

# THE BIOCHEMISTRY OF THE CAROTENOIDS

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Volume II Animals

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## Volume II Animals

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#### Volume II

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# CONTENTS

Preface to the First Edition	xi
Preface to the Second Edition	xv
<b>1. CAROTENOID-PROTEIN COMPLEXES</b>	1
1.1 Introduction	1
1.2 Carotenolipo (glyco) proteins	4
1.3 Carotenoproteins	10
1.3.1 General	10
1.3.2 Lobster pigments	12
(a) Crustacyanin	12
(b) Ovooverdin	13
(c) Yellow pigments	13
(d) Chromoproteins <i>in vivo</i>	14
1.3.3 Starfish pigments	14
(a) <i>Asterias rubens</i>	14
(b) <i>Marthasterias glacialis</i>	15
1.3.4 <i>Velella</i> mantle pigment	16
1.3.5 <i>Pomacea</i> pigment, ovorubin	16
1.3.6 <i>Salpa cylindrica</i> pigment	17
1.3.7 <i>Rhynchosciara americana</i> complex	17
1.3.8 Coral pigments	18
1.4 Nature of bonding of pigments to apoproteins	18
1.5 <i>References</i>	18
<b>2. PORIFERA</b>	22
2.1 Introduction	22
2.2 Nature and distribution	22
2.3 Source of sponge carotenoids	27
2.4 Chemosystematics of sponge carotenoids	33
2.5 <i>References</i>	33

## vi Contents

3.	COELENTERATES	35
3.1	Class Hydrozoa	35
3.1.1	Distribution	35
3.1.2	Formation	36
3.2	Class Scyphozoa	36
3.3	Class Anthozoa	37
3.3.1	Sub-class Alcyonaria	37
3.3.2	Sub-class Hexacorallaria	37
(a)	<i>Distribution</i>	37
(b)	<i>Formation</i>	38
(c)	<i>Function</i>	39
3.4	<i>References</i>	39
4.	ECHINODERMATA, ANNELIDA, SIPUNCULIDA, PRIAPULIDA, PLATYHELMINTHES AND BRYOZOA	42
4.1	Echinodermata	42
4.1.1	Asteroidea	42
4.1.2	Ophiuroidea	44
4.1.3	Holothuroidea	45
4.1.4	Crinoidea	46
4.1.5	Echinoidea	46
4.1.6	Formation, metabolism and function	47
4.2	Annelida	48
4.3	Sipunculida	48
4.4	Priapulida	48
4.5	Platyhelminthes	48
4.6	Bryozoa	48
4.7	Formation and metabolism	50
4.8	<i>References</i>	50
5.	MOLLUSCA	52
5.1	Pelecypoda (Bivalvia, Lamellibranchia, Acephala)	52
5.1.1	Nature and distribution	52
5.1.2	Formation and metabolism	53
5.2	Gastropoda	56
5.2.1	Marine gastropods	56
5.2.2	Fresh-water gastropods	58
5.2.3	Terrestrial gastropods	59
5.3	Amphineura	60
5.4	Cephalopoda	60

5.5	Function of carotenoids	61
5.6	References	62
6.	C R U S T A C E A	64
6.1	Nature and distribution	64
6.1.1	Sub-class Branchiopoda	64
(a)	<i>Anostraca</i>	64
6.1.2	Sub-class Ostracoda	66
6.1.3	Sub-class Copepoda	66
6.1.4	Sub-class Cirripedia	67
6.1.5	Sub-class Malacostraca	67
(a)	<i>Isopoda</i>	67
(b)	<i>Amphipoda</i>	68
(c)	<i>Euphausiacea</i>	68
(d)	<i>Mysidacea</i>	68
(e)	<i>Decapoda</i>	73
(f)	<i>Stomatopoda</i>	76
6.2	Localization	77
6.2.1	Overall picture	77
6.2.2	Quantitative distribution	77
6.2.3	Integument	80
(a)	<i>Carapace</i>	80
(b)	<i>Epidermis</i>	80
6.2.4	Haemolymph	81
6.2.5	Hepatopancreas	81
6.2.6	Digestive tract	82
6.2.7	Gonads	83
6.3	Metabolism	83
6.3.1	Modification of food carotenoids	83
6.3.2	Metabolism during sexual cycle	86
6.3.3	Metabolism resulting in loss of pigments	86
6.4	Hormonal control of pigmentation	86
6.4.1	Eye stalk secretions	86
6.4.2	Androgens	87
6.5	Sexual dimorphism	87
6.6	Colour variants	87
6.7	Environmental and ecological considerations	88
6.7.1	Seasonal variations	88
6.7.2	Diurnal variations	89
6.7.3	Background and illumination	89
6.8	Crowding	89
6.9	Parasitization	90
6.10	Function	90
6.11	References	91

## viii Contents

7.	A R A C H N I D S   A N D   I N S E C T S	97
7.1	Arachnida	97
7.1.1	Acarina	97
(a)	<i>Distribution</i>	97
(b)	<i>Mutants</i>	97
(c)	<i>Metabolism</i>	100
7.2	Insecta	101
7.2.1	Distribution	101
(a)	<i>Orthoptera</i>	101
(b)	<i>Phasmida</i>	102
(c)	<i>Hemiptera</i>	104
(d)	<i>Coleoptera</i>	106
(e)	<i>Diptera</i>	109
(f)	<i>Lepidoptera</i>	109
(g)	<i>Hymenoptera</i>	111
7.2.2	Metabolism of ingested carotenoids	111
(a)	<i>Astaxanthin formation</i>	111
(b)	<i>Carotenoids with oxygen at C-2</i>	112
(c)	<i>Lutein derivatives</i>	115
(d)	<i>Synthesis by symbiotic micro-organisms</i>	116
7.2.3	Insect coloration	116
(a)	<i>Carotenoid contribution</i>	116
(b)	<i>Hormonal and environmental factors</i>	118
7.3	Function	118
7.4	References	118
8.	T U N I C A T E S   A N D   F I S H	122
8.1	Tunicates	122
8.2	Fish	123
8.2.1	Distribution	123
(a)	<i>Skin</i>	123
(b)	<i>Muscle</i>	134
(c)	<i>Eggs</i>	134
(d)	<i>Sperm</i>	134
(e)	<i>Liver</i>	137
(f)	<i>Other organs</i>	138
(g)	<i>Quantitative distribution</i>	139
(h)	<i>Qualitative variations</i>	139
8.2.2	Formation of specific carotenoids	141
(a)	<i>Astaxanthin</i>	141
(b)	<i>Tunaxanthins</i>	144
(c)	<i>Parasiloxanthin</i>	145
(d)	<i>2-Hydroxy-β-carotene</i>	145

8.2.3	Pigment function	146
(a)	<i>Colour pattern</i>	146
(b)	<i>Vision</i>	147
(c)	<i>As vitamin A precursors</i>	147
8.3	<i>References</i>	148
9.	<b>A M P H I B I A A N D R E P T I L E S</b>	154
9.1	Amphibia	154
9.1.1	Distribution	154
9.1.2	Metabolism	157
9.2	Reptiles	157
9.2.1	Distribution	157
(a)	<i>Snakes</i>	157
(b)	<i>Lizards</i>	157
(c)	<i>Turtles</i>	158
9.2.2	Function	158
9.3	<i>References</i>	158
10.	<b>B I R D S</b>	160
10.1	Introduction	160
10.2	Distribution	160
10.2.1	Feathers	160
10.2.2	Eggs	162
10.2.3	Skin	163
10.2.4	Eyes	164
10.2.5	Other tissues	164
10.3	Formation	165
10.4	Metabolism	167
10.5	Function	168
10.6	Coloration of poultry foods	168
10.7	<i>References</i>	168
11.	<b>M A M M A L S</b>	173
11.1	Introduction	173
11.2	Carotenoid accumulators	173
11.2.1	Indiscriminate accumulators	173
(a)	<i>Distribution</i>	173
(b)	<i>Metabolism</i>	174
(c)	<i>Pathological conditions</i>	174
(d)	<i>Absorption</i>	176
11.2.2	Carotene accumulators	176
(a)	<i>Distribution</i>	176
(b)	<i>Metabolism</i>	178
(c)	<i>Function</i>	178

## x Contents

11.3	Non-accumulators	179
11.3.1	Distribution	179
11.3.2	Metabolism	179
11.4	Conversion of carotenoids into Vitamin A	180
11.4.1	Structural requirements	180
11.4.2	Site of conversion	182
11.4.3	Enzymology of conversion	183
11.4.4	Factors controlling conversion	184
11.5	<i>References</i>	185
	General Index	197
	Species Index	213

## PREFACE TO THE FIRST EDITION

The carotenoids are not only amongst the most widespread of the naturally occurring groups of pigments, but probably also have the most varied functions; witness their known roles in photokinetic responses of plants, in phototropic responses of fish and as vitamin A precursors in mammals and birds. Pigments with such wide distribution and such diverse functions are obviously of great interest to biological scientists with very different specializations, especially as it is unlikely that the study of the functions of carotenoids is anywhere near complete.

The primary aim of the present work is to discuss the distribution, biogenesis and function of the carotenoids throughout the plant and animal kingdoms in such a way that, because of, rather than in spite of its biochemical bias, it will be of value to workers interested in all the biological aspects of these pigments. The biochemical approach is considered the most effective because, generally speaking, most progress in the study of carotenoids in living material has been achieved using biochemical techniques, be they applied by zoologists, botanists, entomologists, microbiologists or other specialists; what is even more important is that a consideration of the present position makes it certain that further fundamental progress will also be made along biochemical lines.

Although many good accounts of the pure chemistry of the carotenoids are available, the most recent and comprehensive being Karrer and Jucker's *Carotinoide* (Birkhäuser, Basel, 1948), (now available in an English translation by E. A. Braude and published by Elsevier) sufficient descriptive chemistry has been included to make this book adequately self-contained and to allow the discussion to be followed without undue difficulty. The most up-to-date spectrographic data have also been included, because spectrophotometric techniques are of great importance in identifying carotenoids in biological systems.

The first comprehensive survey of the biochemistry of carotenoids was made in 1922 by the late L. S. Palmer (*Carotenoids and Related Pigments*, Chemical Catalog Co., New York); this was followed in 1934 by Zechmeister's *Carotinoide* (Springer, Berlin) and Lederer's *Les Caroténoides*

*des Plantes* (Hermann, Paris), and in 1935 by Lederer's *Les Caroténoides des Animaux* (Hermann, Paris). Since then a survey such as the present one has not appeared. In order to present a full picture, much of the pre-1934 work has been reconsidered and, as far as is known, every important contribution which has appeared since that date has been discussed. Two peripheral aspects of the subject have, however, been omitted, namely (a) the qualitative and quantitative changes which the carotenoids of plant materials undergo in storage or during processing into food and (b) the carotene (pro-vitamin A) requirements of different animal species; it was felt that the former, about which a great deal has been written, was too technological to be suitable for inclusion in the present volume, whilst the latter is more suitable for a monograph on vitamin A.

The very wide distribution of the carotenoids in Nature suggests that, in spite of the superficially diverse functions ascribed to them in different living tissues, there may be some factor or property through which all these functions will eventually be correlated; any suggestion as to the nature of this common property can perhaps come most readily from a comparative approach. Apart from critically surveying the literature this book has been constructed so as to focus attention on comparative data and their possible implications. If the comparative aspects do not always appear to have been given sufficient explicit consideration it is because essential data are still lacking; it may even be hoped that when research workers realize fully the lacunae, they will be stimulated to carry out investigations on comparative lines. If this does occur then the author will feel that the book has served one of its main purposes.

To many biochemists the word 'carotenoid' stimulates the mental response 'vitamin A precursor' and no more. There is a need, which it is hoped this book fulfils, to emphasize to all concerned, directly or indirectly, with carotenoid biochemistry that a much wider view must now be taken of these pigments and that in the course of elucidating their biogenesis, metabolism, and functions, very significant advances with wide implications for our understanding of living processes are to be expected.

My sincere thanks for considerable help during the writing of this book are due to many friends and colleagues; it should be emphasized however, that none of them can be considered in any way responsible for any peculiarities which may exist in the book. Professor R. T. Williams (St. Mary's Hospital Medical School) read and criticized the original typescript; Mr. D. A. Coul (Department of Botany, The University of Liverpool) read the section on plant carotenoids and corrected many errors of nomenclature; Dr. J. Glover (Department of Biochemistry, the University of Liverpool) devoted considerable time to correcting both the galley and the page proofs, and made many valuable suggestions. Miss B. M. Morris and Miss M. W. Boggiano between them produced an unblemished typescript from a far-from-perfect manuscript; the Staff of the Liverpool University Library (especially Miss E.

Whelan) went to considerable trouble to trace and obtain obscure journals and monographs.

My greatest debt of gratitude is, however, due to Professor R. A. Morton, F.R.S. His encouragement stimulated me to begin this book and his continued unstinting help during the writing of it has been invaluable.

Conditions in the British publishing world are today extremely difficult and the long delays in publishing Scientific Books, especially monographs, tend to make them out of date before they appear. My Publishers have been most tolerant in dealing with my attempts to reduce this delay to a minimum. It is entirely due to their wholehearted co-operation, that it has been possible eventually to include information available in this country up to the end of September 1951.

T.W.G.

## PREFACE TO THE SECOND EDITION

It is just over twenty-five years since the first edition of this book was published and, as in most fields of biochemistry, profound developments have occurred in carotenoid biochemistry in the intervening years. So great have these developments been that the original small book has developed into two large volumes. In the first edition, complete coverage of the literature was aimed at and probably to a great extent achieved; in the present edition I hope that the main developments have been fully covered and documented but in order to keep within a reasonable size, some selectivity has been observed.

The present volume (Volume II) deals with carotenoids in animals; higher plants and Protista have already been dealt with in Volume I, published in 1980. The basic chemistry and properties of carotenoids were discussed in Chapter 1 of Volume I so they are not covered again in this volume. However Chapter 1 is once more a general chapter dealing this time with carotenoproteins which are very characteristic carotenoid derivatives found in animals, particularly in invertebrates. In the chapters which follow, the nature of carotenoids and their distribution in the major animal divisions are described in detail although emphasis is put on the carotenoids recently completely characterized by modern biochemical and physico-organic methods. In particular the stereochemistry of these compounds, which is of great interest and often somewhat unexpected, is emphasized.

The central dogma of carotenoid biochemistry is that animals cannot synthesize the pigments *de novo* but they can only alter the molecules by oxidation, as in the conversion of  $\beta$ -carotene into astaxanthin or, if the structure is appropriate, by central fission to form vitamin A. The first premise of the dogma appears still to be true but within the last few years two new metabolic activities have been revealed: one, resulting in the conversion of  $\beta$ -rings into  $\epsilon$ -rings in birds for example (see Chapter 10), a reaction which appears not to happen in higher plants and protista; and the other, resulting in a change of chirality as in the formation of 3'-epilutein from lutein in fish for example (see Chapter 8). Considerable progress is expected from investigations in this new and exciting field.

xvi Preface to the second edition

I am grateful to a number of people for help in the preparation of this book; to Miss B. T. Foulkes for typing numerous drafts of manuscripts, Miss M. A. Ommeney for careful subediting, and Dr G. Britton for much helpful information. Finally I wish to make a special acknowledgement to my wife who has lived through thirty years of carotenoids; without her sustained support and encouragement during that period this book and very many other things in my life would have never been possible.

T.W.G.  
March, 1983

# [ I ]

## CAROTENOID-PROTEIN COMPLEXES

### 1.1 INTRODUCTION

The existence in nature of lipochromes solubilized by attachment to protein was known long before lipochromes were chemically characterized as carotenoids. The water-solubility of various pigments from invertebrates was first demonstrated in 1883 by Merejkowsky [1] who also showed that solutions of these pigments underwent profound changes when heated or treated with acid, alkali or alcohol with the liberation of the red *zoöerythrin* (astaxanthin) (1.1). Newbigin [2,3] at the turn of the century felt that the lipochrome was attached to an unstable organic base but it was not until the 1920s that the non-pigment component was identified as a protein [4–6]. There followed a descriptive period in which the existence of many carotenoproteins was established [see e.g. 7–10]; these pigments are listed in Table 1.1. More detailed studies developed which involved protein purification, the identification of the carotenoid present and the measurement of the absorption spectrum of the complex. The observations at this level are summarized in Table 1.2. During this time it was also becoming clear that two main types of pigments existed, one in which the pigment was bound to the protein in stoichiometric amounts in non-covalent linkages, and one in which the carotenoid was dissolved in the lipid component of a lipoprotein or lipoglycoprotein. The first group represents true carotenoproteins whilst the latter are better described as carotenoid-lipoproteins or carotenoid-lipoglycoproteins.

In the most recent research on carotenoproteins sophisticated spectroscopic techniques have been used in conjunction with modern protein biochemistry to elucidate the chemical nature of the pigment-protein complex and these have been reviewed in detail by Zagalsky [11] and Britton *et al.* [12].

## 2 The biochemistry of the carotenoids

Table 1.1 Animals in which carotenoid–protein complexes have been detected

<i>Species</i>	<i>Organ</i>	<i>Colour</i>	<i>Reference</i>
<b>Porifera</b>			
<i>Ficulina ficus</i>	—	Brown–orange	10
<i>Ficulina</i> spp.	—	—	13
<i>Suberites</i> spp.	—	—	13
<i>Tragosia</i> spp.	—	—	13
<b>Hydrozoa</b>			
<i>Clava squamata</i>	—	—	14
<i>Hydractinia echinata</i>	—	—	14
<i>Sertularolla gaudichaudi</i>	Eggs	Violet, brown, grey	14
<b>Siphonophora</b>			
<i>Porpita</i> spp.	—	Blue	—
<b>Anthozoa</b>			
<i>Epiactis prolifera</i>	—	Green	15
<b>Gastropoda</b>			
<i>Cerithidium californica</i>	Mantle	Blue–green	16
<i>Flabellina iodinea</i>	Skin	Blue	15
<i>Littorina</i> spp.	—	—	13
<i>Neptunea</i>	—	—	13
<i>Patella depressa</i>	Ovary	Olive–green	17
<i>Patella vulgata</i>	—	—	17
<b>Lamellibranchata</b>			
<i>Cultellus</i> spp.	—	—	13
<i>Lima</i> spp.	—	—	13
<i>Mytilus</i> spp.	—	—	13
<i>Volsella modiolus</i>	Gonads	Red	18
<i>Volsella</i> spp.	—	—	13
<b>Branchiopoda</b>			
<i>Artemia salina</i>	Blood	Green	19
<i>Branchipus stagnalis</i>	Blood, eggs	Green	19, 20
<i>Caenestheria</i> sp.	Eggs	Pink	19
<i>Cladocera</i> sp	Eggs	Brown, grey, blue, green	21
<i>Daphnia magna</i>	Eggs, ovary, blood	Blue, green	21
<i>Daphnia pulex</i>	Eggs	Green	14
<i>Limnadia lenticularis</i>	Blood	Green	19
<i>Pontella mediterranea</i>	—	—	113
<i>Scapholebris aurita</i>	Blood, ovary, eggs	Blue	21
<i>Sida</i> sp.	Blood	Green	19
<i>Simocephalus vetulus</i>	Blood, ovary, eggs, fat cells, epidermis	Brown, green, purple	22, 23
<i>Triops</i> sp.	Eggs	Pink	19
<b>Copepoda</b>			
<i>Anomalocera patersoni</i>	—	Blue	1, 113
<i>Diaptomus vulgaris</i>	—	Blue	24
<i>Hemidiaptomus amblyodon</i>	Eggs, tissues	Blue, pink	25
<i>Heterocope saliens</i>	—	Blue	26
<i>Idya furcata</i>	Epidermis, retina	Blue	6, 27
<i>Pontellina fera</i>	Integument, epidermis	Blue	28
<i>Pontellina gigantea</i>	—	Green }	1

<i>Species</i>	<i>Organ</i>	<i>Colour</i>	<i>Reference</i>
<b>Malacostraca</b>			
<i>Aristeomorpha foliacea</i>	Eggs	Violet, red	26, 29
<i>Aristeus antennatus</i>	Eggs	Violet, blue	26, 29
<i>Astacus fluviatilis</i>	Hypodermis	Blue	5
<i>Astacus nobilis</i>	Hypodermis	Blue	
	Carapace	Grey-brown }	2, 3, 30
<i>Astacus pallipes</i>	—	Green-brown	24
<i>Athanus</i> sp.	—	Blue	1, 4, 5
<i>Caprella dentatum</i>	—	Blue	1
<i>Carcinus maenas</i>	Hepatopancreas	Brown-green }	5, 19, 31-33
	Blood	Red-orange	
<i>Carcinus</i> sp.	—	—	13
<i>Crangon</i> sp.	Carapace	Violet	5
<i>Dromia</i> sp.	—	Red-brown	4
<i>Emerita analoga</i>	—	Blue	15
<i>Galathea</i> sp.	—	Blue	4, 5
<i>Gammarus lacustris</i>	—	Blue	108
<i>Gammarus pulex</i>	—	Olive-brown, blue	26, 34
<i>Gammarus</i> sp.	—	—	13
<i>Gebbia littoralis</i>	—	Blue	1
<i>Hippolyte</i> sp.	Carapace	Blue	4, 5, 35
<i>Hippolyte varians</i>	Body wall	Blue	19, 35
<i>Iodothea</i> sp.	—	—	13
<i>Iodothea viridis</i>	Eggs, blood	Green	19
<i>Macrobrachium roseenbergii</i> (= <i>Palaemon carcinus</i> )	—	Blue	24
<i>Marinogammarus marinus</i>	Blood	Pink, orange, blue	36
<i>Meganyctiphanes</i> sp.	—	—	13
<i>Nephrops norvegicus</i>	Carapace	Orange-red }	2, 3, 4,
	Eggs	Blue	37, 38
	Ovary	Green	
<i>Orchestia gammarella</i>	Blood	Pink, orange, blue	36
<i>Pagurus pollicaris</i>	Eye	Blue	39
<i>Pagurus</i> sp.	—	—	13
<i>Palaemon serratus</i>	Hypodermis	Blue	5
<i>Palaemon</i> sp.	—	—	13
<i>Palaemon viridis</i>	Hypodermis	Blue	1
<i>Palaemonetes vulgaris</i>	—	Blue	40
<i>Pandalus borealis</i>	Eggs	Red }	13, 24
	Ovary	Blue	
<i>Parapenaeus longirostris</i>	Eggs	—	26, 29
<i>Plesionika edwardsii</i>	Eggs	Blue	29
<i>Porcellana</i> sp.	—	—	4, 13
<i>Portunus puber</i>	—	Blue	4
<i>Portunus</i> sp.	—	—	13
<i>Scyllarus latus</i>	Eggs	—	26, 29
<i>Squilla mantis</i>	—	—	29
<i>Stomatopoda</i>	Carapace, eggs, hypodermis	—	4
<b>Insecta</b>			
<i>Locusta</i> spp.	Wings, integument, haemolymph	Green, brown. yellow, red }	41, 42
<i>Oedipoda</i> spp.	Wings	Blue, red, yellow	43

## 4 The biochemistry of the carotenoids

Table 1.1 cont'd

<i>Species</i>	<i>Organ</i>	<i>Colour</i>	<i>Reference</i>
<i>Plusia gamma</i>	Haemolymph	Green	44
<i>Schistocerca gregaria</i>	Wings, integument haemolymph	—	41, 42
<b>Acari</b>			
<i>Eylais extendens</i>	—	Orange–pink	45
<b>Holothuroidea</b>			
<i>Cucumaria</i> spp.	Gonads	Green, blue–green	13, 46
<i>Holothuria</i> spp.	Ovaries	Red–violet	46
<i>Mesothuria</i> spp.	—	—	13
<i>Psolus</i> spp.	—	—	13
<i>Thyone</i> spp.	—	—	13
<b>Asteroidea</b>			
<i>Asterias rubens</i>	Dorsal skin	Blue, violet, brown	18, 47, 48
<i>Asterias</i> sp.	—	—	13
<i>Asterina gibbosa</i>	Skin	Green	1, 24
<i>Asterina panceri</i>	Skin	Green	49
<i>Astrotmetis sertulifera</i>	Spines	Blue	15
<i>Astropecten aurantiacus</i>	—	Grey	1, 3
<i>Astropecten bispinosus</i>	—	Violet	1
<i>Astropecten</i> spp.	—	—	13
<i>Echinaster</i> spp.	—	Red	1
<i>Henricia sanguinolenta</i>	Skin	Red, purple	18, 24, 47
<i>Henricia</i> spp.	—	—	13
<i>Luidia</i> spp.	—	—	13
<i>Marthasterias glacialis</i>	Skin	Green or violet	24
<i>Pisaster giganteus</i>	Skin	Blue, yellow, purple	50
<i>Solaster</i> spp.	—	—	13
<b>Ophiuroidea</b>			
<i>Amphiina</i> spp.	—	—	13
<i>Ophioderma longicauda</i>	—	Brown	1
<i>Ophiotholus</i> sp.	—	—	13
<i>Ophiothrix</i> sp.	—	—	13
<i>Ophiora</i> sp.	—	—	13
<b>Crinoidea</b>			
<i>Antedon</i> sp.	—	—	13

### 1.2 CAROTENOLIPO(GLYCO)PROTEINS

In these complexes carotenoids are dissolved non-stoichiometrically in the lipid component of the lipoproteins. They tend to reflect the pigment intake of the animal and exhibit a main absorption maximum around 450–500 nm, which is close to that of astaxanthin (1.1) in hexane (472 nm) or pyridine (492 nm). Astaxanthin is the most common component of these complexes. Typical examples, which are also listed in Table 1.2, are the complexes from *Cancer pagurus* [55], *Pagurus prideauxi* [7] and *Emerita analoga* [64]. In some cases, for example, *Pecten maximus* [55] and certain birds [91, 92], polar carotenoids are preferentially accumulated in the lipoproteins.

Table 1.2 Carotenoid-protein complexes characterized by absorption spectra and the nature of the carotenoid prosthetic group

Source	Organ	Colour	Absorption maxima <sup>a</sup> (nm)	Carotenoid(s) present	Reference
Hydrozoa					
<i>Velella lata</i>	Mantle	Purple	585–588	1	51
<i>Velella</i> spp.	Mantle	Purple	630	1	52
	Mantle	Purple	620	1	52
	Mantle and tentacles	Purple	650	1	52
Gastropoda					
<i>Pollicipes polymerus</i>	—	—	470	1	53
<i>Pomacea canaliculata</i>	Eggs	Red	(330), 480, 510, 545	1	54
Lamellibranchata					
<i>Peccen maximus</i>	Ovary	Orange-red	(318), (435), 472, 498	2, 3	55
Branchiopoda					
<i>Arenimia salina</i>	—	—	470	4	56
<i>Branchinecta packardi</i>	Blood	Green	300, 400–500, 580	4, 5	20
<i>Branchipus stagnalis</i>	Blood	Green	300, 400–500, 675	4, 5	20
<i>Chiropeltatus diaphanus</i>	Blood	Blue	(340), (460), (480), (690)	4, 5	20
	Blood	Purple	372, 497, 683	(?)	20
<i>Tanymastix lacunae</i>	Blood	Blue	370, 485, 685	4	20
	Blue-green	Blue	371, 460, 685	4	20
	Green	Green	370, 458, 685	4, 5	20
Copepoda					
<i>Anomalocera patersoni</i>	Hypodermis	—	650	57	
<i>Cyclops vernalis</i>	Eggs	Black, grey, brown, blue, purple, green, blue	400–420, 470–492 600–620	{ 71	58
		Blue	—	1	110
<i>Eudiaptomus amblyodon</i>	—	—	—	—	54
<i>Labidocera acutifrons</i>	Hypodermis	—	650	—	57
<i>Labidocera</i> spp.	Hypodermis	—	640	—	28
	Integument	Blue	640	—	
Cirripeda					
<i>Lepas anatifera</i>	Eggs	Blue	600	{ 71	59
<i>Lepas fascicularis</i>	Eggs	Blue	600	{ 71	

Source	Organ	Colour	Absorption maxima <sup>a</sup> (nm)	Carotenoid(s) present	Reference
<b>Malacostraca</b>					
<i>Acanthephyra</i> sp.	—	—	486–498	—	60
<i>Astacus astacus</i>	Carapace	Green	(320), 392, (470), (492), 632	1	33
<i>Callinectes sapidus</i>	—	—	—	6	61
<i>Cambarus clarkii</i>	Carapace	—	655	1	62
<i>Cancer pagurus</i>	Ovary, eggs	orange-red	(325), 470, 490	1, 5	55
<i>Carcinus maenas</i>	Carapace	Green	(320), (408), 500, 560, 625	1	33
<i>Clibanarius erythropus</i>	Exoskeleton	—	620	1	63
<i>Emerita analoga</i>	Eggs, ovary, blood	—	463, 472	—	64
<i>Erithia spinifrons</i>	Carapace	Red-purple	536	1	55
<i>Eupagurus bernhardus</i>	Eggs	Purple	465, 495, 580	7	65
<i>Galathea strigosa</i>	Carapace	—	593	1	55
<i>Homarus americanus (vulgaris)</i>	Eggs, ovaries	Green	(330), (440), 464–468	1	66–74
<i>Homarus gammarus</i>	Carapace	Blue	632	1	75
<i>Idothea granulosa</i>	Carapace	Yellow	409	1	67, 74–76
<i>Idothea monterevensis</i>	Epidermis, blood, eggs	Yellow	398, 470	1	77
<i>Idothea resectata</i>	Eggs, blood	Green	400–500, (625), 680	4(5)	78
<i>Orconectes limous</i>	Exoskeleton	Green	(430), (455), (480), (625)	4	79
<i>Pachygrapsus marmoratus</i>	Blood	—	680	—	80
<i>Pagurus prideauxi</i>	Carapace	Yellow/red	335, 460, 675	5	81, 109
<i>Palinurus vulgaris</i>	Carapace	Blue/purple	520,	1, 4	63
<i>Plesionika edwardsii</i>	Eggs	—	470, 495	1	7
<i>Porania pulillius</i>	Carapace	Red/blue	(350), 560, (600), 616	—	24, 33
<i>Solaster endica</i>	Ovary, eggs	Red	(325), (435), 466, 490	1	63
<b>Astroideidae</b>					
<i>Asterias rubens</i>	Skin	Purple	550–570	1, 8, 9	82–84
<i>Asterina pectinifera</i>	Skin	—	460	1	112
<i>Crossaster papposus</i>	Skin	Red	500	1	85
<i>Lysasterias perrieri</i>	Skin	Blue	570	1	111
<i>Marthasterias glacialis</i>	Skin	Purple	—	1	8
	Skin	Blue	555	1, 10	8
	Skin	Blue	563, 489, 600	1, 1, 10, 11	8

Echinoidea							
<i>Hemicentrotus pulcherrima</i>	—	—	—	—	—	—	—
<i>Sterechinus neumayeri</i>	—	—	—	—	—	—	—
Hydroids and Hydromedusae							
<i>Allopora californica</i>	Skeleton	Violet	545	—	—	—	—
<i>Distichopora coccinea</i>	Skeleton	Red	488	—	—	—	—
<i>Distichopora nitida</i>	Skeleton	Yellow	430, 452, 482	—	—	—	—
<i>Distichopora violacea</i>	Skeleton	Dark red	—	—	—	—	—
<i>Styela elegans</i>	Skeleton	Pale red/pink	(448), 470, (498)	—	—	—	—
<i>Syphaster roseus</i>	Skeleton	Purple/red	540	—	—	—	—
<i>Syphaster sanguineus</i>	Skeleton	Pale pink	(450), 474, (500)	—	—	—	—
Insecta							
<i>Dixippus morosus</i>	Skin	Blue-green	462, 491, 677	—	—	—	—
	Blood	Blue-green	461, 492, 673	—	—	—	—
	Blood	Green	475, 502	—	—	—	—
<i>Meconium varium</i>	Blood	Violet	465, 545	—	—	—	—
<i>Rhynchosciara americana</i>	Skin	Green	478, 510, 678	—	—	—	—
<i>Sphinx ligustri</i>	Skin	Green	470, 501, 671	—	—	—	—
<i>Tettigonia canescens</i>	Skin	Green	470, 501, 671	—	—	—	—
<i>Tunicata</i>							
<i>Salpa cylindrica</i>	—	Purple	560	—	—	—	—
Aves							
<i>Ajaia ajaja</i>	Blood	—	—	—	—	—	—
<i>Guara rubra</i>	Blood	—	—	—	—	—	—

Key

1. Astaxanthin (1.1)
2. Pectenoxanthin (= alloxanthin) (1.2)
3. Peetenolone (1.3)
4. Canthaxanthin (1.4)
5. Mixture of tissue carotenoids (1.5)
6.  $\beta$ -Carotene (1.5)
7. Esterified astaxanthin (1.7)
8. 7,8-Didehydroastaxanthin (1.6)
9. 7,8,7',8'-Tetradehydroastaxanthin (1.7)
10. Adonirubin (1.8)
11. Zeaxanthin (1.9)
12. Lutein (1.10)
13. Echinone (1.11)
14. Unidentified Pigment

Notes

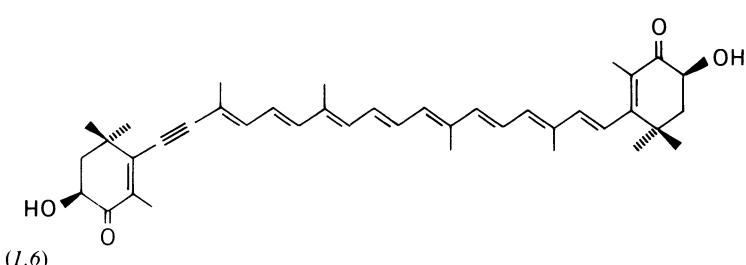
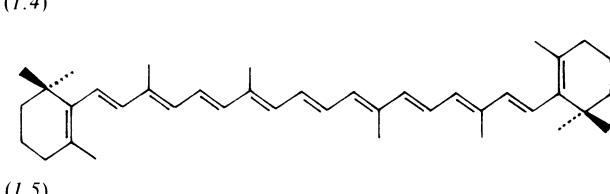
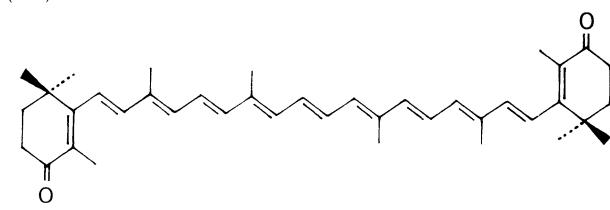
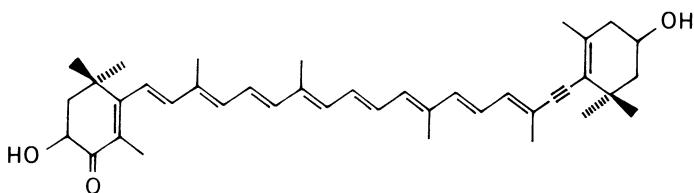
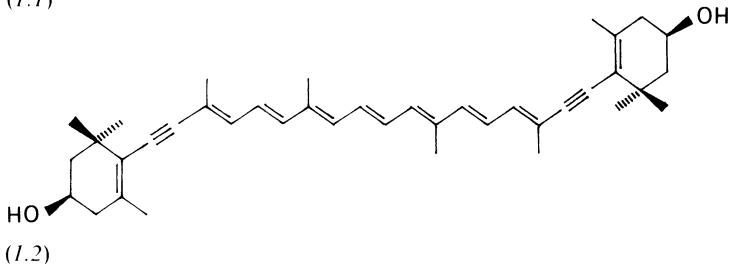
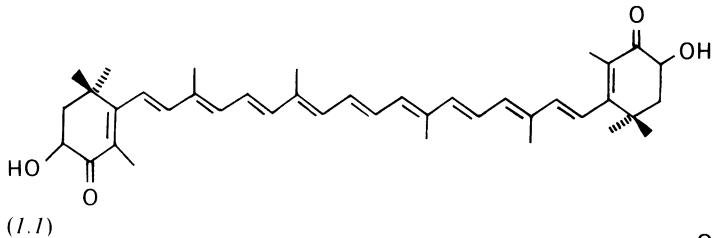
<sup>a</sup> Numbers in parentheses indicate inflexions.

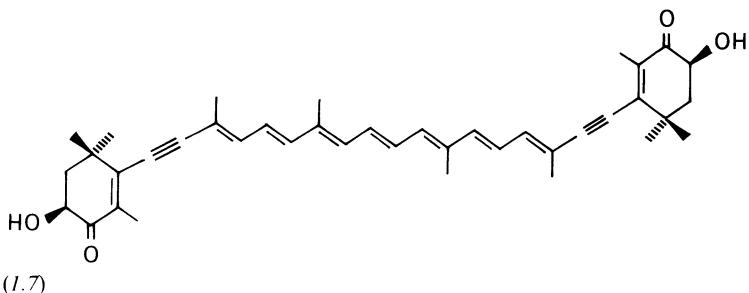
<sup>b</sup> Traces.

<sup>c</sup> Carotenoid and bile pigment associated in a complex sometimes called insectoverdin.

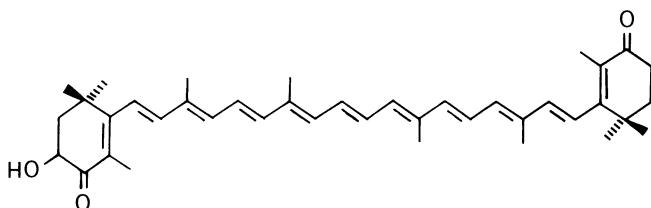
<sup>d</sup> Pure (3S,3'S)-astaxanthin [93].

## 8 The biochemistry of the carotenoids

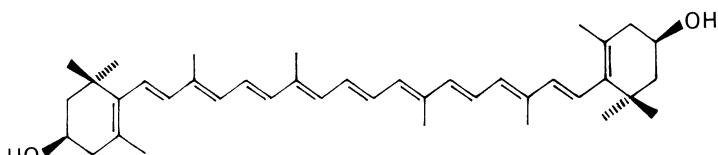




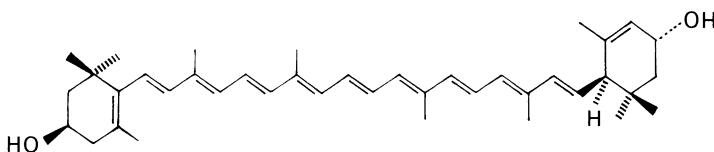
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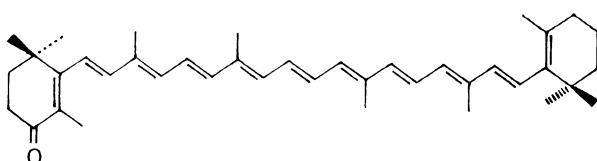
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(I.9)



(I.10)



(I.11)

## 10 The biochemistry of the carotenoids

### 1.3 CAROTENOPROTEINS

#### 1.3.1 GENERAL

With one or two important exceptions, which will be discussed later, carotenoproteins are characterized by a large bathochromic shift in the absorption spectrum of the pigment component compared with that in lipid solvents. If astaxanthin is taken as an example (maximum 492 nm in pyridine) the carotenoproteins exhibit maxima ranging from 536 nm (ex *Erythia spinifrons*) to 650 nm (ex *Porpita* sp.) (see Table 1.2). Two typical spectra of carotenoproteins are recorded in Fig. 1.1. The binding of the pigment to its

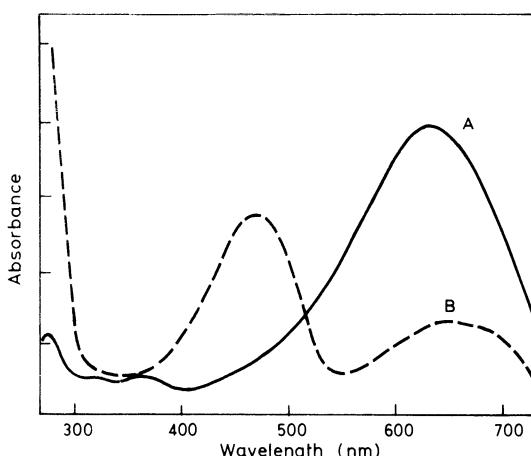


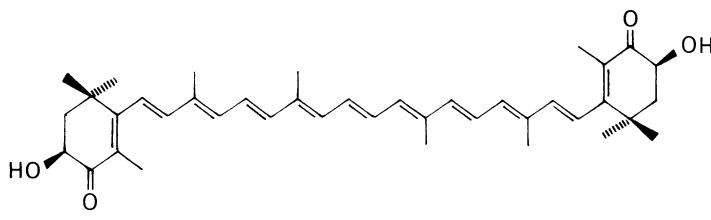
Fig. 1.1. Absorption spectrum of  $\alpha$ -crustacyanin (A) [74] and ovooverdin (B) [33].  $\alpha$ -Crustacyanin in 0.2 M-Na, K phosphate buffer, pH 7; ovooverdin in 0.05 M-Na, K phosphate buffer, pH 7 [Redrawn from reference 9].

apoprotein is, as already indicated, stoichiometric although recent work suggests that the stoichiometry need not be confined to one pigment. For example the chromoprotein from the dorsal skin of the starfish *Asterias rubens* contains not only astaxanthin (1.1) but also its two acetylenic derivatives (1.6 and 1.7) [82–84]. The relative amounts observed reflect the relative amounts present in the food and account for the variations in the absorption maximum of the same chromoprotein isolated at different times and from different locations. This is clearly demonstrated by recombination experiments with purified apoproteins. Table 1.3 indicates the variation in the position of the absorption maxima of the chromoproteins reconstituted from pure apoprotein from the *Pomacea* pigment ovorubin with different carotenoids [12, 52]. The variation is considerable with the maxima ranging from 490 to 517 nm.

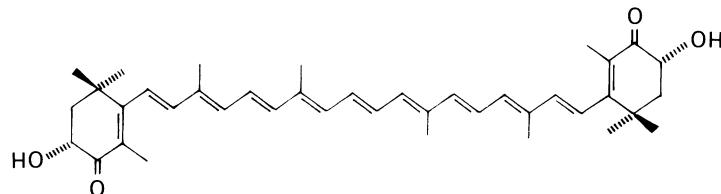
Table 1.3 Absorption maxima of chromoproteins formed by reconstitution from the ovorubin apoprotein and different carotenoids [12]

Carotenoid	Absorption maximum of complex (nm)
(3S,3'S)-Astaxanthin	517
(3R,3'R)-Astaxanthin	517
(3R,3'S)-Astaxanthin	513
7,8-Didehydroastaxanthin	500
7,8,7',8'-Tetrahydroastaxanthin	490

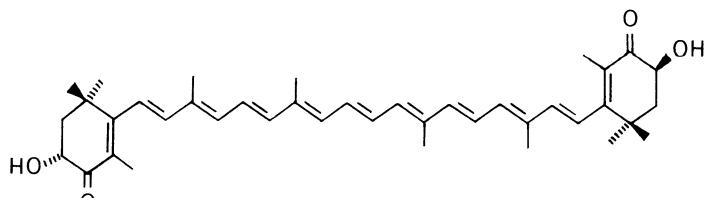
Another important development is the realization that it is insufficient to state that astaxanthin (1.1) is present. Its chirality must be clearly defined. For example that of the chromoproteins of *Marthasterias glacialis* [10] and *Allopora californica* [93] is the (3S,3'S) isomer (1.12) although an earlier report had suggested that the latter pigment was only at least 75% of this isomer [86]. In contrast, all three isomers (3S,3'S), (3R,3'R), (1.13) and (3R,3'S, meso) (1.14) are present in crustacyanin in the ratio 33:28:39 [94]. This confirms the earlier discovery that all three isomers are present in the ‘astaxanthin’ extracted from lobster carapaces [95].



(1.12)



(1.13)



(1.14)

## 12 The biochemistry of the carotenoids

Three important yellow astaxanthin-protein complexes have been obtained from lobster carapace [67, 74-77]; the main absorption bands of these pigments have maxima at wavelengths slightly lower than that of 'astaxanthin' extracted from lobster carapaces [95].

A number of carotenoproteins have now been obtained in the pure state and various modern techniques including advanced spectroscopic techniques are currently being used to obtain information about their overall structure.

### 1.3.2 LOBSTER PIGMENTS

The blue (crustacyanin) and yellow pigments of the carapace and the green (ovoverdin) pigment of the eggs of the lobster have been studied in considerable detail.

#### (a) *Crustacyanin*

Native crustacyanin ( $\alpha$ -crustacyanin,  $\lambda_{\text{max}}$ . 628 nm, Fig. 1.1) dissociates reversibly at low ionic strength to yield purple  $\alpha'$ -crustacyanin ( $\lambda_{\text{max}}$ . 595 nm). On dialysis this is converted irreversibly into  $\beta$ -crustacyanin ( $\lambda_{\text{max}}$ . 585 nm) which is electrophoretically heterogeneous. Each  $\alpha$ -crustacyanin molecule contains eight  $\beta$ -crustacyanin molecules each of which binds two molecules of astaxanthin. Removal of the pigment yields apocrustacyanin which is one half the size of  $\beta$ -crustacyanin, that is about 20000 daltons [74, 75]. Apocrustacyanin separates into five components, three, A<sub>1</sub>, C<sub>1</sub> and C<sub>2</sub>, each having a mass of about 22000 daltons and two, A<sub>2</sub> and A<sub>3</sub> each having a mass of about 19000 daltons. Two of these components, usually one from each group, combine in the presence of astaxanthin to form  $\beta$ -crustacyanins. Astaxanthin probably functions by altering the conformation of the two components rather than directly as a cross linking molecule. The compositions of those already detected are given in Table 1.4. The type of  $\beta$ -

Table 1.4 Subunit composition of the six  $\beta$ -crustacyanins obtained from  $\alpha$ -crustacyanin

$\beta$ -Crustacyanin	Subunits*
$\beta_{1a}$	A <sub>2</sub> ,C <sub>2</sub>
$\beta_{1b}$	A <sub>2</sub> ,C <sub>1</sub>
$\beta_{2a}$	A <sub>3</sub> ,C <sub>1</sub>
$\beta_{2b}$	A <sub>3</sub> ,C <sub>2</sub>
$\beta_3$	A <sub>1</sub> ,A <sub>2</sub>
$\beta_4$	A <sub>1</sub> ,A <sub>3</sub>

\*For description of subunits see the text.

crustacyanin derived from the octameric  $\alpha$ -crustacyanin depends on the way the dissociation is achieved. Electron microscopy suggests two possible structures for  $\alpha$ -crustacyanin (Fig. 1.2), either a double tetramer (a) or a helical coil (b) [96–98]. Circular dichroism (c.d.) studies indicate only 6% of  $\alpha$ -helix in the apoprotein [75] whose secondary structure probably consists mainly of anti-parallel  $\beta$ -pleated sheets with a large number of  $\beta$ -turns [11]. The astaxanthin present in both crustacyanin and ovooverdin is a mixture of optical isomers [94].

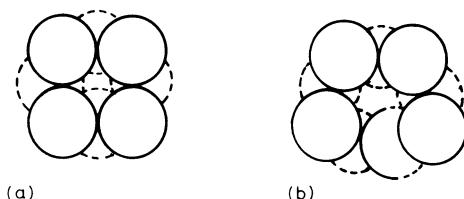


Fig. 1.2. Proposed model for the quaternary structure of  $\alpha$ -crustacyanin. (a) Double tetramer. (b) Helical coil. [Taken from reference 96.]

### (b) Ovooverdin

The lobster egg pigment differs from  $\alpha$ -crustacyanin in exhibiting two absorption maxima at 460 and 640 nm. Recent measurements of the resonance Raman spectrum showed two distinct C=C stretching vibrations at 1500 and 1525  $\text{cm}^{-1}$  obtained by excitation at 647.1 and 488 nm respectively [76]. This demonstrates the existence of two distinct chromophores resulting from the location of astaxanthin in different sites on the apoprotein. The 640 nm chromophore resembles that found in  $\alpha$ -crustacyanin whereas the 460 nm species is similar electronically to free astaxanthin. A molecular weight of ovooverdin reported some time ago as 300 000 [99] from sedimentation measurements has been confirmed by gel filtration techniques [73]. This fits in with the reported minimum molecular weights of 144 000 [100] and 170 000 [33] based on the carotenoid content and with the observations that two astaxanthin molecules must be present in the molecule (see above). A minimum molecular weight of 300 000 has also been reported [101], which may indicate a species difference between *Homarus vulgaris* and *H. americanus*, on which the high values were observed.

### (c) Yellow pigments

The first yellow pigment isolated was characterized by an unusual hypochromic shift of the absorption maximum of the component astaxanthin. It is located at 409 nm, some 70 nm lower than that of the unbound pigment in

## 14 The biochemistry of the carotenoids

acetone. The resonance Raman spectrum of the chromoprotein is the same as that of free astaxanthin, which means that the hypsochromic shift must be due to a destabilized excited state [76]. This has led to the view that in the chromoprotein some 20 astaxanthin molecules are stacked one on top of the other; this would give rise to exciton interactions between the chromophores.

More recently two further yellow astaxanthin–protein complexes have been obtained from lobster carapaces:  $Y_1$  with absorption maxima at 398 and 470 nm, and  $Y_2$  with maxima at 401 and 470 nm.  $Y_1$  is larger than  $Y_2$  but both yield subunits which are very similar in size to those of  $\alpha$ -crustacyanin; one of these subunits is identical with one of the  $\alpha$ -crustacyanin subunits and one is different [75]. There still remains the possibility that these may be artefacts because similar pigments can be obtained from  $\alpha$ -crustacyanin at high pH [67, 75].

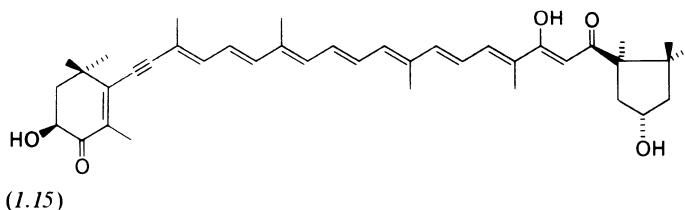
### (d) Chromoproteins in vivo

Photoacoustic spectroscopy [see reference 12] has been used to probe the distribution of chromoproteins across the lobster carapace. It has revealed a near-continuum of astaxanthin absorption wavelengths spanning the visible region of the spectrum. There is a gradual progression from blue-absorbing pigments on the outside of the endocuticle to red pigments on the inside. This is probably due to gradually changing but highly specific pigment–pigment and pigment–protein interactions which are part of the ultrastructure of the endocuticle. This means that it will be impossible to isolate specific chemical species corresponding to each recorded absorption spectrum, but on denaturation a small number of stable species, such as  $\alpha$ -crustacyanin and the yellow pigments, emerge [102, 103].

### 1.3.3 STARFISH PIGMENTS

#### (a) *Asterias rubens*

The purple carotenoprotein (asteriarubin) from the dorsal skin of *A. rubens* exhibits an absorption maximum with a peak varying from 550 to 570 nm according to the relative amounts of the five prosthetic groups present (82–86%). A recent investigation indicated that the mixture contained



canthaxanthin (1.4) (3%), astaxanthin (1.1) (14%), 7,8-didehydroastaxanthin (1.6) (24%), 7,8,7',8'-tetradehydroastaxanthin (1.7) (43%) and 4-oxomytiloxanthin (1.15) (10%) [104]. About 90% of the dehydro-astaxanthins have the (3S,3'S) chirality with small amounts of the *meso* isomers being detected. In the case of astaxanthin itself, 78% is the (3,S,3'S) isomer, 5% the (3R,3'R) isomer and 14% the *meso* compound. The pigment composition clearly reflects the animal's intake of carotenoids; presumably 4-oxomytiloxanthin is a metabolite of mytiloxanthin, a characteristic pigment of mussels (see Chapter 5).

Asteriarubin has a carotenoid/protein ratio of 1:1. The apoprotein (molecular weight 40 000), which has an isoelectric point of 4.5, consists of four identical subunits. The amino acid composition is characterized by a high concentration of aspartic and glutamic acids and the presence of little or no tyrosine or tryptophan (Table 1.5). The first 28 amino acids from the amino-terminus have been sequenced (Fig. 1.3), and two to three disulphide bridges are present in the molecule [12].

*Table 1.5* The amino acid composition of the apoprotein subunit from *Asterias rubens* (The total number of residues present is 129 and numbers in parentheses indicate the number of residues per subunit.)

Lysine (8)	Glutamic acid (10)	Isoleucine (6)
Histidine (2)	Proline (5)	Leucine (6)
Arginine (5)	Glycine (5)	Tyrosine (1)
Aspartic acid (17)	Alanine (10)	Phenylalanine (7)
Threonine (10)	Valine (10)	Cysteine (6)
Serine (8)	Methionine (5)	Tryptophan (0)

Asp – Thr – Gly – Glu – Met – Ala – Ala – Glu – Val –  
 – X – Thr – Cys – Asp – X – Thr – Val – Tyr – X –  
 – Thr – Cys – Leu – Arg – Thr – Ile – X – Ile – Phe/Lys – Asp .....

*Fig. 1.3.* The amino acid sequence of the first 28 residues from the amino-terminus of the apoprotein of the purple carotenoprotein from *Asterias rubens* [12].

### (b) *Marthasterias glacialis*

Two carotenoproteins have been isolated from *M. glacialis* [12, 105, 106]. The purple complex has an absorption maximum at 550 nm and the prosthetic group consists of (3S,3'S)-astaxanthin (1.12) (90–95%) and adonirubin (1.8) (5–10%) with traces of other carotenoids also present. It is extremely soluble in water and very stable in 0.5 M-NaCl. It has a molecular weight of 43 000 and consists of four subunits. The carotenoid/protein ratio is 4:1. In spite of the difference between this ratio and that observed in the *Asterias* pigment (1:1) there are some similarities between the two chromoproteins.

## 16 The biochemistry of the carotenoids

The blue pigment exhibits absorption maxima in water at 463, 489 and 600 nm with the longest wavelength band moving to 612 when the solvent is 1.0 M-NaCl. It is a lipoprotein which results in it being rather insoluble in aqueous solvents and tending to aggregate and precipitate even in solutions of low ionic strengths. It has a molecular weight of 72 000 with a carotenoid/protein ratio of 4:1. The usual prosthetic group mixture is astaxanthin (60–70%), adonirubin (3–6%) with smaller amounts of, *inter alia*, canthaxanthin (1.4) and zeaxanthin (1.9). Two subunits are present, the largest and major component having a molecular weight of 16 000, whereas the minor component has a molecular weight of 13 000.

### 1.3.4 *Velella* MANTLE PIGMENT

The naturally occurring blue pigment ( $V_{620}$ ) from the mantle of *V. velella* exhibits an absorption maximum at 620 nm when measured in the presence of halide ( $Cl^-$ ) ions. On storage in the absence of halide ions this is converted into  $V_{600}$ , a pigment with an absorption maximum at 600 nm measured in the presence of halide ions. Removal of the halide ions converts  $V_{600}$  into the purple  $V_{570}$ . The relationship between these pigments is that  $V_{620}$  is a tetramer of  $V_{600}$  which is an octamer of  $V_{570}$ . Electrophoresis separates  $V_{570}$  into six components each of which appears to be a dimer of the apoprotein. A further pigment  $V_{545}$  is also observed and it and  $V_{570}$  may be artefacts arising from deamidation of acidic amide residues in the native protein. Two astaxanthin molecules are present in each subunit [52]. Electron microscopic studies have recently been made [98] on the crystallized *Velella* pigment [107]. The c.d. spectrum of  $V_{620}$  exhibits exciton splitting which indicates electronic interaction between different chromophores in close proximity to each other: in this case it could be between two molecules on one apoprotein or between molecules on adjacent apoproteins. When  $V_{620}$  dissociates into  $V_{600}$  in the absence of halide ions no exciton splitting is seen in  $V_{600}$ . Thus the interaction most probably is between pigment molecules on adjacent apoproteins, but another possibility is that occupation of the halide binding site alters the orientation of the pigment molecules or the distance between them [52].

### 1.3.5 *Pomacea* PIGMENT, OVORUBIN

Ovorubin, the red protein which accounts for 75% of the total nitrogen of the eggs of the gastropod *Pomacea canaliculata*, is an astaxanthin glycoprotein [54, 108] of minimum molecular weight 330 000 [54]. The bathochromic shift (20–25 nm) is less than that observed with most other carotenoproteins and furthermore there is a pronounced increase in the vibrational fine structure exhibited by the spectrum (Fig. 1.4). The reason for this is not yet clear but reconstitution studies indicate fundamental differences in binding. In

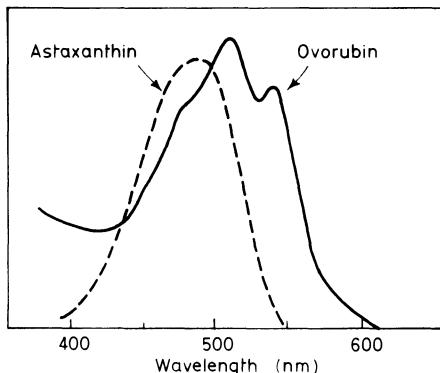


Fig. 1.4. The absorption spectra of free astaxanthin (----) and ovorubin (—) [12].

complexes such as  $\alpha$ -crustacyanin, keto functions at both C-4 and C-4' are necessary for the characteristically large bathochromic effect observed in the complex. In ovorubin, one keto group, as in adonirubin (1.8), is sufficient to produce the 20–25 nm shift; indeed carotenoids without keto groups, e.g. zeaxanthin (1.9), are equally effective [11, 12]. Furthermore the shifts with different chiral astaxanthins ( $3R,3'R;3R,3'S$  and  $3S,3'S$ ) are different, being 27, 23 and 27 nm, respectively [12] (see Table 1.3). In other complexes the shifts are the same with all the chiral astaxanthins.

### 1.3.6 *Salpa cylindrica* P I G M E N T

The pale-blue tunicate *S. cylindrica* changes irreversibly to purple on freezing [90]. A purple water-soluble pigment (absorption maximum 560 nm) which can be extracted from the frozen material behaves in many ways as a carotenoprotein although the very polar prosthetic group (absorption maximum 443 nm) has not yet been identified; it does not correspond to any known carotenoid although the resonance Raman spectrum of the complex is typical of a carotenoid chromophore [12].

### 1.3.7 *Rhynchosciara americana* C O M P L E X

The violet carotenoprotein from the haemolymph of the fly *Rhynchosciara americana* has a molecular weight of 157 000 and consists of four identical subgroups. Four carotenoid molecules, three of echinenone (1.11) and one of canthaxanthin (1.4), are bound to each apoprotein. The absorption spectrum appears complex but on analysis it is revealed as the result of the superposition of two spectra with absorption maxima at 465 and 545 nm, respectively. The complex exhibits circular dichroism in the visible region of the spectrum. As the prosthetic groups are not chiral the c.d. spectrum must

## 18 The biochemistry of the carotenoids

be the result of distortion of the pigments induced by the conformation of the apoprotein. The two absorption maxima in the electronic spectra can thus be ascribed to one molecule of carotenoid bound at an unrestricted site (465 nm) and one at a site which causes distortion of the pigment (545 nm) [89].

### 1.3.8 CORAL PIGMENTS

Alloporin from *Allopora californica* has a molecular weight of 68000, consists of four similar if not identical subunits and exhibits a carotenoid/protein ratio of 1:1 [86]. As indicated in Section 1.3.1 the prosthetic group is (3S,3'S)-astaxanthin [93]. It has a high content of acidic amino acids which probably accounts for its stable arrangement within the aragonite ( $\text{CaCO}_3$ ) skeleton of the coral.

Other chromoproteins have been reported in the hydrocorals *Stylaster roseus*, *S. elegans*, *S. sanguineus* and in *Distichopora coccinea* [86] (See Table 1.2 and Chapter 3).

## 1.4 NATURE OF BONDING OF PIGMENTS TO APOPROTEINS

No final conclusions can yet be made regarding the nature of the pigment–protein binding. A keto group is generally essential and two are frequently necessary for optimal binding and maximal spectral shift as determined by recombination experiments with pure apoproteins and various pigments [11, 12]. These observations have led to the idea that both binding and spectral shifts are mediated through enolization, Schiff base formation or hydrogen bonding to the side chains of the amino acids of the apoprotein. On the other hand the keto groups may merely hold the molecule in position so that other charged regions of the protein interact with the polyene chain and alter its electronic configuration. Another hypothesis is that the shift is due to the distortion of the entire molecule about double bonds. If this situation obtains then strong binding via the keto groups is an essential prerequisite. Much further work is needed to settle this problem and it may well be revealed that different carotenoproteins involve different types of bonding.

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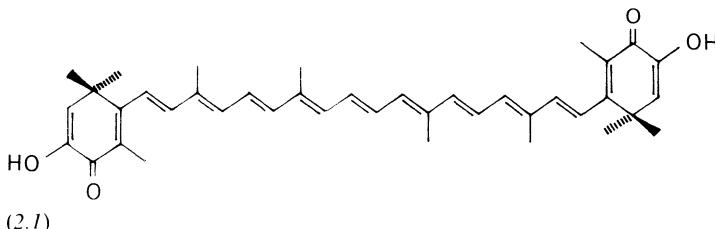
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# [2]

## PORIFERA

### 2.1 INTRODUCTION

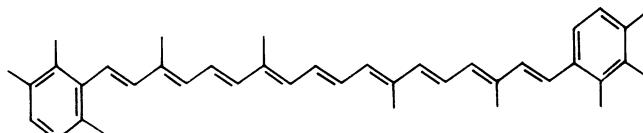
The brilliant orange, red, yellow and purple pigments of many sponges are carotenoids. They were first detected as *lipochromes* towards the end of the last century [1–3]; this early work was summarized by Palmer [4]. However, it was not until 1931 that a study of the visible absorption spectra of sponge extracts clearly indicated the presence of carotenoids [4, 5, 6]. In 1935 the first chemical characterization of a sponge carotenoid was made by Karrer & Solmsen [7] who obtained astacene (2.1) from *Axinella crista-galli*. The naturally occurring pigment is in fact astaxanthin (1.1); it is now known that astacene is an oxidative artefact. From 1935 onwards many new and unexpected pigments have been unequivocally identified in sponges and relatively recently a wide survey using modern analytical techniques has been undertaken [8].



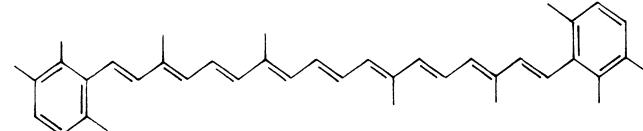
### 2.2 NATURE AND DISTRIBUTION

The general distribution of carotenoids in sponges is given in Table 2.1. The outstanding characteristic of sponge carotenoids is the presence of aromatic residues. The first aromatic carotenoids to be described were renieratene (2.2), isorenieratene (2.3) and renierapurpurin (2.4) which were obtained from *Reniera japonica* [9–12]. These structures have been confirmed by total synthesis [13–15]. Isorenieratene eventually was shown to be identical with leprotene obtained from certain Mycobacteria [16] (see Vol. I, Chapter 9).

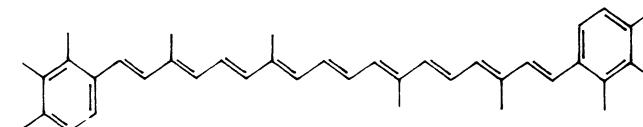
The acetylenic pigments 7,8-didehydrorenieratene (2.5) [18] and 7,8-didehydroisorenieratene (2.6) [17, 18] are minor carotenoid components in *R. japonica* which also contains a pigment renieraxanthin [19] which is now considered to be identical with spheroidenone (2.7), a very characteristic pigment of the purple photosynthetic bacteria (see Vol. I, Chapter 10).



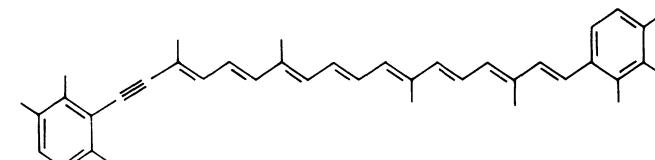
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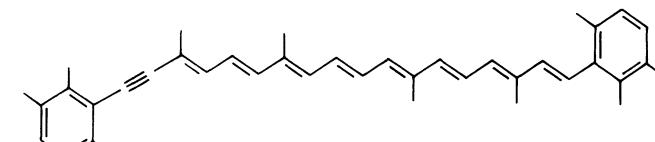
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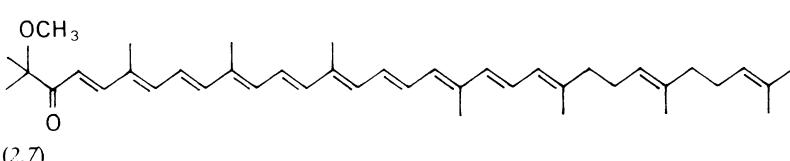
(2.4)



(2.5)



(2.6)

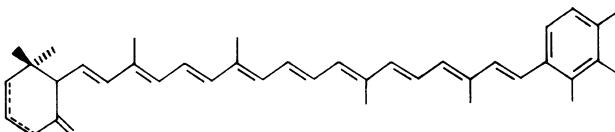
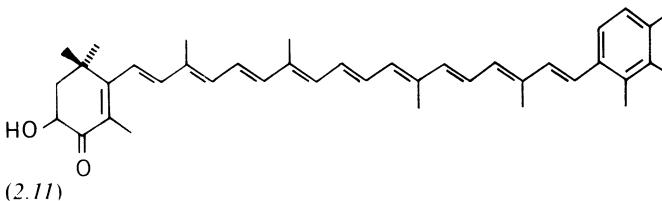
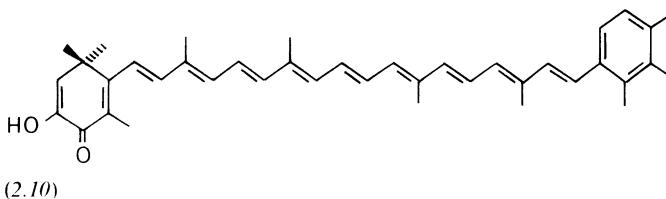
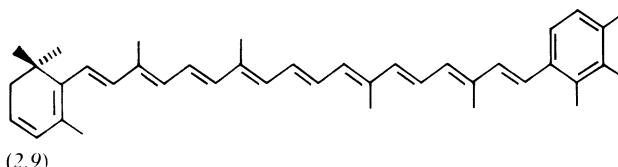
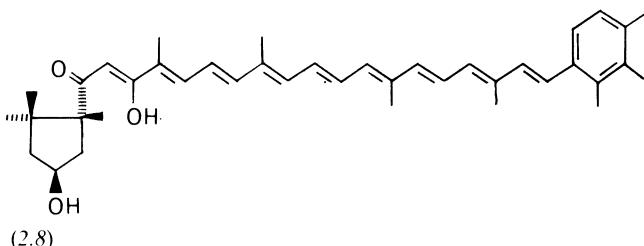


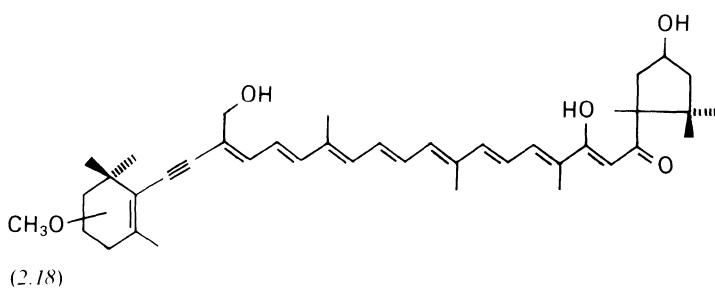
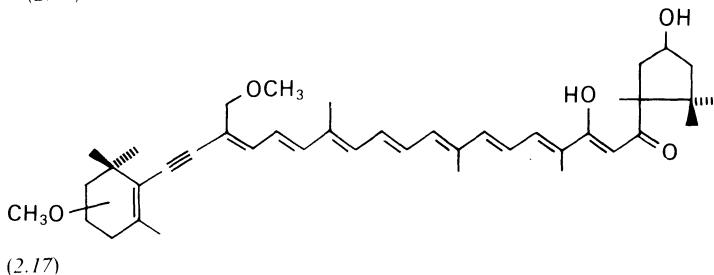
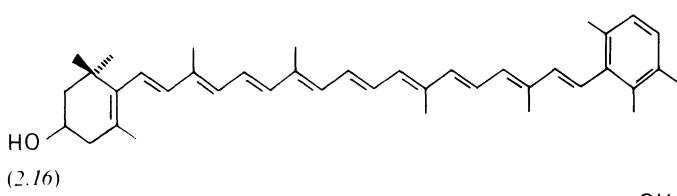
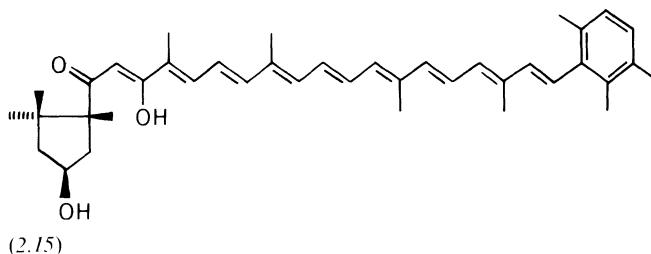
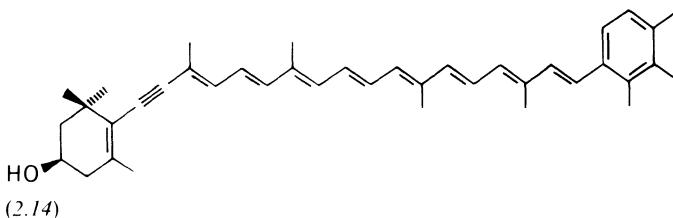
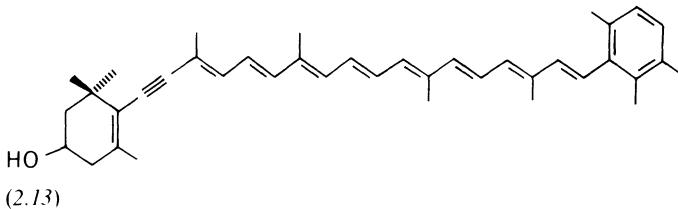
(2.7)

Since the pioneering work on *R. japonica* many other aromatic carotenoids have been isolated from other sponges (Table 2.1); they include triketeniorhodin (2.8) [19–22], tethyatene (2.9) [21, 23], tedanin (2.10) [21,

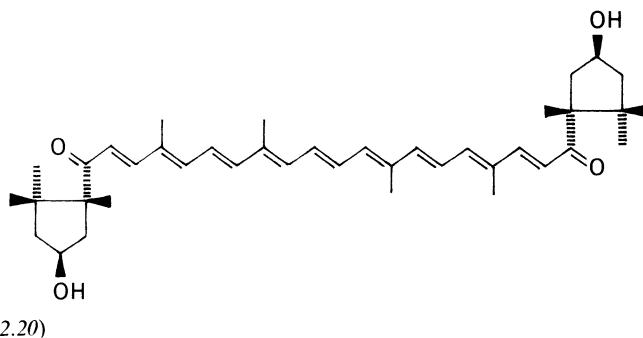
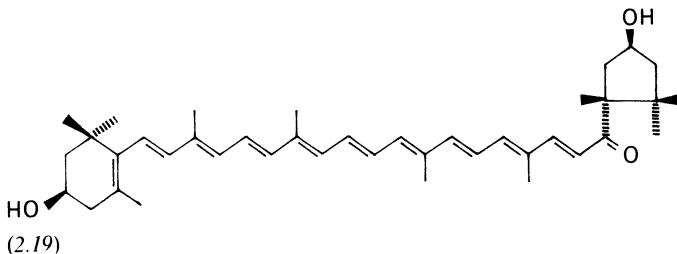
## 24 The biochemistry of the carotenoids

[22], clathriaxanthin (2.11) [21, 24, 25], didehydro- $\gamma, \kappa$ -carotene (2.12) [22], isotedaniaxanthin (2.13) [24], tedaniaxanthin (= allopurpurin) (2.14) [21, 22, 26, 27, 40], triketriophidin (2.15) [22] and agelaxanthins A (2.16), B (2.17) and C (2.18) [18, 20]. Tedanin (2.10) is now considered to be artifactually derived from clathriaxanthin esters on saponification [29]. Apart from the two types of aromatic ring ( $\phi$  as in isorenieratene and  $\chi$  as in renieratene) found in sponges, the existence of the five-membered  $\kappa$  ring, as in triketriorhodin and agelaxanthins B and C, should be noted; previously this ring structure was thought to be confined to capsanthin (2.19) and capsorubin (2.20), the characteristic pigments of red peppers, but is now also found in mussels (see Chapter 5) as well as in sponges.



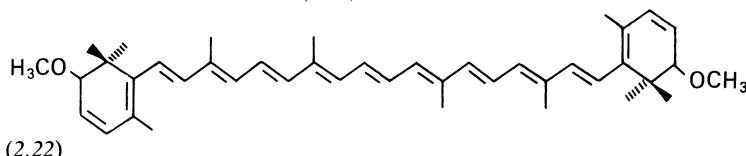
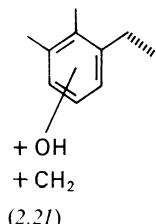


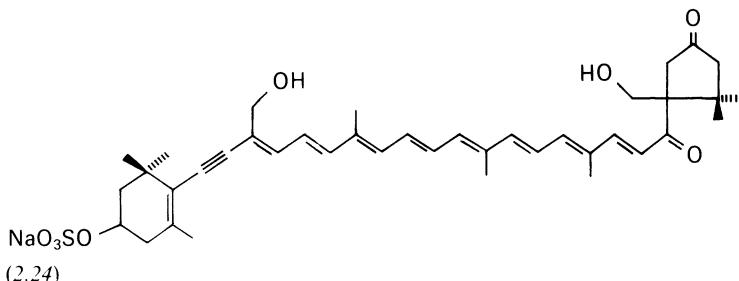
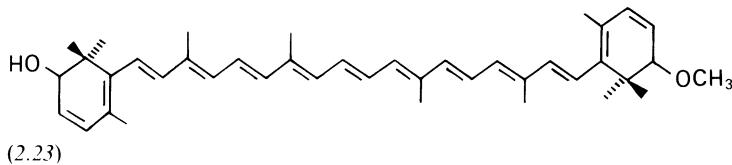
## 26 The biochemistry of the carotenoids



Phenolic carotenoids had previously only been found in one bacterium (see Vol. I) but three partly characterized monoacylcarotenoids with the end group (2.21) have recently been described in a *Ciocalypta* sp. [8].

Methoxycarotenoids were until recently considered characteristic of the purple photosynthetic bacteria, but careful examination has demonstrated their appearance in sponges; apart from agelaxanthins B and C, already mentioned, other methoxycarotenoids found in sponges have the probable structures (2.22) and (2.23) [8] and, as already indicated, the well-known photosynthetic pigment spheroidenone (2.7) has been reported under the name renieraxanthin. Finally O-sulphate esters such as bastaxanthin C (2.24) have been found in one sponge *Ianthella basta* [30]. Many of the more usual carotenoids are also present in sponges and these are listed in Table 2.1. Xanthophylls often exist in the esterified form.





Recently a blue carotenoprotein has been isolated from *Suberites domuncula* [31]; it has a mol. wt. of around 31000 and the carotenoid component is not astaxanthin but possibly a monohydroxymonoepoxy-carotenoid.

### 2.3 SOURCE OF SPONGE CAROTENOIDS

Sponges can be divided into two main groups: (i) those which accumulate food carotenoids unchanged and (ii) those which metabolize food carotenoids to other pigments which are then stored. Subgroups of (i) which can be distinguished are those containing phytoplankton (algal) pigments such as diatoxanthin (7,8-didehydrozeaxanthin), zooplankton pigments such as astaxanthin (1.1) and, possibly, pigments such as zeaxanthin (1.9) which may be derived from symbiotic fungi or bacteria [8]. The main metabolic changes which give rise to the pigments in group (ii) are aromatization of the cyclohexene rings, as in renieratene (2.2) and isorenieratene (2.3) and formation of cyclopentane rings as in agelaxanthin C.

Although aromatic carotenoids are produced by some photosynthetic bacteria (see Vol. I) there is no evidence that these organisms are the source of aromatic carotenoids in sponges [37]. Indeed evidence suggestive that they are the result of the animals' own metabolic activities comes from the isolation of pigments, such as tedaniaxanthin (2.14), which have one algal-type end group and one aryl end group. This type of structure is consistent with the view that such pigments are likely to be intermediates in the production of pigments with two aryl end groups. Furthermore, carotenoids, such as tethyatene (2.9), which have 3,4-dehydro structures, may well be intermediates in the aromatization reaction.

Although the epoxy end group of fucoxanthin is a good candidate for conversion into the  $\kappa$ -rings of agelaxanthin C (2.18), bastaxanthin C (2.24)

## 28 The biochemistry of the carotenoids

Table 2.1 Carotenoid distribution in sponges

<i>Species</i>	<i>Pigments</i>	<i>References</i>
<i>Acanthella</i> sp.	1, 2	8
<i>Acanthella vulgata</i>	49	41
<i>Agelas mauritiana</i>	2, 3, 4, 5 or 21, 6, 50, 51	21
<i>Agelas schmidtii</i>	3, 4, 6, 7, 8, 9, 10, 11, 15	20
<i>Ancorina alata</i>	1	8
<i>Alysina aerophoba</i>	1	1, 2
<i>Axinella crystagalli</i>	3, 4, 12, 13, 14	7
<i>Axinella rugosa</i>	1	4
<i>Axinella verrucosa</i>	4, 8, 15	38
<i>Callyspongia confoederata</i>	4, 7, 16	21
<i>Carteriospongia foliascens</i>	1, 4, 7	8
<i>Carteriospongia pannatula</i>	1, 7	8
<i>Chondropis</i> sp.	1, 2, 4, 7, 15, 17	8
<i>Chondrosia reniformis</i>	1	1, 2
<i>Ciocalypta</i>	1, 4, 18–20	8
<i>Clathria frondifera</i>	2, 3, 4, 5 or 21, 6	21, 25
<i>Clathria</i> spp.	1, 4, 7, 15, 17	8
<i>Clathriopsamma</i> sp.	1	8
<i>Cliona hixonii</i>	1	8
<i>Cocospongia</i> sp.	1	1, 2
<i>Crella incrustans</i>	1, 14	8
<i>Cyamon neon</i>	2, 4, 6, 15, 22	19
<i>Dysidea fragilis</i>	1	4
<i>Dysidea herbacea</i>	1, 4	8
<i>Ectyon oroides</i>	1	35
<i>Esperia foliata</i>	1	4
<i>Ficulina ficus</i>	3, 4, 12, 23, 24	33
<i>Grantia coriacea</i>	1	1, 2
<i>Halichondria albescens</i>	1	1, 2
<i>Halichondria caruncula</i>	1	1, 2
<i>Halichondria incrustans</i>	4, 35	1, 2
<i>Halichondria moorei</i>	1, 26	8
<i>Halichondria panicea</i>	1, 4	1, 2, 37
<i>Halichondria rosea</i>	4	1, 2
<i>Halichondria sanguinea</i>	1	1, 2
<i>Halichondria seriata</i>	4	1, 2
<i>Haliclona permollis</i>	4, 6, 7, 14, 25, 27	21
<i>Halma bucklandi</i>	1	1, 2
<i>Hircina spinulosa</i>	1	1, 2
<i>Hymeniacidon albescens</i>	1	1, 2
<i>Hymeniacidon penicillata</i>	3, 4, 8, 15, 28	21
<i>Hymeniacidon sanguineum</i>	3, 4, 12, 13, 14	7, 32
<i>Ianthella basta</i>	3, 4, 7, 29, 30, 31, 32	8, 30, 39
<i>Iotrochota baculifera</i>	1, 4, 15, 26	8
<i>Leuconia gossei</i>	1	1, 2
<i>Microciona prolifera</i>	2, 3, 4, 5 or 21, 6, 17, 33, 34, 35, 36	22
<i>Myxilla</i> sp.	1	1, 2
<i>Ophlitaspongia tenuis</i>	1, 6	8

<i>Species</i>	<i>Pigments</i>	<i>References</i>
<i>Pachymatisma johnstonia</i>	1	1, 2
<i>Phakellia aruensis</i>	1, 3	8
<i>Pipillina suberea</i>	1	1, 2
<i>Polymastia fusca</i>	1, 3, 4	8
<i>Polymastia granulosa</i>	1, 4	8
<i>Radiera spinolaria</i>	1	1, 2
<i>Raspailia</i> sp.	1	8
<i>Raspailia topsentii</i>	1	8
<i>Reniera aqueductus</i>	1	1, 2
<i>Reniera japonica</i>	3, 4, 8, 15, 37, 38, 39, 47	10–13, 17
<i>Rhaphidophlus typicus</i>	1, 4, 15, 30, 40, 41	8
<i>Spirastrella insignis</i>	3, 7	21
<i>Spirastrella poculooides</i>	1	8
<i>Stylorella</i> sp.	1	36
<i>Suberites domuncula</i>	3, 4, 8, 12, 14, 23, 24	7, 33
<i>Suberites ficus</i>	1	1, 2
<i>Suberites flavus</i>	1	1, 2
<i>Suberites mussa</i>	1	1, 2
<i>Tedania digitata</i>	2, 3, 4, 5 or 21, 6, 15, 47	21, 23, 24, 26, 28
<i>Tedania muggiana</i>	1	1, 2
<i>Tethya amamensis</i>	3, 4, 8, 15, 28, 42, 43, 52, 53	21, 42
<i>Tethya aurantium</i>	1	8
<i>Tethya lyncureum</i>	1	1, 2
<i>Tethyorrhaphis laevis</i>	1, 4	8
<i>Thetorium semisuberites</i>	1	5, 6
<i>Toxochalina</i> sp.	4, 7	8
<i>Trikentrion helium</i>	1, 4, 6, 7, 15	8
<i>Verongia aerophoba</i> (a)*	4, 7, 14, 16, 44, 45	34
<i>Verongia aerophoba</i> (b)†	3, 4, 7, 12, 14, 25, 27, 44, 45, 46	34
<i>Verongia</i> sp.	1	8

**Key**

- |                                      |                                      |        |
|--------------------------------------|--------------------------------------|--------|
| 1. Uncharacterized pigments          | 14. Astaxanthin                      | (1.1)  |
| 2. Tedanixanthin<br>(= Allopurpurin) | 15. Isorenieratene                   | (2.3)  |
| 3. $\alpha$ -Carotene                | 16. Isocryptoxanthin                 | (2.27) |
| 4. $\beta$ -Carotene                 | 17. Alloxanthin                      | (1.2)  |
| 5. Tedanin                           | 18. Partly characterized             |        |
| 6. Trikentriorhodin                  | 19. phenolic carotenoids             |        |
| 7. Zeaxanthin                        | 20. with end group                   | (2.21) |
| 8. Renieratene                       | 21. Clathriaxanthin                  | (2.11) |
| 9. Agelaxanthin A                    | 22. 3,4-Didehydro- $\beta$ -carotene | (2.28) |
| 10. Agelaxanthin B                   | 23. Lycopene                         | (2.29) |
| 11. Agelaxanthin C                   | 24. Torulene                         | (2.30) |
| 12. $\gamma$ -Carotene               | 25. Lutein                           | (1.10) |
| 13. Echinonone                       | 26. Peridinin                        | (2.31) |
|                                      | 27. $\beta$ -Doradexanthin           | (2.32) |

## 30 The biochemistry of the carotenoids

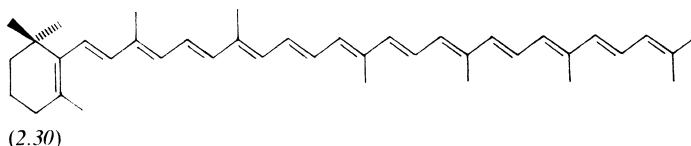
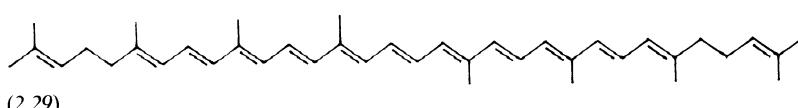
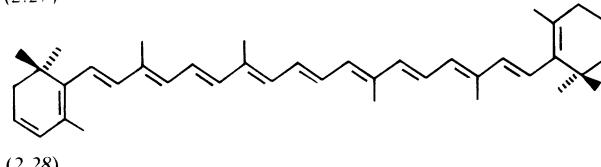
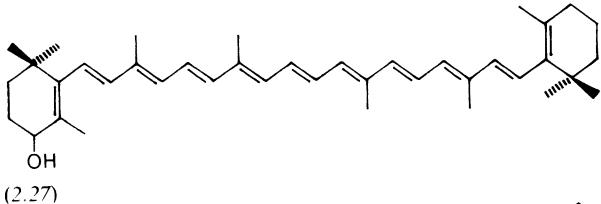
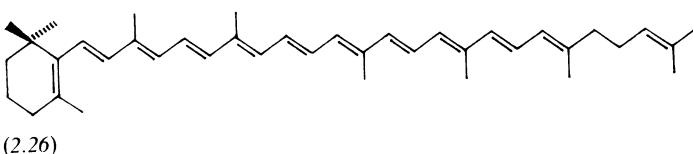
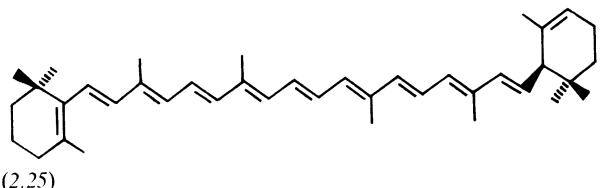
Table 2.1 cont'd

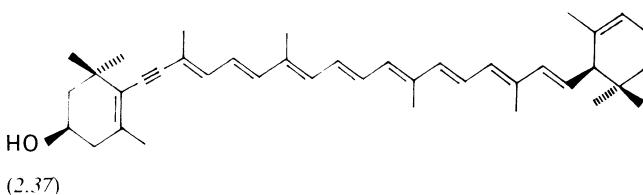
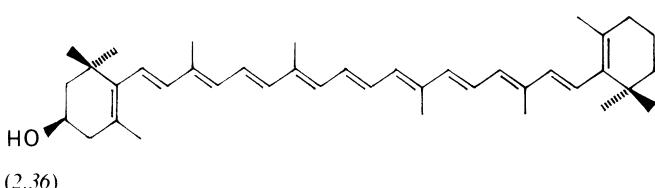
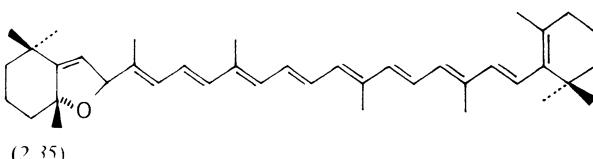
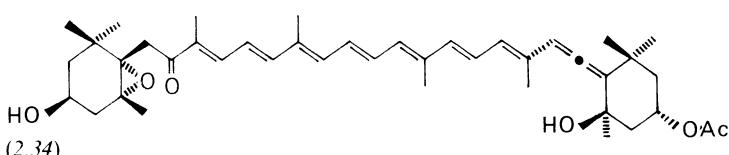
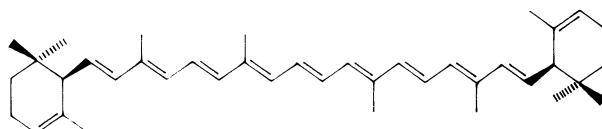
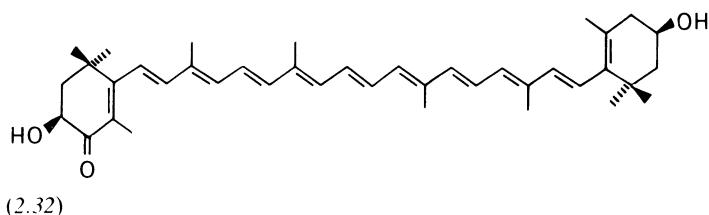
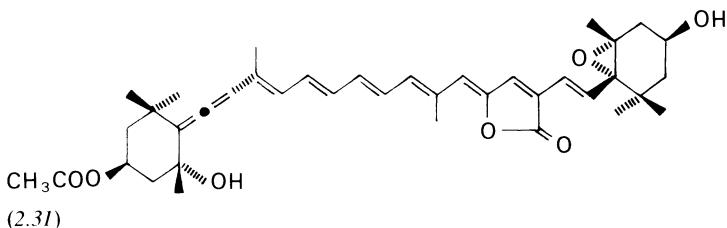
28. $\epsilon$ -Carotene	(2.33)	40. Monomethoxycarotenoid	(2.22)
29. Bastaxanthin C	(2.24)	41. Dimethoxycarotenoid	(2.23)
30. Fucoxanthin	(2.34)	42. Canthaxanthin	(1.4)
31. Mutatochrome	(2.35)	43. Tethyatene	(2.9)
32. $\beta$ -Cryptoxyxanthin	(2.36)	44. Neoxanthin	(2.39)
33. Crocoxanthin	(2.37)	45. Violaxanthin	(2.40)
34. Allobetaxanthin	(2.38)	46. Isozeaxanthin	(2.41)
35. Didehydro- $\gamma$ , $\kappa$ -carotene	(2.12)	47. Isotetradenixanthin	(2.13)
36. Triketriophidin	(2.15)	48. Mutatoxanthin	(see 7.1)
37. Renierapurpurin	(2.4)	49. Isoagelaxanthin A	(2.42)
38. 7,8-Didehydrorenieratene	(2.5)	50. Isotetadanin	(2.43)
39. 7,8-Didehydroisorenieratene	(2.6)	51. Isoclathriaxanthin	(2.44)
		52. Isorenieracistene ( <i>7-cis</i> -isorenieratene)	
		53. Renieracistene ( <i>7-cis</i> -renieratene)	

Note

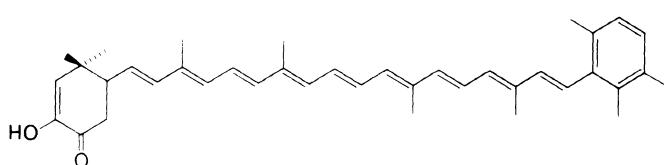
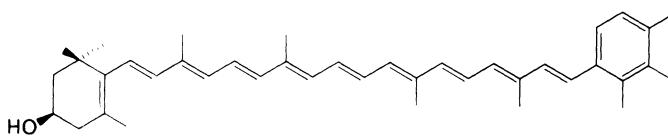
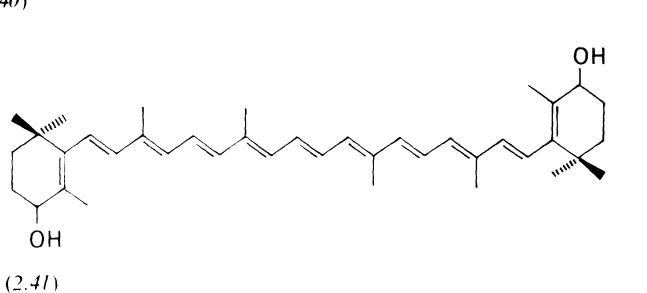
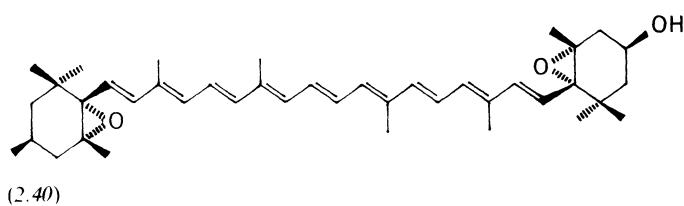
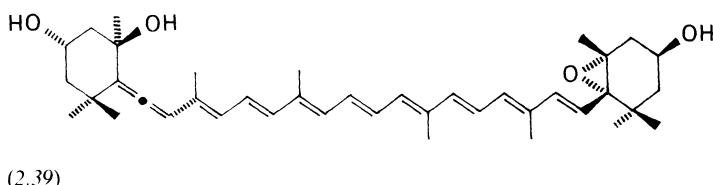
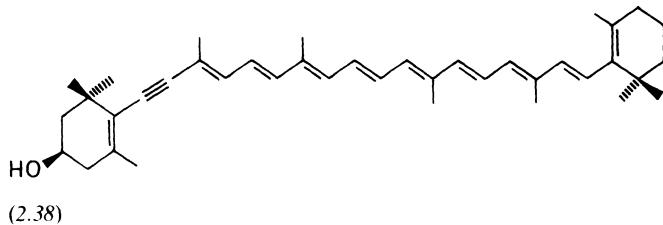
\*Specimens from off West African Coast.

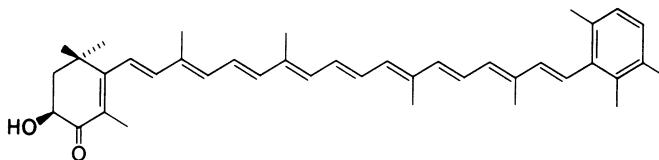
†Specimens from Adriatic sea.





## 32 The biochemistry of the carotenoids





(2.44)

and trikentriophidin (2.15), problems arise when one considers the need to envisage mechanisms to account for the conversion of the second ring of fucoxanthin into the various second ring systems of these pigments.

## 2.4 CHEMOSYSTEMATICS OF SPONGE CAROTENOIDS

The widespread distribution of aryl carotenoids amongst the various orders of sponges renders them of little chemosystematic value [8]; on the other hand the characteristic pigments tedenanin and trikentriorhodin have up to now been located only in the order Poecilosclerida (*Clathria*, *Microciona* and *Tedania*) and Axinellida (*Trikentrion*, *Agelas* spp.). Interestingly the Clathridae, although placed in the Poecilosclerida, exhibit a number of structural features which are also characteristic of some Axinellida [8].

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# [3]

## COELENTERATES

### 3.1 CLASS HYDROZOA \*

#### 3.1.1 DISTRIBUTION

The fact that hydra tend to retain the pigments of their food was known as long ago as 1744 [2] but only in the early part of this century were they recognized by histochemical studies to be carotenoid in nature [3, 4, 5]. Later a pigment with an absorption spectrum similar to that of astaxanthin (1.1) was observed in *Hydra littoralis* [6, 7]. In laboratory-grown specimens of the same polyp fed on *Artemia salina* the main pigment (92.4%) was canthaxanthin (1.4). [This is also the main pigment of *A. salina* (see Chapter 6).] Small amounts of echinenone (1.11) and 4-keto-4'-hydroxy- $\beta$ -carotene together with traces of unidentified xanthophylls were also present [8]. *H. attenuata*, *H. circumcinta* and *H. fusca* fed on *A. salina* and lake plankton accumulated astaxanthin esters as well as canthaxanthin and unidentified pigments [9], whilst *H. vulgaris* fed on *Ceriodaphnia reticulata* maintained on *Chlorella vulgaris* contained astaxanthin, both free and esterified, canthaxanthin and pirardixanthin [8]. The last-named pigment is a carotenoid of unknown structure which, together with hydroxy and keto derivatives, makes up some 62% of the total pigment in *H. pirardi*-fed *A. salina* [8]; small amounts of canthaxanthin were also present. *Chlorohydra viridissima*, which looks colourless when grown on a diet of *A. salina*, yields small amounts of canthaxanthin on extraction (less than 2% of that in *Hydra littoralis*) [8].

The first report of carotenoids in the sub-order Filifera (which now contains the hydrocorals) came in 1925 when Teissier [10] detected them in the eggs of *Clava squamata*. Much more recently astaxanthin has been detected in the skeletons of the purple *Allopora californica*, the scarlet

\*Classification of Bouillon [1].

## 36 The biochemistry of the carotenoids

*Distichopora violacea*, the pink *D. coccinea*, the orange *D. nitida*, the purple *Styloster roseus*, the pale pink *S. sanguineus* and the pink and orange *S. elegans* [11, 12]. In *S. elegans* astaxanthin is accompanied by a neutral carotenoid, probably zeaxanthin (1.9) [9]. Astaxanthin exists as a blue carotenoprotein, alloporin, finely distributed throughout the aragonite skeleton of the coral. Alloporin has an absorption maximum of 545 nm and contains one molecule of astaxanthin per molecule of protein, which has a molecular weight of around 68 000 and is made up of four probably identical subunits [51]. (See Chapter 1 for further details.)

Apparently no carotenoids are present in *Setularella*, *Aglaeophenia* and *Lafoea* spp. [13], although a somewhat later report suggests their presence in *Aglaeophenia* [14].

Lipochromes were first observed in *Tubularia* spp. in 1880 by McMunn [15] and shown to be carotenoids in *T. larynx* and *T. indivisa* in the 1930s [16, 17].

The existence of blue pigments which could be converted into red pigments was first described in *Velella* and *Porpita* in 1883 by Merejkowski [18] and the pigment of *Velella spirans* was also studied in the earlier part of this century [19, 20]. In the late 1940s S. C. Crane in D. L. Fox's laboratory first suggested that the prosthetic group was astaxanthin (1.1) [see reference 21]. Much more recently this has been confirmed [22, 23]. The mantle complex of *V. lata* has a different absorption maximum (585–588 nm) from that extracted from the tentacles [19]. The complex from *V. velella* has been examined in detail [23]. The native protein has an absorption maximum at 620 nm but four components  $\lambda_{\text{max}}$  620, 600, 570 and 545 nm are obtained by gel filtration of extracts. The detailed properties of these complexes are considered in Chapter 1.

### 3.1.2 FORMATION

*H. littoralis* probably accumulates canthaxanthin from its diet of *Artemia salina*, but it is still uncertain whether or not *H. pirardi* synthesizes pira-dixanthin from canthaxanthin and the uncertainty will remain until the structure of this pigment is known [8].

The carotenoid in the eggs of *Clava squamata* occurs as a carotenoprotein and during the development of the embryo the free pigment is released from this complex [24].

## 3.2 CLASS SCYPHOZOA

There are few positive reports of carotenoids in this class although the yellow and red ovaries and testes of *Aurelia flavidula* (*A. aurita*) [25, 26] are said to contain  $\beta$ -carotene (1.5), echinenone (1.11), canthaxanthin (1.4), astaxanthin (1.1), isocryptoxanthin (2.27) and zeaxanthin (1.9) [54].

### 3.3 CLASS ANTHOZOA

#### 3.3.1 SUB-CLASS ALCYONARIA

Early work has indicated that carotenoids are present in a number of alcyonarians *viz.* *Eunicella verrucosa* [27], *Alcyonium digitatum*, *Stenogorgia rosea*, *Pennatula phosphorea* (sea pen) and *Funiculina quadrangularis* [17]. The major pigment in *Alcyonium digitatum* has more recently been established as astaxanthin (1.1); also present are small amounts of the mono- and di-acetylenic derivatives (asterinic acid), a mixture of 1.6 and 1.7 [28]. On the other hand no carotenoids were found in the bright yellow-violet-red pigments of *Heliopora caerulea*, *Corallium rubrum*, *Tubipora musica* [29] or *Alcyonium palmatum* [30]. *Eugorgia ampla* (sea fan) contains an acidic carotenoid eugorgiaenoic acid, the structure of which is unknown [31]. The main pigment of the horny corals *Paragorgia arborea* and *Primnoa resedae formis* is astaxanthin whilst that of the stone coral *Paramuricea* sp. is canthaxanthin (1.4) [28]. Astaxanthin, however, is the main pigment of another stone coral *Lophelia pertusa* [28].

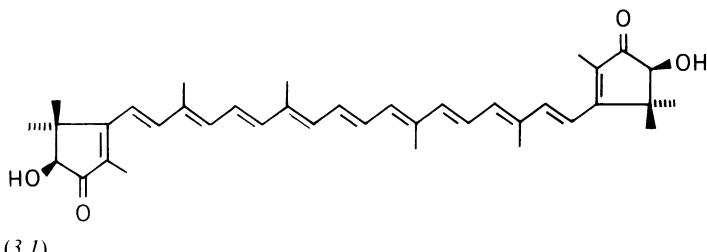
#### 3.3.2 SUB-CLASS HEXACORALLARIA

##### (a) Distribution

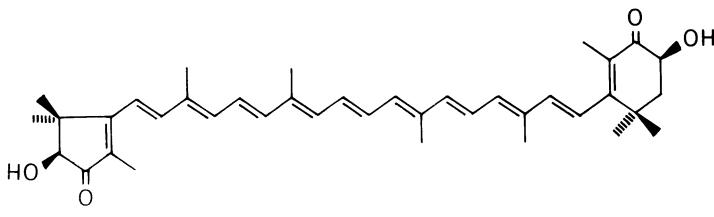
The sea anemone *Actinia equina* has been studied in some detail following the discovery that apart from  $\alpha$ - and  $\beta$ -carotenes (2.25 and 1.5) a red carotenoid named actinioerythrin was the major pigment of the red variants of this animal [32, 33] and that it was present complexed to a protein. These observations were repeatedly confirmed [34–38] and eventually it was shown that actinioerythrin consists of a mixture of several fatty acid esters (the length of the fatty acid varying from  $C_6$  to  $C_{12}$ ) of the alcohol actinioerythrol (3.1) which was identified as 2,2'-bisnorastaxanthin [37] with the absolute configuration, 3S,3'S [39, 40]. Two minor components have been identified as diesters of astaxanthin and 2-norastaxanthin (3.2) [41]; the chirality of the latter has not yet been determined. 2-Norastaxanthin has also been found in *A. tenebrosa* [42]. There are brown and green variants of *A. equina* which do not synthesize actinioerythrin but another pigment [32, 33] which has not been clearly identified. In some specimens from the North Sea astaxanthin esters replace actinioerythrin as the major pigment [38]. Three colour morphs of *Bunodosma granulifera* and *B. cavernata* contain diesters of astaxanthin, 2-norastaxanthin and 2,2'-bisnorastaxanthin in varying proportions [43, 44].

Actinioerythrin has been observed in *Tealia felina* [34], *Epiactis prolifera* [41], *Gyrostoma* sp. [55] and *Bolocera tuediae* [28] and astaxanthin is also found in *T. felina* and *E. prolifera* and *Actinostola callosa* [41] and in

## 38 The biochemistry of the carotenoids



(3.1)



(3.2)

*Metridium senile* [45]. The earlier reported metridene (metridioxanthin) in *M. senile* [45–47] is adonirubin (1.8) [48]. *A. callosa* also accumulates zeaxanthin (1.9) in the ester form [40].

The carotenoid sulcatoxanthin, isolated from *Anemonia sulcata* [34], is known to be identical with peridinin (2.31) [49], a characteristic pigment of dinoflagellates (Volume I, Chapter 7). Clearly the pigment in *A. sulcata* arises from the accompanying commensal algae but it is not known whether that isolated came mainly from the algae or from stored pigment in the animal. The same situation obtained in the Pacific-Coast anemone *Cribrina xanthogrammica* [49].

### (b) Formation

Little experimental work has been done on this aspect of the biochemistry of sea anemones but the general view must be that carotenoids are obtained from the diet and appear in the tissues through selective absorption and/or accumulation. Limited metabolic modification can also occur. Over forty years ago it was elegantly demonstrated that the pigmentation of the colour variants of *A. equina* was of dietary origin [50]. Specimens raised from eggs on a carotenoid-free diet were unpigmented but quickly became pigmented when fed a shrimp (astaxanthin) diet. The colour assumed was that of the parent animals. In the case of *M. senile* the pigmentation is more stable, for no colour changes were observed after long periods on a carotenoid-free diet [46]. The indication from the early work on the red variants of *A. equina* is that astaxanthin can be converted into actinioerythrin and the elucidation of the structure of the latter [37] makes the possibility even more reasonable, and the pathway indicated in Fig. 3.1 has been suggested [51]; it involves a

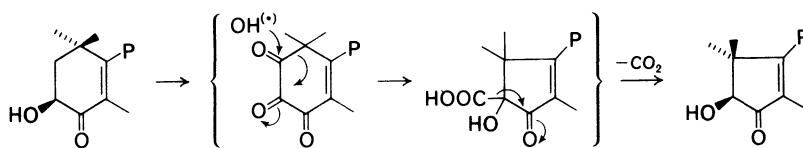


Fig. 3.1. The probable pathway for ring contraction of keto carotenoids in sponges.

benzylic acid rearrangement followed by loss of C-2 as  $\text{CO}_2$ . This has still to be investigated experimentally but support for a stepwise process in which ring contraction occurs sequentially at one and then the other end of the molecule comes from the recent isolation of the putative intermediate 2-norastaxanthin (3.2), in which only one cyclohexene ring has undergone ring contraction [41].

*M. senile* has only very limited ability to transform dietary carotenoids. It will convert canthaxanthin (1.4) into astaxanthin (1.1), but no other of a considerable number of carotenoids investigated was an astaxanthin precursor [52].

Early observations suggested that high light intensity increased the pigmentation of *Anemonia* spp. and of *T. felina* [53]. From what is now known of the existence of commensal algae in the animals a possible explanation of the phenomenon becomes apparent; it is probably due to stimulation of growth of the algae under high light intensity.

### (c) Function

Nothing of real significance is known about the function of carotenoids in sea anemones; even participation in adaptive coloration has been ruled out in *Metridium* [46].

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## [4]

# ECHINODERMATA, ANELIDA, SIPUNCULIDA, PRIAPULIDA, PLATYHELMINTHES AND BRYOZOA

### 4.1 ECHINODERMATA

The older descriptive studies on echinoderm pigments date back to 1881 and continued to the 1930s [1–9]. Many species were examined and shown to contain ‘lipochromes’ either as such or in a water-soluble (protein) complex which liberated the lipochromes on heating or treatment with ethanol.

#### 4.1.1 ASTEROIDEA

In 1881 it was reported [1] that 20 species of echinoderms contained ‘zooerythrine rouge’. However it was not until 1934 that chemical examination of the pigments began. The first identification was that the major pigment of *Ophidiaster ophidianus* was astaxanthin (1.1), isolated as its oxidative artefact astacene (2.1) [10]. Since then astaxanthin has been demonstrated in many other asteroids (Table 4.1).  $\beta$ -Carotene (1.5) is generally present in small amounts [14] as are echinenone (1.11),  $\beta$ -cryptoxanthin (2.36), zeaxanthin (1.9), canthaxanthin (1.4),  $\alpha$ -cryptoxanthin (4.1), lutein (1.10) and diatoxanthin (4.2) [25, 26] (Table 4.2) [17]. Smaller amounts of other pigments have been reported, in particular asteroidenone and hydroxy-asteroidenone, in *O. ophidianus*, *Asterina panceri*, *Astropecten aurantiacus* and *Marthasterias glacialis* [26]. The structures of these pigments have not been unequivocally settled but they are considered to be 3-hydroxy-4'-oxo- $\beta$ -carotene and 3,3'-dihydroxy-4-oxo- $\beta$ -carotene respectively; that is they are hydroxylated derivatives of echinenone.

One of the first pigments to be isolated from a starfish *Asterias rubens* was asterinic acid [15]. A re-examination of the original sample revealed it as being a mixture of the mono- and di-acetylenic derivatives of astaxanthin, that is 7,8-didehydro- and 7,8,7',8'-tetradehydro-astaxanthin (1.6, 1.7), with the absolute configuration indicated [27, 28]. In one sample the relative amounts of astaxanthin (1.1), (1.6) and (1.7) were 5–10%, 25–40% and 50–65% respectively [29]. Optical isomers of these pigments are also

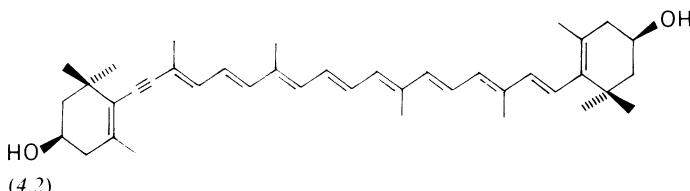
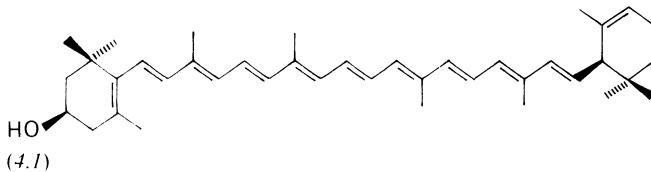
Table 4.1 Asteroids in which astaxanthin has been demonstrated as the dominant carotenoid

Name	Reference
<i>Amphiura filiformis</i>	1
<i>Asterina panceri*</i>	12
<i>Asterina pectinifera*</i>	13
<i>Astrometus sertulifera</i>	14
<i>Astropecten aurantiacus*</i>	15
<i>Astropecten californicus</i>	16
<i>Coscinasterias tenuispina</i>	17
<i>Crossaster (Solaster) papposus*</i>	18, 19
<i>Echinaster sepositus*</i>	20, 21
<i>Henricia sanguinolenta<sup>†</sup></i>	17
<i>Marthasterias gracilis</i>	17, 20, 22, 23
<i>Ophidiaster ophidianus<sup>‡</sup></i>	10
<i>Patiria miniata</i>	16
<i>Piaster giganteus*</i>	16
<i>Piaster ochraceous</i>	16
<i>Porania pulvillus</i>	18
<i>Solaster endica*</i>	18, 24

\* The pigment occurs as a carotenoprotein.

<sup>†</sup> Astaxanthin (1.1) about equal in amount with  $\beta$ -carotene (1.5).

<sup>‡</sup>  $\gamma$ -Carotene (2.26) also reported.



present (see Chapter 1 for details). A number of species known to contain mixtures of unidentified carotenoids are summarized in Table 4.3. It is significant that in *Henricia* spp., which are detritus feeders and not predaceous carnivores, as are most sea stars, astaxanthin is by no means the major pigment [31]. The carotenoids of the sea stars accumulate in the skin generally in the form of carotenoproteins (see Table 4.1 and Chapter 1)

## 44 The biochemistry of the carotenoids

Table 4.2 Carotenoid distribution in *Marthasterias tenuispina* [17]

Pigment	Percentage of total pigments
$\beta$ -Carotene (1.5)	5.2
Echinonone (1.11)	4.8
$\beta$ -Cryptoxanthin (2.36)	1.5
Lutein (1.10)	1.7
Lutein 5,8-epoxide	6.0
4-Hydroxy-4'-oxo- $\beta$ -carotene	11.3
Zeaxanthin (1.9)	29.5
Astaxanthin ester	3.0
Astaxanthin (1.1)	33.0
3,4-Didehydro- $\alpha$ -carotene(?)	4.0

which can vary in colour from green to red and violet [32]. It is likely that in the majority of cases the prosthetic group is astaxanthin but this is not always so as for example in *Asterias rubens* and *Henricia* spp. in which 'asterinic acid' (1.6, 1.7) and unidentified compounds are involved. The skin-colour in colour variants of *Patiria miniata* depends on the concentration of astaxanthin in the skin relative to other carotenoids, the ratio varying from 51:40 to 80:19 in passing from orange to purple specimens [31]. Males of *Henricia leviscula* are generally darker skinned than females [31]. Pigments tend to accumulate in the pyloric caeca as well as the ovaries [32].

Table 4.3 Asteroids containing unresolved mixtures of carotenoids

Name	Reference
<i>Aphelasterias japonica</i>	30
<i>Asterias anurensis</i>	30
<i>Asterias glacialis</i>	5-8
<i>A. mülleri</i>	5-8
<i>Asterina pectinifera</i>	30
<i>Astropecten irregularis</i>	5-8
<i>Dipascaster pretiosa</i>	5-8
<i>Henricia annectens</i>	31
<i>H. leviscula</i>	31
<i>H. palespina</i>	31
<i>Hippasteria phrygiana</i>	5-8
<i>Luidia sarsii</i>	5-8
<i>Solaster borealis</i>	29, 30

### 4.1.2 OPHIUROIDEA

The brittle stars have not yet been examined in great detail by modern

Table 4.4 Ophiuroids known to contain carotenoids

Name	Reference
<i>Amphipholis squamata</i>	11
<i>Amphiura chiajei</i>	7
<i>Ophiocomina nigra</i>	7, 33
<i>Ophioderma longicauda</i>	2
<i>Ophiothrix aculeata</i>	7, 11
<i>Ophiopteris papillosa</i>	16
<i>Ophiothrix fragilis</i>	7, 11
<i>O. rufus</i>	16
<i>O. spiculata</i>	16
<i>Ophiura texturata</i>	7

techniques. Carotenoids are present in the animals listed in Table 4.4. One pigment in *Ophiopteris papillosa* was very similar to pectenoxanthin [14], a molluscan pigment now known to be identical with the acetylenic carotenoid alloxanthin (1.2) (see Chapter 5). The major pigment in *Amphipholus squamata* and *Ophiothrix aculeata* is 'asterinic acid' (a mixture of 1.6 and 1.7) and in *Ophiothrix* it is astaxanthin (1.1) [11].

A pioneering report suggests that the carotenoid (lipochrome) in *Ophioderma longicauda* is in the form of a brown carotenoprotein [2].

#### 4.1.3 HOLOTHUROIDEA

Carotenoids have been found in various tissues of a number of holothurians (Table 4.5) but again definitive modern work is lacking. Echinonone (1.11)

Table 4.5 Holothurians known to contain carotenoids

Species	Tissue	Reference
<i>Cucumaria elongata</i> *	—	9
<i>Cucumaria lactea</i>	Gonads	9
<i>Cucumaria lubrica</i>	—	31
<i>Holothuria forskali</i>	Mesentery, intestine, gonads	34
<i>Holothuria nigra</i>	blood, 'liver'	4
<i>Holothuria polii</i>	Ovaries, blood vessels	3, 34
<i>Holothuria tubulosa</i>	Mesentery, intestine, gonads	1, 34
<i>Mesothuria* intestinalis</i>	Ovaries	9
<i>Ocnus brunneus</i> *	—	9
<i>Phyllophorus pollucidus</i>	—	9
<i>Psolus fabricii</i>	—	—
<i>Psolus phantalus</i>	—	9, 35
<i>Stichopus parvimensis</i>	—	16
<i>Thyone fusus</i> *	—	9

\*Indicates presence of carotenoproteins.

## 46 The biochemistry of the carotenoids

may be present in the integument of *Stichopus tremula* [16] and astaxanthin (1.1) in *Cucumaria lubrica* [31].  $\beta$ -Carotene (1.5), echinenone (1.11), canthaxanthin (1.4) and astaxanthin (1.1) have been obtained from the testes and gonads of *Holothuria leucospilota*; the concentration of total carotenoids is 3  $\mu\text{g/g}$  and 10  $\mu\text{g/g}$  in the testes and ovaries respectively [36]. Early work somewhat unexpectedly suggests that carotenes tend to preponderate over xanthophylls.

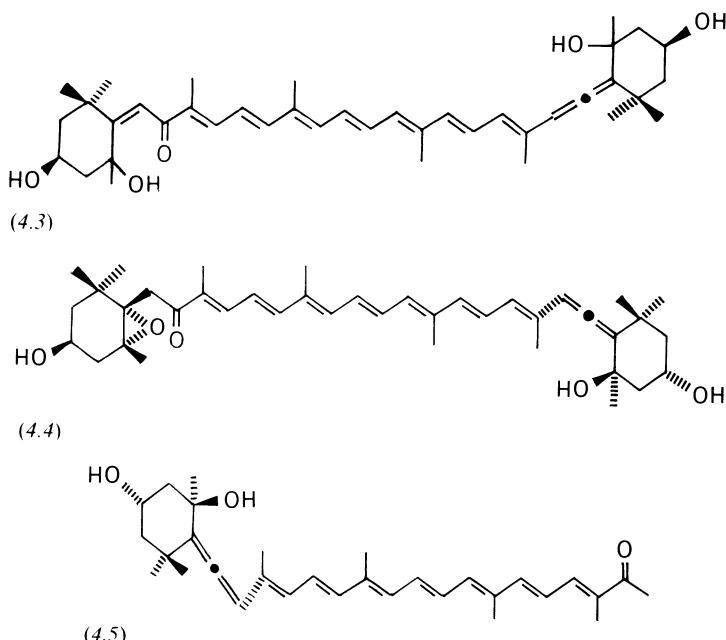
### 4.1.4 CRINOIDEA

Carotenoids have been observed in *Antedon rosacea (bifida)* by some workers [4, 37] but not by others [20, 38]. They have also been noted in *A. petasus* [5, 9, 11]. Positive identifications of echinenone (1.11), canthaxanthin (1.4) and astaxanthin (1.1) were made in *Florometra serretissima* [39]. These represented the major pigments which were accompanied by a smaller amount of  $\beta$ -carotene (1.5), zeaxanthin (1.9) and lutein (1.10). Small amounts of a complex mixture of carotenoids were observed in the calyx (20  $\mu\text{g/g}$ ) and arms (50  $\mu\text{g/g}$ ) of *Lamprometra kluzingeri* [40]. The main components of the yellow colour of crinoids are however anthraquinones.

### 4.1.5 ECHINOIDEA

With the exception of the Asteroidea this class has been examined in more detail than other classes of the Echinodermata. Echinenone (1.11), now known to be identical with myoxanthin and aphanin [37] (see Volume I), was first isolated from the gonads of *Paracentrotus (Strongylocentrotus) lividus* [31, 41, 42, 43]. It has also been found in the gonads of *Dendraster excentricus* [43], *Echinocardium cordatum* [44], *Lytechinus pictus* [16], *Sphaerechinus granularis* [21, 39], *Strongylocentrotus purpuratus* [16], *S. dröbachiensis* [45], *Hemicentrotus pulcherrimus* [13] and *Tripneustes gratila* [46]. It is also present in whole animals of *Dendraster excentricus* and *Strongylocentrotus franciscanus* [16].  $\beta$ -Carotene (1.5) is usually present (in one species, *Echinocardium cordatum*, it is the major carotenoid [11]) and so are other xanthophylls. The amounts of  $\beta$ -carotene plus echinenone are always greater than the remaining xanthophylls which, except in one case, have not been fully identified but are probably mainly derived from the marine algal plankton which the animals eat [39]. In particular pentaxanthin isolated from *P. lividus* [38] is isofucoxanthinol (4.3) [47]; it may have been produced artefactually from fucoxanthinol (4.4), a metabolite of the algal carotenoid fucoxanthin (2.34) (see Volume I). Indeed fucoxanthinol and another possible metabolite paracentrone (4.5) have been isolated from the coelomic epithelium of *P. lividus* [47]. Two other pigments of undetermined structure paracentrotins A and B have been reported in the ovaries and eggs

of *P. lividus*; they are however absent from the testes of these animals [48]. Astaxanthin (1.1) has been reported in *P. lividus* and *Sphaerechinus granularis* [39] and in *Echinocardium cordatum* and *Spatangus purpureus* [11], and *Peronella japonica* [49]; it is the major pigment of *Spatangus purpureus*. Compared with violet forms of *P. lividus*, the green forms contain no echinenone (1.11),  $\beta$ -cryptoxanthin (2.36) or zeaxanthin (1.9) [39]. The pigments in the ovaries of *H. pulcherrima* are in the form of carotenoproteins [13].



#### 4.1.6 FORMATION, METABOLISM AND FUNCTION

Little is known about the formation of carotenoids in echinoderms and our information is still to a great extent based upon classical work published in 1941 [16]. The herbivorous echinoids, crinoids and holothuroids accumulate on average five times less carotenoid than the carnivorous asteroids and sphaeroids. Hydroxylated carotenoids predominate in the carnivores and carotenes plus echinenone in the herbivores. Male *Dendraster* accumulate more carotenoids than do females and this is more marked in the xanthophyll fraction than the carotene fraction. Generally the ovaries contain far more pigment than the testes but the opposite situation was noted in *Strongylocentrotus franciscanus*. In spite of the mobilizing of carotenoids into the testes the spermatozoa are colourless.

In *S. dröbachiensis* up to 85% of the total carotenoids occurs in the ovaries. The detection of isocryptoxanthin (2.27) in the ovary of *S.*

## 48 The biochemistry of the carotenoids

*dröbachiensis* but not in the gut wall suggests that echinenone is formed from  $\beta$ -carotene via isocryptoxanthin in the ovary rather than in the gut wall [45]. Echinenone is preferentially incorporated into the eggs of *S. dröbachiensis* and into the unfed larvae of *Psammechinus miliaris* [49].

### 4.2 ANNELIDA

The annelida are characterized by the number of porphyrin pigments which they produce (see [50] for a review) but their carotenoids, if they exist, have only been given cursory examination. They are found extensively only in the class Polychaeta and in most cases have not been fully characterized (Table 4.6). Most of the orders within the class Polychaeta are characterized by the accumulation of mainly  $\beta$ -carotene (1.5); the exceptions seem to be found within the order Sabellida in which astaxanthin (1.1), sometimes together with an unidentified ketocarotenoid, preponderates over  $\beta$ -carotene.

Four species of leech (order Hirudinea) have been reported to contain astaxanthin (1.1) [57].

### 4.3 SIPUNCULIDA

Lipochromes are present in the digestive juice of *Siphonostoma diplochaitos* [3] and carotene in *Golfingia* (*Phascolosoma*) *elongata* [9].

### 4.4 PRIAPULIDA

The only species reported to contain carotene is *Priapulus caudatus* [5].

### 4.5 PLATYHELMINTHES

In the class Turbellaria lipochromes were reported in a flat worm *Turbellaria* sp. [4]. The carotenoids in certain Polycladida are said to be derived from the Ascidia which they parasitize [58].

$\beta$ -Carotene (1.5), echinenone (1.11) and lutein (1.10) have been reported in the trematode *Fasciola hepatica* (class Trematoda) [59].

### 4.6 BRYZOZA

Lipochromes were early reported in the epidermis of *Bugula neritina* [3] but later work failed to substantiate the presence of carotenoids in this animal; furthermore they were not present in *B. flabellata* [60]. Carotenes were the main pigments in *Schizoporella unicornis*, *Steganoporella magnilabris* and *Trigonospora* sp.; however, some xanthophyll esters are present in the last-named species [60]. On the other hand the main pigment of *Lepralia foliacea* and *Flustra foliacea* might well be related to astaxanthin (1.1) [60].

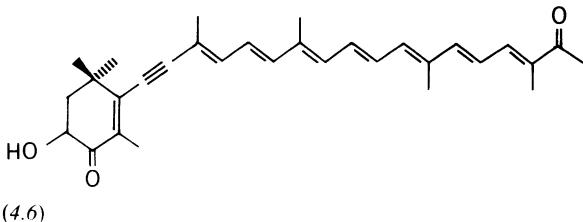
Table 4.6 Carotenoids in Polychaeta

<i>Species</i>	<i>Pigments</i>	<i>Reference</i>
<b>Phyllodocida</b>		
<i>Aphrodite</i>	Present	5
<i>Glycera goessii</i>	$\beta$ -Carotene (1.5) & lutein (1.10)	5
<i>Harmothoe sarsis</i>	Carotene*	9
<i>Laetmonice filicornis</i>	Carotene	9
<i>Nephthys caeca</i>	Lipochromes	4
<i>Nephthys ciliata</i>	$\beta$ -Carotene	5
<i>Nereis pelagica</i>	Carotene	5
<i>Nereis virens</i>	$\beta$ -Carotene	5
<i>Nereis zonata</i>	Numerous	62
<i>Polynome spinifera</i>	Lipochromes	4
<b>Capitellida</b>		
<i>Arenicola piscatorum (marina)</i>	Lipochromes	4
<i>Thoracophelia (Euzorus) mucronata</i>	$\beta$ -Carotene (1.5)	51, 52
<b>Spionida</b>		
<i>Chaetopterus</i>	$\beta$ -Carotene (1.5)	53
<b>Eunicida</b>		
<i>Eunice</i> sp.	Carotenoids	9
<i>Lubriconereis fragilis</i>	$\beta$ -Carotene (1.5)	5
<b>Trebellida</b>		
<i>Neoamphitrite agulus</i>	Carotenoids†	5, 53, 54
<i>Neoamphitrite figulus</i>	$\beta$ -Carotene (1.5)	5
<i>Terebellides stroemii</i>	Carotene	9
<i>Thelepus cincinnatus</i>	Carotene	5
<b>Flabelligerida</b>		
<i>Flabelligera diplochaitus</i>	Carotenoids as protein complex	3
<b>Sabellida</b>		
<i>Chone infundibuliformis</i>	$\beta$ -Carotene (1.5), astaxanthin (1.1)	56
<i>Eudistyla polymorpha</i>	$\beta$ -Carotene (1.5), astaxanthin (1.1)	56
<i>E. vancouveri</i>	$\beta$ -Carotene (1.5), astaxanthin (1.1)	56
<i>Melgalomma (Branchiomma) vesiculosum</i>	$\beta$ -Carotene (1.5), astaxanthin 1.1	56
<i>Myxicola infundibulum</i>	$\alpha$ , $\beta$ -Carotene (2.25, 1.5), astaxanthin (1.1), ketocarotenoid	55, 56
<i>Pomatoceros triqueter</i>	$\beta$ -Carotene (1.5), astaxanthin (1.1)	56
<i>Protula intestinalis</i>	$\beta$ -Carotene (1.5), astaxanthin (1.1)	56
<i>Pseudopotamilla occelata</i>	Astaxanthin (1.1)	56
<i>Sabella penicillatus</i>	$\beta$ -Carotene (1.5), isocryptoxanthin (2.27), echinenone (1.11), 4'-hydroxyechinenone, canthaxanthin (1.4), zeaxanthin (1.9), lutein (1.10)	55
<i>Sabella spallanzani</i>	$\alpha$ , $\beta$ -Carotene (2.25, 1.5)	54, 56

\*‘Carotene’ indicates that isomers were not identified.

†Part of the pigment present as a carotenoprotein.

## 50 The biochemistry of the carotenoids



(4.6)

The pink *Eurystomella bilabiata* accumulates the apo-carotenoid hopkinsiaxanthin (4.6) as its major carotenoid pigment [61].

### 4.7 FORMATION AND METABOLISM

Apart from the Echinodermata (see Section 4.1.6), there is no evidence that the majority of animals in all the Phyla just discussed do other than specifically accumulate  $\beta$ -carotene (1.5) from their food. This was experimentally demonstrated in the case of *Thoracophelia mucronata* [51]. The exceptions would appear to be the order Sabellidae, members of which accumulate astaxanthin (1.1) or canthaxanthin (1.4), and one member, *Neoamphiprute figulus*, of the order Terebellida (Annelida) which can convert dietary  $\beta$ -carotene in the coelomocytes into an astaxanthin-like compound. The reality of the specific absorption of carotenoids in this animal was demonstrated by the fact that dietary lycopene never appeared in the coelomocytes [56].

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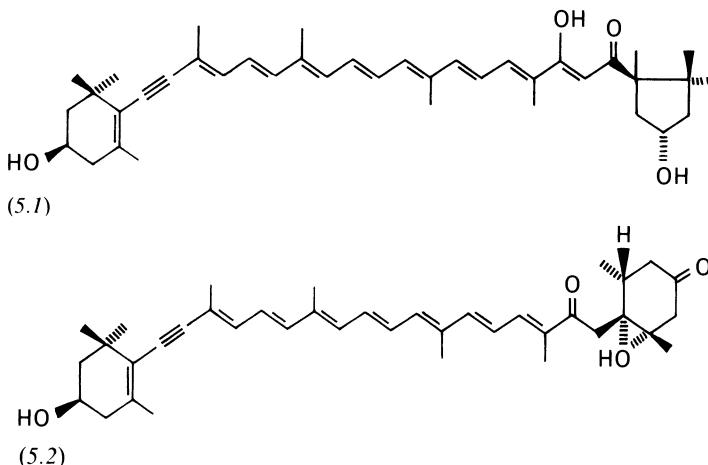
## MOLLUSCA

### 5.1 PELECYPODA (BIVALVIA, LAMELLIBRANCHIA, ACEPHALA)

#### 5.1.1 NATURE AND DISTRIBUTION

Early work [1] showed that a number of Pelecypoda gave positive tests for carotenoids but it was not until the 1930s that the pigments were examined with any chemical rigour.

The gonads of *Pecten maximus* contain a characteristic xanthophyll pectenoxanthin [2] which was eventually shown to be the acetylenic carotenoid alloxanthin (1.2) [3] and it thus must have originated as a component of the animal's algal food (see Volume I). Pectenolone, which accompanies pectenoxanthin in *P. maximus*, is 4'-ketodiatoxanthin (1.3) [3] and is clearly a metabolite of dietary diatoxanthin (4.2). The structure of glycymerin, the xanthophyll characteristic of the gonads of the scallop *Pectunculus glycymeris* [4], has not yet been clarified but it is probably closely related to if not identical with pectenolone [5]; *Mytilus californianus* contains the unique pigments mytiloxanthin (5.1) and isomytiloxanthin (5.2) whose structures emerged as indicated [7]. The pigment reported in *M. californianus* as zeaxanthin (1.9) may well turn out to be the acetylenic diatoxanthin when it is re-examined using modern techniques. The 'zeaxanthin' content of the animals increased when they were fed *Nitzschia closterium* [6], a diatom rich in diatoxanthin (see Volume I). The level of mytiloxanthin also increased on feeding *N. closterium* so this pigment also probably arises by oxidative metabolism of diatoxanthin. The pigment pectenol (3,4,3'-trihydroxy-7',8'-didehydro- $\beta$ -carotene) found in a number of molluscs [20, 54] is also clearly a metabolite of diatoxanthin. Astaxanthin (1.1) was reported in *Pleurobranchus elegans* [8] and in the feet of *Lima excavata* [9]; in both cases the pigment was isolated as its artefact astacene (2.1). A survey of a large number of Pelecypoda was undertaken in 1956 [10] but the xanthophylls were not identified. The known distribution of carotenoids in marine



Pelecypoda is given in Table 5.1. Carotenoids exist as chromoproteins in the neurones of *Mytilus* sp. [23].

Very few fresh-water Pelecypoda have been examined but the information available is collected in Table 5.2. In *Anodonta cygnea* carotenoids accumulate in the neurones [27, 28] where they can reach a concentration as high as 10 mg/100 g of wet tissue [29].

### 5.1.2 FORMATION AND METABOLISM

It has already been indicated in the previous section that Pelecypoda carotenoids arise from the food; frequently the unchanged pigments tend to accumulate as in the case of alloxanthin (1.2) (pectenoxanthin). However the discovery of pectenolone (1.3) and its structural elucidation indicates that in *Pecten maximus*, at least, oxidation of the food carotenoids can take place with the insertion of a keto group. This is a reaction reminiscent of that which occurs in many other marine invertebrates, particularly the crustaceans (see Chapter 6).

The only detailed study of carotenoid metabolism in Pelecypoda is that of Scheer in 1940 [6] on *Mytilus californianus*. No marked seasonal variations in carotenoid levels were noted nor did the concentration drop on prolonged fasting. On a diet of carotenoid-rich *Nitzschia closterium* levels gradually increased but a carotenoid-free diet resulted in a greater loss than that observed in starving animals. After the animals have spawned the carotenoids in the spent ova are qualitatively and quantitatively the same as in the ripe gonads but the total amount in the spent gonads plus that in the eggs does not reach the total found in the ripe gonads. A characteristic of mussels is the high concentration of xanthophylls relative to carotenes and there is evidence from Scheer's work that the animals preferentially absorb food xanthophylls from the intestinal tract.

## 54 The biochemistry of the carotenoids

Table 5.1 Marine Pelecypoda reported to contain carotenoids

<i>Species</i>	<i>Pigments</i>	<i>References</i>
<i>Anadara broughtoni</i>	2, 3, 6, 8	11, 61
<i>Anadara subarenata</i>	8	61
<i>Anomia ephippium</i>	1	1
<i>Astarte sulcata</i>	1	1
<i>Cardium echinatum</i>	1, 2	1
<i>Cardium edule</i>	1, 3	10
<i>Cardium tuberculatum</i>	2	1, 2
<i>Chlamys nippensis azakara</i>	4, 8, 9, 13	59
<i>Chlamys septemradiatus</i>	3	10
<i>Chlamys nobilis</i>	4, 8, 9, 13	59
<i>Cochleodesma praetense</i>	1	1
<i>Cultellus pellucidus</i>	1, 2	1
<i>Dosinia exoleta</i>	2	1, 12
<i>Flexopecten ponticus</i>	Trace	13
<i>Gryphaea angulata</i>	1, 2	14, 15
<i>Laqueatus sowerbyi</i>	1, 2 (?5)	11, 60
<i>Leda parvula</i>	1, 2	1, 10
<i>Lima doscombei</i>	1, 2	1
<i>Lima excavata</i>	4	9
<i>Lima mians</i>	3	10
<i>Lucina borealis</i>	1	1
<i>Meretrix lusoria</i>	1, 2, 5	16
<i>Modiolaria marmorata</i>	1, 2	1
<i>Modiolus modiolus</i>	1, 2	1
<i>Mya arenaria</i>	1, 3	10
<i>Mya truncata</i>	1, 2	1
<i>Mytilus californianus</i>	5, 6	6
<i>Mytilus coruscus</i>	6, 8, 9, 12, 13	20
<i>Mytilus edulis</i>	1, 2, 3, 4, 5, 6, 7, 8	3, 7, 10, 17
<i>Mytilus galloprovincialis</i>	2, 5, 6, 14	13, 18
<i>Nucula sulcata</i>	1, 2	1
<i>Ostrea edulis</i>	1, 3	10
<i>Patinopecten yessonensis</i>	4, 8, 9, 12, 13	37, 59, 61, 63
<i>Pecten albicans</i>	4, 8, 9, 13	59
<i>Pecten jacobaeus</i>	8	3, 8, 19
<i>Pecten maximus</i>	1, 8, 9	3, 10
<i>Pecten opercularis</i>	1, 2	1
<i>Pecten strictus</i>	1	1
<i>Pectunculus glycymeris</i>	10	2
<i>Psammobia ferroensis</i>	1, 2	1
<i>Saxicava rugosa</i>	1, 2	1
<i>Scapharca broughtonii</i>	8, 9, 12, 13	20
<i>S. globosa ursus</i>		
<i>S. satowi</i>		
<i>S. sub-crenata</i>		
<i>Scribicularia plana</i>	1, 3	10
<i>Solen ensis</i>	1, 2	1
<i>Spisula solidula</i>	1, 2	1

Table 5.1 cont'd

Species	Pigments	References
<i>Spisula subtruncata</i>	1, 2	1
<i>Tapes pullastra</i>	1, 2	1
<i>Tellina crassa</i>	1	1
<i>Venus fasciata</i>	1	1
<i>Venus gallina</i>	1	1
<i>Venus japonia</i>	1, 3, 5, 11	21
<i>Venus ovata</i>	1	1
<i>Volsella barbata</i>	1, 2	1
<i>Volsella modiolus</i>	8	22

*Key to pigments*

- |   |       |   |        |
|---|-------|---|--------|
| 1. $\beta$ -Carotene                    | (1.5) | 9. Pectenolone  | (1.3)  |
| 2. Lutein-like pigment                  |       | 10. Glycymerin  | (?= 9) |
| 3. Mixture of unidentified xanthophylls |       | 11. Flavoxanthin  | (5.3)  |
|   |       | 12. Diatoxanthin  | (4.2)  |
| 4. Astaxanthin                          | (1.1) | 13. 3,4,3'-Trihydroxy-7',8'-didehydro- $\beta$ -carotene (pectenol) |        |
| 5. Zeaxanthin (?)                       | (1.9) |   |        |
| 6. Mytiloxanthin                        | (5.1) | 14. Lutein 5,6-epoxide  |        |
| 7. Isomytiloxanthin                     | (5.2) |   |        |
| 8. Pectenoxanthin<br>(= alloxanthin)    | (1.2) |   |        |

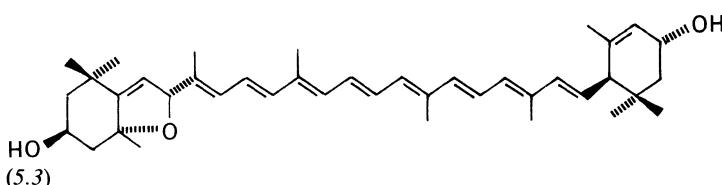
Table 5.2 Carotenoids in fresh-water bivalves

Species	Pigments	References
<i>Anodonta cygnea</i>	1, 2, 3, 4, 5	24–26
<i>Dreissena polymorpha</i>	1, 2, 4, 6, 7, 8	25
<i>Unio pictorum</i>	1, 2, 3, 4, 7	25, 26
<i>Unio rostratus gentilis*</i>	5	62

*Key*

- |                      |        |                       |        |
|----------------------|--------|-----------------------|--------|
| 1. $\beta$ -Carotene | (1.5)  | 5. Unidentified       |        |
| 2. Lutein            | (1.10) | 6. $\alpha$ -Carotene | (2.25) |
| 3. Zeaxanthin        | (1.9)  | 7. Lutein 5,6-epoxide |        |
| 4. Astaxanthin       | (1.1)  | 8. Alloxanthin        | (1.2)  |

\*More in males than females.



## 56 The biochemistry of the carotenoids

Infection of *Unio rostratus gentilis* with a trematode results in a drop in the carotenoid tissue levels [62].

### 5.2 GASTROPODA

#### 5.2.1 MARINE GASTROPODS

Lönnberg [1, 30] has reported carotenoids in a number of marine gastropods but one of the first detailed studies was that on the limpets *Patella vulgata* and *P. depressa* [31, 32]. They contain  $\alpha$ -carotene (2.25),  $\beta$ -carotene (1.5), echinenone (1.11),  $\beta$ -cryptoxanthin (2.36) and zeaxanthin (1.9) which are accumulated mainly in the testes and ovaries in the ratio 1:5:3:3:3. The total concentration is extremely high being around 280 mg/100 g fresh weight of gonads, male or female.

In 1949 Strain [33] reported a new pigment hopkinsiaxanthin in the nudibranch *Hopkinsia rosacea*. The structure (4.6) of this pigment was elucidated by McBeth [34, 35] who found it together with an analogous pigment triophaxanthin (structure not yet determined) in the nudibranch *Triopha carpenteri*. Another californian slug *Flabellinopsis iodinea* accumulates only astaxanthin; the free and esterified pigment is found in the red rhinophores (tentacle-like projections from the head) and in the orange cerata (finger-like gills over the dorsal surface of the body), whereas the free pigment only is present in the pink eggs and as a component of the blue-violet integumentary carotenoprotein [34, 35]. On the other hand  $\alpha$ - and  $\beta$ -carotenes represent a large proportion of the total carotenoids in *Anisodoris nobilis*, *Dendrodoris fulva* and *Doriopsilla albopunctata*; the aromatic isorenieratene (2.3), a characteristic pigment of sponges (see Chapter 2), is also present in significant amounts (Table 5.3). All these animals seem to accumulate food carotenoids unchanged. The carotenoids in *Aplysia* sp. are located in discrete granules within the neural cytoplasm [40]. The marine gastropods known to contain carotenoids are listed in Table 5.4.

Table 5.3 Distribution of carotenoid hydrocarbons in three Californian nudibranchs [34, 35] (% of total carotenoids present)

Species	Pigments		
	$\alpha$ -Carotene	$\beta$ -Carotene	Isorenieratene
<i>Anisodoris nobilis</i>	21.0	22.9	22.1
<i>Dendrodoris fulva</i>	15.5	41.8	21.8
<i>Doriopsilla albopunctata</i>	6.8	21.0	18.7

Table 5.4 Marine gastropods known to contain carotenoids

<i>Species</i>	<i>Pigment</i>	<i>Reference</i>
<i>Anisodoris nobilis</i>	1, 2, 3	34, 35
<i>Aplysia depilans</i>	1, 4	10
<i>Aporrhais pes-pelecani</i>	4	10
<i>Archidoris montereyensis</i>	6	55
<i>Astea undosa</i>	1, 4	10
<i>Buccinum undatum</i>	1, 4, 5	1, 10, 30
<i>Capulus hungaricus</i>	1, 5	1, 30
<i>Cerithidea californica</i>	6	36
<i>Clione limacina</i>	1, 4	10
<i>Crepidula fornicata</i>	1, 4	10
<i>Cypraea spadicea</i>	1, 4	10
<i>Cyprina islandica</i>	1	1, 4, 30
<i>Dendrodoris fulva</i>	1, 2, 3	34, 35
<i>Diodora graeca</i>	1, 2, 7, 11, 15	57
<i>Doriopsilla albopuncta</i>	1, 2, 3	34, 35
<i>Flabellinopsis iodinea</i>	7	34, 35
<i>Gibbula cineraria</i>	1, 4	8
<i>Gibbula tumida</i>	1, (?)5	1, 30
<i>Haliotis discus hanneli</i>	2, 13, 14	58
<i>Haliotis fulgens</i>	1, 4	10
<i>Hopkinsia rosacea</i>	8	33–35
<i>Lima excavata</i>	7	9
<i>Lima loscombi</i>	1, 5	1, 30
<i>Limacina retroversa</i>	4	1, 30
<i>Littorina littoralis</i>	1, 4	10
<i>Littorina littorea</i>	1, 4, 5	10, 30, 57
<i>Littorina planaxis</i>	6	38
<i>Littorina rufa</i>	1, 4	10
<i>Megathura crenulata</i>	1, 4	12
<i>Nassa incrassata</i>	1, 4	12
<i>Nassa reticulata</i>	1	1, 30
<i>Natica nitida</i>	1, 5	1, 30
<i>Osilinus lineatus</i>	1, 4	10
<i>Patella depressa</i>	1, 9, 10, 11	32
<i>Patella vulgata</i>	1, 9, 10, 11	10, 32
<i>Philine aperta</i>	1, (?)5	1, 30
<i>Pleurobranchus</i> sp.	7	8
<i>Purpura lapillus</i>	1, 5	1, 30
<i>Rissoa</i> spp.	1, 5	1, 30
<i>Triopha carpenteri</i>	12	34, 35
<i>Trivia europaea</i>	1	1, 30
<i>Trochus zizyphinus</i>	1, 5	1, 30
<i>Tugalia gigas</i>	7	39
<i>Key</i>		
1. $\beta$ -Carotene	(1.5)	8. Hopkinsianthin (4.6)
2. $\alpha$ -Carotene	(2.25)	9. Echinone (1.11)
3. Isorenieratene	(2.3)	10. $\beta$ -Cryptoxanthin (2.36)
4. Unidentified xanthophylls		11. Zeaxanthin (1.9)
5. Lutein		12. Trirophaxanthin (unknown structure)
6. Present		13. Fucoxanthin (2.34)
7. Astaxanthin	(1.1)	14. Isofucoxanthin (5.4)
		15. $\gamma$ -Carotene (2.26)

## 58 The biochemistry of the carotenoids

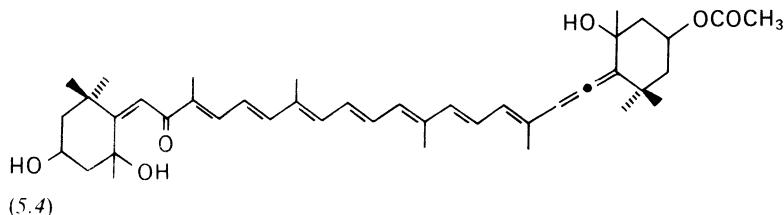


Table 5.5 Carotenoids in fresh-water gastropods

Species	Pigments	References
<i>Helisoma nigricans</i>	1, 2, 3, 4, 5, 6, 7, 8	20
<i>Limnaea stagnalis*</i>	2, 4, 5, 7, 8, 9, 10	20, 62
<i>Planorbarius corneus*</i> <i>v. rubra</i>	8	62
<i>Planorbarius planorbis</i>	1, 2, 5, 7, 8, 9, 10	20
<i>Pomacea canaliculatus</i> <i>australis</i>	7	22
<i>Pomacea doliooides</i>	11	23
<i>Pomacea (Pila) glauca</i>	12	24
<i>Pomacea haustrum</i>	11	23
<i>Pomacea sordia</i>	1, 2	23

*Key*

1. $\alpha$ -Carotene	(2.25)	7. Astaxanthin	(1.1)
2. $\beta$ -Carotene	(1.5)	8. Unknown	
3. $\gamma$ -Carotene	(2.26)	9. 4-Keto- $\alpha$ -carotene	
4. Lutein	(1.10)	10. Isozeaxanthin	(2.41)
5. Lutein 5,6-epoxide		11. Exclusively xanthophylls	
6. Alloxanthin	(1.2)	12. Present	

\*More in males than in females.

### 5.2.2 FRESH-WATER GASTROPODS

The bright red, orange or green eggs of *Pomacea* spp. contain carotenoids [41–43]. In omnivorous species chiefly xanthophylls are stored whereas in the mainly herbivorous *P. sordia* only  $\alpha$ - and  $\beta$ -carotenes (2.25 and 1.5) are stored [42]. The main pigment of *P. canaliculatus australis* is astaxanthin (1.1). It is attached to a glycoprotein and the complex is known as ovorubin [40]. It is discussed in detail in Chapter 1. The fresh-water gastropods known to accumulate carotenoids are listed in Table 5.5. Carotenoids are present in the neurones of *Planorbarius corneus* and *Limnaea stagnalis* [26, 45] where they specifically accumulate in organelles which were originally called cytosomes because they contain respiratory pigments [46] but which have now been renamed carotenoxyosomes [26]. The nerve tissue of *Limnaea stagnalis* contains 30–40 mg/100 g wet weight [26] whereas the overall concentration

in the animal is some hundred times less [25]. A carotenoprotein has also been observed in ganglia of *L. stagnalis* [40, 47]. Infection of *L. stagnalis* and *Planorbarius corneus* with trematodes results in a fall in carotenoid levels in the tissues, somewhat similar to that observed in fasting animals [62].

### 5.2.3 TERRESTRIAL GASTROPODS

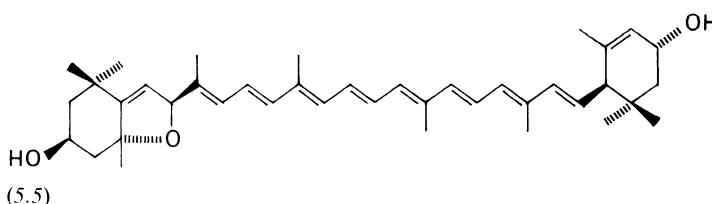
Only one recent survey on the carotenoids of terrestrial gastropods has been reported [44]. The results are summarized in Table 5.6. Modern analytical methods are needed to confirm some of the pigment identifications. In *Helix* spp. the carotenoids accumulate within the neural cytoplasm [48].

Table 5.6 Carotenoids in terrestrial gastropods  
[42]

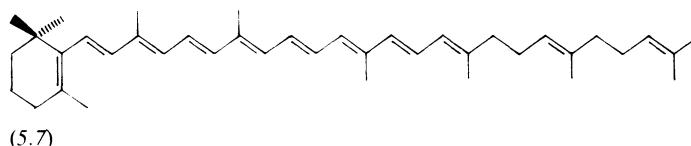
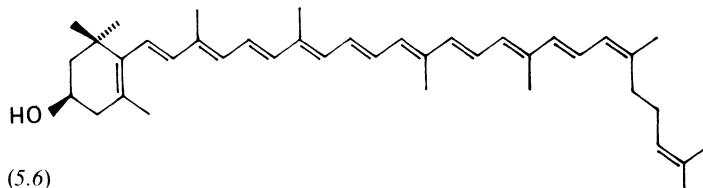
Species	Pigments
<i>Arion empiricorum</i>	2, 3, 4, 11, 12, 13, 14, 15
<i>A. subfuscus</i>	1, 11, 15, 16, 17, 18
<i>Cepaea hortensis</i>	3, 9, 10
<i>Deroceras agrestis</i>	6, 18, 19, 20, 21, 22
<i>Helicella candicans</i>	1, 4, 5, 6
<i>Helicella derbentina</i>	1, 2, 3, 4
<i>Helix aspersa</i>	Present [ref. 45]
<i>Helix pomatia</i>	1, 3, 4, 7, 8
<i>Limax cereus</i>	3, 10, 12, 15, 22
<i>Limax cinerer-niger</i>	3, 5
<i>Limax maximus</i>	1, 3, 5

#### Key

1. $\beta$ -Carotene	(1.5)	12. $\alpha$ -Cryptoxanthin	(4.1)
2. Lutein	(1.10)	13. Canthaxanthin	(1.4)
3. Lutein 5,6-epoxide		14. Capsanthin	(2.19)
4. Astaxanthin	(1.1)	15. Zeaxanthin	(1.9)
5. $\beta$ -Cryptoxanthin	(2.36)	16. $\alpha$ -Carotene	(2.25)
6. 4-Keto- $\alpha$ -carotene		17. 3,4,4'-Trihydroxy- $\beta$ -carotene	
7. Chrysanthemaxanthin	(5.5)	18. 4-Hydroxy- $\alpha$ -carotene	
8. Taraxanthin (= Lutein 5,6-epoxide; see Vol. I)		19. $\gamma$ -Carotene	(2.26)
9. Gazanixanthin	(5.6)	20. $\epsilon$ -Carotene	(2.33)
10. 3,4-Diketo- $\alpha$ -carotene		21. Isocryptoxanthin	(2.27)
11. $\beta$ -Zeacarotene	(5.7)	22. Isozeaxanthin	(2.41)



## 60 The biochemistry of the carotenoids



### 5.3 AMPHINEURA

*Chaetoderma nitidulum* contains  $\beta$ -carotene [30].

### 5.4 CEPHALOPODA

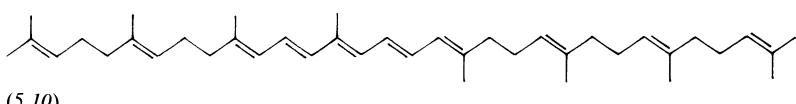
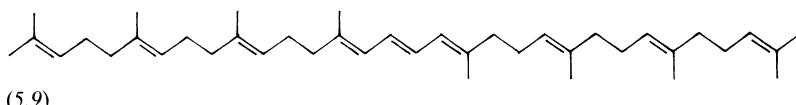
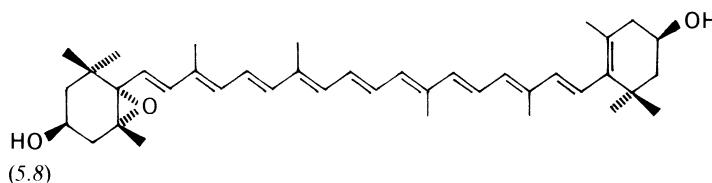
A general characteristic of this class of Mollusca is the rare appearance of carotenoids and then only in trace amounts. The information available on pigment distribution is summarized in Table 5.7. However, large amounts of a complex mixture were found in *Loligo vulgaris* [44]; the components were  $\alpha$ ,  $\beta$ , and  $\gamma$ -carotenes (2.25, 1.5, 2.26),  $\alpha$ -cryptoxanthin (4.1), isocryptoxanthin (2.27), isorenieratene (2.3), capsanthin (2.19), capsorubin (2.20), triophaxanthin (structure unknown), zeaxanthin (1.9), 4-hydroxy- $\alpha$ -carotene, astaxanthin and 4-keto- $\alpha$ -carotene. The precise identification of some of these pigments remains to be confirmed. *Loligo forbesi* and *L. opalescens*, on the other hand, only contain traces of carotenoids [49, 50].

Table 5.7 Cephalopods in which carotenoids have been detected

Species	References
<i>Eledone cirrosa</i>	51, 52
<i>Loligo forbesi</i>	49
<i>L. opalescens</i>	50
<i>L. vulgaris</i>	44
<i>Ommastrephes pteropus</i>	52
<i>Parasepia elegans</i>	52
(Par) <i>Octopus bimaculatus</i>	50, 51
<i>Rossia macrosoma</i>	51, 52
<i>Sepia officinalis</i>	44, 52
<i>Sepiola scandica</i>	51
<i>Sepiola</i> sp.	52
<i>Todaropsis eblanae</i>	52

Other major exceptions to the generalization just enunciated are the liver and, to a lesser extent, the ink of *Octopus bimaculatus*, where large amounts of carotenoids, particularly xanthophylls accumulate [50]. The concentration in the liver ranged between 3.4 and 23.3 mg/100 g of fresh tissue and in the ink it was 1.5–2.0 mg/100 g of fresh fluid [50]. The liver carotenoids reflect the pigment intake and the octopus is an animal which is non-selective in its storage of carotenoids [53].

The two main pigments in the liver of *Sepia officinalis* are  $\beta$ -carotene (1.5) and astaxanthin (1.1) which are associated with traces of  $\alpha$ -carotene (2.25),  $\beta$ -cryptoxanthin (2.36), echinenone (1.11), antheraxanthin (5.8) and lutein 5,6-epoxide [54]. In the adult female *Sepia* the accessory nidamental gland is orange-red and the main pigment is sepiaxanthin, the structure of which is not yet fully understood. It appears to be of bacterial origin and of six strains of symbiotic bacteria isolated from the gland [55] the main pigment in five is  $\beta$ -carotene and in the sixth it is adonixanthin (=  $\beta$ -doradexanthin) (2.32) [54]. Other carotenoids present in the nidamental gland are  $\beta$ -carotene,  $\gamma$ -carotene (2.26), phytoene (5.9), phytofluene (5.10), and lycopene (2.29) [56].



### 5.5 FUNCTION OF CAROTENOIDS

Following the observation of the specific accumulation of carotenoids in the carotenoxysomes of certain gastropoda, considerable effort has been made to find an appropriate function for them. The absorption spectrum of these particles increases in the carotenoid-absorbing region when the neurones of *Limnaea stagnalis* are rendered anaerobic. Access to oxygen allows the spectrum to return to its original shape. From this it is concluded that carotenoids act in the respiratory chain of neurones [26]. In particular, the concentration of carotenoids and  $\text{Ca}^{2+}$  in the modified part of mitochondria called carotenoid containing membranes suggests that carotenoids play a role in the transfer of calcium across membranes [64].

## 62 The biochemistry of the carotenoids

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# [6]

## CRUSTACEA

### 6.1 NATURE AND DISTRIBUTION

Information on the nature and distribution of carotenoids in Crustacea is rather more extensive than in many other invertebrates but occasionally pigment identification has not always been unequivocal. Recent investigations which use modern physicochemical techniques are gradually revealing a general pattern of distribution and the information is summarized in the accompanying Tables. The most important general feature is the wide distribution of relatively large amounts of carotenoids which are keto derivatives of  $\beta$ -carotene. A considerable number of carotenoproteins are found in the Crustacea but these are discussed in detail in Chapter 1.

In particular the major characteristic pigment is astaxanthin and its chirality ( $3S,3'S$ ) was established in 1974 (1.12). However, recent investigations have shown that the enantiomeric ( $3R,3'R$ )-astaxanthin (1.13) and the meso form (1.14) are also present in lobster eggs [1]; these isomers are also present in the tissues of some other crustaceans (see later) [2]. The implications of these important observations have not yet been fully explored and in most of this chapter the term *astaxanthin* means that the chirality of the pigment being discussed has not been established.

#### 6.1.1 SUB-CLASS BRANCHIOPODA

##### (a) Anostraca

In this Order canthaxanthin (1.4) is the most widely distributed and most abundant carotenoid. Astaxanthin (1.1) has occasionally been reported but is never the major pigment present (Table 6.1). Some strains of the same organism vary in their ability to synthesize astaxanthin. For example Californian *Artemia salina* accumulate mainly canthaxanthin, with two oxygen atoms, whilst the Canadian specimens synthesize in addition some

astaxanthin with four oxygen atoms, indicating that they can carry the oxidation of  $\beta$ -carotene further than can the Californian animals [4].

Table 6.1 Carotenoid distribution in Branchiopoda

Species	Pigments	Reference
<b>Anostraca</b>		
<i>Artemia salina</i>	1–14 <sup>b, c</sup>	3–10
<i>Branchinecta packardi</i>	1, 8, 11 <sup>b</sup>	10
<i>Branchinecta paludosa</i>	1, 2, 3, 4, 11 <sup>b</sup> , 15	11
<i>Branchipus stagnalis</i>	1, 8, 11 <sup>b</sup>	10
<i>Chirocephalus diaphanus (stagnalis)</i>	1, 3, 5, 8, 11, 15, 16	10, 12, 13, 14
<i>Tanytarsus lacunae</i>	1, 8, 11 <sup>b</sup>	10
<b>Diplostraca</b>		
<i>Daphnia longostra</i>	1	15
<i>Daphnia magna</i> <sup>a</sup>	1, 2, 3, 8, 9, 11 <sup>b</sup> , 12 <sup>b</sup>	16, 17, 18
<i>Daphnia pulex</i>	2, 3, 15	7, 19
<i>Holopedium gibberum</i>	1	20
<b>Nostrostraca</b>		
<i>Apus cancriformis</i>	2, 3, 9, 11 <sup>b</sup> , 15	21
<i>Lepidurus apus</i>	Present	22

#### Key

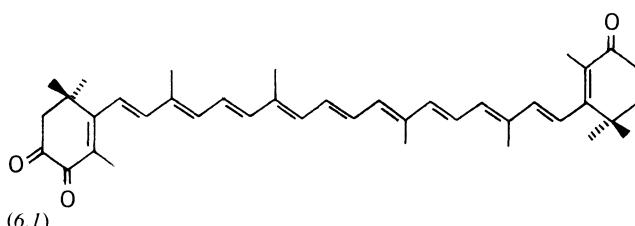
1. Astaxanthin	(1.1)	9. $\gamma$ -Carotene	(2.26)
2. Echinenone	(1.11)	10. Violaxanthin	(2.40)
3. Canthaxanthin	(1.4)	11. Lutein	(1.10)
4. Isocryptoxanthin	(2.27)	12. Neoxanthin	(2.39)
5. Isozeaxanthin	(2.41)	13. Diadinoxanthin	(6.3)
6. Phoeniconone	(6.1)	14. Fucoxanthin	(2.34)
7. Crustaxanthin	(6.2)	15. $\beta$ -Carotene	(1.5)
8. Phoenicoxanthin (= adonirubin)	(1.8)	16. $\alpha$ -Doradexanthin	(6.4)

#### Notes

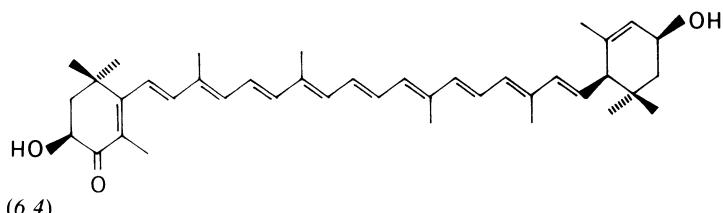
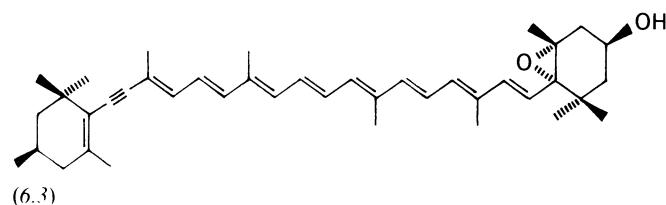
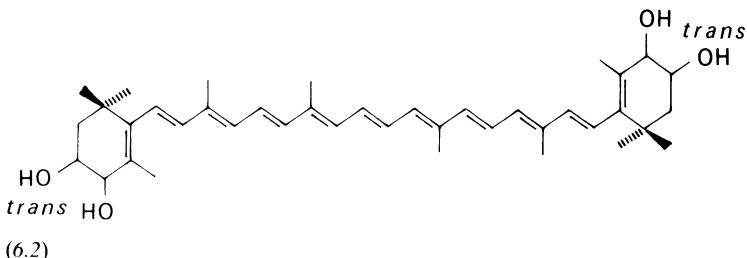
<sup>a</sup> Species not always clearly indicated.

<sup>b</sup> Pigments 10–14 may well be present as a result of algal contamination of the specimens.

<sup>c</sup> A wide survey over eight geographical regions revealed the presence of only echinenone and canthaxanthin [232].

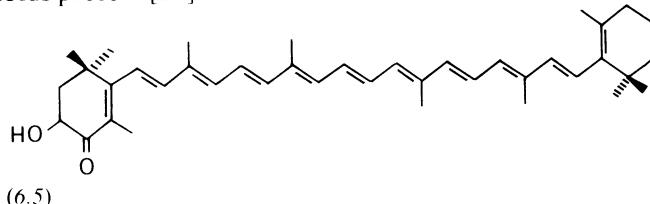


## 66 The biochemistry of the carotenoids



### 6.1.2 SUB-CLASS OSTRACODA

Investigations on only two members of this sub-class have been reported. *Heterocypris incongruens* contains astaxanthin (1.1) and  $\beta$ -carotene (1.5) [23] and *Cyclocypris laevis* accumulates these two pigments and in addition canthaxanthin (1.4);  $\beta$ -carotene predominates representing 70% of the total carotenoids present [24].



### 6.1.3 SUB-CLASS COPEPODA

The wide distribution of astaxanthin (1.1), characteristic of the Crustacea, is again observed in the Copepoda (Table 6.2) although it is not universally present. Canthaxanthin (1.4) is only rarely observed and echinenone (1.11), a possible intermediate in canthaxanthin formation, has not yet been reported. 2-Norastaxanthin (3.2) has recently been observed in a copepod, *Euchaeta russellii*, from the Great Barrier Reef [221].

Table 6.2 Carotenoid distribution in Copepoda

Species	Pigments	Reference
<i>Anomalocera patersoni</i>	1	25
<i>Arctodiaptomus bacillifer</i>	1, 2, 3, 4, 5	26, 27
<i>Arctodiaptomus salinus</i>	1, 2, 4, 6,	28, 29
<i>Argulus foliaceus</i>	(?) 8, 9	30
<i>Calanus finmarchicus</i>	1, 10, 11	31, 32
<i>Centropages furcatus</i>	1	221
<i>Cyclops strenuus strenuus</i>	1, 2, 7, 8, 11, 13	33
<i>Diaptomus bacillifer</i>	1, 2, 10, 12	26, 34
<i>Diaptomus castor</i>	2, 12	34
<i>Euchaeta russelli</i>	1, 5, 6, 13, 15, 16, 17	221
<i>Eudiaptomus amblydon</i>	1, 2, 7, 8, 12	35, 236
<i>Hemidiaptomus amblydon</i>	1, 2, 10, 12	34
<i>Labidocera acutifrons</i>	1	25
<i>Labidocera nerii</i>	1	25
<i>Labidocera woolastoni</i>	1	25
<i>Pontellopsis regalis</i>	1	25
<i>Pontellopsis villosa</i>	1	25
<i>Temora turbinata</i>	1	221
<i>Tigriopus fulvus</i>	1	36
<i>Undinula vulgaris</i>	1	221

**Key**

1. Astaxanthin	(1.1)	9. Neoxanthin	(2.39)
2. $\beta$ -Carotene	(1.5)	10. Violaxanthin	(2.40)
3. Zeaxanthin	(1.9)	11. $\alpha$ -Carotene	(2.25)
4. 3-Hydroxyechinenone	(6.5)	12. $\gamma$ -Carotene	(2.26)
5. Adonixanthin (= $\beta$ -Doradexanthin)	(2.32)	13. Canthaxanthin	(1.4)
6. Crustaxanthin	(6.2)	14. Isocryptoxanthin	(2.27)
7. Isozeaxanthin	(2.41)	15. Phoenicoxanthin (= Adonirubin)	(1.8)
8. Lutein	(1.10)	16. 3,4,3'-Trihydroxy- $\beta$ -carotene	
		17. 2-Norastaxanthin	(3.2)

**6.1.4 SUB-CLASS CIRRIPEDIA**

The information on carotenoid distribution in this class is not extensive; it is collected in Table 6.3. Astaxanthin (1.1) is present in a number of species. In *Lepas* spp. it occurs as a blue carotenoprotein [39, 41]. (See also Chapter 1.)

**6.1.5 SUB-CLASS MALACOSTRACA****(a) Isopoda**

The genus *Iodothea* has been examined in some detail and it is clear that in all species investigated astaxanthin (1.1) does not accumulate but that canthaxanthin (1.4) is the most oxidized pigment produced. Astaxanthin is also absent from all other isopods examined except *Oniscus asellus* [51]. The details of pigment distribution in this sub-class are given in Table 6.4.

## 68 The biochemistry of the carotenoids

Table 6.3 Carotenoids in Cirripedia

Species	Pigments	Reference
<i>Balanus balanus</i>	Present	37, 38
<i>Chthamalus fragilis</i>	1, 3, 6	38
<i>Conchoderma virgatum</i>	1, 8	38
<i>Elminius modestus</i>	1, 3, 6	38
<i>Lepas anacles</i>	2	38
<i>Lepas anatifera</i>	1, 2, 3, 6, 7	38–40
<i>Lepas fascicularis</i>	1, 2, 3, 6, 8	38–43
<i>Lepas pectinata</i>	1, 3, 7	38
<i>Pollicipes polymerus</i>	1, 3, (?4), 5	44, 45
<i>Sacculina carcinii</i>	6	46
<i>Sacculina neglecta</i>	6	96
<i>Scalpellum scalpellum</i>	Present	37

**Key**

- |                  |        |                      |        |
|------------------|--------|----------------------|--------|
| 1. Astaxanthin   | (1.1)  | 6. $\beta$ -Carotene | (1.5)  |
| 2. Fucoxanthin   | (2.34) | 7. Phoenicoxanthin   | (1.8)  |
| 3. Zeaxanthin    | (1.9)  | (= adonirubin)       |        |
| 4. Isozeaxanthin | (2.41) | 8. Peridinin         | (2.31) |
| 5. Lutein        | (1.10) |                      |        |

(b) *Amphipoda*

Both astaxanthin (1.1) and canthaxanthin (1.4) are well distributed in this order and other keto carotenoids have also been reported (Table 6.5). The presence of unexpected carotenoids, such as gazanixanthin (5.6), remains to be confirmed. A blue crustacyanin-type carotenoprotein is found in *Gammarus lacustris* [233].

(c) *Euphausiacea*

Astaxanthin (1.1) [and occasionally  $\beta$ -carotene (1.5) in traces], has been found in all Euphausiacea so far examined (Table 6.6)

(d) *Mysidacea*

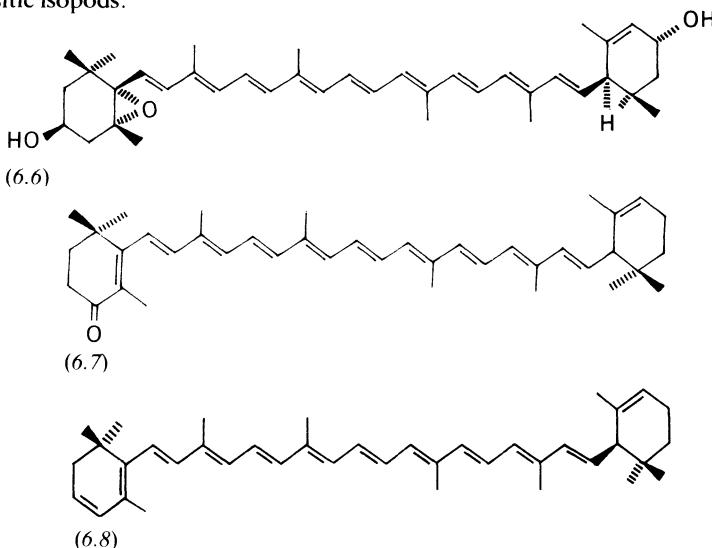
This order differs from others in the sub-class Malacostraca in that no species so far examined synthesizes the usual keto carotenoids, canthaxanthin and astaxanthin (Table 6.7). Originally less common keto carotenoids, such as phoenicoxanthin (= adonirubin) (1.8), had been reported, but their presence has not yet been confirmed.

Table 6.4 Carotenoid distribution in Isopoda

Species	Pigments	Reference
<i>Asellus aquaticus</i>	1,2	46
<i>Idothea ballica</i>	3, 4, 5	47
<i>Idothea chelipes</i>	3, 4, 6, 7	47
<i>Idothea emarginata</i>	1, 3	37
<i>Idothea granulosa</i>	3, 6, (?8)	48, 49
<i>Idothea metallica</i>	1, 9, 10, 11, 12, 18	50
<i>Idothea montereyensis</i>	3, 4, 6, (?8)	49, 51
<i>Idothea neglecta</i>	1, 3, 12	37
<i>Idothea resecata</i>	4, 8, 10, 13, 14	49, 52
<i>Idothea viridis</i>	Present	53
<i>Mesiothea entomon</i>	Present	40
<i>Oniscus asellus</i>	3, 6, 12, 15, 16, 17	54
<i>Pliophryxus philonitiae<sup>a</sup></i>	1, 12	222
<i>Sphaeroma hookeri</i>	3, 10	45, 47
<i>Sphaeroma rugicauda</i>	3, 4, 6	45, 47
<i>Urobopyrus processae<sup>a</sup></i>	1	222

**Key**

1. $\beta$ -Carotene	(1.5)	10. Zeaxanthin	(1.9)
2. $\beta$ -Cryptoxanthin	(2.36)	11. Idoxanthin	(6.10)
3. Lutein	(1.10)	12. Astaxanthin	(1.1)
4. Lutein 5,6-epoxide	(6.6)	13. Violaxanthin	(2.40)
5. 4-Keto- $\alpha$ -carotene	(6.7)	14. $\alpha$ -Carotene	(2.25)
6. Isozeaxanthin	(2.41)	15. Canthaxanthin	(1.4)
7. 3,4-Didehydro- $\alpha$ -carotene	(6.8)	16. 4-Hydroxy-3',4'-didehydro- $\beta$ -carotene	(6.11)
8. 2-Hydroxy- $\beta$ -carotene	(6.9)	17. $\alpha$ -Cryptoxyanthin	(4.1)
9. Crustaxanthin	(6.2)	18. Isocryptoxanthin	(2.27)

**Note**<sup>a</sup>Parasitic isopods.

## 70 The biochemistry of the carotenoids

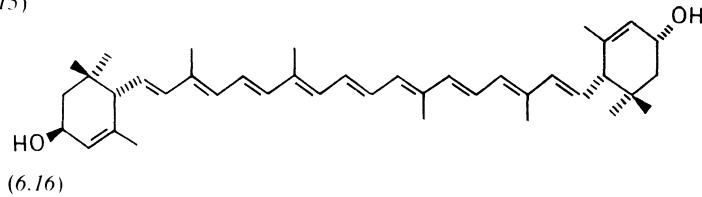
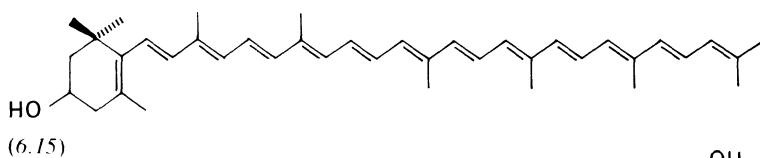
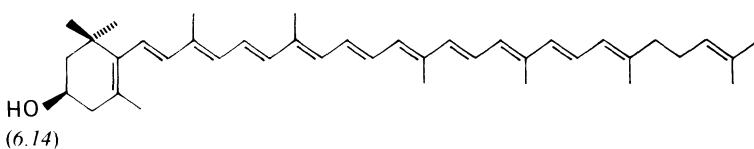
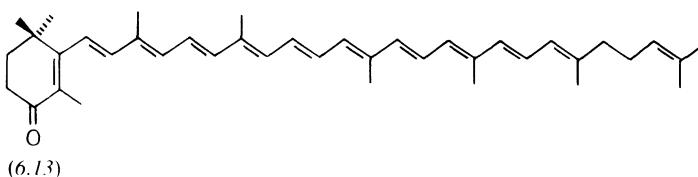
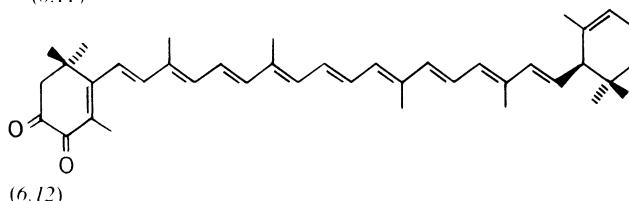
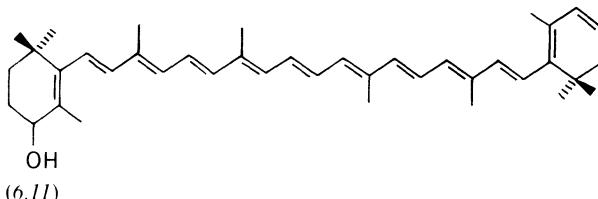
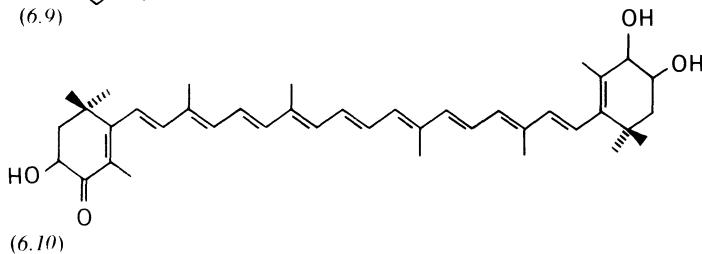
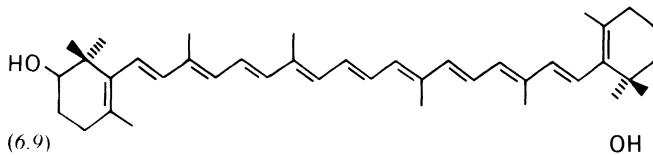


Table 6.5 Carotenoid distribution in Amphipoda

<i>Species</i>	<i>Pigments</i>	<i>Reference</i>
<i>Acanthogammarus albus</i>	1, 2, 3	56
<i>Ampelisca tenuicornis</i>	4, 5	37
<i>Brandtia lata</i>	1, 2, 3, 4, 5, 6, 7	56
<i>Calliopius laeviusculus</i>	5	57
<i>Cryptouropus pachytus</i>	1, 2, 4, 8, 9, 10	56
<i>Corophium volutator</i>	7	47
<i>Eulimnogammarus cruentus</i>	1, 2, 5, 7, 11	56
<i>Eulimnogammarus grandimanus</i>	1, 3, 5, 7, (?12)	56
<i>Eulimnogammarus maacki</i>	1, 4, 5, 6, 7	56
<i>Gammarus duebeni</i>	13	47
<i>Gammarus locusta</i>	14	47
<i>Gammarus marinus</i>	1	40, 57
<i>Gammarus oceanicus</i>	5, 11, 14	56, 58
<i>Gammarus pulex</i>	5	59
<i>Gammarus salinus</i>	7, 14	47
<i>Gammarus zaddachi</i>	7, 11, 14, 15	47
<i>Gmelinoides fasciatus</i>	1, 2, 3, 7, 11	56
<i>Haploops tubicula</i>	Present	37
<i>Hyale perieri</i>	1, 2, 4, 5, 7, (?16)	60
<i>Macrohectopus branickii</i>	1, 8	55
<i>Micruropus vortex</i>	1, 5, 7, 8, 11	55
<i>Micruropus wahli</i>	1, 3, 4, 5, 11	55
<i>Neohela monstrosa</i>	Present	37
<i>Niphargus aquilex</i>	8, 17	61
<i>Niphargus tatrensis</i>	17, 18	61
<i>Orchestia gammarellus</i>	1	40, 57, 60
<i>Pallasea cancelloides</i>	1, 2, 3, 5, 7, 19	56
<i>Pallasea cancellus</i>	3, 4, 5, 6, 20	56
<i>Pallasea viridis</i>	1, 2, 3	56
<i>Pontoporeia affinis</i>	10, 14	47
<i>Pontoporeia femorata</i>	8, 10, 14	47
<i>Talitrus saltator</i>	1	60

**Key**

- |  |        |  |        |
|--|--------|--|--------|
| 1. Astaxanthin                             | (1.1)  | 11. $\gamma$ -Carotene                           | (2.26) |
| 2. Canthaxanthin                           | (1.4)  | 12. Gazaniaxanthin (?)                           | (5.6)  |
| 3. Zeaxanthin                              | (1.9)  | 13. 3,4-Diketo- $\alpha$ -carotene               | (6.12) |
| 4. $\beta$ -Carotene                       | (1.5)  | 14. 4-Keto- $\alpha$ -carotene                   | (6.7)  |
| 5. Lutein                                  | (1.10) | 15. 4-Keto- $\gamma$ -carotene                   | (6.13) |
| 6. Isocryptoxanthin                        | (2.27) | 16. Violaxanthin                                 | (2.40) |
| 7. Lutein 5,6-epoxide                      | (6.6)  | 17. Rubixanthin                                  | (6.14) |
| 8. Isozeaxanthin                           | (2.41) | 18. Celaxanthin                                  | (6.15) |
| 9. $\beta$ -Cryptoxanthin                  | (2.36) | 19. 4-Hydroxy-3',4'-didehydro- $\beta$ -carotene | (6.11) |
| 10. 4-Keto-4-ethoxy- $\beta$ -carotene (?) |        | 20. Tunaxanthin                                  | (6.16) |

## 72 The biochemistry of the carotenoids

Table 6.6 Carotenoid distribution in Euphausiacea

<i>Species</i>	<i>Pigments</i>	<i>Reference</i>
<i>Euphausia americana</i>	1	25
<i>Euphausia brevis</i>	1	25
<i>Euphausia gibboidea</i>	1	25
<i>Euphausia hemigibba</i>	1	25
<i>Euphausia pacifica</i>	1	62
<i>Euphausia superba</i>	1	62–64
<i>Meganyctiphanes norvegica</i>	1, 2	57, 64
<i>Nematobrachion hoopis</i>	1	25
<i>Nematobrachion microps</i>	1	25
<i>Nematobrachion sexspinosus</i>	1	25
<i>Nematobrachion tenella</i>	1	25
<i>Nematoscelis difficilis</i>	1	64, 65, 66
<i>Stylocheiron abbreviatum</i>	1	25
<i>Stylocheiron elongatum</i>	1	25, 64
<i>Stylocheiron maximum</i>	1	25, 64
<i>Thysanoessa gregaria</i>	Traces	64
<i>Thysanoessa inermis</i>	1	64, 65
<i>Thysanoessa raschii</i>	1, 2	64
<i>Thysanoessa spinifera</i>	1	64
<i>Thysanopoda acutifrons</i>	1	64
<i>Thysanopoda cristata</i>	1	25
<i>Thysanopoda microphthalma</i>	1	25
<i>Thysanopoda monacantha</i>	1	25
<i>Thysanopoda obtusifrons</i>	1	25
<i>Thysanopoda pectinata</i>	1	25
<i>Thysanopoda subaequalis</i>	1	25

*Key*

1. Astaxanthin (1.1)      2.  $\beta$ -Carotene (1.5)

Table 6.7 Carotenoids in the Mysidacea

<i>Species</i>	<i>Pigments</i>	<i>Reference</i>
<i>Mysidea</i> sp.	1	68
<i>Mysis flexuosa</i>	2	47, 57
<i>Mysis mixta</i>	3	47
<i>Mysis relicta</i>	3, 4, 5, 7	47
<i>Neomysis integer</i>	3	47
<i>Praunus flexuosus</i>	3, 6	47

*Key*

- |                                   |       |                       |        |
|-----------------------------------|-------|-----------------------|--------|
| 1. Phoenicoxanthin (= adonirubin) | (1.8) | 5. Lutein 5,6-epoxide | (6.6)  |
| 2. $\beta$ -Carotene              | (1.5) | 6. Isozeaxanthin      | (2.41) |
| 3. 4-Keto- $\alpha$ -carotene     | (6.7) | 7. $\alpha$ -Carotene | (2.25) |
| 4. Zeaxanthin                     | (1.9) |                       |        |

## (e) Decapoda

Many Decapoda have been examined in detail and the known distribution in the Caridea, Macrourea, Anomura and Brachyura is summarized in Tables 6.8–6.11 respectively.

Table 6.8 Carotenoid distribution in Decapoda – Caridea

Species	Pigments	Reference
<i>Acanthephyra acanthitelsonis</i>		
<i>Acanthephyra curtirostris</i>		
<i>Acanthephyra exima</i>		
<i>Acanthephyra pelagica</i>		
<i>Acanthephyra purpurea</i>		
<i>Acanthephyra sexspinosa</i>		
<i>Acanthephyra stylorostratis</i>		
<i>Ephyrina hoskynii</i>		
<i>Glyphus marsupialis</i>		
<i>Heterocarpus<sup>a</sup> ensifer</i>	3	67
<i>Heterocarpus grimaldii</i>		
<i>Hymenodora gracilis</i>		
<i>Meningodora miccylus</i>		
<i>Meningodora mollis</i>		
<i>Meningodora vesca</i>		
<i>Nematocarcinus cursor</i>		
<i>Notostomus auriculatus</i>	1, 2	47
<i>Notostomus elegans</i>	1, 3, 4	37
<i>Notostomus gibbosus</i>	1, 2, 3, 5	37, 40, 68
<i>Oplophorous spinosus</i>	3, 4	65, 66
<i>Palaemon adspersus</i>	3	37, 53, 235
<i>Palaemon fabricii</i>	3	67
<i>Palaemon serratus</i>	3	67
<i>Pandalus bonnieri</i>	3	67
<i>Pandalus borealis</i>	3	67
<i>Parapandalus richardi</i>	3	67
<i>Parapaspheaa sulcatifrons</i>	3	67
<i>Plesionika ensis</i>	3	67
<i>Plesionika martia</i>	3	67
<i>Processa edulis</i>	3	222
<i>Spirontocarthus spinus</i>	3, 4	65, 66
<i>Systellaspis cristata</i>	3	67
<i>Systellaspis debilis</i>	3	67

## Key

- |                |        |                      |        |
|----------------|--------|----------------------|--------|
| 1. Lutein      | (1.10) | 4. $\beta$ -Carotene | (1.5)  |
| 2. Zeaxanthin  | (1.9)  | 5. Isozeaxanthin     | (2.41) |
| 3. Astaxanthin | (1.1)  |                      |        |

## Note

<sup>a</sup>*Heterocarpus dorsalis* is said to contain 18 carotenoids [145].

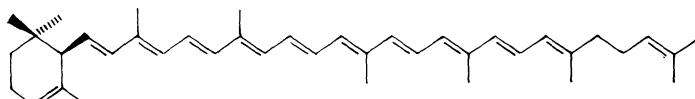
## 74 The biochemistry of the carotenoids

Table 6.9 Carotenoid distribution in Decapoda – Macrourea

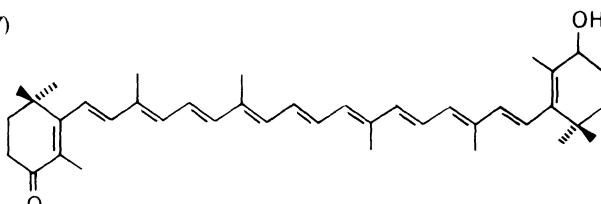
Species	Pigments	Reference
<i>Astacus astacus</i> [fluvialis]	1, 2, 6, 11	31, 64, 69, 70
<i>Astacus leptodactylus</i>	2, 3, 4, 5	71
<i>Astacus nobilis</i>	Present	73, 74
<i>Astacus pallipes</i>	(?)	72
<i>Calocaris meandreae</i>	2, 6	37
<i>Cambarus bartonii tenebrosus</i>	2	75, 76
<i>Crangon allmanni</i>	1, 2, 6	37, 61, 64
<i>Crangon crangon</i>	1, 2, 3, 5, 6, 7, 15	56, 77
<i>Crangon vulgaris</i>	8	61, 64
<i>Homarus americanus</i>	1	73, 78–91
<i>Homarus gammarus</i> [vulgaris]	1, 6, 26, 27	37, 92–96
<i>Leander</i> [Palaemon] <i>serratus</i>	2, 8, 10	31, 97
<i>Metapenaeus affinis</i>	2, 6	156
<i>Nephrops norvegicus</i>	1, 2, 5, 6	31, 37, 74, 96, 97
<i>Orconectes limosus</i>	1, 2, 3, 4, 5, 9, 10, 11, 12, 13, 14, 24, 25	98–100, 234
<i>Orconectes pellucidus</i>	2, 6	75, 76
<i>Orconectes rusticus</i>	1, 2	75, 76, 101
<i>Palaemon adspersus</i>	1, 28	31
<i>Palinurus japonicus</i>	1, 2, 5, 6, 8, 9, 15, 16, 17, 18, 19, 21	103–105
<i>Palinurus vulgaris</i>	1	31, 72, 102
<i>Parribacus antarcticus</i> ( <i>ursus major</i> )	2, 5, 6	106
<i>Penaeus japonicus</i>	1, 6, 8, 9, 15	107–109
<i>Penaeus orientalis</i>	1, 8, 11, 13, 21, 28	68, 235
<i>Scyllarides latus</i>	1, 2	110
<i>Scyllarides squamosus</i> ( <i>Syllarus sieboldi</i> )	2, 5, 8, 20, 21, 24	104
<i>Upogebia deltaura</i>	5, 10, 22, (?)	111

### Key

1. Astaxanthin	(1.1)	15. Canthaxanthin	(1.4)
2. Lutein	(1.10)	16. Isocryptoxanthin	(2.27)
3. Violaxanthin	(2.40)	17. 4-Keto- $\gamma$ -carotene	(6.13)
4. Diadinoxanthin	(6.3)	18. Rubixanthin	(6.14)
5. Zeaxanthin	(1.9)	19. Celaxanthin	(6.15)
6. $\beta$ -Carotene	(1.5)	20. Alloxanthin	(1.2)
7. 4-Keto- $\alpha$ -carotene (= Phoenicopterone)	(6.7)	21. $\beta$ -Doradexanthin	(2.32)
8. Phoenicoxanthin (= adonirubin)	(1.8)	22. $\gamma$ -Carotene	(2.26)
9. Echinenone	(1.11)	23. Gazaniamixanthin	(5.6)
10. Isozeaxanthin	(2.41)	24. 4-Keto-4'-hydroxy- $\beta$ -carotene (4'-hydroxyechinenone)	(6.18)
11. Crustaxanthin	(6.2)	25. $\epsilon$ -Carotene	(2.33)
12. Lutein 5,6-epoxide	(6.6)	26. 7,8-Didehydroastaxanthin	(1.6)
13. Tunaxanthin	(6.16)	27. 7,8,7',8'-Tetrahydro- astaxanthin	(1.7)
14. $\delta$ -Carotene	(6.17)	28. Idoxanthin	(6.10)



(6.17)



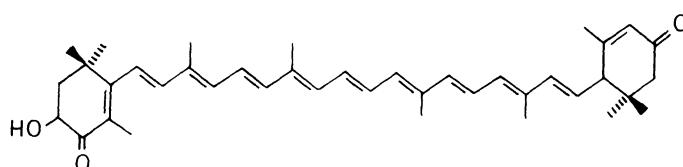
(6.18)

Table 6.10 Carotenoid distribution in Decapoda – Anomura

Species	Pigments	Reference
<i>Anapagurus chiroacanthus</i>	1	40
<i>Clibanarius erythropus (misanthropus)</i>	1, 2, 3, 4, 5, 6, 7, 8, (9)	97, 112, 113
<i>Dardanus arrosor</i>	2, 3, 6	114
<i>Emerita analoga</i>	1, 8, 10, 11, 12	115
<i>Eupagurus bernhardus</i>	1, 4, 11, 13, 14	37, 111, 116
<i>Galathea intermedia</i>	1, 4, 6	37
<i>Pagurus pollicaris</i>	Present	117
<i>Pagurus prideauxi</i>	1	58, 97, 115
<i>Pagurus rubescens</i>	4	37, 40
<i>Paralithodes brevipes</i>	(?) 15	118
<i>Pleuroncodes planipes</i>	1, 5	119
<i>Porcellana longicornis</i>	4	96
<i>Rhithropanopeus harrisii tridentatus</i>	1, 3, 5, 6, 11, 13, 16	120

## Key

- |                                      |                        |   |        |
|--------------------------------------|------------------------|---|--------|
| 1. Astaxanthin                       | (1.1)                  | 10. $\alpha$ -Carotene  | (2.25) |
| 2. Echinenone                        | (1.11)                 | 11. Zeaxanthin  | (1.9)  |
| 3. Canthaxanthin                     | (1.4)                  | 12. Diatoxanthin  | (4.2)  |
| 4. Phoenicoxanthin<br>(= adonirubin) | (1.8)                  | 13. Lutein 5,6-epoxide  | (6.6)  |
| 5. $\beta$ -Carotene                 | (1.5)                  | 14. 4-Keto-4-ethoxy- $\beta$ -carotene                            | (?)    |
| 6. Lutein                            | (1.10)                 | 15. Papilioerythrinone (3-hydroxy- $\alpha$ -carotene-4,3'-dione) | (6.19) |
| 7. $\alpha$ -Doradexanthin           | (6.4)                  | 16. $\gamma$ -Carotene  | (2.26) |
| 8. Alloxanthin                       | (1.2)                  |   |        |
| 9. Plioxanthophyll                   | (structure<br>unknown) |   |        |



(6.19)

## 76 The biochemistry of the carotenoids

Table 6.11 Carotenoid distribution in Brachyura

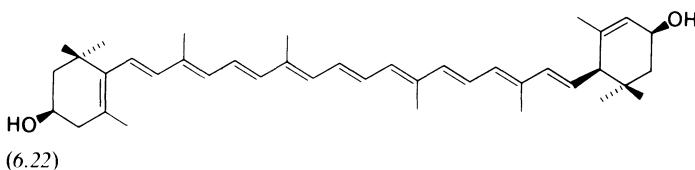
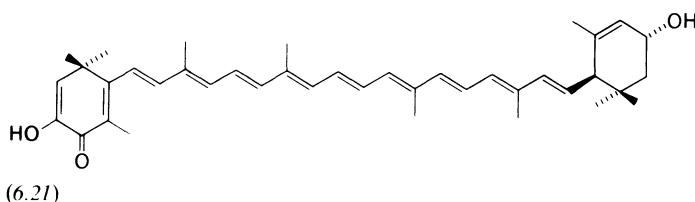
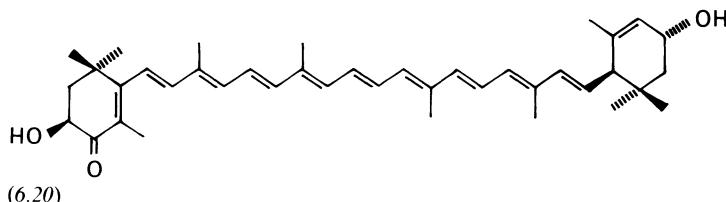
Species	Pigments	Reference
<i>Callinectes sapidus</i>	1	121
<i>Cancer pagurus</i>	1, 2	47, 96, 122
<i>Carcinus maenas</i>	1, 2, 5, 6, 8, 9, 11, 15, 16	40, 96, 102, 123–128
<i>Carcinus mediterraneus</i>	2, 5, 6, 7, 9, 10, 15	129, 130
<i>Chionectes opilio</i>	2, 5, 12	235
<i>Eriphia spinifrons</i>	2, 5, 6, 7, 9, 10	102, 131
<i>Geryon quinquedens</i>	6, 12	132
<i>Hyas coarctatus</i>	5, 7	111
<i>Macropipus holsatus</i>	1, 2, 5, 6, 15	130, 133
<i>Maja squinado</i>	1, 2	134, 135
<i>Pachygrapsus marmoratus</i>	1, 2, 5, 6, 10, 15	97, 124, 129–131, 136–138
<i>Pinnotheres pisum</i>	1, 2, 5, 7, 9, 15	139
<i>Portunus brevirostris</i>	1	40
<i>Portunus depurator</i>	15	40
<i>Portunus longicornis</i>	1, (?5)	40
<i>Portunus persillus</i>	1, 5	40
<i>Portunus puber</i>	2	31
<i>Portunus trituberculatus</i>	2, 12, 13, 14, 15, 16	140, 235
<i>Potamon dehaari</i>	1, 2, 5, 6, 10, 17, 18, 19, 21	238
<i>Potamon edulis</i>	1, 2, 5	141
<i>Sesarma (Holmetopus)</i>	2, 5, 6, 7, 10, 12, 17, 19, 20	142, 143, 239
<i>haematocheir</i>		
<i>Sesarma intermedia</i>	5, 6, 7, 10, 17	142
<i>Taliepus nuttalii</i>	13	144
<i>Xantho poressa</i>	5, 6	130, 133

### Key

1. $\beta$ -Carotene	(1.5)	12. $\beta$ -Doradexanthin	(2.32)
2. Astaxanthin	(1.1)	13. Phoenicoxanthin	(1.8) (= adonirubin)
3. Isozeaxanthin	(2.42)	14. 4'-Hydroxyechinenone	(6.18)
4. $\gamma$ -Carotene	(2.26)	15. Canthaxanthin	(1.4)
5. Lutein	(1.10)	16. 3-Ketocanthaxanthin	(6.1)
6. Zeaxanthin	(1.9)	17. Flavoxanthin	(5.3)
7. Lutein 5,6-epoxide	(6.6)	18. Papilioerythrinone	(6.19)
8. $\delta$ -Carotene	(6.17)	19. Fritschiallassanthin	(6.20)
9. Echinonene	(1.11)	20. 2,3-Didehydrofritschiallassanthin	(6.21)
10. $\alpha$ -Doradexanthin	(6.4)	21. 3'-Epilutein	(6.22)
11. 7,8,7',8'-Tetrahydro-	(1.7)		
astaxanthin			

### (f) Stomatopoda

The only species so far reported to contain a known carotenoid is *Squilla mantis* which accumulates astaxanthin (1.1) [80].



## 6.2 LOCALIZATION

### 6.2.1 OVERALL PICTURE

Carotenoids exist in three forms in the Crustacea: (1) as free pigments, that is carotenes and unesterified xanthophylls; (2) as xanthophylls esterified to long-chain fatty acids; (3) as xanthophylls attached to proteins as carotenoproteins. All three types have been detected in many species. The free pigments appear to accumulate in the hepatopancreas whilst the carotenoproteins have been observed in eggs, ovaries, hypodermis, cuticle (chitin), retina, gut and, to some extent, the hepatopancreas. The distribution of well-characterized chromoproteins in these organs is given in Table 6.12. A full list of all reported carotenoproteins up to 1967 was collected by Cheeseman and his colleagues [89] and the properties of these pigments are fully displayed in Chapter 1.

The carotenes and esterified xanthophylls appear to be storage forms and accumulate dissolved in lipids in the hepatopancreas from which they are transferred to other sites in the body via the haemolymph [146, 147].

### 6.2.2 QUANTITATIVE DISTRIBUTION

The most thorough investigation is that of Herring on decapod samples, particularly from the specimens of Caridea and Penaeidea collected during

## 78 The biochemistry of the carotenoids

Table 6.12 Carotenoprotein distribution in Crustacean tissues

Species	Colour of pigment	Absorption maxima (nm) (visible)	Carotenoid component	Reference
<b>Haemolymph</b>				
<i>Chirocephalus diaphanus</i>	Blue	(460), (480), 680	Canthaxanthin	148
<i>Emerita analoga</i>	Orange	463, 472	Astaxanthin + $\beta$ -carotene	149
<i>Idothea granulosa</i>	Green	(400–500), (625)	Canthaxanthin	48
<i>Idothea montereyensis</i>	Green	(430), (455), 489, (625), 680	Canthaxanthin	51
<i>Tanymastix lacunae</i>	Blue/purple	485, 685	Canthaxanthin	148
<b>Ovaries, eggs</b>				
<i>Artemia salina</i>	Orange/red	470	Canthaxanthin	128, 172
<i>Branchipus stagnalis</i>	Blue	625, (675)	Canthaxanthin	148, 173
<i>Cancer pagurus</i>	Orange	470, 490	Astaxanthin + other xanthophylls	102, 174
<i>Emerita analoga</i>	Orange	463, 472	Astaxanthin	149
<i>Eupagurus bernhardus</i>	Purple	465, 495, 580	Astaxanthin ester	116
<i>Homarus americanus</i>	Green (ovoverdin)	(440), 464–468	Astaxanthin	78–91
<i>Homarus gammarus</i>		(500), 650–670		
<i>Idothea granulosa</i>	Green (480)	(430), (455), (625), 68	Canthaxanthin	48
<i>Idothea montereyensis</i>		470, 495		51
<i>Pagurus prideauxi</i>	Orange	470, 495	Mixed	150
<i>Palinurus vulgaris</i>	Red(blue)	560, (600)	Astaxanthin	31, 72, 102
<b>Exoskeleton</b>				
<i>Astacus astacus</i>	Green	(470), (492), 632	Astaxanthin	31, 102
<i>Carcinas maenas</i>	Green	(480), 460, 625	Astaxanthin	102, 128, 151, 152
<i>Eriphia spinifrons</i>	Red/purple	(400), 625	Astaxanthin	102
<i>Homarus vulgaris</i>	Blue	633	Astaxanthin	(See <i>H. americanus</i> )
<i>Idothea granulosa</i>	Green (480)	(430), (455), 640	Astaxanthin	48
<i>Idothea montereyensis</i>		(625), 680		51
<i>Labidocera acutifrons</i>	Blue	—	Astaxanthin	153
<i>Orconectes limosus</i>	—	—	Astaxanthin canthaxanthin	98–100
<i>Palinurus vulgaris</i>	Red(blue)	560, (600)	Astaxanthin	31, 72, 102

various voyages of RRS *Discovery* [67]. A selection of his data is given in Table 6.3. The total concentrations in the animals surveyed ranged from 60  $\mu\text{g/g}$  to 500  $\mu\text{g/g}$  (fresh wt.) in various species but individual variation is considerable; for example values within the range 116 to 379  $\mu\text{g/g}$  (mean 215) (Table 6.13) were observed in *Acanthephyra purpurea*. In all cases the

carapace and hypodermis represented the major reservoir of body pigments but in some cases this could fall to as low as 58% of the total as in the case of *Sergestes corniculum* (Table 6.13). The amount in the eyes of the species examined in this survey was very low, varying from 1 to 5% of the total, which contrasts sharply with the situation in some euphausiids where up to 94% of the total pigment is concentrated in the eyes [64, 66]. The concentration in the eggs of some species was occasionally much greater than in the rest of the adult animal; the extreme was *Oplophorous spinosus* when the values were 2447 µg/g and 244 µg/g respectively [67].

Table 6.13 Carotenoid distribution and concentration in some adult decapods [67]

Species	Total pigment concn. (µg/g)		Pigment distribution (% of total)			
	Adults	Eggs	Eyes	Gut	Hepato-pancreas	Residue*
<b>Caridea</b>						
<i>Acanthephyra purpurea</i>	215	353	1	11	2	87
<i>Systellaspis debilis</i>	274	1271	1	11	2	86
<i>Plesionika ensis</i>	56	32	3	22	6	68
<b>Penaeidea</b>						
<i>Parapenaeus longirostris</i>	58	—	1	27	5	67
<i>Gennadas valens</i>	499	—	1	9	0	90
<i>Sergestes corniculum</i>	113	—	1	25	17	58

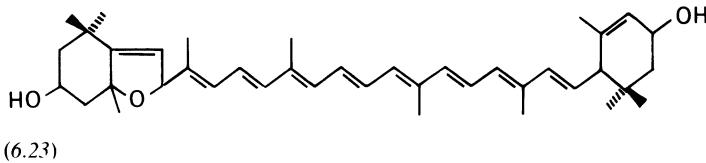
\*Essentially hypodermis and carapace.

Concentrations can vary within the exoskeleton as in *Astacus leptodactylus* where the concentration in the antennae is twice that in the carapace [71]. A study with *Carcinus maenas* [127] revealed marked quanti-

Table 6.14 Carotenoid distribution (% of total present) in various organs of *Carcinus maenas* [127]

Pigment		Hepatopancreas	Ovary	Epidermis
β-Carotene	(1.5)	81	71	8
α-Carotene	(2.25)	9	3	—
Echinone	(1.11)	Trace	1	—
Isocryptoxanthin	(2.27)	Trace	4	—
Canthaxanthin	(1.4)	Trace	Trace	10
Lutein	(1.10)	3	13	24
Lutein 5,8-epoxide	(6.23)	2	—	1
Zeaxanthin	(1.9)	—	2	1
Astaxanthin	(1.1)	4	6	56
Unknown		1	5	10

## 80 The biochemistry of the carotenoids



tative differences in the carotenoid distribution in various organs (Table 6.14). For example,  $\beta$ -carotene preponderates in the hepatopancreas whereas astaxanthin is the major pigment in the epidermis. Similarly about 90% of the total pigment in the carapaces of *Pandalus borealis* [153] and *Penaeus japonicus* [108, 154] is astaxanthin.

### 6.2.3 INTEGUMENT

#### (a) Carapace

As just stated above in most crustaceans free astaxanthin represents the bulk of the pigment in the carapace. Other keto carotenoids such as canthaxanthin (1.4), 4'-hydroxyechinenone (6.18) and 3-keto-canthaxanthin (6.1) are found along with astaxanthin in some species, e.g. *Portunus trituberculatus* [140] and *Panulirus japonicus* [103]. Canthaxanthin is also present in some *Iodothea* [51] and a new pigment papilioerythrinone (6.19) is found in the crab *Paralithodes brevipes* [118]. Traces of esterified astaxanthin occasionally occur as for example in *Pagurus prideauxi* [155]. The keto carotenoids exist mainly in the form of carotenoproteins (see Table 6.2). The prawn *Metapenaeus affinis* appears to be an exception in that it accumulates lutein (1.10) and  $\beta$ -carotene (1.5) in its carapace [156].

#### (b) Epidermis

In contrast to the carapace, the subepithelial tissues contain mainly esterified carotenoids localized in the chromatophores. Esterified astaxanthin has been reported in the epidermis of *Homarus vulgaris* and *Nephrops norvegicus* [36] and of *Plesiopenaeus edwardsii* [157]. Some free astaxanthin is found in the epidermis of *Aristeomorpha (Penaeus) foliacea* and *Aristeus antennatus* [158, 159].

The problem of transfer of carotenoids from epidermis to carapace can only be discussed in relation to moulting, probably one of the most important metabolic activities of Crustacea. The actual shedding of the cuticle is known as ecdysis and the overall process including the metabolic activity leading up to ecdysis is known as moulting. The process has been visualized diagrammatically by Castillo *et al.* [160] (Fig. 6.1) and this representation will be used in the following discussion. There seems no doubt that the

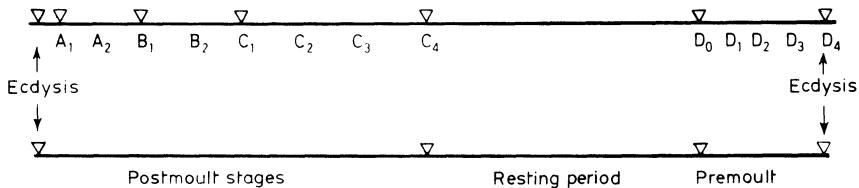


Fig. 6.1. Diagrammatic representation of the intermoult cycle in crustaceans [160].

pigments are transferred from the epidermis to the carapace during moulting and the qualitative changes, which are often observed between the epidermal and carapace carotenoids, take place in the carapace itself [160]. A detailed study of *Carcinus maenas* indicates that at stage D<sub>2</sub> (Fig. 6.1) the pigments in the epidermis and carapace are identical but during stages D<sub>3</sub> and D<sub>4</sub> specific pigments appear in the carapace. However, the complete conversion of epidermal pigments into carapace pigments only takes place after ecdysis during the A<sub>1</sub> and B intermoult stages [161]. The same pattern of changes is observed with *Pachygrapsus marmoratus* [162].

Changes in the appearance of *C. maenas* during moulting varies markedly from green (A<sub>2</sub>) to yellow (C<sub>1</sub>) to red (D<sub>1</sub>). This is probably due to changes in amount or type of carotenoproteins present rather than to marked quantitative changes in the free pigments [163].

#### 6.2.4 H A E M O L Y M P H

Haemolymph transports material between the hepatopancreas and the integument [160] and it is therefore not surprising that its carotenoid content varies according to the stage of moult. In *Astacus fluviatilis* it is deep orange-red before and during ecdysis and is colourless when ecdysis is complete [164]. A low level of carotenoids in the haemolymph of *Carcinus maenas* is observed at the C<sub>1</sub>-C<sub>2</sub> stage (Fig. 6.1); it increases during the C<sub>3</sub> stage and falls again during the C<sub>4</sub> stage [165, 166].

#### 6.2.5 H E P A T O P A N C R E A S

The hepatopancreas not only plays an important part in the absorption of carotenoids from the animals' food but also shows marked changes during the moulting cycle and egg production. Between stages C<sub>1</sub> and D<sub>1</sub> (Fig. 6.1) the organ becomes highly coloured. At the D<sub>2</sub> stage the animals stop feeding and the gland becomes less coloured and smaller as reserves are metabolized for elaboration of new integument and for vitellogenesis [147, 160]. The distribution of carotenoids in the hepatopancreas of various crustaceans is given in Table 6.15. The role that the hepatopancreas plays in the conversion

## 82 The biochemistry of the carotenoids

Table 6.15 Carotenoids found in the hepatopancreas of crustaceans

Species	Pigment	Reference
<i>Carcinus maenas</i>	1 (major component)	127, 161
<i>Carcinus mediterraneus</i>	1 (major component)	129
<i>Homarus vulgaris</i>	1 (traces)	93
<i>Pachygrapsus marmoratus</i>	2, 3, 4, 5	162
<i>Pagurus prideauxi</i>	Traces	127
<i>Penaeus japonicus</i>	Large amounts	155
<i>Xantho poressa</i>	1 (major component)	145

*Key*

1. $\beta$ -Carotene	(1.5)	4. Canthaxanthin	(1.4)
2. Lutein (unesterified)	(1.10)	5. Carcinoxanthin	(Unknown structure)
3. Astaxanthin	(1.1)		

of food carotenoids into the more oxidized carotenoids, e.g. astaxanthin, characteristic of the integument of crustaceans, seems to vary with species which can be divided into two main groups [160]. The first group can metabolize  $\beta$ -carotene through to astaxanthin, as in the case of *Penaeus japonicus* [106], whereas the second group, characterized by *Panulirus japonicus* [104], *Portunus trituberculatus* [167] and *Pagurus prideauxi* [155], can take the metabolic sequence only as far as echinenone (1.11) (see also Section 6.3).

### 6.2.6 DIGESTIVE TRACT

The gut wall can act as a storehouse in some crustaceans. Carotenoids are found in fat globules in the cells of the gut wall of *Daphnia* [16] and in the fat body of *Simocephalus vetulus* where they can exist as carotenoproteins [168]. Carotenoproteins are also found in the stomach wall of *Aristeus antennatus* [169] and of *Plesiopenaeus edwardsii* [157]. Not much information is available about the nature of the carotenoids in the digestive tract although it is known that astaxanthin, both free and esterified, is present in *Plesiopenaeus edwardsii* and that  $\beta$ -carotene is the major component in *Astacus leptodactylus* [170].

The transfer of carotenoids from gut to hepatopancreas is probably mediated by a carrier protein [171] which may be structurally similar to the apoprotein of  $\alpha$ -crustacyanin [91].

### 6.2.7 GONADS

A characteristic of crustaceans is the accumulation of carotenoids in the gonads and eggs in the form of chromoproteins. The distribution of these

well characterized chromoproteins has already been summarized in Table 6.14. The metabolic changes occurring during the sexual cycle are discussed in Section 6.3.2.

### 6.3 METABOLISM

#### 6.3.1 MODIFICATION OF FOOD CAROTENOIDS

There is little doubt that the ultimate source of the carotenoid pigments in the phylum Crustacea is the food. Loss of pigment on fasting [175] or on a carotenoid-free diet [176, 177] was demonstrated in the 1920s and repigmentation on feeding carotenoid-rich diets was achieved experimentally soon afterwards [178]. As already indicated the characteristic pigments of crustaceans contain one or two keto groups at C-4, and/or C-4' with or without additional hydroxyl groups at C-3 and/or C-3'. It was pointed out in the preceding section that some organisms characteristically produce non-hydroxylated keto pigments, e.g. canthaxanthin (1.4), whereas others produce keto carotenoids, such as astaxanthin (1.1), hydroxylated at C-3. The great majority of keto carotenoids are  $\beta$ -carotene derivatives and as keto carotenoids are not significantly present in the diet of Crustacea feeding on phytoplankton they must arise from  $\beta$ -carotene or its hydroxylated derivatives present in the food. However, in pelagic species the food (small crustaceans) contains large amounts of keto carotenoids and most if not all of the pigments of these species arrive preformed in their food. However, there is no doubt that, given the opportunity under experimental conditions, pelagic animals can synthesize keto carotenoids from  $\beta$ -carotene.

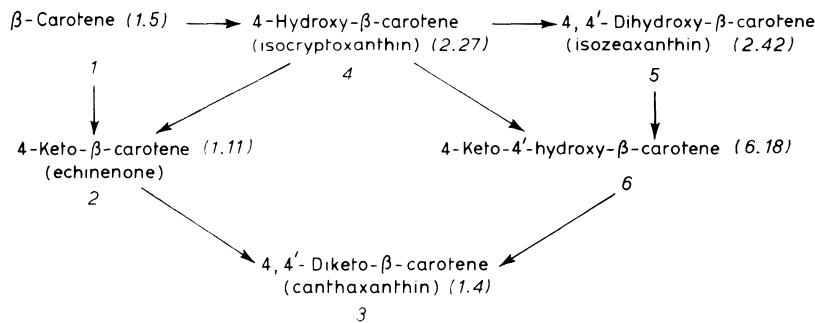


Fig. 6.2. Possible pathway for echinenone and canthaxanthin formation from  $\beta$ -carotene in crustaceans.

For those organisms which make only non-hydroxylated keto carotenoids the number of possible biosynthetic pathways from  $\beta$ -carotene is limited (Fig. 6.2). Experiments designed to elucidate the functioning pathway have been three in type: (i) detection of presumptive intermediates; (ii) feeding

## 84 The biochemistry of the carotenoids

proposed precursors and following changes in levels of possible intermediates and end products; (iii) administering  $^{14}\text{C}$ -labelled intermediates and isolating radioactive products. No enzymic studies have yet been reported. The last two methods have clearly defined the direct pathway  $1 \rightarrow 2 \rightarrow 3$  (Fig. 6.2) as that operating in the brine shrimp *Artemia* (179–181). It was also shown that isozeaxanthin (2.41) could not be further metabolized and isocryptoxanthin (2.27) could not be converted into echinenone (1.11) or canthaxanthin ( $4 \rightarrow 2 \rightarrow 3$ ), although it could be converted into 4-keto-4'-hydroxy- $\beta$ -carotene (6.18) ( $4 \rightarrow 6$ ) which appears to be a metabolic dead-end. So it is clear that in these experiments Californian *Artemia* cannot easily oxidize a free hydroxyl group at C-4, although it can insert a keto group directly into this position. The fact that traces of astaxanthin (1.1) are found in a Canadian strain of *Artemia* [7] indicates that further oxidation of canthaxanthin can take place to a slight extent in some strains.

In the case of *Daphnia magna*, on the other hand, isocryptoxanthin and isozeaxanthin are rapidly converted into echinenone and canthaxanthin ( $4 \rightarrow 2$  and  $5 \rightarrow [6] \rightarrow 3$ ) (Fig. 6.2), respectively [18]. So it is apparent that in some genera hydroxylation followed by further oxidation can occur and that, presumably, direct insertion of keto groups does not take place. However, it is still not clear whether  $4 \rightarrow 5$  or  $4 \rightarrow 6$  is the main pathway involved *in vivo*. As with *Artemia* occasionally some *Daphnia* carried the oxidation as far as astaxanthin. The labelling pattern in the pigments of *Iodothea granulosa* after feeding [ $^{14}\text{C}$ ]- $\beta$ -carotene suggests that in this animal pathways  $1 \rightarrow 4 \rightarrow 2$  and  $1 \rightarrow 4 \rightarrow 6 \rightarrow 3$  (Fig. 6.2) are the main routes of synthesis [182].

The Decapoda are characterized by the accumulation of astaxanthin (1.1). The additional oxidation steps required to produce this pigment increases considerably the possible number of pathways involved. Many proposals have been made [see 160, 183] but unequivocal biochemical facts are few. Suggestions that in the macrourean *Panulirus japonicus* there is direct introduction of keto groups [105] appear to have been invalidated by isotope experiments which indicate that hydroxylation immediately precedes oxidation [103, 104] so that the pathway is probably  $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 6 \rightarrow 7$ , as indicated in Fig. 6.3. Similar proposals have been made on the basis of pigment analysis for other macroureans e.g. *Scyllarides latus* [110] and *Penaeus japonicus* [106, 108]. In the latter species confirmation by isotope experiments followed [104]. The absence of detectable hydroxylated derivatives in the Anomoureans *Dardanus arrosor* [114] and *Emerita analoga* [115] suggested the direct step  $5 \rightarrow 7$ , rather than  $5 \rightarrow 6 \rightarrow 7$  (Fig. 6.3), in which two hydroxyl groups are inserted directly into canthaxanthin. However, the detection of phoenicoxanthin (= adonirubin) (1.8) in *Penaeus japonicus* [184], *Clibanarius misanthropus* [112, 185], *Panulirus japonicus* [104] and *Portunus trituberculatus* [167] satisfies the requirement for a stepwise hydroxylation of canthaxanthin with the overall probable pathway from  $\beta$ -carotene being  $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 6 \rightarrow 7$  (Fig. 6.3).

All the indications in the brachyureans examined, *Carcinus maenas* [186], *Pinnotheres pisum* [139], *Portunus trituberculatus* [140] and *Pachygrapsus marmoratus* [138], are that the basic pathway is again 1→2→3→4→5→6→7 (Fig. 6.3) and this has been confirmed by isotope experiments in *P. trituberculatus* [140].

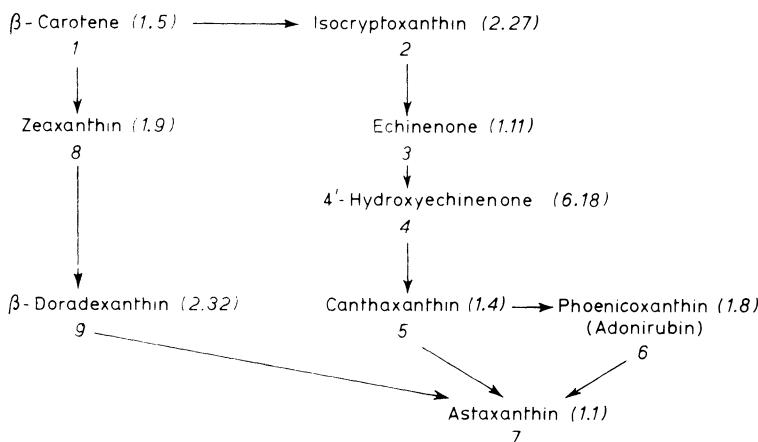


Fig. 6.3. Some possible metabolic pathways from  $\beta$ -carotene to astaxanthin in Crustacea.

A further possibility (1→8→9→7) (Fig. 6.3) is that zeaxanthin can be converted into astaxanthin by the direct insertion of keto groups in *Panulirus japonicus* [105], *Penaeus japonicus* [184] and *Geryon quinquedens* [132]. The intermediate would be  $\beta$ -doradexanthin (2.32) which has been reported in *Panulirus japonicus* [105]. In *G. quinquedens* the interconversions are considered to take place at the ester level.

There is no clear evidence yet that carotenoids with  $\epsilon$ -rings, e.g.  $\alpha$ -carotene (2.25) or lutein (1.10), can be converted into crustacean keto carotenoids, although the possibility now exists following the work on fish and birds (see Chapters 7 and 10); lutein can, however, be stored selectively by *Idothea* spp. and used in the production of coloured lipoproteins in the carapace [184].

The conversion of  $\beta$ -carotene into echinenone in *Panulirus japonicus* takes place in the internal organs, mainly the hepatopancreas, whilst the final steps leading from echinenone to canthaxanthin are localized in the carapace [103, 104]. On the other hand all the steps occur in the inner organs of *Penaeus japonicus* [107]. Nothing is known of the site of synthesis of carotenoproteins. Purified amino acids in the diet, in particular methionine, can raise carotenoid levels of crustaceans; however high levels decrease the pigment content [237].

## 86 The biochemistry of the carotenoids

### 6.3.2 METABOLISM DURING SEXUAL CYCLE

During egg production by Crustacea there is a very marked increase in carotenoid levels in the ovaries; in the case of *Plesiopenaeus edwardsii*, for example, the concentration rises from 20–40 µg/g in a period of sexual repose to 430–518 µg/g in mature ovaries [187]. The transfer takes place in *Artemia salina* at a very precise stage of development [181]. About 50% of the total body carotenoids are transferred from the mother to the egg sac in *Daphnia magna* [18], *Simocephalus vetulus* [168] and *Tigriopus fulvus* [93]. The transfer is said to be effected by carotenoproteins via the haemolymph [124, 181].

There is no marked change in the carotenoid content of the eggs of the lobster [123], *Daphnia magna* [18], *Emerita analoga* [115] or *Acanthephyra* spp. [188] during embryogenesis. However, in the first two species the carotenoprotein is disrupted just before hatching [16, 18] and this is probably a general phenomenon [189]. About 30 days before hatching in *Acanthephyra purpurea* the xanthophylls in the yolk are esterified and transferred to the chromatophores of the developing embryo [188]. Some qualitative changes were, however, noted in *Artemia* [190], including the synthesis of canthaxanthin (1.4), but no such changes occurred in the lobster [123] or *Daphnia* [18]; in *E. analoga* [115] astaxanthin represents a higher proportion of the total pigments in eggs produced late than those formed early in the season. Changes in carotenoids during the annual cycle of *Gammarus lacustris* have recently been reported [191].

### 6.3.3 METABOLISM RESULTING IN LOSS OF PIGMENTS

Ablation of the eye stalks during development of the ovaries in *Rithropanopeus harrisii* results in an increase in ovarian weight and a darkening of colour; however, if removal is carried out during the resting period, the ovary increases in weight but not in colour [192].

The amount of pigment lost during a moult will depend on the amount of carotenoid present within the chitin which is discarded; very little was lost by *Systellaspis debilis* [148] although the spring-lobster *Panulirus interruptus* lost 16–63% of its total astaxanthin at the first moult and 32–85% of the remainder at the second moult [193].

## 6.4 HORMONAL CONTROL OF PIGMENTATION

### 6.4.1 EYE STALK SECRETIONS

The effects of neurosecretions of the eye stalk on pigment metabolism in crustaceans are complex and still mainly at the descriptive stage. In *Palaemon serratus* there is a reduction in the number of pigment granules in

the chromatophores in specimens which had had their eye stalks removed; this is accompanied by a loss of xanthophylls and increase in  $\beta$ -carotene [194]. In *Uca pugilator* bilateral removal of the eye stalks leads to a drop in total carotenoids although there is an increase in the levels in the hepatopancreas and then in the hypodermis just prior to the moult [195]. Bilateral eye stalk ablation results in lowered amounts of esterified astaxanthin in *Dardanus arrosor* [196] whereas in *Macrobrachium rosenbergii* a large increase in both free and esterified astaxanthin is observed [197].

#### 6.4.2 ANDROGENS

When the androgen glands are grafted on to female *Talitrus saltator* and *Orchestia gammarellus* the masculinization of the animals is accompanied by the accumulation of astaxanthin in the second antennae II as noted in normal males [63] (see Section 6.5). Extracts of the androgen glands have the same effect as implantation of the intact gland [198].

### 6.5 SEXUAL DIMORPHISM

Early workers indicated that female Crustacea contained more carotenoids than the corresponding males [126, 199] and recently this has been confirmed [145]. Furthermore qualitative differences have been noted in *Emerita analoga* [115] where  $\beta$ -carotene appeared in the females in addition to astaxanthin and other xanthophylls, although it was absent from males. An important specific observation is that the orange colour of the second antennae in the females of *Orchestia gammarellus* and *Talitrus saltator* is due to the accumulation of astaxanthin in these structures [198].

### 6.6 COLOUR VARIANTS

The contribution of carotenoids, both free and as protein complexes, to the overall colour of crustaceans is self-evident but their contribution to subtle variations in colour has been examined in detail only in a few cases. The red varieties of the littoral *Iodothea montereyensis* accumulate free canthaxanthin (1.4) in the exocuticle and endocuticle whereas in the green varieties the free carotenoid is replaced to a considerable extent by a green canthaxanthin-protein complex, the former predominating; the brown varieties represent a transition stage between the red and green forms, containing a mixture of free and protein-bound canthaxanthin; no pigment was observed in the epidermis in any colour variant [51, 200]. In *I. granulosa*, on the other hand, the colour changes are associated with the epidermis for, unlike *I. montereyensis*, the cuticle is orange in all colour variants owing to the presence of

## 88 The biochemistry of the carotenoids

free canthaxanthin and other xanthophylls in the exocuticle and lutein in the endocuticle. The red, green and blue variants arise mainly from the varying amounts of free canthaxanthin and a green chromoprotein in the epidermis although the chromatophores do play some part in the colouration [48, 200]. *I. resecata* exists in brown and green forms and the pigment distribution in the latter is similar to that in *I. montereyensis*, in that the pigments contributing to the colour are located in both endo- and exo-cuticle; in the brown variant canthaxanthin is confined to the exocuticle and the green carotenoprotein to the endocuticle [200]. The variants differ in that the chromatophores in the brown specimens are moderately to fully expanded whereas in the green animals they are punctate. The ecological implications of these pigmentation patterns in the three littoral *Idothea* have been discussed in detail [200] and it was concluded that selection plays an important part in basic structural and biochemical aspects within a group of closely related species. It is noteworthy that the pelagic *I. metallica* does not accumulate keto carotenoids to any significant extent but that the main pigment is  $\beta$ -carotene and that it uses its chromatophores to control its pigmentation [50].

The pigment concentration in oceanic copepods, euphausiids and decapods shows no correlation with the day depths of the species concerned, although in the case of the decapods the deeper-living species appear to be more heavily pigmented. The reason for this is the differential distribution pattern of pigments. For example *Sergia* spp. existing below 650–700 m have orange coloured chitin with many small chromatophores which gives an overall uniform red appearance: on the other hand *Sergestes* spp. with a population maximum above 650–700 m have colourless chitin and a relatively small number of chromatophores. This gives the latter group a much greater capacity for colour change [201].

## 6.7 ENVIRONMENTAL AND ECOLOGICAL CONSIDERATIONS

### 6.7.1 SEASONAL VARIATIONS

The seasonal variations of carotenoid content of the ovaries have already been discussed. Variation was also observed with whole specimens of *Emerita analoga* [115]; maximum content was recorded in both males and females in July–August and minimal levels in the winter months. Maximum and minimum levels in whole *Orconectes limosus* [47] and in the hepatopancreas of *Plesiopanaeus edwardsii* [187] were noted in spring and autumn respectively. A maximum was observed in winter in *Diaptomus claripes* and *D. pallidus* [202]. No obvious changes were noted in *Artodiaptomus salinus* [28]. Seasonal changes in colour have been recorded in *Acanthodiaptomus denticornis* [203], *Diaptomus sicilis* and *D. nevadensis* [204].

### 6.7.2 DIURNAL VARIATIONS

Diurnal variation in carotenoid content has been reported in *Penaeus japonicus* [205], *Acanthodiaptomus denticornis* [206], *Daphnia longispina* [207] and *Chirocephalus diaphanus* [159]. In *D. longispina* a minimum was observed during the day whereas in *C. diaphanus* it occurred at 06.00–10.00 h with a maximum at 14.00 h. The diurnal variation in carotenoids in the zooplankton in Lake Pavin (France) is probably due to the change in ratio of the pigmented *Acanthodiaptomus denticornis* and the unpigmented *Cyclops* present than to changes in amount of pigment in the organisms [231].

### 6.7.3 BACKGROUND AND ILLUMINATION

Some species, for example *Palaemonetes* [208] and *Palaemon (Leander) serratus* [209, 210], retain their pigments when placed on a black background and lose them on a white background; this is reflected in the increased number of chromatophores in animals kept on a black background compared with those on a light background [211]. This response is mediated by light falling on the eye stalks which act as photoreceptors [212]. The presumed hormonal factor which would be liberated on illumination appears in *Dardanus arrosor* to stimulate the conversion of  $\beta$ -carotene (1.5) into astaxanthin (1.1) and to increase the excretion of lutein (1.10) esters [195].

The effect of light on *Daphnia* is to stimulate pigment accumulation although the eyes are not, in this case, the photoreceptors [213]; possibly direct illumination of the brain is required. *Gammarus puleanus* loses its pigment when placed in darkness [214] as does *G. duebeni* [215]; the latter regains its pigment on being illuminated [215]. The hypogean isopod, *Asellus aquaticus caverniculus* and the amphipods *Niphargus* spp. are colourless although their diet contains adequate amounts of carotenoid [46, 216]. *N. puleanus* but not *N. plateaui* recovers its colour on illumination [216]. In the case of *Gammarus pulex subterraneus* [217] and *Procambarus simulans simulans* [218] the colour of the animals depends only on the nature of the food. Hypogean *Cambarus bartonii tenebrosus* retains small amounts of carotenoid, mainly astaxanthin, but the levels are lower than in epigean specimens [219]. One cavernicolous species *Orconectes pellucidus pellucidus* accumulates  $\beta$ -carotene and lutein; apparently it lacks the enzymes which convert  $\beta$ -carotene into keto carotenoids [219].

## 6.8 CROWDING

The crowding of populations of *Daphnia* results in reduction of their carotenoid levels [213]; this may reflect lowered feeding activity under these adverse conditions.

## 6.9 PARASITIZATION

Many years ago it was noted that the rose colour of the haemolymph of *Inachus mauritanicus* was greatly enhanced when the crab was parasitized by *Sacculina neglecta* [220]; this is probably due to the degeneration of the ovarian cycle and the alteration of the inter-moult cycles [147]. The cirripede itself accumulated only  $\beta$ -carotene (1.5) when parasitizing *Carcinus maenas* in which astaxanthin (1.1) is the predominating pigment [96]. Similarly the acanthocephalan worm *Polymorphus minutus* contains only astaxanthin when parasitizing *Gammarus pulex* which also accumulates pigments other than astaxanthin [59]. The isopod *Pliophryxus philonika* which parasitizes *Processa edulis* contains both  $\beta$ -carotene and astaxanthin whereas the chromatophores of the host contain only astaxanthin; in contrast *Urobopyrus processae*, which also lives on *P. edulis*, accumulates only  $\beta$ -carotene [222].

## 6.10 FUNCTION

Apart from the fact that some carotenoids are an essential primary source of vitamin A (see Chapter 11) little is known of their function *per se*. This was the situation when the first edition of this book was published thirty years ago and today we are little further forward. It is perhaps sensible to summarize the various suggestions made over the years in Table 6.16 without comment or prediction.

*Table 6.16 Proposed carotenoid functions in Crustacea*

<i>Function</i>	<i>Reference</i>
Light perception	199
Electron acceptor	89
Protective	
Chromatic adaptation	48, 51, 89, 223–226
Eggs from radiation*	16, 87, 115, 223, 224
High temperatures	115
Reducing reflectivity	227
Masking luminescence of prey in stomach	89
Gut wall against digestive enzymes	89
Stabilization of proteins	89, 223
Stabilization of chitin	43, 228
Transfer of pigments (carotenoprotein)	165
Reproduction	123, 189, 229, 230
Chemoreception in antennae	63

\*Probably not in *Daphnia* spp. [213].

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[7]

## ARACHNIDS AND INSECTS

### 7.1 ARACHNIDA

#### 7.1.1 ACARINA

##### (a) *Distribution*

Investigations on carotenoids in mites have not been numerous but some recent work has been extremely thorough. Most mites examined belong to the group Prostigmata of the sub-order Trombidiformes. The known distribution in this group is given in Table 7.1 from which it is clear that the pigments present can be separated into two groups, those which arise directly and unchanged from the food and those which are oxidative metabolites of  $\beta$ -carotene. In this respect Trombidiformes are similar to many other arthropods (see Chapter 6 and Section 7.2 of this chapter). Carotenoproteins are probably present in *Tetranychus* spp. [19]. Some predaceous mites also contain carotenoids; these include *Anystis* sp. [1, 2], *Erythraeus* spp. [1], *Balaustium* sp. [2] and *Phytoseiulus persimilis* [12].

##### (b) *Mutants*

A number of pigment mutants of *Tetranychus pacificus* and *T. urticae* have been examined in detail. The mutants of both mites, which have been given the same descriptive names because of their close resemblance one to the other, show different carotenoid patterns which are summarized in Table 7.2. A number of conclusions emerge from a consideration of this Table: (a) an *albino* mutation blocks the oxidation of  $\beta$ -carotene to keto carotenoids; (b) the *lemon* mutation also blocks this oxidation but allows the accumulation of large amounts of  $\beta$ -carotene in the haemolymph and this is the cause of the characteristic colour of the mutant; (c) the block in the *stork* and, to a great extent, the *flamingo* mutants is the step resulting in the

## 98 The biochemistry of the carotenoids

Table 7.1 Carotenoid distribution in Acarina (sub-order Trombidiformes)

Species	Pigments	References
<i>Bryobia praetiosa</i>	Present	1, 2
<i>Dermacentor pictus<sup>a</sup></i>	3, 4 <sup>b</sup> , 5, 6, 7, 8	3, 4
<i>Eotetranychus lewisi</i>	Present	1
<i>Eylais extendans</i>	1, 2, 9	5
<i>Eylais hamata</i>	1, 2, 5, 9 <sup>b</sup> , 10, 11, 12	4, 6, 7
<i>Hydrachna dispar</i>	1, 2, 9, 10, 11	8
<i>Hydrachna geografica</i>	1, 2, 4, 9, 10, 11	9
<i>Metatetranychus (Panonychus) ulmi</i>	1, 8, (13?)	1, 2, 10, 11
<i>Panonychus lewisi</i>	Present	1
<i>Piona nodata</i>	1, 2, 4, 9, 10, 11	9
<i>Schizonobia sycophanta</i>	1, 2, 9, 10, 13, 14, 15, 16, 17, 18	12
<i>Tetranychus atlanticus</i>	Present	1
<i>Tetranychus cinnabarinus</i>	1, 2, 9, 10, 13, 14, 15, 16, 17, 18	13, 14
<i>Tetranychus pacificus</i>	1, 2, 9, 10, 13, 14, 15, 16, 17, 18	15
<i>Tetranychus telarius (= urticae)</i>	1, 2, 9, 10, 13, 14, 15, 16, 17, 18	16
<i>Trombidium</i> sp.	9	17, 18

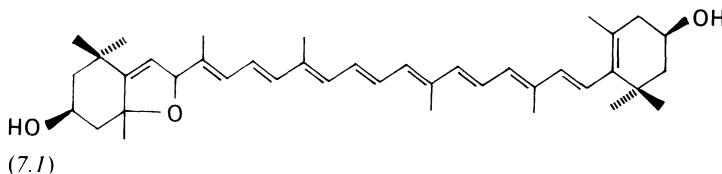
### Key

1. $\beta$ -Carotene	(1.5)	11. Canthaxanthin	(1.4)
2. Lutein	(1.10)	12. Zeaxanthin	(1.9)
3. $\beta$ -Zeacarotene	(5.7)	13. $\alpha$ -Carotene	(2.25)
4. $\beta$ -Cryptoxanthin	(2.36)	14. Lutein 5,6-epoxide	(6.6)
5. Isocryptoxanthin	(2.27)	15. Violaxanthin	(2.40)
6. $\alpha$ -Cryptoxanthin	(4.1)	16. Neoxanthin	(2.39)
7. Mutatoxanthin	(7.1)	17. 3-Hydroxy-4-keto- $\beta$ -carotene (= 3-hydroxyechinenone)	(6.5)
8. 4-Keto- $\gamma$ -carotene	(6.13)	18. 3-Hydroxy-4,4'-diketo- $\beta$ -carotene (= adonirubin = phoenicoxanthin)	(1.8)
9. Astaxanthin	(1.1)		
10. Echinone	(1.11)		

### Notes

<sup>a</sup>Predaceous species.

<sup>b</sup>Major pigment present.



esterification of hydroxy keto carotenoids; this results in an aberrant distribution of haemolymph pigments, all of which appear in the legs of the mites in the form of irregular red granules. The reason why esterification is apparently necessary for normal haemolymph pigmentation is still not clear. The existence of some astaxanthin esters in *flamingo* mutants but not in

Table 7.2 Carotenoid composition of mutants of *Tetranychus pacificus* and *T. urticae* [15, 16]

Mutant	Carotenoid pattern
<i>Albino</i> <sup>a</sup>	Keto carotenoids absent
<i>Pigmentless</i> <sup>a</sup>	
<i>Lemon</i>	Only food carotenoids present; high level of $\beta$ -carotene in haemolymph
<i>White eye</i>	Astaxanthin absent
<i>Stork</i>	Esterified keto carotenoids absent
<i>Flamingo</i>	Reduced levels of esterified keto carotenoids
<i>Rose</i> <sup>b</sup>	Pigment involved not carotenoid

Notes

<sup>a</sup>*Albino* 1 and *albino* 2 respectively in *T. urticae*.

<sup>b</sup> Known only in *T. pacificus*.

*stork* mutants is considered the cause of the phenotypic difference between the mutants; *stork* lacks eyespots whereas almost normal eyespots are present in *flamingo*; (d) in *white eye* mutants astaxanthin, but not other keto carotenoids, is absent which suggests that the final step in astaxanthin synthesis is blocked [15, 16]. The quantitative differences in carotenoids of the wild type and mutant strains of *T. pacificus* are clearly demonstrated in Table 7.3.

Table 7.3 Relative amounts of carotenoids in wild type and mutant *Tetranychus pacificus* [15]

Carotenoid	Relative amount (% of total pigment)					
	Wild type	a	l	we	st	f
$\alpha$ -Carotene (2.25)	3	4	5	4	4	4
$\beta$ -Carotene (1.5)	25	30	38	25	22	26
3,4-Diketo- $\beta$ -carotene (= 3-ketoechinone) (7.2)	7	—	—	6	7	5
3,4,4'-Triketo- $\beta$ -carotene (= 3-ketocanthaxanthin) (6.1)	3	—	—	6	4	2
Astaxanthin* (1.1)	5	—	—	tr	3	4
Lutein (1.10)	38	45	41	42	42	42
Lutein 5,6-epoxide (6.6)	3	4	3	4	3	3
Violaxanthin (2.40)	8	9	8	7	8	8
Neoxanthin (2.39)	8	8	5	6	7	6

Key

a = *albino*

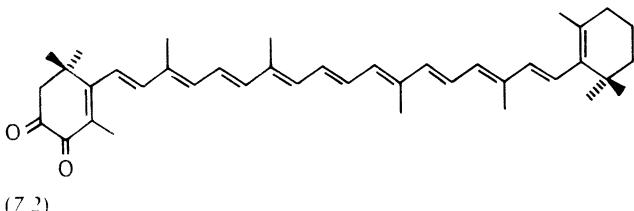
st = *stork*

l = *lemon*

f = *flamingo*

we = *white eye*

\*Isolated as astacene (2.1).



### (c) Metabolism

No keto carotenoids are present in newly laid eggs of mites but they appear during development, with oxidation probably taking place firstly at one  $\beta$ -end group to yield echinenone (1.11) and then 3-hydroxy-4-keto- $\beta$ -carotene (3-hydroxyechinenone) (6.5). Eventually the other end group is similarly oxidized and astaxanthin (1.1) results. This pathway is summarized in Fig. 7.1. In *albino* mutants, eggs develop normally even in the complete absence of carotenoids [16].

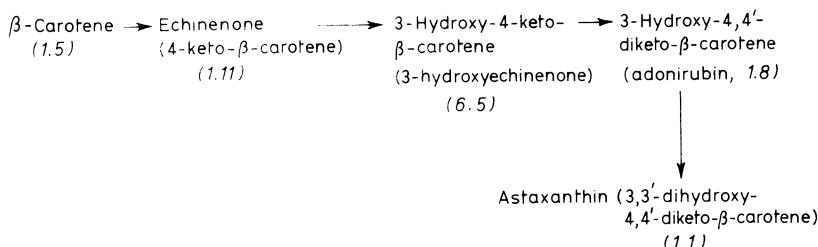


Fig. 7.1. The probable conversion of  $\beta$ -carotene into astaxanthin in mites [15, 16].

The marked change in colour from greenish yellow to deep orange on transition from summer females to diapausing females in *T. urticae* is accompanied by an increase in the concentration of keto carotenoids by between two and three times [16]. Similar colour changes in *Metatetranychus ulmi* [19] and *Schizotetranychus schizophorus* [20] may also be due to quantitative carotenoid changes. As the diapause induction response triggered by a regime of short-day photoperiods [21] is considerably reduced in albino *T. urticae* a case can be made for the involvement of carotenoids in this phenomenon either *per se* or after conversion into an active metabolite [22, 23]. Similar results have been obtained when the predaceous mite *Amblyseius potentillae* is fed for two generations on a carotenoid-free diet of albino mutants of *T. urticae* [24].

It seems clear from all these observations that a carotenoid-containing diet is necessary to provide an intact carotenoid (probably  $\beta$ -carotene) which the mites can then metabolize further.

## 7.2 INSECTA

### 7.2.1 DISTRIBUTION

#### (a) *Orthoptera*

The reported carotenoid distribution in Orthoptera is given in Table 7.4. It will be seen that  $\beta$ -carotene is accumulated specifically from the plant food of these insects. A detailed study of *Locusta migratoria migratorioides* and *Schistocerca gregaria* revealed that  $\beta$ -carotene was distributed amongst all tissues but that astaxanthin was present only in the integument, wings and eyes [34–37]. As astaxanthin does not exist in the food it must be formed from  $\beta$ -carotene which is absorbed specifically from the plant food. The xanthophylls are rejected. The formation of astaxanthin from  $\beta$ -carotene in the developing embryo and the contribution of carotenoids to locust coloration are discussed later in Sections 7.2.2 and 7.2.3 respectively.

*Table 7.4* Carotenoid distribution in Orthoptera

<i>Organism</i>	<i>Pigment</i>	<i>Reference</i>
<i>Acrida turrita</i>	1	25
<i>Acrotylus insubricus</i>	1	26
<i>Amblycorypha</i> sp.	2(?)	27
<i>Calaphenus italicus</i>	1	26
<i>Isophya krausii</i>	1	25
<i>Locusta migratoria</i>	3, 4	28
<i>Meconema varium</i>	1	29
<i>Melanoplus bivittatus</i>	3	30, 31
<i>Oedipoda aurea</i>	1	26
<i>Oedipoda miniata</i>	3, 5	25, 32, 33
<i>Oedipoda schochii</i>	1	25
<i>Phaneroptera quadripunctata</i>	1	26
<i>Schistocerca gregaria</i>	3, 4, 6(?)	34, 35, 36, 37, 38
<i>Tettigonia cantans</i>	1	29
<i>Tettigonia viridissima</i>	1, 7(?)	39

#### *Key*

- |                            |                 |                                  |
|----------------------------|-----------------|----------------------------------|
| 1. Carotenoprotein         | 5. Unidentified |                                  |
| 2. $\alpha$ -Cryptoxanthin | (4.1)           | 6. Lutein (1.10)                 |
| 3. $\beta$ -Carotene       | (1.5)           | 7. $\beta$ -Cryptoxanthin (2.36) |
| 4. Astaxanthin             | (1.1)           |                                  |

The reported presence of lutein (1.10) in *S. gregaria* [38] may have been that remaining in undigested food in the intestinal tract.

Carotenoproteins have been reported in the hind wings of *Oedipoda* spp. and other orthopterans [25, 26].

(b) *Phasmida*

Recent investigations on phasmids have revealed a series of carotenoids characterized by oxygen functions at positions 2 and 2' (Table 7.5). It is now clear that the pigments in *Carausius morosus* originally reported as isocryptoxanthin (2.27) and isozeaxanthin (2.42) are in fact 2-hydroxy- $\beta$ -carotene (6.9) and 2,2'-dihydroxy- $\beta$ -carotene respectively (7.3). In the stick insect *Ectatosoma tiaratum* these compounds are partly racemic at C-2 with no preferred configuration, whereas the 2S configuration preferentially accumulates in the moth *Cerura vinula*; the corresponding pigments from algae (see Volume I) have the 2R-configuration. The structure proposed for the red pigment first described by Willig [39], 2,2'-diketo-3,4,3',4'-tetra-dehydro- $\beta,\beta$ -carotene (7.4) [40] has been confirmed by total synthesis [44].

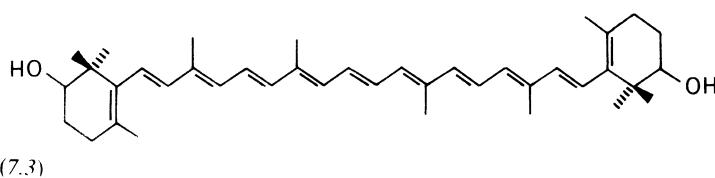
One stick insect examined, *Sipyloidea sipylus*, contained no carotenoids although the animals were feeding on leaves [41].

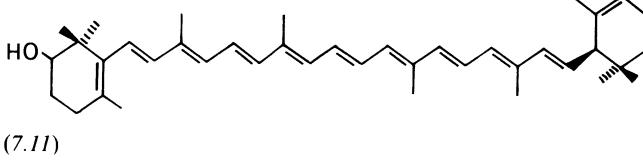
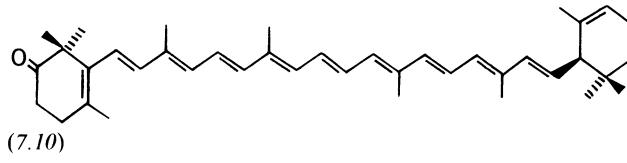
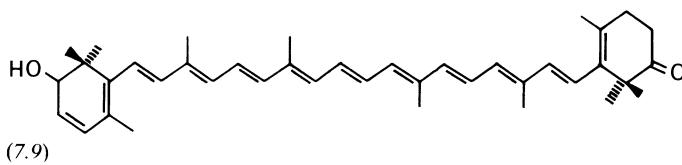
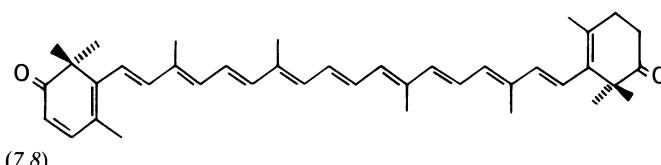
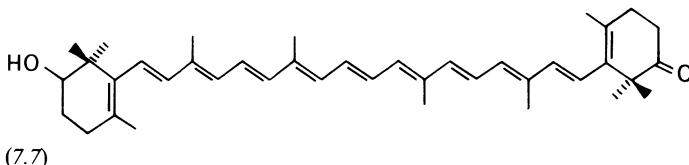
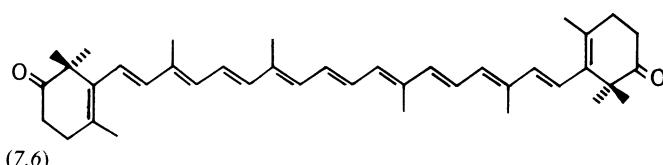
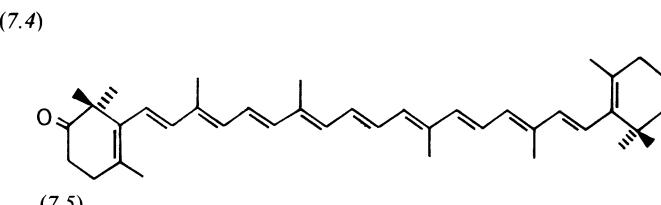
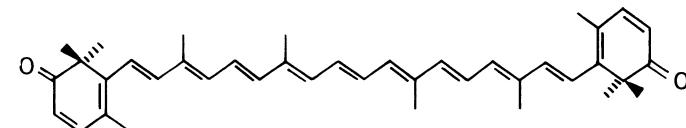
Table 7.5 Carotenoid distribution in Phasmida

Species	Pigments	Reference
<i>Acrophylla wulfgangi</i>	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15	40, 41, 144
<i>Bacillus rossius</i>	1, 2, 3, 6, 7, 10–15	144
<i>Carausius morosus</i>	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15	29, 42, 43, 44, 144
<i>Ctenomorphodes brieveus</i>	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15	40, 41, 144
<i>Ectatosoma tiaratum</i>	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15	40, 41, 45, 144
<i>Sipyloidea sipylus</i>	Absent	41, 144

## Key

- |   |       |                                   |
|---|-------|-----------------------------------|
| 1. 2-Hydroxy- $\beta$ -carotene         | (6.9) | 8. 2-Hydroxy-2'-keto-3,4-dide-    |
| 2. 2,2'-Dihydroxy- $\beta$ -carotene    | (7.3) | hydro- $\beta$ -carotene          |
| 3. 2,2'-Diketo-3,4,3',4'-tetra-de-      |       | 9. 2-Keto- $\alpha$ -carotene     |
| hydro- $\beta$ -carotene                | (7.4) | 10. 2-Hydroxy- $\alpha$ -carotene |
| 4. 2-Keto- $\beta$ -carotene            | (7.5) | 11. $\alpha$ -Carotene            |
| 5. 2,2'-Diketo- $\beta$ -carotene       | (7.6) | 12. $\beta$ -Carotene             |
| 6. 2-Hydroxy-2'-keto- $\beta$ -carotene | (7.7) | 13. 2,2'-Dihydroxy-3,4-didehydro- |
| 7. 2,2'-Diketo-3,4-didehydro-           |       | $\beta$ -carotene                 |
| $\beta$ -carotene                       | (7.8) | 14. Zeaxanthin                    |
|   |       | 15. Lutein                        |





## 104 The biochemistry of the carotenoids

### (c) *Hemiptera*

The general distribution of carotenoids in the Hemiptera (Heteroptera and Homoptera) is given in Table 7.6 and Table 7.7 respectively. Very little modern work has been carried out on the Heteroptera but in the Homoptera one encounters for the first time pigments which may be synthesized by endosymbiotic micro-organisms rather than being provided in the food. The significance of this is discussed in more detail in Section 7.2.2. The green *Macrosiphum liliodendri* contains  $\beta\gamma$ -carotene (7.12) and  $\gamma\gamma$ -carotene (7.13), pigments only found previously in certain fungi (see Volume I); the pink forms accumulate lycopene (2.29),  $\gamma$ -carotene (2.26) and 3,4-didehydrolycopene (7.14), which are not found in green tissues but are also well distributed in fungi (Volume I). In the other species included under Homoptera in Table 7.7 only those pigments not found in the diet are listed. In most cases pigment identification was not always unequivocal and more critical investigations are awaited. The indications are that in the Heteroptera the pigments arise from the retention of food carotenoids:  $\beta$ -carotene in *Perillus bioculatus*, for example, comes from the blood of its prey, the Colorado beetle, which only contains  $\beta$ -carotene [51] (see also Section 7.2.2). It would seem that in the Homoptera only aphids and some coccoids accumulate carotenoids [57, 58].

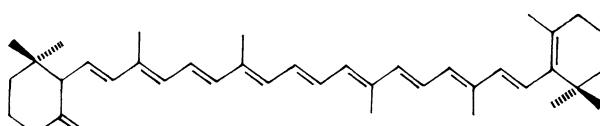
Table 7.6 Carotenoid distribution in Heteroptera

Species	Pigments	References
<i>Dysdercus</i> sp.	1	46, 47
<i>Eurydema ornata</i>	2	48
<i>Nezara viridula</i>	2*	49, 50
<i>Perillus bioculatus</i>	2	52
<i>Pyrrhocoris apterus</i>	3	51

#### Key

1. Unidentified
2.  $\beta$ -Carotene (1.5)
3. Lycopene (2.29)

\*Present as a carotenoprotein.



(7.12)

Table 7.7 Carotenoid distribution in Homoptera<sup>a</sup>

Species	Pigments	References
<i>Acysthosiphon pelargonii</i>	1, 2	53
<i>Aphis fabae</i>	1, 2 <sup>b</sup> , 3 <sup>b</sup> , 4, 5 <sup>b</sup> , 6	53, 54
<i>Aphis intyfi</i>	1	53
<i>Aphis sambuci</i>	6, 7, 8(?)	53
<i>Aphis solanella</i>	—	53
<i>Aphis urticata</i>	1	53
<i>Brachycaudus cardini</i>	2, 9, 10, 11	53
<i>Brachycaudus helichrysi</i>	1	53
<i>Chaitophorus populeti</i>	6, 7, 12	53
<i>Eriosoma lanuginosum</i>	2, 13	53
<i>Eriosoma ulmi</i>	2, 6, 13	53
<i>Longiunguis pyrarius</i>	2	53
<i>Macrosiphoniella millifolii</i>	14	53
<i>Macrosiphum liliodendri</i>		
(a) green	20, 21	27, 55
(b) pink	6, 8 <sup>c</sup> , 22 <sup>c</sup>	27, 55
<i>Macrosiphum rosae</i>	—	53
<i>Myzus cerasi</i>	15	53
<i>Pemphigus spirothecae</i>	1	53
<i>Periphyllus lyropictus</i>	2, 16	53
<i>Pterocomma salicis</i>	1	53
<i>Pterocomma steinheili</i>	1, 4, 17	53
<i>Tetraneura ulmi</i>	1, 2, 18, 19(?)	53, 56

**Key**

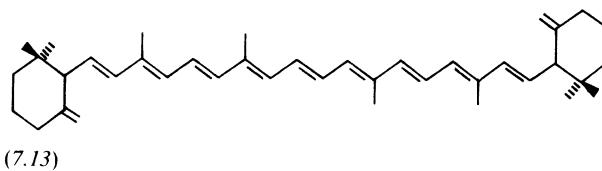
- |  |        |                                       |        |
|--|--------|---------------------------------------|--------|
| 1. Isozeaxanthin   | (2.42) | 12. $\alpha$ -Cryptoxanthin           | (4.1)  |
| 2. Astaxanthin   | (1.1)  | 13. Canthaxanthin                     | (1.4)  |
| 3. $\beta$ -Zeacarotene  | (5.7)  | 14. 4-Hydroxy- $\alpha$ -carotene     | (7.16) |
| 4. Mutatochrome  | (2.35) | 15. Rhodopin                          | (7.17) |
| 5. Torulene  | (2.30) | 16. 3,4-Dihydroxy- $\alpha$ -carotene | (7.18) |
| 6. $\gamma$ -Carotene  | (2.26) | 17. Echinone                          | (1.11) |
| 7. $\delta$ -Carotene  | (6.17) | 18. Isocryptoxanthin                  | (2.27) |
| 8. Lycopene  | (2.29) | 19. Phoenicoxanthin                   |        |
| 9. Chrysanthemaxanthin   | (5.5)  | (= adonirubin)                        | (1.8)  |
| 10. 4-Hydroxy-4'-keto- $\beta$ -carotene<br>(= 4'-hydroxyechinone) | (6.18) | 20. $\beta\gamma$ -Carotene           | (7.12) |
| 11. 3,4,4'-Trihydroxy- $\beta$ -carotene                           | (7.15) | 21. $\gamma\gamma$ -Carotene          | (7.13) |
|  |        | 22. 3,4-Didehydrolycopene             | (7.14) |

**Note**

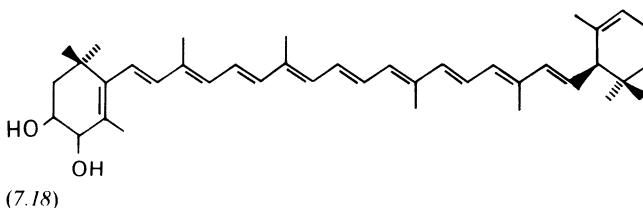
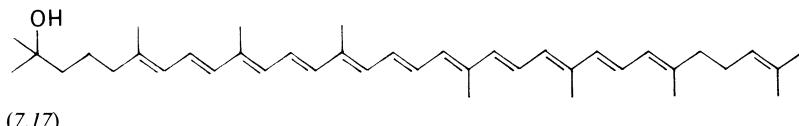
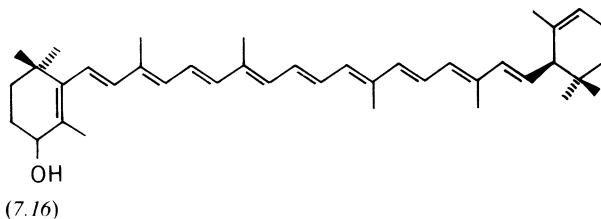
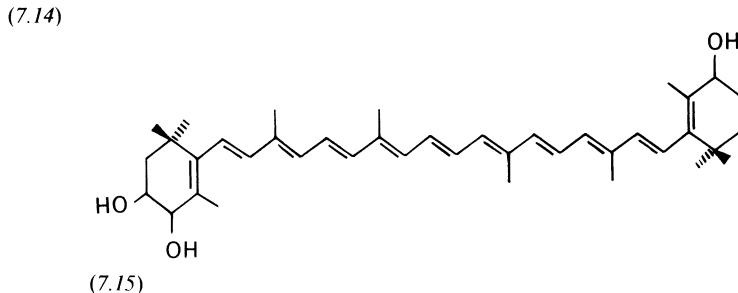
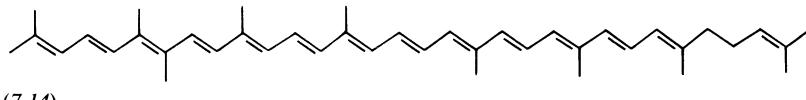
<sup>a</sup>Only those pigments not normally found in aphids' food are listed.

<sup>b</sup>Not observed in a later study [54].

<sup>c</sup>Present only in traces.



## 106 The biochemistry of the carotenoids



### (d) Coleoptera

The main carotenoids found in the Coleoptera are listed in Table 7.8. In the family Coccinellidae the ladybird beetle *Coccinella septempunctata* has recently been investigated thoroughly using modern methods which revealed the presence of lycopene (2.29), first reported forty years previously [51], and some twenty other pigments, many of them with novel structures [61, 62]. A number of these pigments are characteristic of red yeasts (see Volume I) and it is highly likely that such micro-organisms, which grow symbiotically in *C. septempunctata*, are the source of the pigmentation in the elytra of this insect. This view is supported by the fact that, although ladybirds are catholic in their tastes, their main food is aphids, of which only one special colour type of *Macrosiphum liliodendri*, (Table 7.7) contains the

Table 7.8 Carotenoids present in Coleoptera

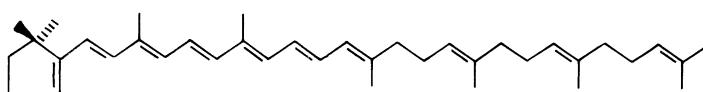
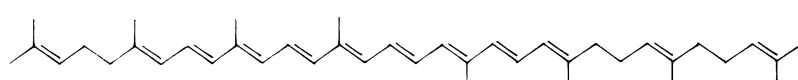
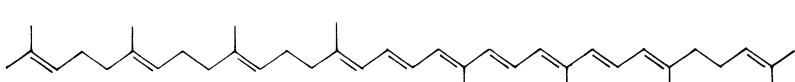
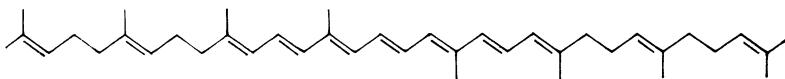
Species	Pigments	References
<b>Coccinellidae</b>		
<i>Coccinella quinquepunctata</i>	1	59
<i>Coccinella septempunctata</i>	1–22	52, 54, 61, 62
<i>Subcoccinella vigintiquatuorpunctata</i>	23	63
<b>Chrysomelidae</b>		
<i>Cassida murraea</i>	1, 19	64, 65
<i>Crioceris duodecimpunctata</i>	1 <sup>a</sup> , 23	66
<i>Gastrophysa cyanea</i> (eggs)	1	60
<i>Leptinotarsa</i> spp.	24, 25, 26	75
<i>Leptinotarsa decemlineata</i>	1, 19, 24, 25	51, 59, 68–74
<i>Lilioceris (Criocersis) lili</i>	1, 24, 25, 26, 27, 28	67
<i>Phytodecta fornicata</i>	24, 29, 30	76
<b>Tenebrionidae</b>		
<i>Tenebrio molitor</i>	21	47
<b>Dytiscidae</b>		
Various water beetles	27 <sup>b</sup> , 28 <sup>b</sup>	77
<b>Key</b>		
1. $\beta$ -Carotene	(1.5)	15. $\gamma\psi$ -Carotene (7.25)
2. Phytoene	(5.9)	16. 3',4'-Didehydro- $\gamma\psi$ -carotene (7.26)
3. Phytofluene	(5.10)	17. $\beta\gamma$ -Carotene (7.12)
4. $\zeta$ -Carotene	(7.19)	18. $\gamma\gamma$ -Carotene (7.13)
5. 7,8,11,12-Tetrahydrolycopene	(7.20)	19. Lutein (1.10)
6. Neurosporene	(7.21)	20. Zeaxanthin (1.9)
7. Lycopene	(2.29)	21. Unidentified carbonyl compound
8. 3,4-Didehydrolycopene	(7.14)	22. $\alpha$ -Carotene (2.25)
9. 7',8',11',12'-Tetrahydro- $\gamma$ -carotene	(7.22)	23. Food carotenoids only
10. $\beta$ -Zeacarotene	(5.7)	24. Echinone (1.11)
11. $\gamma$ -Carotene	(2.26)	25. Canthaxanthin (1.4)
12. Torulene	(2.30)	26. Astaxanthin (1.1)
13. 7',8'11',12'-Tetrahydro- $\gamma\psi$ -carotene	(7.23)	27. Isocryptoxanthin (2.27)
14. 7',8'-Dihydro- $\gamma\psi$ -carotene	(7.24)	28. Isozeaxanthin (2.41)
		29. 3,4-Diketo- $\beta$ -carotene (3-ketoechinone) (7.2)
		30. 3,4,4'-Triketo- $\beta$ -carotene (3-ketocanthaxanthin) (6.1)

**Notes**<sup>a</sup>Only pigment present in elytra.<sup>b</sup>These may have been wrongly identified [41].

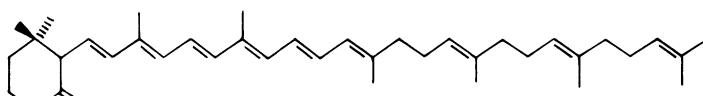
characteristic ladybird pigments. Furthermore intermediates in the *de novo* synthesis of carotenoids, such as phytoene (5.9) and phytofluene (5.10), have only rarely been reported and then only in traces in the insect's potential food, whereas they are relatively abundant in red yeasts (see

## 108 The biochemistry of the carotenoids

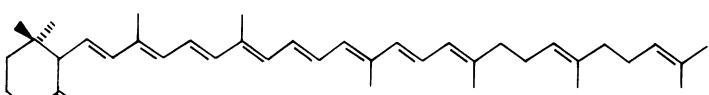
Volume I). The only other coccinellid examined recently was *Subcoccinella vigintiquatuorpunctata* which is not a predator but a plant feeder; it accumulates only the pigments in its diet [63].



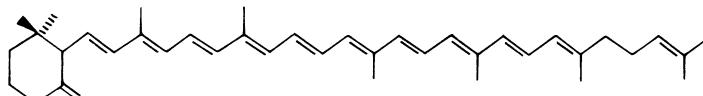
(7.22)



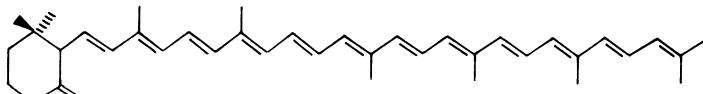
(7.23)



(7.24)



(7.25)



(7.26)

When the Chrysomelids, which are plant eaters, are considered it is apparent that most oxidize their dietary carotenoids to keto carotenoids (Table 7.8). Only in *Crioceris duodecimpunctata* [66] and *Cassida murraea*

[64, 65] were unaltered food carotenoids detected. Oxidation to keto carotenoids presumably takes place during embryogenesis or, in the case of *Phytodecta formicata* later, because oxo carotenoids are not found in the undeveloped eggs or larvae of this species [75].

### (e) Diptera

Only very few Diptera have been examined recently in detail. The available information is collected in Table 7.9. The most thorough investigation has been on *Rhynchosciara* spp. which accumulate  $\beta$ -carotene in the mid gut and keto carotenoids in the haemolymph where they exist as chromoproteins. A violet carotenoprotein, which binds echinenone (1.11) and canthaxanthin (1.4) in a 3:1 ratio, and a yellow lipoprotein, associated with  $\beta$ -carotene (1.5),  $\beta$ -cryptoxanthin (2.36) and echinenone (1.11), are present. It is these proteins which give the larvae of this insect their characteristic colour [82–84] (see also Chapter 1).

Table 7.9 Carotenoids in Diptera

Species	Pigments	References
<i>Chironomus annularius</i>		
(1) eggs	1, 2, 3, 4	78
(2) larvae	1, 2, 3, 5, 6, 7	79
<i>Musca domestica</i>	8 <sup>a</sup>	80
<i>Pollenia</i> sp.	2, 3, 5, 9	81
<i>Rhynchosciara</i> spp.	3, 4, 5, 6, 10 <sup>b</sup> , 11 <sup>b</sup>	82–84

#### Key

1. $\alpha$ -Carotene	(2.25)	7. Astaxanthin	(1.1)
2. Lutein	(1.10)	8. Unidentified xanthophylls	
3. $\beta$ -Cryptoxanthin	(2.36)	9. Zeaxanthin	(1.9)
4. Echinenone	(1.11)	10. Isocryptoxanthin	(2.27)
5. $\beta$ -Carotene	(1.5)	11. 4-Hydroxy-4'-keto- $\beta$ -carotene	
6. Canthaxanthin	(1.4)	(4'-hydroxyechinenone)	(6.18)

#### Notes

<sup>a</sup>In the head.

<sup>b</sup>Minor components.

### (f) Lepidoptera

Some large-scale surveys of carotenoids in various Lepidoptera have been reported and in the majority of cases the pigments in the insects reflect qualitatively rather closely those in their food plants. The families examined in which this generalization is followed are listed in Table 7.10. Considerable quantitative differences are, however, encountered and in some species the food carotenoids tend to be either specifically accumulated or specifically

## 110 The biochemistry of the carotenoids

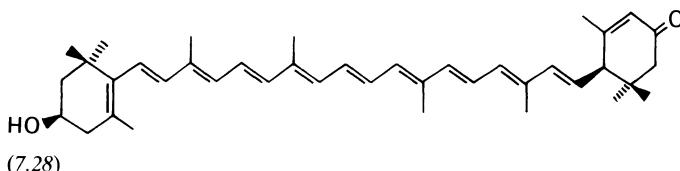
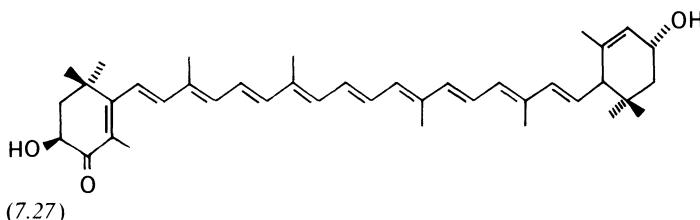
Table 7.10 Lepidoptera families in which their carotenoids reflect those in the diet

Family	Number of genera examined	References
Arctiidae	5	85
Danaidae	1	85
Geometridae	2	85
Lasiocampidae	1	86
Lycaenidae	1	87
Lymantriidae	4	85, 86
Noctuidae	6	49, 85, 88
Notodontidae	2	85, 86, 89–92
Nymphalidae	5	85, 86, 93, 94
Papilionidae	8	95–99
Pieridae	10	49, 85, 86, 100–104
Saturniidae	9	85, 86, 105–110
Tortricidae	1	49
Zygaenidae	3	85, 111

rejected, whereas in others the pigments are absorbed indiscriminately. For example,  $\beta$ -carotene (1.5) and lutein (1.10) occur in about equal amounts in *Pieris brassicae* [103] whereas lutein is by far the major pigment in *Aglais urticae* [93]. *Philosamia ricini* larvae apparently only absorb  $\beta$ -carotene and violaxanthin (2.40) from the food and  $\beta$ -carotene accumulates in the skin [112].

There are one or two important exceptions to the generalization subsumed in Table 7.10. East Asian species of *Papilio* can oxygenate food carotenoids for, apart from leaf carotenoids, canthaxanthin (1.4), astaxanthin (1.1) and papilioerythrin (4-ketolutein) (7.27) were isolated from the orange diapausing pupae of *P. xuthus* [97, 98] and *P. protenor demetrius* [95]. In *P. alcinous* the keto carotenoids present were echinenone (1.11), crustaxanthin (6.2) and canthaxanthin (1.4) [99]. A new pigment *philosamiaxanthin*, (3' O-dehydrolutein, 3-hydroxy-3'-keto- $\alpha$ -carotene) (7.28), first reported in the moth *Philosamia cynthia* [106, 107], has now been reported in *P. xuthus* [97], *Actias selene* and *Cerura vinula* [110] and in the silkworm *Bombyx mori* [107]. A further oxidation product of lutein, papilioerythrinone (6.19), has been isolated from *P. xuthus* [97].

Two notodontids have particularly interesting carotenoid features. *Cerura vinula* was the first example of an insect containing a carotenoid with an oxygen function at C-2 (see also Section 8.2.2). 2-Hydroxy- $\beta$ -carotene (6.9) and 2-keto- $\beta$ -carotene (7.5) were isolated from this insect and fully characterized [90, 92]. Although as is the case with the 2-hydroxy- $\beta$ -carotene from stick insects (Section 8.2.2) *C. vinula* produces both the 2R and 2S enantiomers, they differ in that the S isomer predominates in *C. vinula* whereas the stick insect shows no stereoselective synthesis [41].



*Phalera bucephala* accumulates  $\beta$ -cryptoxanthin (2.36) [85, 91] which is formed from the insect's dietary  $\beta$ -carotene by hydroxylation at C-3 and is not due to selective accumulation of the xanthophyll from the diet [91].

#### (g) Hymenoptera

Very little modern work has been carried out on members of this order but it does seem that their carotenoids reflect the source of their food supply. This is the case with the parasitic *Apanteles flaviconchae* [51], *A. glomeratus* [104] and *Microgaster conglomatus* [100, 113]. Similarly the honey bee *Apis mellifica* reflects the pigments of the collected pollen [114–117] although in one investigation echinenone (1.1) and canthaxanthin (1.4) have been reported together with many other pigments [142].

### 7.2.2 METABOLISM OF INGESTED CAROTENOIDS

#### (a) Astaxanthin formation

The first indication that  $\beta$ -carotene (1.5) was converted into astaxanthin (1.1) in insects was the observation that in the developing locust egg, a closed system,  $\beta$ -carotene disappeared and astaxanthin was formed [34, 35] (Fig. 7.2). The conclusion that astaxanthin was formed from  $\beta$ -carotene was based on the view that animals cannot synthesize carotenoids *de novo*, a concept that has not been seriously challenged during the thirty years which have elapsed since these experiments were carried out.

Almost all possible pathways have been proposed for the conversion of  $\beta$ -carotene into astaxanthin [66, 67, 71, 97] but the scheme indicated in Fig. 7.3 does not involve either  $\beta$ -cryptoxanthin (2.36) or zeaxanthin (1.10) because neither appears to be an intermediate in the conversion which is the

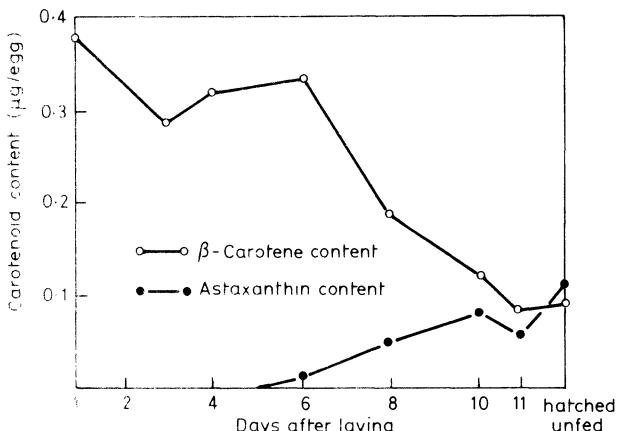


Fig. 7.2. Carotenoid metabolism in the developing egg of the desert locust (*Schistocerca gregaria*) [28].

major pathway. The mono- and di-hydroxy intermediates involved are isocryptoxanthin (A, Fig. 7.3), isozeaxanthin (B, Fig. 7.3) and 3,4-dihydroxy- $\beta$ -carotene (C, Fig. 7.3). The later stages in Fig. 7.3 are all possible ones and only isotope and enzyme experiments will finally settle which is the major pathway. A possible route from lutein to astaxanthin is outlined later in Fig. 7.5 (see p. 115).

### (b) Carotenoids with oxygen at C-2

Direct experiments using [ $^{14}\text{C}$ ] $\beta$ -carotene clearly demonstrated that a number of stick insects and a moth, *Cerura vinula*, can synthesize from the parent hydrocarbon a xanthophyll carrying an oxygen function at C-2 [41, 91, 145], but no indication of the intermediates involved was obtained. One suggestion is that insertion of a keto group (A and B, Fig. 7.4) is the first step and that hydroxy carotenoids arise from the reduction of keto carotenoids (C, D and E, Fig. 7.4). The desaturation at C-3,4 and C-3',4' which occurs in these insects would generally appear to take place at a late stage in the biosynthetic sequence (F, G, H and I, Fig. 7.4), when either two keto groups or one keto group and one hydroxyl group are present in the molecule. Further information was obtained by returning to the embryo as the experimental system; in *Ectatosoma tiaratum* all the pigments present in the newly laid eggs are also present in the newly hatched first instar larvae. However, although marked quantitative changes are observed during the development of the embryos as the carotenoids are metabolized no clear-cut evidence for a biosynthetic pathway emerged. An explanation must be eventually found for the existence in these insects of partly racemic 2-hydroxy carotenoids: lack of any experimental evidence at the moment suggests the acceptance as a working model of the simplest possibility that

two reductases A and B with different stereospecificities are operating according to the reaction indicated in equation (7.1).

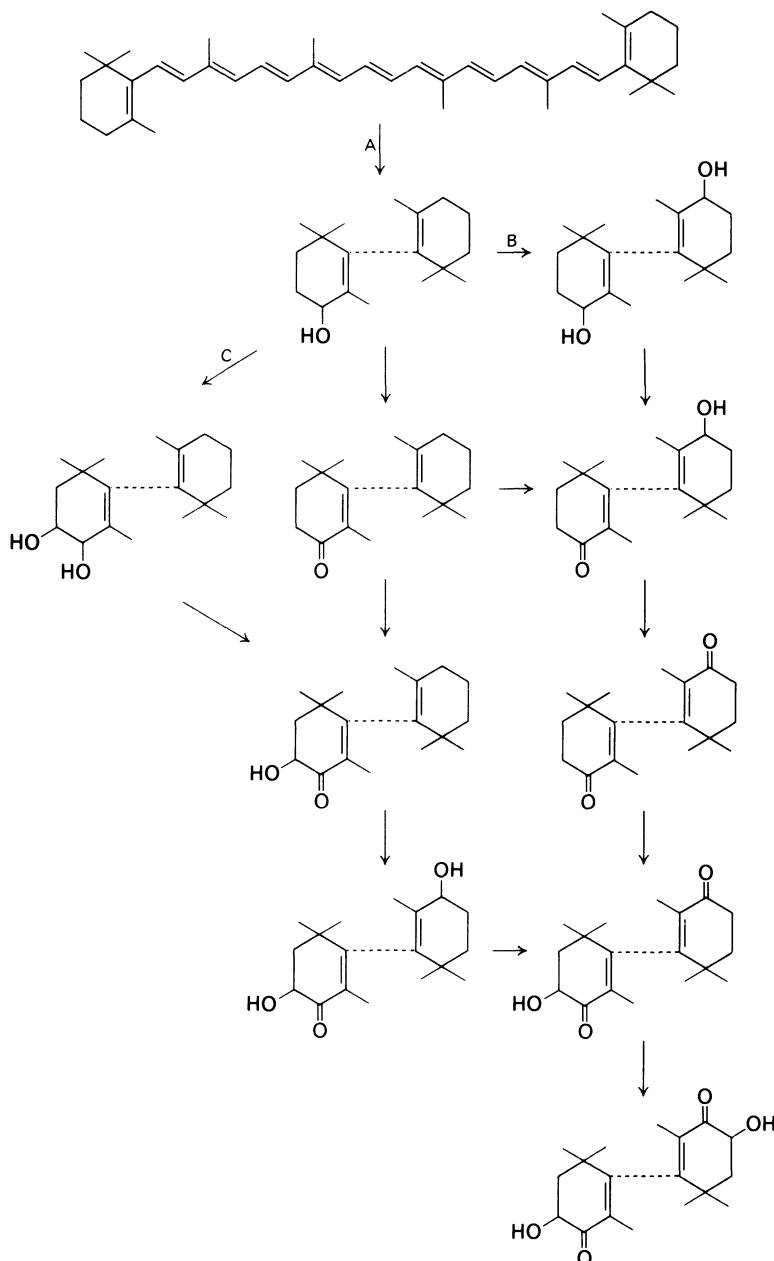


Fig. 7.3. Possible routes for the conversion of  $\beta$ -carotene into astaxanthin in insects [41].

114 The biochemistry of the carotenoids

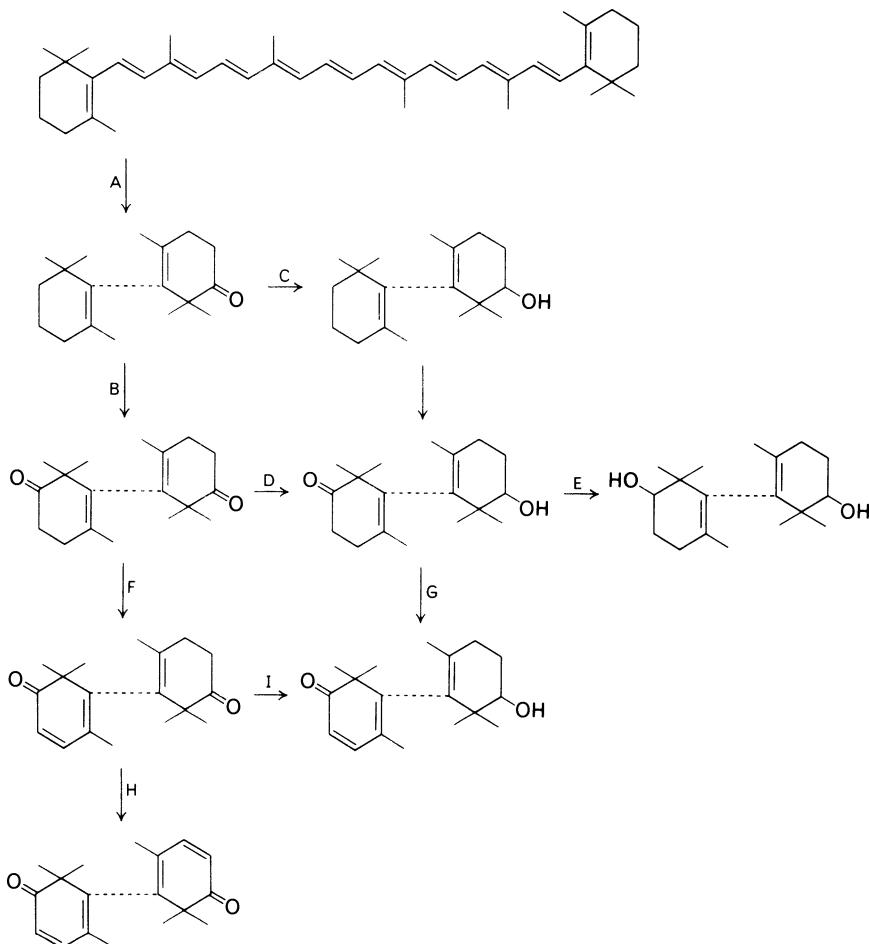
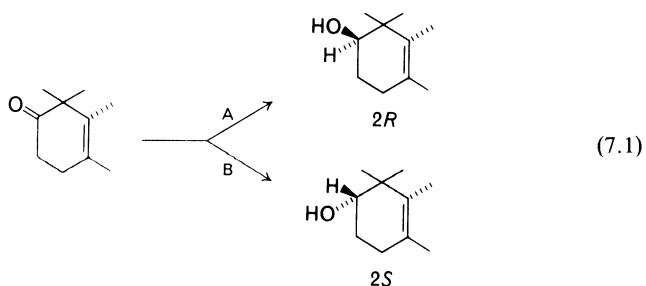
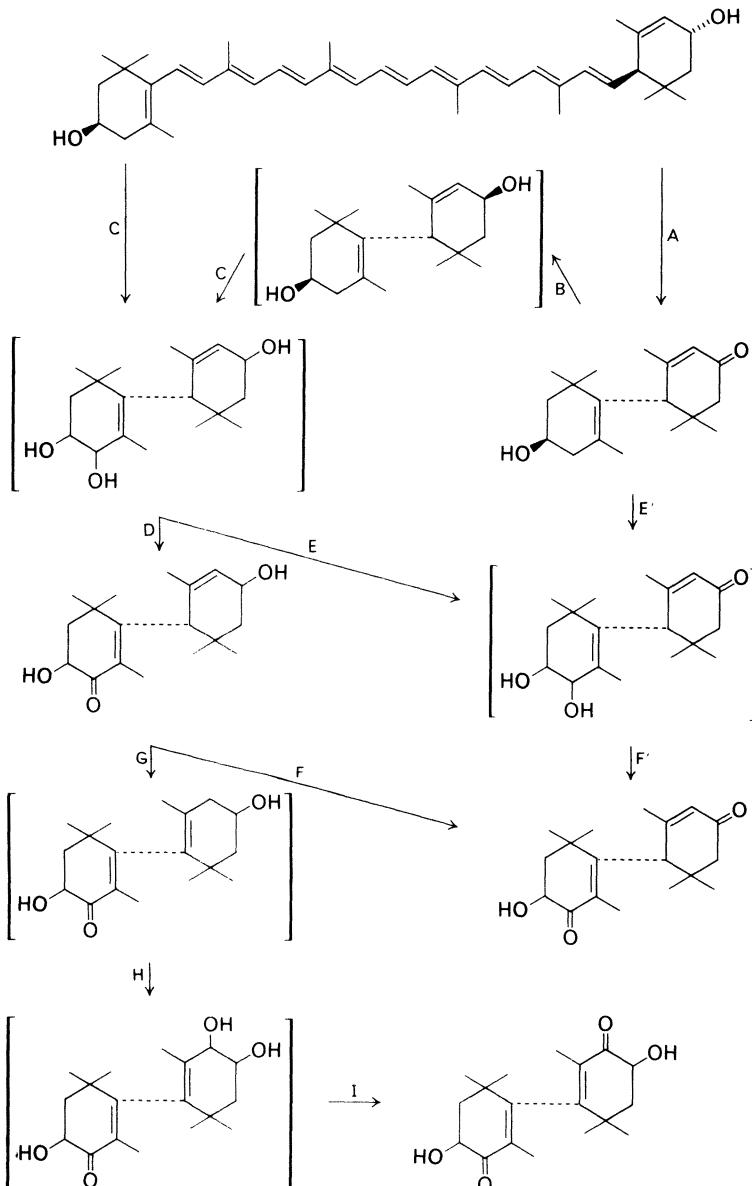


Fig. 7.4. Conversion of  $\beta$ -carotene into 2-substituted and 3,4-didehydrocarotenoids in stick insects [44].



(c) *Lutein derivatives*

Figure 7.5 represents an obvious paper pathway for the formation of 3'-epilutein (7.28) (A, B, Fig. 7.5), papilioerythrin (7.27) (C, D, Fig. 7.5), papilioerythrinone (6.19) (E, F; E', F', Fig. 7.5) and astaxanthin (G, H, I,



*Fig. 7.5.* Possible routes for the conversion of lutein into 3'-epilutein, papilioerythrin, papilioerythrinone and astaxanthin in insects (Pigments in square brackets have not been isolated.) [41].

## 116 The biochemistry of the carotenoids

Fig. 7.5) from lutein. However, the chirality of these pigments at C-6' has not yet been established, nor indeed has that of insect 'lutein'. Similar biosynthetic problems exist in fish and birds (see Chapters 8 and 10) and it is clear that the stereochemical structural problems of insect carotenoids must be settled before exact biochemical pathways can be elucidated.

### (d) *Synthesis by symbiotic micro-organisms*

It should be emphasized here that not all insect carotenoids arise from food carotenoids; some are the result of the biosynthetic activities of symbiotic yeasts. This has been clearly demonstrated in the homopteran *Macrosiphum liliodendri* [27, 55] and in the coccinellid *Coccinella septempunctata* [61, 62]. In the former the presence or absence of the carotenogenic yeasts probably controls the colour of the pupae, the green specimens containing no yeast carotenoids whereas they are the major components in the rose-coloured specimens [27].

### 7.2.3 INSECT COLORATION

#### (a) *Carotenoid contribution*

An assessment of the contribution of various pigments to the colour of insects is a complex matter [118], but in many cases the contribution of carotenoids to the pigmentation pattern is clear. A carotenoid is the yellow component of the green pigment which is observed in many insects under the general name *insectoverdin*; the blue component is a bile pigment. Insects in which insectoverdins are known to occur are listed in Table 7.11. The significance of the carotenoid contribution to the colour of green insects has been emphasized by the study of various blue mutants in which the amount of carotenoid present is either zero or very low; the reason may be failure to absorb carotenoids because the amount excreted in the frass is much greater in mutants than in normals [124]. The mutants examined were of *Colias philodice* [120], *Hyalophora cecropia* [105, 125, 126] and *Papilio* spp. [96, 123]. In *H. cecropia*, for example, the carotenoid levels in pupae of a blue mutant and a normal strain reared on the same diet were 3.8 and 266 µg/g respectively [126]. In native strains of many Lepidoptera the absence of carotenoids from an artificial diet gives rise to blue larvae [122, 127, 128]. The blue colour can be changed to the normal green colour by feeding carotenoid, particularly xanthophylls [122]. Carotenoproteins, with astaxanthin as the prosthetic group, play a major part in the red coloration of the wings of *Oedipoda miniata* and other Orthoptera, whereas the striking yellow colour of adult male *Schistocerca gregaria* is due to accumulation of β-carotene in the integument [37, 129, 130].

Free carotenoids also play a major part in the coloration of female silkworm (*Bombyx mori*) larvae; males are colourless [131]. The silkworm silk is yellow owing to the presence of carotenoids [132–137] as is the silk of *Apanteles flaviconchae* [51]. Two genes control the pigmentation of silk in *B. mori*: *C* determines that the blood contains carotenoids and *Y* determines that these are transferred to the serogenous glands [132–134]. The prediction from this view that insects with yellow haemolymph and white silk should exist has been experimentally verified [120].

Table 7.11 Insects known to contain insectoverdin with a carotenoid as the yellow component

<i>Species</i>	<i>Reference</i>
<i>Acrida turrita</i>	25
<i>Callosamia promethea</i>	119
<i>Carausius morosus</i>	29, 33, 46
<i>Chrysopa peila</i>	25, 50
<i>Colias philodice</i>	120
<i>Locusta migratoria</i>	37
<i>Mantis religiosa</i>	121
<i>Nezara viridula</i>	50
<i>Papilio</i> spp.	96, 122, 123
<i>Phaneroptera quadripunctata</i>	25
<i>Plusia gamma</i>	88
<i>Schistocerca gregaria</i>	37
<i>Sphinx ligustri</i>	29
<i>Tettigonia viridissima</i>	29

Adult female *S. gregaria* contain the same amount of  $\beta$ -carotene as males but the pigment does not migrate into or closely under the cuticle as it does in the male [37]. Thus the characteristic female colour is not yellow but brownish-pink owing to the superficial presence of ommochromes. When locusts swarm, that is change from the solitary to the gregarious phase, they undergo marked colour changes [37, 138], the most impressive of which is the disappearance of the green colour characteristic of the solitary phase and its replacement by a much darker coloration. The green pigment is a typical insectoverdin containing blue and yellow chromoproteins with biliverdin and carotenoids, respectively, as their prosthetic groups [36]. In the gregarious insects the bile pigment complex has disappeared and the carotenoids, although present in the same amounts as in the solitaires are masked, except in mature males, as just indicated, by melanin and ommochromes [37].

(b) *Hormonal and environmental factors*

The changes in carotenoid distribution in locusts on sexual maturation have already been considered in the preceding section. Many colour changes in insects from green to brown are connected with the changes in carotenoid content and localization in the animals. These changes are mediated by light, temperature or relative humidity in *Carausius morosus* [39], and by diapause in *Hestina japonica* [139], *Pieris rapae crucivora* [101] and *Chrysopa carnea* [140, 141]. However, the changes in *Papilio xuthus* brought about by the environment result from qualitative changes in the component carotenoids (see Table 7.4). Keto carotenoids, absent from the green pupae, appear in the brown pupae [101]. The marked colour changes brought about by crowding in locusts and *Plusia gamma* are not caused by changes in carotenoid metabolism [37].

## 7.3 FUNCTION

Apart from the important role of carotenoids in coloration of insects, which has just been discussed, any metabolic function of a carotenoid appears to be related to the ability of the insect to convert it into vitamin A (see Chapter 11). For example in the silk worm (*Bombyx mori*) carotenoid deficiency did not affect development of the pupae or the specific time of eclosion which is regulated by the photoperiod conditions at the pupal stage; however, carotenoid deficiency did cause loss of the phototactic response of the insects but this could be restored by the addition to the diet of vitamin A alone [143].

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## [8]

## TUNICATES AND FISH

## 8.1 TUNICATES

Very little work on these animals has been reported since the first edition of this book. An important observation, however, is that cynthiaxanthin first isolated from *Halocynthia (Cynthia) papillosa* [1–5], and pectenoxanthin from *Botryllus schlosseri* [2] are identical with the acetylenic carotenoid alloxanthin (1.2) [6]. Astaxanthin (1.1) is the major pigment in *H. papillosa* [1, 7, 8] and *Dendrodoa grossularia* [1]. Two new pigments halo-

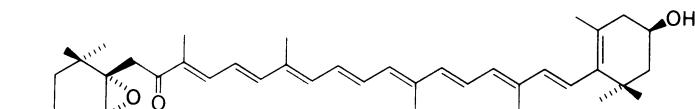
Table 8.1 Carotenoid distribution in tunicates

Species	Pigments	Reference
<i>Botryllus schlosseri</i>	1, 2, 3, 4	1, 9
<i>Ciona intestinalis</i>	1	9
<i>Clavellina lepadiformis</i>	1, 5	9
<i>Corella parallelogramma</i>	1, (?)5	1
<i>Dendrodoa grossularia</i>	5, 6, 7	1
<i>Halocynthia papillosa</i>	4, 7	1–5, 7, 8
<i>Halocynthia roretzi</i>	8, 9	8a, 8b
<i>Microcosmus sulcatus</i>	?6, ?10	1
<i>Molgula occulata</i>	?1, ?5	1
<i>Myxilla mammillaris</i>	?1, ?5	1
<i>Styela rustica</i>	?1, 5	1

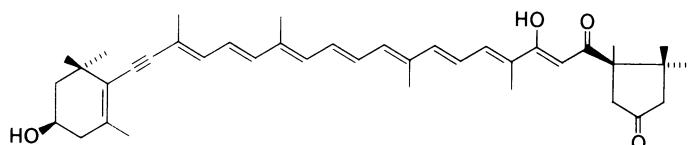
## Key

- |  |        |                        |        |
|--|--------|------------------------|--------|
| 1. Lutein  | (1.10) | 5. $\beta$ -Carotene   | (1.5)  |
| 2. Capsanthin  | (2.19) | 6. $\alpha$ -Carotene  | (2.25) |
| 3. Capsorubin  | (2.20) | 7. Astaxanthin         | (1.1)  |
| 4. Alloxanthin<br>(= cynthiaxanthin<br>= pectenoxanthin) | (1.2)  | 8. Halocynthiaphanthin | (8.1)  |
|  |        | 9. Mytiloxanthone      | (8.2)  |
|  |        | 10. Echinenone         | (1.11) |

cynthiaxanthin (8.1) and mytiloxanthone (8.2) have recently been reported in *H. roretzi* [8a, 8b]. Capsanthin (2.19) and capsorubin (2.20) were also found in *B. schlosseri* [2] probably because the specimens were collected from a harbour in which red pepper wastes had been dumped. However, the possibility remains that the pigments were formed in the animals by enzymic oxidation of carotenoids, for example fucoxanthin (2.34), present in their phytoplankton food. Certainly the pentacyclic ring system of these pigments also appears in sponges and is apparently produced endogenously (see Chapter 2). The reported distribution of carotenoids in tunicates is given in Table 8.1.



(8.1)



(8.2)

## 8.2 FISH

### 8.2.1 DISTRIBUTION

#### (a) Skin

The bright external colour patterns of fish have attracted the attention of biologists for many years and it is clear that the orange and red skin and fin colours are almost always due to the presence of carotenoids in specialized cells, the chromatophores. The known qualitative distribution of carotenoids in fish skin is summarized in Table 8.2. The reserve with which some carotenoid identifications in early publications must be treated today is particularly important in the case of fish pigments because of the recent observations that stereoisomers exist together in the same species. Some rather recent wide-ranging distribution studies have also yielded unexpected identifications which need critical assessment with modern physicochemical methodology.

Table 8.2 Distribution of carotenoids in the integument of fish

Species	Pigments	Reference	Common name
<i>Acanthopagrus schlegelii</i>	1-9	9	
<i>Amanses modestus</i>	10, 32, 33	10	
<i>Ambloplites rupestris</i>	4	176	Sun fish
<i>Ammodytes lanceolatus</i>	4, 11	11	
<i>Ammodytes tobianus</i>	4, 11	11	Sand eel
<i>Anguilla anguilla</i>	1, 3, 4, 8, 12, 13, 14	12, 13	Eel
<i>Aphiga minuta</i>	11	14	
<i>Apodichthys flavidus</i>	3 (90% of total)	15	Marine gunnel
<i>Auxis thazard</i>	1-9	9	
<i>Barboursia rufa</i>	8	16	Whole fish
* <i>Bartus nigrofasciatus</i>	8	10	
<i>Beryx decadactylus</i>	8	17	Marine dorado
<i>Beryx splendens</i>	3, 8	18	Alfoncino
* <i>Betta splendens</i>	4, ?15	19, 20	Siamese Fighting fish
<i>Bothus maximus</i>	11	14	
<i>Bothus rhombus</i>	4, 11	14	
<i>Branchiostegus japonicus</i>	3, 16, 17, 18, 19	21	Tile fish
<i>Callionymus lyra</i>	11	12, 14	
<i>Callionymus punctatus</i>	1-9	9	
<i>Caranx trachurus</i>	4	14	
* <i>Carassius auratus</i>	1, 4, 5, 8, 9, 14, 20, 21, 22	22-28	Goldfish
<i>Carassius carassius buergeri</i>	1, 2, 3, 6, 7,		Golden crucian carp
<i>Carassius carassius grandoculis</i>	14, 24, 25, 26,		Round crucian carp
<i>Carassius cuvieri</i>	27+unidentified	29, 122	Deep bodied crucian carp
<i>Carassius gibelio</i>	triols and tetros		Silver crucian carp
<i>Centrolabrus exoletus</i>	3, 4, 11	14	
<i>Cetostomus regans</i>	8	16	Whalefish
<i>Chaenobrytus gulosus</i>	4	177	Sun fish
<i>Chaenocephalus aeratus</i>	1, 2, 3, 4, 6, 7, 8, 12, 13, 14,	30, 170	Ice fish
<i>Champscephalus gunnari</i>	24, 28, 29, 30, 31		
<i>Channa maculata</i>	10, 32, 33	31	Formosan snake- head cichlid
<i>Chelidonichthys kumu</i>	3, 4, 8, ?15	18	Gurnard
<i>Chichlasoma citrinellum</i>	4, 10, 12, 25, 32, 33, 34	31, 32	Flamingo cichlid
<i>Chichlasoma elisalium</i>	10, 12, 32, 33	31	Red devil
<i>Chrysophrys major</i>	3, 4, 8, 9, 12, 14, 23, 34, 52, 56	33-37 175	Sea bream
<i>Clupanodon punctatus</i>	1, 2, 3, 4, 6, 7, 8, 9, 14 (+ triols)	38	
<i>Clupea harengus</i>	4, 11	6	Herring
<i>Clupea pallasi</i>	1, 2, 3, 4, 6, 7, 9, 14 (+ triols)	38	
<i>Coilia mystus</i>	1, 2, 3, 4, 6, 7, 8, 9, 14 (+ triols)	38	

<i>Species</i>	<i>Pigments</i>	<i>Reference</i>	<i>Common name</i>
* <i>Colisia fasciata</i>	4, (?)15	19	Striped gourami
* <i>Colisia lalia</i>	4, (?)15	19	Dwarf gourami
<i>Cololabris saira</i>	1, 2, 3, 4, 6, 8, 9, 14, 24	39	
* <i>Copeina guttata</i>	4	11	
<i>Coregonus autumnalis migratorius</i>	1, 3, 8	13, 40	
* <i>Coreoperca kawamebari</i>	3, 4, 6, 7, 8, 9, 14, 21	39	Japanese perch
<i>Coryphaena hippurus</i>	1–9	9	
<i>Crenilabrus melops</i>	4 or 11	14	
<i>Crenilabrus suillus</i>	4 or 11	14	
<i>Cyclopterus lumpus</i>	8	14	Lump fish
<i>Cymatogaster aggregatus</i>	11	14	Surf perch
<i>Cyprinus carpio</i>	4, 8, 9, 14	173	Fancy red carp
<i>Dissotichus eleginoides</i>	1, 2, 3, 8, 12, 13, 14, 28, 29, 30, 31	30	
<i>Ditrema temminicki</i>	1–9	9	
<i>Doderleinia berycoides</i>	3, 8	18	
<i>Engraulis japonica</i>	1, 2, 3, 4, 6, 8, 8, 14, 24	39	Anchovy
<i>Entosphenus japonicus</i>	3, 8	18	Lamprey
<i>Epinephelus akaara</i>	3, 8	18	Grouper
<i>Epinephelus fasciatus</i>	3, 8	18	Red hata
<i>Eptatretus stoutii</i>	Absent	42	Pacific hagfish
* <i>Esox lucius</i>	3, 8, 10, 31	17, 43	Pike
<i>Etrumeus micropus</i>	1, 2, 3, 4, 6, 7, 8, 9, 14 (+ triols)	38	
<i>Exocoetus volitans</i>	1, 2, 3, 4, 6, 8, 9, 14, 24	39	
<i>Fistularia petimba</i>	3, 8	18	Flute mouth
<i>Fundulus parvipinnis</i>	11	44–46	Killifish
<i>Gadus aeglefinus</i>	11	14	
<i>Gadus callarias</i>	4, 11	14	
<i>Gadus merlangus</i>	11	14	
<i>Gadus minutus</i>	4, 11	14	
<i>Gadus virens</i>	11	14	
<i>Gaidropsarus cimbrius</i>	4	12	
<i>Gaidropsarus mustela</i>	4	14	
<i>Gambusia holbrooki</i>	8	48	
<i>Gasterosteus aculeatus</i>	1, 4, 8, 9, 12, 14, 20, 24	47	Three spined stickleback
<i>Gephyroberix japonicus</i>	3, 8	18	
<i>Gillichthys mirabilis</i>	11	46	Long jawed goby
<i>Girella nigricans</i>	11	46	Opal eye
<i>Gobius niger</i>	4, 11	12	
<i>Gyrinomismus</i> sp.	8	16	Whalefish
<i>Harengula tunasi</i>	1, 2, 3, 4, 6, 7, 8, 9, 14 (+ triols)	38	
<i>Helicolenus hilgendorfi</i>	3, 8, 15	18	
<i>Heterodontus francisci</i>	14	42	Horned shark
<i>Hexagrammos otakii</i>	1–9	9	
<i>Hypomesus transpacificus</i>	6, 7, 14, 21, 24	172	

## 126 The biochemistry of the carotenoids

Table 8.2 cont'd

Species	Pigments	Reference	Common name
* <i>Hypsypops rubicunda</i>	11	47	Garibaldi
<i>Ilisha elongata</i>	1, 2, 3, 6, 7, 8, 9, 14 (+ triols)	38	
<i>Ischikauia steenackeri</i>	1, 4, 7, 8, 9, 14, 14 (+ triols)	49	Herbivorous chub
<i>Isurus glaucus</i>	Absent	42	
<i>Labrus bergylta</i>	4	14	
<i>Labrus melops</i>	4	12	
<i>Labrus ossifagus</i>	4	14	
* <i>Lampetra fluviatilis</i>	4	50	Lamprey
* <i>Lampetra japonica</i>	4, 6, 7, 14	51	Arctic lamprey
* <i>Lampetra planeri</i>	3, 4, 8, 13, 14	50, 52	
<i>Latimeria chalumnae</i>	Absent	42	
<i>Latealabrax japonicus</i>	1, 2, 3, 4, 6, 7, 8, 9, 14 (+ triols)	38, 53	Sea bass
<i>Lepidotrigla guntheri</i>	3, 8	18	Sea robin
<i>Lepomis cyanellus</i>	4	176	Sun fish
<i>Lepomis macrochirus</i>	4, 10, 32, 33	31, 176	Blue gill
<i>Lepomis megalotis</i>	4, 8	176	Sun fish
<i>Limanda limanda</i>	20, 33, 39, 50–1, 11 others	54	Dab
<i>Lota lota</i>	11	55	Eel pout
* <i>Macropodus opercularis</i>	4, (?)14	19	Paradise fish
<i>Micropodus salmoides</i>	1, 2, 3, 4, 8, 9, 12, 14, 21, 24, 35, 36, 37, 38	56	
<i>Micropterus punctulatus</i>	4	176	
<i>Moroco steindachneri</i>	1, 2, 3, 4, 6, 7, 8, 9, 14 (+ triols)	38	
<i>Mullus barbatus</i>	57 (esters)	184	
<i>Muraenolepis microps</i>	1, 2, 3, 8, 11, 12, 13, 14, 28, 29, 30, 31	30	
<i>Navodon modestus</i>	1–9	9	
<i>Nerophis acequoreus</i>	4	12	
<i>Nerophis ophidion</i>	3, 4, 8, 11, 12, 14, 39	14, 57	
<i>Neothunnus albacora</i>	42	3, 41	Yellowfin tunny
<i>Notothenia gibberifrons</i>	1, 2, 3, 8, 11, 12, 13, 14, 28, 29, 30, 31	30	
<i>Notothenia rossi-marmorata</i>			
<i>Odotobutis obscura</i>	24, 40, 41, 42	58	
<i>Oncorhynchus keta</i>	1, 4, 6, 7, 9, 10, 12, 14, 15,	58, 59, 60	Chum salmon
<i>Oncorhynchus kisutch</i>	24, 26, 32, 33, 35, 40, 43, 44	61, 62	Coho salmon
<i>Oncorhynchus masu masu</i>			Masou salmon
<i>Oncorhynchus masu macrostomus</i>			Kokane
<i>Oncorhynchus nerka</i>			(Sockeye salmon)
<i>Oncorhynchus</i> sp.	44, 45, 46, 47	62	
<i>Oncorhynchus tshawytscha</i>	8	98	Chinook salmon
<i>Opsarichthys unicirrostris</i>	1, 2, 3, 4, 6, 7, 8, 9, 14 (+ triols)	38	Piscivorus char

<i>Species</i>	<i>Pigments</i>	<i>Reference</i>	<i>Common name</i>
<i>Oryzias latipes</i>	1, 2, 3, 4, 6, 8, 9, 14, 24	39, 63	Medaka
<i>Osmerus eperlanus</i>	2, 3, 4, 13, 14, 55	64, 65	Smelt
<i>Oxyjulis californica</i>	10, 32, 33	10, 66	
* <i>Paracottus kessleri</i>	1, 4, 8, 14	13, 40	Bull head
* <i>Paracottus kneri</i>	4, 8, 14	13, 40	
<i>Parapristiopoma filineatum</i>	1, 2, 3, 4, 5, 6, 7, 8, 9, 14 (+ triols)	9, 38, 53	
<i>Parasilurus asotus</i>	48, 49	67	Japanese catfish
<i>Percha fluviatilis</i>	8, 11	17	Fresh water perch
<i>Pholis gunellus</i>	4, 11	14	
<i>Phoxinus lagowski</i>	40	58	
<i>Pimelometopon pulchrum</i>	3, 8, 14	68	California sheep-head
<i>Plattessa platessa</i>	1, 8+2 others	54	Plaice
<i>Platichthys flesus</i>	1, 4, 8, 9, 12, 51+9 others	54	Flounder
* <i>Platypoecilus maculatus</i>	4, (?)14	17	Platyfish
<i>Platyrrhinoidis triseriata</i>	14	42	Thornback ray
<i>Pleuronectes flesus</i>	4	12, 64	
<i>Pleuronectes kitti</i>	4, 11	12, 14	
<i>Pleuronectes limanda</i>	4, 11	12, 14, 65	
<i>Pleuronectes microcephalus</i>	Lipochromes	65	
<i>Pomoxis annularis</i>	4	172	Sun fish
<i>Pomoxis nigromaculatus</i>	4	172	Sun fish
<i>Priacanthus boopis</i>	3, 8	18	Big eye
<i>Pristipomoides amoenus</i>	3, 8	63	
<i>Pristipomoides filamentosus</i>	1, 9	9	
<i>Prognichthys agoo</i>	1, 2, 3, 4, 6, 8, 9, 14, 24	39	Flying fish
<i>Pseudochaenichthys georgianus</i>	1, 2, 3, 8, 11, 12, 13, 14, 28, 29, 30, 31	30	
<i>Pungitus pungitus</i>	1, 8, 14, 38, 52	47	
<i>Pungitus sinensis</i>	1, 2, 3, 4, 6, 8, 9, 14, 24	39	Chinese eight spined stickleback
<i>Raja batis</i>	4	14	
<i>Raja clavata</i>	4	14	
<i>Raja georgiana</i>	1, 2, 3, 8, 11, 12, 13, 14, 28, 29, 30, 31	30	
<i>Raniceps raninus</i>	4	14	
<i>Regalescus glesne</i>	8	69	Oar fish
<i>Rhoxinuslagorski oxycephalus</i>	24, 40, 41, 42	58	
<i>Roccus saxatilis</i>	1, 2, 3, 4, 6, 7, 8, 9, 14 (+ triols)	38, 53	
<i>Rhinogobius brunneus</i>	1, 2, 3, 8, 11, 12, 13, 14, 28, 29, 30, 31, 40	30, 58	
<i>Rondeletia bicolor</i>	8	16	Whalefish
<i>Salmo fario</i>	1, 4, 8, 9, 12, 14, 20, 24	70	

Table 8.2 cont'd

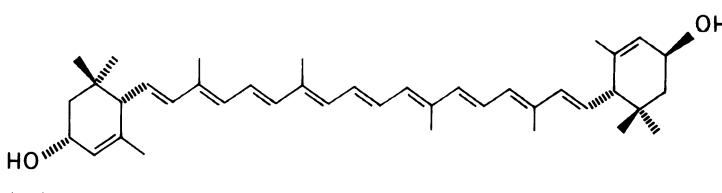
Species	Pigments	Reference	Common name
* <i>Salmo gairdneri (irideus)</i>	1, 4, 8, 11, 12, 14, 24, 25, 35	62, 72–77, 178, 179, 180	Rainbow trout
<i>Salmo salar</i>	4, 8	78, 79, 179, 180	Atlantic salmon
<i>Salmo trutta</i>	4, 8, (?)11, 12, 14, 25	14, 62, 80, 81, 181	Sea trout
<i>Salmo trutta morpho fario</i>	8, 12, 39	82	
* <i>Salvelinus fontinalis</i>	12, 14, 25	62, 108	Brook trout
* <i>Salvelinus leucomaenoides</i>	12, 14, 24, 25, 40, 41, 42	58, 62	Japanese char
* <i>Salvelinus malma malma</i>	24, 40, 41, 42	58, 62	
* <i>Salvelinus namaycush</i>	12, 14, 25	62	Lake trout
<i>Salvelinus</i> sp	8	83	Trout
<i>Sardina pilchardus</i>	1, 8, 11, 11, 14, 24, 38, 51	84	Pilchard
<i>Sardinops melanosticta</i>	4, (?)15	19, 63	
<i>Sarotherodon mossambicus</i>	8	85	
<i>Scomber japonica</i>	1–9	9	
<i>Scomber scombrus</i>	4, 11	12, 14, 15	Mackerel
<i>Scombrobs boopis</i>	1–9	9	
<i>Scophthalmus norvegicus</i>	11	12, 14	
<i>Scorpaena scrofa</i>	(?)8	86	
<i>Scorpaenodes littoralis</i>	1–9	9	
<i>Sebastes baramenuke (maramenuke)</i>	3, 8	18	
<i>Sebastes flavidus</i>	3, 4, 8, 14	10, 65	
<i>Sebastes marinus</i>	4, 53	17, 66, 87	Rock cod
<i>Sebastes miniatus</i>	3, 8, 14	152	
<i>Sebastes umbrosus</i>	3, 8, 14	152	
<i>Sebastiscus marmoratus</i>	3, 8, 14	9	
<i>Sebastolobus macrochir</i>	3, 8	63	
<i>Seriola quinqueradiata</i>	10, 32, 33	10, 65	
* <i>Serrasalmo nattereri</i>	8, 9, 25	31	Piranha
<i>Silurus glanis</i>	17 pigments present	88	
<i>Siphonostoma typhle</i>	4, 11	14	
<i>Sparus sabra</i>	1–9	9	
<i>Stephanolepis cirrhifer</i>			
<i>Stolephorus japonicus</i>	1, 2, 3, 4, 6, 7, 8, 9, 14 (+ triols)		
<i>Syngnathus acus</i>	4, 11	14	
<i>Theragra chalcogramma</i>	1–9	9	
<i>Thunnus thynnus</i>	3, 10, 32, 33	10, 65, 89	Tunny
* <i>Tilapia mossambica</i> }	1, 4, 6, 7, 8, 9, 14, 24, 25, 32, 54	90	
* <i>Tilapia nihotica</i>	8, 14	91	Tench
<i>Tinca tinca</i>	11	14	Greater weaver
<i>Trachinus draco</i>	1, 2, 3, 8, 11, 12, 13, 14, 28, 29, 30, 31	30	
<i>Tribolodon hakonensis</i>	1, 2, 3, 4, 6, 7, 8, 9, 14 (+ triols)	38	
<i>Trigla gurnardus</i>	11	14	Gurnard

Species	Pigments	Reference	Common name
<i>Xiphophorus helleri</i>	4, 14	19	Sword tail
<i>Xiphophorus maculatum</i> X. <i>belleri</i>	1, 4, 14	92	
<i>Zacco platypus</i> }	1, 2, 3, 4, 6, 7,	38	Place chub
<i>Zacco temminke</i> }	8, 9, 14 (+ triols)		Dark chub
<i>Zoarces viviparus</i>	4, 11	14	

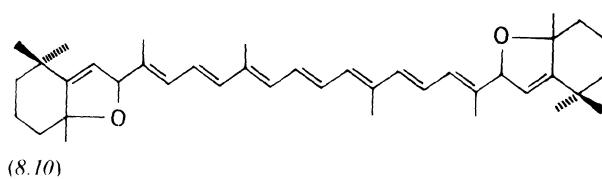
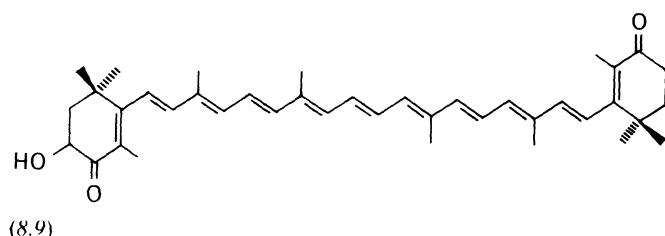
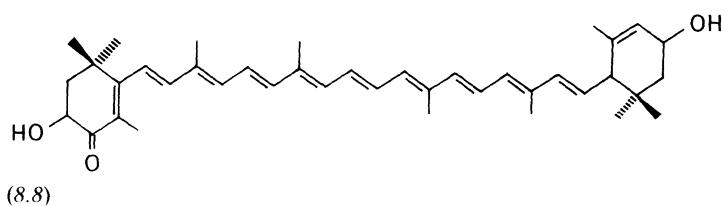
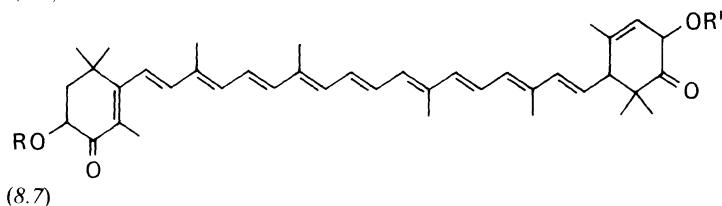
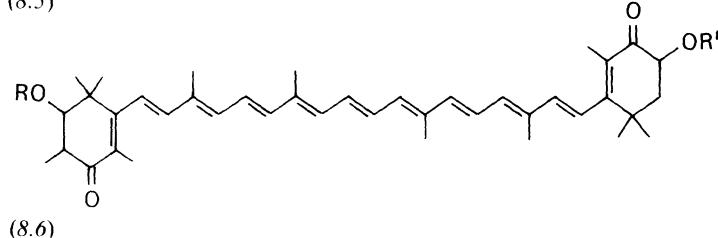
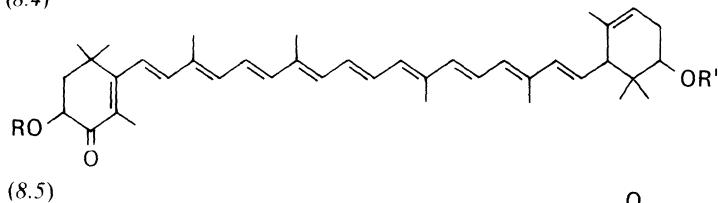
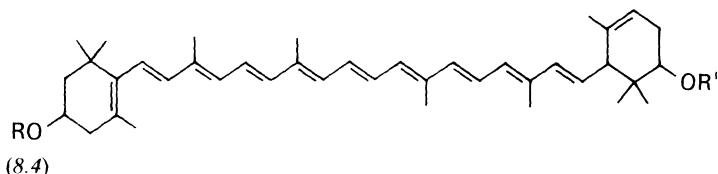
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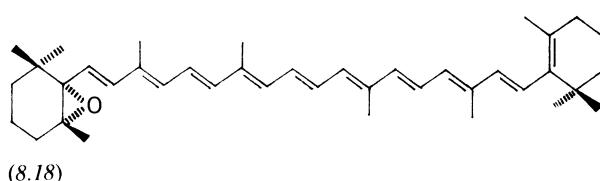
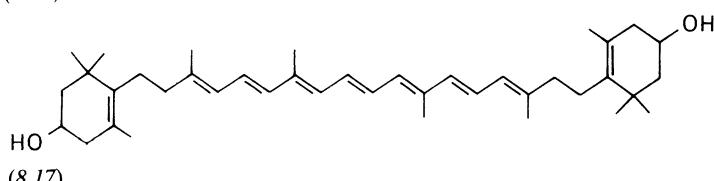
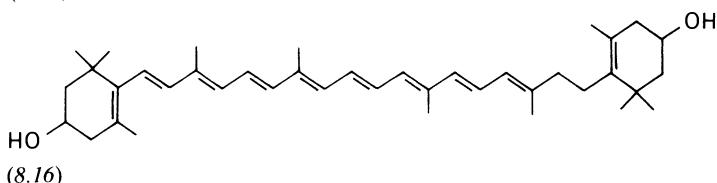
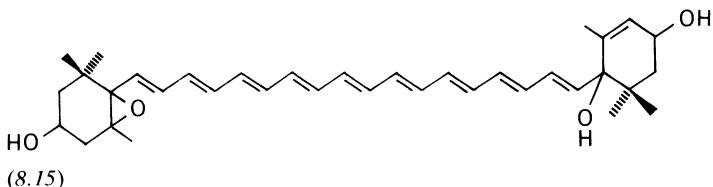
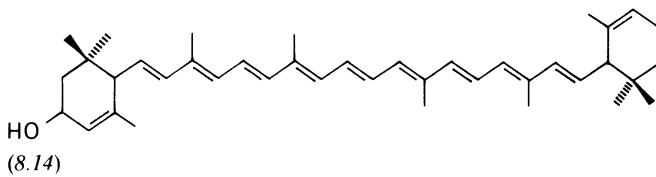
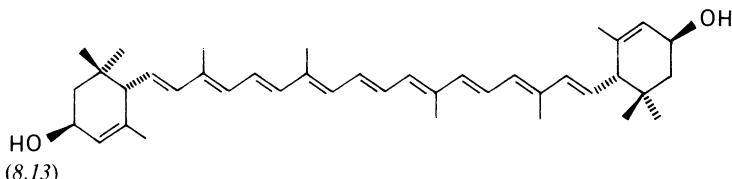
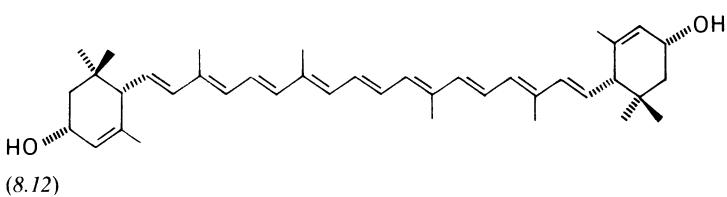
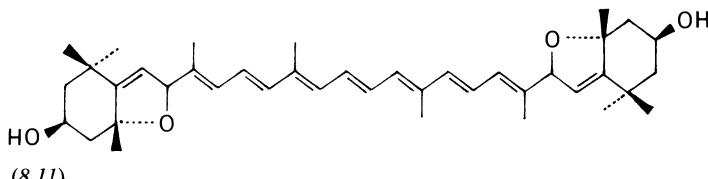
1. $\beta$ -Carotene	(1.5)	27. Idoxanthin	(6.10)
2. $\alpha$ -Cryptoxyanthin	(4.1)	28. Flavoxanthin	(5.3)
3. Tunaxanthin	(6.16)	29. Aurochrome	(8.10)
4. Lutein	(1.10)	30. Auroxanthin	(8.11)
5. 4-Ketolutein (= fritschillaxanthin)	(6.20)	31. 4-Hydroxy- $\alpha$ -carotene	(7.16)
6. Diatoxanthin	(4.2)	32. Tunaxanthin A (3R,6S,3'R,6'S)	(8.12)
7. Alloxanthin (= cynthiaxanthin = pectenoxanthin)	(1.2)	33. Tunaxanthin B (3S,6S,3'S,6'S)	(8.13)
8. Astaxanthin	(1.1)	34. $\epsilon$ -Carotene	(2.33)
9. $\alpha$ -Doradexanthin	(6.4)	35. Echinone	(1.11)
10. Tunaxanthin C (3R,6S,3'S,6'S)	(8.3)	36. Neoxanthin	(2.39)
11. Taraxanthin (= lutein 5,6-epoxide)	(6.6)	37. Mutatoxanthin	(7.1)
12. Canthaxanthin	(1.4)	38. Mutatochrome	(2.35)
13. Isozeaxanthin	(2.41)	39. 4-Keto-4'-hydroxy- $\beta$ -carotene	(6.18)
14. Zeaxanthin	(1.9)	40. 2-Hydroxy- $\beta$ -carotene	(6.9)
15. Violaxanthin	(2.40)	41. Isocryptoxanthin	(2.27)
16. Tilefishxanthin I	(8.4) <sup>†</sup>	42. 3-Hydroxy- $\epsilon$ -carotene (= $\alpha$ , $\alpha$ -cryptoxanthin)	(8.14)
17. Tilefishxanthin II	(8.5) <sup>†</sup>	43. Salmoxanthin	(8.15)
18. Tilefishxanthin III	(8.6) <sup>†</sup>	44. Antheraxanthin	(5.8)
19. Tilefishxanthin IV	(8.7) <sup>†</sup>	45. (3R,3'R)-Astaxanthin	(1.13)
20. Phoenicoxanthin (= adonirubin)	(1.8)	46. (3S,3'S)-Astaxanthin	(1.12)
21. $\beta$ -Doradexanthin (= adonixanthin)	(2.32)	47. (3R,3'S)-Astaxanthin	(1.14)
22. 3,3'-Dihydroxy-4-keto- $\alpha$ -carotene	(8.8)	48. Parasiloxanthin	(8.16)
23. 3-Hydroxy-4,4'-diketo- $\beta$ -carotene	(8.9)	49. 7,8-Dihydroparasiloxanthin	(8.17)
24. $\beta$ -Cryptoxyanthin	(2.36)	50. $\gamma$ -Carotene	(2.26)
25. 3'-Epilutein	(6.22)	51. $\beta$ -Carotene 5,6-epoxide	(8.18)
26. Diadinoxanthin	(6.3)	52. $\alpha$ -Carotene	(2.25)
		53. Chiriquixanthin B (3S,6R,3'S,6'R)	(8.19)
		54. Rhodoxanthin	(8.20)
		55. 4-Keto- $\alpha$ -carotene (= phoenicopterone)	(6.7)
		56. 3,3'-Dihydroxy- $\epsilon$ -carotene	(8.21)
		57. Actinioerythrin	(3.1)

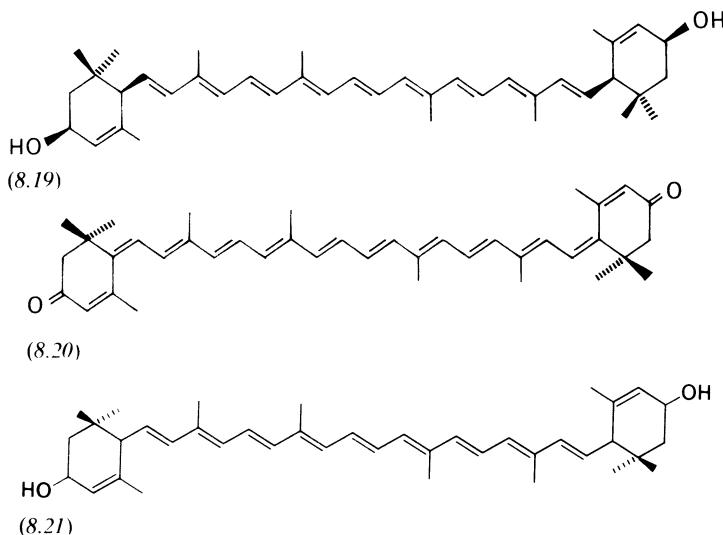
\*Freshwater species.

<sup>†</sup>R and R' are fatty acid residues.

(8.8)







The bulk of the skin pigments are xanthophylls mostly in the ester form; only traces of carotenes are occasionally encountered. In the first edition of this book it was stated that the major fish pigments were astaxanthin (1.1), lutein (1.10) and taraxanthin (6.6). This generalization is still true to the extent that ‘astaxanthin’ and ‘lutein’ are widespread but it is imprecise because it is now clear that enantiomers of these pigments exist, frequently, as just indicated, in the same species. For example three stereoisomers of astaxanthin are found in the flesh (see also Table 8.3) of Atlantic (*Salmo salar*) and Pacific (*Oncorhynchus* spp.) salmon. The relative amounts were very similar in both genera: 80% of the (3S,3'S)-enantiomer (1.12), 15% of the (3R,3'R)-enantiomer (1.13) and 5% of the meso (3R,3'S) compound (1.14) [61]. A similar situation in lobster eggs has already been discussed (Chapter 1). On the other hand astaxanthin from various plant sources is stereochemically pure (see Volume I).

In the case of ‘lutein’, the epimer of lutein, 3'-epilutein (6.22) (*S*-configuration at 3'), has been isolated from goldfish (*Carassius citrinellum*) [31, 32], Pacific salmon (*Oncorhynchus* spp.) [59, 60, 62], various trout species [59, 60, 62, 123], piranha (*Serrasalmo nattereri*) [31] and *Tilapia* spp. [90]. So the widely reported pigment ‘lutein’ in fish may well turn out to be in many cases 3'-epilutein. The plant pigment calthaxanthin from *Caltha palustris* is also 3'-epilutein [124].

The position of taraxanthin (5,6-epoxylutein) (6.6) as a compound of fish skin carotenoids is even more equivocal and it seems to have disappeared from many recent surveys. However, tunaxanthin (6.16) has emerged as a widely distributed pigment particularly in marine fish. An earlier view that it was entirely confined to marine species had to be abandoned when it was

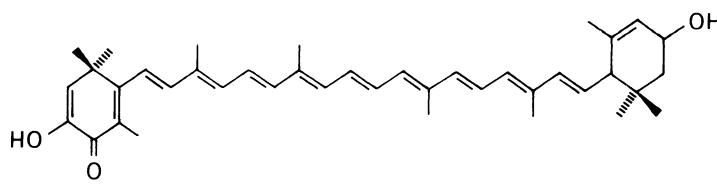
reported in various goldfish and perch (Table 8.2). Once again enantiomers have been encountered and tunaxanthins A ( $3R,6S,3'R,6'S$ ) (8.9), B ( $3S,6S,3'S,6'S$ ) (8.12) and C ( $3R,6S,3'S,6'S$ ) (8.3) have been isolated from, for example, *Amanses modestus* [10] (see also Table 8.2). All these pigments involve different chiralities at C-3 and C-3' whilst the C-6,6' chirality is constant (*S*). However, an enantiomer which involves a change in chirality at C-6 and C-6' has been encountered in *Sebastes marinus* [66]; this compound was first obtained from a frog and has been named chiriquixanthin B ( $3S,6R,3'S,6'R$ ) (8.19) [125] (see also Chapter 9). It is emphasized that tunaxanthins A, B and C have the opposite chirality at C-6 and C-6' to that observed at C-6' in lutein and 3'-epilutein. In contrast  $\alpha$ -doradexanthin (6.4) has the  $6'R,3S,3'S$  configuration which is the same as that of 3'-epilutein [122].

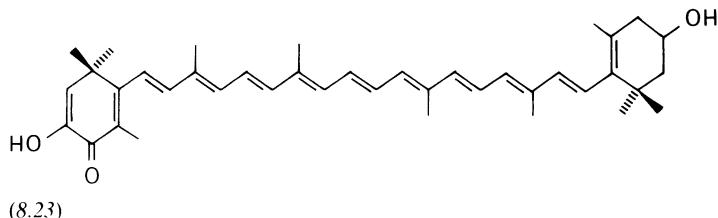
A new group of fish xanthophylls recently reported are the tilefishxanthins I–IV (8.4–8.7) isolated from the Japanese tilefish *Branchiostegus japonicus* [21]. They are keto derivatives of hydroxylated  $\alpha$ -carotenes with, as yet, undetermined stereochemistry.

Other unique pigments recently reported in fish are salmoxanthin (2'-hydroxy-5,6-epoxylutein) (8.15), a major component of Salmonidae carotenoids [60], and 2-hydroxy- $\beta$ -carotene (6.9) from *Odontobutis obscura* [58]. In neither case has the chirality been determined but 2-hydroxy- $\beta$ -carotene, which presumably arises from the insect food of the fish, probably has the same chirality as the insect pigment (see Chapter 7). Carotenoids saturated at C-7,8 have been reported in the Japanese catfish *Parasilurus asotus* [67]. Parasiloxanthin (8.16), said to be 7,8-dihydrozeaxanthin, and 7,8-dihydroparasiloxanthin (8.17) are both present. The recent report of actinioerythrin (3.1) in red mullet (*Mullus barbatus*) [184] is the first record of the occurrence of this pigment outside the sea anemones (Chapter 3).

Most recent work indicates that except for fish which accumulate astaxanthins the major carotenoids in fish contain either one or two  $\epsilon$ -rings. This, combined with the varying chirality at C-3 and C-6 just discussed, poses important biosynthetic questions (see Section 8.2.2).

It should be emphasized that  $\alpha$ - and  $\beta$ -doradexanthins were first reported as the diosphenol artefacts  $\alpha$ - and  $\beta$ -doradecins (8.22, 8.23) [33]. These bear the same relationships to the naturally occurring pigments as does astacene (2.1) to astaxanthin (1.1).





There is as yet no clear evidence for the existence of carotenoproteins in fish integument which is in marked contrast with the situation in marine invertebrates (see Chapter 1).

*Localization in skin.* The carotenoids in fish skin are localized in their xanthophores and non-carotenoid pigments generally in their erythrophores [19]. In the brown trout, on the other hand, lutein is concentrated in the xanthophores and astaxanthin in the erythrophores. Microspectroscopic studies indicated that one xanthophore contained between 11 and 28 pg of lutein; the amount of astaxanthin in an erythrophore was between 200 and 340 pg. The xanthophores are distributed equally through the dermal layers whereas the erythrophores are confined to the outer layers [81]. In lampreys (*Lampetra* spp.) lutein accumulates in the non-expansile lipophores found in the dermal and sub-dermal layers of skin [50]. Carotenoids are present in the xanthophores of the teleost *Oryzias latipes* [126].

Experiments have begun on cultured xanthophores of goldfish [127, 128] and erythrophores of the sword tail *Xiphophorus letteri* [129]; they have been planned to examine the detailed mechanism of pigment movement and accumulation in the formation of chromatophores.

#### (b) Muscle

Carotenoids are not widely distributed in the muscle of fish in great amounts but some salmon and trout species do contain significant quantities. The known qualitative distribution in muscle is given in Table 8.3.

#### (c) Eggs

The nature of the carotenoids found in the eggs of various fish is summarized in Table 8.4. In one case, the goldfish (*Carassius auratus*), the existence of a carotenoprotein was suspected [26]. Although xanthophylls predominate in fish eggs, β-carotene is nearly always present in small amounts. This contrasts with the situation in skin and muscle.

#### (d) Sperm

Early work suggested that the milt (sperm) of brown trout *Salmo trutta* [50]

Table 8.3 Carotenoid distribution in fish muscle

Species	Pigment	Reference	Common name
<i>Aristichthys nobilis</i>	1-5	93	Spotted silver carp
<i>Carassius auratus</i>	4, 6 (traces)	26	Goldfish
<i>Coregonus albula</i>	7	94	
<i>Coregonus lavaretus</i>	4, 6, 8, 9	94	
<i>Ctenopharyngodon idella</i>	1, 2, 3, 4, 5, 10	93	Grass carp
<i>Esox lucius</i>	6, 7, 11	43	Pike
<i>Gadus callarias</i>	2, 4, 6, 7, 11	95	Cod
<i>Hypophthalmichthys molitrix</i>	1, 2, 3, 4, 5, 7, 9	93	Silver carp
<i>Lophius piscatorius</i>	1	96, 97	Angler fish
<i>Oncorhynchus gorbusa</i>	7	182	Pink salmon
<i>Oncorhynchus keta</i>	7	182	Chum salmon
<i>Oncorhynchus kisutch</i>	7	182	Coho salmon
<i>Oncorhynchus masu</i>	7	182	Cherry salmon
<i>Oncorhynchus nerka</i>	7	71, 98	Pacific salmon
<i>Oncorhynchus</i> sp.	7, 12, 13, 14	61, 99, 100	Pacific salmon
<i>Oncorhynchus tshawytscha</i>	7	98	Chinook salmon
<i>Osmerus eperlanus</i>	11	64	Smelt
<i>Salmo gairdneri/irideus</i>	4, 6, 7	72, 73, 74, 185	Rainbow trout
<i>Salmo salar</i>	?1, 2, 4, 6, 7 13, 14	78, 79, 80, 96, 101-105 61	Atlantic salmon Sea trout
<i>Salmo trutta</i>	1, 2, 4, 7	76, 81, 106	
<i>Salmo trutta morpha fario</i>	4, 7, 9, 15	82, 107	
<i>Salvelinus fontinalis</i>	2, 4, 7	72, 108	Brook trout
<i>Sebastodes atrovirens</i>	6, 7, 11	152	
<i>Sebastodes carnatus</i>	2, 4, 7	152	
<i>Sebastodes constellatus</i>	2, 4, 7	152	
<i>Sebastodes eos</i>	2, 4, 7	152	
<i>Sebastodes flavidus</i>	2, 4, 7	152	
<i>Sebastodes miniatus</i>	2, 4, 7	152	
<i>Sebastodes umbrosus</i>	2, 4, 7	152	
<i>Tinca tinca</i>	9	91	Tench

**Key**

- |   |        |                            |        |
|---|--------|----------------------------|--------|
| 1. $\beta$ -Carotene                            | (1.5)  | 10. ?Violaxanthin          | (2.40) |
| 2. Canthaxanthin                                | (1.4)  | 11. Tunaxanthin            | (6.16) |
| 3. Isozeaxanthin                                | (2.41) | (Chirality not stated)     |        |
| 4. Lutein                                       | (1.10) | 12. (3R,3'R)-Astaxanthin   | (1.13) |
| 5. Polioxanthophyll<br>(undetermined structure) |        | 13. (3S,3'S)-Astaxanthin   | (1.12) |
| 6. Zeaxanthin                                   | (1.9)  | 14. (3R,3'S)-Astaxanthin   | (1.14) |
| 7. Astaxanthin                                  | (1.1)  | 15. $\beta$ -Cryptoxanthin | (2.36) |
| 8. 4-Hydroxy- $\alpha$ -carotene                | (7.16) |                            |        |
| 9. Taraxanthin                                  | (6.6)  |                            |        |

Table 8.4 Carotenoid distribution in the eggs and ovaries

Species	Pigment	Reference	Common name
* <i>Acipenser ruthenus ruthenus</i>	1, 2, 3, 4, 5	109	
<i>Acipenseridae</i> sp.	2, 3, 4, 6, 7	109	'Caviar'
<i>Ammodytes tobianus</i>	1, 2	11	Sand eel
* <i>Carassius auratus</i>	3, 4 (trace)	26	Goldfish
<i>Clupea harengus</i>	4	169	Herring
<i>Coregonus albula</i>	1, 2, 3, 6, 9	94, 110	
<i>Cyclopterus lumpus</i>	Present	111	Lumpfish
<i>Cyprinus carpio</i>	Present	111	Fancy red carp
<i>Eleginops navaga</i>	1+3 unidentified xanthophylls	17, 111	
* <i>Esox lucius</i>	1, 4, 7	43, 112	Pike
<i>Gadus callarias</i>	1, 4	112	
<i>Gadus morrhua</i>	1, 2, 4, 5, 6, 13	113, 174	Cod
<i>Hippoglossus hippoglossus</i>	1, 4, 6	112	
<i>Hucho hucho</i>	1, 2, 4, 5, 7, 9	94	Beluga
<i>Karcius bicolor</i>	2, 3, 4, 13, 14, 15	174	Flounder
<i>Katsuwonus pelamis</i>	2, 3, 5, 15	174	Skipjack
<i>Lota vulgaris</i>	1, 4	14	
<i>Oncorhynchus keta</i>	2, 5, 6, 8, 9, 10, 13, 14	114, 174	Pacific salmon
<i>Oncorhynchus tshawytscha</i>	2	98	Chinook salmon
<i>Osmerus eperlanus</i>	2, 3, 16, 17	64	Smelt
<i>Pneumatophorous japonicus</i>	3, 4, 13, 14, 15	174	Mackerel
<i>Prognichthys agoo</i>	2, 3, 5, 14, 15	174	Flying fish
<i>Salmo gairdneri/irideus</i>	1, 2, 4, 6, 8, 11, ?12	94, 115, 195	Rainbow trout
<i>Salmo salar</i>	2, 3, 4, 26, 8	94, 116	Atlantic salmon
* <i>Salmo trutta m. trutta</i>	1, 2, 3, 4, 6, 7	94	Brown trout
* <i>Salmo trutta n. fario</i>	1, 2, 4, 6, 8, 9	94	
<i>Sardinops melanosticta</i>	2, 3, 14, 15	174	Sardine
<i>Seriola quinqueradiata</i>	4, 15	174	Yellow tail
<i>Solea vulgaris</i>	1	112	Sole
<i>Theragra chalcogramma</i>	1, 2, 4, 13	174	Pollock
<i>Thymallus thymallus</i>	1, 2, 4, 5	94	Grayling
<i>Tilapia mossambica</i>	3, 4		

**Key**

- |   |        |   |            |
|---|--------|---|------------|
| 1. $\beta$ -Carotene                    | (1.5)  | 10. Asterinic acid (mixture)                          | (1.6, 1.7) |
| 2. Astaxanthin                          | (1.1)  | 11. 4-Keto- $\alpha$ -carotene<br>(=phoenicopoterone) | (6.7)      |
| 3. Zeaxanthin                           | (1.9)  | 12. $\gamma$ -Carotene                                | (2.26)     |
| 4. Lutein                               | (1.10) | 13. $\alpha$ -Doradexanthin                           | (6.4)      |
| 5. Tunaxanthin                          | (6.16) | 14. Idoxanthin  | (6.10)     |
| 6. Taraxanthin                          | (6.6)  | 15. Triols and tetrols (unidentified)                 |            |
| 7. Isozeaxanthin                        | (2.41) | 16. $\beta$ -Cryptoxanthin                            | (2.36)     |
| 8. Canthaxanthin                        | (1.4)  | 17. $\beta$ -Zeacarotene                              | (5.7)      |
| 9. 4-Keto-4'-hydroxy- $\beta$ -carotene | (6.18) |   |            |

\*Fresh water species.

and sand eels (*Ammodytes tobianus*) [11] did not contain carotenoids, but that they could be detected in pike (*Esox lucius*) milt [14]. More recent surveys indicate the presence of carotenoids in milt of herring (*Clupea harengus*) and sprat (*Sprattus sprattus*) as well as of the rainbow trout (*Salmo gairdneri/irideus*) and lavaret (*Coregonus lavaretus*) [117, 118].

### (e) Liver

The known distribution of carotenoids in fish livers is summarized in Table 8.5. The major components are xanthophylls which, in the main, exist in the unesterified form.

Table 8.5 Carotenoid distribution in fish livers

Species	Pigments	Reference	Common name
<i>Anguilla anguilla</i>	1, 2, 3, 4	13	Eel
<i>Aristichthys nobilis</i>	1, 3, 4, 5, 6, 7, 8	93	Spotted silver carp
<i>Carassius auratus</i>	1, 3, 9+unknown	26	Goldfish
<i>Careharinus glaucus</i>	Present	183	Blue shark
<i>Centrophorus squamosus</i>	Present	183	Shark
<i>Centroscyllium fabricii</i>	Present	183	Black dogfish
<i>Centroscymnus coelolepis</i>	Present	183	Portuguese shark
<i>Cetorhinus maximus</i>	Present	183	Basking shark
<i>Chimaera monstrosa</i>	Present	183	Rabbit fish
<i>Clupea harengus</i>	1, 3, 4, 5, 6, 7	118	Herring
<i>Ctenopharyngodon idella</i>	1, 3, 4, 5, 6, 8, ?10	93	Grass carp
<i>Cyclopterus lumpus</i>	4	14, 119	Lump fish
<i>Esox lucius</i>	3, 4, 9, 11	43, 120	Pike
<i>Etmopterus spinax</i>	Present	183	Shark
<i>Gadus callarias</i>	3, 4, 5, 6, 7, 9	95	Cod
<i>Gasterosteus aculeatus</i>	3, 12	47	Three spined stickleback
<i>Heterodontus francisci</i>	9	42	Horned shark
<i>Hexanchus griseus</i>	Present	183	Six gilled shark
<i>Hypophthalmichthys molitrix</i>	1, 3, 4, 5, 7, 8	93	Silver carp
<i>Lamna cornubica</i>	Present	183	Porbeagle
<i>Leuciscus rutilus</i>	3, 7	14, 120	
<i>Lophius piscatorius</i>	4, 7	14, 23, 96	Angler fish
<i>Mustelus mustelus</i>	Present	121	Smooth hound
<i>Myliobatis aquila</i>	Present	121	Eagle ray
<i>Orthagoriscus mola</i>	4, ?13	121	Sun fish
<i>Oryzias latipes</i>			
<i>Osmerus eperlanus</i>	2, 3, 6, 9, 14, 15	64	Smelt
<i>Platyrrhinoidis triseriata</i>	9	42	
<i>Pristiurus melanostomus</i>	Present	183	Black mouth dogfish
<i>Raja batis</i>	Present	183	Blue skate
<i>Raja brachura</i>	Present	183	Blonde ray

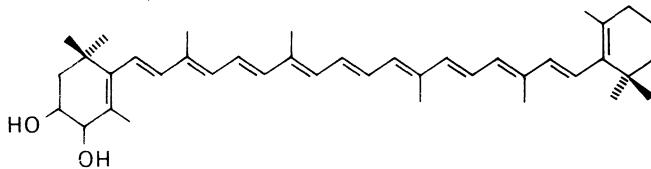
## 138 The biochemistry of the carotenoids

Table 8.5 cont'd

Species	Pigments	Reference	Common name
<i>Raja circularis</i>	Present	183	Sandy ray
<i>Raja clavata</i>	Present	183	Thornback ray
<i>Raja fullonica</i>	Present	183	
<i>Raja lineata</i>	Present	183	
<i>Raja montagui</i>	Present	183	Spotted ray
<i>Raja naevus</i>	Present	183	Cuckoo ray
<i>Raja oxyrhynchus</i>	Present	183	Long-nosed skate
<i>Raja radiata</i>	Present	183	Starry skate
<i>Regalecus glesne</i>	4	96	
<i>Salmo gairdneri/irideus</i>	4	185	Rainbow trout
<i>Salmo salar</i>	3	120	Atlantic salmon
<i>Salmo trutta</i>	1, 3	81	Brown trout
<i>Scymnodon jonesii</i>	Present	183	Shark
<i>Scymnorhinus licha</i>	Present	183	
<i>Somniosus microcephalus</i>	Present	183	
<i>Sprattus sprattus</i>	1, 3, 4, 6, 7	118	Sprat
<i>Squalus acanthias</i>	Present	183	Piked dogfish
<i>Squatina squatina</i>	Present	183	Angel ray
<i>Tinca tinca</i>	4	91	Tench
<i>Torpedo nobiliana</i>	Present	183	Electric ray
<i>Trygon pastinaca</i>	Present	183	Sting ray

### Key

- |  |        |                                      |        |
|--|--------|--------------------------------------|--------|
| 1. $\beta$ -Carotene                           | (1.5)  | 9. Zeaxanthin                        | (1.9)  |
| 2. Tunaxanthin                                 | (6.16) | 10. Violaxanthin                     | (2.40) |
| 3. Lutein                                      | (1.10) | 11. 3,4-Dihydroxy- $\beta$ -carotene | (8.24) |
| 4. Astaxanthin                                 | (1.1)  | 12. Neoxanthin                       | (2.39) |
| 5. Canthaxanthin                               | (1.4)  | 13. $\alpha$ -Carotene               | (2.25) |
| 6. Isozeaxanthin                               | (2.41) | 14. $\alpha$ -Cryptoxanthin          | (4.1)  |
| 7. Taraxanthin                                 | (6.6)  | 15. 4-Ketolutein                     | (6.7)  |
| 8. Polioxyxanthophyll<br>(structure not known) |        |                                      |        |



(8.24)

### (f) Other organs

Carotenoids have been reported in the eyes of *Prionatus carolinus*, *Centropristes striatus* and *Stenotomus chrysops* [130], *Salmo trutta* [50] and *Osmerus eperlanus* [64]. Complex mixtures exist in the brains of *Anguilla anguilla*, *Carassius auratus*, *Cyclopterus lumpus*, *Cyprinus carpio*, *Esox lucius*, *Ctenopharyngodon idella*, *Leuciscus delineatus*, *Misgurnus fossilis*,

*Nemachilus barbatulus*, *Salmo gairdneri/irideus* and *Tinca tinca* [130], and a large number of intestines have been analysed by Czeczuga (see reference list). Astaxanthin is present in the intestines of *Salmo gairdneri/irideus* and is accompanied by zeaxanthin and lutein in the kidneys [185]. Carotenoids were first noted in mouth mucus in *Beryx decadactylus* [17], and later work suggests that they may be widespread in this secretion [18, 131].

### (g) Quantitative distribution

It is difficult to give authoritative values for the carotenoid content in fish organs, not only because of lack of data but also because dietary variation can cause marked changes in the accumulation of ingested pigments as can changes in the physiological state of the animals. An impressive example of this is the results recorded for prespawning and spawning Pacific salmon (Table 8.6). There is a massive movement from muscle to skin in males during spawning and a similar but somewhat less dramatic movement in females, where the major redistribution is from muscle into ovary [132]. Some typical reported values for carotenoids in various tissues of a number of fish are collected in Table 8.7, although possible variations must always be borne in mind.

Table 8.6 Carotenoid distribution in prespawning and spawning *Oncorhynchus nerka* [132]

	Concentration in skin ( $\mu\text{g/g}$ )	% of total	Concentration in muscle ( $\mu\text{g/g}$ )	% of total	Concentration in gonad ( $\mu\text{g/g}$ )	% of total
<b>Male</b>						
Prespawning	2.9	2	28	98	—	—
Spawning	45.0	75	0.3	5	—	—
<b>Female</b>						
Prespawning	3.2	1	23	90	9.2	9
Spawning	11.0	14	0.3	5	29.5	85

### (h) Qualitative variations

Qualitative as well as quantitative differences have been recorded between different organs of the same fish. Results obtained on the pike *Esox lucius* [43] (Table 8.8) illustrate a characteristic pattern. Changes are also sometimes observed during growth; in *Carassius auratus*, for example, the developing fish changes in colour from grey through black and orange to fully orange. Only hydroxycarotenoids are found in the grey stage but with the onset of orange coloration keto carotenoids such as astaxanthin appear and eventually dominate the pigment pattern [26].

Table 8.7 Carotenoid levels in fish tissues

Species	Concentration ( $\mu\text{g/g}$ fresh weight)					Reference
	Integument	Muscle	Liver	Eggs	Milt	
<i>Ammodytes tobianus</i>	—	—	—	8.3	0	11
<i>Aristichthys nobilis</i>	—	1.34	8.88	—	—	93
<i>Coregonus lavaretus</i>	0.90	0.88	2.61	—	1.02	94
<i>Ctenopharyngodon idella</i>	—	0.66	1.76	—	—	93
<i>Gadus callarias</i>	—	0.79	0.89	—	—	95
<i>Heterodontus francisci</i>	19.2	—	45.7	—	—	42
<i>Hoploptthalmichthys molitrix</i>	—	1.59	18.83	—	—	93
<i>Osmerus eperlanus</i>	0.24	0.04	4.17	2.88	2.06	64
<i>Platyrrhinoidis triseriata</i>	0.17	—	7.86	—	—	42
<i>Salmo gairdneri/irideus</i>	12–19 <sup>a</sup>	1.2 <sup>a</sup>	—	—	—	74
	15.9 <sup>a</sup>	2.1 <sup>a</sup>	—	—	—	75
	1.05	0.21	—	—	—	114
	0.44 <sup>b</sup>	0	—	—	—	72
<i>Salmo trutta</i>	80–120 <sup>c</sup>	3.6	19.5	174	—	50
	300 <sup>c</sup>	—	—	—	—	—
	1600 <sup>c</sup>	—	—	—	—	—
<i>Salmo trutta morpha fario</i>	2.56	—	—	—	—	84
<i>Salvelinus fontinalis</i>	—	0.5–1.4	—	—	—	108

*Notes*<sup>a</sup>Measured on a dry wt. basis.<sup>b</sup>Including fins.<sup>c</sup>Yellow skin – almost entirely lutein.<sup>d</sup>Red fin tips – lutein content.<sup>e</sup>Red fin tips – astaxanthin content.Table 8.8 Quantitative differences between carotenoids of different organs of the pike (*Esox lucius*) [43]

Pigment	% of total pigment present			
	Skin	Muscle	Liver	Intestine
Tunaxanthin (6.16)	2.7	3.2	—	1.7
Astaxanthin (1.1)	94.7	61.8	48.5	81.8
4-Hydroxy- $\alpha$ -carotene (7.16)	2.6	—	—	—
Zeaxanthin (1.9)	—	35.0	8.8	—
Canthaxanthin (1.4)	—	—	22.1	3.4
3,4-Dihydroxy- $\beta$ -carotene (8.24)	—	—	13.8	—
Unidentified	—	—	6.8	—
Phenicoxanthin (1.8) (= adonirubin)	—	—	—	9.0

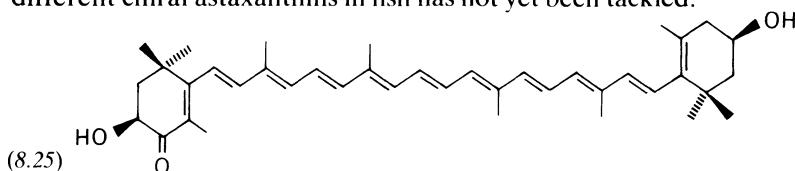
### 8.2.2 FORMATION OF SPECIFIC CAROTENOIDS

It is generally assumed that animals cannot synthesize carotenoids, so the question of the formation of carotenoids which are specific to fish raise fascinating biosynthetic problems which are not yet fully resolved.

#### (a) Astaxanthin

There is reasonable evidence that astaxanthin (1.1) is formed from  $\beta$ -carotene in goldfish (*Carassius auratus*) via the pathway (steps *A* ----> *F*) indicated in Fig. 8.1 [133–135]. Isocryptoxanthin (2.27), echinenone (1.11) and canthaxanthin (1.4) when fed to pigment-depleted goldfish cause a rise in the astaxanthin content of the animals, whereas isozeaxanthin (2.41), which can be formed from  $\beta$ -carotene [133], is not metabolized to astaxanthin [136]. So far 4'-hydroxyechinenone (step *C*, Fig. 8.1), a key intermediate in the proposed pathway, has not been detected. The astaxanthin formed by this pathway would have the chirality of the major enantiomer known to be present. Other investigations suggest that this pathway is only of minor importance and that zeaxanthin (1.9) is the main precursor of astaxanthin with 4-ketozeaxanthin (8.25) as intermediate [137]. Similarly alloxanthin (1.2) is converted into 7,8-didehydroastaxanthin (1.6) and 7,8,7',8'-tetradehydroastaxanthin (1.7) (together previously known as asterinic acid) via the analogous 4-keto derivatives [137].

Recent studies on the conversion of 'lutein' into 'astaxanthin' have revealed unexpected reactions involving a change in configuration at C-3' and the probable isomerization of an  $\epsilon$ -ring into a  $\beta$ -ring. Neither reaction appears to occur in plants. The first stages in the conversion (steps *A* ----->*C*, Fig. 8.2) are well established. [ $^{14}\text{C}$ ]Lutein is converted into  $\alpha$ -doradexanthin in goldfish and fancy red carp [134, 135, 137, 138]. 'Lutein' in goldfish in fact 3'-epilutein so the epimerization of lutein to 3'-epilutein [122], which is then converted into  $\alpha$ -doradexanthin with the same chirality at 3' (step *C*, Fig. 8.2), could take place via 3'-*O*-dehydrolutein (steps *A, B*, Fig. 8.2); this putative intermediate has been isolated from goldfish [122]. The conversion of  $\beta$ -doradexanthin into astaxanthin (step *E*, Fig. 8.2) has also been well documented [134, 135, 139], so the only doubtful step in Fig. 8.2 is *D*. The channelling of zeaxanthin into  $\beta$ -doradexanthin in this pathway is probably via idoxanthin (4-hydroxy-4'-ketozeaxanthin) (6.10) [139]. The problem of the nature of the mechanism of the formation of different chiral astaxanthins in fish has not yet been tackled.



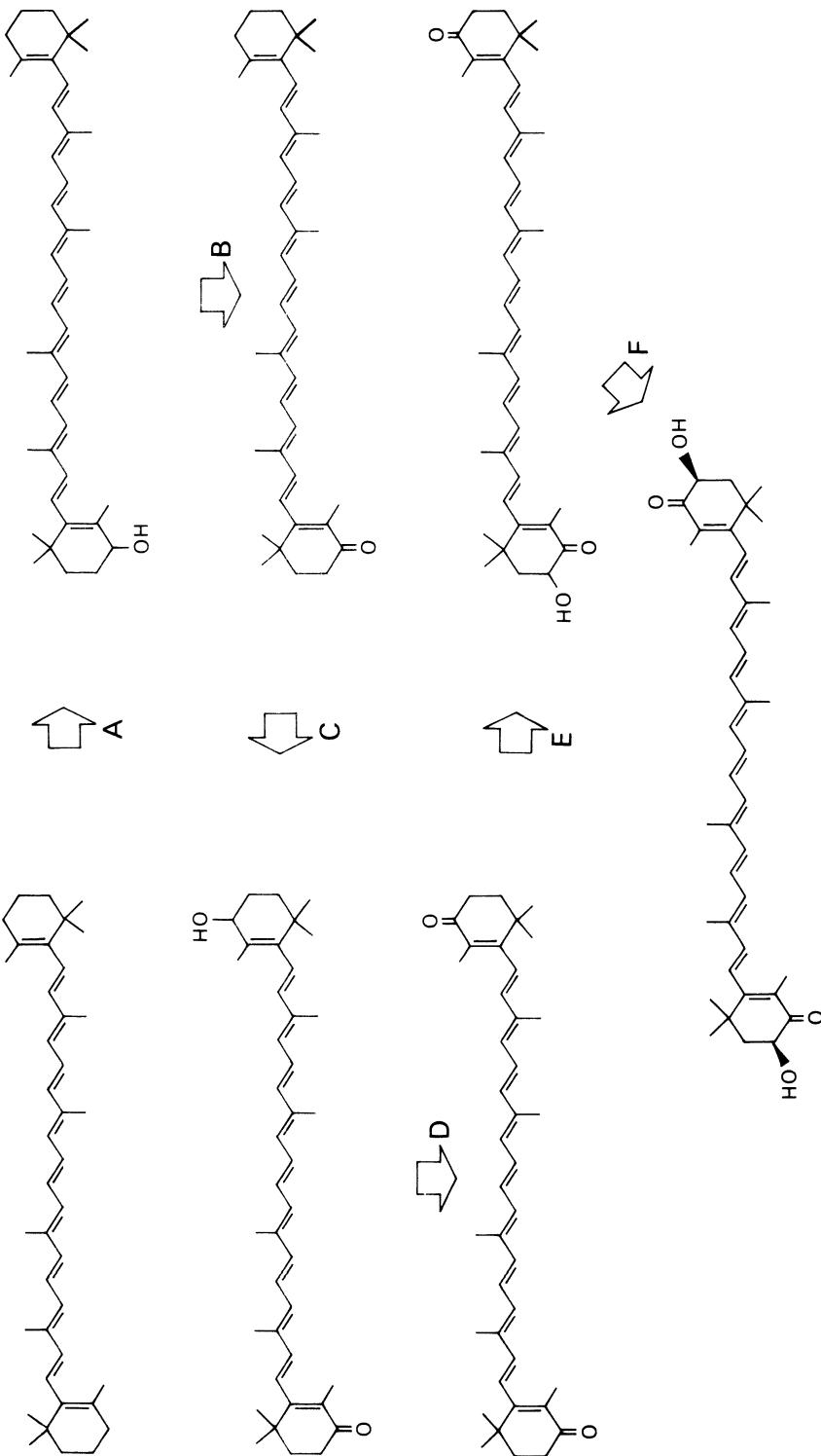


Fig. 8.1. Pathway of conversion of  $\beta$ -carotene into astaxanthin in goldfish [186].

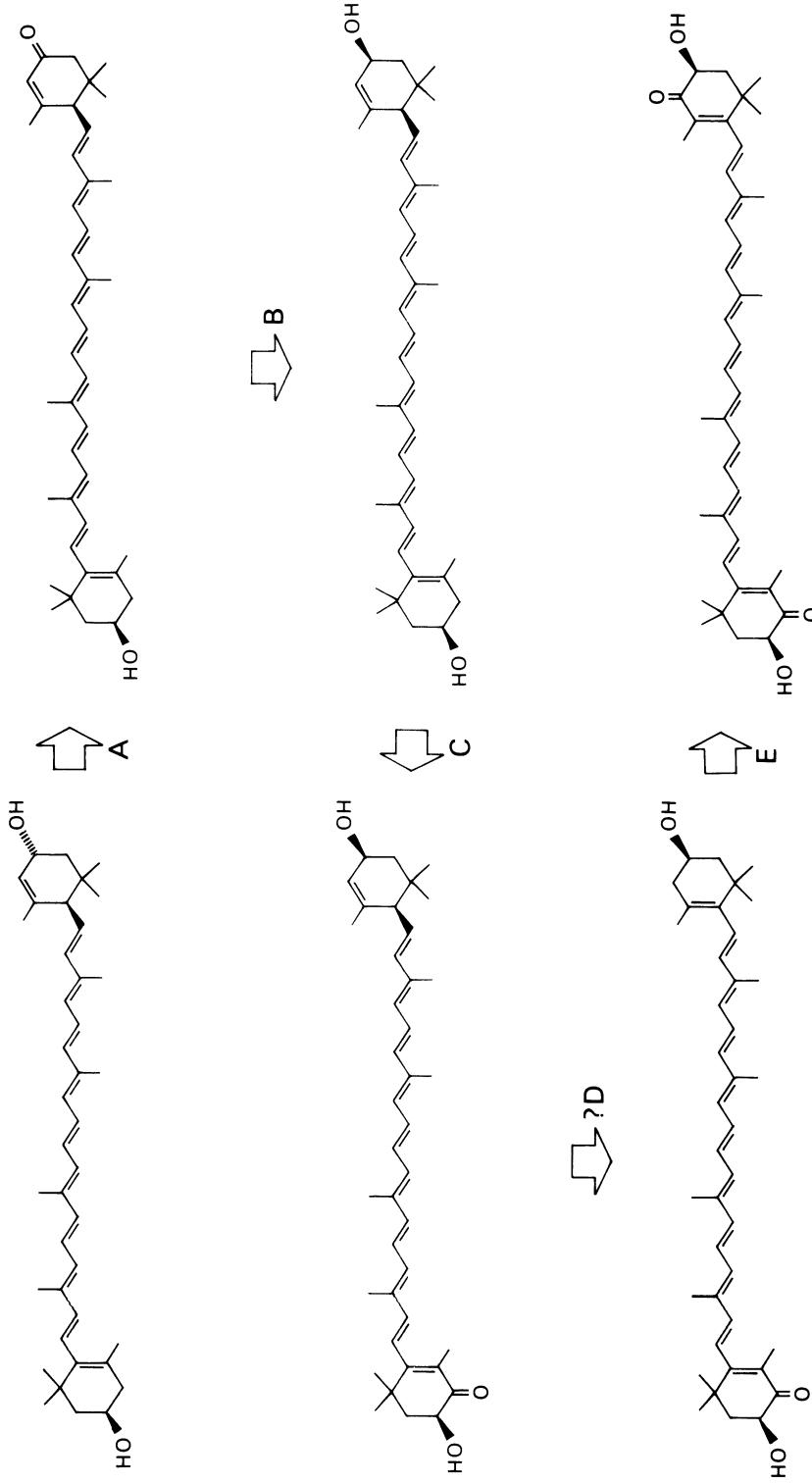
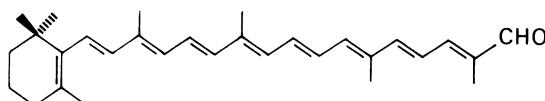


Fig. 8.2. Probable pathway of conversion of lutein into astaxanthin in goldfish [186].

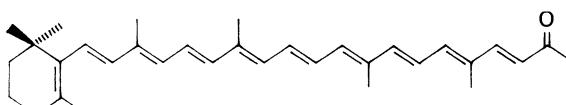
## 144 The biochemistry of the carotenoids

In the Salmonidae the situation is different from that in the carp family, the red coloration in trout and salmon being due to the intake of preformed keto carotenoids, canthaxanthin and astaxanthin in the food [50, 140]. Rainbow trout (*S. gairdneri/irideus*) cannot convert either lutein [171] or canthaxanthin into astaxanthin [141]. This inability to metabolize food carotenoids has led to numerous problems in the pisciculture industry. They have been overcome mainly by feeding the fish either crustacean residues or food containing synthetic carotenoids such as canthaxanthin [140, 142].

It seems that the appearance of astaxanthin in marine fish (e.g. sea bream) is also due to the absorption of this pigment from the diet; non-ketonic carotenoids, although absorbed, are not converted into astaxanthin [143, 144]. The ability of marine fish to absorb carotenoids is sometimes unexpectedly evident in nature. For example, abnormally coloured sea bass were caught in Tokyo Bay in 1979. This was traced to the fact that they were eating large amounts of the carotenoid-rich crab *Tritodynii horvathi* which, in that year, appeared in the Bay in great numbers. However, not all carotenoids are absorbed. Rainbow trout (*Salmo gairdneri/irideus*) do not accumulate either  $\beta$ -apo-8'-carotenal (8.26) [146] or citranaxanthin (8.27) [103] in their tissues. Similarly the medaka (*Oryzias latipes*) will not accumulate  $\beta$ -apo-8'-carotenal and stores  $\beta$ -carotene only to a very small extent [147].



(8.26)



(8.27)

Evidence has been published which suggests that tunaxanthin (6.16) is converted into astaxanthin in the Californian sheepshead *Pimelometopon pulchrum* [148].

### (b) Tunaxanthins

The widely distributed tunaxanthins (8.2, 8.9, 8.10) with two  $\epsilon$ -rings pose the question of whether fish can convert  $\beta$ -rings into  $\epsilon$ -rings because no precursor with two epsilon rings exists to any significant extent in phyto-

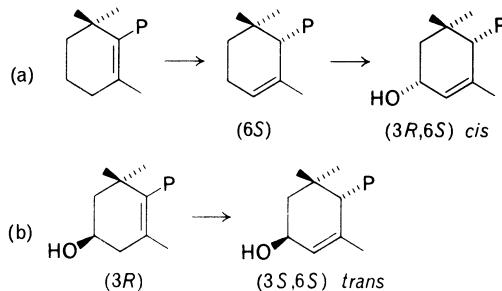


Fig. 8.3. Possible mechanism for formation of the tunaxanthins in fish (see text for details).

plankton, which is ultimately the source of all fish carotenoids. Furthermore the tunaxanthins all exhibit *S* chirality [10, 66] whereas, as far as is known, in all plant carotenoids with  $\epsilon$ -rings such as  $\alpha$ - and  $\epsilon$ -carotenes (2.25, 2.33) and lutein (1.10) the configuration at C-6 is *R*. The need to explain the chemically unexpected 3,6-*cis* substitutions in tunaxanthins A and C still exists. No experimental evidence has yet been presented for any proposed biosynthetic pathway to the tunaxanthins but two reasonable possibilities have been suggested. The isomerization of a  $\beta$ -ring to an  $\epsilon$ -ring with *S* configuration at C-6 in an unsubstituted pigment could be followed by *cis* hydroxylation at C-3 [(a), Fig. 8.3]. On the other hand a 3-hydroxy end group such as that found in zeaxanthin could be converted directly into the 3,6-*trans* compound by allylic rearrangement [(b), Fig. 8.3]. Thus it follows that  $\beta$ -carotene could give rise to tunaxanthin A,  $\beta$ -cryptoxanthin to tunaxanthin C and zeaxanthin to tunaxanthin B. There remains the added problem of explaining the formation of chiriquixanthin B (*6'R* chirality) in *Sebastes marinus* [66].

#### (c) *Parasiloxanthin*

It is reported that the Japanese catfish *Parasilurus asotus* can desaturate administered zeaxanthin at C-7,8 to yield both *parasiloxanthin* (8.16) and 7,8-dihydroparasiloxanthin (8.17) [149].

#### (d) *2-Hydroxy-beta-carotene*

The fish which are reported to contain this pigment (Table 8.2) (Section 8.2.1) are all insectivorous and it is assumed that this pigment, 2-hydroxy- $\beta$ -carotene, is taken in with their food [58] because it has previously been reported in insects (Chapter 6). It is also present in a few algae (see Volume I).

## 8.2.3 PIGMENT FUNCTION

## (a) Colour pattern

It is well established that many fish owe their bright yellow, orange and red colorations to the carotenoid pigments concentrated in the integumentary chromophores [see Section 8.2.1(a)]. It has already been indicated that this was elegantly demonstrated some thirty years ago when it was found that trout xanthophores accumulate lutein and the erythrophores accumulate astaxanthin [50]. A somewhat different type of differential distribution was noted in the fancy red carp (*Cyprinus carpio*). Administration of lutein to these fish results in the white areas of the skin becoming yellowish owing to the deposition of small amounts of esterified lutein. On the other hand considerable amounts of esterified lutein were stored in the areas which were originally red [150]. Larvae of the medaka (*Oryzias latipes*) which have developed from colourless eggs have no pigmented xanthophores, whereas those developing from coloured (carotenoid-containing) eggs produce normal xanthophores, thus demonstrating the transfer of pigments from yolk to embryo [151].

Variations in the carotenoid levels in the skin of *cobalt* and *albino* mutants of trout are noted in comparison with levels in native strains [144], and it has already been pointed out that the orange colour only appears in developing goldfish when the animals begin to synthesize astaxanthin. Similarly although the correlation between general body colour and the carotenoid content in some *Sebastes* spp. is not particularly marked, the percentage of keto carotenoids in the total amount of pigment present is very highly correlated with body colour (Table 8.9) [152].

In the Salmonidae the pigments are mobilized from the muscle and possibly the liver into the eggs during spawning (Table 8.6) [132, 153, 154] and, after fertilization of the eggs, they are gradually transferred to the

Table 8.9 Carotenoid distribution in *Sebastes* spp. caught off La Jolla, California [152]

Species	Overall colour	Carotenoid total concn. ( $\mu\text{g/g}$ of skin)	% of total pigments present		
			Astaxanthin	Tunaxanthin	Zeaxanthin
<i>S. atrovirens</i>	Olive	19	0	87.6	12.4
<i>S. flavidus</i>	Grey–brown	49	20.1	46.7	33.2
<i>S. carnatus</i>	Olive–brown	12	22.9	60.5	16.6
<i>S. umbrosus</i>	Light orange	47	28.6	38.2	33.2
<i>S. eos</i>	Pale pink	45	47.5	33.3	19.3
<i>S. constellatus</i>	Orange	20	55.3	24.5	20.2
<i>S. miniatus</i>	Vermilion	7.5	76.8	11.6	11.6

developing embryo [50, 155]. Similar changes have been reported in *Cyclopterus lumpus*, *Cyprinus carpio*, *Gasterosteus aculeatus* and *Eleginops navaga* [156].

The function of carotenoids in eggs is primarily to provide developing embryos with sufficient pigment to produce the colour pattern in the skin which is usually observed in nature. Young trout which are grown from eggs in which the carotenoids of the yolk were metabolically isolated from the embryo develop normally but with an aberrant colour pattern which makes them very conspicuous in their natural environment [50]. Any other functions in reproduction and development which have been assigned to carotenoids are only tenuously based and proposals made earlier [see 11 and 83] have not been substantiated [157]. Recently, however, an adaptive significance of carotenoids in the reproductive cycle of some fresh-water teleosts has been proposed [158] and the significance of carotenoids on natural selection based on colour patterns has been considered [159].

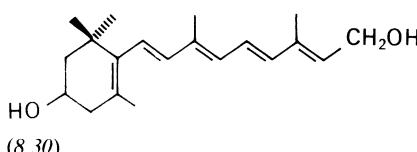
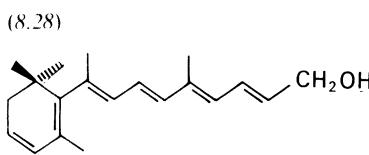
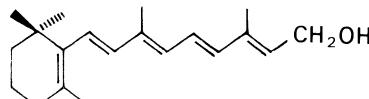
### (b) Vision

The existence of carotenoids in the retina of fish has not attracted much attention and was not considered of great significance [160]; however, their presence may increase visual acuity by reducing chromatic aberration and glare [161]. The corneas of some puffer fish, *Tetradon steindachneri*, *T. nigroviridis* and *Sphaeroides lunaris*, are colourless in the light and become yellow in the dark. This is due to the migration of carotenoids in the chromatophore cells which line the corneal margins. The increase in optical sensitivity by removing the pigment in the light has obvious advantages for fish living in clear waters [162].

### (c) As vitamin A precursors

There is no doubt from direct experimentation that  $\beta$ -carotene can be converted into the biologically active retinol (vitamin A) (8.28) and dehydroretinol (vitamin A<sub>2</sub>) (8.29) in fresh-water fish [163, 164] and into retinol in marine fish [165]. Furthermore  $\beta$ -carotene can substitute for vitamin A in preventing eye lesions in Salmonids fed cataractogenic (vitamin A-deficient) diets; oddly enough this effect is only observed when the fish are kept in warm (12.4°C) water; in colder water (9.0°C) no prevention is noted [166].

There still exists in older literature the unconfirmed claim that astaxanthin (1.1) and other xanthophylls are, contrary to experience with other animals (see Chapter 11), active as vitamin A precursors [167, 168]. If this claim were substantiated it would go a long way to explaining the accumulation of such large amounts of vitamin A in fish such as the cod and the halibut because the amount of vitamin A or its conventional precursors (e.g.  $\beta$ -carotene) in their



food is very limited [168]. Of some significance is the report that lutein, usually considered as inactive as a vitamin A precursor, is converted into dehydroretinol (8.29) as well as into 3-hydroxyretinol (8.30) in the freshwater fish *Saccabranchus fossilis* [164]; the latter compound would not normally be considered to be biologically inactive.

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# [9]

## AMPHIBIA AND REPTILES

### 9.1 AMPHIBIA

It is generally assumed that the yellow skin colours of amphibia are due to the deposition of carotenoids in these areas but investigations are not numerous and recent reports are few indeed.

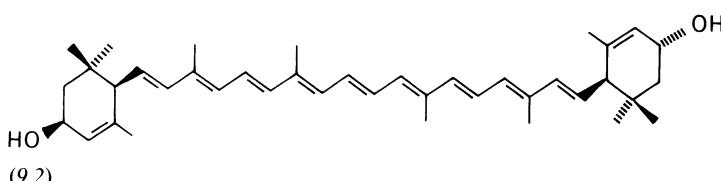
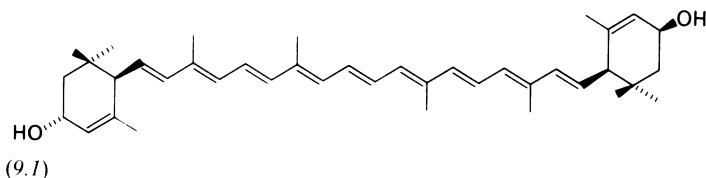
#### 9.1.1 DISTRIBUTION

Early studies [1–5] had demonstrated the presence of ‘lipochromes’ in the skin of the frogs *Hyla arborea*, *Rana esculenta* and *Rana temporaria*, and toads *Alytes obstetricans*, *Bufo viridis*, *B. calamuta* and *B. vulgaris*, and the salamanders *Triton cristatus* and *Salamandra maculosa*. Later carotene was reported in liver and ovaries of *R. temporaria* [6], and carotene and xanthophylls, both free and esters, were found in the skin of *R. temporaria*, *R. esculenta* and *H. arborea* [7, 8]. It remained for Rand [9] to show that frogs were a veritable storehouse of carotenoids which are found in skin, liver, kidney, lungs, ovaries, ova, oviduct, testes and fat bodies of both summer and winter frogs. This was later confirmed [10, 11, 12] and extended to include muscle, tongue, lungs, pancreas and eyes [12].  $\alpha$ -Carotene (2.25),  $\beta$ -carotene (1.5), lutein (1.10) and zeaxanthin (1.9) are the major pigments present [11] and the xanthophylls are present as mono- and di-esters as well as in the free form [13]. In the bullfrog (*R. catesbeiana*) eye, lutein is present in the retina [14] (possibly as a protein complex [15, 16]), in the pigment epithelium and in the choroid [14]; it is also found in the pigment epithelium of the edible frog *R. esculenta* [17].

Carotenoids have been reported in the medullated nerves of frogs [18] and in particular  $\beta$ -carotene, lutein and zeaxanthin are present in the brachial and sciatic nerves of *R. catesbeiana*. The maximum concentration is 60  $\mu\text{g/g}$  which is equally divided between carotene plus esterified xanthophylls and unesterified xanthophylls [16]. Carotenoids are present in the phagocytes in the intestinal wall of frogs [15]. Other Ranidae that contain numerous

carotenoids are *R. arvalis*, *R. lessonae* and *R. ridibunda* [19]. *Bufo bufo* also contains a similar mixture of pigments [19].

Recently the subject of carotenoids in frogs has been re-opened by the demonstration that three new xanthophylls exist in *Atelopus chiriquiensis* [20]. They are the chiriquixanthins A (9.1), B (8.19) and C (9.2). They are  $\epsilon$ -carotene derivatives and have the same chirality at C-6 as has lutein which is the opposite chirality to that exhibited by the tunaxanthins (Chapter 8). The chiriquixanthins differ one from the other in the chirality at C-3 and C-3'. The question of the source of these pigments for the animal is an important unsolved one. Furthermore these results should stimulate a re-appraisal of the pigments of other amphibia examined earlier and also new investigations into species not previously investigated.



Carotenoids in conjunction with a blue pigment or structure is said to contribute to the green colour of the tree frog (*Hyla coerulea*) [39].

*Proteus anguineus*, a blind and nearly colourless salamander which inhabits dark caves in Yugoslavia and North Italy, contains small amounts of  $\beta$ -carotene and unesterified xanthophylls located in the liver and body (excluding intestines) respectively [21].

Carotenoids are widely distributed in newts as, for example, in *Triturus cristatus*. *T. carnifex* and *T. vulgaris* [19, 22] (Salamandridae), *Bombyx mori* (Discoyliosidea) [8] and *Pelobates fuscus* (Pelobatidea) [19].

Some typical values for the quantitative distribution of carotenoids in two species of frog and one species of newt are given in Table 9.1. These should only be considered as an indication of levels because the season at which the samples were taken must have a considerable effect on the pattern of distribution obtained. However, it is clear that a considerable proportion of the carotenoids present are carotenes and that the major part of the xanthophyll fraction is esterified.

Table 9.1 Distribution of carotenoids in some amphibia

Organ	<i>Rana esculenta</i> [11]			<i>Rana temporaria</i> [13]			<i>Triton carolinifex</i> [22]		
	Total carotenoids ( $\mu\text{g/g}$ of tissue)	% of carotenes in mixture	% of xanthophylls esterified	Total carotenoids ( $\mu\text{g/g}$ of tissue)	% of carotenes in mixture	Total carotenoids ( $\mu\text{g/g}$ of tissue)	Total carotenoids ( $\mu\text{g/g}$ of tissue)	% of carotenes in mixture	
Liver	43.7	36.6 (30) <sup>a</sup>	70	12.35	18.8	93.5	—	63.1	
Skin	13.6	25.4 (78)	96	38.72	12.2	—	—	—	
Ovaries	26.9	27.5 (70.4)	66	—	—	13.7	46	—	
Fat Body	96.4	29.5 (95.4)	68	1.56	10.1	54.4	47.8	—	
Testes	—	—	—	1.01	45.1	9.9	38.4	—	
Spleen	—	—	—	—	—	2.5	44	—	
Muscle	—	—	—	8.47	10.2	—	—	—	

Note

<sup>a</sup>Values in parentheses taken from reference [10].

### 9.1.2 METABOLISM

Seasonal variations in carotenoid levels in *R. temporaria* are slight for most organs, viz. kidney, skin, muscle, tongue, lungs, pancreas and eye. Females differ from males in that during the spawning season they metabolize relatively large amounts of carotenoids into the eggs mainly from the fat body, which indicates the importance of this organ in ovarian nutrition. The levels of carotenoids in the fat bodies in both male and female frogs drop during hibernation which indicates that some metabolism or transport of carotenoids is taking place even in the hibernating animal. The carotene/xanthophyll ratio varies markedly during the development of frogs but the significance of this is not yet obvious. Contradictory reports exist on liver carotenoids during hibernation; one records no change [13] and the other a fall followed by a sharp rise during spring [15].

## 9.2 REPTILES

### 9.2.1 DISTRIBUTION

#### (a) Snakes

The early work of a century ago indicated that the pigments of many snakes were not typical lipochromes because they exhibited a strong green fluorescence [2]. Later reports confirmed the presence of xanthophylls in the blood of the rattlesnake *Crotalus terrificus* and the boipeva *Xenodon merremii*; however, no carotenoids are present in the blood of the Brazilian snakes *Bothrops jararaca* and *Eudryas bifossatus* [23].

#### (b) Lizards

A typical carotenoid (lipochrome) is present in a number of lizards, *Lacerta muralis*, *L. agilis*, *Chameleon vulgaris* and *Bombinator igneus* [2]. This pigment named lacertofulvin is considered to be similar but not identical with that found in frogs. The green colour in lizards is due to a yellow carotenoid in combination with a blue structural colour. Lacertofulvin was later found crystalline in the chromatocytes of, *inter alia*, *Lacerta vivipara* [24]. Lacertofulvin, which occurs together with lutein and  $\beta$ -carotene in the skin of *Lacerta sicula*, is considered to be identical with 'chlorophane' extracted from chicken retinas (see Chapter 10, Section 10.2.4) [25]. The chemical nature of this pigment is still obscure and the later investigations do not mention its presence. For example, a study of an African chameleon (probably *Lacerta viridis*) revealed that the skin contained predominantly xanthophyll esters (20  $\mu\text{g/g}$  fresh weight) of which the major component was lutein, with the levels of free xanthophylls and  $\beta$ -carotene being one-quarter and one-tenth of that value respectively [26]. In contrast, the pigments in the

## 158 The biochemistry of the carotenoids

eggs consist entirely of free xanthophylls accompanied by traces of  $\beta$ -carotene. The liver content is much higher than that of the eggs or skin (104  $\mu\text{g/g}$  fresh weight).

Furthermore a recent study on *L. agilis* and *L. vivipara* indicated the presence of  $\beta$ -carotene (1.5),  $\beta$ -carotene epoxide (8.18),  $\beta$ -cryptoxanthin (2.36), lutein (1.10) (in the former only), lutein epoxide (6.6), zeaxanthin (1.9) and astaxanthin (1.1); in the latter canthaxanthin (1.4) and diatoxanthin (4.2) were also reported [27].

The spiny-tailed iguana (*Ctenosaura hemilopha*) possesses a number of femoral pores in the ventral skin of each thigh. In the case of the male the pores produce a waxy exudate which contains a xanthophyll, possibly taraxanthin (lutein 5,6-epoxide) [28]. The lizards *Anguis fragilis* [27] and *Agama agama* [29] also contain carotenoids.

### (c) Turtles

Lipochromes were demonstrated in the serum and body fat of turtles in 1885 [30, 31] but it was not until 53 years later that a thorough investigation was carried out on the Japanese turtle *Chrysemys scripta elegans* [32]. The red spots on the skin near the eye probably contain  $\gamma$ -carotene, whereas the yellow dorsal carapace contains only  $\alpha$ -carotene, both  $\alpha$ -carotene and lutein are present in the intestine. A reinvestigation of this animal with modern methods and with more material than was originally available would be well worthwhile.

The retinas of *Clemmys insculpta* may contain astaxanthin [33] and the intensely coloured retinal oil droplets of the green turtle (*Chelonia mydas*), which were first examined microspectroscopically [34], have now been shown to contain  $\epsilon$ -carotene (2.33) of as yet undetermined chirality at C-6 and C-6' [35]. Carotenoids are found in the livers of the monitor *Varanus komodensis* [36] and the tortoise *Testudo graeca* [37].

### 9.2.2 FUNCTION

Carotenoids are present in the chromatophores of chameleons and lizards and therefore probably play an important part in the colour changes in these animals [2, 39]. In these changes melanin, guanine and an unidentified pigment also play a significant role [38]. In the case of *Agama agama* the change in colour of the male is due to mobilization of lutein into the chromatophores [30]. This response is clearly under endocrine control.

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## BIRDS

### 10.1 INTRODUCTION

A metabolic characteristic of many birds which has been appreciated for a number of years is that they specifically accumulate xanthophylls rather than carotenes in their feathers and their body tissues. A notable and important exception is the presence of a unique carotene in the oil droplets of the retina (see Section 10.2.4).

### 10.2 DISTRIBUTION

#### 10.2.1 FEATHERS

The known distribution of carotenoids in feathers is given in Table 10.1. It will be realized that a number of pigments are still not fully characterized;

*Table 10.1* Distribution of carotenoids in feathers of birds

<i>Species</i>	<i>Common name</i>	<i>Pigments</i>	<i>Reference</i>
<i>Ajaia ajaja</i>	Roseate spoonbill	1, 2	7
<i>Bombycilla cedrorum</i>	Cedar waxwing	1	2
<i>Cardinalis cardinalis</i>	Cardinal grosbeak	2	3
<i>Carduelis carduelis</i>	Goldfinch	3	4
<i>Carduelis spinus</i>	Siskin	3, 4	4
<i>Chloris chloris</i>	Greenfinch	3, 4	4
<i>Chloronorus yucatensis</i>		4, 5	4
<i>Colaptes auratus</i>		6	5
<i>Colaptes cafer</i>			
<i>Dryobates major</i>		5	4
<i>Emberiza citrinella</i>	Yellowhammer	4	4
<i>Emberiza icteria</i>		3, 4	4
<i>Euplectes franciscanus</i> (= <i>Pylomelana franscisana</i> )		3, 4, 6	4, 6
<i>Euplectes nigroventris</i>	African bishop birds	6	6
<i>Euplectes orix</i>		2	14

<i>Species</i>	<i>Common name</i>	<i>Pigments</i>	<i>Reference</i>
<i>Guara guara</i>	Scarlet ibis	1, 2	1
<i>Hypoxanthus rivolii</i>		5	4
<i>Laniarius atrococcineus</i>	Cross bill	3, 4	4
<i>Megaloprepia magnifica</i>	Flame footed fruit pigeon	7	3, 8
<i>Melanerpes erythrocephalus</i>	Woodpecker	6	6
<i>Melopsittacus undulatus</i>	Parakeet	Trace	7
<i>Motacilla cinerea</i>	Grey wagtail	4	4
<i>Oriolus auratus</i>	African oriole	4	5
<i>Oriolus oriolus</i>	Golden oriole	3, 4	4
<i>Oriolus xanthomus</i>		3	9
<i>Parus caeruleus</i>	Blue tit	3, 4	4
<i>Parus major</i>	Great tit	3, 4	4, 9
<i>Pharomacrus mocino</i>	Quetzal	2	3
<i>Phoenicircus nigricollis</i>	Jewel bird	1, 2, 8	1
<i>Phoenicoparrus andinus</i>	Andean flamingo	1, 2, 8	1
<i>Phoenicoparrus jamesi</i>	James' flamingo	1, 2, 8	1
<i>Phoeniconaias minor</i>	Lesser flamingo	7	8
<i>Phoenicopterus antiquorum</i>	Greater flamingo	1, 2, 8	1
<i>Phoenicopterus chilensis</i>	Chilean flamingo	1, 2, 8	1
<i>Phoenicopterus ruber</i>	American flamingo	1, 2, 8	1
<i>Phylloscopus sibilatrix</i>	Wood warbler	4	4
<i>Picus canis</i>	Woodpecker	5	4
<i>Picus viridis</i>	Green woodpecker	5	4
<i>Ploceus cucullatus</i>		4	4
<i>Poephila gouldiae</i>	Gouldian finch	2, 4, ? 9, ? 10	10
<i>Ptilinopus monachus</i>		7	3, 8
<i>Ptilinopus porphyreus</i>		7	3, 8
<i>Ptilinopus superbus</i>		7	3, 8
<i>Pyrrhula pyrrhula</i>	Bullfinch	3, 4	4
<i>Ramphocelus carbo</i>		1	14
<i>Ramphocelus costaricensis</i>		{ } 24 or 11	11
<i>Ramphocelus flammigerus</i>			
<i>Ramphocelus icteronotus</i>			
<i>Regulus regulus</i>	Gold crest	4	4
<i>Rhamphastos toco</i>	Toucan	4, 7, 11	12, 13
<i>Rupicola peruviana</i>	{ } Cock of the rock	2, ?12	3
<i>Rupicola rupicola</i>		4	3
<i>Serinus canaria canaria</i>	Canary	5	4
<i>Serinus canaria serinus</i>	Canary	4	4
<i>Spinus cucullatus</i>		2	8
<i>Xipholena</i>		4, 7, 11	14

*Key*

- |                       |        |                       |        |
|-----------------------|--------|-----------------------|--------|
| 1. Astaxanthin        | (1.1)  | 7. Rhodoxanthin       | (8.20) |
| 2. Canthaxanthin      | (1.4)  | 8. Adonirubim         | (1.8)  |
| 3. Canary xanthophyll |        | 9. Lutein 5,6-epoxide | (6.6)  |
| 4. Lutein             | (1.10) | 10. Violaxanthin      | (2.40) |
| 5. Picofulvin         |        | 11. Zeaxanthin        | (1.9)  |
| 6. Complex mixture    |        | 12. Phoeniconone      | (6.1)  |

these include canary xanthophyll and picrofulvin and the complex mixtures found in such birds as *Colaptes* and *Euplectes*. Picrofulvin was originally described in 1882 [13] so it has reached its centenary without having its structure elucidated. It is highly likely that some of the pigments described as 'lutein' may not have the expected chirality at C-3' (*R*) of the plant pigment. In other words 3'-epilutein (*S*) (6.22) may be widespread as has recently been demonstrated in fish (see Chapter 8). The 6*S'* enantiomers may also be waiting to be detected and furthermore the stereochemical purity or otherwise of avian astaxanthin (1.1) also needs to be assessed.

The contribution of carotenoids to the yellow, orange and pink feather colours of birds is considerable. Different feathers from the same bird can contain different pigments as for example the yellow ventral feathers of the finch *Poephila gouldiae* contain a lutein-like pigment whereas canthaxanthin (1.4) is present in the red face feathers [10]. Differences are sometimes observed in the same feather: the under surface of the plumes of *Chlororus yucatensis* accumulates picrofulvin whereas the upper surface accumulates lutein (1.10) [4]. Frequently the differences in hue between species is due to the presence of different amounts of the same pigment, as in the case of flamingos [12] and perhaps more impressively in *Ramphocelus flammigerus* and *R. icteronotus* [11]: the rump feathers of the former are scarlet and of the latter lemon-yellow although they both contain a lutein-like pigment. The quantitative aspect of colour difference is emphasized by the report that feathers of the orange-red *Rupicola rupicola* contain 20 µg of canthaxanthin per g of feathers whereas the concentration of the same pigment in the deep-red feathers of *R. peruviana* is 360 µg/g [3]. The green colours of feathers are often the result of the superposition of yellow carotenoids on a structure which gives rise to Tyndall scattering or surface diffraction [12]. Picrofulvin is prominent in this phenomenon. (See also [131].)

### 10.2.2 EGGS

It has been known for many years that the yolks of hens' eggs are yellow because of the presence of xanthophylls, mainly lutein (1.10) and zeaxanthin (1.9), in the ratio of about 4:1 when the hens are on a normal diet [15–17]; over 90% of the xanthophylls are esterified [18]. Little or no carotene is present [19–21] and hens, like other birds, are specific accumulators of xanthophylls [22].  $\beta$ -Cryptoxanthin (2.36) [23–25], capsanthin (2.19) [105, 25–27], neoxanthin (2.39), flavoxanthin (5.3), zeaxanthin, lutein [17, 121] and lutein 5,6-epoxide (isolutein) (6.6) [28] if present in the diet are all laid down in the eggs. On the other hand carotenes are not significantly absorbed [3, 23]. Small amounts of  $\beta$ -carotene are found in pheasants' eggs [9, 29], up to 119 µg/100 g, compared with up to 7074 µg of xanthophylls/100 g [30]. This general pattern is also observed in goose eggs [31, 32, 122].

Lutein has been specifically reported in eggs of ducks [33–35, 123], gulls [33–35] and canaries [4], astaxanthin in eggs of black-headed gulls (*Laridibus ridibundus*) [36] and storks (*Ciconia ciconia*), phoenicopterone (6.7) in scarlet ibis eggs [12] and canthaxanthin (1.4) in flamingo eggs [12]. The chirality of the lutein reported in eggs needs to be checked (see Section 10.2.1). Phillipine duck eggs contain  $\beta$ -carotene (1.5), canthaxanthin (1.4) and echinenone (1.11) in addition to lutein,  $\beta$ -cryptoxanthin and zeaxanthin. The high levels of the first two pigments give the dark colour of the yolk [124].

From a quantitative point of view yolks of chicken eggs contain more carotenoids than do those of duck and goose [125]. Furthermore levels in Russian white chicken eggs are higher than in Leghorns [126] which in turn are lower than in Rhode Island eggs [126].

### 10.2.3 SKIN

The yellow colour of the shanks and claws of the domestic hen has long been known to be ‘lutein’ [37] and this conclusion was later extended to geese and ducks [4]. On the other hand the pheasant *Phasianus colchicus* accumulates astaxanthin in its red facial papillae. Fox’s extensive work on flamingo and related species revealed the distribution of keto carotenoids in skins indicated in Table 10.2. The yellow-legged *Phoenicoparrus andinus* stores, in addition to keto carotenoids, considerable amounts of fucoxanthin (2.34), or possibly fucoxanthinol (4.4), which can represent up to 22% of the total pigment present in its tarsal skin. Fucoxanthin is also present to a lesser extent both relatively and absolutely in the skin of the related *P. jamesi* [12].

Table 10.2 Distribution of keto carotenoids in skin of flamingo and related species [1].

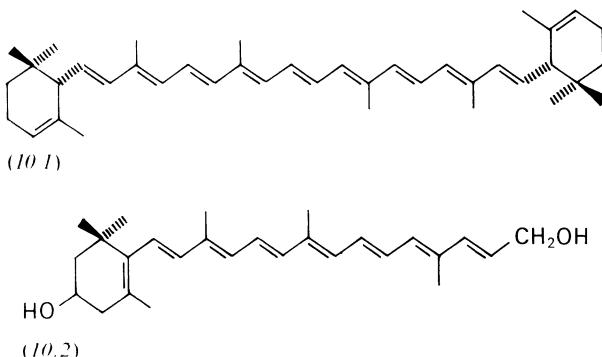
Species	Pigments
<i>Ajaia ajaja</i>	1
<i>Guara rubra</i>	2
<i>Phoeniconaias minor</i>	2, 3
<i>Phoenicoparrus andinus</i>	1, 2
<i>Phoenicoparrus jamesi</i>	1, 2, 3, 4
<i>Phoenicopterus ruber</i>	2, 3, 4

Key	
1	Canthaxanthin (1.4)
2	Astaxanthin (1.1)
3	Phoenicoxanthin (1.8) (adonirubin)
4	Echinone (1.11)

## 10.2.4 EYES

The presence of different coloured droplets in the retinas of the eyes of many diurnal birds has been frequently recorded since the middle of the last century [38, 39]. The existence of red, yellow and greenish droplets is well authenticated [40–42], but recently improved microspectrometric methods indicate that six types of droplet exist [43]. Early investigators reported carotenoids in the eyes of a number of birds without specifying the nature of the pigments [44, 45], but the first detailed work on chicken retinas yielded a carotene similar to sarcinene (see Volume I), astaxanthin (1.1), and a mixture of lutein (1.10), zeaxanthin (1.9) and a new greenish-yellow pigment named galloxanthin [46]. These observations were later confirmed [47–50] and extended to include pigeon [51] and turkey [52, 53] retinas. The carotene has now been clearly established as (6S,6'S)- $\epsilon,\epsilon$ -carotene (10.1) [53], an observation which raises important biosynthetic problems. Galloxanthin is probably 10'-apo- $\beta$ -carotene-3,10'-diol (10.2) [52]. Zeaxanthin and astaxanthin are also present in quail retinas [54, 55].



## 10.2.5 OTHER TISSUES

Carotenoids are present in the blood plasma of hens [56], ducks [57], flamingos [12], the scarlet ibis (*Guara rubra*) [58] and the roseate spoonbill (*Ajaia ajaja*) [59]. In the last two named species they are associated with a high-density lipoprotein (HDL) and can reach very high values, 5–7 mg/100 ml and 0.88–1.4 mg/100 ml respectively [60, 61]. The level in newly born ducklings is 1.23 mg/100 ml [56]. Genetic variability in carotenoid plasma levels has been reported in broilers [130]. No significant amounts of carotenoids are found in pheasants' blood [4] or in that of the Indian black-headed ibis (*Theskiornis melanocephala*) [61].

The crop milk, used for feeding young flamingos, is bright red and contains mainly canthaxanthin (1.4) with traces of  $\beta$ -carotene (1.5) and hydroxycarotenes [12].

The livers of *G. rubra* can accumulate very large amounts of carotenoids, up to 2.8 mg/g fresh weight [52], and values of the same order were reported in goose livers [62]. On the other hand pheasants apparently store no carotenoids in their liver [4].

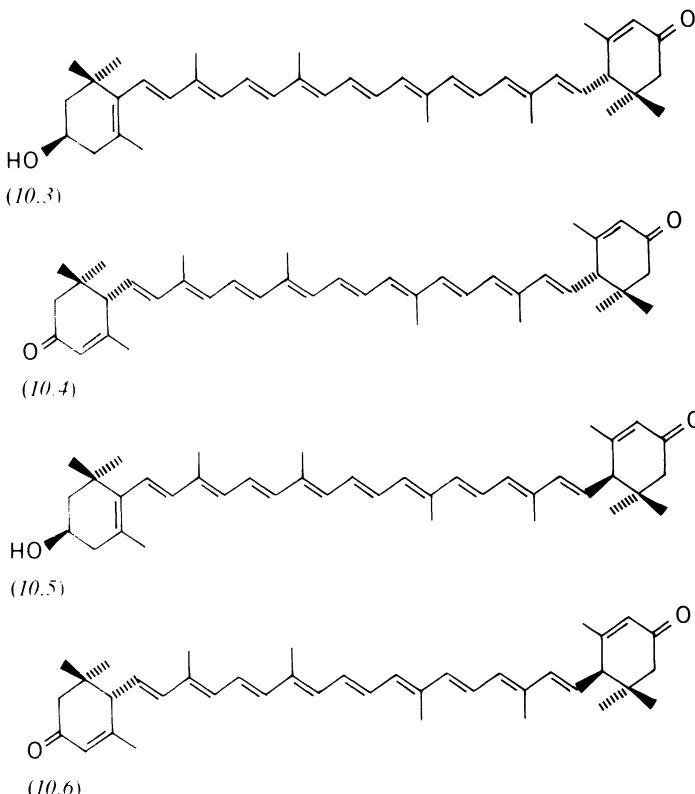
### 10.3 FORMATION

There is no reason to question the well-established view that carotenoids found in birds arise directly from or as a result of modification of food carotenoids. However, some of the recently revealed metabolic transformations appear to occur only in birds and, possibly, turtles (see Chapter 9).

As already indicated birds can be considered xanthophyll accumulators. For example domestic hens on a diet containing carotenes and xanthophylls in the ratio of 1:3 will accumulate a mixture in the ratio of 1:30 [63]. This is due mainly to the poor absorption of carotenes [22] but also to the fact that they are converted into vitamin A (see Chapter 11) [64–66]. Carotenoids are transferred to the yolk with varying degrees of efficiency [67] although in general apart from the carotenes, they are well absorbed [68, 69, 121, 127] and the amounts accumulated are a simple function of the level of intake [70]. The main sites of absorption of carotenoid are jejunum and ileum [71].

A considerable amount of effort has gone into finding which carotenoids in poultry feeds produce eggs with yolks which are most attractive to the customer. This cosmetic problem will not be dealt with here but one report summarizes the general view that  $\beta$ -carotene is ineffective, that lutein and zeaxanthin are highly effective with the latter providing a slightly more intense colour, and that canthaxanthin is effective but produces a less acceptable shade [72].

Recently it has been shown that zeaxanthin (1.9) can be converted into ( $3R,6'S$ )-3-hydroxy- $\beta\epsilon$ -carotene-3'-one (10.3) and ( $6S,6'S$ )- $\epsilon\epsilon$ -carotene-3,3'-dione (10.4), whereas lutein (1.10) is converted into ( $3R,6'R$ )-3-hydroxy- $\beta\epsilon$ -carotene-3'-one (10.5) and ( $6S,6'R$ )- $\epsilon\epsilon$ -carotene-3,3'-dione (10.6) [73]. Similarly avian  $\epsilon$ -carotene [( $6S,6'S$ )- $\epsilon\epsilon$ -carotene (10.1)], which has the opposite chirality to that found in higher plants and algae [74, 75], must be made in the animal from endogenous pigments because none is present in yolk carotenoids [53]. The enzymes concerned with the formation of ( $6S,6'S$ )- $\epsilon\epsilon$ -carotene must be formed (or derepressed) very early in the life of the embryo because the yellow droplets in the retina, where the pigment is found, appear soon after the 19th day of incubation [41]. Furthermore in quail the pigments disappear from the retina when the birds are placed on a carotenoid-free diet; they reappear on feeding  $\beta$ -carotene [54, 55]. It now seems clear therefore that a  $\beta$ -ring can be transformed into an  $\epsilon$ -ring in birds as well as in fish (see Chapter 8). Such a situation does not exist in plants (see Volume I). The mechanism involved in the intramolecular change is not known.



Astaxanthin in the retinas of hens and in the red papillae of pheasants must also be formed from dietary carotenoids. The most likely precursor in pheasants is zeaxanthin (1.9) which is the main pigment of maize on which game reserve birds are usually reared [3]. However, investigations into the chirality of avian astaxanthin are urgently required.

The question of whether flamingos which accumulate such large amounts of keto carotenoids do so exclusively from their food as preformed pigments or whether they transform non-ketonic food carotenoids, such as  $\beta$ -carotene or zeaxanthin, into keto derivatives is still to some extent open. The likely probability is that both processes are proceeding simultaneously to varying extents according to the nutritional situation the birds find themselves in. In the case of the African flamingo *Phoeniconaias minor*, the first situation probably predominates in the wild, for the mud in Kenya on which they feed contains essentially all the pigments present in the birds, *viz.*  $\beta$ -carotene, lutein, echinenone and canthaxanthin. In *Phoenicopterus ruber*, on the other hand,  $\beta$ -carotene can be converted into echinenone and canthaxanthin as demonstrated by the increase in blood levels of these pigments when  $\beta$ -carotene is fed to carotenoid-depleted birds. On the other hand, neither  $\gamma$ -carotene (2.26), lycopene (2.29) nor zeaxanthin (1.9) was assimilated.

lated. Astaxanthin was not taken in to any great extent but canthaxanthin (1.4) was absorbed and converted into phoenicoxanthin (adonirubin) (1.8) and astaxanthin;  $\alpha$ -carotene was absorbed and converted into phoenicocpterone (6.7) [1, 76, 77]. The probable metabolic transformations in flamingos is summarized in Fig. 10.1. The source of  $\epsilon$ -carotene in *Phoenicoparrus andinus* liver is still not yet clear.

Only xanthophylls are precursors of the feather pigments of canaries. White birds are produced on a carotenoid-free diet and only xanthophylls added to the diet will restore the colour [4].

#### 10.4 METABOLISM

In hens esterified xanthophylls are normally laid down from food in the skin and shanks whence they can be rapidly mobilized into the blood by oestrogens and these are probably the trigger for transfer of the pigments to eggs when hens come into lay [78, 79]. Transfer of pigments to feathers is also under hormonal control, for example the post-nuptial plumage of bishop birds can be converted into nuptial display plumage by treatment with pregnant mare's serum: this involves rapid mobilization of stored carotenoids into the feathers [6, 80].

The presence of zinc in the diet improves the absorption of food carotenoids [81] and results in higher levels in eggs [82]. However, on the other hand zinc deficiency is said to have no effect on carotene levels in poultry [81] and its presence appears to lower the levels in duckling livers [83]. Selenium, on the other hand, has little effect on liver or serum levels but would appear to improve the conversion of  $\beta$ -carotene into vitamin A [84]. Vitamin E and certain other anti-oxidants also improve yolk pigmentation [85, 86] as does vitamin B<sub>12</sub> [87]. Feeding of glutamate, lysine or nitrate reduces carotenoid levels in broilers [88, 89], although arsenicals, such as roxarsone, added to increase growth has no effect on absorption [90].

It seems that in hens a number of infections reduce the carotenoid blood levels, which are normally a good measure of body pigmentation [91]. An example is infection with *Eimeria* spp. [92, 93]. Similar effects are noted with coccidiosis infection and chronic respiratory disease [92–105]. It is therefore not surprising to find that the administration of the antibiotic streptoxanthin increases carotenoid absorption as indicated by increased skin coloration [106]. Aflatoxin reduces blood levels and causes the appearance of pale carcasses [107, 129] as does ochratoxin A [108, 128]. Terramycin inhibits the conversion of carotenes into vitamin A [129].

Temperature appears to be one important environmental factor controlling egg yolk colour; on a standard diet a particularly hot summer will result in a drop in pigmentation [109, 110].

### 10.5 FUNCTION

There is no doubt that carotenoids function in birds in two ways. In the first, those carotenoids which have the appropriate structure are converted into vitamin A (see Chapter 11) and in the second place, xanthophylls, either as obtained in the food or after metabolic modification are used to contribute to the natural colour pattern of birds' plumage (see Section 10.2.1). In this latter way they play an important part in the sexual dimorphism so frequently noted in birds. This is particularly marked in bishop birds (see Section 10.4).

No particular metabolic requirement for carotenoids *per se* has ever been unequivocally demonstrated for birds. The absence of such a requirement was clearly shown by the classic experiments of Palmer and Kempster [111] as long ago as 1919 in which they managed to rear normal chicks on a xanthophyll-free diet. These birds laid fertile eggs with almost colourless yolks from which carotenoid-free healthy chicks were hatched. This fundamental observation has frequently been confirmed [see e.g. 112–114].

However, claims for functions which seem not to have been pursued include:

- (i) lutein is converted into a growth factor similar to vitamin A [115];
- (ii) absence of lutein reduces the sperm competitiveness of cocks [116];
- (iii) xanthophylls increase hatchability in hens, ducks and turkeys [117];
- (iv) carotenoids stimulate the absorption of copper [118].

### 10.6 COLORATION OF POULTRY FOODS

The importance of xanthophylls in the biochemical economy of hens is minimal as indicated in the previous section but their importance in the acceptability of poultry products to the public is of considerable interest to the food industry. Consumers in most parts of the world demand deeply coloured yolks of the appropriate hue [119]. Similarly broilers with highly coloured skins and shanks are generally considered to indicate good quality [120], although in some areas of the world pure white broilers are demanded. The interesting phenomenon of food selection by colour, which has no nutritional significance, has led to the industrial development of appropriately coloured carotenoids for addition to poultry rations and the technology of this has been considered in detail elsewhere [119, 131].

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## 172 The biochemistry of the carotenoids

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## [ II ]

# MAMMALS

### 11.1 INTRODUCTION

All the available evidence points to the conclusion that mammalian carotenoids are of dietary origin. There is no confirmed report of any mammal manufacturing a specific carotenoid either *de novo* or by oxidative metabolism of any ingested carotenoid. The latter failure separates mammals sharply from most other animals which exhibit a marked ability to produce oxidized pigments. However, mammals do have the ability to convert carotenoids with appropriate structures into vitamin A (see Section 11.4). Apart from this common metabolic feature mammals can be separated into two main groups according to whether or not they accumulate carotenoids in their body tissues. Those which do accumulate carotenes and xanthophylls indiscriminately and those which accumulate mainly carotenes.

### 11.2 CAROTENOID ACCUMULATORS

#### 11.2.1 INDISCRIMINATE ACCUMULATORS

##### (a) *Distribution*

The only mammal which accumulates both carotenes and xanthophylls and which has been studied in detail is the human. The presence of *lipochromes* in blood and milk was first observed in 1869 [1] but the first detailed investigation was that of Palmer and Eckles in 1914 [2] who reported the presence of both carotene and xanthophylls in blood plasma (but not in red cells) and milk. In blood they are attached to a protein [3–7] mainly (75–88%) to the low-density lipoprotein [8] although small amounts are present in the very-low-density lipoprotein and the high-density lipoprotein [9, 10]. The classic observations of Palmer and Eckles have been confirmed many times and the view that blood carotenoid levels closely reflect the nature and amount of pigments in the diet is now accepted without dissent

[11–13]. This view also probably applies to the milk [14–21], body fat [14, 22, 23], adrenals [4, 24, 25], seminal vesicles [26], placenta [22, 27], heart muscle [28], liver [27, 29], pancreas [30], nerve tissue [31], bone marrow [32], spleen [33] and skin [34]. In skin the epidermis contains more than the dermis [34, 423] and in the adrenals the concentration is higher than in other tissues [24, 35]. Two tissues diverge qualitatively from the general pattern: the corpus luteum accumulates mainly  $\beta$ -carotene [3, 33, 36] whereas in the macular region of the retina the main pigment is lutein [37]. No carotenoids have been observed in sweat [33], spermatozoa [33, 407] or cerebrospinal fluid [33].

The only other mammals which appear to be indiscriminate carotenoid accumulators are the fox (*Canis vulpes*) [38] (but see Table 11.2), fitchet (*Mustela putorius*) [38], field mouse (*Apodemus flavicollis*) [39] and bank vole (*Clethrionomys glareolus*) [39] although there are indications that the badger (*Meles taxus*) and roedeer (*Capreolus capreolus*) fall into the same category [38].

Some typical quantitative values for humans are: blood plasma 10–420  $\mu\text{g}/100 \text{ ml}$  [40]; colostrum 25–250  $\mu\text{g}/100 \text{ ml}$  [20, 21, 41–43]; milk 15–150  $\mu\text{g}/100 \text{ ml}$  [20, 21]; liver 0.7–6.0  $\mu\text{g}/100 \text{ ml}$  [44, 45]; spleen 2  $\mu\text{g}/100 \text{ g}$  [33]; adrenals 4.2–15.6  $\mu\text{g}/100 \text{ g}$  [33]; fat 7.5  $\mu\text{g}/100 \text{ g}$  [33]; corpus luteum 4 mg/100 g [33]. The variation in blood plasma levels according to the carotenoid content of the diet has been reported from many parts of the world, e.g. Poland [46], Canada [47], Czechoslovakia [48], USA [49], UK [13, 21, 50], Batavia [51], Bataan [52], Germany [53], USSR [54] and the Phillipines [17]. Similar variations are noted in human milk [55, 56].

### (b) Metabolism

It has already been emphasized that carotenoid blood levels merely mirror the intake of the pigments and this is underlined by the observation that during the later stages of pregnancy and at parturition the carotenoid levels do not vary markedly although blood vitamin A levels drop [57, 58]. However, a foetal barrier seems to exist, for the foetal blood level is very much lower than that of the mother [59–68] and the level cannot be raised by massive doses of  $\beta$ -carotene [68]. Characteristic corresponding plasma values are foetal blood 16  $\mu\text{g}/100 \text{ ml}$  and maternal blood 127  $\mu\text{g}/100 \text{ ml}$  [68]. The high levels of carotenoids in colostra [20, 21, 41–43, 56, 64, 69–73] ensures that the baby's plasma carotenoids soon rise to normal values. Indeed the transfer of carotenoids from breast milk to infants is so efficient that there are reports of sucklings developing carotenaemia [74, 75].

Carotenoids accumulate in the fat depots of the body through life which accounts for the fact that adult fat is yellow and infant fat almost white [76].

The effect of steroid contraceptives on carotenoid plasma levels is not yet

clear; the combined oral oestrogen–progestogen is said to have no effect in one investigation [431] and to lower the levels in another [432]. Some lowering with depot progestogens were reported in both cases.

### (c) *Pathological conditions*

Although it is clear that excess or lack of carotenoids has no pathological effects provided that sufficient vitamin A is available in the diet, changes in the accumulation pattern can be observed in certain pathological conditions. The changes can generally be clearly separated from any variations occurring in the dietary intake although this is a variable which is often difficult to control. In a number of fevers for example, plasma levels fall rapidly and equally rapidly recover when the fever subsides [61, 77] whilst in others the changes are much less obvious [78]. It is particularly marked in children suffering from pneumonia [78, 79].

Carotenaemia (accompanied by carotenoid deposition in the skin leading to a pseudoicterus) (see [80] for early references) is almost always due to excessive intake of carotenoids and is without ill effect. It disappears on removing carotenoids from the diet [75]. The excess carotenoids are distributed amongst the lipoproteins in a very similar pattern to that observed in normal blood [10]. A claim that carotenaemia is accompanied by a carotenuraemia [81] has not been substantiated [82]. There is one reported case of carotenaemia in an adult apparently caused by a failure to convert  $\beta$ -carotene into vitamin A. The amount of carotene which escaped transformation into vitamin A and appeared in the blood was so great that the usual carotene/xanthophyll ratio of (about 1:3) was reversed [83]. A child which responded to vitamin A but not  $\beta$ -carotene had raised blood plasma levels [84].

Carotenaemia has long been associated with hypothyroidism [85–93] and myxoedema [94–96]. This is due to impaired conversion (see below).

The early observations that many diabetics accumulate carotenoids in the skin (xanthosis diabetica) [97–104] led to the conclusion that the conversion of carotene into vitamin A was impaired in this disease [105]. More recent wide-ranging surveys, however, revealed a normal distribution of plasma levels [106–110]. The earlier high levels reported were almost certain the result of a high carotenoid intake in diabetes designed to avoid excessive amounts of carbohydrate.

Carotenoids accumulate in the subcutaneous tissue and stratum corneum of the epidermis in uraemic patients [111]. Blood levels are low in sprue [112, 113] and jaundice [88, 114], a situation to be expected when lipid absorption is reduced. Low blood values have been reported in cystic fibrosis [115], liver cirrhosis [116], tuberculosis [117, 118] and hyper-vitaminosis D [119].

(d) *Absorption*

In humans as in all mammals examined carotenoids are much less well absorbed from the diet than is vitamin A [13, 120–126]. The general view is that between 25 and 75% of the intake is excreted in the faeces [11] and that qualitatively the faecal carotenoids are very similar to those found in the food [13, 120], although one report suggests a preferential excretion of carotenes [126]. Nutritional factors which affect carotenoid absorption in humans are summarized in Table 11.1.

*Table 11.1* Dietary factors controlling absorption of carotenoids in humans (adapted from [80])

<i>Absorption increased</i>	<i>References</i>	<i>Absorption reduced</i>	<i>References</i>
Administration in oil	11, 38	In indigestible vegetables	13, 127, 128
Readily digested fat in diet	122	Absence of fat in diet	40, 127
Presence of anti-oxidants particularly tocopherols in moderate amounts	129	Pro-oxidants (methyl inolenate)	80
Lecithin	130	Excessive amounts of anti-oxidants	80
Adequate protein	72	Raw soya bean (lipoxidase)	80
Absence of mineral oils	40	Inadequate protein	74
		Presence of mineral oils	40

The low plasma levels in jaundice and hypothyroidism already referred to are due to a reduced efficiency of absorption. The need for the presence of bile for absorption has been demonstrated experimentally in rats in both isolated intestinal loops and choledochocolostomized animals [131, 132].

### 11.2.2 CAROTENE ACCUMULATORS

(a) *Distribution*

*Cattle.* Once again it was the pioneering work of Palmer & Eckles [2] which clearly demonstrated that domestic cattle accumulate in their tissues mainly  $\beta$ -carotene from their feed [133, 134], although traces (5–8%) of xanthophylls are always present [134–143]. Plasma levels reflect the  $\beta$ -carotene content of the feed under many varied nutritional and environmental conditions as reported in the USA [133, 140, 142, 143], UK [139, 144], New Zealand [145], USSR [146–156], Latvia [157–159, 412], Italy [160–162], India [163–165], Czechoslovakia [166–169], Greece [170], Hungary [171] and Yugoslavia [172].

The seasonal variations observed in the plasma are clearly reflected in the carotenoid content of the milk [139, 169, 171, 173–179, 406, 408, 424]. In the

Northern Hemisphere the levels are at their lowest in late winter and rise rapidly during the spring; a slight drop during high summer is followed by a further rise in the autumn. The extent of the rise is a reflection of the rainfall in August [176]. Similar seasonal variations have been reported in New Zealand [180] and Australia [181].

On average the concentration of carotenoids in cow's milk is only about one-half that in human milk [182]. However,  $\beta$ -carotene represents about 85% of the total pigment in cow's milk whereas the corresponding value for human milk is about 25%; the vitamin A potential of both types of milk is very similar.

There are marked variations in the carotenoid content of milk from different breeds of cattle. Jersey and Guernsey cows produce milk having up to twice the concentration of carotenoids in other breeds [41, 133, 140, 163, 176, 183–193]. The concentration in bull's plasma is generally very much less than in cow's [135, 142].

The carotenoid content of colostrum is some five to ten times that in mature milk [138, 141, 169, 179, 194–197], which stabilizes some 1–4 weeks after parturition [144, 179–181, 198–201].

The seasonal and breed variations noted in milk carry over into butter [139, 146, 180, 188, 202–207] and cheese [208]. Some 85% of milk carotenoids are transferred to cheese and they persist through ripening [209, 210].

The following cattle tissues also accumulate carotenoids, almost exclusively  $\beta$ -carotene; body fat [211–213], ovaries [214–216], testes [16, 217], adrenals [212, 216, 218–220], corpus luteum [215, 221–225], corpus rubrum [226], thymus [219], liver [218, 227, 228] which does not exhibit seasonal variations [424], pigment epithelium and iris [227, 229], pituitary [216, 230, 231], bile [40, 232], muscle [233], kidney [212, 218, 219], placenta [2, 60, 234], thyroid [216] and skin [3]. There is one report of carotenoids in the red blood cells [235] but the spleen does not accumulate more than traces [4, 227]. The yellow patches of olfactory tissue in the upper region of the nasal cavity contain carotenoids [228, 236] as does ear wax [15].

The concentration of  $\beta$ -carotene in the *corpus luteum* and *corpus rubrum* can reach 6 and 120  $\mu\text{g}/100 \text{ g}$  of tissue respectively. Ovaries contain five times as much carotene as do the testes [139] which reflects the differences noticed in cow's and bull's blood [138, 142].

There is a marked accumulation of carotenoids in various tissues on ageing of cattle [161] and other animals [434].

*Other mammals.* Horses accumulate mainly  $\beta$ -carotene in their serum [4, 237], body fat [238], adrenals [4] and liver [4] in relatively large amounts. The plasma levels show the same seasonal variation as that just noted for cattle [239]. The corporea lutea of asses contain  $\beta$ -carotene [36]. Small but significant amounts of  $\beta$ -carotene were found in the wapiti (*Cervus canadensis*) (54–120  $\mu\text{g}/100 \text{ ml}$ ) [240] and hedgehog [241]. In the latter the blood levels drop during hibernation.

## 178 The biochemistry of the carotenoids

### (b) Metabolism

A drop in blood carotene levels at parturition is well established in cows [141, 146, 242–251]. The significance of this is not clear because other components of blood also vary under these conditions [141]. The blood levels return to normal within about 3 weeks post-partum [246, 251]. The view that the decline at parturition coincides with a rapidly filling udder [246] cannot be a major controlling factor because the same pattern was noted when a mammectomized cow gave birth to a premature calf [252]. The normal drop does not occur in cows with milk fever [247]; the levels can indeed increase during the fever, but fall back to normal when the condition subsides [253].

The blood carotene levels in newly born calves are very low [167, 168, 254, 255], a typical value being 22 µg/100 ml [254], but they rise very rapidly with the intake of carotene-rich colostrum [168, 169]. Breed differences become obvious within 8 days of birth [256]. It is claimed that plasma carotene levels in calves increase on feeding the amino acid methionine [257].

The reason for the selective accumulation of carotenes by cattle and horses is still not clear. About 70–80% of the ingested carotenes and 60% of the xanthophylls are excreted in horse faeces [258], but even after a large intake of carotenoids no xanthophylls appear in the portal or jugular blood [259, 260]. This means that the xanthophylls which are not excreted are destroyed either in the intestinal tract or as they cross the intestinal wall, or both.

Soya bean and soya bean extracts [261, 262] and excess vitamin A [263–265] probably reduce the absorption of  $\beta$ -carotene in cows. Liquid paraffin, in particular, even at a level of 0.08% in the feed (that is just enough to prevent dustiness in lucerne leaf meal or salt licks) has a marked deleterious effect on carotene absorption [266]. Even under normal conditions about 85% of the ingested  $\beta$ -carotene is excreted in the faeces [404] so any factors which reduce absorption can be critical. Destruction of carotenoids in the intestinal tract has not been examined in great detail but lipoxygenase activity (which destroys carotenoids, see Volume I) has been demonstrated in clear stomach extracts; less activity is noted in intestinal extracts [267].

### (c) Function

The only clear-cut biological function for carotenoids in mammals is as vitamin A precursors and this is considered in a separate section (11.4). However, there is some evidence that the  $\beta$ -carotene levels fall after injections of cloprostenol, to synchronize oestrous, followed by fertilization [268–270], and that low  $\beta$ -carotene intake produces irregularities in the ovarian cycle [410]. This has stimulated research on the possible role of  $\beta$ -carotene in reproduction in dairy cows. Positive claims [411, 417, 418] have been

seriously challenged [419–421, 425, 426] and a detailed review has recently been published [427].

The increase in carotenoid levels in the tissues of ground squirrels and voles living in the high mountain regions of the USSR compared with those of animals living at lower altitudes is considered to indicate a role of carotenoids in the intracellular oxygen supply to nervous tissues [309]. A possible role in nervous transmissions is indicated by the fact that electric stimulation of cerebral cortex slices yields a luminescence spectrum ( $\lambda_{\text{max}}$  560–570 nm) said to be due to carotenoids [428]. Furthermore excitation of nerves leads to changes in the Raman spectrum of the constituent carotenoids [429].

### 11.3 NON-ACCUMULATORS

#### 11.3.1 DISTRIBUTION

In this section we shall deal with species which normally accumulate little or no carotenoid in their tissues although in some cases the pigments appear under pathological conditions. The main species which have been examined and which have emerged as non-accumulators are listed in Table 11.2. To expand a little on the tabulated information it should be noted that one case of carotenaemia has been reported in a dog [277] and that the same condition occurs in sheep parasitized with Trichostrongylidae [323]. A strain of rabbit (*Lepas cuniculus*) is known in which xanthophylls but not carotene accumulate in the subcutaneous fat [324, 325]. The condition is recessive to the normal dominant white in which no carotenoids accumulate in the tissue (Table 11.2) [324].  $\beta$ -Carotene is said to be present in pig's retinas [188].

No carotenoids were ever encountered in a wide ranging investigation on whale liver oils [320] and they are also absent from the flesh and milk [319] and ovaries [321]. Astaxanthin (1.1) was only very occasionally encountered in other investigations on body oils and liver oils [316, 317] and the existence of red oils, which contain astaxanthin, is taken as an indication of some unknown pathological condition [317]. It is clear that the major food carotenoid of the toothed whales, astaxanthin, is excreted in the faeces [318].

#### 11.3.2 METABOLISM

Apart from the conversion of  $\beta$ -carotene into vitamin A in the rat (Section 11.4) very little work has been carried out on the general metabolism of carotenoids in non-accumulators. It is known that, as with the other groups, absorption from the food in the rat [326–332] and sheep [308] is low. Normally it amounts to about 50% [332] and 5–13% [308] respectively. In rats even under optimal conditions and at extremely low doses (1–2  $\mu\text{g}$  of

Table 11.2 Mammals which accumulate little or no carotenoid pigments in their tissues

<i>Species</i>	<i>Comments</i>	<i>References</i>
Buffalo	Milk levels 0–1/10th of cattle	271–274
Camel*	None	164, 275
Caribou	Flesh levels – about 1/10th of cattle levels	233, 276
Cat	Traces	4
Dog	Traces or none	277–280
Elephant	Traces in fat	40, 281
Fox	Generally very low plasma levels	282
Goat	Traces in fat	217, 237, 283–287
Guinea pig	Traces in milk (11 µg/100 ml)	288–290
Hare	Absent	291
Mule deer	Blood levels (0–4.25 µg/ml)	292
( <i>Odocoileus hemionus</i> <i>nemorinus</i> )		
Pig	Absent	203, 237, 293–301
Rabbit	Present in a mutant (see text)	286–301
Rat		302–306
Reindeer	Some seasonal variation noted	307
Sheep	Blood levels 0–18 µg/100 ml	3, 169, 237, 308–315, 306, 312–316
Whale	Accumulates in pathological conditions	316–321
White tailed deer ( <i>Odocoileus virginianus</i> )	Absent	322

\*Arabian camels are reported to have blood plasma carotene levels of around 100 µg/100 ml [409].

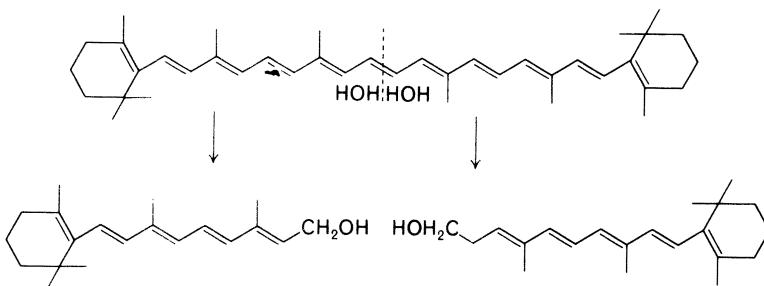
$\beta$ -carotene per day) at least 10–15% of the dose is excreted [330, 331]. The  $\beta$ -carotene which does get absorbed must be efficiently converted into vitamin A because no pigment appears in the circulating blood plasma. The absorption of  $\beta$ -carotene is controlled by the thyroid as already indicated for humans in Section 11.2.1(d). This is also evident for rats [333], goats [334] and sheep [335]. The utilization of  $\beta$ -carotene by rats drops considerably with age; for example only 16% of the vitamin A formed in young rats from a standard dose of  $\beta$ -carotene is found in old rats [405].

## 11.4 CONVERSION OF CAROTENOIDS INTO VITAMIN A

### 11.4.1 STRUCTURAL REQUIREMENTS

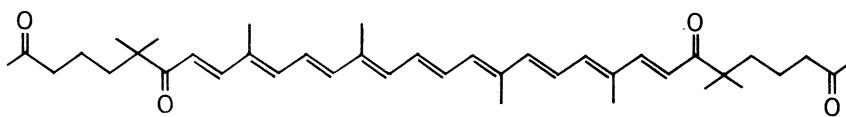
Early investigations which led to the conclusion that  $\beta$ -carotene (1.5) was a precursor of vitamin A (retinol) (8.28) have been fully summarized else-

where [80, 336] and we can begin with the first unequivocal demonstration of this in 1929 by Moore [337–339]. Confirmation was soon forthcoming in chickens [340]. The elucidation of the chemical structures of the various major plant carotenoids in the 1930s by Karrer and Kuhn and their colleagues allowed detailed structure/function studies to be made and it soon became clear that in mammals and chickens, at least, the structural requirements for a carotenoid to exhibit vitamin A activity were restricted. In fact one-half of the carotenoid structure must already contain the basic 15-carbon structure of retinol [40, 341]. This is emphasized in Fig. 11.1,

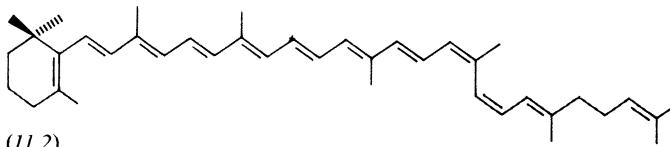


*Fig. 11.1.* Simplified scheme for conversion of one molecule of  $\beta$ -carotene into two molecules of vitamin A (retinol).

which outlines the conversion of one molecule of  $\beta$ -carotene into two molecules of vitamin A. The two essentials are therefore an unsubstituted  $\beta$ -ring and a side chain of conjugated double bonds at least as long as that in retinol. For example  $\alpha$ -carotene (2.25) [342–344],  $\beta$ -cryptoxanthin (2.36) [345, 346] and  $\beta$ -apocaroten-8'-al (8.26) [345, 346] are all active whereas zeaxanthin (1.9), lutein (1.10) and  $\beta$ -carotenone (11.1) are all inactive [347]. However, desaturation at C-3, as in vitamin A<sub>2</sub> (8.29) does not destroy activity. This vitamin is characteristic of fresh-water fish [341].



(11.1)



(11.2)

Furthermore saturation of a double bond in the side chain or removal of a methyl group, for example that at C-13, eliminated activity entirely [341]. It is probably true that  $\beta$ -carotene, which is the only carotenoid which can

## 182 The biochemistry of the carotenoids

theoretically give rise to two molecules of vitamin A, is nutritionally twice as valuable as any other active carotenoid, but the problems of inefficient absorption and the possibility of non-specific degradation of the molecule still lead to difficulties from the point of view of assessing activity from a practical nutritional angle [see 80].

The usual form of carotenoids in nature is the *all-trans* form (see Volume I) but some *cis*-isomers do exist and, with one exception, the *cis*-pigments which are vitamin A-active are less active than the corresponding *all-trans* isomers [348, 349]. The exception is pro- $\gamma$ -carotene (11.2) which has a potency equal to that of *all-trans*- $\gamma$ -carotene [350]. When this work was reported the exact structure of pro- $\gamma$ -carotene was not known; it differs from the *all-trans* pigment in containing hindered *cis*-double bonds. The structure supports the view that only *trans* pigments are active as vitamin A precursors because one half of the molecule has all the structural requirements of a vitamin A precursor. However isomerization of pro- $\gamma$ -carotene [351] and neo- $\beta$ -carotene U [352] can occur in the intestinal tract. For further details of nutrition requirements of animals for carotenes see [435].

### 11.4.2 SITE OF CONVERSION

The fact that, after feeding  $\beta$ -carotene to mammals, vitamin A accumulated in the liver led to the reasonable conclusion that the conversion of the pigment into the vitamin occurred in that organ. Evidence for and against this view frequently appeared in the literature of the late 1930s and early 1940s [see 30, 40 for reviews]. However, with one or two results to the contrary [340, 353], it became accepted that intravenous or intramuscular injection of  $\beta$ -carotene did not give rise to the accumulation of vitamin A in the livers of rats, dogs and chickens [354–361]. Finally a thorough investigation by Deuel's group [362] demonstrated without doubt the ineffectiveness of parenterally administered carotene; indeed in their experimental animals vitamin A deficiency symptoms were obvious although substantial amounts of  $\beta$ -carotene had reached the liver and were stored there. This strongly suggested that the carotene was being converted as it crossed the intestinal wall, a possibility which had been mooted earlier [319, 363]. Proof of this based on two approaches followed rapidly. In the first, vitamin A was detected in the intestinal wall soon after dosing with  $\beta$ -carotene in rats [364–367], pigs [368] and chicks [369, 370]. In the second approach animals were fitted with thoracic cannulae and the appearance of vitamin A in the thoracic lymph was demonstrated after feeding  $\beta$ -carotene to goats [286], rats [369, 371], sheep [368] and cattle [372, 373]. Conversion also occurs in isolated intestinal loops and slices [374–376] and in germ-free rats [377]. In everted gut sacs in the rat, bile salts are necessary for the conversion [376].

### 11.4.3 ENZYMOLOGY OF CONVERSION

The first indication that the splitting of  $\beta$ -carotene involved vitamin A aldehyde (retinal) (11.3) as an intermediate was the demonstration that the intestinal mucosa could convert retinal into retinol [378, 379]. The enzyme which catalyses the splitting of  $\beta$ -carotene with the formation of retinal is  $\beta$ -carotene 15,15'-oxygenase; it is assumed (Fig. 11.2) that a transient 15,15'-peroxide is formed which is rapidly cleaved to two molecules of retinal. The enzyme has been extensively examined from many mammalian species including the rat [380, 381], rabbit [382–385], pig [382, 386] and guinea pig [382, 385]. It is also present in the intestines of fish, tortoise, chicken and monkey [382]. Traces of the enzyme are also probably present in liver and kidney [385] and possibly in blood plasma [416]. However, it is absent from cat intestinal walls [381] which adds support to the claim that  $\beta$ -carotene cannot cure vitamin A deficiency in this animal [386]. A similar situation may exist in mink [387]. A possible relationship of this deficiency with the fact that these animals are omnivores has been suggested. One case is reported of a child who did not respond to  $\beta$ -carotene but did to vitamin A;

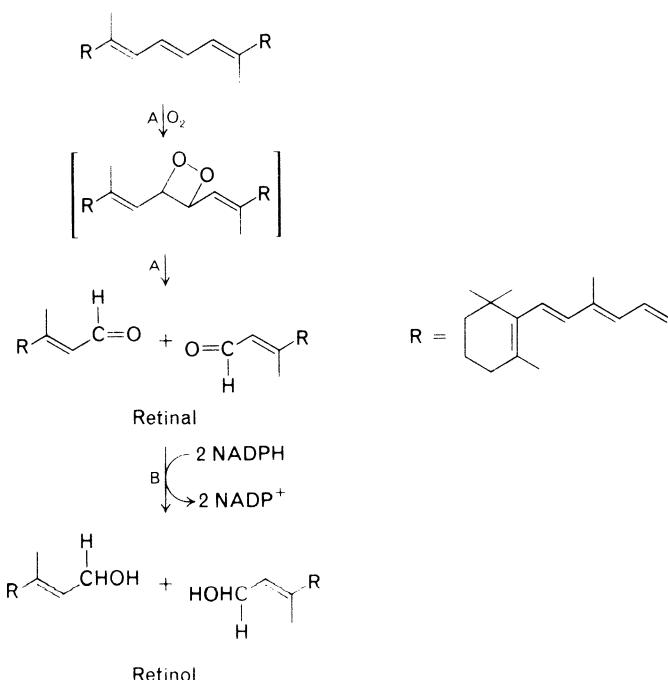
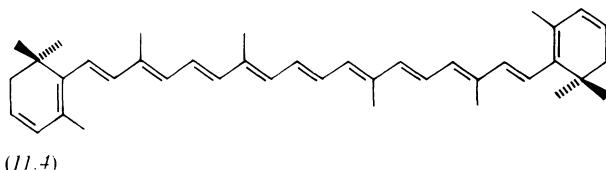
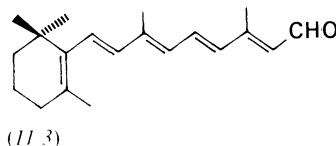


Fig. 11.2. Mechanism for the conversion of  $\beta$ -carotene into vitamin A (retinol) via vitamin A aldehyde (retinal). A,  $\beta$ -carotene 15,15'-oxygenase; B, retinal reductase.

## 184 The biochemistry of the carotenoids

it was assumed that the most likely explanation was the absence of  $\beta$ -carotene 15,15'-oxygenase [84].

The rabbit enzyme will also convert 3,4,3',4'-tetradehydro- $\beta$ -carotene (11.4) into vitamin A<sub>2</sub> (8.28) [383].



The retinal so produced by the  $\beta$ -carotene 15,15'-oxygenase is, as indicated earlier, converted into vitamin A; the enzyme, which can utilize either NADH or NADPH [388], is not a classical dehydrogenase because it will not reduce acetaldehyde to ethanol [389]. The retinol is esterified as it passes across the intestinal wall and the esters are transferred via the lymph to the plasma which transports them to the liver attached to a specific protein, retinol-binding protein [see 390 for review].

### 11.4.4 FACTORS CONTROLLING CONVERSION

The metabolic state of the thyroid has long been known to control the conversion of  $\beta$ -carotene into vitamin A [391–393]. The major action appears to be on the absorption of the pigment rather than on the enzyme system itself. Feeding of thyroxine or related compounds stimulates absorption whereas the thyroid inhibitor thiouracil reduces absorption [333, 394].

There is little doubt that dietary protein intake affects the carotene  $\rightarrow$  vitamin A conversion [395–403] and that the effect is directly on the production of the oxygenase [404]. An optimal dietary protein concentration is about 10% [400]. The nutritional implications of these observations, particularly for the third world, are starkly clear.

Anabolic androgens appear to increase the conversion of  $\beta$ -carotene into vitamin A in the rat [403] as does the increase in dietary zinc in cattle [413], goats [414] and rats [415]. The lowered carotene plasma levels in bulls after zinc feeding might be related to improved conversion into vitamin A [433].

Rabbits with the recessive *bu* gene resulting in hereditary buphthalmus, do not have impaired conversion of  $\beta$ -carotene into vitamin A [430].

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# GENERAL INDEX

- Acephala (*see* Pelecypoda)  
Actinioerythrin  
formation, 38, 39  
in fish integument, 134–139  
in sea anemones, 37  
Adonirubin (3-hydroxy-4,4'-diketo- $\beta$ -carotene, phoenicoxanthin)  
formation, 84–86, 100, 167  
in Anomura, 75  
in Arachnida, 98  
in birds' skins, 163  
in Brachyura, 76  
in Branchiopoda, 65  
in carotenoprotein complexes, 4–6, 15, 16  
in Cirripedia, 68  
in Copepoda, 67  
in Decapoda, 74–76  
in fish integument, 124–129, 140  
in Homoptera, 105  
in Insecta, 105  
in Macrourea, 74  
in Mysidacea, 68, 72  
Adonixanthin (*see*  $\beta$ -Doradexanthin)  
Agelaxanthin A  
in sponges, 24, 28, 29  
structure, 25  
Agelaxanthin B, 26  
in sponges, 24, 28, 29  
structure, 25  
Agelaxanthin C, 26, 27  
in sponges, 24, 28, 29  
structure, 25  
Alcyonarians, 37  
Alfoncino, 124  
Allobetaxanthin, 30  
in sponges, 28, 29  
structure, 32  
Alloporin, 18, 36  
Alloxanthin (cynthiaxanthin, pectenoxanthin)  
in Anomura, 75  
in brittle stars, 44, 45  
in carotenoproteins, 4–6  
in Decapoda, 75  
in fish integument, 124–129  
in fresh water gastropods, 58  
in Mollusca, 52, 54, 55  
in sponges, 28, 29  
in tunicates, 122–123  
metabolism, 141  
structure, 8  
Amphibia, 154–157  
Anchovy, 125  
Angler fish, 135, 137  
Annelida, 48, 49, 50  
Antheraxanthin  
in Cephalopoda, 61  
in fish integument, 124–129  
structure, 61  
Anthozoa, 37–39  
Aphanin (*see* Echininone)  
10'-Apo- $\beta$ -carotene-3,10'-diol (*see* Galloxanthin)  
 $\beta$ -Apo-8'-carotenal  
conversion into retinol, 181  
structure, 144  
Astacene, 52  
structure, 22  
Astaxanthin, 1, 2, 10, 86, 87, 144, 147, 148  
formation from canthaxanthin, 39, 84–85  
formation from  $\beta$ -carotene, 50, 100, 111–115, 141–144  
formation in birds, 166, 167  
in alcyonarians, 37  
in Amphipoda, 68, 71, 90  
in Anomura, 75  
in Arachnida, 98–100  
in birds, 160, 161, 163, 164  
in birds' eggs, 163  
in birds' skin, 163  
in Brachyura, 76, 79, 80  
in Branchiopoda, 64, 65  
in Bryozoa, 48  
in Caridea, 73

## 198 The biochemistry of the carotenoids

- Astaxanthin. *cont.*
- in carotenoprotein complexes, 4–6, 13, 16, 18, 78
  - in Cephalopoda, 60, 61
  - in Cirripedia, 67, 68
  - in Coleoptera, 107
  - in Copepoda, 66, 67
  - in Crinoidea, 46
  - in Decapoda, 73–76, 79, 82
  - in Diptera, 109
  - in Echinoidea, 46, 47
  - in Euphausiacea, 68, 72
  - in feathers, 160, 161
  - in fish eggs, 136
  - in fish integument, 124–129, 132, 134, 139, 140, 146
  - in fish intestines, 139, 140
  - in fish muscle, 135, 140
  - in fish ovaries, 136
  - in Holothuria, 46
  - in Homoptera, 105
  - in hydra, 35, 36
  - in Insecta, 101, 105, 107, 109, 110
  - in Isopoda, 67, 69
  - in leeches, 48
  - in Lepidoptera, 110
  - in lizards, 158
  - in Macrourea, 74
  - in Malacostraca, 67–69, 71–76
  - in mammals, 179
  - in Mollusca, 52, 54, 55
  - in Mysidacea, 68, 72
  - in Orthoptera, 101
  - in Ostracoda, 66
  - in Polychaeta, 48, 49
  - in reptiles, 158
  - in Scyphozoa, 36
  - in sea anemones, 37
  - in sea slugs, 56, 57
  - in sea stars, 42–44
  - in sponges, 28, 29
  - in Stomatopoda, 76
  - in tunicates, 123
  - in turtles, 158
- (3*R*,3'*R*)-Astaxanthin
- in fish integument, 124–129, 132
  - in fish muscle, 135
  - in lobsters, 64
  - in ovorubin, 17
  - structure, 11
- (3*R*,3'*S*)-Astaxanthin
- in fish integument, 124–129, 132
  - in fish muscle, 135
  - in lobsters, 64
  - in ovorubin, 17
  - structure, 11
- (3*S*,3'*S*)-Astaxanthin, 8
- in carotenoproteins, 15, 17
  - in fish integument, 124–129, 132
- in fish muscle, 135
  - in lobsters, 64
  - structure, 11
- Asteriarubin, 14–15
- Asterinic acid (*see* Didehydro- and tetra-dehydroastaxanthin)
- Asteroidene (? 3-hydroxy-4'-oxo- $\beta$ -carotene), in sea stars, 42, 44
- Aurochrome
- in fish integument, 124–129
  - structure, 130
- Auroxanthin
- in fish integument, 124–129
  - structure, 131
- Bass, sea, 126, 144
- Bastaxanthin C, 30
- in sponges, 26, 28, 29
  - structure, 27
- Beluga, 136
- Big eye, 127
- Biliverdin, 117
- Bishop birds, African, 160, 162
- (3*S*,3'*S*)-2,2'-Bisnorastaxanthin, 37
- structure, 38
- Bivalvia (*see* Pelecypoda)
- Blue gill, 126
- Bream, sea, 124
- Bryzoa, 48, 50
- Buffalo, 180
- Bullfinch, 161
- Bullfrog, 154
- Bullhead, 127
- Calthaxanthin (*see* 3'-Epilutein)
- Camel, 180
- Canary, 161, 162
- Canaryxanthophyll
- in birds, 160–162
  - in feathers, 160–162
- Canthaxanthin, 30, 50, 144
- conversion into astaxanthin, 39, 85, 86, 141, 142
  - formation, 83–86
  - in Amphipoda, 68, 71
  - in Anomura, 75
  - in Arachnida, 98
  - in birds, 160–164, 166, 167
  - in birds' eggs, 163
  - in birds' skin, 163
  - in Branchiopoda, 64, 65
  - in Brachyura, 76, 79
  - in brittle stars, 45
  - in carotenoprotein complexes, 4–6, 15, 16, 17, 78
  - in colour variants in Crustacea, 87, 88
  - in Coleoptera, 107
  - in Copepoda, 66, 67

- Canthaxanthin, cont.**
- in Crinoidea, 46
  - in Decapoda, 74–76, 79, 80, 82
  - in Diptera, 109
  - in feathers, 160–162
  - in fish integuments, 124–129
  - in fish livers, 137, 138, 140
  - in fish muscle, 135
  - in fish ovaries, 136
  - in Holothuria, 46
  - in Homoptera, 105
  - in hydra, 35, 36
  - in Hymenoptera, 111
  - in Insecta, 105, 107, 109–111
  - In Isopoda, 69
  - in Lepidoptera, 110
  - in lizards, 158
  - in Macrourea, 74
  - in Malacostraca, 68, 69, 71, 74–76
  - in Ostracoda, 66
  - in Polychaeta, 49
  - in reptiles, 158
  - in sea stars, 42, 44
  - in Scyphozoa, 36
  - in sponges, 28, 29
  - in terrestrial gastropods, 59
  - structure, 8
- Capsanthin, 24**
- in birds' eggs, 162
  - in Cephalopoda, 60
  - in terrestrial gastropods, 59
  - in tunicates, 123
  - structure, 26
- Capsorubin, 24**
- in Cephalopoda, 60
  - in tunicates, 123
  - structure, 26
- Carcinoxanthin, 82**
- Carotenaemia, 174, 175, 179**
- $\alpha$ -Carotene, 145**
- conversion into retinol, 181
  - in amphibia, 154
  - in Anomura, 75
  - in Arachnida, 98, 99
  - in Brachyura, 79
  - in Cephalopoda, 60, 61
  - in Coleoptera, 107
  - in Copepoda, 67
  - in Decapoda, 75, 79
  - in Diptera, 109
  - in Euphausiacea, 72
  - in fish integument, 126–129
  - in fish livers, 137, 138
  - in fresh water gastropods, 58
  - in fresh water molluscs, 55
  - in Insecta, 102, 107, 109
  - in Isopoda, 69
  - in limpets, 56, 57
  - in Malacostraca, 69, 72, 75
  - in marine gastropods, 56, 57
  - in Phasmida, 102
  - in Polychaeta, 48, 49
  - in reptiles, 158
  - in sea anemones, 34
  - in sponges, 28, 29
  - in terrestrial gastropods, 59
  - in tunicates, 122
  - in turtles, 158
  - structure, 30
- $\beta$ -Carotene**
- conversion into astaxanthin, 50, 84–85
  - conversion into canthaxanthin, 83–85, 166
  - conversion into tunaxanthin A, 145
  - conversion into vitamin A (retinol), 147–148, 167, 175
  - factors controlling conversion into retinol, 184
  - in amphibia, 154, 155
  - in Amphineura, 60
  - in Amphipoda, 71, 90
  - in Anomura, 75
  - in Arachnida, 97–100
  - in birds, 166
  - in Brachyura, 76, 79
  - in Caridea, 73
  - in carotenoprotein complexes, 4–6, 78
  - in cattle tissues, 176, 177
  - in Cephalopoda, 60, 61
  - in Cirripedia, 68, 90, 71–76
  - in Coleoptera, 107
  - in Copepoda, 67
  - in Crinoidea, 46
  - in Decapoda, 73–76, 79, 80, 82
  - in Diptera, 109
  - in Echinoidea, 46, 48
  - in Euphausiacea, 68, 72
  - in fish eggs, 134, 136
  - in fish livers, 137, 138
  - in fish muscle, 135
  - in fish ovaries, 136
  - in fresh water gastropods, 58
  - in Hemiptera, 104
  - in human tissues, 174, 175
  - in Insecta, 101, 102, 104, 107, 109–112, 117
  - in Isopoda, 69
  - in Lepidoptera, 110, 111
  - in limpets, 56, 57
  - in lizards, 157, 158
  - in Macrourea, 74
  - in Malacostraca, 68, 69
  - in mammals, 174–178
  - in marine gastropods, 56, 57
  - in Mollusca, 54, 55
  - in Mysidacea, 72
  - in nudibranchs, 57, 58
  - in Orthoptera, 101
  - in Ostracoda, 66
  - in Phasmida, 102

## 200 The biochemistry of the carotenoids

- $\beta$ -Carotene, *cont.*  
in Platyhelminthes, 48  
in Polychaeta, 48, 49  
in reptiles, 154  
in sea anemones, 37  
in sea stars, 42, 44  
in sponges, 28, 29  
in terrestrial gastropods, 59  
in tunicates, 123  
metabolism in cattle, 179, 180  
structure, 8
- $\beta$ -Carotene 5,6-epoxide  
in fish integument, 124–129  
in lizards, 158  
in reptiles, 158  
structure, 131
- $\beta$ -Carotene 15,15'-oxygenase, 183, 184
- $\beta\gamma$ -Carotene  
in Coleoptera, 107  
in Hemiptera, 104, 105  
in Insecta, 104, 105, 107  
structure, 104
- $\gamma$ -Carotene, 166  
in Amphipoda, 71  
in Anomura, 75  
in Branchiopoda, 65  
in Cephalopoda, 60, 61  
in Coleoptera, 107  
in Copepoda, 67  
in Decapoda, 74–76  
in fish eggs, 136  
in fish integument, 124–129  
in fish ovaries, 136  
in fresh water gastropods, 58  
in Hemiptera, 104, 105  
in Macrourea, 74  
in Malacostraca, 71, 75, 76  
in marine gastropods, 57  
in sea stars, 43  
in sponges, 28, 29  
in turtles, 158
- $\gamma\gamma$ -Carotene  
in Coleoptera, 107  
in Hemiptera, 104, 105  
in Insecta, 104, 105, 107  
structure, 105
- $\gamma\psi$ -Carotene  
in Coleoptera, 107  
in Insecta, 107  
structure, 108
- $\delta$ -Carotene  
in Brachyura, 76  
in Decapoda, 74, 76  
in Homoptera, 105  
in Insecta, 105  
in Macrourea, 74  
structure, 75
- $\epsilon$ -Carotene, 30, 145  
in bird liver, 167
- in Decapoda, 74  
in fish integument, 129  
in Macrourea, 74  
in reptiles, 158  
in sponges, 28, 29  
in terrestrial gastropods, 59  
in turtles, 158  
structure, 31
- (6S,6'S)- $\epsilon,\epsilon$ -Carotene, 165  
in birds' eyes, 164  
structure, 164
- (6S,6'R)- $\epsilon,\epsilon$ -Carotene-3,3'-dione  
formation, 165  
structure, 166
- (6S,6'S)- $\epsilon,\epsilon$ -Carotene-3,3'-dione  
formation, 165  
structure, 166
- $\zeta$ -Carotene  
in Coleoptera, 107  
in Insecta, 107  
structure, 108
- Carotenoid–protein complexes, 1–18
- Carotenoids  
absorption in birds, 167  
absorption in humans, 176  
absorption in mammals, 176, 180  
conversion into vitamin A, 180–185  
formation in Arachnida, 100  
formation in birds, 165–167  
formation in Crustacea, 83–85  
formation in Echinodermata, 47–48  
formation in fish, 141–145  
formation in Mollusca, 53  
formation in Polychaeta, 48, 49  
function in Arachnida, 100  
function in birds, 168  
function in Crustacea, 90  
function in Echinodermata, 47–48  
function in fish, 146–148  
function in Insecta, 118  
function in mammals, 178, 179  
function in mollusca, 61  
in birds' eggs, 162, 163  
in birds' eyes, 164  
in birds' skin, 163  
in coloration of fish, 139, 146, 147  
in coloration of insects, 116–119  
in colour patterns in birds, 167  
in colour variants in Crustacea, 87–88  
in digestive tract of Crustacea, 82  
in feathers, 160–162  
in fish eggs, 134, 136, 139  
in fish eyes, 138  
in fish gonads, 136, 139  
in fish integument, 124–129, 131–134  
in fish intestine, 139  
in fish mouth mucus, 139  
in fish muscle, 134, 135, 139  
in fish sperm, 134, 136

- Carotenoids, *cont.*
- in gonads of Crustacea, 82, 83
  - in haemolymph of Crustacea, 81
  - in hepatopancreas of Crustacea, 81
  - in integument of Crustacea, 80, 81, 87
  - in moulting in Crustacea, 80, 81
  - in sexual cycle in Crustacea, 86
  - in sexual dimorphism in birds, 167
  - in sexual dimorphism in Crustacea, 87
  - localization in cattle, 176, 177
  - localization in crustacean tissues, 77–83
  - localization in fish integument, 134
  - localization in humans, 173
  - localization in mammals, 173, 174, 176, 177, 179
  - metabolism in amphibia, 157
  - metabolism in birds, 167–168
  - metabolism in cattle, 178
  - metabolism in Crustacea, 83–86, 89
  - metabolism in Echinodermata, 47, 48
  - metabolism in humans, 176
  - metabolism in mammals, 174, 175, 178, 179
  - metabolism in Mollusca, 53
  - quantitative distribution in amphibia, 156
  - quantitative distribution in Crustacea, 77–80, 88, 89
  - quantitative distribution in mammals, 174, 176, 177
- Carotenolipo(glyco)proteins, 4
- $\beta$ -Carotenone, structure, 181
- Carotenoproteins, 10–18, 77
- distribution in crustacean tissues, 78
  - in Amphipoda, 68
  - in Arachnida, 97
  - in Cirripedia, 67
  - in coloration of insects, 116–118
  - in colour variants in Crustacea, 87
  - in coral, 18, 35, 36
  - in fresh water gastropods, 58, 59
  - in Insecta, 101, 116, 117
  - in lobsters, 12–14
  - in Malacostraca, 68
  - in Mollusca, 53
  - in moulting in Crustacea, 81
  - in pigment transport in Crustacea, 86
  - in pigment transport in mammals, 177
  - in *Pomacea* spp., 16, 17
  - in *Rhynchosciara americana*, 17, 18
  - in *Salpa cylindrica*, 17
  - in sea slugs, 56
  - in sponges, 27
  - in star fish, 14–16, 43, 44
  - in *Veabella*, 16, 36
- Carp, 124, 144
- crucian, 124
  - fancy red, 125, 136, 141, 146
  - grass, 135, 137
  - silver, 135
  - silver crucian, 124
- Cat, 180, 183
- Catfish, Japanese, 127, 145
- Cattle, 176–179
- Celaxanthin
- in Amphipoda, 71
  - in Decapoda, 74
  - in Macrourea, 74
  - in Malacostraca, 71
  - structure, 70
- Chameleon, 157, 158
- Char
- Japanese, 128
  - piscivorus, 126
- (3*R*,6*R*,3'*R*,6'*R*)-Chiriquixanthin (chiriquixanthin C)
- in amphibia, 155
  - structure, 155
- (3*R*,6*R*,3'*S*,6'*R*)-Chiriquixanthin (chiriquixanthin A)
- in amphibia, 155
  - structure, 155
- (3*S*,6*R*,3'*S*,6'*R*)-Chiriquixanthin (chiriquixanthin B), 145
- in amphibia, 155
  - in fish integument, 124–129, 133
  - structure, 132
- Chlorophane, 157
- Chrysanthemaxanthin
- in Homoptera, 105
  - in Insecta, 105
  - in terrestrial gastropods, 59
  - structure, 59
- Chub, herbivorous, 126
- Cichlid
- Flamingo, 124
  - Formosan snake-head, 124
- Citranaxanthin, structure, 144
- Clathriaxanthin
- in sponges, 24
  - structure, 24
- Cod, 135–137, 147
- rock, 128
- Cock of the rock, 161
- Coelentrates, 35–39
- Crinoids, 46
- Crocoxanthin, 30
- in sponges, 28, 29
  - structure, 31
- Crossbill, 161
- Crucian
- golden, 124
  - round, 124
- Crustacea, 64–90
- $\alpha$ -Crustacyanin, 11, 82
- absorption spectrum of, 10
  - structure, 12, 13
- $\beta$ -Crustacyanin, 12
- Crustaxanthin
- in Branchiopoda, 65

## 202 The biochemistry of the carotenoids

- Crustaxanthin, *cont.*  
    in Copepoda, 67  
    in Decapoda, 74  
    in Insecta, 110  
    in Isopoda, 69  
    in Lepidoptera, 110  
    in Macrourea, 74  
    in Malacostraca, 69  
    structure, 66
- $\alpha$ -Cryptoxanthin  
    in Arachnida, 98  
    in Cephalopoda, 60  
    in fish integument, 124–129  
    in fish livers, 137–138  
    in Homoptera, 105  
    in Insecta, 101, 105  
    in Isopoda, 69  
    in Malacostraca, 69  
    in Orthoptera, 101  
    in sea stars, 42  
    in terrestrial gastropods, 59  
    structure, 43
- $\alpha,\alpha$ -Cryptoxanthin (*see* 3-Hydroxy- $\alpha$ -carotene)
- $\beta$ -Cryptoxanthin, 30, 47  
    conversion into retinol, 181  
    conversion into tunaxanthin C, 145  
    in Amphipoda, 71  
    in Arachnida, 98  
    in Cephalopoda, 61  
    in Diptera, 109  
    in fish eggs, 136  
    in fish integument, 124–129  
    in fish muscle, 135  
    in fish ovaries, 136  
    in Insecta, 101, 109, 111  
    in Lepidoptera, 111  
    in limpets, 56, 57  
    in lizards, 158  
    in Malacostraca, 71  
    in marine gastropods, 56, 57  
    in Orthoptera, 101  
    in reptiles, 158  
    in sea stars, 42, 44  
    in sponges, 28, 29
- Cynthianthrin (*see* Alloxanthin)
- Dab, 26
- 3-O-Dehydrolutein (*see* Philosamiaxanthin)
- Dehydroretinol (vitamin A<sub>2</sub>), 147, 181, 184  
    structure, 148
- Diadinoxanthin  
    in Branchiopoda, 65  
    in Decapoda, 74  
    in fish integument, 124–129  
    in Macrourea, 74
- Diatoxanthin, 27, 53  
    in Anomura, 75  
    in Decapoda, 75
- in fish integument, 124–129  
    in lizards, 158  
    in Mollusca, 54, 55  
    in reptiles, 158  
    in sea stars, 142  
    structure, 43
- 7,8-Didehydroastaxanthin  
    formation, 141  
    in Alcyonaria, 37  
    in brittle stars, 45  
    in carotenoprotein complexes, 4–6, 11  
    in Decapoda, 74  
    in fish eggs, 136  
    in fish ovaries, 136  
    in Macrourea, 74  
    structure, 8
- (3S,3'S)-7,8-Didehydroastaxanthin, in carotenoproteins, 15
- 3,4-Didehydro- $\alpha$ -carotene, 43  
    in Isopoda, 69  
    in Malacostraca, 69
- 3,4-Didehydro- $\beta$ -carotene, in sponges, 28, 29
- Didehydro- $\gamma,\kappa$ -carotene, 30  
    in sponges, 24, 28, 29  
    structure, 24
- 2,3-Didehydrofrtschiellaxanthin  
    in Brachyura, 76  
    in Decapoda, 76  
    structure, 77
- 7,8-Didehydroisorenieratene, 30  
    in sponges, 23, 28, 29
- 3,4-Didehydrolycopene  
    in Coleoptera, 107  
    in Hemiptera, 104, 105  
    in Insecta, 104, 105, 107  
    structure, 196
- 7',8'-Dihydro- $\gamma\psi$ -carotene  
    in Coleoptera, 107  
    in Insecta, 107  
    structure, 108
- 7,8-Dihydropsasilocanthin  
    formation, 148  
    in fish integument, 127, 133  
    structure, 131
- 3,4-Dihydroxy- $\alpha$ -carotene  
    in Insecta, 105  
    in Phasmida, 105  
    structure, 106
- 2,2'-Dihydroxy- $\beta$ -carotene  
    in Insecta, 102  
    in Phasmida, 102  
    structure, 102
- 3,4-Dihydroxy- $\beta$ -carotene  
    in fish livers, 138, 140  
    structure, 138
- 3,3'-Dihydroxy- $\epsilon$ -carotene  
    in fish integument, 124–129  
    structure, 132

- 2,2'-Dihydroxy-3,4-didehydro- $\beta$ -carotene  
in Insecta, 102  
in Phasmida, 102
- 3,3'-Dihydroxy-4-keto- $\beta$ -carotene, 42
- 3,4-Diketo- $\alpha$ -carotene  
in Amphipoda, 71  
in Malacostraca, 71  
in terrestrial gastropods, 59  
structure, 70
- 2,2'-Diketo- $\beta$ -carotene  
in Insecta, 102  
in Phasmida, 102  
structure, 103
- 3,4-Diketo- $\beta$ -carotene  
in Arachnida, 99  
in Coleoptera, 107  
in Insecta, 107  
structure, 100
- 2,2'-Diketo-3,4-didehydro- $\beta$ -carotene  
in Insecta, 102  
in Phasmida, 102  
structure, 103
- 2,2'-Diketo-3,4,3',4'-tetrahydro- $\beta$ -carotene  
in Insecta, 102  
in Phasmida, 102  
structure, 103
- Deer  
mule, 80  
white tailed, 180
- Dog, 179, 180
- Dogfish  
black, 137  
black mouth, 137  
pike, 138
- $\alpha$ -Doradecin, 133  
structure, 133
- $\beta$ -Doradecin, 133  
structure, 134
- $\alpha$ -Doradexanthin (4-keto-3'-epilutein)  
formation, 141, 143  
in Anomura, 75  
in Brachyura, 76  
in Branchiopoda, 65  
in Decapoda, 75, 76  
in fish eggs, 136  
in fish integument, 124–129, 133  
in fish ovaries, 136  
structure, 66
- $\beta$ -Doradexanthin  
conversion into astaxanthin, 141, 143  
formation, 85, 86  
in Brachyura, 76  
in Cephalopoda, 61  
in Copepoda, 67  
in Decapoda, 74, 76  
in fish integument, 124–129, 133  
in Macrourea, 74  
in sponges, 28, 29
- structure, 31
- Dorado, marine, 124
- Duck, 163, 164
- Echinone, 164  
conversion into astaxanthin, 141, 142  
formation in Arachnida, 100  
formation in Crustacea, 83–86  
formation in Echinodermata, 47, 48  
in Anomura, 75  
in Arachnida, 98  
in birds' skins, 163  
in Brachyura, 76, 79  
in Branchiopoda, 65  
in carotenoprotein complexes, 4–6, 17  
in Cephalopoda, 61  
in Coleoptera, 107  
in Crinoidea, 46  
in Decapoda, 74–76, 79  
in Diptera, 109  
in Echinoidea, 46  
in fish integument, 124–129  
in Holothuroidea, 45  
in hydra, 35, 36  
in Hymenoptera, 111  
in Insecta, 105, 107, 109–111  
in Lepidoptera, 110  
in limpets, 56, 57  
in Macrourea, 74  
in marine gastropods, 56  
in Platyhelminthes, 48  
in sea stars, 42–44  
in Scyphozoa, 36  
in sponges, 28, 29  
in tunicates, 122  
structure, 9
- Echinoderms, 42–48
- Eel, 137
- Elephant, 180
- 3'-Epilutein  
formation, 115  
in Brachyura, 76  
in Decapoda, 76  
in fish integument, 124–129, 132, 133  
structure, 77
- Eugorgiaenoic acid, 37
- Finch, 161, 162
- Gouldian, 161
- Fish, 123–127  
flying, 127  
ice, 124  
oar, 127  
Paradise, 126  
Siamese fighting, 124  
sun, 124, 126, 127  
tile, 124  
whale, 124
- Flamingo, 162–164, 166

- Flamingo, *cont.*
  - American, 161
  - Andean, 167
  - Chilean, 161
  - James', 161
  - Lesser (African), 161, 166
- Fritschellaxanthin (4-ketolutein)
  - in Brachyura, 76
  - in Decapoda, 76
  - in fish integument, 126–129
  - in fish liver, 137, 138
  - structure, 77
- Flute mouth, 125
- Flavoxanthin
  - in birds' eggs, 162
  - in Brachyura, 76
  - in Decapoda, 76
  - in fish integument, 124–129
  - in Mollusca, 54, 55
  - structure, 55
- Flounder, 127, 136
- Flying fish, 136
- Fox, 180
- Fucoxanthin, 27, 30
  - in birds' skin, 163
  - in Branchiopoda, 65
  - in marine gastropods, 57
  - in sponges, 28, 29
  - structure, 31
- Fucoxanthinol, 46, 47
  - in birds' skin, 163
- Galloxanthin (10'-apo- $\beta$ -carotene-3,10'-diol)
  - in birds' eyes, 164
  - structure, 164
- Garibaldi, 126
- Gastropoda
  - function of carotenoids in, 61
  - freshwater, 58, 59
  - marine, 56–58
  - terrestrial, 59
- Gazaniaxanthin
  - in Amphipoda, 71
  - in Macrourea, 74
  - in terrestrial gastropods, 59
  - structure, 60
- Glycymerin, in Mollusca, 53–55
- Goats, 180, 182
- Goby, long-jawed, 125
- Goldcrest, 161
- Goldfinch, 160
- Goldfish, 124, 132, 135–137, 141
- Goose, 162
- Gourami
  - dwarf, 125
  - striped, 125
- Grayling, 136
- Greenfinch, 160
- Grosbeak, cardinal, 160
- Grouper, 125
- Guinea pig, 180, 183
- Gull, black-headed, 163
- Gunnel, marine, 124
- Gurnard, 124, 128
- Hagfish, Pacific, 125
- Halibut, 147
- Halocynthiaxanthin
  - in tunicates, 123
  - structure, 123
- Hare, 180
- Hedgehog, 177
- Hens, 162–164, 182, 183
- Herring, 124, 136, 137
- Holothuria, 46
- Hopkinsiaxanthin
  - in Bryozoa, 50
  - in marine gastropods, 56, 57
  - in nudibranchs, 56, 57
  - structure, 50
- Hormones
  - effect on carotenoid metabolism, 86, 87
  - effect on coloration in insects, 118
- Horse, 177, 178
- Hydra, carotenoids in, 35, 36
- Hydroxyasteroidenone, 42
- 2-Hydroxy- $\alpha$ -carotene
  - in Insecta, 102
  - in Phasmida, 102
  - structure, 103
- 4 Hydroxy- $\alpha$ -carotene
  - in Cephalopoda, 60
  - in fish integument, 124–129, 140
  - in fish muscle, 135
  - in Insecta, 105
  - in Phasmida, 105
  - in terrestrial gastropods, 59
  - structure, 106
- 2-Hydroxy- $\beta$ -carotene, 145
  - formation, 112, 114
  - in fish integument, 124–129, 133
  - in Insecta, 102, 110
  - in Isopoda, 69
  - in Lepidoptera, 110
  - in Malacostraca, 69
  - in Phasmida, 102
- (2R)-2-Hydroxy- $\beta$ -carotene, 102, 110
- (2R,S)-2-Hydroxy- $\beta$ -carotene, 102, 110
- (2S)-2-Hydroxy- $\beta$ -carotene, 102, 110
- (3R,6'R)-3-Hydroxy- $\beta$ , $\epsilon$ -carotene-3'-one
  - formation from lutein, 165
  - structure, 166
- (3R,6'S)-3-Hydroxy- $\beta$ , $\epsilon$ -carotene-3'-one
  - formation from zeaxanthin, 165
  - structure, 166

- 3-Hydroxy- $\alpha$ -carotene ( $\alpha,\alpha$ -cryptoxanthin)**  
   in fish integument, 124–129  
   structure, 131
- 4-Hydroxy-3',4'-didehydro- $\beta$ -carotene**  
   in Amphipoda, 71  
   in Isopoda, 69  
   in Malacostraca, 69, 71  
   structure, 70
- 3-Hydroxy-4,4'-diketo- $\alpha$ -carotene**  
   in fish integument, 124–129  
   structure, 130
- 3-Hydroxy-4,4'-diketo- $\beta$ -carotene (see Adonixanthin)**
- 3-Hydroxyechinenone**  
   in Arachnida, 98, 100  
   in Copepoda, 67
- 4'-Hydroxyechinenone**, 141  
   formation in Arachnida, 100  
   in Brachyura, 76  
   in Decapoda, 74–76  
   in Diptera, 109  
   in fish eggs, 136  
   in fish integument, 124–129  
   in fish ovaries, 136  
   in Homoptera, 105  
   in Insecta, 105, 109  
   in Macrourea, 74  
   in Polychaeta, 49  
   structure, 68
- 3-Hydroxy-3'-keto- $\alpha$ -carotene (see Philosamiaxanthin)**
- 2-Hydroxy-2'-keto- $\beta$ -carotene**  
   in Insecta, 102  
   in Phasmida, 102  
   structure, 103
- 3-Hydroxy-4'-keto- $\beta$ -carotene**, 42
- 2-Hydroxy-2'-keto-3,4-didehydro- $\beta$ -carotene**  
   in Insecta, 102  
   in Phasmida, 102  
   structure, 103
- 3-Hydroxyretinol**, 148
- Ibis**  
   scarlet, 161–164  
   Indian blackheaded, 164
- Idoxanthin**, 141  
   in Isopoda, 69  
   in Malacostraca, 69, 74  
   in Decapoda, 74  
   in Macrourea, 74  
   in fish integument, 124–129  
   in fish eggs, 136  
   in fish ovaries, 136  
   structure, 70
- Insectoverdin**, 116, 117
- Iguana**, spiny tailed, 158
- Isoagelaxanthin A**, 30
- in sponges**, 28, 29  
**structure**, 32
- Isocryptoxanthin**  
   conversion into astaxanthin, 141, 142  
   formation, 83–86  
   in Amphipoda, 71  
   in Arachnida, 98, 112, 113  
   in Brachyura, 79  
   in Branchiopoda, 65  
   in Cephalopoda, 60  
   in Coleoptera, 107  
   in Copepoda, 67  
   in Decapoda, 74, 79  
   in Diptera, 109  
   in Echinodermata, 47, 48  
   in fish integument, 124–129  
   in Homoptera, 105  
   in Insecta, 105, 107, 109  
   in Isopoda, 69  
   in Macrourea, 74  
   in Malacostraca, 69, 71  
   in marine gastropods, 59  
   in Polychaeta, 49  
   in Scyphozoa, 36  
   in sponges, 28, 29
- Isocryptoxanthin, structure**, 30
- Isofucoxanthin**, in marine gastropods, 57
- Isofucoxanthinol (pentaxanthin)**, 46, 47
- Isolutein (see Lutein 5,6-epoxide)**
- Isomytiloxanthin**  
   in Mollusca, 52, 54, 55  
   structure, 53
- Isorenieracistene (7-cis-isorenienatene)**, 30  
   in sponges, 29
- Isorenieratene**, 24, 27  
   in Cephalopoda, 60  
   in marine gastropods, 56  
   in sponges, 22, 28, 29  
   structure, 23
- Isotedianixanthin**, 30  
   in sponges, 24, 28, 29  
   structure, 25
- Isotedanin**, 30  
   in sponges, 28, 29  
   structure, 33
- Isozeaxanthin**, 30  
   formation, 83, 84, 112, 141  
   in Amphipoda, 71  
   in Brachyurea, 76  
   in Branchiopoda, 65  
   in Caridea, 73  
   in Cirripedia, 68  
   in Coleoptera, 107  
   in Copepoda, 67  
   in Decapoda, 73, 74, 76  
   in fish eggs, 136  
   in fish integument, 124–129  
   in fish liver, 137, 138  
   in fish muscle, 135

## 206 The biochemistry of the carotenoids

- Isozeaxanthin, *cont.*  
  in fish ovaries, 136  
  in fresh water gastropods, 58  
  in Insecta, 107  
  in Isopoda, 69  
  in Macrourea, 74  
  in Malacostraca, 69, 71, 72  
  in Mysidacea, 72  
  in sponges, 28, 29  
  in terrestrial gastropods, 59  
  structure, 22
- Japanese turtle, 158
- Jewel bird, 161
- 3-Ketocanthaxanthin (*see* Phoeniconone)
- 2-Keto- $\alpha$ -carotene  
  in birds' eggs, 163  
  in fish eggs, 136  
  in fish ovaries, 136  
  in fish integument, 124–129  
  in Insecta, 102  
  in Phasmida, 102  
  structure, 103
- 4-Keto- $\alpha$ -carotene  
  in Amphipoda, 71  
  in Cephalopoda, 60  
  in Decapoda, 74  
  in fresh water gastropods, 58  
  in Isopoda, 69  
  in Macrourea, 74  
  in Malacostraca, 69, 71, 72, 74  
  in Mysidacea, 72  
  in terrestrial gastropods, 59  
  structure, 69
- 2-Keto- $\beta$ -carotene  
  in Insecta, 102, 110  
  in Lepidoptera, 110  
  in Phasmida, 102  
  structure, 103
- 4-Keto- $\gamma$ -carotene  
  in Amphipoda, 71  
  in Arachnida, 98  
  in Decapoda, 74  
  in Macrourea, 74  
  in Malacostraca, 71  
  structure, 70
- 4'-Ketodiatoxanthin (*see* Pectenolone)
- 3-Ketoechinenone (*see* 3,4-Diketo- $\beta$ -carotene)
- 4-Keto-3'-epilutein (*see*  $\alpha$ -Doradexanthin)
- 4-Keto-4-ethoxy- $\beta$ -carotene (?), 71, 75
- 4-Keto-4'-hydroxy- $\beta$ -carotene  
  formation, 83–86  
  in hydra, 35, 36
- 4-Ketolutein (*see* Fritschellaxanthin)
- 4-Ketozeaxanthin, structure, 141
- Killifish, 125
- Kokane (Sockeye Salmon), 126
- Lacertofulvin, 157
- Lamellibranchia (*see* Pelecypoda)
- Lamprey, 125, 126  
  Arctic, 126
- Leeches, 48
- Leprotene (*see* Isorenieratene)
- Light, effect on carotenoid metabolism, 89, 100, 118
- Limpets, 56, 57
- Lump fish, 125, 136, 137
- Lutein, 144  
  conversion into astaxanthin, 141, 143  
  conversion into dehydroretinol, 148  
  in amphibia, 155  
  in Amphipoda, 71  
  in Anomura, 75  
  in Arachnida, 98, 99  
  in birds, 160–164, 166  
  in birds' eggs, 162, 163  
  in birds' eyes, 164  
  in birds' skin, 163  
  in Brachyura, 76, 79  
  in Branchiopoda, 65  
  in Caridea, 73  
  in carotenoprotein complexes, 4–6  
  in Cirripedia, 68  
  in Coleoptera, 107  
  in Copepoda, 67  
  in Decapoda, 73–76, 79, 80, 82  
  in Diptera, 109  
  in feathers, 160, 161  
  in freshwater gastropods, 58  
  in fish eggs, 136  
  in fish integument, 124–129, 132, 134, 140, 146  
  in fish livers, 137–138  
  in fish muscle, 135  
  in fish ovaries, 136  
  in Insecta, 101, 102, 107, 109, 110  
  in Lepidoptera, 110  
  in lizards, 157, 158  
  in Macrourea, 74  
  in Malacostraca, 69, 71, 73, 76  
  in marine gastropods, 57  
  in Orthoptera, 101  
  in Phasmida, 102  
  in reptiles, 157  
  in sea stars, 42, 44  
  in sponges, 28, 29  
  in terrestrial gastropods, 59  
  in tunicates, 122  
  in turtles, 158  
  structure, 9
- Lutein 5,6-epoxide  
  in Amphipoda, 71  
  in Anomura, 75  
  in Arachnida, 98, 99  
  in birds, 160–162  
  in birds' eggs, 162

- Lutein 5,6-epoxide, *cont.*  
   in Brachyura, 76  
   in Cephalopoda, 61  
   in Decapoda, 74–76  
   in feathers, 160, 161  
   in fish eggs, 136  
   in fish integument, 124–129  
   in fish livers, 137, 138  
   in fish muscle, 135  
   in fish ovaries, 136  
   in fresh water gastropods, 58  
   in Isopoda, 69  
   in lizards, 158  
   in Macrourea, 74  
   in Malacostraca, 69, 71  
   in Mollusca, 54, 55  
   in Mysidacea, 72, 74–76  
   in reptiles, 158  
   in terrestrial gastropods, 59  
   structure, 69
- Lutein 5,8-epoxide  
   in Brachyura, 79  
   in Decapoda, 79  
   in Platyhelminthes, 48  
   in Polychaeta, 49  
   in sea stars, 43  
   structure, 80
- Lycopene, 166  
   in Cephalopoda, 61  
   in Coleoptera, 107  
   in Hemiptera, 104, 105  
   in Insecta, 104, 105, 107  
   in sponges, 28, 29
- Mackerel, 128  
 Medaka, 127, 144, 146  
 Melanin, 117  
 Methoxycarotenoids, 30  
   in sponges, 26, 28, 29
- Metridene (metridioxanthin) (*see*  
   Adonirubin)
- Mink, 183  
 Mollusca, 52–61  
 Monkey, 183  
 Mutatochrome, 30  
   in fish integument, 124–129  
   in Homoptera, 105  
   in Insecta, 105  
   in sponges, 28, 29  
   structure, 31
- Mutatoxanthin, 30  
   in Arachnida, 98  
   in fish integument, 124–129  
   in sponges, 28, 29  
   structure, 98
- Mytiloanthin  
   in Mollusca, 52, 54, 55  
   structure, 53
- Mytiloanthone
- in tunicates, 123  
   structure, 123
- Myroxanthin (*see* Echinonone)
- Neo- $\beta$ -carotene U, 182  
 Neoxanthin, 30  
   in Arachnida, 98, 99  
   in birds' eggs, 162  
   in Branchiopoda, 65  
   in Copepoda, 67  
   in fish integument, 129  
   in fish livers, 137, 138  
   in sponges, 28, 29  
   structure, 32
- Neurosporene  
   in Coleoptera, 107  
   in Insecta, 107  
   structure, 108
- Newts, 155
- 2-Norastaxanthin, 39  
   in Copepoda, 66, 67  
   in sea anemones, 37  
   structure, 38
- Nudibranchs, 66, 67
- Ommochromes, 117  
 Opal eye, 125  
 Oriole  
   African, 161  
   golden, 161  
 Ostracods, 66  
 4-Oxomytiloanthin, structure, 14  
 Ovorubin, 10  
   absorption spectrum of, 17  
   in fresh water gastropods, 58  
   properties, 16, 17
- Ovoverdin  
   absorption spectrum of, 10  
   structure, 13
- Papilioerythrin (4-ketolutein)  
   formation, 115  
   in Insecta, 110  
   in Lepidoptera, 110  
   structure, 111
- Papilioerythrinone (3-hydroxy- $\alpha$ -carotene-4,3'-dione)  
   formation, 115  
   in Anomura, 75  
   in Brachyura, 76  
   in Decapoda, 75, 76, 80  
   in Insecta, 110  
   in Lepidoptera, 110  
   structure, 75
- Paracentrone  
   in echinoderms, 46  
   structure, 47
- Paracentrotin A, 46  
 Paracentrotin B, 46  
 Parakeet, 161

## 208 The biochemistry of the carotenoids

- Parasiloxanthin  
  in fish integument, 127  
  formation, 145  
  structure, 131, 133
- Parasitization, effect on carotenoid metabolism, 90
- Pectenol (3,4,3'-trihydroxy-7',8'-didehydro- $\beta$ -carotene), in Mollusca, 52, 54, 55  
  54, 55
- Pectenolone, (4'-ketodioatoxanthin)  
  in carotenoprotein complexes, 4–6  
  in Mollusca, 53–55
- Pectenoxanthin (*see* Alloxanthin)
- Pelecypoda, 52–56
- Pentaxanthin (isofucoxanthinol)  
  in echinoderms, 46  
  structure, 47
- Perch  
  fresh water, 127  
  Japanese, 125  
  surf, 125
- Peridinin  
  in Cirripedia, 68  
  in sea anemones, 38  
  in sponges, 28, 29  
  structure, 31
- Pheasant, 162, 163
- Phenolic carotenoids, in sponges, 26
- Philosamiaxanthin (3'*O*-dehydrolutein, 3-hydroxy-3'-keto- $\alpha$ -carotene)  
  in fish, 141  
  in Insecta, 110  
  in Lepidoptera, 110  
  structure, 111
- Phoeniconone (3-ketocanthaxanthin)  
  in Arachnida, 99  
  in Brachyura, 76  
  in Branchiopoda, 65  
  in Coleoptera, 107  
  in Decapoda, 76, 80  
  in feathers, 160, 161  
  in Insecta, 107  
  structure, 65
- Phoenicoterone (*see* 4-Keto- $\alpha$ -carotene)
- Phoenicoxanthin (*see* Adonirubin)
- Photoacoustic spectroscopy, 11
- Phytoene  
  in Cephalopoda, 61  
  in Coleoptera, 107  
  in Insecta, 107
- Phytofluene  
  in Cephalopoda, 61  
  in Coleoptera, 107  
  in Insecta, 107  
  structure, 61
- Picofulvin, 160–162
- Pig, 179, 180, 182, 183
- Pigeon, 164  
  flame footed fruit, 161
- Pike, 125, 135–137, 140
- Pilchard, 128
- Piranha, 128, 132
- Platyfish, 127
- Platyhelminthes, 48
- Plioxyanthin, 75
- Polioxanthin, 135, 138
- Polychaeta, 48, 49
- Pollock, 136
- Porbeagle, 137
- Plaice, 127
- Pirardixanthin, in hydra, 35, 36
- Priapulids, 48
- Pro- $\gamma$ -carotene, structure, 182
- Pufferfish, 147
- Quail, 164
- Quetzel, 161
- Rabbit, 179, 180, 183
- Rabbit fish, 137
- Rat, 179, 180, 182, 183
- Rattlesnake, 157
- Reindeer, 180
- Ray  
  angel, 138  
  blonde, 137  
  cuckoo, 138  
  eagle, 137  
  electric, 138  
  sandy, 137  
  spotted, 138  
  sting, 138  
  thornback, 127, 128
- Red devil, 124
- Red hata, 125
- Red mullet, 133
- Renieracistene (*7-cis*-renieratene), 30  
  in sponges, 29
- Renierapurpurin, 30  
  in sponges, 22, 28, 29  
  structure, 23
- Renieratene, 24, 27  
  in sponges, 22, 28, 29  
  structure, 23
- Renieraxanthin (spheroidenone)  
  in sponges, 23  
  structure, 23
- Resonance Raman spectroscopy, 14, 17
- Retinal, 183, 184
- Retinol (vitamin A), 147, 165  
  formation, 180–184  
  structure, 148
- Rhodopin  
  in Homoptera, 105  
  in Insecta, 105  
  structure, 106
- Rhodoxanthin

- Rhodoxanthin, *cont.*  
     in birds, 160–161  
     in feathers, 160–161  
     in fish integument, 124–129  
         structure, 132
- Rubixanthin  
     in Amphipoda, 71  
     in Decapoda, 74  
     in Macrourea, 74  
     in Malacostraca, 71  
     structure, 70
- Salamander, 155
- Salmon, 144  
     Atlantic, 128, 132, 135–137  
     cherry, 135  
     Chinook, 126, 135, 136  
     Chum, 126, 135  
     Coho, 126, 135  
     Masou, 126  
     Pacific, 132, 135, 136, 139  
     sockeye, 126
- Salmoxanthin  
     in fish integument, 124–129, 133  
         structure, 131
- Sand eel, 136
- Sarcinene, 164
- Sardine, 136
- Sea anemones, 37  
     carotenoid formation in, 38  
     carotenoid function in, 39
- Sea robin, 126
- Sea stars, 42–44
- Scyphozoa, 36
- Sepiaxanthin, in Cephalopoda, 61
- Shark, 137, 138  
     basking, 137  
     blue, 137  
     horned, 125, 137  
     Portuguese, 137  
     six gilled, 137
- Sheep, 179, 182
- Sheephead, California, 127, 144
- Sipunculids, 48
- Siskin, 160
- Skate  
     blue, 137  
     long-nosed, 138  
     starry, 138
- Smelt, 127, 135–137
- Smooth hound, 137
- Sole, 136
- Sponges, 22–23
- Spoonbill, roseate, 160, 164
- Sprat, 137, 138
- Stickleback  
     Chinese eight-spined, 127  
     three-spined, 125, 137
- Stork, 163
- Sulcatoxanthin (*see* Peridinin)
- Sunfish, 137
- Taraxanthin (*see* Lutein 5,6-epoxide)
- Tedaniaxanthin (allopurpurin), 27  
     in sponges, 24, 28, 29  
         structure, 25
- Tedanin, in sponges, 23, 28, 29, 33
- Tethyatene  
     in sponges, 23, 27–29  
         structure, 24
- Tench, 128, 135, 138
- (3S,3'S)-7,8,7',8'-Tetrahydroastaxanthin  
     formation, 141  
     in alcyonarians, 37  
     in Brachyura, 76  
     in brittle stars, 45  
     in carotenoproteins, 15  
     in carotenoprotein complexes, 4–6, 11  
     in Decapoda, 74, 76  
     in Macrourea, 74  
         structure, 9
- 3,4,3',4'-Tetrahydro- $\beta$ -carotene, 184
- 7',8',11',12'-Tetrahydro- $\gamma$ -carotene  
     in Coleoptera, 107  
     in Insecta, 107  
         structure, 108
- 7',8',11',12'-Tetrahydro- $\gamma\psi$ -carotene  
     in Coleoptera, 107  
     in Insecta, 107  
         structure, 107
- 7,8,11,12-Tetrahydrolycopene  
     in Coleoptera, 107  
     in Insecta, 107  
         structure, 108
- Tilefishxanthins, I–IV  
     in fish integument, 124  
         structures, 130
- Tit  
     blue, 161  
     great, 161
- Tortoise, 158, 183
- Toluene  
     in Coleoptera, 107  
     in Homoptera, 105  
     in Insecta, 105, 107  
     in sponges, 28, 29  
         structure, 30
- Toucan, 161
- Treefrog, 155
- Trematodes, 58
- 3,4,3'-Trihydroxy- $\beta$ -carotene  
     in Copepoda, 67
- 3,4,4'-Trihydroxy- $\beta$ -carotene  
     in Homoptera, 105  
     in Insecta, 105  
     in terrestrial gastropods, 9  
         structure, 106

## 210 The biochemistry of the carotenoids

- 3,4,3'-Trihydroxy-7',8'-didehydro- $\beta$ -carotene (*see* Pectenol)
- Triketriophidin, 30, 33  
in sponges, 24, 28, 29  
structure, 25
- Triketriorhodin, 33  
in sponges, 23, 28, 29  
structure, 24
- Triphaxanthin  
in Cephalopoda, 59  
in nudibranchs, 56, 57
- Trout, 144  
brook, 128, 135  
brown, 136, 137  
lake, 128  
mutants, 146  
rainbow, 128, 135–137, 144
- Tunaxanthin  
formation, 144, 145  
in Amphipoda, 71  
in Decapoda, 74  
in fish eggs, 136  
in fish integument, 124–129, 132, 140, 146  
in fish intestines, 140  
in fish muscle, 135, 140  
in fish livers, 137, 138  
in fish ovaries, 136  
in Macrourea, 74  
in Malacostraca, 71  
structure, 70
- (3*R*,6*S*,3'*R*,6'*S*)-Tunaxanthin (tunaxanthin A)  
formation, 145  
in fish integument 124–129, 133  
structure, 131
- (3*R*,6*S*,3'*S*,6'*S*)-Tunaxanthin (tunaxanthin C)  
formation, 145  
in fish integument, 124–129, 133  
structure, 131
- (3*R*,6*S*,3'*R*,6'*S*)-Tunaxanthin (tunaxanthin B)  
formation, 145  
in fish integument, 124–129, 133  
structure, 129
- Tunicates, 122–123
- Tunney, 128  
yellowfin, 126
- Turkey, 164
- Violaxanthin, 30  
in Amphipoda, 71  
in Arachnida, 98, 99  
in birds, 160, 161  
in Branchiopoda, 65  
in Copepoda, 67  
in Decapoda, 74  
in feathers, 160, 161  
in fish integument, 124–129
- in fish livers, 137, 138  
in fish muscle, 134  
in Isopoda, 69  
in Macrourea, 74  
in Malacostraca, 69, 71, 74  
in sponges, 28, 29  
structure, 32
- Vitamin A (*see* Retinol)
- Vitamin A<sub>2</sub> (*see* Dehydroretinol)
- Vitamin A aldehyde (*see* Retinal)
- Wagtail, grey, 161
- Wapiti, 177
- Warbler, wood, 161
- Waxwing, cedar, 160
- Weaver, greater, 128
- Whale, 179, 180  
toothed, 179
- Whalefish, 124, 125, 127
- Woodpecker, 161  
green, 161
- Yellowhammer, 160
- Yellow tail, 136
- $\beta$ -Zeacarotene  
in Arachnida, 98  
in Coleoptera, 107  
in Homoptera, 105  
in Insecta, 105, 107  
in terrestrial gastropods, 59  
structure, 60
- Zeaxanthin, 27  
conversion into astaxanthin, 141, 142, 166  
conversion into 7,8-dihydroparasinoxanthin, 145  
conversion into parasiloxanthin, 145  
conversion into tunaxanthin B, 145  
formation, 85, 86  
in amphibia, 154  
in Amphipoda, 71  
in Anomura, 75  
in Arachnida, 98  
in birds, 160–162, 163  
in birds' eggs, 162  
in birds' eyes, 163  
in Brachyura, 76, 79  
in Caridea, 73  
in carotenoprotein complexes, 4–6, 16  
in Cephalopods, 60  
in Cirripedia, 68  
in Coleoptera, 107  
in Copepoda, 67  
in Crinoidea, 46  
in Decapoda, 73–76, 79  
in Diptera, 109  
in feathers, 160, 161  
in fish eggs, 136

*Zeaxanthin, cont.*

- in fish integument, 124–129, 146
- in fish liver, 137, 138
- in fish muscle, 135
- in fish ovaries, 136
- in Insecta, 102, 107, 109
- in Isopoda, 69
- in limpets, 56, 57
- in lizards, 158
- in Macrourea, 74
- in Malacostraca, 69, 71–76
- in Mysidacea, 72
- in marine gastropods, 56, 57
- in Mollusca (?), 52, 54, 55
- in Phasmida, 102
- in Polychaeta, 49
- in reptiles, 158
- in sea anemones, 38
- in sea stars, 42, 44
- in Scyphozoa, 36
- in sponges, 28, 29
- in terrestrial gastropods, 59
- structure, 9

Zoöerythrin, 1, 43

# SPECIES INDEX

- Acanthella* sp., 28  
  *vulgaris*, 28  
*Acanthephyra* sp., 6, 86  
  *acanthitelsonis*, 73  
  *curtirostris*, 73  
  *exima*, 73  
  *pelagica*, 73  
  *purpurea*, 73, 78, 79, 86  
  *sexspinosa*, 73  
  *stylorstratis*, 73  
*Acanthodiaptomus denticornis*, 88, 89  
*Acanthogammarus albus*, 71  
*Acanthopagrus schlegelii*, 124  
*Acipenser ruthenus ruthenus*, 136  
*Acrida turrita*, 101, 117  
*Acrophyllo wulffingi*, 102  
*Acrotylus insubricus*, 101  
*Actias selene*, 110  
*Actinia equina*, 37, 38  
  *tenebrosa*, 37  
*Actinostola callosa*, 37, 38  
*Acysthosiphon pelargonii*, 105  
*Agama agama*, 158  
*Agelias* sp., 33  
  *mauritania*, 28  
  *schmidtii*, 28  
*Aglaeophenia*, 36  
*Aglais urticae*, 110  
*Ajaia ajaja*, 7, 160, 163, 164  
*Alcyonium digitatum*, 37  
  *pulmatum*, 37  
*Allopora californica*, 7, 11, 18, 35  
*Alysina aerophoba*, 28  
*Alytes obstetricans*, 154  
*Amanses modestus*, 124, 133  
*Ambloplites rupestris*, 124  
*Amblycorypha* sp., 101  
*Amblyseius potentillae*, 100  
*Ammodytes lanceolatus*, 124  
  *tobianus*, 124, 136, 137, 140  
*Ampelisca tenuicornis*, 71  
*Amphiuna* sp., 4  
*Amphipholis squamata*, 45  
*Amphiura chiajei*, 45  
  *filiformis*, 43  
*Anadara broughtoni*, 54  
  *subarenata*, 54  
*Anapagurus chiroacanthus*, 75  
*Ancorina alata*, 28  
*Anemonia*, sp., 39  
  *sulcata*, 38  
*Anguilla anguilla*, 124, 137, 138  
*Anguis fragilis*, 158  
*Anisodoris nobilis*, 56, 57  
*Anodonta cygnea*, 53, 55  
*Anomalocera patersoni*, 2, 5, 67  
*Anomica ephippium* 54  
*Antedon* sp., 4  
  *petasus*, 46  
  *rosacea*, 46  
*Anystis* sp., 97  
*Apanteles flaviconchae*, 111, 117  
  *glomeratus*, 111  
*Aphelasterias japonica*, 44  
*Aphiga minuta*, 124  
*Aphis fabae*, 105  
  *intyfi*, 105  
  *sambuci*, 105  
  *solanella*, 105  
  *urticata*, 105  
*Aphrodite* sp., 49  
*Apis mellifica*, 111  
*Aplysia* sp., 56  
  *depilans*, 57  
*Apodemus flavicollis*, 174  
*Apodichthys flavidus*, 124

## 214 The biochemistry of the carotenoids

- Aporrhais pes-pelecani*, 57  
*Apus cancriformis*, 65  
*Archidoris montereyensis*, 57  
*Arctodiaptomus bacillifer*, 67  
    *salinus*, 67  
*Arenicola marina*, 49  
    *piscatorum*, 49  
*Argulus foliaceus*, 67  
*Arion empiricorum*, 59  
    *subfuscus*, 59  
*Aristeomorpha foliacea*, 3, 80  
*Aristeus antennatus*, 3, 80, 82  
*Aristichthys nobilis*, 135, 137, 140  
*Artemia* sp., 84, 86  
    *salina*, 2, 5, 35, 36, 64, 65, 78, 86  
*Artediaptomus salinus*, 88  
*Asellus aquaticus*, 69  
    *aquaticus cavernicolus*, 89  
*Astacus astacus*, 6, 74, 78  
    *fluvialis*, 3, 74, 81  
    *leptodactylus*, 74, 79, 82  
    *nobilis*, 3, 74  
    *pallipes*, 3, 74  
*Astarte sulcata*, 54  
*Astea undosa*, 57  
*Asterias* sp., 4  
    *anurensis*, 44  
    *glacialis*, 44  
    *müllerii*, 44  
    *rubens*, 4, 6, 10, 14, 15, 42, 44  
*Asterina gibbosa*, 4  
    *panceri*, 4, 42, 43  
    *pectinifera* 6, 43, 44  
*Astrometis sertulifera*, 4, 43  
*Astropecten* sp., 4  
    *aurantiacus*, 4, 42, 43  
    *bispinosus*, 4  
    *irregularis*, 44  
*Atelopus chiriquiensis*, 155  
*Athanus* sp., 3  
*Aurelia aurita*, 36  
    *flavidula*, 36  
*Auxis thazard*, 124  
*Axinella crista-galli*, 22, 28  
    *rugosa*, 28  
    *verrucosa*, 28
- Bacillus rossius*, 102  
*Balanus balanus*, 68  
*Balanstium* sp., 97  
*Barbourisia rufa*, 124  
*Bartus nigrofasciatus*, 124  
*Beryx decadactylus*, 124, 139  
    *splendens*, 124  
*Betta splendens*, 124  
*Bolocera tuediae*, 37  
*Bombia bombia*, 157
- Bombinator igneus*, 157  
*Bombycilla cedrorum*, 160  
*Bombyx mori*, 110, 117, 118  
*Bothrops jararaca*, 157  
*Bothus maximus*, 124  
    *rhombus*, 124  
*Brachycaudus cardini*, 105  
    *helichrysi*, 105  
*Branchinecta packardi*, 5, 65  
    *paludosa*, 65  
*Branchiomma vesiculosum*, 49  
*Branchiostegus japonicus*, 124, 133  
*Branchipus stagnalis*, 2, 5, 65, 78  
*Brandtia lata*, 71  
*Bryobia praetiosa*, 98  
*Buccinum undatum*, 57  
*Bufo bufo*, 155  
    *calamuta*, 154  
    *viridis*, 154  
    *vulgaris*, 154  
*Bugula flabellata*, 48  
    *neritina*, 48  
*Bunodosma cavernata*, 37  
    *granulifera*, 37
- Caenestheria* sp., 2  
*Calanus finmarchicus*, 67  
*Callinectes sapidus*, 6, 76  
*Callionymus lyra*, 124  
    *punctatus*, 124  
*Calliopius laeviusculus*, 71  
*Callosamia promethea*, 117  
*Callyspongia confaederata*, 28  
*Calocaris meandreae*, 74  
*Calophenus italicus*, 101  
*Caltha palustris*, 132  
*Cambarus bartoni tenebrosus*, 74, 89  
    *clarkii*, 6  
*Cancer pagurus*, 4, 6, 76, 78  
*Canis vulpes*, 174  
*Caprella dentatum*, 3  
*Capreolus capreolus*, 174  
*Capulus hungaricus*, 57  
*Caranx trachurus*, 124  
*Carassius auratus*, 124, 134–139, 141  
    *carassius buergeri*, 124  
    *carassius grandoculis*, 124  
    *citrinellum*, 132  
    *cuvieri*, 124  
    *gibeli*, 124  
*Carausius morosus*, 102, 117, 118  
*Carcinus* sp., 3  
    *maenas*, 3, 6, 76, 78, 79, 81, 82, 85, 90  
    *mediterraneus*, 76, 82  
*Cardinalis cardinalis*, 160  
*Cardium echinatum*, 54

- edule*, 54
- tuberculatum*, 54
- Carduelis carduelis*, 160
- spinus*, 160
- Careharinus glaucus*, 137
- Carteriospongia foliascens*, 28
- pennatula*, 28
- Cassida murraea*, 106, 107
- Centrolabrus exoletus*, 124
- Centropages furcatus*, 67
- Centrophorus squamosus*, 137
- Centropristes striatus*, 139
- Centroscyllium fabricii*, 137
- Centroscymus coelolepis*, 137
- Cepaea hortensis*, 59
- Cerithidua californica*, 2, 57
- Cerrodaphnia reticulata*, 35
- Cerura vinula*, 102, 112, 113
- Cervus canadensi*, 177
- Cetorhinus maximus*, 137
- Cetostomus regans*, 124
- Chaenobrytus gulosus*, 124
- Chaenocephalus aeratus*, 124
- Chaetoderma nitidulum*, 60
- Chaetopterus* sp., 49
- Chaitophorus populeti*, 105
- Chameleon vulgaris*, 157
- Champscephalus gunneri*, 124
- Channa maculata*, 124
- Chelidonichthys kumu*, 124
- Chelonia mydas*, 158
- Chichlasoma elisalium*, 124
- Chimaera monstrosa*, 137
- Chionectes opilio*, 76
- Chirocephalus diaphanus*, 5, 65, 78, 89
- Chironomus annularius*, 106
- Chlamys nipponensis azakara*, 54
- nobilis*, 54
- septemradiatus*, 54
- Chlorella vulgaris*, 35
- Chloris chloris*, 160
- Chlorohydra viridissima*, 35
- Chlororherpes yucatanensis*, 160, 162
- Chondropsis* sp., 28
- Chondrostria reniformis*, 28
- Chone infundibuliformis*, 49
- Chrysemys scripta elegans*, 158
- Chrysopa carnea*, 118
- peila*, 117
- Chrysophris major*, 124
- Ciconia ciconia*, 163
- Ciocalypta* sp., 26, 28
- Ciona intestinalis*, 122
- Cladocera* sp., 2
- Clathria* sp., 28, 33
- frondifera*, 28
- Clathriopsamma*, sp., 28
- Clava squamata*, 2, 35, 36
- Clavellina lepadiformis*, 122
- Clemmys insculpta*, 158
- Clethrionomys glauvovolus*, 174
- Clibanarius erythropus*, 6, 75
- misanthropus*, 75, 84
- Cliona hixonii*, 28
- Clione limacina*, 57
- Clupanodon punctatus*, 124
- Clupea harengus*, 124, 136, 137
- pallasii*, 124
- Coccinella quinquepunctata*, 107
- septempunctata*, 106, 107
- Cochleodesma praetense*, 54
- Cocospongia* sp., 28
- Coilia mystus*, 124
- Colaptes* sp., 162
- auratus*, 160
- cafer*, 160
- Colias philodice*, 116, 117
- Colisia fasciata*, 125
- lalia*, 125
- Cololabris saira*, 125
- Conchoderma virgatum*, 68
- Copeina guttata*, 125
- Corallium rubrum*, 37
- Coregonus albula*, 135, 136
- autumnalis migratorius*, 125
- lavaretus*, 135, 137, 140
- Corella parallelogramma*, 122
- Coreoperca kawambari*, 125
- Corophium volutator*, 71
- Coryphaena hippurus*, 125
- Coscinasterias tenuispina*, 43
- Crangon* sp., 3
- allmanni*, 74
- crangon*, 74
- vulgaris*, 74
- Crella incrustans*, 28
- Crenilabrus melops*, 125
- suillus*, 125
- Crepidula fornicata*, 57
- Cribrina xanthogrammica*, 38
- Croceris duodecimpunctata*, 106, 107
- lili*, 107
- Crossaster papposus*, 6, 43
- Crotalus terrificus*, 157
- Cryptouropus pachytus*, 71
- Cithamus fragilis*, 68
- Ctenomorpodes brieveus*, 102
- Ctenopharyngodon idella*, 135, 137, 138, 140
- Ctenosaura hemilopha*, 158
- Cucumaria* sp., 4
- elongata*, 45
- lactea*, 45
- lubrica*, 45, 46
- Cultellus* sp., 2
- pellucidus*, 54
- Cyamon neon*, 28

## 216 The biochemistry of the carotenoids

- Cyclocypris laevis*, 66  
*Cyclops* sp., 89  
    *strenuus*, 67  
    *vernalis*, 5  
*Cyclopterus lumpus*, 125, 136–138, 147  
*Cymatogaster aggregatus*, 125  
*Cynthia papillosa*, 122  
*Cypraea spadicea*, 57  
*Cyprina islandica*, 57  
*Cyprinus carpio*, 125, 136, 138, 146, 147
- Daphnia* sp., 82, 86, 89, 90  
    *longispina*, 89  
    *longostra*, 65  
    *magna*, 2, 65, 84, 86  
    *pulex*, 2, 65  
*Dardanus arrosor*, 75, 84, 87, 89  
*Dendraster excentricus*, 46, 47  
*Dendroda grossularia*, 122  
*Dendrodoris fulva*, 56, 57  
*Dermacentor pictus*, 98  
*Deroceras agrestis*, 59  
*Diaptomus bacillifer*, 67  
    *castor*, 67  
    *claripes*, 88  
    *nevadensis*, 88  
    *pallidus*, 88  
    *sicilis*, 88  
    *vulgaris*, 2  
*Dipacaster pretiosa*, 44  
*Diodora graeca*, 57  
*Disidea fragilis*, 28  
    *herbacea*, 28  
*Dissotichus eleginoides*, 125  
*Distichophora coccinea*, 7, 18, 36  
    *nitida*, 7, 36  
    *violacea*, 7, 36  
*Ditrema temminicki*, 125  
*Dixippus morosus*, 7  
*Doderleinia berycooides*, 125  
*Doriopsilla albopunctata*, 56, 57  
*Dosinia exoleta*, 54  
*Dreissena polymorpha*, 55  
*Dromia* sp., 3  
*Drybates major*, 160  
*Dysdercus* sp., 104
- Echinaster* sp., 4  
    *sepositus*, 43  
*Echinocardium cordatum*, 46, 47  
*Ectasoma tiaratum*, 102, 112  
*Ectyon oroides*, 28  
*Eimeria* sp., 167  
*Eledone cirrosa*, 60  
*Eleginus navaga*, 136, 147  
*Elminius modestus*, 68
- Emberiza citrinella*, 160  
    *icteria*, 160  
*Emerita analoga*, 3, 4, 6, 75, 78, 84, 86–88  
*Engraulis japonica*, 125  
*Entosphenus japonicus*, 125  
*Eotetrahyalus lewisi*, 98  
*Ephyrina hoskynii*, 73  
*Epiactis prolifera*, 2, 37  
*Epinephelus akaara*, 125  
    *fasciatus*, 125  
*Eptatretus stoutii*, 125  
*Eriosoma lanuginosum*, 105  
    *ulnii*, 105  
*Eriphia spinifrons*, 6, 10, 76, 78  
*Erythraeus* sp., 97  
*Esox lucius*, 125, 135–140  
*Esperia foliata*, 28  
*Etomopterus spinax*, 136  
*Etrumeus micropus*, 125  
*Euchaeta russellii*, 66, 67  
*Eudiaptomus amblyodon*, 5, 67  
*Eudistylia polymorpha*, 49  
    *vancouveri*, 49  
*Eudryas bifossatus*, 157  
*Eugorgia ampla*, 37  
*Eulimnogammarus cruentus*, 71  
    *grandimanus*, 71  
    *maacki*, 71  
*Eunice* sp., 49  
*Eunicella verrucosa*, 37  
*Eupagurus bernhardus*, 6, 75, 78  
*Euphausia americana*, 72  
    *brevis*, 72  
    *gibboides*, 72  
    *hemigibba*, 72  
    *pacifica*, 72  
    *superba*, 72  
*Euplectes* sp., 161  
    *francisanus*, 160  
    *nigroventis*, 160  
    *orix*, 160  
*Eurydema ornata*, 104  
*Eurystomella bilabiata*, 48  
*Euzorus mucronata*, 49  
*Exocoetus volitans*, 125  
*Eylais extendens*, 4, 98  
    *hamata*, 98
- Fasciola hepatica*, 48  
*Ficulina* sp., 2  
    *ficus*, 2, 28  
*Fistularia petimba*, 125  
*Flabelligera diplochaitus*, 49  
*Flabellina iodinea*, 2  
*Flabellinopsis iodinea*, 56, 57  
*Flexopecten ponticus*, 54  
*Florometra serretissima*, 46  
*Flustra foliacea*, 48

- Fundulus parvipinnis*, 125  
*Funiculina quadrangularis*, 37
- Gadus aeglefinus*, 125  
 callarias, 125, 135, 136, 137, 140  
 minutus, 125  
 morrhua, 136  
 virens, 125
- Gaidropsarus cimbrius*, 125  
 mustela, 125
- Galathea* sp., 3  
 intermedia, 75  
 strigosa, 6
- Gambusia hollbrookii*, 125
- Gammarus* sp., 3  
 duebeni, 71, 89  
 lacustris, 3, 68, 86  
 locusta, 71  
 marinus, 71  
 oceanicus, 71  
 pulex, 3, 71, 90  
 pulex subterraneus, 89  
 puteanus, 89  
 salinus, 71  
 zaddachi, 71
- Gastrophysa cyanea*, 107
- Gastrostomus aculeatus*, 125, 137, 147
- Gebbia littoralis*, 3
- Gennadas valens*, 79
- Gephyroberix japonicus*, 125
- Geryon quinquedens*, 76, 85
- Gibbula cineraria*, 57  
 tumida, 57
- Gillichthys mirabilis*, 125
- Girella nigricans*, 125
- Glycera goessii*, 49
- Glyphus marsupialis*, 73
- Gmelinoides fasciatus*, 71
- Gobius niger*, 125
- Golfingia elongata*, 48
- Grania coriacea*, 28
- Gryphaea angulata*, 54
- Guara guara*, 161  
 rubra, 7, 163–165
- Gyrinomismus* sp., 125
- Gyrostoma* sp., 37
- Halichondria albescens*, 28  
 caruncula, 28  
 incrustans, 28  
 moorei, 28  
 panicea, 28  
 rosea, 28  
 sanguinea, 28  
 seriata, 28
- Haliclona permollis*, 28
- Haliotis discus-hanlei*, 57  
 fulgens, 57
- Halma bucklandi*, 28
- Halocynthia papillosa*, 122  
 roretzi, 122, 123
- Haplooops tubicula*, 71
- Harengula tunasi*, 125
- Harmothoe sarsis*, 49
- Helicella candidans*, 59  
 derbentina, 59
- Helicolenus hilgendorfi*, 125
- Heliopora caerulea*, 37
- Helisoma nigricans*, 58
- Helix* sp., 59  
 aspersa, 59  
 pomatia, 59
- Hemicentrotus pulcherrima*, 6, 46, 47
- Hemidiptomus amblyodon*, 2, 67
- Henricia* sp., 4, 43, 44  
 annectens, 44  
 levigata, 44  
 paleopina, 44  
 sanguinolenta, 4, 43
- Hestina japonica*, 118
- Heterocarpus doralis*, 73  
 ensifer, 73  
 grimaldii, 73
- Heterocope saliens*, 2
- Heterocypris incongruens*, 66
- Heterodontus francisci*, 125, 137, 140
- Hexagrammos otakii*, 125
- Hexanchus griseus*, 137
- Hippasteria phrygiana*, 44
- Hippoglossus hippoglossus*, 136
- Hippolyte* sp., 3  
 varians, 3
- Hircina spinulosa*, 28
- Holmetopus haematocheir*, 76
- Holopedium gibberum*, 65
- Holothuria* sp., 4  
 forskali, 45  
 leucospilota, 46  
 nigra, 45  
 polii, 45  
 tubulosa, 45
- Homarus americanus*, 6, 13, 74, 78  
 gammarus, 6, 74, 78  
 vulgaris, 6, 13, 74, 78, 80, 82
- Hopkinsia rosacea*, 56, 57
- Hucho hucho*, 136
- Hyale perieri*, 71
- Hyalophora cecropia*, 116
- Hyas coarctatus*, 76
- Hydra attenuata*, 35  
 circumcincta, 35  
 fusca, 35  
 littoralis, 35, 36  
 pirardi, 35  
 vulgaris, 35
- Hydrachna dispar*, 98  
 geografica, 98

## 218 The biochemistry of the carotenoids

- Hydractinia echinata*, 2  
*Hyla arborea*, 154  
  *coerulea*, 155  
*Hymeniacidon albescens*, 28  
  *penicillata*, 28  
  *sanguineum*, 28  
*Hymenodora gracilis*, 73  
*Hypomesus transpacificus*, 125  
*Hypophthalmichthys molitrix*, 135, 137, 140  
*Hypoxanthus rivoli*, 161  
*Hypsypops rubicunda*, 126
- Ianthea basta*, 26, 28  
*Iodothea* sp., 3, 67, 80, 85, 88  
  *baltica*, 69  
  *chelipes*, 69  
  *emarginata*, 69  
  *granulosa*, 6, 69, 78, 84, 87  
  *metallica*, 69, 88  
  *montereyensis*, 6, 69, 78, 87, 88  
  *neglecta*, 69  
  *resecata*, 6, 69, 87  
  *viridis*, 3, 69  
*Idya furcata*, 2  
*Ilisha elongata*, 126  
*Inachus mauritanicus*, 90  
*Iotrochota baculifera*, 28  
*Ischikauia steenackeri*, 126  
*Isophya krausii*, 101  
*Isurus glaucus*, 126
- Karcius bicolor*, 136  
*Katsuwonus pelamis*, 136
- Labidocera* sp., 5  
  *acutifrons*, 67, 78  
  *nerii*, 67  
  *woollastoni*, 67  
*Labrus bergylta*, 126  
  *melops*, 126  
  *ossifagus*, 126  
*Lacerta agilis*, 157, 158  
  *muralis*, 157  
  *sicula*, 157  
  *viridis*, 157  
  *vivipara*, 157, 158  
*Laetmonice filicornis*, 49  
*Lafoea* sp., 36  
*Lamna cornubica*, 137  
*Lampetra* sp., 134  
  *fluvatilis*, 126  
  *japonica*, 126  
  *planeri*, 126
- Lamprometra kluzingeri*, 46  
*Laniarius atrococcineus*, 161  
*Laqueatus sowerby*, 54  
*Laradibus ridibundus*, 163  
*Latealabrax japonicus*, 126  
*Latimeria chalumnae*, 126  
*Leander serratus*, 74, 89  
*Leda parvula*, 54  
*Lepas* sp., 67  
  *anacles*, 68  
  *anatifera*, 5, 68  
  *cuniculus*, 179  
  *fascicularis*, 5, 68  
  *pectinata*, 68  
*Lepidotrigla guntheri*, 126  
*Lepidurus apus*, 65  
*Lepomis cyanellus*, 126  
  *macrochirus*, 126  
  *megalotis*, 126  
*Lepralia foliacea*, 48  
*Leptinotarsa* sp., 107  
  *decemlineata*, 107  
*Leucespicus delineata*, 138  
*Leuciscus rutilus*, 137  
*Leuconia gossei*, 28  
*Lilioceris lili*, 107  
*Lima* sp., 2  
  *doscombei*, 54  
  *excavata*, 52, 54, 57  
  *loscombi*, 57  
  *mians*, 54  
*Limacina retroversa*, 57  
*Limanda limanda*, 126  
*Limax cereus*, 59  
  *cinerer-niger*, 59  
  *maximus*, 59  
*Limnadia lenticularis*, 2  
*Limnaea stagnalis*, 58, 59, 61  
*Littorina* sp., 2  
  *littoralis*, 57  
  *littorea*, 57  
  *planaxis*, 57  
  *rudis*, 57  
*Locusta* sp., 3  
  *migratoria migratorioides*, 101, 117  
*Loligo forbesi*, 60  
  *opalescens*, 60  
  *vulgaris*, 60  
*Longiunguis pyrarius*, 105  
*Lophelia pertusa*, 37  
*Lophius piscatorius*, 135, 137  
*Lota lota*, 126  
  *vulgaris*, 136  
*Lubriconereis fragilis*, 49  
*Lucina borealis*, 54  
*Luidia* sp., 4  
  *sarsi*, 44  
*Lysasterias perrieri*, 6

- Lytechinus pictus*, 46
- Macrobrachium rosenbergi*, 3, 87
- Macro hectopus branickii*, 71
- Macropipus holsatus*, 76
- Macropodus opercularis*, 126
- Macrosiphonella millifolii*, 105
- Macrosiphum liliodendri*, 104–106, 116  
  *rosae*, 105
- Maja squinado*, 76
- Mantis religiosa*, 117
- Marinogammarus marinus*, 3
- Marthasterias glacialis*, 4, 6, 11, 15, 42, 43  
  *tenuispina*, 44
- Meconema varium*, 101
- Meconium varium*, 7
- Megalomma vesiculosum*, 49
- Megaloprepia magnifica*, 161
- Meganyctiphantes* sp., 3  
  *norvegica*, 72
- Megathuria crenulata*, 57
- Melanerpes erythrocephalus*, 161
- Melanoplus bivittatus*, 101
- Meles taxus*, 174
- Melopsittacus undulatus*, 161
- Meningodora miccylus*, 73  
  *mollis*, 73  
  *vesca*, 73
- Meretrix lusoria*, 54
- Mesiothea entomon*, 69
- Mesothuria* sp., 33  
  *intestinalis*, 45
- Metapenaeus affinis*, 74, 80
- Metatetranychus ulmi*, 98
- Metridium senile*, 38, 39
- Microciona* sp., 33  
  *prolifera*, 28
- Microcosmus sulcatus*, 122
- Microgaster conglomeratus*, 111
- Micropterus punctulatus*, 126  
  *salmoides*, 126
- Micruropus vortex*, 71  
  *wahli*, 71
- Misgurnus fossilis*, 138
- Modiolaria marmorata*, 54
- Modiolus modiolus*, 54
- Molgula acculata*, 122
- Moroco steindachneri*, 126
- Motocilla cinerea*, 161
- Mullus barbatus*, 126, 133
- Muraenalepis micros*, 126
- Musca domestica*, 106
- Mustela putorius*, 174
- Mustelus mustelus*, 137
- Mya arenaria*, 54  
  *truncata*, 54
- Myliobatis aquila*, 137
- Mysidea* sp., 72
- Mysis flexuosa*, 72  
  *mixta*, 72  
  *relicta*, 72
- Mytilus* sp., 2, 53  
  *californianus*, 52–54  
  *coruscus*, 54  
  *edulis*, 54  
  *galloprovincialis*, 54
- Myxicola infundibulum*, 49
- Myxilla* sp., 28  
  *mammillaris*, 122
- Myzus cerasi*, 105
- Nassa incrassata*, 57  
  *reticulata*, 57
- Natica nitida*, 57
- Navodon modestus*, 126
- Nemachilus barbatulus*, 138
- Nematobrachion boopis*, 72  
  *microps*, 72  
  *sexspinosis*, 72  
  *tenella*, 72
- Nematocarcinus* sp., 73
- Nematoscelis difficiles*, 72
- Neoamphitrite agulus*, 49  
  *figulus*, 49, 50
- Neohela monstrosa*, 71
- Neomysis integer*, 72
- Neothunnus albacora*, 126
- Nephrops norvegicus*, 3, 74, 80
- Nephthys caeca*, 49  
  *ciliata*, 49
- Neptunea* sp., 2
- Nereis pelagica*, 49  
  *virens*, 49  
  *zonata*, 49
- Nerophis acequorius*, 126  
  *ophidion*, 126
- Nezara viridula*, 104, 117
- Niphargus* sp., 89  
  *aquilex*, 71  
  *plateaui*, 89  
  *puteanus*, 89  
  *tatrensis*, 71
- Nitzschia closterium*, 52, 53
- Notostomus auricularius*, 73  
  *elegans*, 73  
  *gibbosus*, 73
- Notothenia gibberifrons*, 126  
  *rossi-masmorata*, 126
- Nucula sulcata*, 54
- Ocnius brunneus*, 45
- Octopus bimaculatus*, 60, 61

## 220 The biochemistry of the carotenoids

- Odocoileus hemionus nemonius*, 180  
  *virginianis*, 180
- Odotobutis obscura*, 126, 133
- Oedipoda* sp., 3, 101  
  *aurea*, 101  
  *miniata*, 101, 116  
  *schochii*, 101
- Ommastrephes pteropus*, 60
- Onychyrhynchus* sp., 126, 132, 135  
  *gorbusa*, 135  
  *keta*, 126, 135  
  *kisutch*, 126, 135  
  *masu*, 135  
  *masu masu*, 126  
  *masu macrostomus*, 126  
  *nerka*, 126, 135, 139  
  *tschawytscha*, 126, 135, 136
- Oniscus asellus*, 67, 69
- Ophidiasster ophidianus*, 42, 43
- Ophiocornis nigra*, 45
- Ophioderma longicauda*, 4, 45
- Ophiopholis* sp., 4  
  *aculeata*, 45
- Ophiopterus papillosa*, 44, 45
- Ophiothrix* sp., 4  
  *fragilis*, 45  
  *rudis*, 45  
  *spiculata*, 45
- Ophiura* sp., 4  
  *texturata*, 45
- Ophelitaspongia tenuis*, 28
- Oplophorous spinosus*, 73, 79
- Opsarichthys unicirrostris*, 126
- Orchestia gammarellus*, 3, 71, 87
- Orconectes limosus*, 6, 74, 78, 88  
  *pellucidus*, 74, 89  
  *rusticus*, 74
- Oriolus auratus*, 161  
  *oriolus*, 161  
  *xanthomus*, 161
- Orthagoriscus mola*, 137
- Oryzias latipes*, 127, 133, 144, 146
- Osilinus lineatus*, 57
- Osmerus eperlanus*, 127, 135–138, 140
- Ostrea edulis*, 54
- Oxyjulis californica*, 127
- Pachygrapsus marmoratus*, 6, 76, 81, 82, 85
- Pachymatista johnstonia*, 29
- Pagurus* sp., 3  
  *pollicaris*, 3, 75  
  *prideauxi*, 4, 6, 75, 78, 80, 82  
  *rubescens*, 75
- Palaemon* sp., 3  
  *adspersus*, 73  
  *carcinus*, 73  
  *fabricii*, 73
- serratus*, 3, 73, 74, 86, 89  
  *viridis*, 3, 74
- Palaemonetes vulgaris*, 3
- Palaemontes* sp., 89
- Palinurus japonicus*, 74  
  *vulgaris*, 6, 74, 78
- Pallasea cancelloides*, 71  
  *cancellus*, 71  
  *viridis*, 71
- Pandalus bonnieri*, 73  
  *borealis*, 3, 73, 80
- Panonychus lewisi*, 98  
  *ulmi*, 98
- Panulirus interruptus*, 86  
  *japonicus*, 80, 82, 84, 85
- Papilio* sp., 110, 116, 117  
  *alcinous*, 110  
  *protenor demetrius*, 110  
  *xuthus*, 110, 118
- Paracentrotus lividus*, 46, 47
- Paracottus kessleri*, 127  
  *kneri*, 127
- Paragorgia arborea*, 37
- Paralithodes brevipes*, 75, 80
- Paramuricea* sp., 37
- Parapandalus richardi*, 73
- Parapaspheae sulcatafrons*, 73
- Parapenaeus longirostris*, 3, 79
- Parapristiopoma filineatum*, 127
- Parasepia elegans*, 60
- Parasilurus asotus*, 127, 133, 145
- Parribacus antarctica*, 74  
  *ursa major*, 74
- Parus caeruleus*, 161  
  *major*, 161
- Patella depressa*, 2, 56, 57  
  *vulgata*, 2, 56, 57
- Patinopecten yessoensis*, 54
- Patiria miniata*, 43, 44
- Pecten albicans*, 54  
  *jacobaeus*, 54  
  *maximus*, 4, 5, 52–54  
  *opercularis*, 54  
  *strictus*, 54
- Pectunculus glycymeris*, 52, 54
- Pelobastes fuscus*, 155
- Pemphigus spirothecae*, 105
- Penaeus foliacea*, 80  
  *japonicus*, 74, 80, 82, 84, 85, 89  
  *orientalis*, 74
- Pennatula phosphorea*, 37
- Percha fluviatilis*, 127
- Perillus bioculatus*, 104
- Periphyllus lyropictus*, 105
- Peronella japonica*, 47
- Phakellia aruensis*, 29
- Phalera bucephala*, 111
- Phaneroptera quadripunctata*, 101, 117

- Pharomacrus mocino*, 161  
*Phascolosoma elongata*, 48  
*Phasianus colchicus*, 163  
*Philine aperta*, 57  
*Philosamia cynthia*, 110  
  *ricini*, 110  
*Phoenicircus nigricollis*, 161  
*Phoeniconaias minor*, 161, 163, 166  
*Phoenicoparrus andinus*, 161, 163, 167  
  *jamesi*, 161, 163  
*Phoenicopterus antiquorum*, 161  
  *chilensis*, 161  
  *ruber*, 161, 163, 166  
  *sibilatrix*, 161  
*Pholis gunellus*, 127  
*Phoxinus lagowski*, 127  
*Phyllophorus pollucidus*, 45  
*Phylloscopus sibilatrix*, 161  
*Phytodecta fornicate*, 106, 107  
*Phytoseiulus persimilis*, 97  
*Piaster ochraceous*, 43  
*Picus canis*, 161  
  *viridis*, 161  
*Pieris brassicae*, 110  
  *rapae crucivora*, 118  
*Pila glauca*, 58  
*Pimelometopon pulchrum*, 127, 144  
*Pinnotheres pisum*, 76, 85  
*Piona nodata*, 98  
*Pipillina suberea*, 29  
*Pisaster giganteus*, 4, 43  
*Planorbarius corneus*, 58, 59  
*Planorbis corneus*, 58  
  *planorbis*, 58  
*Platichthys flesus*, 127  
*Plattessa platessa*, 127  
*Platypoecilus maculatus*, 127  
*Platyrhinoidis triseriata*, 127  
*Plesionika edwardsii*, 36  
  *ensis*, 73, 79  
  *martia*, 73  
*Plesiopenaeus edwardsii*, 80, 82, 86, 88  
*Pleurobranchus* sp., 57  
  *elegans*, 52  
*Pleuroncodes planipes*, 75  
*Pleuronectes flesus*, 127  
  *kitt*, 127  
  *limanda*, 127  
  *microcephalus*, 127  
*Pliophryxus philonika*, 69, 90  
*Ploceus cucullatus*, 161  
*Plusia gamma*, 4, 117, 118  
*Pneumatophorous japonicus*, 136  
*Poephila gouldiae*, 161, 162  
*Pollenia* sp., 106  
*Pollicipes polymerus*, 5, 68  
*Polymastia fusca*, 29  
  *granulosa*, 29  
*Polymorphus minutus*, 90  
*Polynone spinifera*, 49  
*Pomacea* sp., 10, 16  
  *canaliculatus*, 5, 58  
  *doliooides*, 58  
  *glauca*, 58  
  *haustum*, 58  
  *sordia*, 58  
*Pomatoceros triqueter*, 49  
*Pomoxis annularis*, 127  
  *nigromaculatus*, 127  
*Pontella mediterranea*, 2  
*Pontellina fera*, 25  
  *gigantea*, 2  
*Pontellopsis regalis*, 67  
  *villosa*, 67  
*Pontoporeia affinis*, 71  
  *femorata*, 71  
*Poranita pulvillus*, 6, 43  
*Porcellana* sp., 3  
  *longicornis*, 75  
*Porpita* sp., 2, 5, 10, 36  
*Portunus* sp., 3  
  *brevirostris*, 76  
  *depurator*, 76  
  *longicornis*, 76  
  *persillus*, 76  
  *puber*, 3, 76  
  *tuberculatus*, 76, 80, 82, 84, 85  
*Potamon dehaari*, 76  
  *edulis*, 76  
*Praunus flexuosus*, 72  
*Priacanthus boops*, 127  
*Priapulus caudatus*, 48  
*Primnoa resedae formis*, 37  
*Prionatus carolinus*, 138  
*Pristipomoides amoenum*, 127  
  *filamentosus*, 127  
*Pristiurus melanostomus*, 137  
*Procambarus simulans simulans*, 89  
*Processa edulis*, 73, 90  
*Prognichthys agoo*, 127, 136  
*Proteus anguineus*, 155  
*Protula intestinum*, 49  
*Psammechinus miliaris*, 48  
*Psammobia ferroensis*, 54  
*Pseudochaenichthys georgianus*, 127  
*Pseudopotamilla occelata*, 49  
*Psolus* sp., 4  
  *fabricii*, 45  
  *phantalus*, 45  
*Pterocomma salicis*, 105  
  *steinheili*, 105  
*Ptilinopus monachus*, 161  
  *porphyreus*, 161  
  *superbus*, 161  
*Pungitius pungitius*, 127  
  *sinensis*, 127

## 222 The biochemistry of the carotenoids

- Pylomelana fransciana*, 160  
*Pyrrhocoris apterus*, 104  
*Pyrrhula pyrrhula*, 161
- Radiera springolaria*, 29  
*Raja batis*, 127, 137  
    *brachura*, 137  
    *circularis*, 138  
    *clavata*, 127, 138  
    *fullonica*, 138  
    *georgiana*, 127  
    *lintea*, 138  
    *montagui*, 138  
    *naevus*, 138  
    *oxyrhynchus*, 138  
    *radiata*, 138  
*Ramphastus toco*, 161  
*Ramphocelus carbo*, 161  
    *costaricensis*, 161  
    *flammingerus*, 161, 162  
    *icteronotus*, 161, 162  
*Rana arvalis*, 155  
    *catesbeiana*, 154  
    *esculenta*, 154, 156  
    *lessonae*, 155  
    *ridibunda*, 155  
    *temporaria*, 154, 156, 157  
*Raniceps raninus*, 127  
*Raspailia* sp., 29  
    *topsentii*, 29  
*Regaleucus glesne*, 127, 138  
*Regulus regulus*, 161  
*Reniera aquaeductus*, 29  
    *japonica*, 22, 23, 29  
*Rhaphidophorus typicus*, 29  
*Rhinogobius brunneus*, 127  
*Rhithropanopeus harrisi tridentatus*, 75, 86  
*Rhoxinustlagorski oxycephalus*, 127  
*Rhynchosciara americana*, 7, 17  
*Rissoa* sp., 57  
*Roccus saxatilis*, 127  
*Rondeletia bicolor*, 127  
*Rossia macrosoma*, 60  
*Rupicola peruviana*, 161, 162  
    *rupicola*, 161, 162
- Sabella penicilllus*, 49  
    *spallanzani*, 49  
*Saccabranthus fossilis*, 148  
*Sacculina carcinii*, 68  
    *neglecta*, 68  
*Salamandra maculosa*, 154  
*Salmo fario*, 127  
    *gaidneri*, 128, 135–140, 144  
    *salair*, 128, 132, 135, 136, 138  
    *trutta*, 128, 134–136, 138, 140  
    *trutta morpho fario*, 128, 135, 136, 140
- Salpa cylindrica*, 7, 17  
*Salvelinus* sp., 128  
    *fontinalis*, 128, 135, 140  
    *leucomaenis*, 128  
    *malma malma*, 128  
    *namaycush*, 128  
*Sardinia pilchardus*, 128  
*Sardinops melanosticta*, 128, 136  
*Sarotherodon mossambicus*, 128  
*Saxicava rugosa*, 54  
*Scalpellum scalpellum*, 68  
*Scapharca broughtonii*, 54  
    *globosa ursus*, 54  
    *satowi*, 54  
    *sub-crenata*, 54  
*Scapholebris aurita*, 2  
*Schistocerca gregaria*, 4, 101, 111, 112, 116,  
    117  
*Schizonobia sycophanta*, 98  
*Schizophorella unicornis*, 48  
*Schizotetrahyalus schizophorus*, 100  
*Scomber japonicus*, 128  
    *scombrus*, 128  
*Scombrids* *boobs*, 128  
*Scophthalmus norvegicus*, 128  
*Scorpaena scrofa*, 128  
*Scorpaenodes littoralis*, 128  
*Scribicularia plana*, 54  
*Scyllarus latus*, 3  
    *squamulosus*, 74  
*Sycomodon jonsonii*, 138  
*Sygnorhinus licha*, 138  
*Sebastes* sp., 146  
    *atrovirens*, 146  
    *baramenuke*, 128  
    *carnatus*, 146  
    *constellatus*, 146  
    *eos*, 146  
    *flavidus*, 128, 146  
    *marinus*, 128, 133, 145  
    *miniatu*, 146  
    *umbrosus*, 128, 146  
*Sebastiscus marmoratus*, 128  
*Sebastodes atrovirens*, 135  
    *carnatus*, 135  
    *constellatus*, 135  
    *eos*, 135  
    *flavidus*, 135  
    *miniatu*, 135  
    *umbrosus*, 135  
*Sebastolobus macrochir*, 128  
*Sepia officinalis*, 60, 61  
*Sepiola* sp., 60  
    *scandia*, 60  
*Sergestes* sp., 88  
    *corniculum*, 79  
*Sergia* sp., 88

- Serinus canaria canaria*, 161  
*canaria serinus*, 161
- Seriola quinqueradiata*, 128, 136
- Serrasalmo natterei*, 128, 132
- Sertularolla gaudichaudi*, 2
- Sesarma haematocheir*, 76  
*intermedia*, 76
- Setularella* sp., 36
- Sida* sp., 2
- Silurus glanis*, 128
- Simocephalus vetulus*, 2, 82, 86
- Siphonostoma diplochaitos*, 48  
*typhle*, 128
- Sipyloidea sipylus*, 102
- Solaster* sp., 4  
*borealis*, 44  
*endica*, 6, 43  
*papposus*, 43
- Solea vulgaris*, 136
- Solen ensis*, 54
- Somniosus microcephalus*, 138
- Sparus sabra*, 128
- Spatangus purpureus*, 47
- Sphaerechinus granularis*, 46, 47
- Sphaerooides lunaris*, 147
- Sphaeroma hookeri*, 69  
*rugicauda*, 69
- Sphinx ligustri*, 7, 117
- Spinus cucullatus*, 161
- Spirastrella insignis*, 29  
*poculoides*, 29
- Spirontocarous spinus*, 73
- Spisula solida*, 54  
*subtruncata*, 54
- Sprattus sprattus*, 137, 138
- Squalus acanthias*, 138
- Squatina squatina*, 138
- Squilla mantis*, 3, 76
- Steganoporella magnilabris*, 48
- Stenogorgia rosea*, 37
- Stenotomus chrysops*, 138
- Stephanolepis cirrifer*, 128
- Sterechinus neumayeri*, 6
- Stichopus parvimensis*, 45  
*tremula*, 45
- Stolephorus japonicus*, 128
- Stomatopoda*, 3
- Strongylocentrotus dröbachiensis*, 46–48  
*franciscanus*, 46, 47  
*lividus*, 46  
*purpuratus*, 46
- Styela rustica*, 122
- Styaster elegans*, 7, 18, 36  
*roseus*, 7, 18, 36  
*sanguineus*, 7, 18, 36
- Styloccheiron abbreviatum*, 72  
*elongatum*, 72
- Stylorella* sp., 29
- Subcoccinella vigintiquatuorpunctata*, 106, 107
- Suberites* sp., 2  
*domuncula*, 27, 29  
*ficus*, 29  
*flavus*, 29  
*mussa*, 29
- Syllarus sieboldi*, 74
- Syngnathus acus*, 128
- Systellaspis cristata*, 73  
*debilis*, 73, 79, 86
- Taliepus nuttallii*, 76
- Talitrus saltator*, 71, 87
- Tanymastix lacunae*, 5, 65, 78
- Tapes pullastra*, 55
- Tealia felina*, 37, 39
- Tedania* sp., 33  
*digitata*, 29  
*muggiana*, 29
- Tellina crassa*, 55
- Temora turbinata*, 67
- Tenebrio molitor*, 107
- Terebellides stroemii*, 49
- Testudo graeca*, 158
- Tethya amamensis*, 29  
*aurantium*, 29  
*lyncreum*, 29
- Tethyorraphis laevis*, 29
- Tetradon nigroviridis*, 147  
*steindachneri*, 147
- Tetraneura ulmi*, 105
- Tetranychus* sp., 97  
*atlanticus*, 98  
*cinnabarinus*, 98  
*pacificus*, 97–99  
*telarius*, 98  
*urticæ*, 97–100
- Tettigonia cantens*, 7, 101  
*viridissima*, 7, 101, 117
- Thelepus cincinnatus*, 49
- Theragra chalcogramma*, 128, 136
- Theskiiorais melanocephala*, 164
- Thetorium semisuberites*, 29
- Thoracophelia mucronata*, 49, 50
- Thunnus thynnus*, 128
- Thymallus thymallus*, 136
- Thyone* sp., 4  
*fusus*, 45
- Thysanoessa gregaria*, 72  
*inermis*, 72  
*raschii*, 72  
*spinifera*, 72
- Thysanopoda acutifrons*, 72  
*cristata*, 72

## 224 The biochemistry of the carotenoids

- monacantha*, 72  
*obtusifrons*, 72  
*pectinata*, 72  
*subaequalis*, 72  
*Tigriopus fulvus*, 67, 86  
*Tilapia* sp., 132  
    *mossambica*, 128, 136  
    *nihotica*, 128  
*Tinca tinca*, 128, 135, 138, 139  
*Todaropsis eblanae*, 60  
*Torpedo nobiliana*, 138  
*Toxochalina* sp., 29  
*Trachinus draco*, 128  
*Tragosia* sp., 2  
*Trematomus hansonii*, 128  
*Tribolodon hankoneensis*, 128  
*Trigla gurnardus*, 128  
*Trigonospora* sp., 48  
*Trikentriton* sp., 33  
    *helium*, 29  
*Triopha carpenteri*, 56, 57  
*Triops* sp., 2  
*Tripneustes gratila*, 46  
*Tritodynii horvathi*, 144  
*Triton cristatus*, 154, 155  
*Triturus carnifex*, 155, 156  
    *vulgaris*, 155  
*Trivia europaea*, 57  
*Trochus zizyphinus*, 57  
*Trombidium* sp., 98  
*Trygon pastinaca*, 138  
*Tubipora musica*, 37  
*Tubularia* sp., 36  
    *indivisa*, 36  
    *larynx*, 36  
*Tugalia gigas*, 57  
*Turbellaria* sp., 48  
*Uca pugilator*, 87  
*Undinula vulgaris*, 67  
*Unio pictorum*, 55  
*Unio rostratus gentilis*, 55, 56  
*Upogebia deltaura*, 74  
*Urobopyrus processae*, 69, 90  
*Varanus comodensis*, 158  
*Vellella* sp., 5, 16, 36  
    *lata*, 5, 36  
    *spirans*, 36  
    *velella*, 16, 36  
*Venus fasciata*, 55  
    *gallina*, 55  
    *japonica*, 55  
    *ovata*, 55  
*Verongia* sp., 29  
    *aerophobia*, 29  
*Volsella* sp., 2  
    *barbata*, 55  
    *modiolus*, 2, 55  
*Xantho poressa*, 76, 82  
*Xenodon merrenii*, 157  
*Xipholena*, 161  
*Xiphophorus helleri*, 129  
    *letteri*, 134  
    *maculatum*, 129  
*Zacco platypus*, 129  
    *temminke*, 129  
*Zoarces viviparus*, 129