3 Antitumor Activity of Dietary Carotenoids, and Prospects for Applications in Therapy: Carotenoids and Cancer by Raman Imaging 31
Halina Abramczyk and Jakub Surmacki

3.1 Results 33
3.2 Conclusions 38
3.3 Perspectives 38
References 39

4 Photoprotection and Radiation Protection by Dietary Carotenoids 43
Fritz Boehm, Ruth Edge, Terence George Truscott, and Christian Witt

4.1 Introduction 43
4.2 Carotenoids and singlet oxygen 44
4.2.1 Organic solvents 44
4.2.2 Cell models 46
4.2.3 Cells 47
4.3 Radicals 48
4.3.1 Radical cations 48
4.3.2 Carotenoid–radical adducts 49
4.3.3 Neutral radicals 49
4.3.4 Radical anions 50
4.3.5 The interaction of CARs with the superoxide radical and its protonated conjugated acid 51
4.4 Future prospects and challenges 53
4.5 Conclusion 53
Acknowledgments 54
References 54

5 Macular Carotenoids: Human Health Aspects 59
Aruna Gorusupudi and Paul S. Bernstein

5.1 Introduction 59
5.2 Macular pigment distribution 60
5.3 Human health aspects 61
5.4 Age-related macular degeneration (AMD) 61
5.5 Macular carotenoid absorption 63
5.6 Stereocarotenoid and metabolism of macular carotenoids 65
5.7 Measurement of macular carotenoids 67
5.8 Conclusions and perspectives 68
References 68

Part II Spectroscopy 75

6 Vibrational Spectroscopy as a Tool to Investigate Carotenoids 77
Jan Cz. Dobrowolski

6.1 Introduction 77
6.2 Vibrations of carotenoids 77
6.2.1 Geometry 78
6.2.2 Geometrical cis-trans isomerism 78
6.2.3 Syn-periplanar (s-cis) or anti-periplanar (s-trans) conformations 79
6.2.4 π-electron delocalization 79
6.2.5 The nature, shape, and energy of the electronic ground and excited states 79
6.2.6 Electron affinity, ionization, reduction, and oxidation potentials 80
6.2.7 The nature and shape of molecular vibrations and vibrational coupling patterns 80
6.2.8 The role of methyl groups attached to the polyene chain and the end groups 81
6.3 Recent applications of vibrational spectroscopy to study natural carotenoids 81
6.3.1 Bacteria lichens and algae 83
6.3.2 Corals and pearls 87
6.3.3 Art and archeology 90
6.4 Perspectives 91
Acknowledgments 92
References 92

7 Structural Studies of Carotenoids in Plants, Animals, and Food Products 103
Takashi Maoka
7.1 Introduction 103
7.2 Extraction and pre-preparation of carotenoids 103
7.3 Chromatography and separation of carotenoids 105
7.3.1 Column chromatography and thin-layer chromatography 105
7.3.2 High-performance liquid chromatography 105
7.4 Quantification of carotenoids 106
7.5 Identification and structural elucidation of carotenoids 106
7.5.1 Chemical dramatization 107
7.5.2 UV-Vis, IR, and Raman spectrometry 107
7.5.3 Mass spectrometry 108
7.5.4 NMR spectrometry 111
7.6 Determination of absolute configuration of carotenoids 120
7.6.1 Circular dichroism (CD) spectroscopy 120
7.6.2 NMR spectrometry using the modified Mosher method 122
7.6.3 Synthetic approach 123
7.6.4 X-ray crystallography 124
7.6.5 Examples of structural determination of natural carotenoids 124
7.7 Conclusion (future prospects and challenges) 126
Acknowledgments 126
References 127

8 In Situ Studies of Carotenoids in Plants and Animals 131
Malgorzata Baranska, Jan Cz. Dobrowolski, and Grzegorz Zajac
8.1 Introduction 131
8.2 Plants 131
8.3 Animals 134
8.4 Humans 137
8.4.1 Skin 137
8.4.2 Macular pigment 139
8.4.3 Carotenoids in single human cells 140
8.5 Perspectives 142
Acknowledgments 143
References 143


9 Carotenoids in Pigment–Protein Complexes: Relation between Carotenoid Structure and Function
Wieslaw I. Gruszecki

9.1 Biological functions of carotenoids 147
9.2 Carotenoids in pigment–protein complexes 149
9.3 Final remarks 154
9.4 Perspectives 155
Acknowledgments 155
References 155

Part III Technology

10 Carotenoid Biosynthesis and Regulation in Plants
Rafal Baranski and Christopher I. Cazzonelli

10.1 Biosynthetic pathways 161
  10.1.1 Occurrence in nature 161
  10.1.2 Cellular localization and compartmentalization 162
  10.1.3 Pathways to generate isoprenoid precursors for carotenoid biosynthesis 163
  10.1.4 The main pathway toward carotenoid biosynthesis 165
  10.1.5 Specialty branches of the pathway 169
10.2 Regulation of carotenoid biosynthesis 170
  10.2.1 Cross-talk between and within the carotenoid and MEP pathways 171
  10.2.2 Environmental and developmental control 171
  10.2.3 Regulation by epigenetic and posttranscriptional mechanisms 172
  10.2.4 Carotenoids in plastid biogenesis, differentiation, and control 173
  10.2.5 Enzyme localization and metabolon compartmentalization 174
  10.2.6 Carotenoid degradation and production of signaling metabolites 175
10.3 Biofortification and health perspectives 178
Acknowledgments 179
References 179

11 Carotenoid Bioavailability from the Food Matrix: Toward Efficient Extraction Procedures
Hartwig Schulz

11.1 Introduction 191
11.2 Occurrence of carotenoids in food materials 193
11.3 Bioavailability and bioefficiency of carotenoids 194
11.4 Extraction of carotenoids from various food matrices 197
11.5 Conclusions 210
11.6 Perspectives 211
References 211

12 Carotenoid Production by Bacteria, Microalgae, and Fungi
Ralf Martin Schweiggert and Reinhold Carle

12.1 Introduction 217
12.2 Microbial biosynthesis of carotenoids 218
12.3 Carotenoid-rich microorganisms
  12.3.1 Microalgae 223
  12.3.2 Yeasts and filamentous fungi 225
  12.3.3 Bacteria 226
12.4 Selected examples of biotechnological carotenoid production 228
12.4.1 Production of β-carotene 228
12.4.2 Production of astaxanthin 230
12.4.3 Production of lycopene 232
12.4.4 Production of lutein and zeaxanthin 233
12.5 Perspectives and conclusions 234
References 235

13 Impact of Stress Factors on Carotenoid Composition, Structures, and Bioavailability in Microbial Sources 241
Agnieszka Kaczor and Marta Z. Pacia
13.1 Introduction 241
13.2 Light 242
13.3 Temperature 246
13.4 Carbon and nitrogen sources 249
13.5 Aerobic versus anaerobic conditions 250
13.6 Inorganic and organic salts 250
13.7 Other chemical agents 253
13.8 pH 253
13.9 Multiple stress factors 254
13.10 Perspectives and conclusions 254
Acknowledgments 255
References 255

14 Syntheses with Carotenoids 261
Hans-Richard Sliwka and Vassilia Partali
14.1 Introduction 261
14.2 Reaction with double bonds 263
14.2.1 Hydrogenation 263
14.2.2 Halogenation 263
14.2.3 Oxidation 263
14.2.4 Electron transfer from and to carotenoids 264
14.2.5 Iron carbonyl 264
14.2.6 Nitration 265
14.2.7 In-chain modification 265
14.3 Transformation of substituents 265
14.3.1 –C=O → –C=C– 265
14.3.2 –CH=O → CH=S 267
14.3.3 –C=O → –C=S 268
14.3.4 –C=O → –C=OH 268
14.3.5 Inversion of –OH 269
14.3.6 –OH → –F, –Cl, –Br, and –I 269
14.3.8 –OH → –OR 270
14.3.9 –OH → glycides 271
14.3.10 Reactions with carotenoid epoxides 271
14.3.11 Reactions with halogen carotenoids 271
14.3.12 Metal complexes with carotenols, carotenals, and carotenones 272
14.4 Preparative derivatization 272
14.5 Syntheses with carotenoid acids and carotenols 272
14.5.1 –COOH → –COCl 273
14.5.2 –COOH → COO– M+ 273
14.5.3 −COOH → COOR 273
14.5.4 −COOR → −COOH 277
14.5.5 −COOH → −CONH₂ 279
14.5.6 −COOH → −CO–O–OC– (carotenoid anhydrides) 279

14.6 Carotenoid reactions with Au 280
14.7 Valuation and conclusion 281
Acknowledgments 282
References 283

Index 291