

Handbook of Natural Colorants

Edited by

THOMAS BECHTOLD

and

RITA MUSSAK

Leopold-Franzens University, Austria



A John Wiley and Sons, Ltd., Publication

Handbook of Natural Colorants

**Wiley Series
in
Renewable Resources**

Series Editor

Christian V. Stevens, Department of Organic Chemistry, Ghent University, Belgium

Titles in the Series

Wood Modification: Chemical, Thermal and Other Processes

Callum A. S. Hill

Renewables-Based Technology: Sustainability Assessment

Jo Dewulf and Herman Van Langenhove (Editors)

Introduction to Chemicals from Biomass

James H. Clark and Fabien E. I. Deswarte (Editors)

Biofuels

Wim Soetaert and Erick Vandamme (Editors)

Handbook of Natural Colorants

Thomas Bechtold and Rita Mussak (Editors)

Forthcoming Titles

Starch Biology, Structure and Functionality

Anton Huber and Werner Praznik

Industrial Application of Natural Fibres: Structure, Properties and Technical Applications

Jörg Müssig (Editor)

Surfactants from Renewable Resources

Mikael Kjellin and Ingegärd Johansson (Editors)

Thermochemical Processing of Biomass

Robert C. Brown (Editor)

Bio-based Polymers

Martin Peter and Telma Franco (Editors)

Handbook of Natural Colorants

Edited by

THOMAS BECHTOLD

and

RITA MUSSAK

Leopold-Franzens University, Austria



A John Wiley and Sons, Ltd., Publication

Copyright © 2009

John Wiley & Sons Ltd,

The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at www.wiley.com.

The right of the author to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book. This publication is designed to provide accurate and authoritative information in regard to the subject matter covered. It is sold on the understanding that the publisher is not engaged in rendering professional services. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

The publisher and the author make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of fitness for a particular purpose. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for every situation. In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. The fact that an organization or Website is referred to in this work as a citation and/or a potential source of further information does not mean that the author or the publisher endorses the information the organization or Website may provide or recommendations it may make. Further, readers should be aware that Internet Websites listed in this work may have changed or disappeared between when this work was written and when it is read. No warranty may be created or extended by any promotional statements for this work. Neither the publisher nor the author shall be liable for any damages arising herefrom.

Library of Congress Cataloging-in-Publication Data

Bechtold, Thomas.

Handbook of natural colorants / Thomas Bechtold, Rita Mussak.

p. cm.

Includes bibliographical references and index.

ISBN 978-0-470-51199-2 (cloth : alk. paper) 1. Dyes and dyeing. 2. Dye plants.

3. Dyes and dyeing—Chemistry. I. Mussak, Rita. II. Title.

TP919.B43 2009

667'.26—dc22

2008053906

A catalogue record for this book is available from the British Library.

ISBN 978-0-470-511992

Set in 10/12pt Times by Integra Software Services Pvt. Ltd, Pondicherry, India

Printed and bound in Great Britain by CPI Antony Rowe, Chippenham, Wiltshire

Contents

List of Contributors	xv
Series Preface	xix
Preface	xxi
Part I Historical Aspects	1
1 History of Natural Dyes in the Ancient Mediterranean World	3
<i>Maria J. Melo</i>	
1.1 Introduction	3
1.1.1 Ancient Mediterranean World	3
1.1.2 Dyes from Antiquity	4
1.1.3 Unveiling the Secrets of Ancient Dyes with Modern Science	5
1.2 Ancient Reds	6
1.2.1 Anthraquinone Reds	6
1.2.2 Redwoods	8
1.2.3 Flavylum/Anthocyanin Reds	8
1.3 Ancient Blues	10
1.3.1 Indigo Blues	10
1.3.2 Anthocyanin Blues	12
1.4 Ancient Purple (Tyrian Purple)	13
1.5 Ancient Yellows	15
1.5.1 Flavonoid Yellows	15
1.5.2 Carotenoid Yellows	17
1.5.3 Chalcone and Aurone Yellows	17
Acknowledgement	17
References	17

2 Colours in Civilizations of the World and Natural Colorants: History under Tension	21
<i>Dominique Cardon</i>	
2.1 Introduction	21
2.2 The Triumph of Mauvein: Synthetic Fulfilment of the Antique Purplemania	22
2.3 Blue: from Kingly Regional to Globally Democratic	23
2.4 Red and Yellow: from Micro to Macro Scales	24
2.5 What Future for Natural Colorants in the Dawning Era of Renewable Resources?	25
Acknowledgement	26
References	26
3 History of Natural Dyes in North Africa ‘Egypt’	27
<i>Harby Ezzeldeen Ahmed</i>	
3.1 Introduction	27
3.2 Natural Dyes in Pharaonic Textiles	28
3.3 Dyeing Techniques	28
3.4 Dye Sources	29
3.4.1 Woad	29
3.4.2 Indigo	30
3.4.3 Red	30
3.4.4 Yellow	30
3.4.5 Black	31
3.4.6 Brown	31
3.4.7 Green	31
3.4.8 Purple	31
3.5 Dyeing in Coptic Textiles	31
3.6 Wool Dyed Fabric with Natural Dye	33
3.7 Dyes in Islamic Textiles	33
3.8 Mordants	34
References	36
Part II Regional Aspects of Availability of Plant Sources	37
4 Dye Plants in Europe	39
<i>Andrea Biertümpfel and Günter Wurl</i>	
4.1 Introduction	39
4.2 Potential European Dye Plants	39
4.3 Cultivation of Dye Plants Yesterday and Now	40
4.4 Modern Cultivation Methods for Important European Dye Plants	41
4.4.1 General Facts	41
4.4.2 Blue Dyeing Plants	42

4.4.3	Red Dyeing Plants	43
4.4.4	Yellow Dyeing Plants	44
4.4.5	Brown Dyeing Plants	46
4.5	Production of Dye Extracts	48
4.6	Relevant Examples for the Application	50
4.7	Conclusions, Discussion and Summary	50
	References	51
5	Dyes in South America	53
	<i>Veridiana Vera de Rosso and Adriana Zerlotti Mercadante</i>	
5.1	Introduction	53
5.2	Annatto	55
5.3	Turmeric	57
5.4	Marigold	59
5.5	Cochineal and Carmine	60
	Acknowledgements	62
	References	62
6	Natural Dyes in Eastern Asia (Vietnam and Neighbouring Countries)	65
	<i>Hoang Thi Linh</i>	
6.1	Introduction	65
6.2	Annatto (Botanical Name <i>Bixa orellana</i> L., Family Bixaceae)	65
6.3	Tea (Botanical Name <i>Camellia sinensis</i> (L.) Kuntze, Family Theaceae)	67
6.4	Umbrella Tree (Botanical Name <i>Terminalia catappa</i> L., Family Combretaceae)	67
6.5	<i>Diospyros mollis</i> – Mackloeur (Botanical Name <i>Diospyros mollis</i> L. Griff, Family Ebenaceae)	68
6.6	Indigo (Botanical Name <i>Indigofera</i> L., Family Fabaceae)	68
	6.6.1 <i>Indigofera tinctoria</i> L.	68
	6.6.2 <i>Indigofera galeoides</i> DC.	69
	6.6.3 <i>Strobilanthes cusia</i> (<i>Baphicacanthus</i>)	69
6.7	Henna (kok khan, or khao youak in Laos) (Botanical Name <i>Lawsonia spinosa</i> L., Family Lythraceae)	69
6.8	Nacre (Botanical Name <i>Khaya senegalensis</i> , Family Meliaceae)	69
6.9	Sappan Wood (Botanical Name <i>Caesalpinia sappan</i> L., Family Fabaceae)	69
6.10	<i>Sophora japonica</i> Flowers (Botanical Name <i>Sophora japonica</i> L., Family Leguminosae)	70
6.11	Turmeric (Botanical Name <i>Curcuma longa</i> L., Family Zingiberaceae)	70
6.12	Sapodilla (Botanical Name <i>Manilkara zapota</i> L. or <i>Achras zapota</i> , Family Sapotaceae)	70
6.13	Betel (Botanical Name <i>Piper betle</i> L., Family Piperaceae)	71
6.14	Eucalyptus (Botanical Name <i>Eucalyptus</i> , Family Myrtaceae)	71

6.15	Caesalpinia Yellow (Botanical Name <i>Caesalpinia pulcherrima</i> L., Family Fabaceae)	71
6.16	Brow-tuber (Botanical Name <i>Dioscorea cirrhosa</i> Lour, Family Dioscoreaceae)	71
Part III Colorant Production and Properties		73
7	Indigo – Agricultural Aspects	75
	<i>Philip John and Luciana Gabriella Angelini</i>	
7.1	Introduction	75
7.2	<i>Isatis</i>	76
	7.2.1 Introduction	76
	7.2.2 Agronomy	77
7.3	<i>Persicaria (Polygonum)</i>	92
	7.3.1 Introduction	92
	7.3.2 Agronomy	93
7.4	<i>Indigofera</i>	101
	Acknowledgements	103
	References	103
8	Indigo – Extraction	105
	<i>Philip John</i>	
8.1	Introduction	105
8.2	Methods of Determining Indigo	106
8.3	Precursors in the Plants and Indigo Formation	108
8.4	Extraction Procedures	114
	8.4.1 Traditional Process Using Crushed Leaf Material	114
	8.4.2 Steeping in Water	117
8.5	Purity of Natural Indigo	126
	Acknowledgements	130
	References	130
9	Anthocyanins: Nature’s Glamorous Palette	135
	<i>Maria J. Melo, Fernando Pina and Claude Andary</i>	
9.1	Chemical Basis	135
	9.1.1 Chemical Structures	135
	9.1.2 Equilibria in Solution	137
	9.1.3 Colour and Colour Stability	140
	9.1.4 Anthocyanins as Antioxidants	141
9.2	Natural Sources for Anthocyanins	142
	9.2.1 Plant Sources, Content, Influencing Parameters	142

9.3	Applications	144
9.3.1	Food Colorants	144
9.3.2	Other Uses	145
9.4	Examples of Commercial Products and Processing	146
	References	147
10	Natural Colorants – Quinoid, Naphthoquinoid and Anthraquinoid Dyes	151
	<i>Thomas Bechtold</i>	
10.1	Introduction	151
10.2	Benzoquinone Dyes	151
10.3	Naphthoquinone Dyes	152
10.3.1	Lawson (2-hydroxy-1,4-naphthoquinone, CI Natural Orange 6)	153
10.3.2	Juglone (5-hydroxy-1,4-naphthoquinone, CI Natural Brown 7)	156
10.4	Anthraquinone Dyes	157
10.4.1	Main Components Emodin and Chrysophanol – <i>Rheum</i> Species and <i>Rumex</i> Species	157
10.4.2	Main Components Alizarin and/or Pseudopurpurin/Purpurin	159
10.5	Other Sources of Anthraquinoid Dyes	171
	References	171
11	Dyes from Lichens and Mushrooms	183
	<i>Riikka Räisänen</i>	
11.1	Use of Lichen and Mushroom Dyes in the Past	183
11.2	Cultivation of Lichens and Mushrooms	184
11.3	Dyestuffs in Lichens and Mushrooms	185
11.3.1	Lichen Dyestuffs: Orchils and Litmus	185
11.3.2	Yellowish, Brownish and Reddish Colorants from Lichen	191
11.3.3	Benzoquinone Derivatives	192
11.3.4	Anthraquinones	192
11.3.5	Other Colorants of Fungi	196
11.4	Colour-fastness of Lichen and Mushroom Dyes	197
11.5	New Approaches to Lichen and Fungal Natural Dyes	198
	References	198
12	Tannins and Tannin Agents	201
	<i>Riitta Julkunen-Tiitto and Hely Häggman</i>	
12.1	Introduction	201
12.2	Chemical Structure, Biosynthesis and Degradation	203
12.3	Properties of Tannins	207
12.4	Chemical Activities of Tannins	208

12.5	Analysis of Tannins	209
12.5.1	Sample Preservation	209
12.5.2	Extraction and Purification	209
12.5.3	Quantification of Tannins	210
12.6	Use, Toxicology and Safety Aspects of Tannins	212
	References	214
13	Carotenoid Dyes – Properties	221
	<i>U. Gamage Chandrika</i>	
13.1	Introduction	221
13.1.1	Occurrence of Carotenoids	221
13.1.2	Chemistry of Carotenoids	221
13.1.3	Chemical Characteristics of Natural Carotenoids	222
13.2	Properties and Functions of Carotenoids	225
13.2.1	Carotenoids Role as Pro-vitamin A	225
13.2.2	Use of Carotenoids as Markers of Dietary Practices	227
13.2.3	Carotenoids as Antioxidants	227
13.2.4	Carotenoids in the Macular Region of the Retina	227
13.2.5	Carotenoids as Anticancer Agent	228
13.2.6	Carotenoids as a Natural Colorant	228
13.3	General Procedure for Carotenoid Analysis	228
13.3.1	Sampling	228
13.3.2	Extraction	230
13.3.3	Saponification of Carotenoids	230
13.3.4	Chromatographic Separation	230
13.3.5	Chemical Tests	231
13.3.6	Detection and Identification of Carotenoids	231
13.3.7	Quantification of Carotenoids	233
13.4	Problems in Carotenoid Analysis	233
	References	234
14	Carotenoid Dyes – Production	237
	<i>U. Gamage Chandrika</i>	
14.1	Factors Influencing Carotenoid Composition in Plant Sources	237
14.1.1	Stage of Maturity	237
14.1.2	Cultivar or Varietal Differences	238
14.1.3	Climatic or Geographic Effects	238
14.1.4	Post-harvest Storage and Packing	239
14.1.5	Changes in Processing/Cooking	239
14.1.6	Effect of Agrochemicals	241
	References	241

15 Chlorophylls	243
<i>Ursula Maria Lanfer Marquez and Daniela Borrmann</i>	
15.1 Introduction	243
15.2 Chlorophylls as Colorants	244
15.3 Other Applications of Chlorophylls and their Derivatives	247
15.4 Chemical Structures and Physicochemical Properties	247
15.5 Stability and Analysis	250
15.6 Sources, Storage and Handling	250
15.7 Purity, Standardization and Quality Control	251
15.8 Toxicological and Safety Aspects	252
References	253
Part IV Application in Technical Use and Consumer Products	255
16 Flavonoids as Natural Pigments	257
<i>M. Monica Giusti and Taylor C. Wallace</i>	
16.1 Introduction	257
16.2 Role of Localized Flavonoids in the Plant	258
16.3 General Flavonoid Chemical Structure	258
16.4 Biosynthesis of Flavonoids	259
16.5 Anthocyanins as Natural Colorants	261
16.5.1 Color Stability	261
16.5.2 Structure	261
16.5.3 Structural Transformation and pH	263
16.5.4 Temperature	264
16.5.5 Oxygen and Ascorbic Acid	264
16.5.6 Light	265
16.5.7 Enzymes and Sugars	265
16.5.8 Sulfur Dioxide	266
16.5.9 Co-pigmentation and Metal Complexation	267
16.6 Other Flavonoids as Natural Colorants	268
16.6.1 Yellow Flavonoid Pigments	268
16.6.2 Tannins	269
16.7 Therapeutic Effects of Flavonoids in the Diet	270
16.8 Regulations on the Use of Flavonoid Colorants	271
References	272
17 Application of Natural Dyes in the Coloration of Wood	277
<i>Martin Weigl, Andreas Kandelbauer, Christian Hansmann, Johannes Pöckl, Ulrich Müller and Michael Grabner</i>	
17.1 Introduction	277
17.1.1 General Basics	278
17.1.2 Color Measurement	282
17.1.3 Color Stability	283

17.2	Coatings	283
17.3	Dyes	285
17.3.1	Dyeing for Analytical Purposes	285
17.3.2	Impregnation	286
17.4	Color Modification	290
17.4.1	Drying	291
17.4.2	Steaming	295
17.4.3	Thermal Treatment	297
17.4.4	Ammoniation	298
17.4.5	Bleaching	301
17.4.6	Enzymatic Treatment	303
17.4.7	Radiation	305
17.5	Outlook	308
	References	308
18	Natural Colorants in Textile Dyeing	315
	<i>Rita A. M. Mussak and Thomas Bechtold</i>	
18.1	Introduction	315
18.2	Reasons for Natural Coloration	316
18.3	Analysis of a Dyeing Process	317
18.3.1	Water	318
18.3.2	Energy	318
18.3.3	Dyestuff and Chemicals (Mordants and Auxiliaries)	319
18.3.4	Machinery	321
18.4	Basics of Natural Dyeings	321
18.4.1	Requirements of the Dyestuff	321
18.4.2	Dye-ability of Substrates	321
18.4.3	Standardization of the Dyestuff	326
18.4.4	Ecological Aspects	327
18.4.5	Aspects of Application	328
18.4.6	Dyeing Technology	329
18.4.7	Mordanting	330
18.4.8	Standardization of the Coloration Process	331
18.4.9	Mixtures of Plant Material	331
18.5	Natural Dyes on an Industrial Scale	332
18.5.1	Hank Dyeing of Woolen Yarn and Production of Woolen Caps	332
18.5.2	Dyeing of Cones in a Yarn Dyeing Machine	333
18.5.3	Dyeing of Cotton Fabric on a Jet Dyeing Machine	333
18.5.4	Dyeing of Cotton Fabric on a Jig Dyeing Machine	333
18.5.5	Fabric Dyeing on a Garment Dyeing Machine	333
18.5.6	Dyeing of Polyamide Tights in a Paddle Dyeing Machine	334
18.6	Conclusion	334
	Acknowledgment	334
	References	335

19	Natural Colorants in Hair Dyeing	339
	<i>Thomas Bechtold</i>	
19.1	Introduction	339
19.2	Human Hair	340
19.3	General Requirements on Hair Dyeing Concepts	340
19.4	Chemical Principles of Dyestuff Binding	341
19.5	Relevant Natural Dyes for Hair Dyeing	342
19.5.1	Naphthoquinone Dyes – Henna and Walnut	342
19.5.2	Indigo	343
19.5.3	Metal Complexes	345
19.5.4	Metal Reaction Dyes	346
19.5.5	Anthraquinoid Dyes	347
19.6	Specialities	347
19.7	Regulations	347
	References	347
Part V	Environmental	351
20	Environmental Aspects and Sustainability	353
	<i>Erika Ganglberger</i>	
20.1	Introduction	353
20.2	Supply of Plant Material	354
20.2.1	Cultivation of Dye Plants	354
20.2.2	Residual Materials and By-products	355
20.2.3	Selection Process for a Sustainable Supply of Plant Material	356
20.3	Processing to Dyestuff	357
20.3.1	Energy Consumption	358
20.3.2	Water Consumption	359
20.4	Application of Colouring Matter	360
20.4.1	Dyeing Procedure	361
20.5	Considerations Concerning the Life Cycle	361
20.5.1	Raw Material	361
20.5.2	Processing of Raw Material	362
20.5.3	Extraction of Dyestuff	362
20.5.4	Dyeing Procedure	363
20.5.5	Transport	363
20.6	Conclusion	364
20.6.1	Dealing with Sustainability	364
	References	365
21	Economic Aspects of Natural Dyes	367
	<i>Susanne Geissler</i>	
21.1	Introduction	367
21.2	Basic Requirements for the Industrial Use of Natural Colorants	368

21.3	Challenges for the Industrial Use of Natural Colorants	370
21.3.1	Quality of Raw Material and Reproducibility of Colours	370
21.3.2	Range of Available Colours	370
21.4	Consumer Expectations	371
21.4.1	Market Research for Naturally Dyed Products	372
21.5	Production Costs of Natural Colorant Products	375
21.5.1	Cost Categories	375
21.5.2	Aspects Influencing Production Costs	376
21.5.3	Prices of Synthetic Dyes – How Much Are Textile Companies Prepared to Pay for Dyes?	378
21.5.4	Acceptable Production Costs through a Mixed Portfolio (Agricultural Primary Production and Residues from Other Production Processes)	379
21.6	Closed-Loop Economy: Towards a Zero-Emission and Zero-Waste Society	381
21.7	Conclusion: Aspects Influencing Market Development for Natural Colorants	382
	References	383
	Index	385

List of Contributors

Harby Ezzeldeen Ahmed Department of Conservation, Faculty of Archeology, Cairo University, Giza, Egypt. Present address: Tomes IV, Biotechnology–Chemical Engineering School, National Technical University of Athens, 9 Iroon Polytechniou, 15780, Zografou, Athens, Greece

Claude Andary Laboratoire de Botanique, Phytochimie et Mycologie, Faculte de Pharmacie, UMR 5175 (CEFE)*, 15, Ave Charles Flahault, FR-34093 Montpellier Cedex 5, France

Luciana Gabriella Angelini Dipartimento di Agronomia e Gestione dell' Agroecosistema, University of Pisa, Via S. Michele degli Scalzi, 2 I-56127 Pisa, Italy

Thomas Bechtold Research Institute for Textile Chemistry and Textile Physics, University Innsbruck, Hoehsterstrasse 73, A-6850 Dornbirn, Austria

Andrea Biertümpfel Thüringer Landesanstalt für Landwirtschaft, Apoldaer Straße 4, D-07778 Dornburg, Germany

Daniela Borrmann Department of Food and Experimental Nutrition, Faculty of Pharmaceutical Science, University of São Paulo, Av. Prof Lineu Prestes, 580, Bloco 14, 05508-900 São Paulo, SP, Brazil

Dominique Cardon Le Vert, 30460 Cognac, France

U. Gamage Chandrika Department of Biochemistry, Faculty of Medical Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka

Erika Ganglberger Austrian Society for Environment and Technology, Hollandstrasse 10/46, 1020 Vienna, Austria

Susanne Geissler University of Applied Sciences Wiener Neustadt FHWN, Wieselburg, Zeiselgraben 4, A-3250 Wieselburg, Austria

M. Monica Giusti The Ohio State University, Parker Food Science and Technology, Room 110, 2015 Fyffe Road, Columbus, OH 43210, USA

Michael Grabner BOKU – University of Natural Resources and Applied Life Sciences Vienna, Peter Jordan Str. 82, A-1190 Vienna, Austria

Hely Häggman University of Oulu, Department of Biology, PO Box 3000, FIN-90014 Oulu, Finland

Christian Hansmann Wood Kplus, Competence Center for Wood Composites and Wood Chemistry, St. Peter Str. 25, A-4021 Linz, Austria c/o BOKU – University of Natural Resources and Applied Life Sciences Vienna, Peter Jordan Str. 82, A-1190 Vienna, Austria

Philip John School of Biological Sciences, Harborne Building, University of Reading, Whiteknights, Reading RG6 6AS, UK

Riita Julkunen-Tiitto University of Joensuu, Faculty of Biosciences, PO Box 111, FIN-80101 Joensuu, Finland

Andreas Kandelbauer BOKU – University of Natural Resources and Applied Life Sciences Vienna, Peter Jordan Str. 82, A-1190 Vienna, Austria c/o Wood Carinthian Competence Center, Klagenfurter Str. 87-89, A-9300 St. Veit/Glan, Austria

Hoang Thi Linh Faculty of Textile–Garment Technology and Fashion Design, Hanoi University of Technology, 1-Dai co Viet, Hanoi, Vietnam

Ursula Maria Lanfer Marquez Department of Food and Experimental Nutrition, Faculty of Pharmaceutical Science, University of São Paulo, Av. Prof Lineu Prestes, 580, Bloco 14, 05508-900 São Paulo, SP, Brazil

Maria J. Melo Department of Conservation and Restoration, Requitme and CQFB, Faculty of Sciences and Technology, New University of Lisbon, Campus Caparica, 2829-516 monte da Caparica, Portugal

Adriana Zerlotti Mercadante Department of Food Science, Faculty of Food Engineering, University of Campinas – UNICAMP, CP: 6121, 13083-862, Campinas, Brazil

Ulrich Müller Wood Kplus, Competence Center for Wood Composites and Wood Chemistry, St. Peter Str. 25, A-4021 Linz, Austria c/o BOKU – University of Natural Resources and Applied Life Sciences Vienna, Peter Jordan Str. 82, A-1190 Vienna, Austria

Rita A. M. Mussak Institute for Textile Chemistry and Textile Physics, University of Innsbruck, Hoehsterstrasse. 73, A-6850 Dornbirn, Austria

Fernando Pina REQUIMTE, CQFB, Chemistry Department, Faculty of Sciences and Technology, New University of Lisbon, 2829-516 Monte da Caparica, Portugal

Johannes Pöckl Wood Kplus, Competence Center for Wood Composites and Wood Chemistry, St. Peter Str. 25, A-4021 Linz, Austria c/o BOKU – University of Natural Resources and Applied Life Sciences Vienna, Peter Jordan Str. 82, A-1190 Vienna, Austria

Riikka Räisänen Department of Home Economics and Craft Science, PO Box 8, University of Helsinki, Fin-00014 Helsinki, Finland

Veridiana Vera de Rosso Department of Health Science, Federal University of São Paulo – UNI FESP, 11030-400, Santos, Brazil

Taylor C. Wallace The Ohio State University, Parker Food Science and Technology, Room 110, 2015 Fyffe Road, Columbus, OH 43210, USA

Martin Weigl Wood Kplus, Competence Center for Wood Composites and Wood Chemistry, St. Peter Str. 25, A-4021 Linz, Austria c/o BOKU – University of Natural Resources and Applied Life Sciences Vienna, Peter Jordan Str. 82, A-1190 Vienna, Austria

Günter Wurl Thüringer Landesanstalt für Landwirtschaft, Apoldaer Straße 4, 07778 Dornburg, Germany

Series Preface

Renewable resources, their use and modification are involved in a multitude of important processes with a major influence on our everyday lives. Applications can be found in the energy sector, chemistry, pharmacy, the textile industry, paints and coatings, to name but a few.

The area interconnects several scientific disciplines (agriculture, biochemistry, chemistry, technology, environmental sciences, forestry, . . .), which makes it very difficult to have an expert view on the complicated interaction. Therefore, the idea to create a series of scientific books, focusing on specific topics concerning renewable resources, has been very opportune and can help to clarify some of the underlying connections in this area.

In a very fast changing world, trends are not only characteristic for fashion and political standpoints but science is also not free from hypes and buzzwords. The use of renewable resources is again more important nowadays; however, it is not part of a hype or a fashion. As the lively discussions among scientists continue about how many years we will still be able to use fossil fuels, opinions ranging from 50 years to 500 years, they do agree that the reserve is limited and that it is essential not only to search for new energy carriers but also for new material sources.

In this respect, renewable resources are a crucial area in the search for alternatives for fossil-based raw materials and energy. In the field of the energy supply, biomass and renewable-based resources will be part of the solution alongside other alternatives such as solar energy, wind energy, hydraulic power, hydrogen technology and nuclear energy.

In the field of material sciences, the impact of renewable resources will probably be even bigger. Integral utilization of crops and the use of waste streams in certain industries will grow in importance, leading to a more sustainable way of producing materials.

Although our society was much more (almost exclusively) based on renewable resources centuries ago, this disappeared in the Western world in the 19th century. Now it is time to focus again on this field of research. However, it should not mean a 'retour à la nature', but it should be a multidisciplinary effort on a highly technological level to perform research towards new opportunities, to develop new crops and products from renewable resources. This will be essential to guarantee a level of comfort for a growing number of people living on our planet. It is 'the' challenge for the coming generations of scientists to develop more sustainable ways to create prosperity and to fight poverty and hunger in the world. A global approach is certainly favoured.

This challenge can only be dealt with if scientists are attracted to this area and are recognized for their efforts in this interdisciplinary field. It is therefore also essential that consumers recognize the fate of renewable resources in a number of products.

Furthermore, scientists do need to communicate and discuss the relevance of their work. The use and modification of renewable resources may not follow the path of the genetic engineering concept in view of consumer acceptance in Europe. Related to this aspect, the series will certainly help to increase the visibility of the importance of renewable resources.

Being convinced of the value of the renewables approach for the industrial world, as well as for developing countries, I was myself delighted to collaborate on this series of books focusing on different aspects of renewable resources. I hope that readers become aware of the complexity, the interaction and interconnections, and the challenges of this field and that they will help to communicate on the importance of renewable resources.

I certainly want to thank the people of John Wiley & Sons, Ltd from the Chichester office, especially David Hughes, Jenny Cossham and Lyn Roberts, in seeing the need for such a series of books on renewable resources, for initiating and supporting it and for helping to carry the project to the end.

Last, but not least, I want to thank my family, especially my wife Hilde and children Paulien and Pieter-Jan for their patience and for giving me the time to work on the series when other activities seemed to be more inviting.

Christian V. Stevens
Faculty of Bioscience Engineering
Ghent University
Belgium
June 2005

Preface

Looking out of the window on a bright and colourful autumn day we can recognize that nature provides us with a firework of yellow, red and green colours, inspiring mankind to bring more colour into the products of daily life. However, we have known for a long time that access to the colours of nature is coupled with laborious procedures and a high number of restrictions.

The invention of synthetic organic chemistry and the desire for more bright and stable colorants can be seen as one of the strong driving forces in the historical development of natural sciences. In the 20th century synthetic colorants dominated almost every field of possible application, such as mass coloration of plastics, textiles, paints, cosmetics and food.

For almost 100 years research on natural colorants was continued by only a few groups who were enthusiastic enough to persist against the straightforward arguments for the use of synthetic dyes, relying on cost, performance, colour strength and brilliance, which can easily be achieved using artificial dyes.

During the last decade more and more new aspects were integrated into the assessment of any chemical product used. Interestingly, every new argument that had to be considered also added to the argument strengthening the position of natural colorants. Increased awareness of product safety and higher attention to the possible adverse impact of a chemical product on human health brought changes in the regulations for the use of colorants in food and cosmetics.

Concentration on renewable resources, sustainability and replacement of oil-based products are driving forces to reassess the potential of natural resources including natural colorants, at least for application in very specific fields. Growing consumer interest in purchasing 'green' products, which exhibit an improved environmental profile, can be seen as the breakthrough force for reintroducing natural colorants into the modern markets.

During our own scientific work on natural dyes for textiles and hair dyeing we learned that knowledge about natural colorants and their possible application, at present, is quite fragmented. There are collections of knowledge about natural colorants like Schweppe's *Handbuch der Naturfarbstoffe*, that summarizes properties and sources of natural dyes from a chemical and more historical aspect. However, for the demands of the future development of natural colorants into applications of the present, there is no useful source of information available that could help to give an overview of the state of the research and knowledge in the field of natural colorants.

The search for scientists working on natural colorants who were able and willing to write a contribution for this book was the major challenge in editing this book. The interdisciplinary range of content that should be covered by the different authors made our work particularly difficult, but is understandingly one of the key aspects of this book. The introduction of natural colorants into modern products is an interdisciplinary task that has to consider farming, dyestuff extraction, analysis, properties and application at the same time. Success will only be achieved if integrative concepts are presented that consider all stages of production at the same time.

The organization of the different chapters follows this order. In the first chapters a short review about plant sources and applications of natural colorants in historical times is given. Aspects of farming crops and product processing are then summarized for the different chemical classes of dyes. In the more application-oriented chapters the use of natural colorants in, for example, food, wood, textile and hair dyeing is presented. Sustainability and consumer aspects are discussed in the final chapters of the book.

We would like to thank all authors for their contributions. Their expertise in their particular field, covering a whole array of specialized knowledge, makes the book a unique source of information, which summarizes the present knowledge about natural colorants in depth.

We are aware that every collection of information will be incomplete and further aspects could have been introduced and considered in more detail. However, we are convinced that the book as it stands will be a useful instrument to overview the fragmented situation of natural colorants and will support a rapid and efficient entry of new researchers into this emerging field of sustainable chemistry. From this point of view we are also convinced that the book will strengthen the position of natural colorants in the future, by facilitating access to information and thereby indirectly helping the revival of natural colorants to gain momentum.

Thomas Bechtold and Rita A. M. Mussak
Dornbirn/Linz
2008

Part I
Historical Aspects

1

History of Natural Dyes in the Ancient Mediterranean World

Maria J. Melo

The colours used on textiles and artifacts, their social significance and the scope of their trade, are part and parcel of a people's overall history.

Jenny Balfour-Paul, in *Indigo*, British Museum Press, 2000

1.1 Introduction

1.1.1 Ancient Mediterranean World

The build-up of *Mare Nostrum* probably began much earlier than the 6th–5th millennium BC and there is material evidence pointing to such activity as early as the 12th–11th millennium BC [1]. *Mare Nostrum*, the Roman name for the Mediterranean Sea, was to become the home for a global market that expanded beyond its natural borders in the 1st millennium BC. The Phoenicians, the Etruscans, the Greeks and finally the Romans shaped *Mare Nostrum*, a geographic as well as a cultural domain. It was also home for the first global dye, Tyrian purple, which was traded by the ingenious and industrious Phoenicians. The purple of Tyre was famous, as were the textiles dyed and produced by the Phoenicians. It is said that the Greeks named the Phoenicians after *Phoinikes*, the ancient Greek word for ‘red colour’, probably as a result of their famous purple trade.

By the time of the founding of the Mediterranean civilizations, what we would consider the classical palette for natural dyes had already been established, and the most valued colours were indigo for the blues, anthraquinone-based chromophores for the reds and 6,6'-dibromoindigo for purple. These colours were traded all over the Mediterranean,

regardless of distance to be travelled or the price to be paid. The natural sources for yellows were much more diverse, so yellows could generally be obtained locally. For dyeing, with the exception of some browns, all other colours and shades, including green and orange, could be obtained with these blue, red, purple and yellow dyes. This classical palette was preserved over centuries, if not millennia. The first adjustment resulted from the loss of Tyrian purple following the fall of Constantinople and the subsequent collapse of the Roman social and commercial web. This was followed by a new entry, cochineal red, brought by the Spanish from the New World [2]. However, even with the introduction of cochineal the chemical nature of the classical palette was maintained, as carminic acid is still a substituted 1,2-dihydroxy anthraquinone. This classical palette was only challenged by the audacity of chemists, who created new molecules, and colours never seen before, from the mid-19th century on [3].

1.1.2 Dyes from Antiquity

Natural dyes, discovered through the ingenuity and persistence of our ancestors, can resist brightly for centuries or millennia and may be found hidden in such diverse places as the roots of a plant, a parasitic insect and the secretions of a sea snail. By contrast, the bright colours that we see in the green of a valley, the red of a poppy, the purple of mauve or the blue of cornflower are less stable. Natural dyes were used to colour a fibre or to paint. It is useful to distinguish between dyes and pigments based on their solubility in the media used to apply the colour; dyes are generally organic compounds that are soluble in a solvent, whereas pigments, used in painting, are usually inorganic compounds or minerals that are insoluble in the paint medium (oil, water, etc.) and are dispersed in the matrix. A lake pigment is a pigment formed by precipitation, namely by complexation with a metal ion, forming a dye on the surface of an inorganic substance.

Dyeing, in red, blue, purple or yellow, is a complex task that requires skill and knowledge [4]; this is true now and has been for several millennia. Colour is obtained by applying a chemical compound called a chromophore or chromogen, something that brings or creates colour. When used as a textile dye, the chromophore must also be captured as strongly as possible into the fibres; i.e. it must be resistant to washing. Dyes can bind to the surface of the fibre or be trapped within them. They are often bound to the textile with the aid of metallic ions known as mordants, which can also play an important role in the final colour obtained. Alum, as a source of the aluminium ion, is an important historical mordant and was widely used in the past. Other important mordants used in the past were iron, copper and tin ions [4,5]. Dyes, like indigo, which are trapped in the fibres due to an oxidation–reduction reaction, without the aid of a mordant, are known as vat dyes.

Natural dyes, as lake pigments, have been widely applied in painting. For example, anthraquinones and their hydroxy derivatives have been used as red dyes and pigment lakes from prehistoric times, and we can find written accounts of the use of anthraquinone reds and purples as dyes in ancient Egypt [5, 6]; anthraquinone lakes (e.g. madder red) were also very popular with Impressionist painters, including Vincent van Gogh. Lake pigments can be prepared by precipitating the dye extract with aluminium or other inorganic salts, such as alum [7]. Pure dyes such as indigo were also used as painting materials, e.g. in medieval illuminations (Figure 1.1).



Figure 1.1 Medieval Portuguese illumination, dating from a 12–13th century, Lorrvão 15, fl. 50 kept at Torre do Tombo (Lisbon). Dark blues were painted with indigo, whereas for the background the inorganic and precious pigment lapis-lazuli was used (See Colour Plate 1)

These *eternal* colours will be described in more detail in the following sections, after a brief account of the analytical techniques used to reveal the secrets of these ancient materials. The natural colorants will be organized according to the colour: first the anthraquinone reds, followed by the blues and purple, where indigo and its bromo derivatives play a major role. Yellows will close this historic overview.

1.1.3 Unveiling the Secrets of Ancient Dyes with Modern Science

Identifying the dyes and dye sources used in the past has only been possible with the development, in the past two decades or so, of sensitive new microanalytical techniques [8,9]. Chromophores are extracted, then separated chromatographically and characterized by UV-Vis spectrophotometry or mass spectrometry; whenever possible comparison with

authentic references is performed. Currently, the use of HPLC-DAD (high-performance liquid chromatography with diode array detection) enables dyestuff characterization from as little as 0.1 mg of thread. For unknown components, or those not characterized before, analysis by HPLC-MS (HPLC with mass spectrometric detection) may provide further information. Recently developed mild extraction methods allow more detailed chemical information to be obtained on the historical natural dyes, and as a consequence it is sometimes possible to identify the natural sources [10, 11].

Mordant analysis can also provide relevant information about the dyeing method or process used. The metal ions can be quantified by inductively coupled plasma separation with atomic emission spectrometric (ICP-AES) or mass spectrometric detection (ICP-MS) of samples (*ca.* 0.25 mg textile strands) previously digested with nitric acid solutions [12, 13]. Before the sample analysis, calibration curves must be constructed using standards. Concentration linearity in the range of ppb to ppm (or higher) can be achieved.

1.2 Ancient Reds

1.2.1 Anthraquinone Reds

The most stable reds used in antiquity are based on the 1,2-dihydroxy anthraquinone chromophore (Figure 1.2), also known as alizarin. Dyes containing anthraquinone and its derivatives are among the most resistant to light-induced fading [5]. These

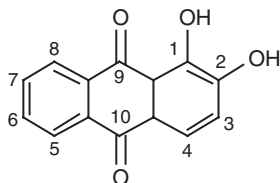


Figure 1.2 Alizarin; 1,2-dihydroxy anthraquinone

dyes were obtained from parasitic insects, such as the famous *Kermes vermilio*, or from the roots of plants belonging to the Rubiaceae or madder family, and were among the reds that dominated the dye markets of Europe [2, 14]. Alizarin and purpurin are the main chromophores in *Rubia tinctorum*, the most important species of the family Rubiaceae. In Persia and India, other red dyes – of animal origin – were also used. These dyes were imported, or sometimes found locally, and were considered luxury goods. Well-known examples are the reds based on the laccic acids, kermesic acid and carminic acid (Table 1.1), from the parasite insects, lac, kermes and cochineal, respectively [2]. The female lac insect secretes a red resin, stick-lac, from which are obtained both the lac dye and the shellac resin. Common or Indian lac, *Kerria lacca* (= *Laccifer lacca*, *Carteria lacca*, *Tachardia lacca* and *Lakshadia lacca*) and *Kerria chinensis* are examples of species that have been widely exploited [5]. In both cochineal (*Dactylopius coccus*) and kermes (*Kermes vermilio*)