

Prof. W. Herz, Department of Chemistry,
The Florida State University, Tallahassee, Florida, U.S.A.

Prof. H. Falk, Institut für Chemie,
Johannes-Kepler-Universität, Linz, Austria

Prof. G. W. Kirby, Chemistry Department,
The University of Glasgow, Glasgow, Scotland

This work is subject to copyright.
All rights are reserved, whether the whole or part of the material is concerned, specifically those of translation, reprinting, re-use of illustrations, broadcasting, reproduction by photocopying machines or similar means, and storage in data banks.

© 2007 Springer-Verlag/Wien
Printed in Austria

SpringerWienNewYork is part of
Springer Science + Business Media
springer.com

Product Liability: The publisher can give no guarantee for the information contained in this book. This also refers to that on drug dosage and application thereof. In each individual case the respective user must check the accuracy of the information given by consulting other pharmaceutical literature. The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Library of Congress Catalog Card Number AC 39-1015

Typesetting: Thomson Press (India) Ltd., Chennai
Printing and binding: Druckerei Theiss GmbH, A-9431 St. Stefan

Printed on acid-free and chlorine-free bleached paper

SPIN: 10975961

With 12 Figures and 1 coloured Plate

ISSN 0071-7886
ISBN-10 3-211-20688-4 SpringerWienNewYork
ISBN-13 978-3-211-20688-1 SpringerWienNewYork

Contents

List of Contributors.	IX
-------------------------------	----

Synthesis Pathways to *Erythrina* Alkaloids and *Erythrina* Type Compounds

E. Reimann	1
1. Introduction	2
2. Structural Classification of <i>Erythrina</i> Alkaloids	4
3. New <i>Erythrina</i> Alkaloids.	18
4. Biosynthesis of <i>Erythrina</i> Alkaloids	18
4.1. Erythrinane Alkaloids.	18
4.2. Homoerythrinane Alkaloids.	20
5. Syntheses of <i>Erythrina</i> Alkaloids and <i>Erythrina</i> Type Compounds	21
5.1. Methodical Classification	22
5.2. Erythrinanes	23
5.2.1. Final Formation of One Ring.	23
5.2.1.1. Ring C (Route C)	23
5.2.1.1.1. Cyclization of <i>N</i> -Phenethylhydroindole Derivatives (Route C(a))	23
5.2.1.1.2. Cyclization of Angular Arylated Hydroindole Derivatives (Route C(b))	29
5.2.1.2. Formation of Ring B (Route B)	32
5.2.1.2.1. Cyclization of <i>N</i> -substituted C5-Spiroisoquinoline Derivatives (Route B(a))	32
5.2.1.2.2. Cyclization of C6-Substituted C5-Spiroisoquinoline Derivatives (Route B(b))	35
5.2.1.3. Formation of Ring A (Route A)	35
5.2.1.3.1. Cycloaddition to Pyrroloisoquinolines (Route A(a))	35
5.2.1.3.2. Intramolecular Aldol Condensation of Angularly Substituted Pyrroloisoquinoline (Route A(b))	37
5.2.2. Simultaneous Formation of More Than One Ring.	38
5.2.2.1. Simultaneous Formation of Rings B and C (Route B/C)	39

5.2.2.1.1. Cyclization of Secondary Diphenethyl- or (Cycloalkyl)ethyl-phenethylamine Derivatives (Route B/C(a))	39
5.2.2.1.2. Cyclization of Tertiary Cyclohexyl-ethyl- phenethyl-amide Derivatives (Route B/C(b))	42
5.2.2.2. Cyclization of N-Substituted 1-Acyldihydroisoquinolinium Derivatives (Route A/B)	44
5.2.2.3. Cyclization of a Highly Functionalized Homoveratrylimide (Route A/B/C)	45
5.3. Homoerythrinanes	45
5.3.1. Biomimetic Routes	47
5.3.2. Final C Ring Formation Starting from N-Substituted Phenylhydroindoles.	49
5.3.3. A Ring Formation by [2 + 2] Photocycloaddition to Pyrrolobenzazepines	50
5.3.4. Simultaneous B Ring Formation/C Ring Expansion Starting from Spiro-2-tetralones	52
6. Pharmacology	53
7. Concluding Remarks.	55
References	56

The Trichothecenes and Their Biosynthesis

J. F. Grove (†)	63
1. Introduction	63
2. The Trichothecenes.	64
2.1. Macrocyclic and Non-Macrocyclic Compounds.	64
2.2. Trichothecene Relatives	90
2.3. Sources.	96
2.4. Oxygenation Pattern.	97
3. Biosynthesis.	98
3.1. Simple Trichothecenes	98
3.1.1. Mevalonic Acid to Trichodiene	98
3.1.2. Trichodiene to 12,13-Epoxytrichothecene and Isotrichodermol	101
3.1.3. Further Oxygenation and Esterification of the Trichothecene Nucleus: Biosynthesis of Specific Metabolites	104
3.1.3.1. Trichothecolone	104
3.1.3.2. Vomitoxin and Derivatives.	104
3.1.3.3. T-2 Toxin.	107
3.1.3.4. Nivalenol and Derivatives	108
3.1.4. Trichothecene Biosynthetic Gene Clusters	108
3.2. Trichoverroids and Macrocyclic Trichothecenes.	109
3.3. Trichothecene Relatives	112
References	113

Melanin, Melanogenesis, and Vitiligo

S. Roy	131
1. Melanin	132
1.1. Introduction	132
2. Chemistry of Melanin	134
2.1. Isolation and Analysis	134
2.2. Solubilization	135
2.3. Protein Content	135
2.4. Carboxylic and Phenolic Function	136
2.5. Chemical Degradation	136
2.5.1. Reductive Methods	136
2.5.2. Oxidative Methods	137
2.5.3. Pyrolytic Methods	137
2.6. Spectroscopic Studies	138
2.6.1. UV and IR Spectroscopy	138
2.6.2. NMR Spectroscopy	138
2.6.3. X-Ray Defraction Study	138
2.6.4. ESR Study	139
2.7. Structure of Melanin	139
2.7.1. Melanin as Homopolymer	139
2.7.2. Melanin as Poikilopolymer	140
2.7.3. Melanin as Bipolymer	141
2.7.4. Biophysical Model of Melanin Structure	141
2.7.5. Structure of Phaeomelanin	143
2.8. Synthesis of Melanin	143
2.8.1. Electrochemical Synthesis	143
2.8.2. Photochemical Synthesis	145
3. Characteristic Biophysicochemical Properties of Melanin	145
3.1. Interaction of Melanin with Light	146
3.1.1. Melanin in UV and Visible Light	146
3.1.2. Melanin in the Photoprotection of Skin	146
3.1.3. Melanin as Light Screen in Eyes	147
3.2. Melanin and Its Redox Function	148
3.3. Binding Complexation and Medicinal Aspects of Melanin	149
3.4. Use of Melanin for Defence	150
4. Melanogenesis	150
4.1. Melanogenesis <i>in vivo</i>	150
4.1.1. Melanocytes	151
4.1.2. The Characteristics of the Enzyme	152
4.1.3. Regulation of Melanogenesis	153
4.1.3.1. Physiological Factors	154
4.1.3.2. Organic Sulfur Compounds	154
4.1.3.3. Metal Ions and Other Chemicals	154
4.1.3.4. Vitamins	154
4.1.3.5. Hormones	155
4.1.3.6. Neural Influence	157
4.1.3.7. Malpighian Cells	157
4.1.3.8. UV Light	157

4.2. Melanogenesis <i>in vitro</i>	157
4.2.1. Enzymatic Melanin Synthesis.	157
4.2.1.1. Rearrangement of Dopachrome.	158
4.2.1.2. Polymerization of DHI	159
4.2.2. Non-Enzymatic Melanin Synthesis: Model Reaction.	161
4.2.2.1. Udenfriend System: A Model for Mixed Function Oxidase	161
4.2.2.2. Melanin Formation Under Udenfriend Conditions.	162
5. Vitiligo	164
5.1. Introduction	164
5.2. Melanocytotoxicity: Antimelanocyte-Antibodies Formation.	164
5.2.1. The Immune Hypothesis	165
5.2.2. The Neural Hypothesis	165
5.2.3. The Self-Destruction Hypothesis	165
5.2.4. The Composite Hypothesis	165
5.3. Chemotherapy of Vitiligo	166
5.3.1. Psoralens	166
5.3.2. Psoralen Action and UV Light.	166
5.3.3. Psoralen Action on Melanogenesis	167
5.4. Abnormal Biochemical Parameters in Vitiligo.	168
5.5. Status of Tryptophan in the Melanogenic System	169
5.6. A Composite Hypothesis on Vitiligo	171
References	171
Author Index	187
Subject Index	201

Fortschritte der Chemie organischer Naturstoffe /
Progress in the Chemistry of Organic Natural Products
88

Herz, W.; Falk, H.; Kirby, G.W. (Eds.)

2007, IX, 212 p. 12 illus. With 1 coloured plate.,

Hardcover

ISBN: 978-3-211-20688-1