Recent Advances in Polyphenol Research

VOLUME 1

Edited by Fouad Daayf and Vincenzo Lattanzio



WILEY-BLACKWELL

Recent Advances in Polyphenol Research

Volume 1

Edited by

Fouad Daayf

Associate Professor, Molecular Plant Pathology Department of Plant Science Faculty of Agricultural and Food Sciences University of Manitoba, Winnipeg, Manitoba, Canada

Vincenzo Lattanzio

Professor, Plant Biochemistry and Physiology
Department of Agro-Environmental Sciences, Chemistry and
Plant Protection
Faculty of Agricultural Sciences
University of Foggia, Foggia, Italy

This edition first published 2008 © 2008 Blackwell Publishing Ltd

Blackwell Publishing was acquired by John Wiley & Sons in February 2007. Blackwell's publishing programme has been merged with Wiley's global Scientific, Technical, and Medical business to form Wiley-Blackwell.

Registered office

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

Editorial offices

9600 Garsington Road, Oxford, OX4 2DQ, United Kingdom

2121 State Avenue, Ames, Iowa 50014-8300, USA

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/wiley-blackwell.

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.

Library of Congress Cataloging-in-Publication Data

Recent advances in polyphenol research / edited by Fouad Daayf, Vincenzo Lattanzio.

p. cm.

Includes bibliographical references.

ISBN-13: 978-1-4051-5837-4 (hardback : alk. paper)

ISBN-10: 1-4051-5837-9 (hardback : alk. paper) 1. Polyphenols—Research. I. Daayf, Fouad.

II. Lattanzio, Vincenzo, 1949-

QK898.P764R43 2008

572'.2-dc22

2008006133

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

Set in 10/13pt Times by Graphicraft Limited, Hong Kong Printed in Singapore by Fabulous Printers Pte Ltd

Recent Advances in Polyphenol Research

Recent Advances in Polyphenol Research

A series for researchers and graduate students whose work is related to plant phenols and polyphenols, as well as for individuals representing governments and industries with interest in this field. Each volume in this biennial series will focus on several important research topics in plant phenols and polyphenols, including Chemistry, Biosynthesis, Metabolic Engineering, Ecology, Physiology, Food, Nutrition, and Health.

Volume 1 editors:

Fouad Daayf and Vincenzo Lattanzio

Series Editor-in-Chief:

Vincenzo Lattanzio, President of 'Groupe Polyphénols' (University of Foggia, Italy)

Series Editorial Board:

Øyvind M. Andersen (University of Bergen, Norway)

Denis Barron (Nestlé Research Centre, Lausanne, Switzerland)

Catherine Chèze (Université Victor Segalen, Bordeaux 2, France)

Richard A. Dixon (The Samuel Roberts Noble Foundation, Ardmore, OK, USA)

Ismaîl El-Hadrami (Cadi Ayyad University, Marrakech, Morocco)

Tadao Kondo (Nagoya University, Japan)

Paul A. Kroon (Institute of Food Research, Norwich, UK)

Stéphane Quideau (IECB, Université Bordeaux 1, France)

Jorge-Manuel Ricardo da Silva (University of Lisbon, Portugal)

Celestino Santos-Buelga (University of Salamanca, Spain)

Dieter Treutter (Technical University of Munich, Freising, Germany)



Dedication

To Michel Bourzeix and his collaborators, Carmen Bataller and Nicolas Hérédia, whose efforts and enthusiasm have been decisive for the life of the Groupe Polyphénols.

Acknowledgments

The editors wish to thank all the members of the Groupe Polyphénols Board Committee (2004–2006) for their guidance and assistance throughout this project.

Groupe Polyphénols Board 2004-2006

Professor Øyvind M. Andersen

Dr Patrice André

Professor Denis Barron

Dr Catherine Chèze

Dr Claire Dufour

Professor Maria Teresa Escribano-Bailón

Dr Hélène Fulcrand

Dr Sylvain Guyot

Dr Paul A. Kroon

Dr Jean-Luc Poessel

Professor Stéphane Quideau

Professor Jorge-Manuel Ricardo da Silva

Professor Celestino Santos-Buelga

Dr Pascale Sarni-Manchado

Contributors

Øyvind M. Andersen, Department of Chemistry, University of Bergen, Allegt. 41, N-5007 Bergen, Norway

Denis Barron, Food Consumer Interaction Department, Nestlé Research Center, P.O. Box 44, CH-1000 Lausanne 26, Switzerland

Maria José Bermúdez-Soto, Research Group on Quality, Safety and Bioactivity of Plant Food, Department of Food Science & Technology, CEBAS (CSIC), P.O. Box 164, Espinardo, Murcia 30100, Spain

Stéphane Bernillon, INRA, UMR619, Centre de Bordeaux, 71, avenue Edouard Bourleaux, BP 81, F-33883 Villenave d'Ornon Cedex, France

Wout Boerjan, Department of Plant Systems Biology, VIB-Ghent University, Gent 9052, Belgium

Gösta Brunow, Department of Chemistry, University of Helsinki, Helsinki, Finland

Jérémy Catinot, Department of Biology, University of Fribourg, Rue du Musée 10, 1700 Fribourg, Switzerland

Begoña Cerdá, Research Group on Quality, Safety and Bioactivity of Plant Food, Department of Food Science & Technology, CEBAS (CSIC), P.O. Box 164, Espinardo, Murcia 30100, Spain

Fouad Daayf, Associate Professor, Molecular Plant Pathology, Department of Plant Science, Faculty of Agricultural and Food Sciences, University of Manitoba, Winnipeg, Manitoba, Canada

Olivier Dangles, UMR A 408 INRA – University of Avignon, Safety and Quality of Plant Products Site Agroparc, Domaine St-Paul, 84914 Avignon Cedex 9, France

Hannelore Daniel, Molecular Nutrition Unit, Department of Food and Nutrition Sciences, Technical University of Munich, Am Forum 5, D-85354 Freising, Germany

Kevin M. Davies, New Zealand Institute for Crop & Food Research Limited, Private Bag 11-600, Palmerston North, New Zealand

Richard A. Dixon, Plant Biology Division, Samuel Roberts Noble Foundation, 2510 Sam Noble Parkway, Ardmore, OK 73401, USA

Claire Dufour, UMR A 408 INRA – University of Avignon, Safety and Quality of Plant Products Site Agroparc, Domaine St-Paul, 84914 Avignon Cedex 9, France

Juan Carlos Espín, Research Group on Quality, Safety and Bioactivity of Plant Food, Department of Food Science & Technology, CEBAS (CSIC), P.O. Box 164, Espinardo, Murcia 30100, Spain

María Teresa García-Conesa, Research Group on Quality, Safety and Bioactivity of Plant Food, Department of Food Science & Technology, CEBAS (CSIC), P.O. Box 164, Espinardo, Murcia 30100, Spain

Christophe Garcion, Department of Biology, University of Fribourg, Rue du Musée 10, 1700 Fribourg, Switzerland

Rocio González-Barrio, Research Group on Quality, Safety and Bioactivity of Plant Food, Department of Food Science & Technology, CEBAS (CSIC), P.O. Box 164, Espinardo, Murcia 30100, Spain

Antonio González-Sarrías, Research Group on Quality, Safety and Bioactivity of Plant Food, Department of Food Science & Technology, CEBAS (CSIC), P.O. Box 164, Espinardo, Murcia 30100, Spain

Sylvain Guyot, INRA, UR117, Unité de Recherches Cidricoles, Domaine de la Motte, BP 35327, F-35653 Le Rheu Cedex, France

Ray Hammerschmidt, Department of Plant Pathology, 107 CIPS Bldg, Michigan State University, East Lansing, MI 48824-1311, USA

Philip J. Harris, School of Biological Sciences, The University of Auckland, Private Bag 92019, Auckland, New Zealand

Samantha I. Hollosy, Department of Plant Pathology, 107 CIPS Bldg, Michigan State University, East Lansing, MI 48824-1311, USA

Sampo Karkola, Laboratory of Organic Chemistry, Department of Chemistry, University of Helsinki, AI Virtasen Aukio 1, P.O. Box 55, FIN-00014 Helsinki, Finland

Colin D. Kay, Diet and Health Group, School of Medicine, Health Policy and Practice, University of East Anglia, Norwich, Norfolk, UK

Alan P. Kozikowski, Department of Medicinal Chemistry and Pharmacognosy, 833 South Wood Street, Room 531, Chicago, IL 60612, USA

Paul A. Kroon, Institute of Food Research, Colney Lane, Norwich NR4 7UA, UK

Elisabeth Lamodière, Department of Biology, University of Fribourg, Rue du Musée 10, 1700 Fribourg, Switzerland

Olivier Lamotte, Department of Biology, University of Fribourg, Rue du Musée 10, 1700 Fribourg, Switzerland

Mar Larrosa, Research Group on Quality, Safety and Bioactivity of Plant Food, Department of Food Science & Technology, CEBAS (CSIC), P.O. Box 164, Espinardo, Murcia 30100, Spain

Vincenzo Lattanzio, Dipartimento di Scienze Agro-Ambientali, Chimica e Difesa Vegetale, Università degli Studi di Foggia, Via Napoli, 25, 71100-Foggia, Italy

Annamaria Lilienkampf, Laboratory of Organic Chemistry, Department of Chemistry, University of Helsinki, AI Virtasen Aukio 1, P.O. Box 55, FIN-00014 Helsinki, Finland

Giuseppe (Joe) Mazza, Agriculture and Agri-Food Canada, Pacific Agri-Food Research Centre, 4200 Highway 97, Summerland, BC, Canada V0H 1Z0

Jean-Pierre Metraux, Department of Biology, University of Fribourg, Rue du Musée 10, 1700 Fribourg, Switzerland

Luzia V. Modolo, Plant Biology Division, Samuel Roberts Noble Foundation, 2510 Sam Noble Parkway, Ardmore, OK 73401, USA

Stéphane Quideau, Institut Européen de Chimie et Biologie, Pôle Chimie Organique et Bioorganique, 2 rue Robert Escarpit, F-33607 Pessac cedex, France

Yongzhen Pang, Plant Biology Division, Samuel Roberts Noble Foundation, 2510 Sam Noble Parkway, Ardmore, OK 73401, USA

Pascal Poupard, INRA, UR117, Unité de Recherches Cidricoles, Domaine de la Motte, BP 35327, F-35653 Le Rheu Cedex, France

John Ralph, Departments of Biochemistry and Biological Systems Engineering, University of Wisconsin, Madison, WI 53706, USA; and US Dairy Forage Research Center, USDA-Agricultural Research Service, 1925 Linden Drive West, Madison, WI 53706-1108, USA

Catherine M.G.C. Renard, INRA, UMR A480 'Sécurité et Qualité des Produits d'Origine Végétale' Domaine St Paul, F-84914 Avignon cedex 09, France

Paul F. Schatz, US Dairy Forage Research Center, USDA-Agricultural Research Service, 1925 Linden Drive West, Madison, WI 53706-1108, USA

Kathy E. Schwinn, New Zealand Institute for Crop & Food Research Limited, Private Bag 11-600, Palmerston North, New Zealand

Li Tian, Plant Biology Division, Samuel Roberts Noble Foundation, 2510 Sam Noble Parkway, Ardmore, OK 73401, USA

Francisco A. Tomás-Barberán, Research Group on Quality, Safety and Bioactivity of Plant Food, Department of Food Science & Technology, CEBAS (CSIC), P.O. Box 164, Espinardo, Murcia 30100, Spain

Dieter Treutter, Center of Life and Food Science Weihenstephan, Technische Universität München, Unit Fruit Science – Fruit Tree Physiology, Alte Akademie 16, D 85350 Freising, Germany

Werner Tückmantel, PsychoGenics, Inc., 765 Old Saw Mill River Road, Tarrytown, NY 10598, USA

Kristiina Wähälä, Laboratory of Organic Chemistry, Department of Chemistry, University of Helsinki, Al Virtasen Aukio 1, P.O. Box 55, FIN-00014 Helsinki, Finland

Uwe Wenzel, Molecular Nutrition Research, University of Giessen, Heinrich-Buff-Ring 26–32, D-35392 Giessen, Germany

Huaibi Zhang, New Zealand Institute for Crop & Food Research Limited, Private Bag 11-600, Palmerston North, New Zealand

Preface

Plant phenolics are secondary metabolites that constitute one of the most common and widespread groups of substances in plants. They represent adaptive characters that have been subjected to natural selection during evolution, when the presence of a particular secondary metabolite has conferred a selection advantage to the plant containing it.

Polyphenols have a large and diverse array of beneficial effects on both plants and humans. For example, they are famous as antioxidants, hormones, constituents of essential oils, natural neurotransmitters, and as having many other biological activities. Their antioxidant ability is known to confer many health benefits such as reducing the risk of cardiovascular disease and cancer. They also provide antimicrobial activity for the plant's own defense against invading pathogens. The diversity of structure and activity of phenolic compounds has resulted in a multiplicity of research areas such as chemistry, biotechnology, ecology, physiology, nutrition, medicine, and cosmetics. The International Conference on Polyphenols, organized under the auspices of 'Groupe Polyphénols', is a unique opportunity for scientists in these and other fields to get together every other year and exchange their ideas and new findings. Apart from the two-page manuscripts - Polyphenols Communications – that comprise the proceedings of this conference, a separate volume has been concurrently published, comprising full chapters by the conference guest speakers. For the first time in the history of the conference, the board of 'Groupe Polyphénols' decided in 2005 that, starting in Winnipeg (ICP 2006), such a volume should be published by a renowned publisher such as Wiley-Blackwell, and given the series title Recent Advances in Polyphenol Research. The present (first) volume in the series is from the 23rd conference, which was hosted by the University of Manitoba in Winnipeg, Manitoba, Canada, from August 22 to August 25 2006, and chaired by Dr Fouad Daayf. The University of Manitoba, established in 1877, is one of the oldest universities in Canada. Its education and research programs are dedicated to many areas including agriculture, art, architecture, medicine, business, and science. The interest in polyphenols involves many departments on campus including the Departments of Plant Science, Chemistry, Food Science, Nutrition, and Human Ecology, as well as other health and functional food-related centers such as the Richardson Center for Functional Foods and Nutraceuticals.

In addition to the guest speakers' chapters, the present volume also includes full chapters from other selected speakers at the 23rd International Conference on Polyphenols, and covers five topics:

1) *Phenols and Polyphenols Chemistry*: (a) Isolation and structural elucidation; (b) Synthesis; (c) Reactivity and physico-chemical properties; (d) Biomolecular interactions.

- 2) Phenols and Polyphenols Biosynthesis and Genetic Manipulation: (a) Metabolic pathways; (b) Enzymology; (c) Biotechnology advances.
- 3) *Ecology and Physiology of Plant Phenolics*: (a) Biotic and abiotic stress; (b) Phenolic functions in plant development; (c) Role of phenolics in soil ecology.
- 4) Food and Nutrition: (a) Dietary intake; (b) Bioavailability; (c) Safety and toxicity; (d) Functional foods and nutraceuticals; (e) Taste.
- Phenolics and Health: (a) Biological activities; (b) Drug discovery and development;
 (c) Cosmetics.

These topics were presented in 59 oral communications and 222 posters, and scientists had the opportunity to debate their results, and sometimes their divergent theories, in an exciting manner.

The 23rd International Conference on Polyphenols would not have been possible without the generous support of public and private donors such as the Manitoba Rural Adaptation Council and the University of Manitoba. Other sponsors include Horphag, l'Agence Universitaire de la Francophonie, Phytochemistry, Cargill, and Monsanto. Our sincere thanks go to all of our sponsors.

Fouad Daayf, Conference Chair Vincenzo Lattanzio, President of 'Groupe Polyphénols'

Contents

Coi	Contributors		
Pre	eface	XX	
1	Plant Phenolics – Secondary Metabolites with Diverse Functions Vincenzo Lattanzio, Paul A. Kroon, Stéphane Quideau and Dieter Treutter	1	
1.1	Secondary metabolism in the interactions between plants and their		
	environment	1	
1.2	and the company of the control of th	5	
	1.2.1 UV sunscreens	6	
	1.2.2 Phenolics as signal compounds	6	
	1.2.3 Phenolics as pigments	8	
	1.2.4 Phenolics and plant growth	9	
	1.2.5 Phenolics and plant defense	11	
	1.2.5.1 Fungal pathogens	13	
	1.2.5.2 Phenolics and plant–insect interactions	17	
1.0	1.2.6 Plant phenolics and health	22	
1.3		24	
1.4	References	24	
2	Lignification: are Lignins Biosynthesized via simple Combinatorial		
	Chemistry or via Proteinaceous Control and Template Replication?	36	
	John Ralph, Gösta Brunow, Philip J. Harris, Richard A. Dixon,		
	Paul F. Schatz and Wout Boerjan		
2.1	Introduction	36	
2.2	The current theory	37	
2.3	Is there a need for a new theory?	37	
	2.3.1 The challenge hypothesis (proteinaceous control and template		
	replication)	38	
	2.3.2 Has the challenge hypothesis become a theory?	38	
2.4	and the second of the second o	38	
	2.4.1 Lignification as a biochemical anomaly	38	

	2.4.2	The β -ether frequency anomaly	39
	2.4.3	'Obligatory' linkages?	40
2.5	Is ther	re anything wrong with the dirigent hypothesis?	40
	2.5.1	Monomer substitution	40
		2.5.1.1 Has monomer substitution been disproven?	41
		2.5.1.2 Malleability of lignification: what makes a good	
		monolignol substitute?	43
	2.5.2	'Well-defined primary structure'	45
		2.5.2.1 Sequencing of lignin oligomers	45
		2.5.2.2 Monomer-independent sequences	46
		2.5.2.3 The 'urgent need to sequence lignin primary structure'	47
	2.5.3	Lignins' racemic nature	47
		2.5.3.1 The 'number of isomers' problem	48
	2.5.4	Comments on template replication	48
	2.5.5	Polymer branching	49
2.6	Why t	the new hypothesis is not in contention	50
2.7	Is lign	nification a biochemical anomaly?	51
	2.7.1	Ferulate dehydrodimerization is combinatorial	51
	2.7.2	Polysaccharide primary structure is NOT absolutely dictated	51
2.8	Summ	nary comments on the dirigent/replication hypothesis	52
2.9	Concl	usions	53
2.10	Notes		55
2.11	Refere	ences	58
0	n Hum	id-Protein Binding Processes and their Potential Impact an Health	67
C	livier L	Dangles and Claire Dufour	
3.1	Introd	luction	67
3.2	Biolog	gically relevant chemical properties of flavonoids	68
3.3		ng processes prior to absorption	71
3.4		ng processes involved in flavonoid bioavailability	72
		Absorption and conjugation	72
		Transport in plasma	73
	3.4.3	Tissue distribution and cellular metabolism	73
3.5	Bindi	ng processes involved in the potential health effects of flavonoids	74
	3.5.1	Inhibition of enzymes involved in ROS production	74
	3.5.2	Modulation of the redox properties of flavonoids by binding to	
		proteins	76
	3.5.3	Inhibition of protein kinases	78
	3.5.4	Inhibition of cytochrome P450 enzymes	79
	3.5.5	Regulation of gene expression	80
3.6	Concl		83
3.7	Refer		83

	lethods for Synthesizing the Cocoa-Derived Oligomeric Epi-Catechins	00
	Observations on the Anticancer Activity of the Cocoa Polyphenols	88
A	lan P. Kozikowski and Werner Tückmantel	
4.1	Introduction	88
4.2	Synthesis of procyanidins	89
	4.2.1 General chemical properties of cocoa procyanidins	89
	4.2.2 Earlier synthetic work	91
	4.2.3 The synthesis of benzyl-protected building blocks	92
	4.2.4 Inter-flavan bond formation using benzyl-protected building blocks	94
	4.2.5 Establishment of inter-flavan bond stereochemistry	97
	4.2.6 Further developments	102
4.3	Anticancer activity	105
4.4	Acknowledgments	109
4.5	References	109
	Gene Discovery and Metabolic Engineering in the Phenylpropanoid	
	athway	113
L	uzia V. Modolo, Yongzhen Pang, Li Tian and Richard A. Dixon	
5.1	Introduction	113
5.2	Biosynthesis and functions of isoflavones	113
5.3	Dietary sources of isoflavones	115
5.4	Metabolic engineering of isoflavones	115
	5.4.1 Metabolic engineering by ectopic expression of IFS	115
	5.4.2 Structural biology-assisted design and metabolic engineering	
	with an artificial bifunctional IFS enzyme	116
5.5	Gene discovery in the proanthocyanidin biosynthetic pathway	117
	5.5.1 Structural genes for PA biosynthesis	118
	5.5.2 Regulatory genes for PA biosynthesis	121
5.6	Metabolic engineering of PAs in plants	122
5.7	Glycosyltransferases for modification of phenylpropanoid compounds	
	- in-vitro biochemistry and in-vivo function	123
	5.7.1 UGTs active with non-flavonoid phenolic compounds	124
	5.7.2 Glycosylation of flavonoid compounds	128
	5.7.3 Problems for the functional annotation of UGTs	130
5.8	Concerted strategies for metabolic engineering	131
5.9	References	132
5.10	Abbreviation list of the pathway genes	138
6 F	Recent Advances in the Molecular Biology and Metabolic Engineering	
	f Flavonoid Biosynthesis in Ornamental Plants	139
	Kevin M. Davies, Huaibi Zhang and Kathy E. Schwinn	

6.1	Introduction	139
6.2	Metabolic engineering of flavonoid production in flowers	142
	6.2.1 Engineering yellow flower colors	143
	6.2.2 Engineering blue flower colors	144
6.3	Anthocyanic vacuolar inclusions	149
6.4	Regulation of anthocyanin biosynthesis	152
6.5	Concluding comments	157
6.6	References	158
		100
7 R	ecent Advances in the Field of Anthocyanins – Main Focus	
01	n Structures	167
Ø	byvind M. Andersen	
7.1	Introduction	167
7.2	Anthocyanidins	168
7.3	Anthocyanidin equilibrium forms	178
7.4	New anthocyanin glycosides	181
7.5	New anthocyanin acylglycosides	183
7.6	Flavonoid complexes including at least one anthocyanidin subunit	187
7.7	Metalloanthocyanins	188
7.8	Biosynthesis and molecular biology	189
7.9	Anthocyanin localization in plant cells	191
7.10	Acknowledgments	192
7.11	Notes	192
7.12	References	193
8 S	alicylic Acid and Induced Plant Defenses	202
	ean-Pierre Métraux, Elisabeth Lamodière, Jérémy Catinot, Olivier Lamotte	202
	nd Christophe Garcion	
8.1	Induced resistance and phenolics	202
8.2	The biosynthesis of SA	203
8.3	The network of signaling and the action of SA	205
8.4	Conclusions	207
8.5	Acknowledgment	207
8.6	References	207
	henols and the Onset and Expression of Plant Disease Resistance	211
R	ay Hammerschmidt and Samantha I. Hollosy	
9.1	Introduction	211
9.2	Biosynthetic origins of defense-associated phenolic compounds	212
9.3	Phenolic compounds as preformed defenses	212