

Handbook of Plant Food Phytochemicals

SOURCES, STABILITY AND EXTRACTION

EDITED BY

B.K. Tiwari • Nigel P. Brunton • Charles S. Brennan



 **WILEY-BLACKWELL**

Handbook of Plant Food Phytochemicals

Handbook of Plant Food Phytochemicals

Sources, Stability and Extraction

Edited by

B.K. Tiwari

Food and Consumer Technology Department
Hollings Faculty
Manchester Metropolitan University
Old Hall Lane
Manchester
UK

Nigel P. Brunton

School of Agriculture and Food Science
University College Dublin
Dublin
Ireland

Charles S. Brennan

Faculty of Agriculture and Life Sciences
Lincoln University
Lincoln
Canterbury
New Zealand



WILEY-BLACKWELL

A John Wiley & Sons, Ltd., Publication

This edition first published 2013 © 2013 by John Wiley & Sons, Ltd

Wiley-Blackwell is an imprint of John Wiley & Sons, formed by the merger of Wiley's global Scientific, Technical and Medical business with Blackwell Publishing.

Registered Office

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

Editorial Offices

9600 Garsington Road, Oxford, OX4 2DQ, UK

The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK

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 authors to be identified as the authors of this work has been asserted in accordance with the UK 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.

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.

Limit of Liability/Disclaimer of Warranty: While the publisher and author(s) have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. It is sold on the understanding that the publisher is not engaged in rendering professional services and neither the publisher nor the author shall be liable for damages arising herefrom. 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

Handbook of plant food phytochemicals : sources, stability and extraction / edited by Brijesh Tiwari, Nigel Brunton, Charles S. Brennan.

p. cm.

Includes bibliographical references and index.

ISBN 978-1-4443-3810-2 (hardback : alk. paper) – ISBN 978-1-118-46467-0 (epdf) –

ISBN 978-1-118-46469-4 (emobi) – ISBN 978-1-118-46468-7 (epub) – ISBN 978-1-118-46471-7 (obook)

1. Phytochemicals. 2. Plants—Composition. 3. Food—Composition. 4. Food industry and trade.

I. Tiwari, Brijesh K. II. Brunton, Nigel. III. Brennan, Charles S.

QK861.H34 2012

580—dc23

2012024779

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

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

Cover image credits, left to right: © iStockphoto.com/KevinDyer; © iStockphoto.com/aluxum; © iStockphoto.com/FotografiaBasica

Cover design by Meaden Creative

Set in 10/12pt Times by SPi Publisher Services, Pondicherry, India

Contents

<i>Contributor list</i>	xiii
1 Plant food phytochemicals	1
B.K. Tiwari, Nigel P. Brunton and Charles S. Brennan	
1.1 Importance of phytochemicals	1
1.2 Book objective	2
1.3 Book structure	2
PART I CHEMISTRY AND HEALTH	5
2 Chemistry and classification of phytochemicals	7
Rocio Campos-Vega and B. Dave Oomah	
2.1 Introduction	7
2.2 Classification of phytochemicals	8
2.2.1 Terpenes	8
2.2.2 Polyphenols	13
2.2.3 Carotenoids	15
2.2.4 Glucosinolates	15
2.2.5 Dietary fiber (non starch polysaccharides)	16
2.2.6 Lectins	17
2.2.7 Other phytochemicals	18
2.3 Chemical properties of phytochemicals	21
2.3.1 Terpenes	21
2.3.2 Polyphenols	22
2.3.3 Carotenoids	23
2.3.4 Glucosinolates	24
2.3.5 Dietary fiber (non starch polysaccharides)	26
2.3.6 Lectins	26
2.3.7 Other phytochemicals	28
2.4 Biochemical pathways of important phytochemicals	34
2.4.1 Shikimate pathway	34
2.4.2 Isoprenoid pathway	37
2.4.3 Polyketide pathway	38
2.4.4 Secondary transformation	40
2.4.5 Glucosinolate biosynthesis	40
References	41
3 Phytochemicals and health	49
Ian T. Johnson	
3.1 Introduction	49

3.2	Bioavailability of phytochemicals	50
3.2.1	Terpenes	51
3.2.2	Polyphenols	52
3.2.3	Carotenoids	53
3.2.4	Glucosinolates	54
3.2.5	Lectins	55
3.3	Phytochemicals and their health-promoting effects	55
3.3.1	Phytochemicals as antioxidants	56
3.3.2	Blocking and suppressing the growth of tumours	59
3.3.3	Modifying cardiovascular physiology	62
3.4	General conclusions	63
	References	64
4	Pharmacology of phytochemicals	68
	José M. Matés	
4.1	Introduction	68
4.2	Medicinal properties of phytochemicals	69
4.2.1	Therapeutic use of antioxidants	73
4.2.2	Phytochemicals as therapeutic agents	75
4.3	Phytochemicals and disease prevention	78
4.3.1	Pharmacologic effects of phytochemicals	80
4.4	Phytochemicals and cardiovascular disease	82
4.5	Phytochemicals and cancer	88
4.6	Summary and conclusions	95
	References	96
	PART II SOURCES OF PHYTOCHEMICALS	105
5	Fruit and vegetables	107
	Uma Tiwari and Enda Cummins	
5.1	Introduction	107
5.2	Polyphenols	107
5.3	Carotenoids	113
5.4	Glucosinolates	117
5.4.1	Variations in glucosinolates	119
5.5	Glycoalkaloids	120
5.6	Polyacetylenes	121
5.7	Sesquiterpene lactones	123
5.8	Coumarins	124
5.9	Terpenoids	125
5.10	Betalains	125
5.11	Vitamin E or tocopherols content in fruit and vegetables	126
5.12	Conclusions	129
	References	129
6	Food grains	138
	Sanaa Ragae, Tamer Gamel, Koushik Seetharaman, and El-Sayed M. Abdel-Aal	
6.1	Introduction	138

6.2	Phytochemicals in cereal grains	139
6.2.1	Dietary fiber	139
6.2.2	Phenolic compounds	141
6.2.3	Other phytochemicals	143
6.3	Phytochemicals in legume grains	144
6.3.1	Dietary fiber	144
6.3.2	Phenolic acids	145
6.3.3	Isoflavones	146
6.3.4	Saponins	146
6.3.5	Anthocyanins	147
6.3.6	Lignans	148
6.3.7	Other phytochemicals	148
6.4	Stability of phytochemicals during processing	149
6.5	Food applications and impact on health	152
6.6	Cereal-based functional foods	152
6.7	Legume-based functional foods	153
	References	154
7	Plantation crops and tree nuts: composition, phytochemicals and health benefits	163
	Narpinder Singh and Amritpal Kaur	
7.1	Introduction	163
7.2	Composition	165
7.3	Phytochemicals content	167
7.4	Health benefits	174
	References	175
8	Food processing by-products	180
	Anil Kumar Anal	
8.1	Introduction	180
8.2	Phytochemicals from food by-products	181
8.2.1	Biowaste from tropical fruit and vegetables	181
8.2.2	Citrus peels and seeds	181
8.2.3	Mango peels and kernels	182
8.2.4	Passion fruit seed and rind	183
8.2.5	Pomegranate peels, rinds and seeds	184
8.2.6	Mangosteen rind and seeds	184
8.3	By-products from fruit and vegetables	187
8.3.1	Apple pomace	187
8.3.2	By-products from grapes	187
8.3.3	Banana peels	188
8.3.4	Tomato	188
8.3.5	Carrot	188
8.3.6	Mulberry leaves	189
8.4	Tuber crops and cereals	189
8.4.1	Cassava	189
8.4.2	Defatted rice bran	189
8.5	Extraction of bioactive compounds from plant food by-products	190

8.6	Future trends	190
	References	192
PART III	IMPACT OF PROCESSING ON PHYTOCHEMICALS	199
9	On farm and fresh produce management	201
	Kim Reilly	
9.1	Introduction	201
9.2	Pre-harvest factors affecting phytochemical content	202
9.2.1	Tissue type and developmental stage	208
9.2.2	Fertilizer application – nitrogen, phosphorus, potassium, sulphur and selenium	210
9.2.3	Seasonal and environmental effects – light and temperature	212
9.2.4	Biotic and abiotic stress	214
9.2.5	Means of production – organic and conventional agriculture	216
9.2.6	Other factors	217
9.3	Harvest and post-harvest management practices	218
9.3.1	Harvest and post-harvest management of onion	218
9.3.2	Harvest and post-harvest management of broccoli	220
9.3.3	Harvest and post-harvest management of carrot	221
9.4	Future prospects	222
9.4.1	Growing bio-fortified crops – optimized agronomic and post-harvest practices	222
9.4.2	Edible sprouts	222
9.4.3	Variety screening and plant breeding for bio-fortified crops	223
9.4.4	Novel uses for crops and crop wastes	224
	References	225
10	Minimal processing of leafy vegetables	235
	Rod Jones and Bruce Tomkins	
10.1	Introduction	235
10.2	Minimally processed products	236
10.3	Cutting and shredding	237
10.4	Wounding physiology	238
10.5	Browning in lettuce leaves	240
10.6	Refrigerated storage	241
10.7	Modified atmosphere storage	242
10.8	Conclusions	243
	References	244
11	Thermal processing	247
	Nigel P. Brunton	
11.1	Introduction	247
11.2	Blanching	248
11.3	Sous vide processing	250
11.4	Pasteurisation	251

11.5	Sterilisation	254
11.6	Frying	255
11.7	Conclusion	257
	References	257
12	Effect of novel thermal processing on phytochemicals	260
	Bhupinder Kaur, Fazilah Ariffin, Rajeev Bhat, and Alias A. Karim	
12.1	Introduction	260
12.2	An overview of different processing methods for fruits and vegetables	261
12.3	Novel thermal processing methods	261
12.4	Effect of novel processing methods on phytochemicals	264
12.4.1	Ohmic heating	265
12.4.2	Microwave heating	266
12.4.3	Radio frequency	268
12.5	Challenges and prospects/future outlook	268
12.6	Conclusion	269
	References	269
13	Non thermal processing	273
	B.K. Tiwari, PJ Cullen, Charles S. Brennan and Colm P. O'Donnell	
13.1	Introduction	273
13.2	Irradiation	273
13.2.1	Ionising radiation	274
13.2.2	Non ionising radiation	274
13.3	High pressure processing	281
13.4	Pulsed electric field	284
13.5	Ozone processing	286
13.6	Ultrasound processing	289
13.7	Supercritical carbon dioxide	291
13.8	Conclusions	292
	References	293
PART IV	STABILITY OF PHYTOCHEMICALS	301
14	Stability of phytochemicals during grain processing	303
	Laura Alvarez-Jubete and Uma Tiwari	
14.1	Introduction	303
14.2	Germination	304
14.3	Milling	307
14.4	Fermentation	312
14.5	Baking	315
14.6	Roasting	323
14.7	Extrusion cooking	324
14.8	Parboiling	327
14.9	Conclusions	327
	References	327

15	Factors affecting phytochemical stability	332
	Jun Yang, Xiangjiu He, and Dongjun Zhao	
15.1	Introduction	332
15.2	Effect of pH	335
15.3	Concentration	337
15.4	Processing	338
	15.4.1 Processing temperature	338
	15.4.2 Processing type	341
15.5	Enzymes	346
15.6	Structure	349
15.7	Copigments	350
15.8	Matrix	353
	15.8.1 Presence of SO ₂	353
	15.8.2 Presence of ascorbic acids and other organic acids	354
	15.8.3 Presence of metallic ions	355
	15.8.4 Others	356
15.9	Storage conditions	357
	15.9.1 Light	357
	15.9.2 Temperature	358
	15.9.3 Relative humidity (RH)	360
	15.9.4 Water activity (a _w)	361
	15.9.5 Atmosphere	361
15.10	Conclusion	363
	References	364
16	Stability of phytochemicals at the point of sale	375
	Pradeep Singh Negi	
16.1	Introduction	375
16.2	Stability of phytochemicals during storage	375
	16.2.1 Effect of water activity	376
	16.2.2 Effect of temperature	376
	16.2.3 Effect of light and oxidation	379
	16.2.4 Effect of pH	381
16.3	Food application and stability of phytochemicals	381
16.4	Edible coatings for enhancement of phytochemical stability	382
16.5	Modified atmosphere storage for enhanced phytochemical stability	383
16.6	Bioactive packaging and micro encapsulation for enhanced phytochemical stability	384
16.7	Conclusions	387
	References	387
PART V	ANALYSIS AND APPLICATION	397
17	Conventional extraction techniques for phytochemicals	399
	Niamh Harbourne, Eunice Marete, Jean Christophe Jacquier and Dolores O’Riordan	
17.1	Introduction	399
17.2	Theory and principles of extraction	399

17.2.1	Conventional extraction methods	400
17.2.2	Factors affecting extraction methods	401
17.2.3	Limitations of extraction techniques	404
17.3	Examples of conventional techniques	405
17.3.1	Roots	405
17.3.2	Leaves and stems	405
17.3.3	Flowers	407
17.3.4	Fruits	407
17.4	Conclusion	409
	References	409
18	Novel extraction techniques for phytochemicals	412
	Hilde H. Wijngaard, Olivera Trifunovic and Peter Bongers	
18.1	Introduction	412
18.2	Pressurised solvents	413
18.2.1	Supercritical fluid extraction	413
18.2.2	Pressurised liquid extraction (PLE)	419
18.3	Enzyme assisted extraction	421
18.4	Non-thermal processing assisted extraction	423
18.4.1	Ultrasound	423
18.4.2	Pulsed electric fields	424
18.5	Challenges and future of novel extraction techniques	426
	References	428
19	Analytical techniques for phytochemicals	434
	Rong Tsao and Hongyan Li	
19.1	Introduction	434
19.2	Sample preparation	436
19.2.1	Extraction	436
19.2.2	Sample clean-up	438
19.3	Non-chromatographic spectrophotometric methods	439
19.3.1	Total phenolic content (TPC)	440
19.3.2	Total flavonoid content (TFC)	440
19.3.3	Total anthocyanin content (TAC)	441
19.3.4	Total carotenoid content (TCC)	441
19.3.5	Methods based on fluorescence	441
19.3.6	Colorimetric methods for other phytochemicals	442
19.4	Chromatographic methods	442
19.4.1	Conventional chromatographic methods	442
19.4.2	Instrumental chromatographic methods	443
	References	447
20	Antioxidant activity of phytochemicals	452
	Ankit Patras, Yvonne V. Yuan, Helena Soares Costa and Ana Sanches-Silva	
20.1	Introduction	452
20.2	Measurement of antioxidant activity	453
20.2.1	Assays involving a biological substrate	453

20.2.2	Assays involving a non-biological substrate	454
20.2.3	Ferrous oxidation–xylenol orange (FOX) assay	455
20.2.4	Ferric thiocyanate (FTC) assay	455
20.2.5	Hydroxyl radical scavenging deoxyribose assay	456
20.2.6	1,1-diphenyl-2-picrylhydrazyl (DPPH•) stable free radical scavenging assay	456
20.2.7	Azo dyes as sources of stable free radicals in antioxidant assays	457
20.2.8	Oxygen radical absorbance capacity (ORAC) assay	458
20.2.9	Total radical-trapping antioxidant parameter (TRAP) assay	459
20.2.10	ABTS•+radical cation scavenging activity	460
20.2.11	Ferric reducing ability of plasma (FRAP) assay	460
20.2.12	Inhibition of linoleic acid oxidation as a measure of antioxidant activity	461
20.2.13	Other assays – methods based on the chemiluminescence (CL) of luminol	462
20.2.14	Comparison of various methods for determining antioxidant activity: general perspectives	462
20.2.15	Discrepancies over antioxidant measurement	463
20.3	Concluding remarks	465
	References	466
21	Industrial applications of phytochemicals	473
	Juan Valverde	
21.1	Introduction	473
21.2	Phytochemicals as food additives	474
21.2.1	Flavourings	475
21.2.2	Sweeteners and sugar substitutes	476
21.2.3	Colouring substances	477
21.2.4	Antimicrobial agents/essential oils	478
21.2.5	Antioxidants	480
21.3	Stabilisation of fats, frying oils and fried products	481
21.4	Stabilisation and development of other food products	488
21.4.1	Anti-browning effect of phytochemicals in foods	488
21.4.2	Colour Stabilisation in meat products	490
21.4.3	Antimicrobials to extends shelf life	491
21.5	Nutraceutical applications	492
21.5.1	Phytosterol and phytostanol enriched foods	492
21.5.2	Resveratrol enriched drinks and beverages	492
21.5.3	Isoflavone enriched dairy-like products	493
21.5.4	β-glucans	493
21.5.5	Flavonoids	494
21.6	Miscellaneous industrial applications	494
21.6.1	Cosmetic applications	494
21.6.2	Bio-pesticides	495
	References	495
	<i>Index</i>	502

Contributor list

Editors

B.K. Tiwari

Food and Consumer Technology,
Manchester Metropolitan University,
Manchester, UK

Nigel P. Brunton

School of Agriculture and Food Science,
University College Dublin,
Dublin, Ireland

Charles S. Brennan

Faculty of Agriculture and Life Sciences,
Lincoln University, Lincoln,
Canterbury, New Zealand

Contributors

El-Sayed M. Abdel-Aal

Guelph Food Research Centre,
Agriculture and Agri-Food Canada,
Guelph, Ontario, Canada

Laura Alvarez-Jubete

School of Food Science and
Environmental Health,
Dublin Institute of Technology,
Dublin, Ireland

Anil Kumar Anal

Food Engineering and Bioprocess
Technology,
Asian Institute of Technology,
Klongluang, Thailand

Fazilah Ariffin

Food Biopolymer Research Group,
Food Technology Division,
School of Industrial Technology,
Universiti Sains Malaysia,
Penang, Malaysia

Rajeev Bhat

Food Biopolymer Research Group,
Food Technology Division,
School of Industrial Technology,
University Sains Malaysia,
Penang, Malaysia

Peter Bongers*

Structured Materials and
Process Science,
Unilever Research and Development
Vlaardingen,
The Netherlands

Charles S. Brennan

Faculty of Agriculture and Life Sciences,
Lincoln University, Lincoln,
Canterbury, New Zealand

Nigel P. Brunton

School of Agriculture and Food Science,
University College Dublin,
Dublin, Ireland

Rocio Campos-Vega

Kellogg Company Km,
Campo Militar,
Querétaro, México

Helena Soares Costa

National Institute of Health Dr Ricardo Jorge, Food and Nutrition Department, Lisbon, Portugal

PJ Cullen

School of Food Science and Environmental Health, Dublin Institute of Technology, Dublin, Ireland

Enda Cummins

UCD School of Biosystems Engineering, Agriculture and Food Science Centre, Dublin, Ireland

Tamer Gamel

Guelph Food Research Centre, Agriculture and Agri-Food Canada, Guelph, Ontario, Canada

Niamh Harbourne

Food and Nutritional Sciences, University of Reading, Reading, UK

Xiangjiu He

School of Pharmaceutical Sciences, Wuhan University, Wuhan, Hubei, China

Jean Christophe Jacquier

School of Agriculture and Food Science University College Dublin, Dublin, Ireland

Ian T. Johnson

Institute of Food Research, Norwich Research Park, Colney, Norwich, UK

Rod Jones

Department of Primary Industries, Victoria, Australia

Alias A. Karim

Food Biopolymer Research Group, Food Technology Division, School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia

Amritpal Kaur

Department of Food Science and Technology, Guru Nanak Dev University, Amritsar, India

Bhupinder Kaur

Food Biopolymer Research Group, Food Technology Division, School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia

Hongyan Li

Guelph Food Research Centre, Agriculture and Agri-Food Canada, Guelph, Ontario, Canada

Eunice Marete

School of Agriculture and Food Science University College Dublin, Dublin, Ireland

José M. Matés

Department of Molecular Biology and Biochemistry, Faculty of Sciences, Campus de Teatinos, University of Málaga, Spain

Pradeep Singh Negi

Human Resource Development, Central Food Technological Research Institute (CSIR), Mysore, India

Colm P. O'Donnell

UCD School of Biosystems Engineering, University College Dublin Belfield, Dublin, Ireland

B. Dave Oomah

Pacific Agri-Food Research Centre,
Agriculture and Agri-Food Canada,
Summerland,
British Columbia, Canada

Dolores O’Riordan

School of Agriculture and Food Science
University College Dublin,
Dublin, Ireland

Ankit Patras

Department of Food Science,
University of Guelph, Guelph
Ontario, Canada

Sanaa Ragae

Department of Food Science,
University of Guelph, Guelph,
Ontario, Canada

Kim Reilly

Horticulture Development Unit,
Teagasc, Kinsealy Research Centre,
Dublin, Ireland

Ana Sanches-Silva

National Institute of Health Dr Ricardo
Jorge, Food and Nutrition Department,
Lisbon, Portugal

Koushik Seethraman

Department of Food Science,
University of Guelph,
Guelph, Ontario, Canada

Narpinder Singh

Department of Food Science and
Technology,
Guru Nanak Dev University,
Amritsar, India

B.K. Tiwari

Food and Consumer Technology,
Manchester Metropolitan University,
Manchester, UK

Uma Tiwari

UCD School of Biosystems Engineering,
Agriculture and Food Science Centre,
Dublin, Ireland

Bruce Tomkins

Department of Primary Industries,
Victoria, Ferntree Gully,
DC, Australia

Olivera Trifunovic

Structured Materials and Process Science,
Unilever Research and Development
Vlaardingen,
The Netherlands

Rong Tsao

Guelph Food Research Centre,
Agriculture and Agri-Food Canada,
Guelph, Ontario, Canada

Juan Valverde

Teagasc Food Research Centre Ashtown,
Dublin, Ireland

Hilde H. Wijngaard

Dutch Separation Technology Institute,
Amersfoort, The Netherlands

Jun Yang

Frito-Lay North America R&D,
PepsiCo Inc.,
Plano, TX, USA

Yvonne V. Yuan

School of Nutrition,
Ryerson University,
Toronto, Ontario, Canada

Dongjun Zhao

Department of Food Science,
Cornell University,
Ithaca, NY, USA

1 Plant food phytochemicals

B.K. Tiwari, Nigel P. Brunton and Charles S. Brennan

1.1 Importance of phytochemicals

Type the word ‘phytochemical’ into any online search engine and it will return literally thousands of hits. This is a reflection of the role plant derived chemicals have played in medicine and other areas since humans have looked to nature to provide cures for various ailments and diseases. While it is often stated, it is worth repeating that the evolution of modern medicine derived from applying scientific principles to herbalism and to this day plants derived compounds provide the skeletons for constructing molecules with the abilities to cure many diseases. In recent times applications of phytochemicals have extended into other areas especially nutraceuticals and functional foods. The focus here is not on curing existing conditions but delaying the onset of new ones and it is not surprising to note that plant foods and plant derived components make up the vast majority of compounds with European Food Safety Authority validated Article 13.1 health claims. Whilst there has been a renewed interest in the use of medicinal plants to treat diseases in recent times and the use of phytochemicals as pharmaceuticals is covered in the present book, this is not the core theme of the book. Given that plant foods are still a major component of most diets worldwide the greatest significance of phytochemicals derives from their role in human diets and health. In fact it is only in relatively recent times that due recognition has been given to the importance of phytochemicals in maintaining health. This has driven a huge volume of work on the subject ranging from unravelling mechanisms of biological significance to discovery and stability studies.

An overview of the health benefits of phytochemicals is essential as many phytochemicals have been reported to illicit both positive and negative biological effects. In recent times some evidence for the role of specific plant food phytochemicals in protecting against the onset of diseases such as cancers and heart diseases has been put forward. Most researchers in this field will however agree that in most cases more evidence is needed to prove the case for the ability of phytochemicals to delay the onset of these diseases. Nevertheless the

increasing awareness of consumers of the link between diet and health has exponentially increased the number of scientific studies into the biological effects of these substances.

1.2 Book objective

The overarching objective, therefore, of the *Handbook of Plant Food Phytochemicals* is to provide a bird's eye view of the occurrence, significance and factors affecting phytochemicals in plant foods. A key objective of the handbook is to critically evaluate some of these with a particular emphasis on evidence for or against quantifiable beneficial health effects being imparted via a reduction in disease risk through the consumption of foods rich in phytochemicals.

1.3 Book structure

The book is divided into five parts. Part I deals with the health benefits and chemistry of phytochemicals, Part II summarises phytochemicals in various food types, Parts III and IV deal with a variety of factors that can affect phytochemical content and stability and Part V deals with a range of analytical techniques and applications of phytochemicals. The subject of the biological activity of phytochemicals is approached both from a disease risk reduction perspective in Chapter 3 and from a more traditional pharmacological viewpoint in Chapter 4. Together these chapters are intended to give the reader a sound basis for understanding the biological significance of these substances and to contextualise their roles either as a medicinal plant or as a nutraceutical/functional food. Key to understanding both the stability and biological role of phytochemicals is a sound knowledge of their chemistry and biochemical origin. This often neglected topic is covered in detail here along with an overview of the classification of these compounds. This reflects the ambition of the book to serve as a reference text for students in the field and is intended to provide a basis for understanding some of the complex subjects covered in earlier chapters.

The chemical diversity and number of plant food phytochemicals with reported abilities to protect against diseases numbers in the many thousands. Therefore, to cover all these substances in detail would be impossible. However, myself and my fellow editors felt that providing readers with a reference manuscript for plant food phytochemicals and a basic understanding of the types of phytochemicals in plant foods was essential. Part II of the handbook covers this subject matter by giving an overview of the phytochemicals present in four food categories – fruit and vegetables, food grains, natural products and tree nuts and food processing by-products. Fruits and vegetables are perhaps the best recognised source of phytochemicals and this is reflected in the depth and volume of literature on this food type. Chapter 5 summarises information on major phytochemicals groups in fruits and vegetables as well as some of the more obscure and recently emerged groups. From a consumption perspective food grains form a huge proportion of most diets worldwide – however, due recognition of grains as sources of phytochemicals has only emerged relatively recently. Chapter 6 summarises the phytochemical composition of both cereals and legumes and underlines the importance of this food group as a source of phytochemicals in human diets. Early humans were of course hunter gatherers and nuts would have been important of their diets. It is therefore perhaps not surprising that tree nuts and other natural products have been shown to contain a range of phytochemicals with the potential to deliver benefits

beyond basic nutrition. The importance of tree nuts as sources of these compounds is hence covered in detail in Chapter 7 along with related food types such as plantation products. Whilst a core objective of the handbook is to cover the breadth of subject matter in phytochemicals from plant foods this is not merely an academic exercise. Phytochemicals have real commercial uses and this is given due recognition in Chapters 7 and 8 where an overview of the application of phytochemicals derived from foods grains and trees is given. In fact throughout the handbook authors provide detailed information and examples of real applications of plant food derived phytochemicals with a view to underlining the commercial importance of these compounds. Food processing by-products do not of course constitute a food group – however, they have become hugely important sources of phytochemicals in recent times and Chapter 8 is dedicated to revealing the potential of food processing by-products as sources of phytochemicals with real commercial potential. Recovering value from by-products is of course hugely significant to food processors as they seek to maximise the value of a resource that hitherto was considered a waste. This also reflects the drive to identify more sustainable food processing practices and increasing pressures from regulators to reduce waste.

As with most other foods, plant foods are often not consumed in their native form. Therefore, investigators have long been interested in developing an understanding of how processing effects phytochemical composition with view to maximising their potential health promoting properties. Today's consumers are demanding foods that are healthy, convenient and appetising. The drive for healthy foods has fuelled interest in the effect of processing on the level of components responsible for imparting this benefit, especially phytochemicals. Therefore, much work has been devoted to assessing the effect of processing and storage on levels of potentially important phytochemicals in foods. In addition, a number of novel thermal and non-thermal technologies designed to achieve microbial safety, while minimising the effects on its nutritional and quality attributes, have recently become available. Minimising changes in phytochemicals during processing is a considerable challenge for food processors and technologists. Thus, there is a requirement for detailed industrially relevant information concerning phytochemicals and their application in food products. In addition, industrial adoption of novel processing techniques is in its infancy. Applications of new and innovative technologies and resulting effects on those food products either individually or in combination are always of great interest to academic, industrial, nutrition and health professionals. Part III gives an oversight as to how processing affects phytochemicals in plant foods. This is an area that has received huge attention recently and this has reflected the number of chapters dedicated to it in the handbook. This part of the handbook also summarises and evaluates an area that is often neglected when in the phytochemicals arena but can have profound impact on final phytochemical content, namely on farm and fresh produce management. Given the investment and scale of research required to carry out replicated field trials elucidating the impact of pre-harvest factors, such as fertiliser application, light, temperature, biotic and abiotic stress, this area has perhaps been the most challenging of any of the 'farm to fork' factors involved in determining the phytochemical content of plant foods. Indeed assessing the relative effects of intensive and organic farming practices is a highly controversial area but one that consumers appear to take an active interest in given the premium demand for organically produced plant foods. Post-harvest management pertains to the period between harvesting of the plant food and its arrival at the processing plant. This covers many operations including mechanical harvesting, storage and transport. Unsurprisingly many of these operations constitute a stress to the still respiring plant food and thus can activate or deactivate pathways leading

to the synthesis of phytochemicals. Ready to eat fruit and vegetables are a relatively recent phenomenon on supermarket shelves. Their emergence is a reflection of consumers' busy lifestyles and the need to provide healthy and convenient solutions for time poor customers who desire a healthy diet. Products of this nature are often referred to as minimally processed and are subjected to a variety of operations ranging from peeling and cutting to washing. Unlike plant foods, which have been subjected to heat processing, minimally processed products remain viable, albeit in many cases in a wounded state. Therefore a wide variety of responses to minimal processing have been reported and these are summarised and evaluated in Chapter 10, with a particular emphasis on salad mixes. A huge spectrum of full processing techniques is available to food processors nowadays. These range from severe (canning) to mild (*sous-vide* processing) to non-thermal examples such as high pressure processing, ultrasound and irradiation. Not surprisingly these can have a range of effects on phytochemical content and Chapters 11, 12 and 13 summarise the work done to date on these processes. Grains and pulses undergo a distinctly different processing route to other plant foods involving germination, milling, fermentation and finally baking. Therefore we have dedicated a standalone chapter to food grains, which reviews reports on the grain processing techniques on the content of phytochemicals. Finally, in tune with the farm to fork approach adopted by the handbook, the last chapter in Part III reviews the stability of foods containing phytochemicals during storage after processing. Like most chemical constituents the nature of the matrix they are contained in has a profound effect on their stability. Therefore, in Chapter 15 the stability of phytochemicals with different properties such as low moisture contents, ethnic foods and of course traditional foods is reviewed.

The final part of the book deals with perhaps the first question a researcher must ask him/herself when entering the field namely how do we extract these compounds and how do we measure them. The chapter on extraction is particularly relevant as this is an important consideration not only when analysing these compounds but also when preparing to include them as an ingredient in another food. Phytochemical analysis techniques are advancing at an exponential rate and therefore a chapter reviewing the state of the art in this discipline was one of the first we put on paper when deciding on the content of the book. Finally, the reason we have dedicated a book to the subject of phytochemicals in plant foods is because they have very real applications in industry and everyday life. The final chapter of the handbook drives this point home by providing real examples of industrial uses for phytochemicals ranging from maintaining stability in oxidatively labile foods to enhancing the health promoting properties of others. To conclude we hope you find the proceeding chapters to be informative, clear, concise and that they provide a clear thinking perspective on a subject matter that has benefitted mankind from many perspectives and will no doubt continue to do so into the future.

Part I

Chemistry and Health

2 Chemistry and classification of phytochemicals

Rocio Campos-Vega¹ and B. Dave Oomah²

¹ Kellogg Company Km. Querétaro, Qro. México

² Pacific Agri-Food Research Centre, Agriculture and Agri-Food Canada, Summerland, British Columbia, Canada

2.1 Introduction

The word ‘biodiversity’ is on nearly everyone’s lips these days, but ‘chemodiversity’ is just as much a characteristic of life on Earth as biodiversity. Living organisms produce several thousands of different structures of low-molecular-weight organic compounds. Many of these have no apparent function in the basic processes of growth and development, and have been historically referred to as natural products or secondary metabolites. The importance of natural products in medicine, agriculture and industry has led to numerous studies on the synthesis, biosynthesis and biological activities of these substances. Yet we still know comparatively little about their actual roles in nature.

Clearly such research has been stimulated by scientific curiosity in the substances and mechanisms involved in the protective effects of fruits and vegetables. Dietary phytonutrients appear to lower the risk of cancer and cardiovascular disease. Studies on the mechanisms of chemoprotection have focused on the biological activity of plant-based phenols and polyphenols, flavonoids, isoflavones, terpenes, and glucosinolates. However, most, if not all, of these bioactive compounds are bitter, acrid, or astringent and therefore aversive to the consumer. Some have long been viewed as plant-based toxins. The analysis of phytochemicals is complicated due to the wide variation even within the same group of compounds, and the metabolic degradation or transformation that may occur during crushing or processing of plants (e.g. for *Allium* and *Brassica* compounds), thus increasing the complexity of the mixture. Many phytochemical analyses require mass spectroscopy and therefore are time-consuming and expensive. Furthermore, some compounds tend to bind to macromolecules, making quantitative extraction difficult. Furthermore, many plant food phytochemicals that are poorly absorbed by humans usually undergo metabolism and rapid excretion. It is clear from *in vitro* and animal data that the actions of some phytochemicals are likely to be achieved only at doses much higher than those present in edible plant foods. Thus, extraction or synthesis of the active ingredient is essential if they are to be of prophylactic or therapeutic value in human subjects.

Handbook of Plant Food Phytochemicals: Sources, Stability and Extraction, First Edition.

Edited by B.K. Tiwari, Nigel P. Brunton and Charles S. Brennan.

© 2013 John Wiley & Sons, Ltd. Published 2013 by John Wiley & Sons, Ltd.

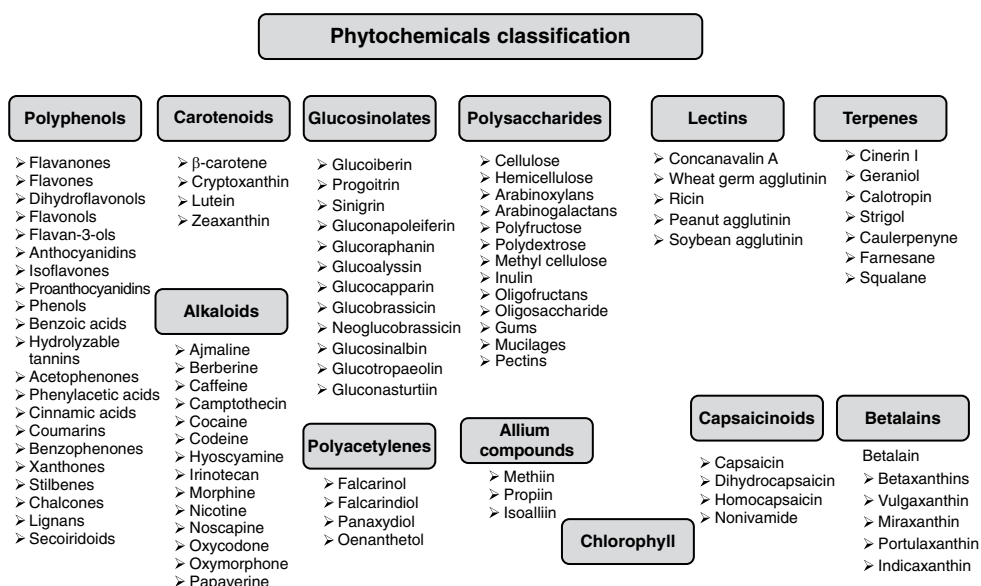


Figure 2.1 Classification of phytochemicals.

2.2 Classification of phytochemicals

Many phytochemicals have a range of different biochemical and physiological effects, isoflavonoids, for example have antioxidant and anti-oestrogenic activities. These activities may require different plasma or tissue concentrations for optimum effects. A diagram illustrating the classification of the phytochemicals covered in this chapter is shown in Figure 2.1.

In addition, plants contain mixtures of phytochemicals (Table 2.1), with considerable opportunity for interaction (Rowland *et al.*, 1999). Plant secondary metabolites are an enormously variable group of phytochemicals in terms of their number, structural heterogeneity, and distribution.

A summary of the main groups of bioactive chemicals in edible plants, their sources, and their biological activities is presented in Table 2.2 (Rowland *et al.*, 1999).

2.2.1 Terpenes

The term terpenes originates from turpentine (*balsamum terebinthinae*). Turpentine, the so-called “resin of pine trees”, is the viscous pleasantly smelling balsam that flows upon cutting or carving the bark and the new wood of several pine tree species (*Pinaceae*). Turpentine contains the “resin acids” and some hydrocarbons, which were originally referred to as terpenes. Traditionally, all natural compounds built up from isoprene subunits and, for the most part, originating from plants are denoted as terpenes (Breitmaier, 2006).

All living organisms manufacture terpenes for certain essential physiological functions and therefore have the potential to produce terpene natural products. Given the many ways in which the basic C_5 units can be combined together and the different selection pressures under which organisms have evolved, it is not surprising to observe the enormous number and

Table 2.1 Phytochemical content of some edible plants (modified from Caragay, 1992; Rowland *et al.*, 1999)

Plants	Flavo- noids	Isofla- vonoids	Lig- nans	Organo- sulphides	Glucosi- nolates	Phenolic acids	Oligo- saccharides	Terpe- nes	NSP	Alka- loids	Poly- acetylenes	Chloro- phyll	Capsaici- noids	Beta- lains	Carote- noids
Soybeans	✓	✓				✓	✓		✓						
Cereals	✓		✓			✓			✓					✓	
Garlic and onions				✓		✓	✓	✓							
Cruciferae	✓			✓	✓	✓		✓	✓						
Solanaceae	✓					✓		✓	✓						
Umbeliderae	✓					✓		✓	✓						
Citrus fruits	✓					✓		✓	✓						
Green tea	✓					✓				✓					
Legumes		✓				✓			✓						
Blueberry	✓														
Grapes					✓										
Tomato															✓
Carrots											✓				
Pepper												✓	✓		
Beets														✓	
<i>Amaranthus</i> <i>caudatus</i>															✓
Flaxseed	✓		✓			✓			✓						

Table 2.2 Sources and biological activities of phytochemicals (adapted from Rowland *et al.*, 1999)

Group	Examples	Main food sources	Activity and functional marker
Fiber and related compounds	NSP Soluble (e.g. pectins, gums) Insoluble (celluloses) Resistant starch, retrograded starch Phytate Oligosaccharides	Fruit (apples, citrus), oats, soybean, algae Cereals (wheat, rye), vegetables High-amylose starches, processed starches, whole grains, and seeds Cereals, grains, soybeans Chicory, soybeans, artichokes, onion	Lowers serum cholesterol Prevents colon and breast cancer, diverticular disease Alleviates constipation Increases butyrate in faeces Prevents colon cancer Binds minerals. Prevents Colon cancer Modifies gut flora, modulates lipid metabolism, Cancer prevention?
Flavonoids	Flavonols: quercetin, kaempferol Flavanones: tangeritin, naringenin, hesperitin Flavanols: catechins, epicatechins	Vegetables (onion, lettuce, tomatoes, peppers) wine, tea Citrus fruits Green tea	Antioxidants, modulate phase 1 enzymes, inhibit protein kinase C. Prevent cancer protect CVD? Modulate immune response?
Tea polyphenols Derived tannins Isoflavonoids Lignans	Catechins, epicatechins Theaflavins, thearubigens Daidzein, genistein Secoisolariciresinol, matairesinol	Green tea Black tea, red wine, roasted coffee Soybean products Rye bran, flaxseed, berries, nuts	Antioxidants prevent CHD? Anti-oestrogenic effects, effects on serum lipids, prevent breast and prostate cancers Antioxidant and anti-oestrogenic effects Prevent colon and prostate cancer?
Glucosinolates Isothiocyanates	Glucobrassicin, indole-3-carbinol Allylisoithiocyanates, indoles, sulforaphane	Cruciferous vegetables (broccoli, cabbage, Brussel sprouts, watercress, mustard)	Induces phase 2 enzymes Cancer prevention?
Simple phenols Phenolic acids, condensed phenols	p-Cresol, ethyl phenol, hydroquinone Gallic acid, tannins, ellagic acid	Raspberry, cocoa beans, green tea, black tea, strawberries	Antioxidants

Monoterpenes	D-Limonene, D-carvone, perillyl alcohol	Citrus fruits, cherries, herbs	Induce Phase I and Phase II enzymes
Hydroxycinnamic acid	Caffeic, ferulic, chlorogenic acids, curcumin	Apples, pears, coffee, mustard, curry	Anti-tumour activity Inhibit nitrosation by trapping nitrite, nucleophiles, antioxidants
Phytosterols	β -Sitosterol, campesterol, stigmasterol	Vegetable oils (soybean, rape seed, maize, sunflower)	Lower serum cholesterol
Alkaloids	Caffeine, Codeine, Noscopine, Quinidine	Berberis vulgaris, Cinchona ledgeriana	Anticancer agents, glycosidase inhibitors, Analgesic
Polyacetylenes	Falcarindiol, Falcarinol, Crepenyic, Stearicolic, Teriric acids	Carrots	Anti cancer properties
Chlorophyll Betalains	Chlorophyll Vulgaxanthin, Miraxanthin, Portulaxanthin, Indicaxanthin	Plants, algae and cyanobacteria Plants: amaranth, cactus fruits	Antioxidant Antioxidant
Organosulphides (allium compounds)	Diallyl sulphide, allyl methyl sulphide, S-allylcysteine	Garlic, onions, leeks	Induce Phase II enzyme, affects serum lipids and platelet aggregation Prevent cancer

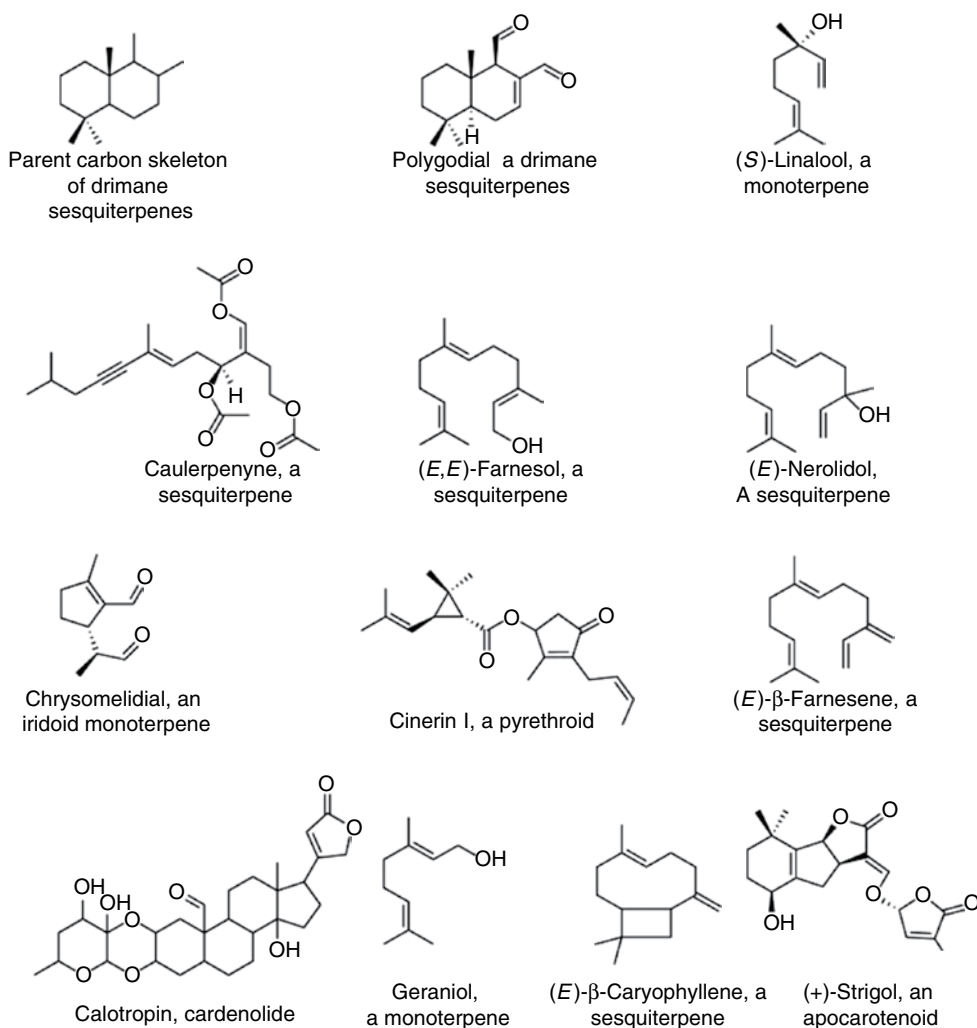


Figure 2.2 Examples of terpenes with established functions in nature (adapted from Gershenzon and Dudareva, 2007).

diversity of structures elaborated (Gershenzon and Dudareva, 2007). Terpenes (also known as terpenoids or isoprenoids) are the largest group of natural products comprising approximately 36 000 terpene structures (Buckingham, 2007), but very few have been investigated from a functional perspective (Figure 2.2).

The classification of terpenoids is based on the number of isoprenoid units present in their structure. The largest categories consist of compounds with two (monoterpenes), three (sesquiterpenes), four (diterpenes), five (sesterterpenes), six (triterpenes), and eight (tetraterpenes) isoprenoid units (see Figure 2.3) (Ashour *et al.*, 2010).

Terpenoids have well-established roles in almost all basic plant processes, including growth, development, reproduction, and defence (Wink and van Wyk, 2008). Gibberellins, a large group of diterpene plant hormones involved in the control of seed germination, stem elongation, and flower induction (Thomas *et al.*, 2005) are among the best-known lower