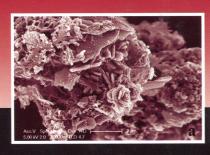
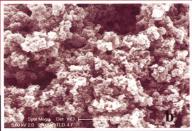
ANTIOXIDANT POLYMERS

Synthesis, Properties, and Applications





Edited by
Giuseppe Cirillo
and Francesca Iemma





Antioxidant Polymers

Synthesis, Properties, and Applications

Edited by

Giuseppe Cirillo

and

Francesca Iemma

Department of Pharmaceutical Sciences, University of Calabria, Italy





Copyright © 2012 by Scrivener Publishing LLC. All rights reserved.

Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts.

Published simultaneously in Canada.

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, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at http://www.wiley.com/go/permission.

Limit of Liability/Disclaimer of Warranty: While the publisher and author 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. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

For more information about Scrivener products please visit www.scrivenerpublishing.com.

Cover design by Russell Richardson

Library of Congress Cataloging-in-Publication Data:

ISBN 978-1-118-20854-0

Printed in the United States of America

Contents

Pre	face			xv
List	of C	ontrib	ıtors	xix
1.	Anti	oxidan	ts: Introduction	1
	Chui	nhuan .	He, Yingming Pan, Xiaowen Ji and	
		gshan I		
			eaning of Antioxidant	1
			ategory of Antioxidants and Introduction	
			n Üsed Antioxidants	2
		1.2.1	BHT	4
		1.2.2	Quercetin	5
		1.2.3	BHA	5
		1.2.4	2- <i>tert</i> -Butylhydroquinone (TBHQ)	6
		1.2.5	Gallic Acid	6
		1.2.6	Resveratrol	6
			Luteolin	7
		1.2.8	Caffeic Acid	7
		1.2.9	Catechin	7
	1.3	Antiox	kidant Evaluation Methods	8
			DPPH Radical Scavenging Assay	8
		1.3.2	ABTS Radical Scavenging Activity	8
		1.3.3	Phosphomolybdenum Assay	9
		1.3.4	Reducing Power Assay	9
		1.3.5	Total Phenols Assay by Folin-Ciocalteu	
			Reagent	10
		1.3.6	Hydroxyl Radical Scavenging Assay	10
		1.3.7	β-carotene-linoleic Acid Assay	11
		1.3.8		11
			Metal Ion Chelating Assay	12
		1.3.10	Determination of Total Flavonoid Content	12

vi Contents

	1.4	Antioxidant and its Mechanisms	13
		1.4.1 Mechanism of Scavenging	
		Free Radicals	13
		1.4.2 Mechanism of Metal Chelating Properties	14
	1.5	Adverse Effects of Antioxidants	15
	Refe	erences	16
2.		ural Polyphenol and Flavonoid Polymers	23
		ly C. Heim	
		Introduction	23
	2.2	7.1	24
		2.2.1 Simple Phenolics	24
		2.2.2 Stilbenes	26
		2.2.3 Lignin	27
		2.2.4 Flavonoids	28
		2.2.5 Tannins	29
	2.3	Polyphenol Biosynthesis and Function	
		in Plants	34
		2.3.1 Biosynthesis	34
		2.3.2 Protective Roles	36
	2.4	Tannins in Human Nutrition	36
		2.4.1 Dietary Sources and Intake	36
		2.4.2 Absorption and Metabolism	37
	2.5	Antioxidant Activity of Tannins	41
		2.5.1 Mechanisms	41
		2.5.2 Structure-activity Relationships	44
	2.6	Protective Effects of Proanthocyanidins	
		in Human Health	45
		Conclusion	46
	Ack	nowledgements	46
	Refe	erences	47
3.	Svn	thesis and Applications of Polymeric Flavonoids	55
	_	oshi Uyama and Young-Jin Kim	
	3.1	0	55
		Polycondensates of Catechin with Aldehydes	57
		Enzymatically Polymerized Flavonoids	69
		Biopolymer-flavonoid Conjugates	76
		Conclusion	84
		prences	84

\sim					
\mathbf{C}	NT	FN	TS	VI	1

4.	Ant	ioxidant	t Polymers: Metal Chelating Agents	87
	Hib	a M. Zai	lloum and Mohammad S. Mubarak	
	4.1	Introdu	action	87
		4.1.1	Antioxidants	87
		4.1.2	Natural Polymers as Antioxidants	88
		4.1.3	Chelating Polymers and Heavy Metal Ions	90
	4.2		and Chitosan	91
		4.2.1	Chitin and Chitosan Derivatives	94
		4.2.2	Chitin and Chitosan as Chelating Agents	95
	4.3	Algina	tes	96
	4.4	Chelat	ion Studies	97
		4.4.1	Chitosan Derivatives as Chelating Agents	101
			Alginates as Chelating Agents	103
	4.5	Conclu	0 0	106
	Refe	erences		107
5.	Ant	ioxidant	t Polymers by Chitosan Modification	115
			šová and Eva Vavříková	
	,	Introdu		115
	5.2		an Characteristics	117
			ve Oxygen Species and Chitosan	
			loxidant	117
	5.4	Structu	are Modifications	120
			N-Carboxymethyl Chitosan Derivatives	120
			Quaternary Salts	121
			Sulphur Derivatives	122
			Chitosan Containing Phenolic Compounds	124
			Schiff Bases of Chitosan	127
	5.5	Conclu	ision	129
	Refe	erences		129
6.	Cell	ulose ai	nd Dextran Antioxidant Polymers	
			ical Applications	133
			bino, Roberta Cassano and Teresa Ferrarelli	
	6.1	Introdu	•	133
	6.2		idant Polymers Cellulose-based	134
			Cellulose	134
			Antioxidant Biomaterials	
			Carboxymethylcellulose-based	135
			Ferulate Lipoate and Tocopherulate Cellulose	136

viii Contents

		6.2.4	Cellulose Hydrogel Containing	
			Trans-ferulic Acid	138
		6.2.5	Polymeric Antioxidant Membranes Based	*
			on Modified Cellulose and PVDF/cellulose	
			Blends	139
		6.2.6	Synthesis of Antioxidant Novel Broom	
			and Cotton Fibers Derivatives	140
	6.3	Antio	oxidant Polymers Dextran-based	142
			Dextran	142
		6.3.2		
			with pH-dependent Antioxidant Properties	143
		6.3.3	Coniugates of Dextran with Antioxidant	- 10
		0.0.0	Properties	145
		6.3.4	Dextran Hydrogel Linking <i>Trans</i> -ferulic	
			Acid for the Stabilization and Transdermal	
			Delivery of Vitamin E	146
	Refe	erences	•	149
	-,,			117
7.	Ant	ioxida	nt Polymers by Free Radical Grafting	
	on l	Vatura:	l Polymers	153
	Mar	nuela (Curcio, Ortensia Ilaria Parisi,	
	Fran	ncesco	Puoci, Ilaria Altimari, Umile Gianfranco	
	Spi	zzirri a	ınd Nevio Picci	
	7.1	Introd	duction	153
	7.2	Graft	ing of Antioxidant Molecules	
			atural Polymers	156
	7.3		ins-based Antioxidant Polymers	157
	7.4		accharides-based Antioxidant Polymers	164
		7.4.1	Chitosan	164
		7.4.2	Starch	166
		7.4.3	Inulin and Alginate	170
	7.5		lusions	175
	Ack	nowle	dgements	176
		erences	C	176
8.	Nat	ural Po	olymers with Antioxidant Properties:	
	Poly	y-/oligo	osaccharides of Marine Origin	179
	Gua	ingling	Jiao, Guangli Yu, Xiaoliang Zhao,	
			hang and H. Stephen Ewart	
	8.1		duction to Polysaccharides	
			Marine Sources	180

_		
((NTENTS	S 1X

		8.1.1	Polysaccharides from Marine Algae	180
		8.1.2	,	181
		8.1.3	, and the second	182
	8.2	Antio	xidant Activities of Marine Polysaccharides	
			heir Derivatives	183
		8.2.1	Antioxidant Evaluation Methods	183
		8.2.2	Marine Sulfated Polysaccharides	187
			Marine Uronic Acid-containing	
			Polysaccharides	188
		8.2.4	Marine Non-acidic Polysaccharides	
			and their Oligomers	189
		8.2.5	Marine Glycoconjugates	189
	8.3	Appli	ications of Marine Antioxidant	
		Polys	accharides and their Derivatives	191
		8.3.1	Applications in Food Industry	191
			Applications as Medicinal Materials	191
			Applications as Cosmetic Ingredients	192
		8.3.4	Applications in Other Fields	193
	8.4	Struct	ture-antioxidant Relationships of Marine	
		Poly-	/oligosaccharides	193
	8.5		lusions	195
	Ack	nowle	dgements	195
	Refe	erences	;	195
9.	Ani	iovida	nt Peptides from Marine Origin: Sources,	
•			and Potential Applications	203
		_	iménez, M. Elvira López-Caballero,	_00
	_		Montero and M. Carmen Gómez-Guillén	
	9.1		duction	204
			le Fish Hydrolysates	207
	9.3		ne Invertebrate Hydrolysates	223
	9.4		Frames Hydrolysates	227
	9.5		ra Hydrolysates	228
	9.6		ele Hydrolysates	232
	9.7		gen and Gelatin Hydrolysates	240
	9.8		eeds Hydrolysates	243
	9.9		ntial Applications	245
			lusions	249
			dgements	250
		erences		250

x Contents

10.	Synt	hetic Ar	ntioxidant Polymers: Enzyme Mimics	259
	Chen	g Wang	, Gang-lin Yan and Gui-min Luo	
	10.1	Introd	uction	260
	10.2	Organ	o-selenium/tellurium Compound Mimics	261
		10.2.1	Chemistry of Organo-selenium/tellurium	261
		10.2.2	Synthetic Organo-selenium/tellurium	
			Compounds as GPX Mimics	263
		10.2.3	Cyclodextrin-based Mimics	272
	10.3	Metal	Complex Mimics	281
			The Role of Metal Ions in Complexes	282
			Manganese Complexes Mimics	283
		10.3.3	•	293
	10.4	Seleno	protein Mimics	295
		10.4.1		295
		10.4.2		305
	10.5	Suprai	molecular Nanoenzyme Mimics	312
		10.5.1	Advantages of Supramolecular	
			Nanoenzyme Mimics	313
		10.5.2	Supramolecular Nanoenzyme Mimics	
			with Antioxidant Acitivity	314
	10.6	Conclu	•	325
	Refer	ences		325
11.	Synt	hetic Po	lymers with Antioxidant Properties	333
	Ashv	een V. N	Nand and Paul A. Kilmartin	
	11.1	Introdu	uction	334
	11.2	Intrins	ically Conducting Polymers	335
	11.3	Intrins	ically Conducting Polymers	
		with A	ntioxidant Properties	336
	11.4	0 .1	esis of Antioxidant Intrinsically	
		Synthe	isis of Antioxidant multisically	
		-	icting Polymers	337
		Condu	•	337 337
		Condu 11.4.1	acting Polymers	
		Condu 11.4.1 11.4.2	acting Polymers Chemical Synthesis	337
	11.5	Condu 11.4.1 11.4.2 11.4.3	cting Polymers Chemical Synthesis Electrochemical Synthesis Other Polymerization Techniques	337 338
		Condu 11.4.1 11.4.2 11.4.3 Polyme	Icting Polymers Chemical Synthesis Electrochemical Synthesis Other Polymerization Techniques er Morphologies	337 338 339
		Condu 11.4.1 11.4.2 11.4.3 Polyme	cting Polymers Chemical Synthesis Electrochemical Synthesis Other Polymerization Techniques er Morphologies Polyaniline	337 338 339 340
		Condu 11.4.1 11.4.2 11.4.3 Polymo 11.5.1	cting Polymers Chemical Synthesis Electrochemical Synthesis Other Polymerization Techniques er Morphologies Polyaniline Polypyrrole	337 338 339 340 340
		Condu 11.4.1 11.4.2 11.4.3 Polymo 11.5.1 11.5.2 11.5.3	cting Polymers Chemical Synthesis Electrochemical Synthesis Other Polymerization Techniques er Morphologies Polyaniline Polypyrrole Poly(3,4-ethylenedioxythiophene)	337 338 339 340 340 342
	11.5	Condu 11.4.1 11.4.2 11.4.3 Polyme 11.5.1 11.5.2 11.5.3 Mecha	Chemical Synthesis Electrochemical Synthesis Other Polymerization Techniques er Morphologies Polyaniline Polypyrrole Poly(3,4-ethylenedioxythiophene) nism of Radical Scavenging	337 338 339 340 340 342 343
	11.5	Condu 11.4.1 11.4.2 11.4.3 Polyme 11.5.1 11.5.2 11.5.3 Mecha	cting Polymers Chemical Synthesis Electrochemical Synthesis Other Polymerization Techniques er Morphologies Polyaniline Polypyrrole Poly(3,4-ethylenedioxythiophene)	337 338 339 340 340 342 343 344

Contents	xi
----------	----

	11.8 11.9 Refer	Polymer	Affecting the Radical Scavenging Activity r Blends and Practical Applications	348 350 351
12.	Hind and H	ered Phe Iindered	Antioxidant Monomers Based on Sterically enols, α-Tocopherols, Phosphites I Amine Light Stabilizers (HALS) oolymerization with Ethylene,	
		lene or		355
	Carl-	Eric Wil	én	
	12.1	Introdu	ction	356
	12.2		is of Antioxidant Monomers to Enhance l Persistence and Performance	
		of Stabil	lizers	361
			Copolymerization of Antioxidants with α-Olefins Using Coordination	
			Catalysts	363
		12.2.2	Synthesis of Antioxidant Monomers	364
	12.3		c Antioxidant Monomers and their	
			merization with Coordination Catalysts Copolymerization of Antioxidant	369
			Monomers with Ethylene or Propylene using Traditional Ziegler-Natta Catalysts	369
	12.4		merization of Antioxidant Monomers with	
			e, Propylene, Styrene and Carbon	
			de Using Single Site Catalysts	372
			Copolymerization of Phenolic Antioxidant Monomers	372
			Copolymerization of HALS Monomers	
			using Single Site Catalysts	376
	12.5	Conclus		379
		owledge	ements	380
	Refer	ences		380
13.	Nove	l Polymo	eric Antioxidants for Materials	385
	Ashis	sh Dhaw	an, Vijayendra Kumar,	
	Virin	der S. Pa	armar and Ashok L. Cholli	
	13.1	Industr	ial Antioxidants	386
	13.2	Antioxi	dants Used in Plastics (Polymer) Industry	386
			Primary Antioxidants	388
		13.2.2	Secondary Antioxidants	389
	13.3	Antioxi	dants Used in Lubricant Industry	389

xii Contents

	13.4	Antiox	idants Used in Elastomer (Rubber) Industry	390
	13.5		idants Used in Fuel Industry	392
	13.6	Antiox	idants Used in Food Industry	393
		13.6.1	Natural Food Antioxidants	393
		13.6.2	Synthetic Food Antioxidants	394
	13.7		tions of Conventional Antioxidants	395
		13.7.1	Performance Issues because of Antioxidant	
			Efficiency Loss	395
			Environmental Issues and Safety Concerns	395
		13.7.3	Compatibility Issues	396
		13.7.4	Poor Thermal Stability	396
	13.8	Trends	towards High Molecular Weight	
		Antiox	idants	396
		13.8.1	Functionalization of Conventional	
			Antioxidants with Hydrocarbon Chains	397
		13.8.2	Macromolecular Antioxidants	397
		13.8.3	Polymer-bound Antioxidants	398
		13.8.4	Polymeric Antioxidants	401
	13.9		tion, Design and Methodology	
			thesis of Novel Polymeric Antioxidant	
		Motiva		407
		13.9.1	Design of the Polymeric Antioxidants	408
		13.9.2	Methodology	408
			llytic Synthesis of Polymeric Antioxidants	409
	13.11		l Procedure for Enzymatic Polymerization	410
		13.11.1	Synthesis and Characterization	
			of Polymeric Antioxidants	411
		13.11.2	Antioxidant Activity of Polymeric	
			Antioxidants	417
		13.11.3	Evaluation of Polymeric Antioxidants	
			in Vegetable Oils by Accelerated	
			Oxidation	420
		Conclu		421
		owledge	ement	422
	Refere	ences		422
14.	Rione	lymeri	c Colloidal Particles Loaded	
1.1.			enolic Antioxidants	427
			tel and Krassimir P. Velikov	74/
	14.1	Introdu		427
	14.1		enols: Antioxidant Properties and Health	74/
	17.4	Benefit		428
		Delicite	U .	740

			CONTENTS	XIII
	14.3	Polyph	enols: Formulation and Delivery Challenges	429
		14.3.1	Solubility	430
		14.3.2	Chemical Reactivity and Degradation	430
		14.3.3		430
		14.3.4	First Pass Metabolism and	
			Pharmacokinetics	431
		14.3.5	Organoleptic Properties and	
			Aesthetic Appeal	431
	14.4	Polyph	nenols Loaded Biopolymeric	
		Colloid	dal Particles	431
		14.4.1	Curcumin Loaded Biopolymeric	
			Colloidal Particles	433
		14.4.2	Silibinin Loaded Biopolymeric	
			Colloidal Particles	441
		14.4.3	Quercetin Loaded Biopolymeric	
			Colloidal Particles	447
	14.5	Conclu	ision	454
	Refer	ences		455
15.			Polymers for Tuning Biomaterial	
			oility: From Drug Delivery to Tissue	450
		neering		459
			ran and Thomas D. Dziubla	
		Introd		459
	15.2		tive Stress in Relation to Biocompatibility	460
			Mechanism of Immune Response	460
			Examples in Practice	464
	15.3		idant Polymers in Drug Delivery	467
			Uses as Active Pharmaceutical Ingredients	467
			Uses as Pharmaceutical Excipients	468
	15.4		idant Polymers in Anti-cancer Therapies	470
	15.5		cidant Polymers in Wound Healing	
			ssue Engineering	472
		15.5.1	Antioxidant Polymers Incorporated into	.=-
			Biomaterials	472
	-			4-7
			isions and Perspectives	476
		Conclu ences	usions and Perspectives	476 479
Ind	Refer		usions and Perspectives	