

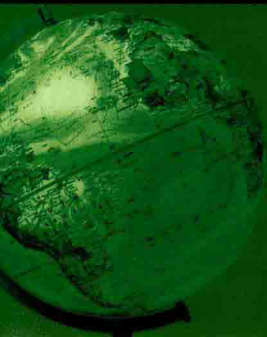
WILEY SERIES IN RENEWABLE RESOURCES

Lignin and Lignans as Renewable Raw Materials

Chemistry, Technology and Applications



Francisco G. Calvo-Flores | José A. Dobado
Joaquín Isac-García | Francisco J. Martín-Martínez



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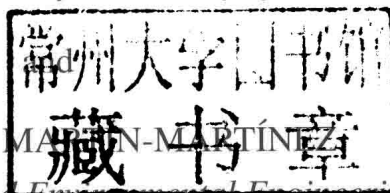
Chemistry, Technology and Applications

FRANCISCO G. CALVO-FLORES, JOSÉ A. DOBADO,
JOAQUÍN ISAC-GARCÍA

Department of Organic Chemistry, University of Granada, Spain

FRANCISCO J. MARTÍN-MARTÍNEZ

*Department of Civil and Environmental Engineering,
Massachusetts Institute of Technology, USA*



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Series Editor

Christian V. Stevens—Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium

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To our families

Series Preface

Renewable resources and their 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 fields.

The broad area of renewable resources connects several scientific disciplines (agriculture, biochemistry, chemistry, technology, environmental sciences, forestry ...), but it is very difficult to take an expert view on their complicated interactions. Therefore, the idea to create a series of scientific books, focussing 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 do not only occur in fashion and politics, hype and buzzwords occur in science too. The use of renewable resources is more important nowadays, however, it is not hype. Lively discussions among scientists continue about how long we will be able to use fossil fuels, opinions ranging from 50 years to 500 years, but they do agree that the reserve is limited and that it is essential to search not only for new energy carriers but also for new material sources.

In this respect, renewable resources are a crucial area in the search for alternatives to 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 utilisation 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 nineteenth 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 does require a multidisciplinary effort at a highly technological level to perform research on 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. The challenge for coming generations of scientists is 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 met 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 so that the use and modification of renewable resources may not follow the path of the genetic engineering concept in terms of consumer acceptance in Europe. In this respect, 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 focussing on different aspects of renewable resources. I hope that readers become aware of the complexity, interactions and interconnections, and challenges of this field and that they will help to communicate the importance of renewable resources.

I would like to thank the staff from Wiley's 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
Series Editor "Renewable Resources"
June 2005

Preface

This book has grown from a mini-review on lignin that we had published in 2010, by invitation from Sarah Higginbotham (nee Hall) at John Wiley & Sons Publishing Group. From the very outset, it was clear to us that tackling the project as authors of a complete work was the most challenging but nevertheless the most robust way of addressing the issue. Conceiving a whole book appeared to be more complete than the common compilation books where the monograph results from the contribution of various authors coordinated by an editor. In our opinion, although these compilation-type books often result in a series of very specific chapters that provide a collection of review articles of high scientific level, they usually lack a strength thread to unify the entire work.

The specific case of lignin is particularly challenging due to the enormous amount of information available, the abundance of undefined concepts, and the diverse areas of knowledge involved in the topic. Native lignin is studied by botanists for its role in plants and plant cells, by biochemists regarding biosynthesis, by chemists concerned with its structure, and even by engineers dealing with lignin coming from paper mill or biorefineries.

A similar situation involves lignans, where these secondary plant metabolites are studied also by botanists, chemists, and even by professionals in biomedical sciences for the biological properties of these molecules in living organisms. A fairly complete description of the nature, structure, properties, synthetic processes, and applications of this family of compounds is provided.

Given such a complex and multidisciplinary outlook, a thorough review was needed of the existing literature, together with classical references, the brainchild of pioneering authors, as well as recent contributions to the topic in order to provide the reader with a broad view of the most comprehensive knowledge on lignin and lignans. As is inevitable with projects of this scope, the final work might not be as complete as it could have been, but we nevertheless trust that the result is thorough enough to be useful to the scientific community interested in the subject.

Throughout the text, lignin is explained from different perspectives, including its role as a structural component of plants, and how it is produced as a by-product of paper industry and a product of biorefineries. Structural models of this biopolymer are disclosed, as well as the developing process that these models have undergone through the years, parallel to the improvement of structural determination methods, both instrumental and chemical ones. This information will provide the reader with an overall idea of the structure of lignin, its origin, its function, its applications, and its potential. The reader will also learn how to appropriately use the term "lignin," as the actual lignin depends on the origin of this material.

During the preparation of the book, special effort was made to review the applications and the potential uses of different lignins, with emphasis on the word "potential." So far, there has been ample academic work on the subject, but the actual results are still relatively modest. Therefore, many topics remain to be developed in the coming years, and they definitely will be, considering the growing importance of renewable raw materials in taking over those of limited availability.

Given our input on lignin, and our experience as authors of the present work, we conclude that this is a highly promising biomaterial, which, in terms of science and technology, still presents many unresolved issues that continue to be investigated. In the literature, terms such as "potential" and

“promising” constantly appear, alongside “difficult,” “complex,” and “underutilized.” These modifiers reflect lignin’s state of the art. In the coming years, great effort must be needed to ensure lignin the central role as source of raw materials, consumer goods, and much more relevant applications that it deserves. We deeply hope that this book will stimulate further interest and research in this promising biopolymer in its various forms.

Finally, we repeat our appreciation to John Wiley & Sons Publishing Group and its staff for their incalculable help, support, and feedback over the course of the project. Last but not least, we would like to give our special thanks to Dr Ángel Sánchez-González for the design of the front cover, and Mr David Nesbitt for his invaluable work on the revision of the English version of the manuscript and his contribution with the “*Podophyllum peltatum*” illustration.

Francisco G. Calvo-Flores
José A. Dobado
Joaquín Isac-García
Francisco J. Martín-Martínez
January 2015

List of Acronyms

2D	two dimensional
3D	three dimensional
4CL	4-coumarate CoA ligase
Ac-CW	acetylated cell wall
ADF	acid detergent fiber
AFEX	ammonia fiber explosion
AOAC	Association of Analytical Communities (formerly Association of Official Agricultural Chemists)
AOP	advanced oxidation process
ARP	ammonia recycle percolation
ASAM	alkaline sulfite, anthraquinone, methanol
ASL	alkali sulfite lignin
BADGE	bisphenol A diglycidyl ether
BTX	benzene, toluene, and xylene
C4H	cinnamate 4-hydroxylase
CAGT	coniferyl alcohol glucosyltransferase
CBG	coniferin- β -glucosidase
CD	circular dichroism
CEHPL	chain-extended hydroxypropyl lignin
CEL	cellulolytic enzyme lignin
CK	cytokinins
DAD	photodiode array detector
DAHPh	3-deoxy-D-arabinose heptulosonic acid-7-phosphate
DBDO	dibenzodioxocin
DCC	<i>N,N'</i> -Dicyclohexylcarbodiimide
DCCC	droplet counter-current chromatography
DCG	dehydrodiconiferyl alcohol-4- β -D-glucoside
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DFRC	derivatization followed by reductive cleavage
DHP	dehydrogenation polymer
DIR	dirigent protein
DMAc	<i>N,N</i> -dimethylacetamide
DMF	dimethylformamide
DMS	dimethyl sulfide
DMSO	dimethyl sulfoxide
DPPH	1,1-diphenyl-2-picrylhydrazyl
EDXA	energy-dispersive X-ray analysis
EMAL	enzymatic mild acidolysis lignin
END	enterodiol
ENL	enterolactone
EPSP	5-enolpyruvylshikimate-3-phosphate

ESR	electron spin resonance
FDA	Food and Drug Administration
FTIR	Fourier transform infrared
G	coniferyl alcohol
GC-MS	gas chromatography-mass spectrometry
GC	gas chromatography
GHG	greenhouse gas
GPC	gel permeation chromatography
H	<i>p</i> -coumaryl alcohol
HBS	high-boiling solvents
HDO	hydrodeoxygenation
HDPE	high-density polyethylene
HMR	7-hydroxymatairesinol
HMTA	hexamethylenetetramine
HPA	Heteropoly acids (e.g., $\text{H}_3\text{PWO}_{12}\text{O}_{40}$)
HPL	hydroxypropyl lignin
HPLC	high-performance liquid chromatography
HPSEC	high-pressure size exclusion chromatography
HPSECI	high-pressure size exclusion chromatography infrared
HRMS	high-resolution mass spectrometry
HRP	hydroxyproline-rich protein
HSCCC	high-speed counter-current chromatography
IAT	indulin AT
IM	interference microscopy
IOR	improved oil recovery
IPTES	3-(triethoxysilyl)propylisocyanate
IR	infrared
KL	Klason lignin
LALLS	laser light scattering
LBS	low-boiling solvents
LC-NMR	liquid chromatography-nuclear magnetic resonance
LDPE	low-density polyethylene
LEM	<i>Lentinus edodes</i> mycelia
LPF	lignin-modified phenolic resin
LPS	lignin process system
LSA	lignin sulfonic acid, lignosulfonic acid
MAE	microwave-assisted extraction
MDF	medium-density fiberboards
MDI	methylene diphenyl isocyanate
MEKC	micellar electrokinetic capillary chromatography
MOF	metal-organic framework
MPP	mesophase pitch
MSn	multiple-stage mass spectrometry
MWL	milled wood lignin
NADH	nicotinamide adenine dinucleotide
NDGA	nordihydroguaiaretic acid
NE	nucleus exchange
NMR	nuclear magnetic resonance
NOESY	nuclear overhauser effect spectroscopy
NP	nanoparticle

OSB	oriented strand boards
PA66	polyamide 66
PAL	L-Phenylalanine ammonia lyase
PAN	polyacrylonitrile
PE	polyethylene
PEG	polyethylene glycol
PF	phenol formaldehyde
PLCG1	phospholipase C γ 1
PLPW	pressurized low-polarity water
PLR	pinoresinol/lariciresinol reductases
PNNL	Pacific Northwest National Laboratory
POM	polyoxometalate
PP	polypropylene
PPG	polypropylene glycol
PPT	podophyllotoxin
PS	polystyrene
PTSA	<i>p</i> -toluenesulfonic acid
PU	polyurethane
PVC	polyvinyl chloride
RP	reverse phase
S	sinapyl alcohol
SAA	soaking in aqueous ammonia
SAR	structure–activity relationship
SDG	secoisolariciresinol diglucoside
SEC	size exclusion chromatography
SECO	secoisolariciresinol
SEL	swelled enzyme lignin
SEM	scanning electron microscopy
SHS	switchable hydrophilicity solvent
SIRD	secoisolariciresinol dehydrogenase
TAL	tyrosine ammonia lyase
TAPPI	Technical Association of the Pulp and Paper Industry
TDMP	2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane
TEM	transmission electron microscopy
THF	tetrahydrofuran
TLC	thin-layer chromatography
TOC	total organic carbon
TPA	tonns per annum
TTFA	thallium(III) trifluoroacetate
UDP	uridine diphosphate
UV/Vis	ultraviolet/visible
VCD	vibrational circular dichroism
VPO	vapor pressure osmometry
WG	water-dispersible granules

List of Symbols

δ	NMR chemical shift
D	dispersity index
ED_{50}	median effective dose
g	contraction factor
IC_{50}	half maximal inhibitory concentration
M_n	average molecular weight
M_w	molecular weight
λ_{max}	The wavelength at which the largest amount of absorption occurs
$\text{Log } P$	partition coefficient
pH	acidity or basicity of an aqueous solution
ppm	parts <i>per</i> million
ppu	parts <i>per</i> unit
T_g	temperature range of glass transition
rt	room temperature

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