This is the first book to describe the scientific basis for the action of plant polyphenols in a wide range of technologically important phenomena.

Basic understanding of plant polyphenols (vegetable tannins) has increased dramatically over the past 30 years. This has opened the way to an understanding of practical polyphenolic phenomena. The book opens with a general summary of polyphenolic structure and a discussion of the physical and chemical basis of non-covalent molecular interactions (the process of molecular recognition) and the means by which polyphenols initiate the many and varied properties they display. There has been a big increase in interest in our ability to understand the importance of polyphenols in areas as diverse as agriculture, ecology and food selection, foodstuffs and nutrition, beverages (astringency and bitterness), natural medicines (the so-called 'French Paradox'), floral pigmentation, natural glues and varnishes and the age-old methods for the manufacture of leather. The role of polyphenols in all of these areas is discussed.

This book will be of value to a wide range of researchers in chemistry, agriculture, food science, ecology, oenology, plant physiology and pharmacology with an interest in polyphenolics.

PRACTICAL POLYPHENOLICS
From Structure to Molecular Recognition and Physiological Action

PRACTICAL POLYPHENOLICS
From Structure to Molecular Recognition and Physiological Action

EDWIN HASLAM
University of Sheffield

CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo

Cambridge University Press
The Edinburgh Building, Cambridge CB2 2RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521465137

First published 1998
This digitally printed first paperback version 2005

A catalogue record for this publication is available from the British Library

Library of Congress Cataloguing in Publication data
Haslam, Edwin.
Practical polyphenolics: from structure to molecular recognition
and physiological action.
p. cm.
Includes bibliographical references.
ISBN 0 521 46513 3 (hb)
1. Phenols. 2. Botanical chemistry. I. Title.
QK898.P57H37 1998
661′.82–dc21 9-8686 CIP

ISBN-13 978-0-521-46513-7 hardback
ISBN-10 0-521-46513-3 hardback

ISBN-13 978-0-521-67559-8 paperback
ISBN-10 0-521-67559-6 paperback

For M

Che faro senza M

Contents

Preface

Over the past three centuries Science has increasingly come to represent one of mankind's most formidable achievements. In areas as diverse as agriculture, materials and medicine its technological applications have transformed the lives of many throughout the world. Science conversely often exacts its own price, for benefits and risks are frequently found to be complementary aspects of the same technological advances; society has to judge between them. A popular misconception fostered by some writers and media pundits is that progress in Science, the accumulation of new and greater knowledge superseding previous discoveries, proceeds exponentially ever upwards and onwards. This is misleading. Science is a human endeavour and scientists are creative beings. Science is therefore spiced with pride and prejudice; it is often subject to personal folly, wrong turns and cul-de-sacs. False dawns, unfortunately not always constrained to the confines of the laboratory, are legion. The odyssey of the science of the vegetable tannins (plant polyphenolics) as its has journeyed from darkness into (comparative) light is littered with examples of the frustrations which underly scientific progress and discovery.

Records show that extracts of a plant origin (vegetable tannins) were employed in Mediterranean regions to convert raw animal hides and skins to durable leathers at least 2000 years ago. Investigations of the chemistry of such extracts, despite the outstanding contributions of the Nobel Laureate Emil Fischer at the turn of the century, merely served to show the complexity of the problems which they posed and by the 1950s this area had become one of the murky and unfashionable corners of organic chemistry. There is often an ebb and flow to scientific research and the advent of new techniques, new ideas and new personnel has, over the past forty years, not only transformed the state of the fundamental knowledge of these compounds but has also revealed their crucial importance to many other areas of science – from ecology and agriculture, nutrition and foodstuffs, to beverages, fruit and floral pigmentation. Thus

particular attention has focused recently on the possible amelioration of long-term degenerative disorders using beverages (such as teas and red wines) and specific diets rich in anti-oxidants (natural phenolics and polyphenolics).

Guardians of the public purse increasingly demand from scientific research a greater poundage of flesh; the emphasis has shifted to one in which short term exploitation of its discoveries is pre-eminent. This text therefore summarises the established chemical knowledge appertaining to plant polyphenols and seeks to use this information to address and interpret the many, important and wide ranging technological and applied phenomena in which plant polyphenols are intimately involved and which have been noted above. The approach adopted is an all inclusive one and is based upon critical evaluation of the physical forces which underly the '*recognition*' by polyphenols of other molecules, often prior to further irreversible chemical reaction. There seems little doubt that this area and that of the genetic and biochemical control of polyphenol synthesis *in vivo* are the ones which, in the future, will come to dominate scientific research involving plant polyphenols. The period from 1950 to 1990 was one in which public attitudes towards the status of science helped to facilitate fundamental research in seemingly arcane areas, such as that of the plant polyphenols. As the turn of the twentieth century approaches and siren voices increasingly beckon a long past rustic Arcadia it is timely, however, to gently remind those same guardians of a seemingly diminished share of the public purse for pure science of the words of Louis Pasteur (whose father was incidentally a tanner) that 'there are no such things as applied sciences, *only applications of science*'.

> We are like dwarfs on the shoulders of giants, so that we can see more than they ... not by virtue of any sharpness of sight on our part, or any physical distinction, but because we are carried high and raised up by their giant size.

As in most scientific fields the expansion in knowledge and ideas is due to the many, amongst whom some major figures stand out. During the past forty years the contributions to the chemistry of plant polyphenols of Schmidt, Mayer and Weinges in Heidelberg, of Okuda and Nishioka in Japan, of Haworth in Sheffield and Roux in Bloemfontein were outstanding. The science of the vegetable tannins also occupies a unique position which borders not only on chemistry, but also botany, food science, agriculture and animal physiology. Two persons, Tony Swain and E. C. Bate-Smith, had the vision to recognise this crucial pivotal relationship and to see the importance which vegetable tannins were destined to play in succeeding years in many areas of applied science. The author had the extreme good fortune to have glimpses of that cherished vision in a long correspondence with one of these figures, E. C.

Bate-Smith. The correspondence was not only of inestimable scientific value but it was also full of encouragement and not a little humour. A few extracts are reproduced herein, not only for their scientific but also their human insights. May they stand for all who follow as a reminder of one of the true pioneers and giants of the science of vegetable tannins.

The sixteenth/seventeenth century poet and later Dean of St. Paul's John Donne did not have scientists in mind when he wrote that 'No man is an Island, entire of it self'. However, one of the most satisfying facets of a career in scientific research is the opportunities which it gives to meet and collaborate with others world-wide; to test one's ideas with like-minds thousands of miles distant. Unlike governments, science does not recognise national boundaries, it thrives on the spirit of intellectual challenge which arises from differences of opinion and interpretation. It is entirely appropriate that the author should note therefore the special contributions made by others to his own travails in this field – most notably Professor T. H. Lilley and Dr. M. P. Williamson (Sheffield), Professor L. G. Butler (Purdue University, U.S.A.), Dr. L. J. Porter (New Zealand) and Dr. Zhaobang Shen (China); to numerous postgraduate students from the original eponymous 'Lord Tannin' to the 'Last of the Mohicans'; to friends and acquaintances in the Phytochemical Society of Europe (and the earlier Plant Phenolics Group), the Phytochemical Society of North America and the Groupe Polyphenols (France); to those in industry with whom it has been the author's privilege to collaborate – Mme Daniele Magnolato (Nestlé Suisse), Dr. M. Saltmarsh (Mars G.B.) and Dr. A. Davies and Dr. Y. Cai (Unilever).

The author would also like to express his thanks to those who have helped in the preparation of this text; to Dr. Simon Capelin, Beverley Lawrence and Ian Sherratt (Cambridge University Press) who have overseen the transformation of the manuscript to the printed text; to Dr. Christopher A. Hunter (University of Sheffield) who read and critically evaluated the two chapters on molecular recognition, and who also abstracted and organised the X-ray structures of simple phenols from the Cambridge X-ray data bank; to David Lodge and Reed Books who gave permission to reproduce an extract from the novel *Small World*; to Verlag Carl Ueberreuter (Vienna) for permission to use the illustration by Ulrik Schramm from *Gullivers Travels* and to the other authors who are specifically noted and who gave permission to use figures, at appropriate parts of the text, from their own scientific publications.

Sheffield, U.K.