PHYTOCHEMISTRY

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Phytochemistry Vol. 68, Nos. 22–24, 2007

Special issue

Highlights in the Evolution of Phytochemistry: 50 Years of the Phytochemical Society of Europe

Editors: Richard J. Robins, Simon Gibbons and Andrew Marston

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PHYTOCHEMISTRY OF PHENOLIC COMPOUNDS

Vegetable tannins - Lessons of a phytochemical lifetime

pp 2713-2721

Edwin Haslam

Vegetable tannins are complex polyphenolic metabolites of plants based upon two principal structural themes - oligomeric flavan-3-ols (proanthocyanidins) and poly-3,4,5trihydroxyaroyl esters (gallotannins and ellagitannins). The remarkable progress made in the last fifty years in the understanding of their chemistry and biochemistry is reviewed.

Evolution and current status of research in phenolic compounds

pp 2722-2735

Alain-Michel Boudet

Several topics of research are discussed in detail:

- The characterization of the enzymatic steps leading to specific branches of phenolic metabolism.
- The use of molecular biology for to probe the changes in gene expression associated with the plasticity of phenolic metabolism.
- The emergence of genomics, showing the diversity of the genes/enzymes involved in phenolic metabolism.
- The exploitation of genetic engineering for optimizing the phenolic profiles of plants.
- The explosion of epidemiological studies supporting the protective role of food polyphenols in human health.

Justicidin B 7-hydroxylase, a cytochrome P450 monooxygenase from cell cultures of *Linum perenne* Himmelszelt involved in the biosynthesis of diphyllin

pp 2736-2743

Shiva Hemmati, Bernd Schneider, Thomas J. Schmidt, Katja Federolf, A. Wilhelm Alfermann, Elisabeth Fuss*

A biosynthetic pathway for the formation of arylnaphthalene lignans like diphyllin is suggested. Justicidin B 7-hydroxylase (JusB7H) which catalyzes the last step in the biosynthesis of diphyllin was characterized as a cytochrome P450 monooxygenase from suspension cultures of *Linum perenne* Himmelszelt.

Coniferin dimerisation in lignan biosynthesis in flax cells

pp 2744-2752

Vickram Beejmohun, Ophélie Fliniaux, Christophe Hano, Serge Pilard, Eric Grand, David Lesur, Dominique Cailleu, Frédéric Lamblin, Eric Lainé, José Kovensky, Marc-André Fliniaux, François Mesnard*

The use of $[8,9^{-13}C_2]$ -coniferin coupled with mass spectrometry and nuclear magnetic resonance showed the ability of a flax cell suspension to biosynthesise differently linked (neo)lignans: 8-8', 8-5' and 8-O-4'. The continuous synthesis and subsequent metabolisation of these coniferin-derived dimers were established all over the culture period.

Homoisoflavanones from *Pseudoprospero firmifolium* of the monotypic tribe Pseudoprospereae (Hyacinthaceae: Hyacinthoideae)

pp 2753-2756

Chantal Koorbanally, Sarisha Sewjee, Dulcie A. Mulholland*, Neil R. Crouch, Anthony Dold

Five homoisoflavanones: 3,5-dihydroxy-7,8-dimethoxy-3-(3',4'-dimethoxybenzyl)-4-chromanone, 3,5-dihydroxy-7-methoxy-3-(3',4'-dimethoxybenzyl)-4-chromanone, 3,5-dihydroxy-7,8-dimethoxy-3-(3'-hydroxy-4'-methoxybenzyl)-4-chromanone, 3,5,6-trihydroxy-7-methoxy-3-(3'-hydroxy-4'-methoxybenzyl)-4-chromanone and 3,5,7-trihydroxy-3-(3'-hydroxy-4'methoxybenzyl)-4-chromanone and the nortriterpenoid, 15-deoxoeucosterol, have been isolated from the bulbs of *Pseudoprospero firmifolium*, the sole representative of the tribe Pseudoprosperae (Hyacinthaceae: Hyacinthoideae).

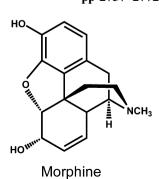
PHYTOCHEMISTRY OF NITROGENOUS COMPOUNDS

Evolution and current status of the phytochemistry of nitrogenous compounds

pp 2757-2772

Meinhart H. Zenk*, Melanie Juenger

With the discovery of nitrogen-containing plant products, 200 years ago, a success story began. Strongly bioactive pure chemicals from plants were isolated and used in medicine and, in parallel, organic and pharmaceutical chemistry developed. This success story continues today and multidisciplinary "phytochemistry" surely has a bright future.



Functional characterisation of genes involved in pyridine alkaloid biosynthesis in tobacco

pp 2773-2785

Suvi T. Häkkinen, Sofie Tilleman, Agnieszka Šwiątek, Valerie De Sutter, Heiko Rischer, Isabelle Vanhoutte, Harry Van Onckelen, Pierre Hilson, Dirk Inzé, Kirsi-Marja Oksman-Caldentey*, Alain Goossens

Potential catalysers of tobacco pyridine metabolism can be discovered by functional genomics-based analysis of a *Nicotiana tabacum* gene platform, established previously by means of integrated transcript and metabolite profiling.



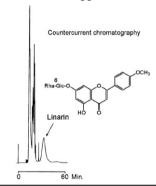
ROLE OF METHODOLOGY IN ADVANCING PHYTOCHEMICAL RESEARCH

Role of advances in chromatographic techniques in phytochemistry

pp 2786-2798

Andrew Marston

Chromatography is essential to phytochemistry and is the key to obtaining pure compounds for structure elucidation (by countercurrent chromatography, for example), for pharmacological testing or for development into therapeuticals. It also plays a fundamental role as an analytical technique for quality control and standardisation of phytotherapeuticals.

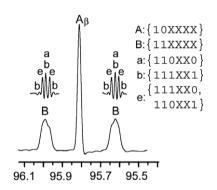


Advances of high-resolution NMR techniques in the structural and metabolic analysis of plant biochemistry

pp 2799-2815

Wolfgang Eisenreich*, Adelbert Bacher

Recent advances in instrumentation have led to a remarkable set of techniques and applications of NMR spectroscopy. This review describes the role of high-resolution NMR spectroscopy in the structural analysis of plant constituents (e.g. proteins and small metabolites) and in the analysis of biosynthetic pathways and metabolite flux.



Biosynthesis of the chromogen hermidin from Mercurialis annua L.

pp 2816-2824

Elena Ostrozhenkova, Eva Eylert, Nicholas Schramek, Avi Golan-Goldhirsh, Adelbert Bacher, Wolfgang Eisenreich*

The isotopologue patterns in hermidin labelled with [U-¹³C₆]glucose or ¹³CO₂ indicate that the alkaloid is derived from the nicotinic acid pathway.

Determination of saponins in *Maesa lanceolata* by LC-UV: Development and validation

pp 2825-2830

Mart H.B.L. Theunis*, Kenn Foubert, Jacob Pollier, Miguel Gonzalez-Guzman, Alain Goossens, Arnold J. Vlietinck, Luc A.C. Pieters, Sandra Apers

A method is described to quantify the saponins in *Maesa lanceolata* extracts. The method is based on a H₂O/MeOH extraction and a purification step on a C₁₈ SPE cartridge. The identification is done by the combination of LC-UV/MS, while quantification is performed by LC-UV, using oleanolic acid as an external standard.

$$\begin{array}{c} \text{OH } \text{O} \longrightarrow R_2 \\ \text{O} \longrightarrow R_1 \\ \text{Gal II} \longrightarrow \text{GlA} \\ \text{Rha} \quad \text{Gal II} \\ \text{Res} \quad \text{Gal II} \\ \end{array}$$

METABOLIC PHYTOCHEMISTRY

From waste products to ecochemicals: Fifty years research of plant secondary metabolism

pp 2831-2846

Thomas Hartmann

The chemical diversity of plant secondary metabolism – formerly understood as part of metabolic excretion – is now recognized as an essential part of survival strategies of plants in a continuously changing environment.



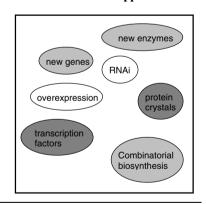
Current status of metabolic phytochemistry

pp 2847-2860

Maike Petersen

Some current topics of research in metabolic phytochemistry will be shown:

- detection, isolation and characterisation of enzymes and genes.
- structure elucidation of enzymes after crystallisation.
- manipulation of natural product formation by overexpression or down-regulation.
- transcription factors in natural product biosyntheses.
- combinatorial biosynthesis of plant natural products in microorganisms.

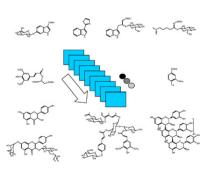


The future of metabolic phytochemistry: Larger numbers of metabolites, higher resolution, greater understanding

pp 2861-2880

Alisdair R. Fernie

This article describes the state of the art in modern phytochemical analysis and affords one potential perspective of where it is heading in the future. Particular stress is given to unravelling the function of metabolites and the genes that control their accumulation or degradation.

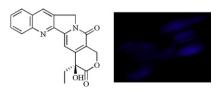


Transport of camptothecin in hairy roots of Ophiorrhiza pumila

pp 2881-2886

Supaart Sirikantaramas, Hiroshi Sudo, Takashi Asano, Mami Yamazaki, Kazuki Saito*

Autofluorescence emitted from camptothecin, an anticancer monoterpene indole alkaloid, in the hairy root of *Ophiorrhiza pumila* suggests its localization in the vacuole. In this paper, we employed a pharmacological approach to elucidate camptothecin transport in the hairy root.



PHYTOCHEMISTRY AND CHEMOSYSTEMATICS

The evolution of chemosystematics

pp 2887-2895

Tom Reynolds

Chemosystematics has been used by animals, including man, to distinguish plants and other beings useful for food and those best avoided. Originally unwritten, this knowledge has been formalized down the ages, until in modern times useful and harmful chemical constituents from relevant taxa have been identified and recorded. In return this knowledge has now been used to aid taxonomic distinctions of these plants, animals and micro-organisms. Advances in analytical instrumentation, in particular chromatography in all its forms, followed by electronic detection methods, has speeded these studies.

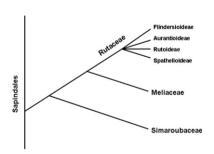


The current status of chemical systematics

pp 2896-2903

Peter G. Waterman

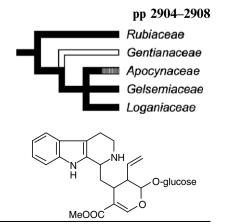
Chemical systematics sets out to interpret the phylogenetic implications of the occurrence and distribution of secondary metabolites. In this review, a number of the major contributions from the 1960's and 1970's are identified and re-assessed in the light of recent evidence gained from DNA studies. It is shown that for the most part conclusions drawn on the basis of secondary metabolite distribution have been confirmed by the new techniques and it is concluded that chemical systematics can continue to provide useful insights into plant phylogeny.



The "new" chemosystematics: Phylogeny and phytochemistry

Sonny Larsson

Recircumscription of plant systematics must be taken into account when drawing chemosystematic conclusions. They are highly dependent on up-to-date botanical classification.

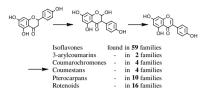


Isoflavonoids in non-leguminous taxa: A rarity or a rule?

pp 2909-2916

Oldřich Lapčík

The number of known isoflavonoid-producers increases slowly but continously. Isoflavonoids have been found in not less than sixty families falling into four classes of multicellular plants. Biosynthetically advanced structural types of isoflavonoids (rotenoids, pterocarpans, etc.) were recorded in both classes and all subclasses of flowering plants.



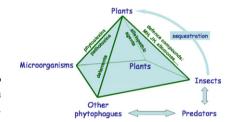
ECOLOGICAL PHYTOCHEMISTRY

Evolution and current status of ecological phytochemistry

pp 2917-2936

Francisco A. Macías*, Jose L.G. Galindo, Juan C.G. Galindo

Phytochemical studies have experienced a great change through the last century. This change has occurred mainly in two key points: the methodologies used in phytochemical studies and the point of view about why and for what reason secondary metabolites are present in plants and, by extension, in the rest of living organisms. The main question is to clarify the role that secondary metabolites play in the plant and if the resources invested in their production have or have not a reasonable reward in terms of advantages for survival. Some considerations in terms of evolution are made.

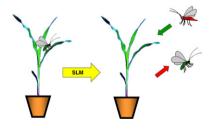


Developments in aspects of ecological phytochemistry: The role of *cis*-jasmone in inducible defence systems in plants

pp 2937-2945

John A. Pickett*, Michael A. Birkett, Toby J.A. Bruce, Keith Chamberlain, Ruth Gordon-Weeks, Michaela C. Matthes, Johnathan A. Napier, Lesley E. Smart, Christine M. Woodcock

Developments in ecological phytochemistry for food production and generation of bioenergy and biofuels will involve processes activated by natural products to "switch on" plant defence pathways. Plant breeding can exploit these systems and heterologous gene expression will eventually give rise to a new range of crops for food and energy.

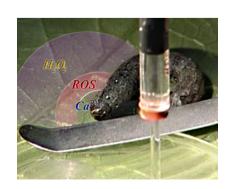


Insects feeding on plants: Rapid signals and responses preceding the induction of phytochemical release

pp 2946-2959

Massimo E. Maffei*, Axel Mithöfer, Wilhelm Boland

The ability of plants to withstand herbivores relies on direct and indirect chemical defense. By using toxic phytochemicals, plants can deter and/or poison herbivores, while by releasing volatile organic compounds (VOCs) into the atmosphere plants can attract predators of the attacking insects. In this review, we will focus on rapid early events following insect feeding on plants that eventually lead to the production and release of phytochemicals.



PHYTOCHEMICALS AND HUMAN HEALTH

Phytochemistry and pharmacognosy

pp 2960-2972

J. David Phillipson

The author met frequently with the first editors of *phytochemistry*, Tony Swain and Jeffrey Harborne, at scientific meetings of the Phytochemical Society. During the first 50 years of the Society there were tremendous advances in biological and chemical techniques that facilitated the isolation and structure determination of biologically active natural products. Today, we continue to rely on plants as sources of medicinal drugs and of herbal medicines. Pharmacognosy maintains strong links with phytochemistry and the Phytochemical Society of Europe.



Phytochemicals: The good, the bad and the ugly?

pp 2973-2985

Russell J. Molyneux*, Stephen T. Lee, Dale R. Gardner, Kip E. Panter, Lynn F. James

The perception of phytochemicals can be good or bad, depending on viewpoint. This review describes phytochemicals isolated from poisonous plants of the genera *Taxus*, *Veratrum*, *Lupinus*, *Swainsona*, *Astragalus*, *Oxytropis*, *Castanospermum* and *Ipomoea*, some of which are currently in clinical use, others that have been used to produce animal models of human disease, and even more that have shown potential for development into drug candidates.

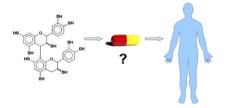


Nutraceuticals: Facts and fiction

pp 2986-3008

Juan Carlos Espín, María Teresa García-Conesa, Francisco A. Tomás-Barberán*

Nutraceuticals are pharmaceutical forms containing food phytochemicals as active principles. Scientific research supports the biological activity of many of these food phytochemicals, but the health claims attributed to the marketed nutraceuticals have often doubtful scientific foundation. Bioavailability and metabolism are key factors to understand the biological effects of these nutraceuticals.



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ISSN 0031-9422

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