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1982 PROCEEDINGS OF THE PHYTOCHEMICAL SOCIETY OF EUROPE

A meeting of the PSE held at The University of Strathclyde, Glasgow, 5–7 April 1982, when the following papers were presented under the general title

CHEMISTRY AND CHEMICAL TAXONOMY OF THE RUTALES

REVIEW LECTURES*

The Concept of the Rutales: A D J MEEUSE Hugo de Vries Laboratory, University of Amsterdam, Amsterdam, Netherlands

The concept of the Rutales as a group of families at the approximate level of an Order became precisely defined only after *ca* 1900 There is still some disagreement regarding the 'size' of the Order, some workers including the Rutales s s in a large assemblage with the Sapindales s s and others distinguishing these as two separate Orders Some authorities now even doubt that these two are as closely allied as is often assumed

The Geraniales are often said to be closely related to the Rutales, but so far there is no cogent evidence either clearly supporting or refuting this point of view

The Rutaceae are the most primitive members of the Order and show certain characteristics strongly suggesting a link with magnolialean–ranunculalean taxa, i e the Rutales shared a progenatorial group with some representatives of the Magnoliid–Ranunculiid assembly In their turn the Rutaceae link up with the Araliales, and the latter with the Asterales–Campanulales aggregate (and conceivably with a few other sympetalous groups), which indicates the artificiality of the assembly of the 'Asteridae' as recognized and delimited in most recent systems of classification of the Angiospermae The central position of the Rutaceae is of interest as a starting point, not only for studies of possible phylogenetic connections with other Rutales and with the Sapindales and Geraniales, but also for the unravelling of connections with the Asterales and Campanulales

Aspects of the Biosynthesis of Coumarins and Quinoline Alkaloids in the Rutaceae: M F GRUNDON School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland, U K

An account of recent studies related to the biosynthesis of quinoline alkaloids and coumarins will include a discussion of the furo- and pyrano-derivatives, of compounds apparently formed by sigmatropic rearrangements, and of dimeric quinolines and coumarins found in the Rutaceae

Structural Diversity and Distribution of Alkaloids in the Rutales: I MESTER Institute of Pharmaceutical Chemistry, University of Munster, Munster, West Germany

The order Rutales contains, according to Dahlgren's system, the families Rutaceae, Cneoraceae, Surianaceae, Simaroubaceae, Kirkiaceae, Burseraceae and Meliaceae So far reports of alkaloids are restricted to species of the Rutaceae, Simaroubaceae and Meliaceae, those from the latter two families being comparatively small in number

The alkaloids obtained to date from simaroubaceous plants are predominantly derived from tryptophan (canthin-6-ones and β-carbolines), those from the Meliaceae are pyridine or pyrrole derivatives The distribution of alkaloids within both families is discussed The most widely examined family of the Order, the Rutaceae, are characterized by the production of a very wide range of alkaloids belonging to several biogenetic classes Their diversity and distribution are reviewed, with particular emphasis being placed on results obtained in the last 5–10 years Two problem areas that will be highlighted are (a) the production of alkaloid artefacts during isolation procedures, and (b) the potential value of alkaloids as taxonomic markers at the family level

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*Review Lectures are to be published in the Phytochemical Society of Europe Symposia series Vol 22

Structural Diversity and Distribution of Coumarins and Chromones in the Rutales

A I Gray School of Pharmacy, Trinity College, Dublin, Eire

To date, just under 300 coumarins and *ca* 40 chromones have been isolated from families which constitute the natural Order Rutales (Rutaceae, Meliaceae, Simaroubaceae, Burseraceae, Ptaeroxylaceae and Cneoraceae) The majority of reports of coumarins have been from the Rutaceae while the chromones have predominated in the Ptaeroxylaceae, Cneoraceae, and in *Spathelia* spp (Rutaceae)

The Rutaceae continues to be the source of new and interesting coumarin types In the past 5 years the majority of *ca* 80 'first reports' of coumarins from the Rutaceae were of novel structures These coumarins vary in complexity from 'simple' to acyl-, alkyl- or alkoxy-substituted types, and further to variously prenylated furano- and pyranocoumarins, glycosides and dimers The diversity of structures encountered has stimulated the development of methods to aid structure elucidation and recent developments in the structural analysis of coumarins are discussed The overall distribution of coumarins in the Rutaceae has changed little since the review by Gray and Waterman [1] Thus simple coumarins account for *ca* 55% of the total with furanocoumarins (*ca* 28%) and pyranocoumarins (*ca* 11%) making up the bulk of the remainder

In comparison to the Rutaceae the other families of the Rutales have yielded very few coumarins In the Simaroubaceae only a single coumarin has been isolated, scopoletin from *Ailanthus altissima* Similarly, only one coumarin has so far been encountered in the Burseraceae, a family better known for its utilization of cinnamate in the production of lignans, resins and volatile oils Two structures have been proposed for this compound, the coumarinolignoid propacin from *Protium opacum*

Within the Meliaceae only a few cinnamate-derived coumarins and two atypical coumarins have been encountered Thus *Melia azedarach* is reported to contain aesculetin, scopoletin and 6-hydroxy-7-methoxycoumarin, *Ekebergia senegalensis* to contain ekersenin, and *Cedrela toona* to contain siderin Both ekersenin and siderin are examples of 4-methoxy-5-methylcoumarins that are probably derived from acetate–pentaketide intermediates

The Ptaeroxylaceae and Cneoraceae show striking similarity in both producing several 6,7-dioxygenated and 6,7-dioxy-8-prenyl coumarins For example, obliquin is reported from *Ptaeroxylon obliquum* and *Cneorum tricoccum* and cedrelopsin from *Cedrelopsis grevei* (Ptaeroxylaceae) and *Neochamelea pulverulenta* (Cneoraceae) Both of these families also yield a range of related chromones, some of which have been found in species of *Spathelia* (Rutaceae)

REFERENCE

1 Gray, A I and Waterman, P G (1978) *Phytochemistry* **17**, 845

The Flavonoids of the Rutales:

J B Harborne Plant Sciences Laboratories, University of Reading, Reading, U K

Diversity of flavonoid structures in the Rutales is exemplified by the large number of extensively *O*-methylated flavones and flavonols reported in plants of the Order The octamethoxyflavonol exoticin from *Murraya exotica* typifies this biosynthetic feature Specific *O*-methyltransferases appear to be responsible for methylating different hydroxyl groups in these flavonoids Isopentenyl and methylenedioxy substitutions are also present in some structures Characteristic glycosides reported in these plants include the rutinose-based rutin, hesperidin and diosmin The isomeric neohesperidose is present attached to several flavanones in *Citrus*, such glycosides being intensely bitter Many more common flavonoid structures have been recorded in most rutalean families

The distribution of different flavonoid types within the Rutales is still imperfectly known so that flavonoid data are at present mainly of taxonomic interest at the generic or species level (e g for distinguishing species hybrids in *Citrus*) There are also some minor variations in flavonoids within the Rutaceae Finally, there are indications that flavonoid patterns may help to sort out relationships at the family level within this taxonomically difficult Order

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The Biological Activity of Some Secondary Metabolites of the Rutaceae.

J R Lewis Department of Chemistry, University of Aberdeen, Aberdeen, U K

For its size the Rutaceae produces an extremely large number of secondary metabolites of different structural types Not surprisingly, individual members of these secondary metabolites possess biological activity ranging from vitamin activity to antitumor, antisickling and photosensitization activity Representative examples of compounds possessing these and other physiological effects are presented

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Chemistry of the Limonoids of the Meliaceae and the Cneoraceae.

J D Connolly Department of Chemistry University of Glasgow Glasgow, U K

In biogenetic terms limonoids (tetranortriterpenoids) can be derived from simple C_{30} tirucallol precursors by apo-rearrangement and loss of four carbon atoms from the side chain with formation of a furan ring Subsequent ring cleavage processes and rearrangements lead to the wide range of known structural types An overall picture of this group will be given, including discussion of representative structures and their chemistry The structural elucidation of several new compounds, which arise by a novel ring cleavage, from *Carapa procera* and *C grandiflora* are detailed Finally the extensively rearranged pentanortriterpenoids of the Cneoraceae are considered

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Chemistry and Biological Activity of the Quassinoids: J Polonsky Institut de Chemie des Substances Naturelles, Gif-sur-Yvette, France

An interest in the bitter principles of the Simaroubaceae, the quassinoids, has gained in popularity in the last decade This interest stems from the identification of new types of quassinoids, due in part to the advent of ^1H NMR at higher fields and ^{13}C NMR, and in part to the discovery of their wide spectrum of biological activity The latter includes antineoplastic, antiviral, antimalarial, antiamoebic, antifeedant and insecticidal properties Many of the structural features required for biological activity have been established, thus leading to research on the chemical modifications of inactive members of the class to afford the biologically active compounds Several research groups are involved in a study of the total synthesis of the biologically active quassinoids Recently success has been achieved in the total synthesis of quassin, which was, interestingly, the first quassinoid to have its structure established

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Chemistry of the Burseraceae: S A Khalid Phytochemistry Research Laboratory, University of Strathclyde, Glasgow, U K

The Burseraceae are a relatively small plant family usually placed within the Rutales in taxonomic treatments of the plant kingdom The limited amounts of phytochemical information available on the family is reviewed and related to the chemistry of the typically rutalean families The natural products are discussed under the following classifications (a) oleo-resins—monoterpenes, sesquiterpenes and diterpenes, (b) triterpenes—ursane, oleane, euphane and lupane types—oxidation levels and opening of ring-A, (c) biflavonoids—a link with the Anacardiaceae? and, (d) lignans—a link with *Amyris* (Rutaceae)?

Chemistry and Systematics of the Bitter Principles of the Rutaceae: D L Dreyer U S D A , Berkeley, California, U S A

New results on limonoid chemistry and biology of the Rutaceae obtained during the past decade are reviewed With minor exceptions the pattern of structures of limonoids isolated during this period follows that previously recognized Thus, most structural differences in rutaceous limonoids, unlike those from the Meliaceae, are confined to the A-ring In addition to the chemical uniformity found in rutaceous limonoids, the botanical distribution largely follows the patterns previously detailed This includes a high frequency of occurrence in the subfamily Aurantioideae and the fact that all species of a limonoid-producing genus yield limonoids Evidence continues to accumulate suggesting that the enzymes involved in limonoid biosynthesis are relatively non-specific in terms of substrate structure

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Advances in the Tissue and Cell Culture of Species of Rutales: J-C Chénieux Laboratoire de Biologie Végétale et Cellulaire, Université de Tours, Tours, France

Tissue culture of members of the Rutales is well-established and has expanded rapidly since the first attempts to culture *Citrus* in 1954 At present, cultures are known to have been produced from more than 30 species, almost all belonging to the Rutaceae, and particularly to the subfamily Aurantioideae

The reasons for culturing plant cells *in vitro* are reviewed and the variable results obtained by different research groups analysed The agronomic applications (vegetative multiplication, production of specific pathogen-free plants) are, of course, of fundamental importance, but work aimed at resolving basic physiological problems has also been considerable The paper emphasizes work on secondary metabolites likely to be of economic interest (alkaloids, coumarins, flavonoids, terpenoids) An example of such a line of research, the bioproduction of quaternary alkaloids in *Choisya*, is used to describe the various steps involved The conditions under which secondary metabolites accumulate are reviewed and some examples will be given to show the influence of genetic, chemical and physical factors, the relationships between growth and metabolism and between metabolism and organogenesis There is room for optimism with regard to future possibilities for tissue and cell culture in the Rutales for the production of high-value metabolites and for the biotransformations of complex molecules Future advances will involve the use of immobilized cells and protoplasts, allowing the manipulation of the genome in a profitable direction

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Chemistry and Biological Significance of Selected *Citrus* Limonoids and Flavonoids: V P MAIER U S D A , Fruit and Vegetable Chemistry Laboratory, Pasadena, California, U S A

World production of *Citrus* fruits in 1979–1980 was *ca* 47 million tonnes, of which 45 % was converted into processed products Juice, in various forms, is the main product In addition, a variety of other processed and manufactured products are made from the fruit endocarp and from the rind, pulp and seeds remaining after juice extraction

The size, diversity and technological sophistication of the citrus industry have been the stimulus for a great deal of research on the chemistry and properties of citrus fruit constituents This work has shown that a broad array of secondary metabolites contribute to the distinctive characteristics that set citrus fruits apart from other fruits and from each other Attention is focused on two classes of secondary metabolites that have been extensively studied because of their taste properties, the limonoids and flavonoids

Studies of these constituents have produced a fund of information from which insights into the origin of fruit constituents and the changes they undergo as the fruit develops can be derived Aspects of the chemistry, biochemistry and physiology of the limonoids and flavonoids are discussed as they relate to growing the crop and producing high quality fruit, fruit products and by-products Specific topics covered are the site of synthesis, transport, accumulation, and metabolism of limonin and naringin during growth, maturation and postharvest storage of the fruit, a comparison of the bitterness problem caused by limonin (juice products) vs naringin (fresh fruit and juice), the chemistry of delayed bitterness in citrus juices caused by the conversion of limonoate A-ring lactone to limonin, the nature of the enzymes that catalyse this reaction and the enzymes that degrade limonoate A-ring lactone and limonin, and bitterness thresholds of limonin and naringin and the suppression of bitterness by taste modulating flavonoids

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Chemical Taxonomy of the Genus *Citrus*: R W SCORA Department of Botany and Plant Sciences, University of California, Riverside, California, U S A

The evolutionary development towards species of freely interbreeding plants in *Citrus* has been complicated by the occurrence of nucellar embryony This has caused extreme difficulty in taxonomic treatments A biotype relationship in *Citrus* species is derived after examining individual species, their origin, migration routes and chemotaxonomic inter-relationships

The origin of the grapefruit, *C paradisi*, the only New World biotype, is deduced by isozyme studies (glutamate oxalacetate transaminase 1 and 2, phosphoglucose isomerase, phosphoglucose mutase, amylase) and monoterpene studies (sabinene) The position of the mandarin, *C reticulata*, as a central species is discussed in relation to isozyme and leaf and rind oil studies The dominance of oxidase browning is used to identify biotypes with mandarin parentage The homozygosity of the Rough lemon, *C jambhiri*, assemblage and its relationships to Khoubs el Arsa and the true lemon, *C limon*, are shown by a statistical divergence diagram of their rind oil The problems of elucidating the ancestry of the lemon are presented and leaf oil data shown to suggest at least a trihybrid combination, including an unknown ancestor The lime, *C aurantifolia*, seems to be another complicated hybrid species

The unique position of the recently described *C halimii* is discussed While ovary morphology places it between the genera *Citrus* and *Fortunella*, its rind oils show an affinity to those of mandarin and sweet oranges, while leaf oils, isoenzymes and leaf protein patterns do not confirm such a relationship A tropical and subtropical area of origin are proposed for the subgenera *Papeda* and *Citrus* Only a few basic species are discernible which are linked with each other through hybrid combinations stabilized by nucellar embryony

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Biogenesis, Distribution and Systematic Significance of Limonoids in the Meliaceae, Cneoraceae and Related Taxa: D A H TAYLOR Department of Chemistry, University of Natal, Durban, S Africa

Limonoids, which are altered triterpenes related to limonin, are confined to species belonging to the Rutales, and are therefore probably truly related and not examples of parallel evolution Their biogenesis is believed to be fairly well understood, although little labelling work has been done It consists of a series of changes to an original triterpene similar to tirucallol, all of which can be represented as peroxidations followed by isomerizations or cyclizations of labile intermediates In the laboratory, these oxidations can be brought about by peracids, in nature peroxidases are presumably responsible

These oxidative changes commonly lead to ring opening by a Baeyer–Villiger mechanism, and the limonoids can be classified on the basis of which of the original four carbocyclic rings are opened When this is done a general agreement is found between chemical and botanical classifications using the recent revision of the Meliaceae by Pennington and Styles Some types of limonoid are widespread, others are, so far as is presently known, linked to one restricted botanical grouping

Attention is directed to points of particular interest

Among these are the sharp chemical distinction between the genera *Cedrela* and *Toona*, which appear closely related morphologically, the distinctive nature of the Swietenioideae, of the Melioideae, of the Melieae, and probably of *Ekebergia* and *Lovoa*, the relationship of *Spathelia*, *Sohnreyia* and *Harrisonia* to other genera, and the relationship between the Meliaceae–Rutaceae and the Simaroubaceae

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Chemical Characters and the Delimitation of Taxa Within the Rutales: P G WATERMAN Phytochemistry Research Laboratory, University of Strathclyde, Glasgow, U K

The Rutales produce an extremely wide spectrum of types of secondary compound many of which appear to have value as taxonomic markers An attempt is made to trace the development of these compounds in the Rutales based on the premise that the order derived from ranalean stock containing 1-benzyltetrahydroisoquinoline alkaloids but devoid of those compounds typical of the Order

Attention is drawn to the distribution of 1-benzyltetrahydroisoquinoline alkaloids in extant taxa and their co-occurrence with three major groups of rutaceous metabolites, anthranilate-derived alkaloids, coumarins and limonoids It is proposed that all three types of compounds arose early in the development of the Rutales with the limonoids developing before any divisions and coumarins and anthranilate alkaloids later in proto-rutaceous stock after separation of the Meliaceae The Simaroubaceae is considered to have separated later from the proto-Rutaceae, with which it shares the rare canthin-6-ones, and to then have developed the biosynthesis of quassinoids from limonoid-like precursors

The distribution of alkaloids and coumarins in the Rutaceae is examined with particular emphasis being placed on the distribution of furoquinolines, acridones, carbazoles and furano- and pyranocoumarins It is concluded that chemical data conforms to accepted taxonomy of the Aurantioideae but that supra-generic distinctions made within the Toddalioideae and Rutoideae are, with the exception of the Rutinae, difficult to maintain

Among the smaller taxonomic units it is concluded that the Flindersioideae is chemically allied to the Rutaceae rather than the Meliaceae The small group of taxa covering the Cneoraceae, Ptaeroxylaceae, *Spathelia* (Rutaceae) and *Harrisonia* (Simaroubaceae) are clearly closely related in their secondary metabolism, and the problems posed by the group are examined

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Chemical Characters and the Classification of the Rutales: R HEGNAUER Laboratorium voor Experimentele Plantensystematiek, University of Leiden, Leiden, The Netherlands

Past proposals for the delimitation and classification of the Rutales are briefly discussed The phytochemistry of the Order (Rutaceae, Cneoraceae, Simaroubaceae, Burseraceae, Meliaceae) and of the Anacardiaceae and Zygophyllaceae is outlined Attention is paid to essential oils, phenylpropanoids and bisarylpropanoids, chromones and phloroglucides (acetogenins), coumarins, flavonoids, tannins and their precursors, amides, amines (= protoalkaloids) and alkaloids, bitter nortriterpenoids and their tetracyclic triterpene precursors, diterpenes and pentacyclic triterpenes, saponins, various minor groups of secondary metabolites (acetylenic compounds, cyanogenic glycosides, quinones, unclassified), mucilages, storage products of seeds and inorganic compounds

The following suggestions for delimitation and classification based mainly on chemical evidence are made (a) Rutales *sensu stricto* and Sapindales *s s* together form the Rutales or Sapindales *sensu lato*, (b) the Burseraceae, Anacardiaceae and Zygophyllaceae belong to the Sapindales *s s* and, (c) the Leguminosae (Fabales) seem to be rather closely allied to the Sapindales

Notwithstanding Cronquist's recent comments [1], an evolutionary line starting with the Magnoliidae and comprising the Sapindales *s s*, Apiales (= Umbelliflorae), and resulting in the Asterales is still believed to be a very acceptable suggestion

REFERENCE

1 Cronquist, A (1980) *Chemosystematics Principle and Practice* (Bisby, F A , Vaughan, J G and Wright, C A , eds) p 1 Academic Press, London

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POSTERS

Canthinone Alkaloid Production in *Ailanthus altissima* Plant Cell Culture: L A ANDERSON, A HARRIS and J D PHILLIPSON Department of Pharmacognosy, The School of Pharmacy, University of London, London, U K

The deciduous tree, *Ailanthus altissima* (Mill) Swingle (Simaroubaceae), has yielded a series of quassinoids, alkaloids, flavonoids and quinones [1] There has been no previous literature report on plant cell culture of this species Callus cultures were initiated from sterile seeds of

A altissima and methanol extracts of the cells showed the presence of a major fluorescent compound when examined by TLC Evidence is presented for the identification of this compound as 1-methoxycanthin-6-one (UV, MS, ^{1}H NMR)

REFERENCE

1 Varga, E , Szendrei, K , Reisch, J and Maroti, G (1980) *Planta Med* **40**, 337

The Quinoline Alkaloids of *Vepris louisii*:

J Ayafor Department of Chemistry, University of Yaoundé, Yaoundé, Cameroun

The stem bark of *Vepris louisii* Gilb (Rutaceae) collected in Cameroun has yielded a number of novel and unusual quinolones and quinolone dimers [1–4] The isolation and biogenesis of these alkaloids are outlined

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1 Ngadjui, T B , Ayafor, J F and Sondengam, B L (1980) *Tetrahedron Letters* 3293
2 Ngadjui, T B , Ayafor, J F and Sondengam, B L (1981) *Tetrahedron Letters* 2685
3 Ayafor, J F , Sondengam, B L and Ngadjui, T B (1982) *Phytochemistry* **21**, 955
4 Ngadjui, T B , Ayafor, J F , Sondengam, B L , Connolly, J D , Rycroft, D S , Khalid, S A , Waterman, P G , Brown, N M D , Grundon, M F and Ramachandran, V N (1982) *Tetrahedron Letters* **23**, 2041

Alkaloids from *Euodia* aff. *triphylla*; a New Caledonian Rutaceae:

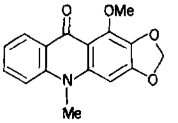
F Bevalot,* J Vaquette* and P Cabalion† *Laboratoire de Pharmacognosie, Faculté de Médecine et de Pharmacie, Besançon, France, †Centre Orstom, Noumea, New Caledonia

Stem bark and leaves of *Euodia* aff *triphylla* DC contain only two alkaloids which are identified, on the basis of spectral date, as evoxanthine (**1**) and 1,3-dimethoxy-*N*-methylacridone (**2**) Total yield from the leaves is *ca* 4 %, from the stem bark lower

The presence of closely related acridones, substituted only in the acetate-derived ring, in this New Caledonian species of *Euodia* suggests a possible phylogenetic relationship to *Euodia* native to Australia [1]

REFERENCE

1 Waterman, P G (1975) *Biochem Syst Ecol* **3**, 149



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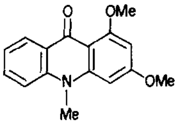
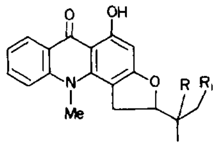


2

Acridone Epoxides in Cell Cultures of *Ruta* Species:

U Eilert*, B Engel†, E Reinhard† and B Wolters* *Institut fur Pharmazeutische Biologie, Technische Universitat Braunschweig, Braunschweig, West Germany, †Pharmazeutisches Institut, Universitat Tubingen, Tubingen, West Germany

Callus cultures of *Ruta graveolens* L yield a number of antimicrobial substances, mostly coumarins and alkaloids Rutacridone-epoxide (**1**) and hydroxy-



1 $R-R_1-O$
2 $R-H, R_1-OH$

rutacridone-epoxide (**2**) are the major active substances in methylene chloride extracts of callus material [1] In tests with mixed cultures of callus and fungi these substances show phytoalexin properties, with up to 10-fold increase in alkaloid content [2] Alkaloid yields are highest after culturing in darkness without phytohormone [2] The screening of suspensions of other *Ruta* species, in an attempt to optimize alkaloid yield, is outlined

Table 1 shows the quantities of (**1**) and (**2**) in suspension cultures of five *Ruta* species Alkaloid content varies markedly in the different species *R graveolens* and *R macrophylla* give the highest yields of both alkaloids, which reach up to *ca* 1 % dry wt Furthermore the media formulations used are shown to influence alkaloid formation in these five species to different extents

Table 1 Production of (1) and (2) in five *Ruta* species under varying culture conditions

Ruta species	C culture medium	Alkaloid production in μg/g dry wt (1)	(2)
R graveolens	E	90	25
	MS	5000	4000
	B5	4000	660
R corsica DC	E	2000	110
	MS	1500	180
	B5	4000	410
R macrophylla Moris	E	2400	490
	MS	2400	8000
	B5	1500	105
R chalapensis L	E	1300	450
	MS	430	190
	B5	150	15
R bracteosa DC	E	1300	450
	MS	430	190
	B5	160	100

E, Eriksson medium with 1 ppm NAA and 0 02 ppm kinetin [3]

MS, Modified Murashige and Skoog medium with 1 ppm 2,4-D and 0 1 ppm kinetin [4]

B5, Gamborg B5 medium with 1 ppm 2,4-D and 0 1ppm kinetin plus 0 2 % casein hydrolysate [5]

Alkaloid content estimated as previously reported [1]

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2 Wolters, B and Eilert, U (in preparation)
3 Scharlmann, W (1972) *Z Naturforsch Teil B* **27** 806
4 Murashige T and Skoog, F (1962) *Physiol Plant* **15**, 473
5 Steck, W, Gamborg, O L and Bailey B K (1973) *Lloydia* **36**, 93

Flavonoids of *Vepris heterophylla*:

E Gomes,* J Dellamonica,† J Gleye,* C Moulis,* J Chopin† and E Stanislas* *Laboratoire de Pharmacognosie, Universite Toulouse, †Laboratoire de Chemie Biologique, Universite Claude Bernard (Lyon I), Villeurbanne, France

Petrol defatted leaves of *Vepris heterophylla* Letouzey (Rutaceae) were extracted with methylene chloride followed by methanol Flavonoids were partially purified by an Amberlite XAD-2 column and then isolated by PC on cellulose The following are identified on the basis of UV spectral date, EIMS of permethylated derivatives, and cochromatography with authentic standards chrysoeriol-7-*O*-β-D-glucoside, chrysoeriol-7-*O*-α-rhamnosyl-7-*O*-β-D-galactoside, 7-*O*-acyl-8-*C*-β-D-glucosylchrysoeriol (7-*O*-acylscoparin), 6-*C*-β-D-glucosylapigenin (isovitexin), 8-*C*-β-D-glucosylapigenin (vitexin), 2″-*O*-β-D-glucosylisovitexin, 2″-*O*-β-D-glucosylvitexin

Coumarins from *Coleonema calycinum*.

A I Gray, C J Meegan and N B O'Callaghan Department of Pharmacognosy, School of Pharmacy, Trinity College, Dublin, Eire

Coleonema calycinum (Steud) Williams (Rutaceae) is a small shrub found in coastal regions of S Africa A petrol extract of the aerial parts was subjected to CC and TLC over Si gel Seven coumarins were isolated and identified on the basis of spectral data as 7-(3,3-dimethylallyloxy)-coumarin, 7-(2,3-epoxy-3-methylbutoxy)-coumarin, 7-(3-methoxycarbonylbut-2-enoxy)-coumarin, 7-methoxy-8-(2,3-epoxy-3-methylbutoxy)-coumarin, epoxysuberosin (TLC only), and 7-methoxy-8-(2,3-dihydroxy-3-methylbutoxy)-coumarin This is the first record of 7-methoxy-8-(2, 3-dihydroxy-3-methylbutoxy)-coumarin, the major product, and 7-(3-methoxycarbonylbut-2-enoxy)-coumarin from a natural source The other coumarins have previously been encountered in the closely allied *C album* Bartl & Wendl [1] In *C album* 7-oxy coumarins appear to predominate and 8-substitution is unusual

REFERENCE

1 Gray A I (1981) *Phytochemistry* **20**, 1711

Further Alkaloids from *Zanthoxylum simulans*:

A I GRAY and J J O'SULLIVAN Department of Pharmacognosy, School of Pharmacy, Trinity College, Dublin, Eire

Recently we reported the occurrence of alkaloid, lignan and sterol constituents in *Zanthoxylum simulans* Hance (Rutaceae) [1] Two of the alkaloids, *N*-acetyl-anonaine and the novel 8-methoxy-*N*-methylflindersine had not previously been found in the Rutaceae Further investigations of the root bark have afforded seven further alkaloids three benzophenanthridines, two pyranoquinolones, the furoquinoline dictamnine and an amide

The benzophenanthridines have been identified as 11-formylmethyl-dihydrochelerythrine, 11-carboxymethyl-dihydrochelerythrine and 1,3-bis-(11-dihydrochelerythrine)-acetone Substituted benzophenanthridines of these types are rare in the Rutaceae (in *Zanthoxylum, Toddalia* and *Fagaropsis*) [2] In some cases they may be artefacts, however, in this case they do appear to be natural products The pyranoquinolones are identified as the novel compounds 5′-(2,3-epoxy-2-methylbutan-4-yl)-*N*-methylflindersine and 3′,4′-dihydroxy-8-methoxy-*N*-methyl-3′,4′-dihydroflindersine The synthesis of the latter from 8-methoxy-*N*-methylflindersine, The major quinolone alkaloid of this species, is described the amide is shown to be (*E*)-*N*-(4-methoxyphenethyl)-*N*-methyl-3, 4-methylenedioxy-cinnamide, another new natural product

REFERENCES

1 Gray, A I and O'Sullivan, J J (1980) *Planta Med* **39**, 209
2 Waterman, P G and Khalid, S A (1981) *Biochem Syst Ecol* **9**, 45

Coumarins and Flavonoids from *Diosma pilosa*:

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Diosma pilosa Williams (Rutaceae) is a small shrub found in S Africa The isolation and characterization of 5,6,7-trimethoxycoumarin, 6,7,8-trimethoxycoumarin and 6,7-dimethoxycoumarin from a petrol extract of the aerial parts is described Further extraction with methanol yielded the flavonol glycoside quercitrin The coumarins of *D pilosa* differ from those of the only other species of the genus studied, *D acmaeophylla* E & Z which has yielded only 7-, 6,7- and 7,8-oxygenated coumarins, of which several have 7-prenyloxy-substituents [1]

REFERENCE

1 Campbell, W E, Provan, G J and Waterman, P G (1982) *Phytochemistry* **21**, 1457

Pentanortriterpenes of the Cneoraceae:

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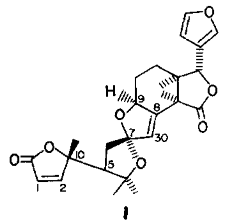
The typical bitter substances of the Cneoraceae such as cneorin B_1 (**1**) have a skeleton of 25 carbon atoms, which at first glance shows little resemblance to those characteristic of other members of the Rutales However, the structures of several less degraded minor constituents of *Neochamaelea pulverulenta* (Vent) Erdt and *Cneorum triccocon* L , some of which are known from other rutalean species, clearly demonstrate the relationship and indicate a biogenetic pathway leading from the tirucallan-type triterpenoids via classical limonoids to the cneoran framework, formulated as in **2** The degradation involves (a) incorporation of the C-30 methyl group into the skeleton, (b) ring opening between C-9 and C-10, (c) loss of C-16, and (d) ring closure between C-18 and C-14, giving rise to a cyclopropane ring A mechanistic interpretation of these steps is put forward



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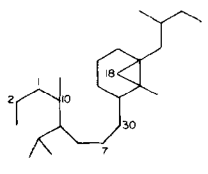


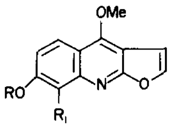
2

Alkaloids from *Melicope lasioneura*, Isolation, Structure, Synthesis:

F TILLEQUIN,* G BAUDOUIN,* M KOCH,* J PUSSET† and T SEVENET† *Laboratoire de Pharmacognosie, Universite René Descartes, Paris, France, †Laboratoire des Plantes Médicinales du C N R S , Noumea, New Caledonia

Seven furoquinoline alkaloids have been isolated from the aerial parts of *Melicope lasioneura* (Baill) Guill (Rutaceae) and characterized as evolitrine, kokusaginine, skimmianine, haplopine, 7-hydroxydictamnine, 7-isopentenyloxy-γ-fagarine and the novel melineurine (**1**) The structure of **1** was established on the basis of spectral data and confirmed by conversion into isomelineurine (**2**) on heating with methyl iodide

Synthesis of **1** is achieved by condensation of 7-hydroxydictamnine (**3**) with 3,3-dimethylallylbromide, a reaction that also yields **4** and **5** Epoxidation of **1** by *m*-



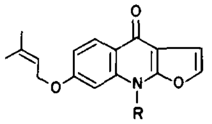
1 $R = CH_2CH\ C(Me)_2, R_1 = H$

3 $R = R_1 = H$

4 $R = R_1 = CH_2CH\ C(Me)_2$

6 $R = CH_2CH{-}C(Me)_2, R_1 = H$

7 $R = CH_2CH(OH)C(OH)Me_2, R_1 = H$



2 $R = Me$

5 $R = CH_2CH\ C(Me)_2$

CPBA leads to the epoxide (**6**) previously isolated from *Euodia xanthoxyloides* F Muell [1] Hydrolysis of **6** gives evellerine (**7**) previously isolated from *Euodia elleryana* F Muell [2]

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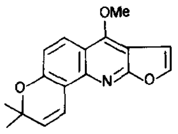
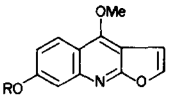
1 Dreyer, D L (1970) *J Org Chem* **35**, 2420

2 Johns, S R, Lamberton, J A and Sioumis, A A (1968) *Aust J Chem* **21**, 1897

Synthesis of Dutadrupine: F Tillequin, G Baudouin and M Koch Laboratoire de Pharmacognosie, Universite Rene Descartes, Paris, France

The alkaloid dutadrupine (**1**) has been isolated from *Dutaillyea drupacea* (Rutaceae) [1] The synthesis of the alkaloid by condensation of 7-hydroxy-dictamnine (**2**) with 3-chloro-3-methylbutyne to give **3** followed by Claisen rearrangement to **1** is described





2 $R = H$

3 $R = C(Me)_2C{\equiv}CH$

REFERENCE

1 Baudouin, G, Tillequin, F, Koch, M, Pusset, J and Sevenet, T (1981) *J Nat Prod* **44**, 546