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PHYTOCHEMISTRY OF THE AUSTRALIAN RUTACEAE: *BORONIA*, *ERIOSTEMON* AND *PHEBALIUM* SPECIES

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Key Word Index—*Boronia*; *Eriostemon*; *Phebalium*; Rutaceae, tribe Boronieae; secondary metabolites; terpenoids; alkaloids; coumarins.

Abstract—The phytochemistry of *Boronia*, *Eriostemon* and *Phebalium* species, three members of the Australian Rutaceae (tribe Boronieae), is reviewed. Aspects of the chemistry, stereochemistry and biogenesis of the more unusual metabolites are discussed. More than 270 secondary metabolites identified in these species are listed, together with their sources, in Fig. 1 and the Appendix. © 1997 Elsevier Science Ltd

INTRODUCTION

The family Rutaceae is distributed throughout the temperate and tropical regions of the world, but certain tribes are largely confined to one continent. Only four of the 11 recognized tribes occur in Australia and these comprise about 40 genera, of which 20 are endemic. The Boronieae, one of several tribes of the subfamily Rutoideae, is largely Australian and is evenly distributed throughout the Australian continent [1–3]. However, the tribe shows a clear and sharp division within Australia into three regions of specific endemism with a high degree of xeromorphic adaptation. The first and largest one of these regions includes the eastern areas of New South Wales and Queensland, the second is in the south west region of Western Australia, and the third includes the northern part of the Northern Territory. Few species are found in more than one region; this pronounced endemism is not found in other tribes of the Rutoideae or in other subfamilies of the Rutaceae. Seventeen genera are included in the tribe Boronieae, the largest being *Boronia*, *Eriostemon* and *Phebalium*.

Boronia is named after Francesco Borone, a young Italian helper of the English botanist John Sibthorp [4]. The genus comprises about 95 species of which only *B. koniambensis* occurs outside Australia and is endemic to New Caledonia [5]. The distribution within Australia consists of three disjunct regions, a northern, east and south east, and a south western region coinciding with the distribution of other sclerophyllous taxa [3, 5, 6]. Western Australia, which contains the south west region, has 49 species, 45 of which are endemic [7]. The majority of *Boronia* species are perennial woody shrubs; a few achieve the size of a small tree, others are herbaceous though arising from woody underground stocks [5]. Generally, species do not grow very far inland but they can grow in a range of soil types and climatic conditions. Some, e.g. *B. coerulescens*, tolerate the hottest and driest regions while others, *B. algida* and *B. citriodora*, are found at higher altitudes. They have proven to be popular in cultivation largely because of the fragrant flowers and long period of bloom of many species; *B. metastigma* being the best known and most widely grown because of its perfume.

The genus *Eriostemon* (Greek *erion*, wool; *stemon*, stamen) was first described by Smith in 1798 [4]. Commonly known as Wax Flower, because of its smooth thickish petals, it consists of about 35 species and occurs in all Australian states including Tasmania. A number of species from New Caledonia have, at different times, been included in *Eriostemon*, but it is now accepted that they should not be considered to belong to the Boronieae [8–10]. Its distribution ranges from the sub-alpine habitats in south-eastern Australia to the semi-arid region of Western Australia [11]. *Eriostemon* species grow as small trees or shrubs, generally as part of an open forest or woodland communities, and can tolerate great variations in temperature ($<0°$ to $>35°$), rainfall (1500 mm to 300 mm) and are resistant to frost.

The genus *Phebalium* (Greek *phibalee*, a kind of myrtle), was first described by E. T. Ventenat in 1805 [4] and consists of approximately 45 species distributed in the south-west and south-east regions of Australia (44 species) with one species, *P. nudum*, being endemic to New Zealand. A number of species are distinguishable only with difficulty from *Erios-*

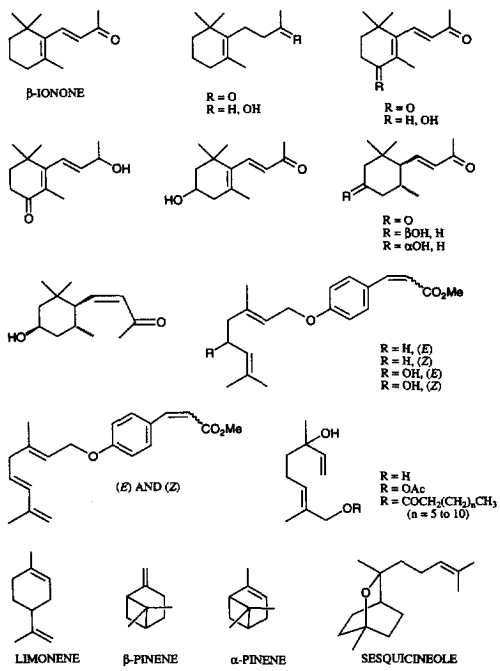


Fig. 1. Terpenes and derivatives from *B. megastigma* [55, 56, 110].

temon. Several sections of the two genera are independently related to other genera, suggesting that *Phebalium* and *Eriostemon* contain a heterogeneous assemblage of species [8–10].

The remaining genera of the Boronieae are: *Acradenia* (2 species), *Asterolasia* (5), *Chorilena* (2), *Correa* (12), *Crowea* (3), *Diplolaena* (6), *Drummondita* (4), *Geleznowia* (1), *Microcybe* (3), *Muiriantha* (1), *Nematolepis* (1), *Philotheca* (2), *Rhadinothamnus* (1), *Zieria* (27).

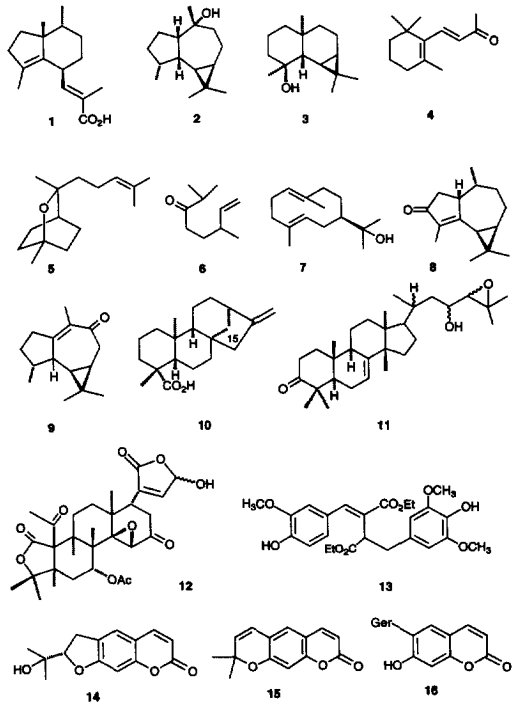
In this review, the secondary metabolites isolated from *Boronia*, *Eriostemon* and *Phebalium* species are considered in terms of the classes of compounds represented, stereochemistry and probable biosynthesis. A complete listing of the metabolites identified from these species is presented in a graphical way in Fig. 1 and the Appendix. It is hoped that this compilation will provide the foundations for a chemotaxonomic study of these unusual members of the Rutaceae.

HISTORICAL PERSPECTIVE

Boronia and *Eriostemon* species were much admired by gardeners and species such as *E. buxifolius*, *E. australasius* and *E. myoporoides* were introduced into England in the period 1822–1824. *B. pinnata* was cultivated as a greenhouse plant in England as early as 1830 [7, 11]. On a historical note, *Diplolaena grandiflora* (Boronieae) was part of the first recorded collection of Australian plants made by an European. The plant was collected by William Dampier in the Shark Bay area of Western Australia in 1699 and described and illustrated in his book 'A Voyage to New Holland' [12].

Boronia, *Eriostemon* and *Phebalium* species possess glands which secrete strongly scented oils and, as much as they captured the attention of the early European settlers, they would have been well known to the Australian Aboriginal people. However, there are only a few reports which indicate the traditional uses of members of the Boronieae. Reportedly, the leaves of *B. lanuginosa* were used to alleviate aches and pains and an infusion of the leaves was rubbed onto the chest to treat colds [13]. The leaves of *E. brucei* were rubbed on the skin or the plant was warmed near a fire and the fumes were inhaled to alleviate colds [14, 15]. In this context, it is interesting to note that the essential oil contains a high proportion of cineole (70%) [15] and the leaves contain the sesquiterpene valerenic acid (**1**) [16, 17], well known as a spasmolytic and sedative agent [18]. Some *Phebalium* species, *P. anceps* and *P. argenteum*, are known as 'blister bushes' since the sap will cause blistering of the skin [12, 19, 20], a reaction induced by the presence of furanocoumarins. *P. nudum*, known to the Maori people as 'Mairehau' was used by them as a body rub and sachets of the fragrant leaves were also worn [21]. The chopped leaves of *B. rhomboideae* were added to fodder and fed to horses as a vermifuge by the early settlers [22]. Given the number of species of the Boronieae, their wide distribution and their often spectacular bloom, it would be surprising if they had not attracted more attention for use in ceremonial and medicinal practices.

Chemical interest in these genera appears to have started in 1896 when the steam distillate of *B. polygalifolia* was investigated [23], and by the early 1920s studies on the essential oils of several *Boronia*, *Erios-*



temon and *Phebalium* species had been conducted. *B. megastigma* is the species that has attracted greatest attention largely because of its perfumery potential. Even so, this did not appear to have been appreciated in those early days; a compilation of 'The Useful Native Plants of Australia' in 1889 suggested the use of this plant as a grave decoration and the flowers as suitable as a flavouring agent for tea [22]. A mention of *B. megastigma* was made in a book entitled 'Sweet Scented Flowers' published in 1895 and by 1922 attempts were made to prepare an extract from the blossoms for the production of a perfume 'different to anything that has yet been offered to the public on the European market' [24]. By 1928, the concrete otto was 'a well known article of commerce' and the results of studies of the chemical composition of this preparation were published [25].

The research carried out by Penfold on the essential oils of *Boronia* species, and those of *Eucalyptus* and *Backhousia*, led him to the concept of physiological forms 'those varieties of... species which cannot be differentiated on botanical evidence but which yield essential oils of diverse chemical composition' [26]. For example, one form of *B. thujona* gave α- and β-thujone whereas a botanically identical form yielded safrole [26]. Polymorphism in terpenoid composition has since been widely recognized and recorded [27].

CLASSES OF SECONDARY METABOLITES

Mono- sesqui- and diterpenes

Much of the early interest in the secondary metabolites of the three genera was concerned with the composition of their essential oils and by the 1930s a number of species had been investigated. The results of those efforts which led to the identification of compounds are summarized in Table 1, but this data must be viewed with some caution. The reliability is questionable because of dubious sampling methods, the uncertain identities of the species collected and the primitive methods of analysis then in use. For example, *B. thujona* var A has been renamed *B. rivularis* [47, 48] and there is some uncertainty whether the specimen of *E. coxii* examined by Penfold was in fact *P. coxii* [49]. Furthermore, the compound supposedly isolated from *E. myoporoides*, and thought to be the sesquiterpene ledol (**2**), has since been shown to be maaliol (**3**) [50].

One result that has withstood the test of time is the isolation of β-ionone (**4**) from the flowers of *B. megastigma*. Initially identified by Penfold, and confirmed by Sabetay [51], β-ionone was recognized as being similar to a synthetic product prepared by Tiemann and Kruger [52] by cyclization of pseudoionone with acid [53, 54]. More recent investigations of *B. megastigma* and various clones have shown that there are distinct chemotypes. Over 150 compounds have been detected in the light petroleum extract of the flowers of the clones. β-Ionone, dodecyl acetate, methyl jasmonate, *Z*-heptadec-8-ene and C21 and C33 hydrocarbons were the major components in all clones. The concentration of α-,β-pinene and limonene varied widely between clones and some produced significant amounts (up to 19.3%) of sesquicineole (**5**) [55]. A detailed analysis of the absolute of *B. megastigma*, obtained by petroleum ether extraction of the flowers, has revealed the presence of a number of β-ionone derivatives (megastigmanes) differing in the degree of unsaturation and oxygenation in the ring and side chain (Fig. 1). Apparently, these compounds are derived by enzymatic degradation of the caro-

Table 1. Early work on essential oils of *Boronia*, *Eriostemon* and *Phebalium* species

Species	Major components	References
B. anemonifolia	*d*-α-pinene	28
B. citriodora	*d*-α-pinene, citronellol	29
B. dentigeroides	*d*-α-pinene, *d*-limonene, ocimene	28
B. ledifolia var a	α-pinene, methyl nonyl ketone, methyl heptyl ketone	30
B. megastigma	β-ionone	25
B. muelleri	elemicin, pinene, geraniol	31, 32
B. pinnata	limonene, *d*-α-pinene	26, 31
B. safrolifera	*d*-α-pinene, methyl eugenol, safrole	31, 34
B. thujona	α-, β-thujone	26, 31, 35
B. thujona var A	safrole, *l*-limonene	26, 30, 33, 35
E. coxii (P. *coxii*)	*d*-α-pinene, ocimene, *d*-myrtenol	36, 37
E. crowei	croweacin	38
E. glasshousiensis	*d*-α-pinene, ocimene	39
E. myoporoides	α-pinene, methyl anthranilate, ledol	40
P. argenteum	geraniol, *d*-limonene, α-pinene, psolaren	41, 42
P. becklerii	α-pinene	43
P. dentatum	*d*-α-pinene, geraniol, citronellol	36
P. filifolium	sabinene	44
P. nudum	citronellal, citral, limonene, camphene	45
P. squameus	ledol	46

tenoids in the flowers. From the distillation residues of the absolute, a range of methyl cinnamates derivatives of monoterpenes have been isolated and identified (see Fig. 1) [56].

Apart from the work on *B. megastigma*, little systematic investigation of the essential oils of these three members of the Rutaceae has been carried out with modern analytical methods. Dihydrotagetone (**6**) is the major component (97.4%) of the essential oil of *P. glandulosum* subsp. *glandulosum* [57]. α-Pinene has been isolated from *B. algida* [58] and (+)-bornyl acetate was found to be the major component (61%) of the essential oil of *B. latipinna* [59].

Among the sesquiterpenes, the most unusual example is sesquicineole (**5**) which was isolated from *B. megastigma* [55]. This compound was first found in *Senecio subrubriflorus* [60] and, subsequently, has been obtained from other plants [61, 62]. Two syntheses have been reported [63, 64] and olfactory evaluation showed that it contributed to the flavour and fragrance of *B. megastigma* absolute [64]. The presence of eudesmols in *E. difformis* [65] and *P. ozothamnoides* [66] can be explained as arising, in part, as artefacts of hedycaryol (**7**) [66]. An alcohol, thought to be α-cadinol has been isolated from *P. drummondii* [67]. A number of guaianes [68] and aromadendrenes [69–72] have been identified, the more unusual ones being the conjugated ketones cyclocolorenone (**8**) from *B. ledifolia* (70% of the essential oil) [70] and squamulosone (**9**) (65%) from *P. squamulosum* [72]. Valerenic acid (**1**) is a rare sesquiterpene which occurs in *E. brucei* [16, 17]. This compound has been isolated from *Valeriana officinalis* and is a component of the alcoholic extract from the roots which has been used for centuries as a mild sedative or tranquilizing agent [73, 74]. From a biosynthetic perspective, most of the sesquiterpenes found so far can be readily derived from the two precursors hedycaryol and bicyclogermacrene as illustrated in Fig. 2.

The first record of the occurence of diterpenes in the Rutaceae was the isolation of (−)-kaurenoic acid (**10**) (0.2%) and its 15β-hydroxylated derivative from the leaves and terminal branches of *P. rude* [75]. Kaurenoic acid is the precursor of the gibberellin phytohormones whereas the 15β-hydroxy derivative does not appear to play a similar role since it is inactive in tests for gibberellin activity. Diterpenes appear to be rare secondary metabolites in the Rutaceae and the only other cases reported are the isolation of the labdanes daniellic acid and corresponding butenolide from *Pamburus missionis* [76], *cis*-clerodanes from *Evodia floribunda* [76] and of gomerol from *Citrus sinensis* [77].

Triterpenes and derivatives

The common triterpenes lupeol, betulonic acid, oleanolic acid and simple derivatives have been isolated from *B. inornata* and *B. gracilipes* [69], *B. crassifolia* [Ghisalberti, unpublished work] and *P. tuberculosum*

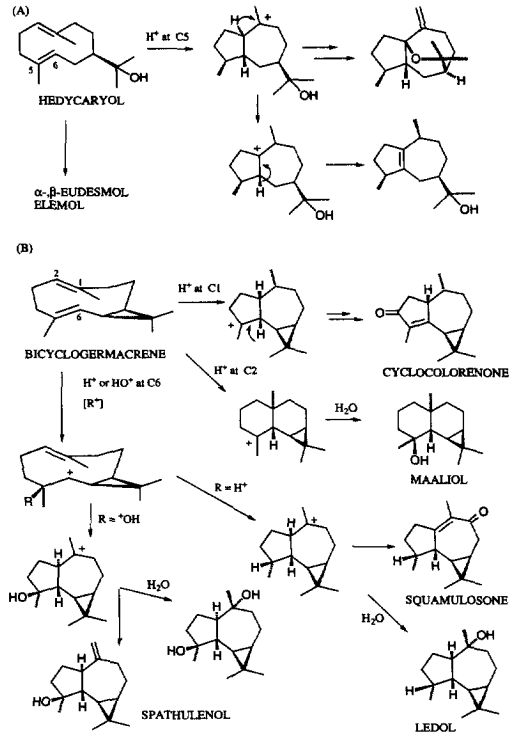


Fig. 2. Biogenetic correlations of sesquiterpenes in *Boronia*, *Eriostemon* and *Phebalium*.

ssp. *megaphyllum* [78]. α-Amyrin, β-amyrin and sitosterol occur in the bark of *P. nudum* [79] and a dammarane triterpene has been isolated from *B. algida* [80]. Limonoids are well represented in the Rutaceae [81] and examples of protolimonoids have been isolated; niloticin from *B. alata* [82] and *B. inornata* [69], piscidinol-A (**11**) from *B. inornata* [69] and phebaloparvilactone from *P. squamulousum* ssp. *parvifolium* [83]. Boronialatenolide (**12**) is a pentanortriterpene isolated from *B. alata* [82]. This type of compound represents a subclass of limonoids which is rare in the Rutaceae [81].

Phenylpropanoid derivatives

Simple C6-C3 derivatives. Simple shikimic acid derived metabolites are well represented in the three genera. These are frequently obtained in the essential oil fraction recovered by steam distillation [49, 84]. Cinnamic acid has been isolated from the bark of *P. nudum* [79], methyl *p*-methoxycinnamate is present in substantial amounts in the essential oil of *E. obovalis* [57] and 3,4-dimethoxy cinnamaldehyde was found in *E. fitzgeraldii* [68]. *E*- and *Z*- isomers of methyl cinnamate with 4-terpenyloxy substitution have been obtained from *B. megastigma* absolute (Fig. 1) [56] and *E. australasius* ssp. *banksii* [85]. Eugenol [86, 87], methyl eugenol [31, 34, 68, 86], isoeugenol [79], safrole [26, 30, 31, 33–35], croweacin [38] and elemicin [31, 32] have all been isolated from these genera. Lignans are quite commonly found in the Rutales [88, 89] but

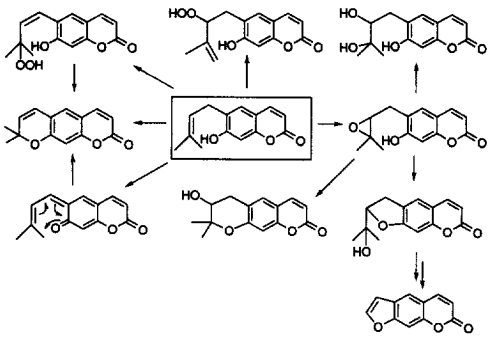


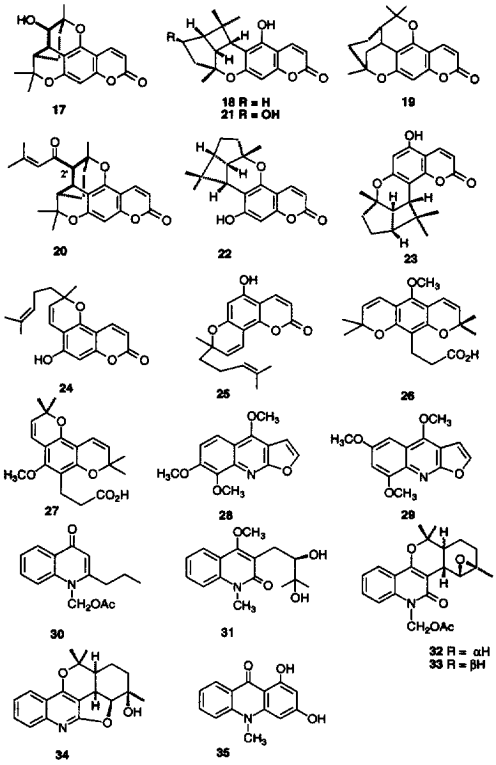
Fig. 3. Elaboration of prenyl side chain in coumarins.

only two examples are available for the genera under consideration; phebalarin from *P. nudum* [90] and (−) suchilactone from *E. fitzgeraldii* [68]. Phebalarin (**13**) is a dibenzylbutane containing an ethyl diester group and is probably an artefact of the ethanol extracting procedure. Nevertheless the corresponding diacid could be derived from an intermediate in the biosynthesis of lignans [91].

Coumarins. Coumarins have been found in all of the families of the order Rutales and, indeed, this class of compounds is the most widely represented in the three genera. In all cases, they exhibit oxygenation at C7 and are derived from the cyclization of (*Z*)-2,4-diglucosyloxycinnamic acid [89, 92]. The hemiterpene unit, generally 3-methylbut-2-enyl, is frequently involved in the modification of the coumarins and is responsible for the wide range of structures which are found in these genera. Coumarins with prenylation at the 6 and/or the 8 positions are common and these prenylated derivatives become the precursors of a large number of other compounds which arise from oxidation, epoxidation, hydrolysis, hydroperoxidation, and ester formation [89, 93] (see Fig. 3). Cyclization processes lead to dihydrofurans or dihydropyrans which give rise to furanocoumarins (**14**) and pyranocoumarins (**15**) (Fig. 3). The geranyl coumarin osthrutin (**16**) was the first example of a coumarin with a ring alkylated by a C10 terpene unit to be isolated from Rutaceous plants [94].

The first naturally occurring coumarins containing a C10 terpene-derived carbocyclic system include the most interesting group of coumarins so far isolated, the bruceol (**17**) [15] and eriobrucinol (**18**) types [17]. The first example of this type was the citran bruceol, isolated from *E. brucei*, whose structure was deduced from chemical studies [15] and confirmed by X-ray crystallography [95, 96]. Deoxybruceol (**19**), initially thought to be the deoxy analogue of bruceol, was later shown to have the terpene unit in the opposite orientation [96]. Both of these compounds occur in optically active forms and their absolute stereochemistry has been tentatively assigned. However, deoxybruceol has also been found to occur as a racemate [95] thus raising interesting biosynthetic questions.

Elegant synthetic work by Crombie's group has



resulted in the synthesis of both **17** and **19** [96] and the proton and ^{13}C NMR spectra of these compounds have been fully assigned [97]. A related group of citrans, e.g. **20**, has been isolated from *E. myoporoides* [98] and differ from bruceol (**17**) by the presence of an oxygenated C5 moiety at C2′. It has been suggested that this unit is introduced following the formation of the bruceol skeleton rather than arising directly from a farnesyl coumarin [98]. An alternative pathway which involves the possible involvement of a C5 unit during the elaboration of the bruceol carbocyclic ring system is illustrated in Fig. 4.

The two related cyclols, eriobrucinol (**18**) and hydroxyeriobrucinol (**21**), have also been discovered in *E. brucei* and their structure fully confirmed from chemical [17], X-ray [99] and synthetic studies [100]. Interestingly, the two regioisomers (**22**) and (**23**) previously prepared synthetically [97, 100] from the chromenes (**24**) and (**25**), have also been isolated from a variety of *E. brucei* [101]. The suggestion that these compounds arise biosynthetically by a (π6s + π2a) process, as indicated from synthetic studies, is worthy of consideration [100] and a probable sequence involving such electrocyclic cyclizations is illustrated in Fig. 4.

In all, coumarins (117) account for almost 43% of the secondary metabolites (274) identified so far in the three genera. It is worth noting that of the courmarins isolated, approximately one quarter have not been fully defined in terms of their stereochemistry. Most of these are coumarins containing an isoprenoid chain which has been modified by hydroxylation, epoxidation or hydroperoxidation.

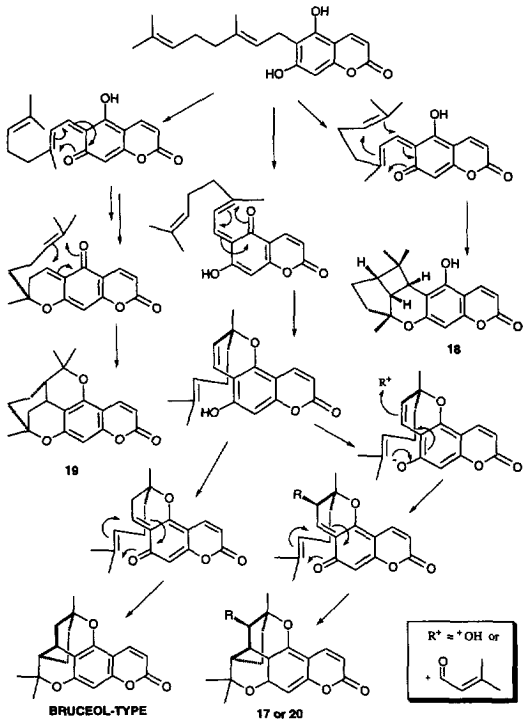


Fig. 4. Hypothetical derivation of citrans and cyclols in *Eriostemon* spp.

Acetophenone and chromone derivatives. These compounds, derived from the acetate/malonate pathway, form a small subset of compounds in the three genera. All but one of the examples so far identified are characterized by C- or O-prenylation of the aromatic ring. The structurally more interesting examples are the linear benzodipyran eriostoic acid (**26**) [102] and the angular analogue eriostemoic acid (**27**), the first natural product shown to possess this carbon skeleton [94]. Both are common components of extract of many *Eriostemon* species (see Appendix).

Flavonoids. Rutin, from *B. cymosa*, was the first flavonoid isolated from the three genera [103]. Some early work indicated the presence of mono- dimono- and bioside derivatives of malvidin and delphinidin anthocyanins in the flowers and fruits of several *Boronia* and *Eriostemon* species [104]. Apart from this, studies on the flavonoid components of these genera has until recently been neglected. Examples of chalcones, flavanones, flavanols and flavones have been isolated [69, 103, 105–108], a number of which have prenyl substitution either in the polyketide or the shikimic acid derived portions (see Appendix).

Alkaloids

The presence of alkaloids in these species was first established by the isolation of a number of furanoquinolines from the bark of the New Zealand species *P. nudum* [79]. Despite unpromising assays for alkaloids in the Western Australian Rutaceae [quoted in 65], subsequent investigations led to the isolation of

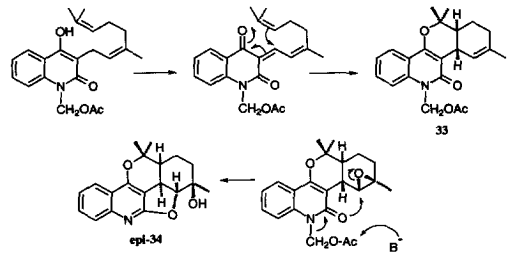


Fig. 5. Correlation of erioaustralasine (**33**) and the epimer of furoerioaustralasine (**34**).

skiammine (**28**) and maculosidine (**29**) from *B. ternata* and a number of *Eriostemon* species [65, 94]. From *B. ternata*, the 2- propyl-4-quinolinone (**30**), with the unusual N-acetoxymethyl substituent, and 2-propyl-4-quinolone were also isolated, but the latter was shown to be an artefact of the isolation procedure [65, 109]. Some 30 years elapsed before any further phytochemical investigations on the alkaloids of the three genera was undertaken and recent results indicate that quinoline and furoquinoline alkaloids are commonly found in species of *Boronia* and *Eriostemon*, but only rarely in *Phebalium*. The quinoline alkaloids originate from anthranilate following condensation with malonate or alkyl malonates. In this respect, it is worthwhile noting that methyl anthranilate has been isolated from *E. glasshousiensis* [39] and *E. myoporoides* [40]. The simplest compound derived in this sequence is the 2,4-dioxygenated quinoline which can undergo prenylation at the C3 position. Further modification can lead to the terpenyl quinolines, e.g. edulinine (**31**) [86], which appears to be optically inactive from its melting point, and the furanoquinolines, e.g. **28**, **29**.

The structurally more interesting compounds of this type are the 3-monoterpenyl derived quinolines, *cis*- and *trans*-erioaustralasine (**32**, **33**) and furoerioaustralasine (**34**), members of an exceptionally rare class of quinoline alkaloids, which have been isolated from *E. australasius* [85]. The biosynthetic elaboration of the terpene portion mimics the events leading to the citran coumarins (Fig. 4) and can be rationalized as shown in Fig. 5. It is tempting to consider that **32** is a precursor of **34**, except that the stereochemistry assigned at C2′ is opposite to that expected from epoxide ring opening by a 2-hydroxy group. In this context, it is worthwhile noting that, in the structural elucidation of **34**, NOESY interactions were apparently observed between H-2′ and both the 8′-axial methyl and 1′-methyl group. The first interaction is, in fact, only possible if H-2′ is in the β-axial orientation, a situation which would be in agreement with a *trans*-epoxide ring opening.

The acridone alkaloids arise by combination of anthranilate with a malonyl CoA derived triketide which condenses to give the tricyclic nucleus typically oxygenated at C1 and C3 as in **35**. To date, acridone alkaloids have only been isolated from *Boronia* spp.

and become the first examples of this type of compound to be isolated from the tribe Boronieae.

Other compounds

A number of other compounds have been isolated from the three genera (Appendix). Of these, the more interesting ones are the diastereomeric methyl cucurbates, from *B. megastigma*, and the methyl jasmonates. The hormonal action of jasmonic acid and related compounds has been much studied [134].

CONCLUDING REMARKS

Boronia, *Eriostemon* and *Phebalium* species are characterized by the presence of glands which secrete essential oils composed of simple monoterpenes and aromatic compounds. A distinguishing feature is the production of a range of megastigmanes and the sesquiterpene sequicineole by *B. megastigma*. Apart from these, the terpenoids produced are, on the whole,structurally unexceptional with the underrepresentation of diterpenes being a puzzling feature. Coumarins modified by prenyl groups are the dominant metabolites in all three genera and many such metabolites appear to arise by processes involving electrocyclic reactions. *Eriostemon* species seem to specialise in this and produce the unique citrans and cyclols exemplified by bruceol and eriobrucinol. *Boronia* and *Eriostemon* species produce a range of quinoline and furoquinoline alkaloids which are rarely found in *Phebalium*. So far, acridone alkaloids appear to be restricted to *Boronia* species. No studies of the biosynthesis of these secondary metabolites appear to have been carried out, although the types and range of compounds produced by the three genera would make efforts along these lines worthwhile.

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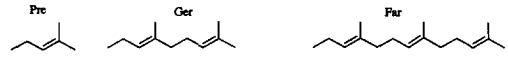
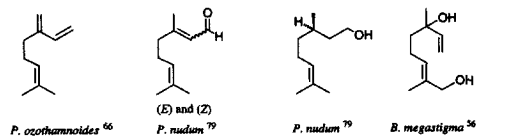
APPENDIX

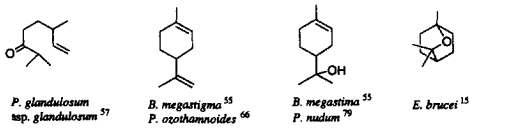
This appendix, together with Fig. 1, contains the structures, sources and literature references for all compounds isolated from *Boronia*, *Eriostemon* and *Phebalium* species. The secondary metabolites are listed according to the structural classes discussed in the text. The following abbreviations have been used:



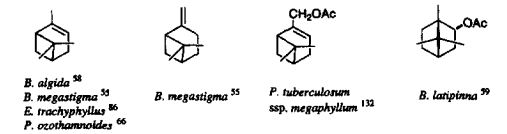
MONOTERPENES



P. ozothamnoides [66] | (*E*) and (*Z*) *P. nudum* [79] | *P. nudum* [79] | *B. megastigma* [56]

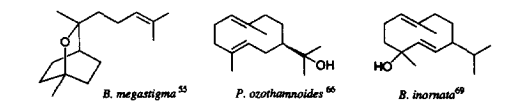


P. glandulosum ssp. *glandulosum* [57] | *B. megastigma* [55] *P. ozothamnoides* [66] | *B. megastima* [55] *P. nudum* [79] | *E. brucei* [15]

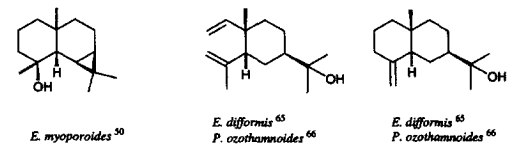


B. algida [58] *B. megastigma* [55] *E. trachyphyllus* [86] *P. ozothamnoides* [66] | *B. megastigma* [55] | *P. tuberculosum* ssp. *megaphyllum* [132] | *B. latipinna* [99]

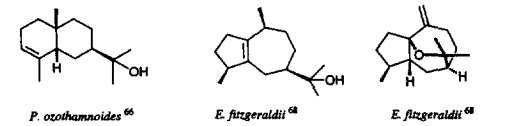
SESQUITERPENES



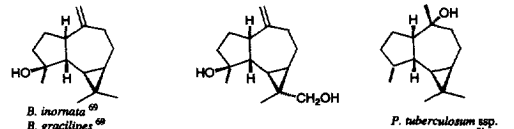
B. megastigma [55] | *P. ozothamnoides* [66] | *B. inornata* [69]



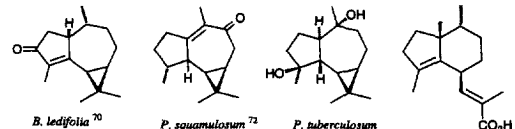
E. myoporoides [50] | *E. difformis* [65] *P. ozothamnoides* [66] | *E. difformis* [65] *P. ozothamnoides* [66]



P. ozothamnoides [66] | *E. fitzgeraldii* [68] | *E. fitzgeraldii* [68]

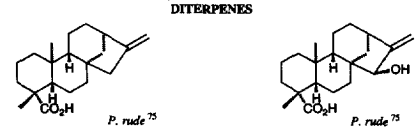


B. inornata [69] *B. gracilipes* [69] *P. tuberculosum* ssp. *megaphyllum* [71] *P. filifolium* [71] | *E. brucei* ssp. *brucei* [71] | *P. tuberculosum* ssp. *megaphyllum* [71] *P. squameus* [46]



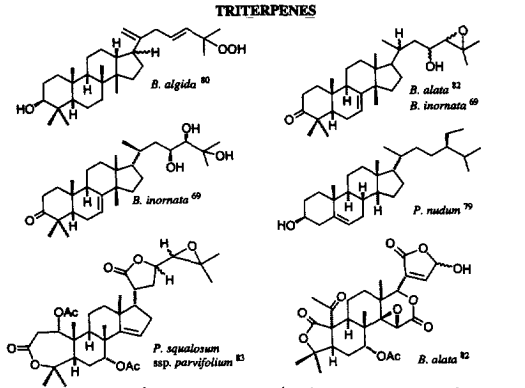
B. ledifolia [70] | *P. squamulosum* [72] | *P. tuberculosum* ssp. *megaphyllum* [71] *P. filifolium* [71] | *E. brucei* [16, 17]

DITERPENES

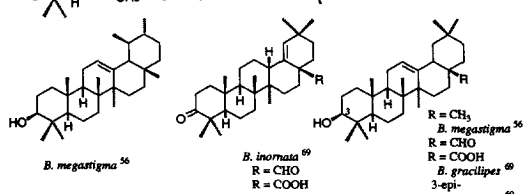


P. rude [75] | *P. rude* [75]

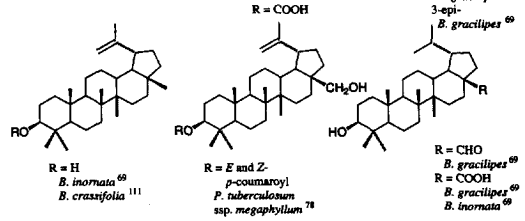
TRITERPENES



B. algida [80] | *B. alata* [82] *B. inornata* [69] | *B. inornata* [69] | *P. nudum* [79] | *P. squalosum* ssp. *parvifolium* [83] | *B. alata* [82]

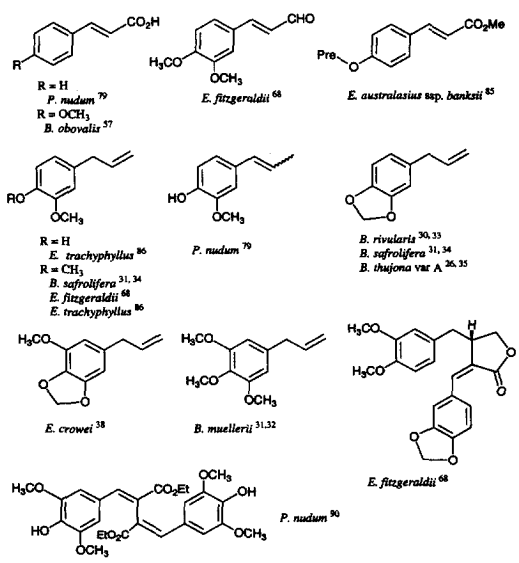


B. megastigma [56] | *B. inornata* [69] R = CHO R = COOH | R = CH_3 *B. megastigma* [56] R = CHO R = COOH *B. gracilipes* [69] 3-epi- *B. gracilipes* [69]



R = H *B. inornata* [69] *B. crassifolia* [111] | R = *E* and *Z*-*p*-coumaroyl *P. tuberculosum* ssp. *megaphyllum* [78] | R = CHO *B. gracilipes* [69] R = COOH *B. gracilipes* [69] *B. inornata* [69]

SIMPLE C6-C3 COMPOUNDS



R = H *P. nudum* [79] R = OCH_3 *B. obovalis* [57] | *E. fitzgeraldii* [68] | *E. australasius* ssp. *banksii* [85]

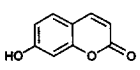
R = H *E. trachyphyllus* [86] R = CH_3 *B. safrolifera* [31, 34] *E. fitzgeraldii* [68] *E. trachyphyllus* [86] | *P. nudum* [79] | *B. rivularis* [30, 33] *B. safrolifera* [31, 34] *B. thujona* var A [26, 35]

E. crowei [38] | *B. muelleriі* [31,32] | *E. fitzgeraldii* [68]

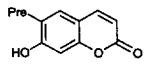
P. nudum [90]

COUMARINS

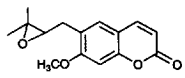
7-OXYGENATED



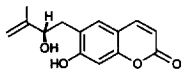
E. apiculatus [113]
E. fitzgeraldii [68]
P. anceps [112]
P. ovatifolium [112]
P. squameum [112]
P. squamulosum ssp. *parvifolium* [83, 112]



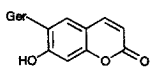
B. algida [80]
B. lanceolata [114]



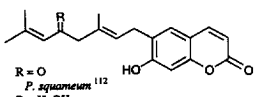
P. phylicifolium [112]



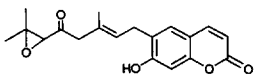
B. lanceolata [114]



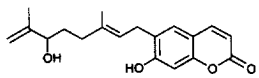
E. tomentellus [94, 115]
P. filifolium [78, 112]
P. squamulosum ssp. *parvifolium* [112]
P. stenophylum [112]
P. tuberculosum [78, 112]



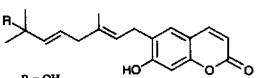
R = O
P. squameum [112]
R = H, OH
P. anceps [112, 117]
P. squameum [112]



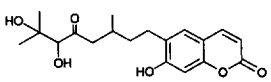
P. squameum [112, 116]



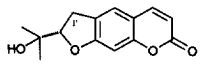
E. tomentellus [115]
P. filifolium [78, 112]
P. tuberculosum [78, 112]



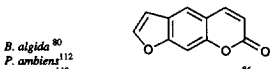
R = OH
E. tomentellus [115]
P. anceps [112]
P. filifolium [78, 112]
P. squamulosum ssp. *parvifolium* [83, 112]
P. stenophyllum [112]
P. tuberculosum [112]
R = OOH
E. tomentellus [115]



P. squameum [116]

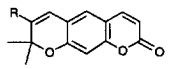


Δ1'-
P. anceps [112, 117]

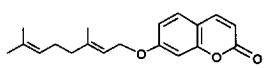


B. algida [80]
P. ambiens [112]
P. anceps [112]
P. squamulosum ssp. *longifolium* [112]
P. whitei [112]

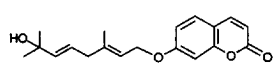
E. trachyphyllus [86]
P. ambiens [112]
P. anceps [112, 117]
P. argenteum [19]



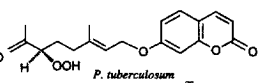
R = H
B. lanceolata [114]
R = OH
B. algida [80]



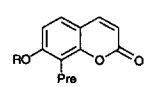
P. tuberculosum ssp. *megaphyllum* [78]
P. filifolium [78]



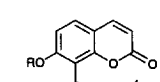
P. tuberculosum ssp. *megaphyllum* [78]
P. filifolium [78]



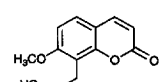
P. tuberculosum ssp. *megaphyllum* [78]
P. filifolium [78]



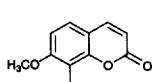
R = Me
P. tuberculosum [78, 112]
P. tuberculosum ssp. *megaphyllum* [78]
R = Pre
E. spicatus [121]



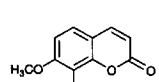
R = CH_3
P. squamulosum ssp. *parvifolium* [83]
R = Pre
E. spicatus [121]
P. stenophyllum [112]



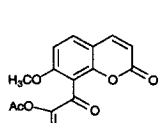
P. canaliculatum [112]
P. coxii [112, 117]
P. tuberculosum [78, 112]



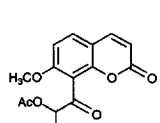
P. coxii [112, 117]



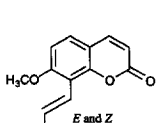
R = H
P. coxii [112]
R = Ac
P. bilobum [112]
Δ3'-
P. bilobum [112]



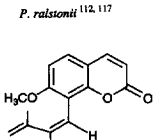
P. ralstonii [112, 117]



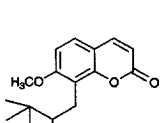
P. ralstonii [112, 117]



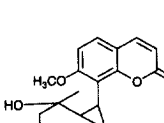
E and *Z*
P. tuberculosum [78, 112]
P. tuberculosum ssp. *megaphyllum* [78]



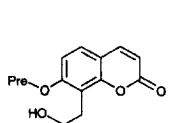
P. ralstonii [117]



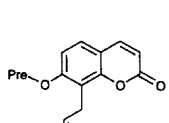
P. coxii [112, 117]



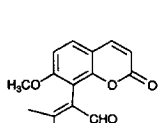
P. coxii [112]



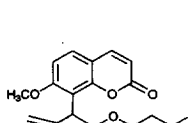
E. spicatus [121]



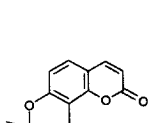
E. spicatus [121]



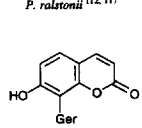
P. coxii [112, 117]
P. filifolium [78, 112]
P. ralstonii [112, 117]



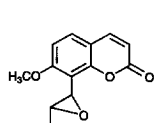
P. filifolium [127]



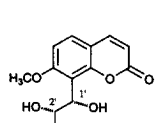
P. anceps [112, 117]
P. argenteum [19]



B. lanceolata [114]
B. inornata [69]
E. tomentellus [115]

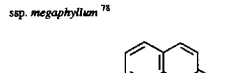


P. bilobum [112]
P. canaliculatum [112]
P. dentatum [105, 112]
P. drummondii [112, 118]
P. filifolium [78, 112]
P. gracile [112]
P. phylicifolium [112]
P. rotundifolium [112]
P. tuberculosum [112, 118]
P. tuberculosum ssp. *megaphyllum* [78]

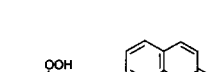


P. bilobum [112]
P. coxii [112, 117]
P. ralstonii [112, 117]
P. tuberculosum [112]
P. tuberculosum ssp. *megaphyllum* [78]

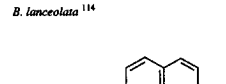
1'-acetate
P. phylicifolium [112]
2'-acetate
P. coxii [112]
P. phylicifolium [112]
P. ralstonii [112, 117]
P. rotundifolium [112]
P. tuberculosum [78, 112]
P. tuberculosum ssp. *megaphyllum* [78]
1', 2'-diacetate
P. coxii [112]
1'-methoxy
P. bilobum [112]
P. dentatum [112]
P. drummondii [112]
P. tuberculosum [78, 112]



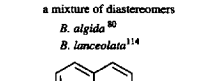
B. lanceolata [114]



a mixture of diastereomers
B. algida [80]
B. lanceolata [114]



B. algida [80]
B. lanceolata [114]



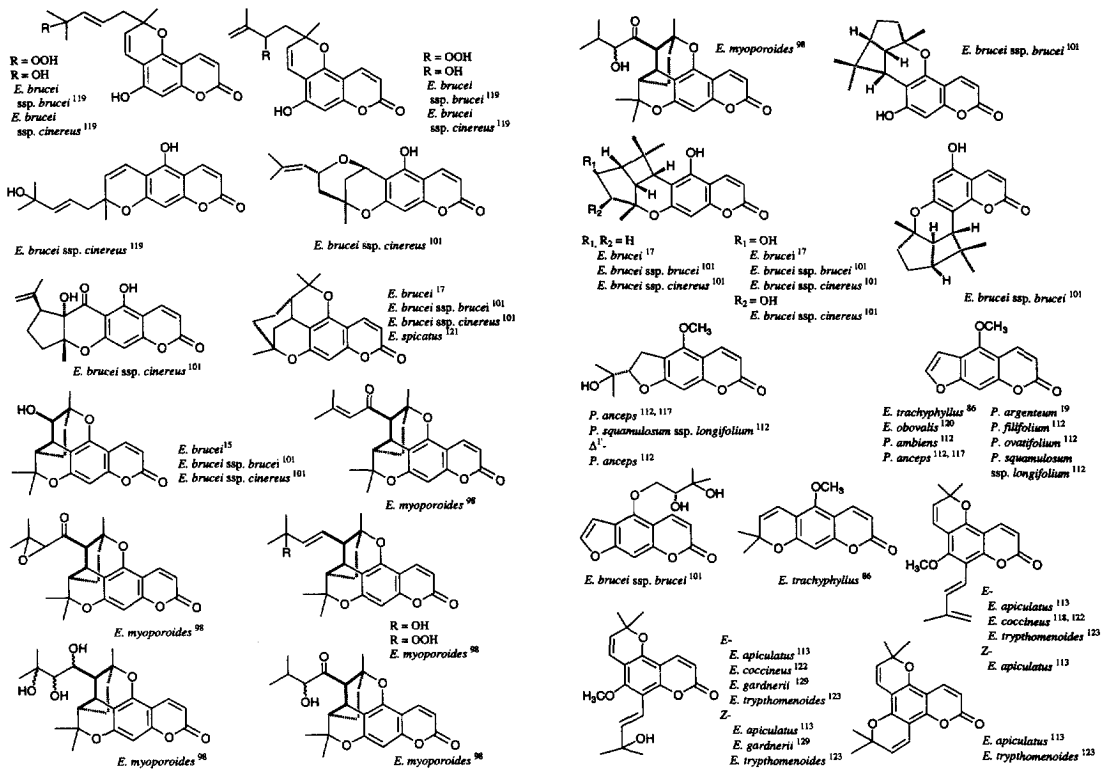
P. stenophyllum [112]

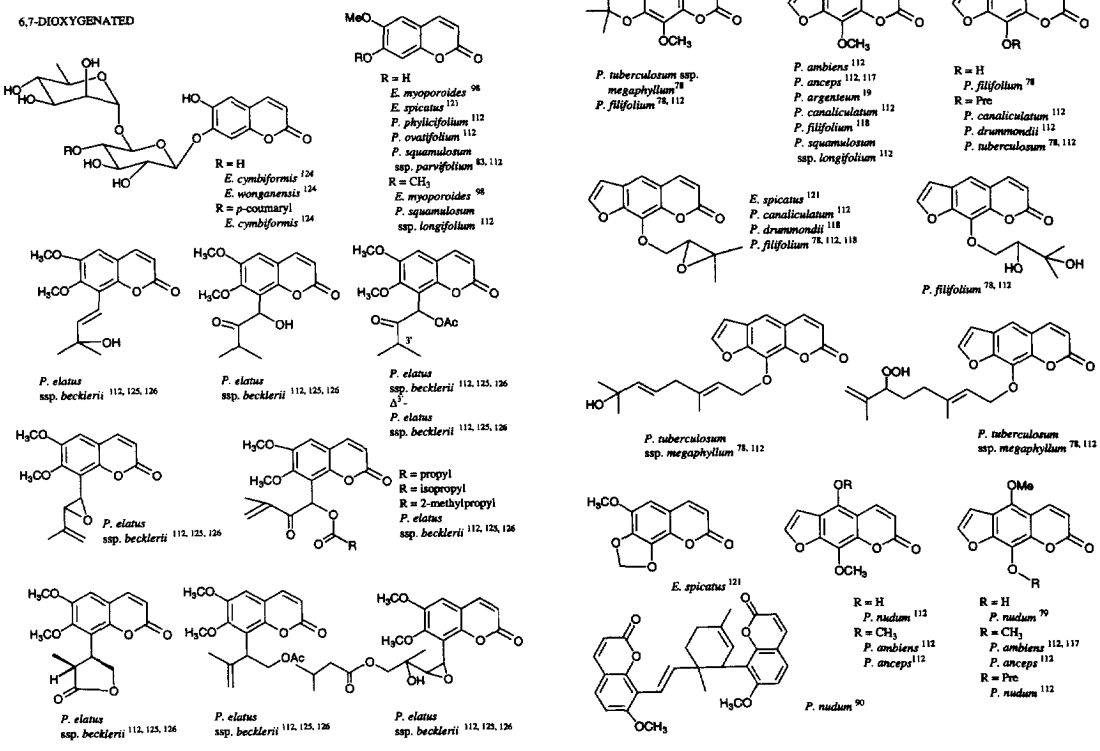
5, 7-DIOXYGENATED

E. obovalis [120]

E. myoporoides [98]

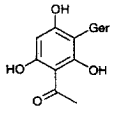
E. brucei ssp. *cinereus* [119]


R = OOH
R = OH
E. brucei ssp. brucei 119
E. brucei ssp. cinereus 119
E. brucei ssp. cinereus 119
E. brucei ssp. cinereus 101
E. brucei 17
E. brucei ssp. brucei 101
E. brucei ssp. cinereus 101
E. spicatus 121
E. brucei ssp. cinereus 101
E. brucei 15
E. brucei ssp. brucei 101
E. brucei ssp. cinereus 101
E. myoporoides 98
E. myoporoides 98
R = OH
R = OOH
E. myoporoides 98
E. myoporoides 98
E. myoporoides 98
E. brucei ssp. brucei 101
E. brucei ssp. cinereus 101
R1 = OH
E. brucei 17
E. brucei ssp. brucei 101
E. brucei ssp. cinereus 101
R2 = OH
E. brucei ssp. cinereus 101
E. brucei ssp. brucei 101
P. anceps 112, 117
P. squamulosum ssp. longifolium 112
Δ1'-
P. anceps 112
E. trachyphyllus 86
E. obovalis 120
P. ambiens 112
P. anceps 112, 117
P. argenteum 19
P. filifolium 112
P. ovatifolium 112
P. squamulosum ssp. longifolium 112
E. brucei ssp. brucei 101
E. trachyphyllus 86
E-
E. apiculatus 113
E. coccineus 118, 122
E. trypthomenoides 123
Z-
E. apiculatus 113
E-
E. apiculatus 113
E. coccineus 122
E. gardnerii 129
E. trypthomenoides 123
Z-
E. apiculatus 113
E. gardnerii 129
E. trypthomenoides 123
E. apiculatus 113
E. trypthomenoides 123

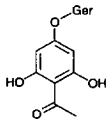

6,7-DIOXYGENATED
R = H
E. cymbiformis 124
E. wonganensis 124
R = p-coumaryl
E. cymbiformis 124
R = H
E. myoporoides 98
E. spicatus 121
P. phylicifolium 112
P. ovatifolium 112
P. squamulosum ssp. parvifolium 83, 112
R = CH3
E. myoporoides 98
P. squamulosum ssp. longifolium 112
P. elatus ssp. beckierii 112, 125, 126
P. elatus ssp. becklerii 112, 125, 126
P. elatus ssp. becklerii 112, 125, 126
Δ3'-
P. elatus ssp. becklerii 112, 125, 126
P. elatus ssp. becklerii 112, 125, 126
R = propyl
R = isopropyl
R = 2-methylpropyl
P. elatus ssp. becklerii 112, 125, 126
P. elatus ssp. becklerii 112, 125, 126
P. elatus ssp. becklerii 112, 125, 126
P. elatus ssp. becklerii 112, 125, 126
P. tuberculosum ssp. megaphyllum 78
P. filifolium 78, 112
P. ambiens 112
P. anceps 112, 117
P. argenteum 19
P. canaliculatum 112
P. filifolium 118
P. squamulosum ssp. longifolium 112
R = H
P. filifolium 78
R = Pre
P. canaliculatum 112
P. drummondii 112
P. tuberculosum 78, 112
E. spicatus 121
P. canaliculatum 112
P. drummondii 118
P. filifolium 78, 112, 118
P. filifolium 78, 112
P. tuberculosum ssp. megaphyllum 78, 112
P. tuberculosum ssp. megaphyllum 78, 112
E. spicatus 121
R = H
P. rudum 112
R = CH3
P. ambiens 112
P. anceps 112
P. rudum 90
R = H
P. rudum 79
R = CH3
P. ambiens 112, 117
P. anceps 112
R = Pre
P. rudum 112

ACETOPHENONES AND CHROMONES

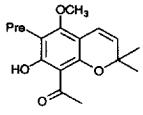
P. filifolium [78]
P. tuberculosum ssp *megaphyllum* [78]



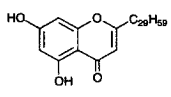
B. ramosa [128]



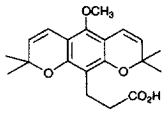
B. ramosa [128]



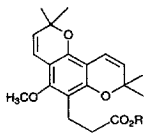
B. coerulescens ssp. *spinescens* [107]



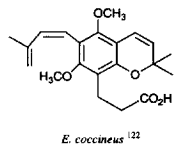
E. brucei ssp. *brucei* [101]



E. coccineus [102, 122]
E. desertii [102]
E. difformis [102]
E. gardnerii [129]
E. hispidulus [106]
E. wonganensis [124]

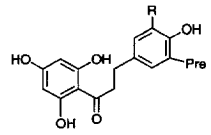


R = H
E. apiculatus [113]
E. cymbiformis [124]
E. gardnerii [129]
E. myoporoides [98]
E. tomentellus [94]
E. tryptomenoides [94, 123]
R =Me
E. wonganensis [124]

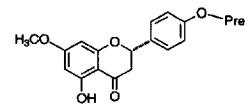


E. coccineus [122]

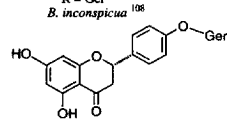
FLAVONOIDS



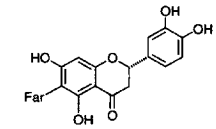
R = Pre
R = Ger
B. inconspicua [108]



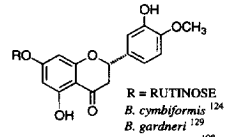
B. coerulescens ssp. *spinescens* [107]



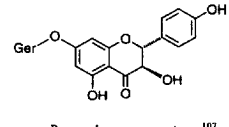
B. coerulescens ssp. *spinescens* [107]



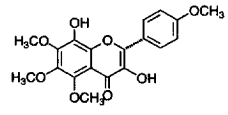
B. ramosa [128]



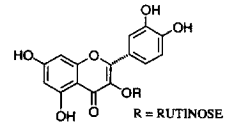
R = RUTINOSE
B. cymbiformis [124]
B. gardneri [129]
B. incospicua [108]



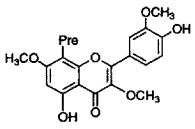
B. coerulescens ssp. *spicata* [107]
B. coerulescens ssp. *spinescens* [107]



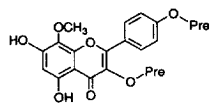
E. buxifolius ssp. *buxifolius* [106]
E. hispudulus [106]



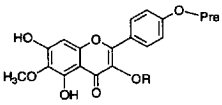
R = RUTINOSE
B. cymosa [103]
B. gracilipes [69]



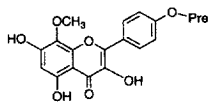
P. deniatum [105]



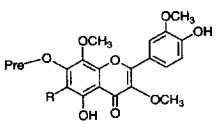
B. coerulescens ssp. *spicata* [107]



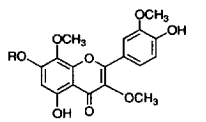
R = H
B. coerulescens ssp. *spicata* [107]
R = CH_3
B. coerulescens ssp. *spicata* [107]
B. coerulescens ssp. *spinescens* [107]



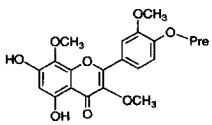
B. coerulescens ssp. *spicata* [107]
B. coerulescens ssp. *spinescens* [107]



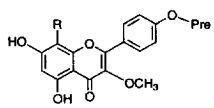
R = H
B. coerulescens ssp. *spicata* [107]
B. coerulescens ssp. *spinescens* [107]
R = OCH_3
B. coerulescens ssp. *spicata* [107]



R = H
R = CH_3
B. coerulescens ssp. *spicata* [107]

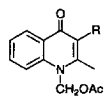


B. coerulescens ssp. *spinescens* [107]

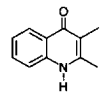


R = H
R = OCH_3
B. coerulescens ssp. *spicata* [107]
B. coerulescens ssp. *spinescens* [107]

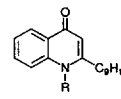
ALKALOIDS



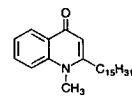
R = H
R = CH_3
B. bowmanii [130]
B. lanceolata [131]



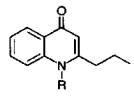
B. bowmanii [130]
B. lanceolata [131]



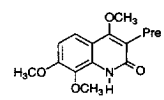
R = H
R = CH_3
R = CH_2OAc
B. bowmanii [130]



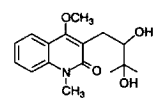
B. algida [80]



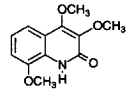
R = H (artefact)
R = CH_2OAc
B. ternata [109]



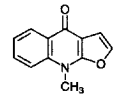
B. bowmanii [130]



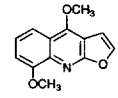
E. trachyphillus [86]



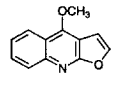
B. gardneri [129]



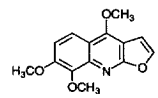
B. inornata [69]



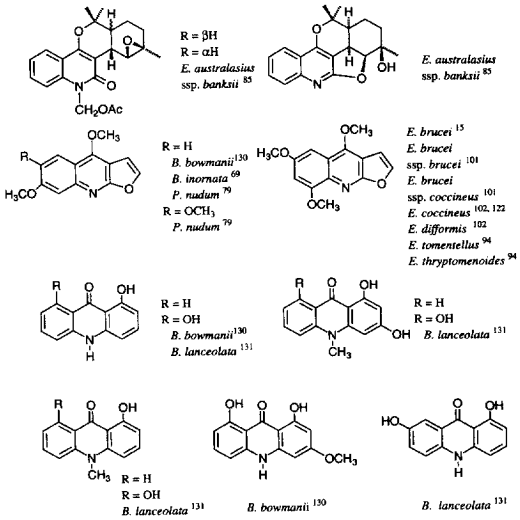
B. bowmanii [130]
E. coccineus [122]
P. nudum [79]



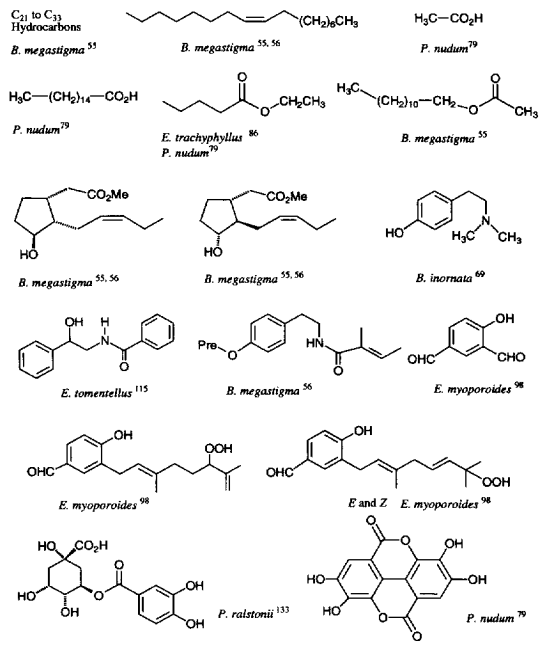
B. bowmanii [130]
B. coerulescens ssp. *spinescens* [107]
B. inornata [69]
P. nudum [79]



B. ternata [109]
E. brucei ssp. *brucei* [101]
E. brucei ssp. *coccineus* [101]
E. coccineus [102]
E. tomentellus [94]
E. thryptomenoides [94]
P. nudum [79]


R = βH
R = αH
E. australasius ssp. banksii [85]
E. australasius ssp. banksii [85]
R = H
B. bowmanii [130]
B. inornata [69]
P. nudum [79]
R = OCH3
P. nudum [79]
E. brucei [15]
E. brucei
ssp. brucei [101]
E. brucei ssp. coccineus [101]
E. coccineus [102, 122]
E. difformis [102]
E. tomentellus [94]
E. thryptomenoides [94]
R = H
R = OH
B. bowmanii [130]
B. lanceolata [131]
R = H
R = OH
B. lanceolata [131]
R = H
R = OH
B. lanceolata [131]
B. bowmanii [130]
B. lanceolata [131]

OTHERS


C21 to C33 Hydrocarbons
B. megastigma [55]
B. megastigma [55, 56]
P. nudum [79]
P. nudum [79]
E. trachyphyllus [86]
P. nudum [79]
B. megastigma [55]
B. megastigma [55, 56]
B. megastigma [55, 56]
B. inornata [69]
E. tomentellus [115]
B. megastigma [56]
E. myoporoides [98]
E. myoporoides [98]
E and Z E. myoporoides [98]
P. ralstonii [133]
P. nudum [79]