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POLYPHENOLS IN THE LEAVES OF *EUCALYPTUS*: A CHEMOTAXONOMIC SURVEY—V.

THE SERIES CORNUTAE AND SUBCORNUTAE OF THE SECTION MACRANTHERAE AND THE SECTION PLATYANTHERAE

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Abstract—Chromatographic examination of the leaves of the forty-three species examined revealed the presence of discoloured flavonols or a characteristic unknown compound or both in twenty-four species. These two groups of species could be further subdivided according to the presence of large amounts of rutin or engelitin, and significant amounts of leucocyanidin or myricetin. Classification based on chemical characters is similar in most cases to that based on morphological characters.

INTRODUCTION

PRYOR[1] has suggested that the eucalypt species found on the newer soils of Australia may be divided into two groups, the "Adnata" and the "Bisectae". The former group are very largely found in north-eastern and eastern Australia and the polyphenolic composition of the leaves of the species found in this group have been described.[2] This present paper describes the composition of the Bisectae in which group Pryor includes most of the series Cornutae and Subcornutae of Blakely's[3] section Macrantherae and the section Platyantherae. Almost all the species are found in the southern portion of Western Australia. Of the fifty-two recorded species in these parts of Blakely's classification, forty-three have been examined.

Hathway[4] has found that the heartwoods of *Eucalyptus cornuta* (Blakely No. 96), *E. lehmannii* (97), *E. gomphocephala* (98) differ from other species of the Cornutae and Subcornutae in that they lack stilbenes.

RESULTS AND DISCUSSION

Blakely's Series VIII. Cornutae

All the species in this series are found in the southern portion of Western Australia and are mallees (shrubby species with a bulbous rootstock, from which ascend several slender stems), such as *Eucalyptus annulata* (102, Table 1) with heights of about 10 ft, or marlocks (dwarf species with a reduced rootstock) with heights between 5–30 ft, for example *E. macrandra* (108), or small trees with heights up to 130 ft such as *E. gomphocephala* (98). The bark may be smooth (*E. platypus* (99)) or rough (*E. gomphocephala*). The wood is pale-yellow or yellow-brown and very hard and durable.

[1] L. D. PRYOR, In *The Evolution of Living Organisms* (Edited by G. W. LEEPER), p. 446. Melbourne University Press (1962).
[2] W. E. HILLIS, *Phytochem.* **6**, 373 (1967).
[3] W. F. BLAKELY, *A Key to the Eucalypts*, 2nd ed., Forestry and Timber Bureau, Canberra (1955).
[4] D. E. HATHWAY, *Biochem. J.* **83**, 80 (1962).

TABLE 1. POLYPHENOLS IN THE LEAVES OF THE CORNUTAE (VIII) AND SUBCORNUTAE (IX) SERIES OF THE SECTION MACRANTHERAE†

‡a	b	c	d	e f g h i j k l m n o p q r s t u v w x y z *a b c d e* *f g h i j k*	Factor§
				Series VIII. CORNUTAE	
				Subseries xx. Sessiles	
96.	*E. cornuta*	(1)	Z	– – – – 2 – 5 2 2 4 3 1 – 1 1 1 – 1 – – – – – – – – 1 1 2 2 1 – – –	
		(1)	Z	– – – 2 5 – 5 2 4 5 3 2 – 1 1 2 – – – – – – – – – 2 1 3 2 1 – – –	
96a.	*E. burdettiana*	(1)	Z	T – – 5 5* – 2 – – 5 2 – – T T T – – – – – – – – – – – – 1 – 1 2 – –	
96b.	*E. megacornuta*	(1)	Z	– T – 4 5* – 4 – 5 5 3 – – 3 1 – – – – – – – – – – – 4 – 3 – 2 1 – –	
97.	*E. lehmannii*	(2)	Z	– – – 1 4* – 5 – – 5 3 1 – – – 3 – – – – 2 – – – – T – 3 2 2 2 1 –	
98.	*E. gomphocephala*	(3)	Me, Z	– – – 1* 3* – 5 3 1 5 3 – – – – – – – – – – – – – – 2 T 3 1 1 – – –	Gomphocephala: 2
99.	*E. platypus*	(1)	Z	– – – 1 3* – 5 5 4 5 3 – – – – 2 – – – – – – – – – 1 – 5 3 2 1 3 –	Platypus: 2
101.	*E. nutans*	(1)	Z	– – – 1 5 – 5 5 4 5 2 – – – – 2 – – – – 1 – – – – – – 3 3 3 – 2 –	Gomphocephala: 2
102.	*E. annulata*	(2)	Me	– – – 4 2 – 4 T – 5 3 – – – – 5 – – – – T – – – – – – 1 2 1 – 2 –	Annulata: 4
				Subseries xxi. Pedicallatae	
103.	*E. spathulata*	(1)	Mc	– – – 5 5 – 5 4 4 5 1 – – – – 3 – T – – T – – – – – – 3 2 3 – 1 –	
105.	*E. eremophila*	(1)	Z	– – – T* 3* – 5 – 5 5 2 – – T T 1 – T – – – – – – – – – 3 3 7 1 1 T	
		(1)	Mc	– – – T* 3* – 5 – 5 5 3 – – – – 1 – – – – – – – – – – – – – – 2 – –	
107.	*E. stowardii*	(1)	Z	– – – 2 5* – 3 – 1 5 2 – – 2 1 1 – – – – – – – – – 2 3 1 3 T 2 –	
108.	*E. macrandra*	(1)	Lb	– – – – 5 2 4 – T 5 2 – – – – 2 – – – – – 5 – 3 1 3 T – 1 1 – –	Platypus: 2
110.	*E. occidentalis*	(1)	Md	– – – 4 4* – 5 5 5 5 1 – – – – 2 – – – – 1 – – – – – – 4 3 4 – 2 –	Annulata: 2
112.	*E. astringens*	(4)	Mc, Z	– T – 1* 5* T 4 – – 5 3 – – – – 1 – T – 2 2 – – – – 1 – 1 – T 2 T –	
113.	*E. sargentii*	(1)	Me	– – – – 3* – 5 4 5 5 3 – – 1 3 2 – – – – – – – – – – 3 – 3 1 2 –	

Series IX. SUBCORNUTAE

114.	*E. xanthonema*			Not examined	
115.	*E. redunca*	(1)	Me	– T – – 5 – 2 – – 3 1 – – – – 2 – – – – – – – – T – – – – – –	1 specific cpd.: 2
119.	*E. gardneri*	(1)	Nc	– T – – 5 – 1 – – 2 2 – – – – – – – – – – – – – – – – 1 – – –	
120.	*E. wandoo*	(6)	Mc, Md, Nc	– – – – 4 – 5 1 3 5 2 – – 2 2 T – – – – – – – – – 2 2 3 – – – – –	
		(3)	Md	– – – – 3 2 5 2 – 5 4 – – 1 1 2 – – – – – – – – – 3 3 2 – – – – –	
		(1)	Mc	– – 2 – 3* – 5 5 3 5 2 2 1 – – – – – – – 1 – 2 – 1 2 2 – – – – – –	

† Numbers (5–1) represent relative amounts; T = trace; – = not present.

‡ a = Blakely's Number
b = Species
c = Number of samples examined
d = Origin (see map, Hillis[7])
e = Leucodelphinidins
f = Leucocyanidins
g = "Leucopelargonidins"
h = Myricetin
i = Quercetin
j = Kaempferol
k = Ellagic acid
l = Unknown compd. A
m = Unknown compd. B
n = Gallic acid
o = Gentisic acid
p = Caffeic acid
q = *p*-Coumaric acid
r = Sinapic acid
s = Ferulic acid
t = Macrantherin
u = Renantherin
v = Unknown compd. C
w = Unknown compd. D
x = Taxifolin
y = Aromadendrin
z = Unknown compd. E
a = Astringin
b = Rhapontin
c = Piceid
d = Chlorogenic acid
e = *p*-Coumarylquinic acid
f = Unknown compd. F
g = Unknown compd. G
h = Unknown compd. H
i = Unknown compd. I
j = Unknown compd. J
k = Unknown compd. K

§ Distinctive components of very limited distribution.

Leucoanthocyanins have been detected in trace amounts in a very few species and kaempferol is present in small amounts in only two species. The only other constant features in the series are the maximum relative amounts of gallic acid, and the presence of unknown compounds F and H. The unidentified compound macrantherin[5] was present in almost all the species examined.

After acid hydrolysis, the myricetin and quercetin obtained from several species appeared on the chromatograms as dull brown-orange or brown-yellow fluorescences under u.v. light instead of the normally bright orange or yellow colours; in this paper they are described as "discoloured flavonols". It has been pointed out previously,[2] that this effect is probably due to other materials having the same or very similar R_f values as these flavonols. In the case of quercetin the material may be the unknown compound I, which in most of the relevant species is partly resolved by the Forestal and butanol:acetic acid:water solvents.

The polyphenols in the leaves of *E. cornuta* (96), *E. lehmannii* (97) and *E. gomphocephala* (98) are not markedly different from the species in the rest of the series, in contrast to Hathway's[4] findings with the heartwood extractives.

The presence of the Platypus Factor in *E. platypus* (99) and in *E. macrandra* (108), the Annulata Factor in *E. annulata* (102) and *E. occidentalis* (110) and the Gomphocephala Factor in *E. gomphocephala* (98) and *E. nutans* (101) indicate a close relationship between the different pairs of species. A close morphological relationship between *E. platypus* and *E. macrandra* has been recognized.[6] Only the latter species contains large amounts of rutin, but as stilbenes are also present this occurrence may be a feature of the variant form.

Blakely's Series IX. Subcornutae

The members of this series, like the previous one, are found in southern Western Australia, and have white deciduous barks and pale-brown, hard and very durable timbers. Their sizes range from small mallees of about 8 ft height (115, Table 1) to small trees of 100 ft height (120). *E. wandoo* (120) and *E. accedens* (125) are the source of the commercial tanning extract "Myrtan".

E. redunca (115) and *E. gardneri* (119) have the very similar composition recorded in Table 1 and in addition contain large amounts of rutin. They are distinctly different from *E. wandoo* in that the amounts of ellagic and gallic acids are considerably lower than that of quercetin and also these species lack chlorogenic and *p*-coumarylquinic acids, and unknown compound G. One of the samples of *E. wandoo* (examined after the previous report[7]) contains small amounts of astringin and piceid and an abnormally coloured quercetin. It is notable that compounds G–J are absent in this series.

Blakely's Series XLIII. Subulatae

As in the above series, the size of the species in the Subulatae ranges from mallees of about 20 ft (*E. gillii*, 582, Table 2) to small trees of 100 ft height (*E. oleosa* var. *longicornis*, 577, formerly *E. longicornis*). The bark is smooth and deciduous (575, 584, 584a), or rough and dark-coloured (576, 578), the timbers are red-brown, very hard and durable. They are found in arid and semi-arid areas of different parts of Australia, namely the southern part of Western Australia (569, 570a, 577, 584a, 585), from Western Australia to South Australia (578, 584), along the border of South Australia and New South Wales ("N.S.W.", 582), in

[5] W. E. HILLIS, *Phytochem.* **5**, 1075 (1966).
[6] L. D. PRYOR, Personal communication.
[7] W. E. HILLIS, *Phytochem.* **5**, 541 (1966).

eastern N.S.W. (576), inland N.S.W. and Queensland (572, 574), the northern part of Northern Territory (575), and in several of the inland parts of Australia (581).

Leucoanthocyanins are absent in significant amounts in all the species examined except those growing in N.S.W. namely *E. bakeri* (572) and *E. squamosa* (576). Kaempferol is present in small amounts in *E. flocktoniae* (584) and absent or in trace amounts in other species; similarly myricetin is present in small amounts in 584 and in one of the chemical variants of *E. oleosa* (578). Quercetin is a major component in only some of the species. The ratio is low in *E. oleosa* var. *longicornis* (577) and some of the chemical variants of *E. oleosa* (578) but particularly low in *E. brockwayi* (584a). Ellagic acid is a major component except in the N.S.W. species (572 and 576) and the Northern Territory species (575). The amount of gallic acid is variable usually with a medium score but particularly low in *E. squamosa* (576). Either chlorogenic or *p*-coumarylquinic acids or both are present and unknown compound G is absent. Macrantherin and compounds H and J are usually present and stilbenes are present in four species.

Most of the Subulatae yield discoloured flavonols and in five species (572, 577, 578, 582, 584) compound I was also resolved. The notable feature is the presence of these characters in *E. bakeri* (572) which is found in the inland semi-arid regions of N.S.W. and Queensland whereas all other similar species are found in the south-western portion of Australia. Other relevant features are the large amounts of rutin (quercetin-3-rhamnoglucoside) in *E. umbra-warrensis* (575) and *E. squamosa* (576), large amounts of epicatechin in the latter also, and engelitin (dihydrokaempferol-3-rhamnoside) in *E. gillii* (582), *E. flocktoniae* (584) and chemical variants of *E. oleosa* (578).

Blakely's Series XLIV. Leptopodae

These are low divaricate mallees with a height of 25 ft or less (species 586, 587, 588, 591, 591a, 592, Table 2) or small trees of 50–80 ft height (589, 590, 593, 594), with smooth, pink or white barks and brown or reddish timbers. They are confined to areas of low rainfall in the southern portion of Western Australia.

Leucoanthocyanins are present in most of the species in significant amounts and leucocyanidin is usually the main representative. Myricetin may be taxonomically significant in *E. leptopoda* (592) and the normal variety of *E. salmonophloia* (593). Quercetin and ellagic acid are major components except in the case of *E. leptopoda* (592), in which the latter compound is weakly present. Gallic acid has a consistently low score in this series. As in the previous series, macrantherin, chlorogenic and *p*-coumarylquinic acids, compounds H and J are almost always present whereas compound G is always absent.

Abnormally coloured flavonols are present in most species as well as compound I in some of them. There is no apparent reason for the lack of these characters in *E. crucis* (587). Rutin was strongly present in *E. lane-poolei* (589), *E. drummondii* (590), *E. leptopoda* (592) whereas this compound was replaced by large amounts of engelitin in the normal variety of *E. salmonophloia* (593).

Blakely's Series XLV. Contortae; XLVI. Quadricostatae

These two series contain only one species each and both species are found in the semi-arid regions of the southern portion of Western Australia. The well-known *E. salubris* (594, Table 2) "Gimlet" is a slender tree 40–80 ft high, with the trunk twisted like a gigantic corkscrew, whereas *E. forrestiana* (596) is a small mallee of about 15 ft height.

TABLE 2. POLYPHENOLS IN THE LEAVES OF THE SUBULATAE (XLIII), LEPTOPODAE (XLIV), CONTORTAE (XLV) AND QUADRICOSTATAE (XLVI) SERIES OF THE SECTION PLATYANTHERAE†

‡a	b	c	d	e f g h i j k l m n o p q r s t u v w x y z *a b c d e* *f g h i j k*	Factor§
				Series. XLIII. SUBULATAE	
569.	*E. jutsonii*			Not examined	
570a.	*E. formanii*			Not examined	
572.	*E. bakeri*	(1)	Lq	3 T – T* 5* T 3 – – 5 2 – – – – T – – – – – – – – 1 3 2 – – 2 2 –	Cullenii: 2 Specific cpd.: 2
574.	*E. pachycalyx*			Not examined	
575.	*E. umbrawarrensis*	(1)	Fi	– – 2 – 5 T 3 1 – 2 1 1 – – – – – – – – – – – 9 T 3 – 2 – – – – –	
576.	*E. squamosa*	(3)	Op, Nq, Z	– 2 1 – 5 T 1 – – 1 2 – – – – 3 – – – – – – – – – 1 1 – – 3 – 2 –	
577.	*E. oleosa* var. *longicornis*	(3)	Nc	– – – T 3* – 5 2 – 5 3 – – 1 1 2 – – – – – T 3 – – 1 4 2 – 2 3 3 –	
		(2)	Nc	– – – T 2* – 5 – – 5 2 1 2 1 1 T – – – – – – – – – 1 3 2 – – 1 1 –	
578.	*E. oleosa*	(4)	Nm, Ok	– T – – 2* – 5 1 2 2 2 1 – 1 – T – – – – – – – – – 3 1 4 – 3 2 T 1	
		(2)	On	– – – 2 4* – 5 – 3 3 2 – – – – 2 – – – 2 – – – – 1 3 3 – 3 – 1 –	
		(1)	Ok	– – – – 5* – 5 – – 2 2 – – – – 1 – T – – – – 2 1 T – 1 1 – 3 – 1 –	
581.	*E. oleosa* var. *glauca*	(2)	Jj, Nm	– T – – 4* – 5 – 1 3 1 – – 1 – 2 – T – – – – – – – 3 1 – – 2 – T –	
582.	*E. gillii*	(1)	Nl	– T – – 5* – 5 2 4 3 2 – – – – 3 – – – – 2 – – – – 1 3 2 – 3 T 1 –	
584.	*E. flocktoniae*	(2)	Me	– T – 2* 5* 1 4 1 2 3 1 – – – – 3 – – – 2 4 – – – – 1 4 3 – 1 1 – –	
584a.	*E. brockwayi*	(1)	Me	– – – – 1 – 5 – – 2 2 – – – – – – – – – – – – 8 – T T 3 1 – 1 – – –	
585.	*E. cooperana*			Not examined	
				Series XLIV. LEPTOPODAE	
586.	*E. orbifolia*	(2)	Z	1 T – – 3* – 5 2 2 2 3 – – – – – – – – – – – – – 2 2 1 – 1 – – –	
587.	*E. crucis*	(2)	Me, Z	– T – T 5 – 5 – 1 2 3 – – – – 1 – – – – – – – – – 2 2 – – 3 – 2 –	

588.	*E. websterana*	(1)	Z	3 3 – – 5 – 4 – – 1 2 – – – – 4 – – – – – – – – – – 3 – – 2 T 4 –
589.	*E. lane-poolei*	(1)	Me	1 2 – – 5* – 4 – 1 2 2 – – – – 2 – – – – – – – – – T T 1 – 3 T 1 –
590.	*E. drummondii*	(4)	Kd, Me	T 2 T T 5* – 4 – – 2 3 2 1 – 1 2 – – – – – – – – – 2 2 – – 3 1 3 –
591.	*E. ewartiana*			Not examined
591a.	*E. oxymitra*			Not examined
592.	*E. leptopoda*	(1)	Md	T 1 – 2* 5 T 2 – – 1 2 1 – – – 3 – – – – 1 – – – – T 1 – – 3 – 1 –
593.	*E. salmonophloia*	(3)	Nd	– – – – 4* – 5 – – 2 2 1 1 T T 1 – 1 – – – – 5 4 1 1 2 1 – 1 1 1 –
		(3)	Nd	– – – – 4* – 5 – – 2 2 1 1 T T 1 – 1 – – – – 2 5 – 1 2 1 – 1 1 1 –
		(2)	Nd	– – – – 4* – 5 – – 2 2 1 1 T T 1 – 1 – – – – 5 – 3 1 2 1 – 1 1 1 –
		(1)	Nd	– – – – 4* – 5 – – 2 2 1 1 T T 1 – 1 – – – – 1 5 3 1 2 1 – 1 1 1 –
		(1)	Nd	– – – 2 4* 4 5 – – 5 1 – – – – – – 1 – 2 7 – – – – 1 2 – – – 1 – –
				Series XLV. CONTORTAE
594.	*E. salubris*	(3)	Nd	– – – 2 4* 3 5 – 2 3 2 T T 1 1 – – 2 – 2 7 – – – – T 2 – – – 1 – –
				Series XLVI. QUADRICOSTATAE
596.	*E. forrestiana*	(2)	Z	– 1 – 2* 5* 1 3 – – 3 2 – – – – 2 – 2 – – 3 – – – – – – 2 – 3 1 1 –

†, ‡, § See footnotes, Table 1.

The very similar polyphenolic composition of *E. salubris* (594) and the normal variety of *E. salmonophloia* (593) can be seen (Table 2). Both species contain large amounts of engelitin and after hydrolysis the leaves of both species yield very large amounts of dihydrokaempferol and smaller amounts of dihydroquercetin. *E. forrestiana* has a similar composition but does not contain large amounts of engelitin.

Blakely's Series XLVII. Xylocardae

The representatives of this series are mallees of 20 ft height or less, usually with slender crooked stems and smooth deciduous bark. The species are found in semi-arid regions of Western Australia (species 597, 599, 600, 604, 605, Table 3), South Australia (600) and north Australia (602, 603).

Leucocyanidin is the major leucoanthocyanin in most of the species just as it is in the series Leptopodae (Table 2). Quercetin is the major or the only flavonol in all species and in some the major component (599, 600, 602, 603, 605). This series differs distinctly from others in this section in that quercetin has the usual bright yellow fluorescence and compound I was not observed.

Another feature of this series is the almost consistently low amounts of ellagic and gallic acids, particularly in *E. sessilis* (603). In common with the rest of the section, chlorogenic and *p*-coumarylquinic acids and compound J are present in all and macrantherin in most species. Rutin is present in large amounts in *E. pachyphylla* (602), *E. sessilis* (603) and *E. kingsmillii* (605) and one of the samples of *E. oldfieldii* (597). The composition of *E. pachyphylla* resembles those of the Macrorhyncha (331, 333, 334)[8] in several aspects although the two groups are morphologically dissimilar.

The Relationship of Polyphenols with Classification

The distinctive features of the polyphenols in the leaves of Pryor's Bisectae are the presence of a large number of species yielding discoloured flavonols on chromatographic examination or compound I or both, and the presence of large amounts of rutin or engelitin or significant amounts of leucocyanidins or myricetin in a number of species. On the basis of these features, the Bisectae may be divided firstly into two groups of species one yielding discoloured flavonols and/or compound I and the other which does not. Although there are a few exceptions these two groups can be further subdivided as shown in Table 4. The closeness of the numbers in the above groups shows that the groups based on polyphenolic characters are similar in many cases to those based on morphological features.

Of the forty-three species examined in this present paper twenty-four species yielded discoloured flavonols or compound I or both and they represent most of the species in the Cornutae, Subulatae, Leptopodae, Contortae and Quadricostatae series. The ten species of the Subcornutae and the Xylocardae series that were examined lack these features and both series have a very similar polyphenolic composition. On the basis of the absence of the above characters, the low amounts of ellagic and gallic acids and presence of leucocyanidin, *E. squamosa* (576) could be included in the latter series and perhaps also *E. umbrawarrensis* (575) and *E. crucis* (587). Although only tentative conclusions regarding the distribution of the discoloured flavonols and compound I can be drawn from a general survey it is evident that further examination of a greater number of samples of these species and further work to

[8] W. E. HILLIS, *Phytochem.* **6**, 259 (1967).

TABLE 3. POLYPHENOLS IN THE LEAVES OF THE XYLOCARDAE SERIES OF THE SECTION PLATYANTHERAE†

‡a	b	c	d	e f g h i j k l m n o p q r s t u v w x y z *a b c d e f g h i j k*	Factor§
597.	*E. oldfieldii*	(1)	Lb	T T – 1 5 – 5 T 5 3 3 3 1 2 – T – – – – – – – – – 4 4 3 – T – T –	
		(1)	Lb	– – – – 2 – 5 – 5 3 2 3 – – – – – – – – – – – – – – – T – 3 – – – – –	
597b.	*E. carnabyi*			Not examined	
598.	*E. rameliana*			Not examined	
599.	*E. macrocarpa*	(3)	Mc, Z	T 3 – – 5 – 2 – – 2 2 1 1 – – 1 – 1 – – – – – – – – 1 – T – – – 1 –	
				Subseries lxxvi. Ptychocarpae	
600.	*E. pyriformis*	(1)	Z	– 2 – – 5 – 2 – – 1 2 – – – T T – – – – – – – – – T 3 – – T – T –	
602.	*E. pachyphylla*	(2)	Jj	– 2 – – 5 – 2 – – 2 2 – – – – – – – – – – – – – – 1 3 – – – – 1 –	
603.	*E. sessilis*	(1)	Z	– 2 – – 5 – T – – T 1 – – – – 1 – – – – – – – – – – 3 – – 2 – 1 –	
604.	*E. burracoppinensis*	(1)	Md	– – – – 3 – 5 – 2 4 2 T T – – 2 – 2 – – 1 – – – – 1 1 1 – 1 – 1 –	
605.	*E. kingsmillii*	(1)	Kd	– 1 – – 5 – 2 – – 2 2 – – – – 3 – – – – – – – – – 1 3 – – – – 1 –	

†, ‡, § See footnotes, Table 1.

TABLE 4. A POSSIBLE REGROUPING OF PRYOR'S BISECTAE

Other polyphenols	Discoloured flavonols and/or compound I: Present	Other polyphenols	Discoloured flavonols and/or compound I: Absent
MYRICETIN present	*E. burdettiana* (96a) *E. megacornuta* (96b) *E. lehmannii* (97) *E. gomphocephala* (98) *E. platypus* (99) *E. eremophila* (105) *E. stowardii* (107) *E. occidentalis* (110)	RUTIN as major component	*E. umbrawarrensis* (575)
		RUTIN and LEUCOCYANIDIN present	*E. reduncа* (115) *E. gardneri* (119) *E. squamosa* (576) *E. leptopoda* (592) *E. oldfieldii* (597) *E. pachyphylla* (602) *E. sessilis* (603) *E. kingsmillii* (605)
MYRICETIN+ ENGELITIN present	*E. astringens* (112) *E. flocktoniae* (584) *E. salmonophloia* (593) *E. salubris* (594) *E. forrestiana* (596)		
MYRICETIN absent	*E. sargentii* (113) *E. bakeri* (572) *E. oleosa* (578) *E. oleosa* var. *longicornis* (577) *E. oleosa* var. *glauca* (581)	LEUCOCYANIDIN present	*E. crucis* (587) *E. macrocarpa* (599) *E. pyriformis* (600)
		RUTIN and LEUCOCYANIDIN absent	*E. wandoo* (120) *E. brockwayi* (584a) *E. burracoppinensis* (604)
MYRICETIN absent LEUCOCYANIDIN present	*E. gillii* (582) *E. orbifolia* (586) *E. websterana* (588) *E. lane-poolei* (589) *E. drummondii* (590)		

improve the chromatographic separation and to identify the compounds should yield information of value in taxonomic and other studies. The species which have been previously reported to contain these characters are *E. foecunda* (442), *E. lansdowneana* (449), *E. porosa* (451), *E. froggattii* (454) and *E. viridis* (465)[2] and chemical variants of *E. apodophylla* (286a),[9] *E. patellaris* (490)[2] and *E. intertexta* (291).[9] These species, like most of the members of the Bisectae, are found in the southern portion of Western Australia, western N.S.W. and Northern Territory. The results from this present survey indicate that they could be included in the Bisectae. However it should be noted that Pryor[1] considers *E. intertexta* should be included in the combined Porantheroideae and Terminales sections[2] ("Adnata") although the anther is not distinctly adnate to the filament. It will be shown in the next paper that several species in the Dumosae and other series also yield discoloured flavonols and compound I.

Whereas the Cornutae and Subcornutae lack significant amounts of leucoanthocyanins, several species in the Platyantherae contain leucocyanidins as the only or major leucoanthocyanins. In this regard they differ from the "Adnata" group of the eastern states, in which more than half the species contain leucodelphinidins as the major representative of this class of compound.

[9] W. E. HILLIS, *Phytochem.* **6**, 275 (1967).

Most of the species in the Cornutae contain myricetin and the presence of this compound possibly has taxonomic significance in this series. Myricetin was consistently absent in the other species examined except in *E. flocktoniae* (584), *E. leptopoda* (592) the normal form of *E. salmonophloia* (593), *E. salubris* (594) and *E. forrestiana* (596). Kaempferol was also present in these species.

Usually, a number of flavonol glycosides are present in the alcohol extracts of the leaves but none is particularly distinctive. However, several of the species examined in this present study contained very large amounts of one of the glycosides, rutin or engelitin. It has been previously noted that some of the species in the Pachyphloiae series of the Renantherae[8,10] contain appreciable amounts of rutin. In addition to the twelve species mentioned in this present paper the other species found in the survey to contain large amounts of rutin are *E. desmondensis* (126) and *E. goniantha* (158) of the series Dumosae and *E. odontocarpa* (6) of the series Eudesmiae, both of which belong to the section Macrantherae. This distribution of rutin indicates the possibility of inter-specific groupings in the renantherous and non-renantherous sections. However, chemical varieties of *E. sideroxylon*,[11] *E. odorata* var. *angustifolia* (456), *E. camaldulensis* (197), *E. woollsiana* (482) and *E. andrewsii* (422) have been found to contain rutin but the amounts are much smaller. Very few (108, 589 and 590) of the species containing rutin give discoloured flavonols or unknown compound I.

Engelitin is a major component in *E. astringens* (112), a chemical variety of *E. oleosa* (578), *E. gillii* (582), *E. flocktoniae* (584), *E. salmonophloia* (593), *E. salubris* (594) and *E. forrestiana* (596). In addition these species also yield discoloured flavonols or compound I or both. The possible taxonomic significance of engelitin will be discussed in the next part of this series.

E. squamosa (576) and *E. bakeri* (572) differ from the rest of the species in the Bisectae in that they are found in the eastern coastal regions of Australia. *E. squamosa* differs from the rest of the series Subulatae (Table 2) as it contains an appreciable amount of leucocyanidin and the amounts of ellagic and gallic acids are very low. These characters show a greater affinity with the Xylocardae, (Table 3) but there is no group of species in the Adnata[2] which possesses a similar composition. *E. bakeri* (572) has been found in several localities in central Queensland and N.S.W. in addition to the small area in the eastern coastal region. The formation of discoloured flavonols and compound I after hydrolysis support the view that it should be included with all the other species which possess these characteristics and are found in the semi-arid regions of central and Western Australia. *E. bakeri* (572) does have some affinity with the Adnata of the eastern states in that the ratio of leucodelphinidins is high and it contains the Culleni Factor in common with *E. cullenii* (512) found in that group.[2]

In common with the Adnata, the Bisectae frequently contain macrantherin, *p*-coumaryl-quinic and chlorogenic acids and compounds F, H and J. Stilbenes have been detected in seven species of the latter group but in only two of the Adnata. Whereas the Adnata has few characteristic polyphenolic features the Bisectae has a number, as mentioned above, and in most cases these features support the groupings drawn up by Pryor or made on the grounds of geographical distribution.

EXPERIMENTAL

The methods used have been described in previous parts of this series. The properties of the uncommon eucalypt polyphenols are given in Table 5.

[10] F. R. HUMPHREYS, *Econ. Botany* **18**, 195 (1964).
[11] W. E. HILLIS and K. ISOI, *Phytochem.* **4**, 541 (1965).

TABLE 5. CHROMATOGRAPHIC PROPERTIES OF SECONDARY EUCALYPT POLYPHENOLS DETECTED IN THE CORNUTAE, SUBCORNUTAE AND PLATYANTHERAE

Polyphenol	$\frac{R_f \times 100^*}{\text{Solvent}}$	Appearance*
Factors	BA/HA	
Gomphocephala	40/25	Orange fl., yellow with pNA
Cullenii	88/04	Yellow fl., strong yellow with pNA
Platypus	80/66	Strong orange with pNA
Annulata	60/24	Mauve-opaque, tan with pNA
Specific compounds		
115. *E. reduncat*	41/77	Yellow with pNA
572. *E. bakeri*	75/75	Orange with pNA

* R_f values ($\times 100$) were taken from chromatograms of mixed components and may be slightly different from those of pure compounds. BA/HA = two-dimensional chromatograms with butanol:acetic acid: water (6:1:2) then 6% acetic acid.
Appearance: fl. = fluorescence in u.v. light (366 mμ), pNA = diazotized *p*-nitroaniline and the colours formed were observed in daylight.

† Properties before acid hydrolysis: other data obtained after hydrolysis.

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