

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

THE SERIES TRANSVERSAE, EXSERTAE, SUBEXSERTAE,  
MICROCARPAE, SEMIUNICOLORES, VIMINALES,  
ARGYROPHYLLAE AND PANICULATAE OF THE  
SECTION MACRANTHERAE

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**Abstract**—The differences in the composition of the polyphenols in the species of the series of eucalypts examined are much less pronounced than those of the Renantherae. The composition of the Paniculatae is more heterogeneous than the other series. The accepted classification on morphological grounds into series or to groups within these series is supported in many cases by the presence or absence of leucoanthocyanins, myricetin and kaempferol.

### INTRODUCTION

BLAKELY<sup>1</sup> divided the Section Macrantherae of the eucalypts into twenty-two series. The composition of the leaves of the series Globulares has been described previously,<sup>2</sup> and this paper describes the species in a number of other series in this section. The series chosen have been arbitrarily grouped together and separated from the other macrantherous series although there are morphological and chemical features to support this grouping. More than 85 per cent of the known species in these series have been examined.

The compounds that have been detected when the leaves were heated with 2 N hydrochloric acid included delphinidin (3:5:7:3':4':5'-hexahydroxyflavylium chloride) from the polymerized leucodelphinidins, and cyanidin (3:5:7:3':4'-pentahydroxyflavylium chloride) from the polymerized leucocyanidins. Another red compound had properties very similar to those of pelargonidin (3:5:7:4'-tetrahydroxyflavylium chloride). Also detected were myricetin (5:7:3':4':5'-pentahydroxyflavon-3-ol), quercetin (5:7:3':4'-tetrahydroxyflavon-3-ol), kaempferol (5:7:4'-trihydroxyflavon-3-ol) and the following acids: ellagic, gallic (3:4:5-trihydroxybenzoic), gentisic (2:5-dihydroxybenzoic), caffeic (3:4-dihydroxycinnamic), *p*-coumaric (4-hydroxycinnamic), sinapic (3:5-dimethoxy-4-hydroxycinnamic) and ferulic (3-methoxy-4-hydroxycinnamic). The constitutions of macrantherin and renantherin which become distinctively yellow when sprayed with diazotized *p*-nitroaniline are at present under investigation. Taxifolin (dihydroquercetin) and aromadendrin (dihydrokaempferol) have also been detected. In the alcohol extracts the following compounds have been observed: astringin (probably 3:5:3':4'-tetrahydroxystilbene glucoside), rhapontin (3:5:3'-trihydroxy-4'-methoxystilbene-3-glucoside), piceid (3:5:4'-trihydroxystilbene-3-glucoside), chlorogenic acid (caffeoylquinic acid) and *p*-coumarylquinic acid (cf. Hillis<sup>2</sup>).

<sup>1</sup> W. F. BLAKELY, *A Key to the Eucalypts*, 2nd edit. Forestry and Timber Bureau, Canberra (1955).

<sup>2</sup> W. E. HILLIS, *Phytochem.* **5**, 1075 (1966).

## RESULTS AND DISCUSSION

*Blakely's Series VI. Transversae*

Members of this series are nearly all large trees (up to 250 ft high) and with one exception (No. 74, a shrubby tree of less than 20 ft high and with a brown wood) have red timbers of commercial importance. Two (No. 56, 57) belong to Western Australia, one (No. 85) to South Australia, and the remainder to the coastal areas of New South Wales and Queensland.

Macrantherin was present in appreciable amounts in most of the samples examined (Table 1). The presence or absence of leucoanthocyanins indicate a possible division into No. 56–64 and 67–85. This possibility is further supported in the case of No. 57–67 which contain small amounts of myricetin although there is an overlap with species No. 67. Kaempferol is present in ten species but not in *E. jacksonii* (56), *E. notabilis* (72), *E. punctata* (78), *E. canaliculata* (80), *E. longifolia* (81) and *E. cosmophylla* (85). *E. canaliculata* (80) is much less widespread than *E. punctata* (78), but they have been found in the same geographical areas. In addition to the absence of both kaempferol and myricetin they have also a very close composition in regard to the low amount of quercetin and other respects (Table 1). This is in accord with their morphology.<sup>3</sup> *E. longifolia* (81) and *E. cosmophylla* (85) resemble each other in polyphenolic composition, although their areas of distribution are separated by a distance of 600 miles. The mainland forms of *E. cosmophylla* (85) were very similar to the Kangaroo Island forms except that one of the latter forms contained large amounts (score 5) of unknown compound H.

Apart from the presence of leucocyanidin, *E. resinifera* (69) and *E. pellita* (73) (and to a lesser extent, *E. notabilis* (72)) are very similar in composition and this supports their association in the subseries Annulares (Table 1; see also Ref. 4). *E. pumila* (74) and *E. propinqua* (75) also are very similar to each other in their polyphenolic composition.

Although *E. robusta* (67) lacks the leucoanthocyanins present in *E. botryoides* (64) and *E. saligna* (60) it is very similar in many other regards (Table 1). In addition these three species contain the Saligna Factor, a compound detected only with the Forestal solvent and previously recorded in a small number of species of the Renantherae.<sup>5</sup> Presumably the compound arose independently in the two sections.

The West Australian species *E. diversicolor* (57) differs from the other members of the Transversae in regard to the low amounts of ellagic and gallic acids and the absence of unknown compounds A and B. Although there are slight differences (the most important being the absence of chlorogenic and *p*-coumarylquinic acids) in the composition of *E. jacksonii* (56) from other members, they are not sufficiently significant to be used in support of the morphological evidence<sup>6, 7</sup> that this species is wrongly classified and that it is close to *E. patens* (299).<sup>5</sup>

Carr and Carr<sup>8</sup> have found a resemblance in the floral morphology of *E. microcorys* (314) with the Transversae. An overall resemblance in the leaf polyphenols of *E. major* (76) (Transversae) with this species<sup>5</sup> can be seen, although there are significant differences in some characters. They<sup>9</sup> also suggested an association of *E. guilfoylei* (305) with this

<sup>3</sup> L. D. PRYOR, personal communication.

<sup>4</sup> L. D. PRYOR, In *The Evolution of Living Organisms* (Edited by G. W. LEEPER), p. 446. Melbourne Univ. Press (1962).

<sup>5</sup> W. E. HILLIS, *Phytochem.* 6, 259 (1967).

<sup>6</sup> E. GAUBA and L. D. PRYOR, *Proc. Linnean Soc. N.S. Wales* 83, 20 (1958).

<sup>7</sup> C. A. GARDNER, *West. Aust. Dept. of Agric. Leaflet* 2064 (1952).

<sup>8</sup> D. J. CARR and S. G. M. CARR, *Australian J. Botany* 7, 109 (1959).

<sup>9</sup> D. J. CARR and S. G. M. CARR, *Nature* 184, 1549 (1959).

TABLE 1. POLYPHENOLS IN THE LEAVES OF THE TRANSVERSARAE SERIES (NO. VI) OF THE MACRANTHERAE SECTION OF THE GENUS *Eucalyptus*<sup>†</sup>

†a	b	c	d	e	f	g	h	i	j	k	Factor†
56.	<i>E. jacksonii</i>	(2) Nc		2 1 - - 5 - 5 3 4 3 2 - - -							
57.	<i>E. diversicolor</i>	(1) Z		3 2 - 1 5 1 4 - - 2 1 T - - T							
58.	<i>E. grandis</i>	(3) Z		2 1 - 1 5 3 5 3 - 3 1 1 - - 1							
60.	<i>E. saligna</i>	(1) Z		3 1 - 1 3 2 5 2 - 5 2 - - T T							
62.	<i>E. deanei</i>			Not examined							
64.	<i>E. botryoides</i>	(6) Oq, Np		3 1 - 1 5 1 5 T - 4 2 - - T -							
67.	<i>E. robusta</i>	(3) Np, Z		- - - 1 4 1 5 3 - 3 1 1 - - -							
69.	<i>E. resinifera</i>	(2) Kr, Z		- - - T 2 1 5 2 2 5 2 1 - - -							
72.	<i>E. notabilis</i>	(1) Np		- 1 - T 3 - 5 1 3 3 2 - - -							
73.	<i>E. pellita</i>	(2) Ip, Z		- 2 - - 3 2 5 2 3 4 1 1 - - -							
74.	<i>E. pumila</i>	(1) Z		- - - - 4 2 5 2 2 5 1 1 - - -							
75.	<i>E. propinqua</i>	(2) Lq, Z		- - - - 5 3 5 2 1 5 2 1 1 - 1							
76.	<i>E. major</i>	(2) Lq		- - - - 2 2 5 3 5 2 1 - 1 1 2							
77.	<i>E. shirensii</i>			Not examined							
78.	<i>E. punctata</i>	(2) Lq, Z		- - - - 2 - 5 3 5 3 1 2 2 - -							
80.	<i>E. canaliculata</i>	(1) Z		- T - - 2 - 5 4 2 5 3 - - 1 -							
81.	<i>E. longifolia</i>	(6) Op, Oq		- T - - 3 - 5 3 3 5 3 - - -							
85.	<i>E. cosmophylla</i>	(5) Ok, Nk, Z		- - - 1 5 - 5 2 4 5 2 1 2 - -							

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

† a = Blakely's number	j = Kaempferol	s = Ferulic acid	b = Rhaipontin
b = Species	k = Ellagic acid	t = Macrantherin	c = Piccid
c = Number of samples examined	l = Unknown compd. A	u = Renantherin	d = Chlorogenic acid
d = Origin (see map, Hillis <sup>16</sup> )	m = Unknown compd. B	v = Unknown compd. C	e = p-Coumaric/quinic acid
e = Leucodelphinidins	n = Gallic acid	w = Unknown compd. D	f = Unknown compd. F
f = Leucocyanidins	o = Gentisic acid	x = Taxifolin	g = Unknown compd. G
g = "Leucopelargonidins"	p = Caffeic acid	y = Aromadendrin	h = Unknown compd. H
h = Myricetin	q = p-Coumaric acid	z = Unknown compd. E	i = Unknown compd. I
i = Quercetin	r = Sinapic acid	a = Astringin	j = Unknown compd. J
			k = Unknown compd. K

† Distinctive components of very limited distribution.

TABLE 2. POLYPHENOLS IN THE LEAVES OF THE EXSERTAE SERIES (NO. XV) OF THE MACRANTHERAE SECTION OF THE GENUS *Eucalyptus*<sup>φ</sup>

†a	b	c	d	e	f	g	h	i	j	k	Factor‡
Subseries xxix. Phaeoxyla											
173. <i>E. exserta</i>	(1) Hj			T	4	2	5	1	5	2	1
175. <i>E. herbertiana</i>	(1) Fi			-	3	3	5	2	4	5	1
176. <i>E. morrisii</i>	(2) Jj, Z			-	1	3	5	5	4	5	2
Subseries xxx. Erythroxylo											
178. <i>E. tereticornis</i>	(3) Do			3	2	5	3	T	2	-	-
	(3) Do			-	2	2	2	5	5	2	1
	(2) Nq, Op			-	-	4	3	5	1	2	5
180. <i>E. glauca</i>	(1) Z			Not examined							
184. <i>E. amplifolia</i>	(3) La, Z			-	2	-	4	2	5	2	-
186. <i>E. blakelyi</i>	(1) Z			-	T	-	4	1	5	2	2
189. <i>E. dealbata</i>	(1) Z			-	-	-	5	1	2	5	2
190. <i>E. dwyeri</i>	(1) Z			-	-	-	2	-	5	1	3
191. <i>E. confuens</i>				Not examined							
Subseries xxxi. Liberivalvae											
192. <i>E. parramattensis</i>	(2) Np, Op			-	T	T	5	1	4	T	3
194. <i>E. seeana</i>	(1) Z			-	1	-	4	2	5	-	2
196. <i>E. bancroftii</i>	(1) Z			-	-	-	2	5	3	5	2
Subseries xxxii. Rostratae											
197. <i>E. camaldulensis</i>				See Hillis <sup>10</sup>							
204. <i>E. rudis</i>	(5) Md, Nc, Z			-	-	-	4	1	5	3	2
205. <i>E. melanoxylon</i>	(1) Z			-	T	-	3	-	5	1	2

φ, †, ‡ See footnote, Table 1.

series, but as our samples of this species were stilbenoid chemotaxa<sup>5</sup> a satisfactory comparison is not possible.

*Blakely's Series XV. Exserta*

This series contains small to large trees from about 20 ft (*E. herbertiana* (175)) to more than 150 ft height (*E. tereticornis* (178)) and most species have red and the rest brown wood. All are eastern Australian species except *E. herbertiana* (175) and *E. confluens* (191) found in the northern part and *E. rudis* (204) and *E. melanoxylon* (205) in the southern part of Western Australia. *E. tereticornis* (178) is found both in Papua and eastern Australia and *E. camaldulensis* (197) is found throughout Australia except Tasmania.

Macrantherin is present in all species (Table 2) and leucoanthocyanins and myricetin are absent in almost all samples. The absence of kaempferol or variations in the score of quercetin have no apparent taxonomic significance. Ellagic acid is almost invariably the major polyphenol and gallic acid has a similar score except in three species (192, 194, 205). Aromadendrin was found in a number of species in this series. The variation in composition of *E. camaldulensis* (197) has been previously reported<sup>10</sup> and although this may be associated with environmental factors the marked differences in *E. tereticornis* (178) can be attributed to the existence of chemotaxa.

*E. deglupta* (437) has been incorrectly classified in the Renantherae<sup>5</sup> and its composition shows several points of resemblance to the composition of members of the Exserta and Subexserta.

*Blakely's Series XVI. Subexserta*

Members of this series are small (No. 206) to medium-sized (No. 210) trees and the wood is usually pale coloured. The Argophloiae (206–209) are found in northern Australia, New Guinea and Timor and the Semidecorticatae (210–215a) are found in southern Australia and Tasmania.

The presence of "leucopelargonidin" in species 206–209 (Table 3) probably has taxonomic significance. All the species in the Argophloiae have a similar composition and it is noteworthy that the absence of chlorogenic and *p*-coumarylquinic acids in *E. alba* (207) and *E. platyphylla* (208) is consistent with the view that the latter is a subspecies of the former. *E. alba* (207) is unique in that samples have been collected from three separated land masses, namely Papua (near Port Moresby), Portuguese Timor and Northern Territory (near Edith River). All samples have a very similar composition.

The recently rediscovered Timor eucalypt (which formerly was called *E. decaisneana*) also has a composition very similar to that of *E. alba* (207). It is of incidental interest that trees of this species were probably the first eucalypts to be utilized by Europeans and seeds of this species were possibly taken to Brazil from Timor by Portuguese travellers early in the sixteenth century. It has been found only in Timor and excellent specimens of 165 ft height growing at 7000 ft altitude have been recorded.<sup>11</sup> The amount of quercetin in *E. brevifolia* (206) is higher than in the other species and the alcohol extract of these leaves contains appreciable amounts of rutin.

All species of the subseries Semidecorticatae (210–215a) contain leucoanthocyanins but apart from this there is no feature to characterize the subseries. The Tasmanian representatives of *E. aggregata* (215) have recently been recognized as the separate species *E. rodwayi*

<sup>10</sup> W. E. HILLIS, *Phytochem.* 5, 541 (1966).

<sup>11</sup> Annual Rep. Forestry Timber Bureau, Dept. Natl Development, p. 47 (1964).

TABLE 3. POLYPHENOLS IN THE LEAVES OF THE SUBSERIES (NO. XVI) OF THE MACRANTHERAE SECTION OF THE GENUS *Eucalyptus*<sup>φ</sup>

†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†					
Subseries xxxiii. Argophloiae																																										
206.	<i>E. brevifolia</i>	(1)	Hj	-	1	-	5	T	5	1	4	5	2	1	1	1	1	1	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
207.	<i>E. alba</i>	(5)	Do, Df, Fi	-	T	T	-	2	2	5	2	5	2	3	1	1	1	1	2	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
208.	<i>E. platyphylla</i>	(1)	Fi	-	1	-	2	4	5	1	-	3	2	-	-	-	-	T	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
209.	<i>E. bigalerita</i>	(1)	Fi	-	T	2	-	2	5	2	3	2	2	1	1	1	1	T	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
	" <i>E. decaisneana</i> "	(1)	Df	-	-	-	-	3	2	5	2	-	5	1	T	T	-	T	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
Subseries xxxiv. Semidecorticae																																										
210.	<i>E. ovata</i>	(4)	On, Pn, Z	1	1	-	4	5	-	2	-	T	3	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
		(1)	Ro	-	3	-	5	-	3	-	5	1	-	-	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
212.	<i>E. camphora</i>	(4)	Nq, Op	-	T	-	4	3	5	1	2	5	3	3	-	1	-	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
		(1)	Nq	4	2	-	T	5	4	-	5	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
215.	<i>E. aggregata</i>	(3)	Nq	4	1	-	3	5	3	3	-	5	4	-	-	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
215a.	<i>E. rodwayi</i>	(1)	Rp	-	T	-	5	-	4	-	5	2	T	T	-	-	-	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				

φ, †, ‡ See footnote, Table 1.

TABLE 4. POLYPHENOLS IN THE LEAVES OF THE MICROCARPAE SERIES (NO. XVII) OF THE MACRANTHERAE SECTION OF THE GENUS *Eucalyptus*<sup>φ</sup>

†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					
216.	<i>E. acaciaeformis</i>	(1)	Z	2	2	-	2	5	T	3	-	3	2	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
217.	<i>E. nicholii</i>	(1)	Z	-	-	-	3	-	5	2	4	5	1	1	-	-	-	-	4	-	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
218.	<i>E. parvifolia</i>			Not examined																																					
219.	<i>E. scoparia</i>	(2)	Z	1	T	-	3	5	2	5	-	1	4	2	-	-	-	-	2	-	1	-	-	-	1	1	-	-	-	-	-	-	-	-	-	-	-				
220.	<i>E. mannifera</i> ssp. <i>maculosa</i>	(3)	Z	-	1	-	2	4	-	5	-	5	2	2	-	1	-	-	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
220a.	<i>E. aromaphloia</i>	(1)	Pm	2	1	-	2	5	-	5	-	5	2	-	-	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
220b.	<i>E. corticosa</i>			Not examined																																					
222.	<i>E. mannifera</i> ssp. <i>praecox</i>			Not examined																																					

φ, † See footnote, Table 1.

(215a)<sup>12</sup> and the latter lacks the myricetin significantly present in the former species. It is interesting that the Tasmanian forms of *E. ovata* (210) and *E. sieberi* (371)<sup>5</sup> also lack the myricetin that is strongly present in the mainland forms.

*Blakely's Series XVII. Microcarpae*

Blakely<sup>1</sup> recognized that the species in this series represent an artificial grouping, but its members could not be merged into any of the other series. Two of the species examined (No. 220 and 220a, Table 4) have a very similar composition, but the heterogeneous nature of the assemblage of species in this series is indicated by the composition of the other three species when compared between themselves and 220 and 220a. There are insufficient characteristic chemical features to indicate regroupings of the species in this series.

The species represented are small to large trees with pale to deep red timbers and growing at high altitudes in the eastern States.

*Blakely's Series XIX. Semiunicolores, Series XX. Viminales, Series XXI. Argyrophyllae, and Series XXII. Paniculatae*

*E. kitsoniana* (264) and *E. neglecta* (265) are dwarf trees of about 30 ft height growing in two small areas in south-eastern Victoria. They have brown to reddish timbers and a very similar leaf composition except the latter species lacks kaempferol but contains a specific compound (Table 5). On the other hand, *E. johnstonii* (269) is a tree reaching a height of 200 ft, having a reddish timber and found in mountainous areas of southern Tasmania, and except for the absence of leucocyanidin has a very similar leaf composition to *E. kitsoniana*.

*E. viminalis* (277) is the most important species in the Viminales (Table 5) reaching a height of 150 ft, possessing a pink to pale yellow wood and found in a wide area from northern New South Wales to South Australia and Tasmania. The other species are smaller trees and found in small areas of this range but they show slight and significant differences in leaf composition from that of *E. viminalis*. Two stilbenoid chemotaxa have been found in this Series (270 and 274).

The Argyrophyllae are found in Victoria and New South Wales (283–285), or in northern Western Australia (286–286a). They are medium-sized trees with reddish timbers. The eastern representatives consistently contain appreciable amounts of myricetin which is absent in the north-western representative. The sample of *E. apodophylla* (286a) collected near Darwin contained a component which gave a characteristic yellow colour with diazotized *p*-nitroaniline but had different *R<sub>f</sub>* values from macrantherin and renantherin. This compound has not been detected yet in other eucalypts and it is intended to determine its relationship to macrantherin and renantherin which are characteristic of many of the species in the two main subdivisions of the genus. The other sample of *E. apodophylla* (286a) contains abnormally coloured “quercetin” and unknown compound *I* which are found in the Dumosae and certain other non-renantherous species (unpublished data).

The Paniculatae (288–295, Table 5) are tropical and subtropical species usually of medium height. The species 288–294 differ from those in the above series in that only *E. michaeliana* (293a) contains macrantherin and in trace amounts. Carr and Carr<sup>9</sup> have suggested on the basis of floral morphology that *E. gamophylla* (288) is misplaced but owing to the variable composition of the species in this series no conclusion from the chemical data can be drawn at this stage although the presence of appreciable amounts of rutin may prove to be significant.

<sup>12</sup> L. A. S. JOHNSON, *Contrib. N.S. Wales Nat. Herb.* 3, 103 (1962).

TABLE 5. POLYPHENOLS IN THE LEAVES OF THE SERIES SEMIUNICOLORES (NO. XIX), VIMINALES (NO. XX), ARGYROPHYLLAE (NO. XXI), PANICULATAE (NO. XXII) OF THE MACRANTHAE SECTION OF THE GENUS *Eucalyptus*<sup>a</sup>

†a	b	c	d	e	f	g	h	i	j	k	Factor†	
Series XIX. SEMIUNICOLORES												
264.	<i>E. kitsoniana</i>	(1) Po		- 2 - - 5 2 4 - - 5 2 3 - 1 -	1 - -	- - - -	- - - -	- - - -	1 - - - -	-		
265.	<i>E. neglecta</i>	(1) Po		- 2 - T 5 - 4 - 1 5 1 3 - - -	1 - -	T - -	T - -	T - -	1 1	T - -	-	
269.	<i>E. johnstonii</i>	(1) Ro		- - - - 5 2 5 - 2 5 2 3 T - -	3 - -	- - - -	- - - -	- - - -	- - - 3 3	3 - - - -	-	
Series XX. VIMINALES												
270.	<i>E. baeuerlenii</i>	(1) Z		- - - - 4 - 5 - - 2 2 - - - -	2 - -	- - - T	- - -	- - -	5 5 4 2 2	- - - - -	-	
272.	<i>E. quadrangulata</i>	(1) Lq		T - - - 5 3 5 1 1 4 2 - - - -	4 - -	- - -	- 2 -	- - -	- - -	3 3 - - -	-	
273.	<i>E. macarthurii</i>	(1) Oq		1 2 - - 5 - 3 - - 5 2 - - - -	2 - -	- - -	- - -	- - -	- - -	- - -	-	
274.	<i>E. smithii</i>	(6) Oq		3 2 - 2 2 - 5 - - 5 2 - - - -	1 - -	- - -	- - -	- - -	- - -	- - -	-	
		(1) Z		2 1 - - 5 - 5 2 2 5 2 - - - -	- - -	- - -	- - -	- - -	5 1 3 3 2	1 - - - -	-	
275.	<i>E. benthamii</i>			Not examined								
277.	<i>E. viminalis</i>	(8) Oo, Po, Ol, Pn, Z		- T - - 3 - 5 2 2 5 2 - - 1 -	1 - -	- - -	- - -	- - -	- - - 1 1	2 - - - -	-	
		(4) Pn, Ro		- T - - 5 1 5 3 1 5 2 2 - - -	2 - -	- - -	- - -	- - -	- - - 1 1	2 - - - -	-	
278.	<i>E. pryoriana</i>	(3) Pn		1 2 - 1 5 T 5 2 3 5 2 - - 1 1	- - -	- - -	- - -	- - -	- - - 1 1	1 - - - -	-	
Series XXI. ARGYROPHYLLAE												
283.	<i>E. cinerea</i>	(5) Z		T 1 - 1 5 - 3 T - 5 2 1 - - -	T - -	- - -	- - -	- - -	- - - 2 -	1 - - - -	-	
284.	<i>E. cephalocarpa</i>	(3) Pn, Po		1 1 - 1 4 - 4 1 2 5 2 - - - -	1 - -	- - -	- - -	- - -	- - - 2 2	1 - - - -	-	
285.	<i>E. nova-anglica</i>	(2) Ma, Z		- - - 2 5 1 4 2 1 4 2 1 - - -	T - -	- - -	- T T	- - -	- - - 1 -	2 2 3 - -	-	
286.	<i>E. houseana</i>			Not examined								
286a.	<i>E. apodophylla</i>	(1) Fi		2 1 - - 4 - 5 2 - 5 2 2 - 1 -	2 - 2	- - -	- - -	- - -	- - - 1 -	1 1 - - -	-	
		(1) Id		- - - T 4 - 5 3 5 5 2 1 2 2 1	- - -	- - -	- - -	- - -	- - - 2 3	4 2 3 1 -	-	
287.	<i>E. mooreana</i>			Not examined								
Series XXII. PANICULATAE												
Subseries xlv. Oliganthae												
288.	<i>E. gamophylla</i>	(1) Jj		- - - - 5 1 5 2 3 5 2 - - 1 -	- - -	- - -	- - -	- - -	- - - 2	3 5 T - -	-	
289.	<i>E. stirleyi</i>	(1) Ip		1 1 - 2 2 - 5 - T 5 2 - - - -	- - -	- - -	- - -	- - -	- - -	- - -	-	

Specific  
Cpd.: 5Specific  
Cpd.: 1



290. <i>E. argillacea</i>	(1) Fi	3 T - 5 3 - 3 T 2 5 3 - 1 - 1	- - -	- - -	- - -	1 3	T - 1 - -	Platyptus : 2	
291. <i>E. intertexta</i>	(1) Jj	3 2 - 1 3 - 5 - 2 5 5 - - -	- - -	- - -	- - -	- - -	1 - 1 T 1 -		
293a. <i>E. michaeliana</i>	(1) Kd	3 T - 2 4 - 5 - * - 5 2 - - -	- - -	- - -	- - -	- - -	1 - - 2 1 -	Tetraptera : 3	
294. <i>E. howittiana</i>	(1) Z	- - - - 3 2 5 2 2 5 2 1 - -	- - -	- - -	- - -	- - -	4 1 2 - -		
		Not examined							
		Subseries xlv. Megalanthae							
295. <i>E. clbeiziana</i>	(1) Z	5 T - 3 - - 5 3 - 5 2 - - -	- 2 -	- - -	- - -	- - -	3 1 - - -		

$\phi$ ,  $\dagger$ ,  $\ddagger$  See footnote, Table 1; \* = abnormally coloured flavonol.

The samples of *E. intertexta* (291) produced quercetin with a yellow brown fluorescence and both contained compound *I*; it will be shown subsequently that these are characteristics of certain members of the Dumosae and this species warrants further investigation. *E. argillacea* (290) differs from the other species as it has high myricetin and low ellagic acid ratios and in addition the Platypus Factor. Compound *I* is possibly present but the amount was too low to be recognized with certainty. *E. cloeziana* (295) contains appreciable amounts of a compound giving an orange-yellow colour with diazotized *p*-nitroaniline and traces of another giving a light yellow colour. The colour reactions and chromatographic properties indicate a relationship of this compound with macrantherin and renantherin. An investigation of this species together with the variety of *E. apodophylla* (286a) mentioned above may reveal a connexion with both the renantherous and non-renantherous species. A high ratio of myricetin and the absence of quercetin is a very unusual combination and in this regard *E. cloeziana* (295) resembles *E. todiana* (298).<sup>5</sup> With the associated high ratio of leucodelphinidin this species has a composition very similar to that of *E. phoenicea* (13, unpublished data). It seems likely that *E. cloeziana* (295) is a remnant of an evolutionary line which existed during the development of the present-day species.

#### *The Relationship of Polyphenols with Classification*

The differences in polyphenolic composition within and between the series reported in the present paper are much less pronounced than those of the Renantherae.<sup>5</sup> Most of the differences are of a small quantitative nature only and the species in the Transversae and the Exsertae show the close similarity in composition previously recorded for those species in the Globulares.<sup>2</sup>

With the exception of the series Paniculatae (Table 5) macrantherin is present in more than 80 per cent of the species. A similar percentage of the species in the series Globulares<sup>2</sup> contain this compound.

Leucoanthocyanins are absent in the majority of species of the Transversae (Table 1) and in most cases the presence or absence of these compounds is associated with the morphological affinity between species. Whereas almost all the Exsertae (Table 2) lack leucoanthocyanin most of the Subexsertae contain them. "Leucopelargonidin", which could have taxonomic significance in the Argophloiae (206–209, Table 3), has been detected in other sections of the genus also, and often when stilbenes are present, but in these other cases there is no apparent association with classification. With the exception of the series Paniculatae, about half of the species in the remaining series contain leucoanthocyanins. Three of the species (290, 291, 295) in the Paniculatae contain leucoanthocyanins in large amounts and there are other chemical data indicating that these species could be wrongly classified.

Myricetin is almost always absent from the Globulares<sup>2</sup> and the Exsertae and Subexsertae (Tables 2 and 3). Kaempferol is usually absent from the Globulares<sup>2</sup> and the Viminalae and the Argyrophyllae (Table 5). The presence of myricetin or kaempferol or both is associated with the morphological affinities of the species in the different series and particularly in the Transversae and the Argophloiae of the Subexsertae. A low ratio of quercetin could be associated with classification in the cases of species 69, 76, 78, 80 on the one hand and species 207, 208 and 209 on the other, although with the latter group the arid and semi-arid environment, may have an effect on the ratio.

With a few exceptions (No. 178, 210, 216, 273, 274, 283, 288, 290) ellagic acid was a major or the main component in the phenolic mixture. On the other hand the ratio of gallic acid was low to medium in several species found in most series.

The low ratio of gallic acid found in *E. melanoxyton* (205, Table 2) and *E. baeuerlenii* (270, Table 5) may be associated with the formation of stilbenes, but in other species (*E. diversicolor* (57, Table 1) and *E. seeana* (194, Table 2)) stilbenes are absent.

The series studied resemble the Globulares<sup>2</sup> in that the distribution of ferulic and sinapic acids is rather erratic whereas chlorogenic and *p*-coumarylquinic acids are almost always present. The presence of aromadendrin is possibly significant in the Exsertae and species No. 75, 76 and 78 of the Transversae but not in the other series. Compound *F* is almost universally present in these series, in Globulares and in the section Renantherae and is without taxonomic significance in these cases. On the other hand, compounds *G*, *H* and *J* and the specific compounds are very occasionally present and also have no significance.

### EXPERIMENTAL

The location of the trees from which the samples were taken has been recorded in Tables 1–5 and can be ascertained by reference to the map previously published.<sup>10</sup> Samples collected from botanic gardens or arboreta are designated by “Z”. The methods of examination have been previously reported<sup>2,10</sup> and the numbers (5–1) in the tables represent relative amounts with 5 being the highest amount, T=trace and —=not present. The term “Factor” is used for those characteristic compounds found in a very small number of species, and they are named after the species with the lowest Blakely number in which it was detected. The properties of the uncommon eucalypt polyphenols are given in Table 6.

TABLE 6. CHROMATOGRAPHIC PROPERTIES OF SECONDARY EUCALYPT POLYPHENOLS DETECTED IN SERIES NO. XI, XV, XVI, XVII AND XIX, XX, XXI AND XXII OF THE SECTION MACRANTHERAE

Polyphenol	$R_f \times 100^*$ Solvent			Appearance†
Factors‡	F	Be	BA/HA	
<i>Saligna</i>	97	—	— —	y. fl.
<i>Herbertiana</i>	—	—	35/05	opaque u.v. → s. y. fl.
<i>Setosa</i>	90	—	55/74	or. pNA
<i>Tetraptera</i>	—	—	45/28	or. y. fl.
<i>Platypus</i>	—	—	80/66	or. pNA
Specific compounds				
192. <i>E. parramattensis</i> §	—	—	72/72	or. pNA
265. <i>E. neglecta</i>	—	—	93/71	canary y. pNA
285. <i>E. nova-anglica</i>	—	88	91/78	bu. m. fl. (254 nm)
286a. <i>E. apodophylla</i>	—	12	69/67	canary y. pNA
295. <i>E. cloeziana</i> (a)	—	43	92/65	or. pNA
295. <i>E. cloeziana</i> (b)	—	—	94/75	canary y. pNA

\* $R_f$  values ( $\times 100$ ) were taken from chromatograms of mixed components and may be slightly different from those of pure compounds.

Solvents: F=Forestal solvent (hydrochloric acid:acetic acid:water 3:30:10); Be=benzene:acetic acid:water (6:7:3); BA/HA=two dimensional chromatograms first with butanol:acetic acid:water (6:1:2) then 6% acetic acid.

†Appearance: bu.=blue; fl.=fluorescence in u.v. light (365 nm); m.=mauve; or.=orange; pNA=diazotized *p*-nitroaniline; s.=strong; u.v.=ultra-violet light (365 nm); y.=yellow; →=fluorescence after exposure to ammonia.

The colours formed with pNA were observed in daylight.

‡ Factors are characteristic compounds found in a very small number of species.

§ Properties before acid hydrolysis; other data obtained after hydrolysis.

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