

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

### THE SECTIONS PORANTHEROIDEAE AND TERMINALES

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**Abstract**—More of the species in these two sections contain leucoanthocyanins than those in other sections of the genus. Agreement exists between the presence or absence of myricetin and the present classification into series. Members of the Heterophloiae series possess a very similar composition which is different from the rest of the two sections and characterized by a high ratio of myricetin and gallic acid and a low ratio of quercetin and ellagic acid.

#### INTRODUCTION

IN THE previous papers of this series<sup>1-3</sup> we have examined the relationship of the polyphenolic composition of the leaves of several classes of eucalypt species with the taxonomy of the genus. In Part I,<sup>1</sup> a close relationship was found between the composition and the classification of the series Globulares in the section Macrantherae. The characteristic features differed in three species and thus provided independent support for recent reclassifications based on morphological features. The botanically distinctive sections Renantherae and Renantheroideae of the genus contain species with a range of polyphenolic compositions which show in most cases a close agreement with the existing classification into series.<sup>2</sup> The distribution of a small number of distinctive compounds suggests certain interspecific relationships.<sup>2</sup> Recent reclassifications based on morphological characters were supported by the polyphenolic composition. In Part III,<sup>3</sup> several series of the section Macrantherae were examined and the differences in composition found to be less pronounced than those of the Renantherae. The accepted classification into series resulting from morphological examination is supported in many cases by the polyphenolic composition.

Except for a very small number of species, the members of the macrantherous series examined so far are found in the eastern and north-eastern parts of Australia. Similarly, only a small number of renantherous species are found in Western Australia.

Pryor<sup>4</sup> has discussed the possibility that the geologically newer soils of Australia carry the more recently evolved species. The large majority of the species occupying such soils in Western Australia are in a group he designated the "Bisectae". This group includes most of the species in the series Cornutae and Subcornutae of the section Macrantherae and also in the section Platyantherae and most of them have distinctly bisected cotyledons, a characteristic which occurs rarely outside the group. In eastern Australia the newer soils on the inland

<sup>1</sup> W. E. HILLIS, *Phytochem.* 5, 1075 (1966).

<sup>2</sup> W. E. HILLIS, *Phytochem.* 6, 259 (1967).

<sup>3</sup> W. E. HILLIS, *Phytochem.* 6, 275 (1967).

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



side of the Great Dividing Range are occupied very largely by species belonging to the comparable but remotely related unit, the "Adnata", containing most of the species in the Porantheroideae and Terminales sections. It is possible that new soils, with fertility levels higher than those of the old, were presented to the eucalypts during the Tertiary period.<sup>4</sup> At that time the climate became increasingly more arid and species were evolved to occupy these sites of changing environmental conditions.

The polyphenols in the leaves of the species included in the "Bisectae" and "Adnata" have been examined to ascertain any support for this grouping. In this paper, the Porantheroideae and Terminales sections of Blakely<sup>5</sup> are examined, and it has been found most convenient to present the data according to the geographical distribution of the species.

The accepted species in the Porantheroideae and Terminales sections number sixty-six, and of these fifty-one have been examined. Some of them are found only in restricted areas in uninhabited, semi-arid regions in northern Australia, and collection of authentic samples is difficult.

#### *Blakely's Section Terminales*

The habitat of most of the species belonging to this section extends from southern Queensland to Victoria in eastern Australia although *E. leucoxylon* (542, Table 1) and *E. fasciculosa* (560) are restricted to areas in eastern South Australia and western Victoria.

*E. paniculata* (537), *E. fergusonii* (538), *E. caleyi* (539), and *E. sideroxylon* (541), are trees of about 100 ft height, with very hard deeply furrowed barks, and reddish-brown, hard and very durable woods. *E. leucoxylon* (542), which has the same height and similar timber properties, is included with the above species but has a flaky brown or smooth grey bark. *E. melliodora* (550) is a tree of 60–100 ft height with a yellow-brown, hard and durable timber and a hard, persistent, fibrous bark. There is no distinctive feature of the composition of the polyphenols of these species (Table 1). It is now recognized that *E. paniculata* (537) includes *E. fergusonii* (538).

The Heterophloiae (Series XL, 555–560), the Red Boxes, are a morphologically distinct group, of 50–100 ft height, with red, hard and durable timbers and rough bark. They have a similar, distinctive polyphenol composition with a low to medium ratio of ellagic acid and quercetin and a high ratio of myricetin and gallic acid. The composition of the Red Boxes is very similar to that of the Piperitales (405–427) of the Renantherae<sup>2</sup> with respect to the high ratios of gallic acid and myricetin and the low to medium ratio of ellagic acid.

With two exceptions (No. 538 and 556) leucoanthocyanins are present in low to medium ratios in the Terminales section. Similarly most of the species contain appreciable amounts of macrantherin. However, the polyphenolic composition of the Heterophloiae stands apart from the rest of the section in which quercetin is the main or only flavonol, ellagic acid is a major component and *p*-coumarylquinic and chlorogenic acids are present.

#### *Blakely's Series XXXVIII. Siderophloiae ("Ironbarks")*

With Blakely's antheral classification this series is found in both the Porantheroideae and Terminales sections but in the latter the species have anthers which lack terminal glands. Whereas the habitat of these latter species extended from southern Queensland to western Victoria, the species in the Porantheroideae are found in the north-eastern part of Australia

<sup>5</sup> W. F. BLAKELY, *A Key to the Eucalypts*, 2nd Ed., Forestry and Timber Bureau, Canberra (1955).



TABLE 1. POLYPHENOLS IN THE LEAVES OF THE SECTION TERMINALES<sup>a</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 lxii. Rhodoxyla																																								
537. <i>E. paniculata</i>		(1)	Lq	2	T	1	3	5	5	3	1	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2		
537a. <i>E. panda</i>				Not examined																																				
538. <i>E. fergusonii</i>		(1)	Kq	2	2	5	3	3	5	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1			
539. <i>E. caleyi</i>		(1)	Lq	2	1	2	5	2	2	5	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		
541. <i>E. sideroxylon</i>		(19)	Po, Pp, Op, Pn, On	3	T	3	5	3	3	2	1	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
		(1)	Lq	3	1	1	5	1	5	5	2	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		
		(25)		1	1	5	4	4	2	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		
Subseries lxiii. Leucoxyla																																								
542. <i>E. leucoxylon</i>		(1)	Pn	1	2	1	5	2	1	1	2	3	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
		(2)	Po, Op	1	1	2	5	2	5	2	5	3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Series XXXIX. MELLIODORAE																																								
550. <i>E. melliodora</i>		(2)	Oo, Op	1	1	1	5	1	5	5	4	2	2	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
		(1)	Lq	1	1	2	T	2	5	5	4	1	1	1	1	1	1	1	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
Series XL. HETEROPHLOIAE																																								
555. <i>E. conica</i>		(1)	Z	3	T	5	3	2	2	T	5	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
556. <i>E. rudderi</i>		(2)	Kq	T	3	4	2	1	5	1	1	1	1	1	1	1	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
557. <i>E. dawsonii</i>		(1)	Z	2	1	4	1	1	1	5	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
558. <i>E. polyanthemus</i>		(6)	On	2	1	4	1	1	2	5	2	2	2	2	2	2	2	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
559. <i>E. bauerana</i>		(6)	Po, Pp, Op	2	T	4	2	2	2	5	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
560. <i>E. fasciculosa</i>		(1)	Ol	2	4	1	1	2	2	5	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	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<sup>7</sup>)

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 = Picoid

d = Chlorogenic acid

e = p-Coumaric 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.

<sup>a</sup> W. E. Hillis and K. Hillis, *Phytochem.* 4, 541 (1965).



and the inland areas of northern New South Wales; *E. pruinosa* (525) has been found in northern Western Australia. They are trees of 40–100 ft height, with very hard deeply furrowed (except 525, 534 and 535, Table 2) barks and reddish-brown, hard and durable woods.

The northern species of *Siderophloiae* contain appreciable ratios of myricetin more often than do the southern species. In other regards there is a similarity in composition between the two areas in that leucoanthocyanins are almost always present whereas kaempferol is rarely present, and ellagic and gallic acids usually present in large amounts. The notable exceptions in regard to the latter acids are *E. orgadophylla* (534) and *E. argophloia* (535, Table 2) and these two species contain unusually large amounts of leucodelphinidins. The only other species so far examined which contain large amounts of leucodelphinidins are *E. baileyana* (12), *E. phoenicea* (13), *E. miniata* (14), *E. falcata* (168), *E. cloeziana* (295), *E. umbra* ssp. *umbra* (311), *E. planchoniana* (377) and *E. fraxinoides* (381). As these species are found in different sections of the genus, it is evident that large amounts of leucodelphinidins when considered alone have little taxonomic value.

It is noteworthy that the three species containing the Cullenii Factor are found in different parts of tropical northern Australia and it is possible that formerly the habitats of these species were contiguous.

#### *Blakely's Series XXXVII. Buxaeales*

These species have a close botanical relationship with the *Siderophloiae* and have a height of 30–80 ft (up to 120 ft with *E. bosistoana* (479)), a box-type bark (except in the case of the smooth bark of *E. behriana*, (480)) and a brownish, hard and durable timber. Almost all species are distributed in northern New South Wales, Northern Territory and Queensland, and *E. microtheca* (507, Table 3) has been found also in northern Western Australia. *E. bosistoana* (479) and *E. behriana* (480) are found largely in the southern portion of the eastern states and *E. moluccana* (484) and *E. albens* (485) have a more southerly limit than the other *Buxaeales*.

In common with the *Siderophloiae*, leucoanthocyanins (with leucodelphinidins predominating) are usually present, chlorogenic and *p*-coumarylquinic acids are almost always present and macrantherin occasionally. Whereas ellagic and gallic acids are more consistently present in large ratios than in the *Siderophloiae*, myricetin is much less frequently present (Table 3). The exceptions to the above general composition are *E. rummeryi* (504) with a composition very similar to the *Heterophloiae* (Table 1), *E. oligantha* (491) found in the most northerly part of Northern Territory and *E. populnea* (501) and *E. microtheca* (507).

*E. tectifera* (493) and *E. spencerana* (494) were collected as different species from localities 400 miles apart in the northern part of Northern Territory. The composition of the samples are appreciably different (Table 3), but without the examination of further samples, it is not possible to confirm or otherwise the current view of the inclusion together of *E. spencerana* and *E. tectifera*.

The sample of the very rare species *E. patellaris* (490) was collected in the same area as the above two species and is distinctive in that the myricetin and quercetin spots on the chromatograms have a brown appearance under u.v. light. In addition, the unknown compound I, with a distinctive brown colour under u.v. light, is resolved. It will be pointed out below in the discussion of the *Fruticosae* and *Subbuxaeales* series, and in subsequent papers, that these features may have some significance.



TABLE 2. POLYPHENOLS IN THE LEAVES OF SIDEROPHLOIAE SERIES (XXXVIII) OF THE SECTION PORANTHEROIDEAE<sup>φ</sup>

†a	b	c	d	e	f	g	h	i	j	k	Factor‡
Subseries Ixviii. Subvirides											
510.	<i>E. decorticans</i>	(1)	Kq	3 2 - 2 5 - 3 - 2 5 1 - - - -	-	-	-	-	-	-	-
512.	<i>E. cullenii</i>	(1)	Ho	- - - T 4 - 5 2 - 5 3 1 2 2 2	3	-	-	-	-	-	Cullenii: 2
514.	<i>E. crebra</i>	(2)	Z	1 1 - 5 5 - 5 - T 4 2 - - - -	1	-	-	-	-	-	-
516.	<i>E. siderophloia</i>			Not examined							-
Subseries Ixix. Subglaucae											
519.	<i>E. jensenii</i>	(1)	Fi	T - - 5 3 - 3 - 2 5 2 1 2 2 -	-	-	-	-	-	-	Cullenii: 3
520.	<i>E. staigerana</i>	(1)	Z	- 2 - - 5 2 4 2 - 5 1 - - - -	-	-	-	-	-	-	-
522.	<i>E. fibrosa</i>										-
	ssp. <i>nubila</i>	(1)	Z	2 T - 4 2 - 3 - - 5 2 - 2 - -	-	-	-	-	-	-	-
523.	<i>E. fibrosa</i>										-
	ssp. <i>fibrosa</i>	(3)	Mr	- 2 - - 3 1 5 2 2 5 2 1 1 - 1	-	-	-	-	-	-	Tetraptera: 2
Subseries Ixx. Jugatae											
524a.	<i>E. tetrapleura</i>			Not examined							-
525.	<i>E. pruinosa</i>	(1)	Hj	- - - 1 5 1 5 1 4 5 2 1 2 1 1	-	-	-	-	-	-	Cullenii: 1
526.	<i>E. melanophloia</i>	(2)	Ko, Z	2 2 - 3 5 T 4 T 2 4 3 1 - - -	1	-	-	-	-	-	-
Subseries Ixxi. Eujugatae											
530.	<i>E. whitei</i>			Not examined							-
532.	<i>E. bowmanii</i>			Not examined							-
533.	<i>E. drepanophylla</i>	(1)	Kq	2 1 - 2 5 - 5 2 2 5 1 1 1 - 1	-	-	-	-	-	-	-
Subseries Ixxii. Submelliiodorae											
534.	<i>E. orgadophila</i>	(1)	Kq	5 1 - 1 3 - 2 - - 2 2 - - - -	-	-	-	-	-	-	-
535.	<i>E. argophloia</i>	(1)	Kq	5 1 - T 4 - 2 - - 3 2 - - - -	2	-	-	-	-	-	-

φ, †, ‡ See footnote, Table 1.



TABLE 3. POLYPHENOLS IN THE LEAVES OF BUXALES SERIES (XXXVII) OF THE SECTION PORANTHEROIDEAE<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 lxiii. Subangustae																																							
470.	<i>E. thoetiana</i>	(2)	Kj, Il	-	-	-	-	3	1	5	3	2	5	2	1	-	-	2	-	-	T	-	-	1	1	-	-	-	3	1	-	-	4	5	-	-	1	Specific cpd. A: 2 Specific cpd. B: 1	
471.	<i>E. pilligaensis</i>	(1)	Z	-	-	-	-	3	-	5	2	4	5	2	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5	1	-	-	-	-	
472.	<i>E. largiflorens</i>	(3)	Nm, Om	1	1	-	T	4	-	5	2	3	5	2	1	-	-	-	2	-	-	-	-	-	-	-	-	-	-	-	-	-	4	3	3	2	2	1	-
474.	<i>E. largeana</i>			Not examined																																			
476.	<i>E. ochrophloia</i>	(1)	Z	-	-	-	-	3	-	5	-	5	2	2	-	-	-	-	T	-	-	-	-	-	-	-	-	-	-	-	-	3	4	2	-	-	-	-	
Subseries lxiv. Subplatyphylae																																							
Not examined																																							
Not examined																																							
		(1)	Pp	-	2	T	4	T	5	T	-	4	2	-	-	-	-	-	2	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
		(2)	Om, Ni	2	1	-	4	-	5	-	2	5	2	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
482.	<i>E. woolistiana</i>	(1)	Z	2	1	-	4	-	5	T	3	5	2	T	2	T	T	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
483.	<i>E. microcarpa</i>	(1)	Z	-	-	-	3	-	5	2	2	5	2	T	1	T	T	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
484.	<i>E. moluccana</i>	(2)	Oo	-	1	-	4	1	5	5	5	1	2	1	T	T	-	-	2	-	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		(2)	Lq	1	-	T	4	-	5	3	3	5	2	-	-	-	-	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
486.	<i>E. albens</i>	(2)	Op	3	T	-	1	5	T	5	2	2	5	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		(1)	Op	1	-	-	5	-	5	3	2	5	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
489.	<i>E. leptophleba</i>	(2)	Jo, Gn	1	2	-	1	5	-	3	-	3	3	-	2	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
				* *																																			
490.	<i>E. patellaris</i>	(1)	Fi	-	T	-	1	5	-	4	-	T	5	3	2	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
491.	<i>E. oligantha</i>	(1)	Fi	1	2	-	4	5	-	3	-	3	4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
491a.	<i>E. fitzgeraldii</i>			Not examined																																			
Subseries lxvi. Boreales																																							
493.	<i>E. tectifera</i>	(1)	Gj	-	-	-	2	-	5	4	4	5	3	1	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
494.	<i>E. spencerana</i>	(1)	Fi	-	2	-	2	5	-	4	-	T	3	2	2	1	-	2	T	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
496.	<i>E. microneura</i>			Not examined																																			
Subseries lxvii. Protrusae																																							
Not examined																																							
498.	<i>E. cyanoclada</i>			Not examined																																			
501.	<i>E. populnea</i>	(1)	Kq	3	1	-	2	5	-	2	-	2	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
504.	<i>E. rummeryi</i>	(1)	Kq	3	1	-	5	3	-	3	-	5	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
505.	<i>E. normantonensis</i>	(1)	Ij	2	-	-	T	5	-	5	2	2	5	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
507.	<i>E. microtheca</i>	(1)	Li	3	1	-	3	5	-	3	1	-	3	1	-	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

<sup>φ</sup>, †, ‡ See footnote, Table 1; \* = abnormally coloured flavonol.



*Blakely's Series Fruticosae (XXXV) and Subbuxaeales (XXXVI)*

The species in these series are found in Western Australia (441, 445, 446, 447, Table 4), extend from that state to western Victoria (442) or are found close to the border of South Australia with Victoria and New South Wales (449, 451, 454, 455, 456, 462, 465, 469). They are slender many-stemmed Mallees of 30 ft height or less, and grow in areas of low rainfall.

There is a considerable variation in the composition of the species (Table 4). The most notable feature is the presence of abnormally coloured flavonols and unknown compound I in species 442, 451, 454 and 465. It will be shown in the next paper of this series that many of the Bisectae found on the newer soils of Western Australia possess these characteristics. Examination of further samples of these series may show subdivision on this basis to be possible. *E. decipiens* (447) differs from several of the other species in the Subbuxaeales in that it lacks unknown compound I. This observation is in partial agreement with Pryor's<sup>4</sup> conclusions drawn from botanical studies that this Western Australian member of the series resembles the eastern species only superficially. However, whereas Pryor considers *E. decipiens* should be included in the Bisectae, the absence of the above components suggests a closer affinity with the Adnata.

The samples of *E. foecunda* warrant special comment. This species has been very recently reinvestigated morphologically<sup>6</sup> and some specimens left in their present classification but with a name-change to *E. oraria* (131). Other specimens have been reclassified from the series Dumosae (section Macrantherae) to the series Fruticosae (section Porantheroideae) and to the species *E. leptophylla* (442) which has been renamed *E. foecunda* (442).<sup>6</sup> One sample collected in the field (Murchison River, Western Australia, see Map Lb<sup>7</sup>) as *E. foecunda* possessed a polyphenolic composition quite different from another sample collected at Fremantle, W.A. (Map Lb), as *E. foecunda* and so identified at that time after herbarium examination. The composition of the latter resembled *E. loxophleba* (129) and *E. accedens* (125) (unpublished data) and is *E. oraria* (131). The composition of the first sample was very similar to a sample of *E. leptophylla* (442) (or as it is now known, *E. foecunda*, 442) previously collected at Encounter Bay, S.A. (Map O1). The difficulties encountered with these samples show the value that the polyphenolic composition has in assisting the identification of some species. In addition, there is a remarkably close resemblance in the composition of these samples of *E. foecunda* (442) which have been collected 1500 miles apart. This species is found in isolated areas on the fringes of the desert or semi-arid regions in Western Australia, South Australia, Victoria and New South Wales, although Encounter Bay, S.A., is farther away from these regions than other localities. The present-day species could be either the relic or the environmental adaptation of a species formerly growing in central Australia in earlier geological periods.

*The Relationship of Polyphenols with Classification*

More than two-thirds of the Porantheroideae contain leucoanthocyanins and more than half contain leucodelphinidins as the major or only representatives. A higher ratio of the Terminales species contain leucoanthocyanins and again leucodelphinidins are the most common major representatives. The ratio of the species in these two sections which contain leucoanthocyanins, and specifically leucodelphinidins, is higher than in any other section.

<sup>6</sup> L. A. S. JOHNSON, *Contrib. N.S.W. Natl Herb.* 3, 103 (1962).

<sup>7</sup> W. E. HILLIS, *Phytochem.* 5, 541 (1966).







Large amounts of myricetin and small amounts of quercetin characterize the Piperitales series of the Renantherae<sup>2</sup> section, and similarly characterize the Heterophloiae of the Terminales (Table 1). Myricetin is usually absent from the remainder of the species in the Terminales section and in the Fruticosae, Subbuxae and Buxae series of the Porantheroideae section except in the cases of *E. foecunda* (442) and *E. rummeryi* (504). Most of the Siderophloiae (Table 2) contain myricetin sometimes as the major flavonol. It has been observed in other series<sup>1,2</sup> that the presence of appreciable amounts of myricetin can be taxonomically significant and apparently it has some significance in the Porantheroideae and Terminales sections. Kaempferol is present in only a few species and occasionally quercetin occurs in low ratios but in neither case is there any apparent taxonomic significance.

It has previously been observed in the Renantherae<sup>2</sup> that low ratios of ellagic acid are characteristic of the Piperitales (405–427) and the Longitudinales (394–401) series. Similarly the Heterophloiae (555–560) contain a low ratio of ellagic acid, although some other species (489, 491, 501, 534, 535 and 539 see Tables 1, 2 and 3) contain small amounts but without taxonomic significance. The amount of gallic acid was much higher than ellagic acid in the Heterophloiae and is apparently characteristic just as it is in the Longitudinales (394–401) and Piperitales (405–427) series of the Renantherae.<sup>2</sup>

Chlorogenic and *p*-coumarylquinic acids are present in most species just as they are in the macrantherous species previously reported,<sup>3</sup> and in contrast to the renantherous species.<sup>2</sup> About 40 per cent of the species contain macrantherin, and stilbenes have been detected in two species (541 and 550).

Aromadendrin has been detected in eleven species but it has no apparent taxonomic significance. Unknown compounds F and to a lesser extent G were found in most species although both were consistently absent in the Heterophloiae and G was absent in the Siderophloiae. Unknown compounds H and J were usually present and more frequently than in the macrantherous and renantherous species previously reported but similarly no taxonomic relationship is evident.

Abnormally coloured flavonols and the unknown compound I are present in six species. Whereas the fluorescences of quercetin and myricetin under u.v. light are normally bright yellow and strong orange respectively, the fluorescence of the flavonols in these species are dull and brown–yellow. The appearance is the same in both the Forestal and butanol:acetic acid:water solvents and is doubtless due to an underlying component which affects the appearance. In the case of quercetin the component may be compound I with very similar chromatographic properties and which is not always discretely resolved. In view of the broad nature of the survey, the cause of the abnormal colour of the flavonols was not studied in detail. The possible taxonomic significance of the characters will be discussed in the next paper.

#### 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>7</sup> Samples collected from botanic gardens or arboreta are designated by “Z”. The methods of examination have been previously reported<sup>1,7</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 5.



TABLE 5. CHROMATOGRAPHIC PROPERTIES OF SECONDARY EUCALYPT POLYPHENOLS DETECTED IN THE SECTIONS PORANTHEROIDEAE AND TERMINALES

Polyphenol	$R_f \times 100^*$ Solvent			Appearance*
	F	Be	BA/HA	
Factors†				
Microcarpa	—	90	80/72	or. pNA
Cullenii‡	—	—	20/02	s. y. fl. → s. or., tan pNA
Tetraptera	—	—	45/28	or. y. fl.
Specific compounds				
442. <i>E. foecunda</i>	—	10	18/02	y. D.L.
470. <i>E. thozetiana</i>				
A.	—	48	67/77	l. y. pNA
B.	—	65	84/80	or. pNA
484. <i>E. moluccana</i>	—	—	76/77	or. pNA

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

Solvent 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:

D.L. = daylight  
 fl. = fluorescence in u.v. light (365 nm)  
 l. = light  
 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.

The compounds that have been detected when the leaves were heated with 2 N HCl included delphinidin from the polymerized leucodelphinidins, and cyanidin from the polymerized leucocyanidins. Another red compound had properties very similar to those of pelargonidin. Also detected were myricetin, quercetin, kaempferol and the following acids: ellagic, gallic, gentisic, caffeic, *p*-coumaric, sinapic and ferulic. 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 been detected also. 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 and *p*-coumarylquinic acid (cf. Hillis<sup>1</sup>).

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