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Distribution and Taxonomic Significance of Major Alkaloids in the Genus *Podalyria*

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Key Word Index—*Podalyria*; Leguminosae; Podalyrieae; quinolizidine alkaloids; variation study; chemotaxonomy.

Abstract—A chemotaxonomic survey of alkaloids in 22 species of the genus *Podalyria* has shown the presence of several different tetracyclic quinolizidine alkaloids and their angelate, tigliate and carboxylic acid esters. Quantitative and qualitative differences were found between the species and also between samples of twigs, leaves, pods and seeds. Most of the species have high concentrations of lupanine as virtually the only alkaloid, but some have a wide range of different compounds, including various hydroxylated lupanines and esters of alkaloids. The three yellow-flowered species differ from all others in the presence of virgiline, oroboidine and virgiline–pyrrolyl carboxylic acid ester as major alkaloids. These three compounds were found to be totally absent in all the pink- and white-flowered species of the genus. In the tribe Podalyrieae, carboxylic acid esters were hitherto known only from the genus *Virgilia* and their distribution agrees with morphological evidence that the yellow-flowered group of species should be excluded from *Podalyria*.

Introduction

As part of a study of generic relationships in the tribe Podalyrieae, we have investigated the taxonomic value of alkaloids in the genus *Podalyria*. This genus is restricted to southern Africa and comprises some 24 species. *Podalyria* is closely related to *Virgilia*, a genus well known for its unique combination of interesting quinolizidine alkaloids (Mears and Mabry, 1971; Van Eijk *et al.*, 1982; Van Eijk and Radema, 1982; Greinwald *et al.*, 1989; Veen *et al.*, 1991). Judged from available literature, however, the alkaloids of *Podalyria* seem rather uninteresting—only three compounds have been reported thus far, namely sparteine, lupanine and aphylline (Nattrass, 1973; Southon and Buckingham, 1988). Our aim with this study was to find reliable data, not only for a comparison with *Virgilia*, but also to determine the taxonomic value of alkaloids within *Podalyria*.

Materials and Methods

Plant materials. Full details of all the samples used for extraction of alkaloids are given in Table 1.

Procedures. Finely ground air-dried material (100–800 mg) was extracted with 15 ml 0.05 M H_2SO_4 and left standing at room temperature for 15 min. After filtration, the plant material was extracted a second time with 5 ml 0.05 M H_2SO_4. The aqueous phases were combined, applied to glass columns with celite (24 g), alkalinized with ammonia and extracted (1×) with 100 ml CH_2Cl_2. The CH_2Cl_2 extracts were dried with anhydrous Na_2SO_4 and the solvent evaporated under reduced pressure to leave an alkaloidal mixture of pale yellow to pale brown oil. For large-scale extractions, finely ground leaves were exhaustively extracted with cold CH_2Cl_2. The extracts were acidified with 0.5 M HCl and re-extracted with CH_2Cl_2 after basifying the aqueous phase with conc. NH_3. Alkaloids were identified by comparative TLC and comparative GC using authentic reference samples obtained in previous studies (Van Wyk *et al.*, 1988; Van Wyk and Verdoorn, 1989a, 1989b; Verdoorn and Van Wyk, 1990) and isolated from extracts of several species of *Podalyria* as shown in Table 2. These reference samples were fully authenticated by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. Two TLC systems were used as described previously (Van Wyk and Verdoorn, 1991; Van Wyk *et al.*, 1992). For column chromatography we used silica gel 60 with $CHCl_3$–cyclohexane–Et_2NH (4:5:1) as eluent. GC spectra were obtained with a DB-1 fused silica capillary column (30 m × 0.25 mm i.d.; N_2 as carrier gas at 4 ml min^{-1}; column temperature 150–320°C at 6°C min^{-1}, 15 min isotherm; injector 230°C; PND detection 300°C; split ratio 30:1; injection volume 1 μl). The identities of all the major alkaloids were confirmed by GC-MS analyses of the following extracts: *P. biflora*

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TABLE 1. MATERIAL OF THE GENUS *PODALYRIA* USED FOR ALKALOID STUDIES AND YIELDS OF ALKALOIDAL MATERIAL OBTAINED

Voucher specimens	Yield (mg g $^{-1}$ dry weight) Twigs	Leaves	Pods	Seeds
a. Section *Nitidae*				
1. *Podalyria speciosa* Eckl. & Zeyh.				
Schlecter 9617 (BOL)		9.41		
Levyns 3287 (BOL)		38.78		
Esterhuysen 3858 (BOL)		26.14		
Stokoe s.n. sub BOL 17249		22.27		
Drewe s.n. (JRAU)		41.46		
2. *Podalyria glauca* (Thunb.) DC.				
Compton 4549 (BOL)		36.53		
Vlok 66 (BOL)		24.56		
Barker 58 (BOL)		39.19		
Fourcade 4485 (BOL)		18.45		
Van Wyk 2576 (JRAU)		29.33		
* *Van Wyk 2945* (JRAU)		42.84		10.09
3. *Podalyria microphylla* E. Mey.				
Levyns 10597 (BOL)		20.07		
Van der Spuy s.n. (BOL)		25.43		
Leipoldt s.n. sub BOL. 18605		17.25		
Boucher 3537 (PRE)		23.13		17.58
4. *Podalyria buxifolia* (Retz.) Willd.				
Schlecter 5548 (BOL)		11.22		
Dahlstrand 392 (PRE)		1.94		
Story 2470 (PRE)		1.96		
5. *Podalyria reticulata* Harv.				
Bolus 6787 (BOL)		24.68		
Barker 1866 (PRE)		25.50		
Galpin 3904 (PRE)		24.56		
b. Section *Villosae*				
6. *Podalyria cordata* (Thunb.) R. Br.				
Esterhuysen 21786 (BOL)		15.69		
Bond 494 (BOL)		13.00		
Levyns 3358 (BOL)		6.66		
Gillett 3594 (BOL)		16.63		
* *Van Wyk 2771* (JRAU)	4.71	11.27	1.15	3.85
7. *Podalyria hirsuta* (Ait.) Willd. (= *P. cordata*?)				
Esterhuysen 1891 (BOL)		19.58		
Esterhuysen 4858 (BOL)		10.08		
Bolus 11252 (BOL)		5.88		
* *Van Wyk 2682* (JRAU)	17.91	24.85		
8. *Podalyria canescens* E. Mey.				
Esterhuysen 8951 (BOL)		15.80		
Compton 17319 (BOL)		17.81		
L. Bolus s.n. (BOL)		18.20		
Bolus 11253 (BOL)		8.38		
9. *Podalyria velutina* Burch. ex Benth.				
Bolus 1931 (BOL)		0.77		
Burtt Davy 15318 (BOL)		1.93		
Van Dam s.n. (BOL)		0.53		
10. *Podalyria burchellii* DC.				
Bean 456 (BOL)		0.30		
Bean 901 (BOL)		0.28		
Compton 10788 (BOL)		0.25		
Esterhuysen 16271 (BOL)		0.39		
Compton 4245 (BOL)		0.66		
Van Wyk 1433b (JRAU)		0.26		

TABLE 1—*CONTINUED*

Voucher specimens	Twigs	Yield (mg g⁻¹ dry weight) Leaves	Pods	Seeds
c. Section *Calyptratae*				
11. *Podalyria calyptrata* (Retz.) Willd.				
Pillans 9353 (BOL)		15.68		
Van Wyk 2743 (JRAU)	4.31	18.16		
Van Wyk 2675 (JRAU)	11.15	34.35		
**Van Wyk 2676* (JRAU)	17.91	34.06		
Van Wyk 2785 (JRAU)	8.04	38.12	3.21	5.41
d. Section *Sericeae*				
12. *Podalyria argentea* Salisb.				
**Van Wyk 2761* (JRAU)	5.00	14.23		
Van Wyk 2762 (JRAU)	8.35	28.52		
13. *Podalyria biflora* (L.) Willd.				
Salter 8769 (BOL)		17.94		
Walgate s.n. sub BOL 23850		9.84		
L. Bolus s.n. (BOL)		16.63		
Thorns s.n. (BOL)		25.13		
Pillans 8478 (BOL)		20.36		
Barker 10258 (BOL)		11.51		
14. *Podalyria myrtillifolia* (Retz.) Willd.				
Levyns 2537 (BOL)		7.73		
Esterhuysen 11871 (BOL)		11.19		
Leighton 45 (BOL)		11.15		
15. *Podalyria cuneifolia* Vent.				
Fourcade 170 (BOL)		24.13		
Levyns 9669 (BOL)		30.26		
Levyns 4476 (BOL)		23.31		
Levyns 10288 (BOL)		8.99		
Schutte 445 (JRAU)		8.87		
* *Van Wyk 2589* (JRAU)	1.42	9.67	2.14	4.50
Van Wyk 2870 (JRAU)	4.35	18.25	2.23	7.63
Van Wyk 2889 (JRAU)	2.91	28.07	2.00	8.86
* *Van Wyk 2890* (JRAU)	4.26	21.26	2.92	10.94
16. *Podalyria sericea* (Andr.) R. Br. ex Ait. f.				
Wolley Dod 1128 (BOL)		14.04		
Leighton 1055 (BOL)		1.90		
Esterhuysen 12833 (BOL)		1.37		
Barker 10872 (BOL)		4.31		
Van Wyk 2461b		9.20		
* *Van Wyk 2461c*	2 .17	5.95	5.41	1.04
17. *Podalyria leipoldtii* L. Bol.				
L. Bolus s.n. sub BOL 23845		0.78		
Leipoldt 1/9/37 (BOL)		1.03		
Leipoldt 8/31 (BOL)		1.20		
Barker 10280 (BOL)		0.96		
Gillett 4070 (BOL)		0.45		
18. *Podalyria pearsonii* Phill.				
Esterhuysen 22135 (BOL)		2.06		
Leipoldt s.n. sub BOL 23844		1.42		
Lavis s.n. sub BOL 19636		27.00		
19. *Podalyria pulcherrima* Schinz				
Levyns 2190a (BOL)		7.79		
Adamson s.n. (BOL)		21.21		
Pillans 7893 (BOL)		8.76		

TABLE 1—*CONTINUED*

Voucher specimens	Twigs	Yield (mg g⁻¹ dry weight) Leaves	Pods	Seeds
e. Yellow-flowered group				
20. *Podalyria chrysantha* Adamson				
Adamson s.n. (BOL)		18.25		
Pocock sub Levyns 2514 (BOL)		1.63		
Levyns 8966 (BOL)		3.36		
21. *Podalyria tayloriana* L. Bol.				
L. Bolus s.n. sub BOL 20839		5.41		
Van Wyk 3169a		18.51		
Van Wyk 3169b		22.26		
22. *Podalyria insignis* Compton				
Walgate s.n. sub BOL 23847		2.71		
Levyns 8025 (BOL)		2.34		
Esterhuysen 1869 (BOL)		2.74		
Levyns 6424 (BOL)		8.05		
NBI, Worcester (ex hort.) A		5.12		
NBI, Worcester (ex hort.) B		9.06		
**Van Wyk 2913* (JRAU)		7.49		

*These materials were used for large-scale extraction and isolation of individual alkaloids (see Table 2).

TABLE 2. LARGE-SCALE EXTRACTS OF SPECIES OF *PODALYRIA* AND YIELDS OF PURE ALKALOIDS THAT WERE ISOLATED AND FULLY AUTHENTICATED BY SPECTRAL METHODS

Species (voucher specimen)	Material extracted (g dry wt)	Alkaloid(s) isolated	Yield obtained (mg)
Podalyria glauca (*Van Wyk 2945*)	Leaves 0.9	Lupanine	39
P. cordata (*Van Wyk 2771*)	Leaves 22.4	Lupanine	253
P. hirsuta (*Van Wyk 2682*)	Leaves 22.3	Lupanine	554
P. calyptrata (*Van Wyk 2676*)	Leaves 49.0	Lupanine	487
P. argentea (*Van Wyk 2761*)	Leaves 25.8	Lupanine	129
P. cuneifolia (*Van Wyk 2589*)	Leaves 63.8	Sparteine	5
		Lupanine	4
P. cuneifolia (*Van Wyk 2890*)	Leaves 1980.0	Sparteine	2080
		Lupanine	457
		17-oxo-Lupanine	81
		3β-Hydroxylupanine	432
		3,13-Dihydroxylupanine	180
		Lupanine-13-angelate	276
		Cajanifoline	2133
		Pearsonine	417
P. sericea (*Van Wyk 2461c*)	Leaves 31.3	Sparteine	69
P. insignis (*Van Wyk 2913*)	Leaves 407.0	Ammodendrine	49
		Isolupanine	61
		13-Hydroxylupanine	17
		Virgiline	35
		Virgiline–pyrrolyl–carboxylic acid ester	3310
		Oroboidine	322

(*Barker 10258*, leaves), *P. cuneifolia* (*Van Wyk 2589*, seeds), *P. cuneifolia* (*Levyns 9669*, leaves), *P. insignis* (ex hort. *A*, leaves), *P. insignis* (*Levyns 8025*, leaves), *P. pearsonii* (*Lavis 19636*, leaves), *P. pulcherrima* (*Levyns 2190a*, leaves), *P. sericea* (*Van Wyk 2461c*, leaves and seeds) and *P. speciosa* (*Stokoe s.n.*, leaves). Unknown minor alkaloids were detected by GC in some of the extracts and studied by GC-MS but none of these occurred in sufficient quantity to allow confirmation of their identities by spectroscopic methods.

Piperidyl alkaloids. Ammodendrine: Rt 15.10, M^+ 208. Minor alkaloid of the yellow-flowered species (see Table 1) and occur only sporadically in trace amounts elsewhere in the genus.

Tetracyclic quinolizidine alkaloids. α-Isosparteine: Rt 12.62, M^+ 234. Trace amounts detected by GC and GC-MS in some extracts. Sparteine: Rt 13.77, M^+ 234. Isolupanine (11-*epi*-lupanine): Rt 19.60, M^+ 248. Lupanine: Rt 20.45, M^+ 248. Aphylline (10-oxo-sparteine): Rt 20.72, M^+ 248. 3β-Hydroxylupanine: Rt 21.95, M^+ 264. 17-oxo-Lupanine: Rt 23.30, M^+ 262. 13α-Hydroxylupanine: Rt 24.27, M^+ 264. Lebeckianine (3β, 4α-dihydroxylupanine): Rt 23.43, M^+ 280. Virgiline (13α-hydroxyaphylline): Rt 24.66, M^+ 264. 3β, 13α-Dihydroxylupanine: Rt 25.75, M^+ 280.

Esters of quinolizidine alkaloids. Lupanine-13α-*O*-angelate: Rt 28.82, M^+ 346. Lupanine-13α-*O*-tigliate: Rt 29.05, M^+ 346. Cajanifoline: Rt 30.30, M^+ 362. Sessiliofoline: Rt 30.85, M^+ 362. Pearsonine: Rt 32.10 M^+ 378. Virgiline-pyrollyl-carboxylic acid ester: Rt 32.08, M^+ 357. Oroboidine: Rt 34.70, M^+ 357.

Results

To ensure that most of the variation within the genus was accounted for, 144 extracts from 22 species were analysed. The sample included, where possible, at least three different provenances of the same species and in some cases also different plants from the same population. For a smaller selection of species, possible differences between twigs, leaves, pods and seeds were investigated. A complete list of voucher specimens of the material used for extraction and the yields of alkaloids obtained are given in Table 1. The genus *Podalyria* is in urgent need of taxonomic revision and care was therefore taken to give accurate voucher specimen information so that identifications can be verified in the future. With the exception of the more recently described yellow-flowered species, the sectional arrangement in Table 1 follows that of the latest available taxonomic treatment by Harvey (1862), which is now very much outdated.

A summary of alkaloid yields obtained from leaf samples is presented in Fig. 1 and a comparison of yields from twigs, leaves, pods and seeds taken from the same individual plants in Fig. 2. The distribution of major alkaloids in 96 leaf samples from 22 species is presented schematically in Fig. 3a–c. Differences in the distribution of major alkaloids in twigs, leaves, pods and seeds of five different species are summarized in Fig. 4.

The following alkaloids were present as major alkaloids in at least some of the samples: sparteine, aphylline (10-oxo-sparteine), lupanine, isolupanine (11-*epi*-lupanine), 17-oxo-lupanine, 3β-hydroxylupanine, 3β,13α-dihydroxylupanine,

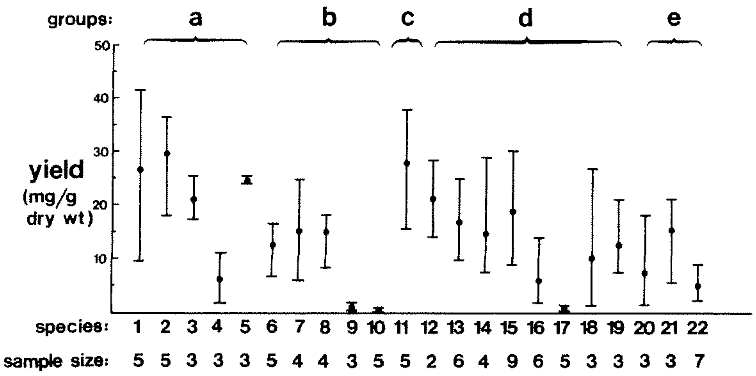

FIG. 1. YIELDS OF ALKALOIDS OBTAINED FROM LEAF SAMPLES OF THE SPECIES OF *PODALYRIA*. Note the high concentrations of alkaloids in most of the species (up to 4% of dry weight) and the diagnostically low concentrations in *P. velutina* (sp. 9), *P. burchellii* (sp. 10) and *P. leipoldtii* (sp. 17). (The range and mean values are shown; species are numbered as in Table 1.)

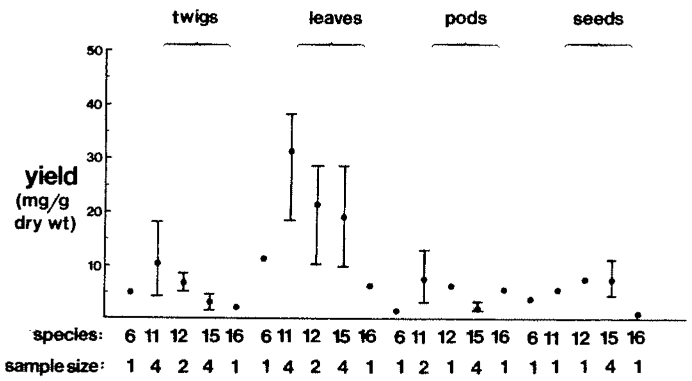

FIG. 2. YIELDS OF ALKALOIDS OBTAINED FROM DIFFERENT PLANT PARTS OF SOME SPECIES OF *PODALYRIA*. Note that in all five species, the highest yields were obtained from leaf samples. (The range and mean values are shown; species are numbered as in Table 1.)

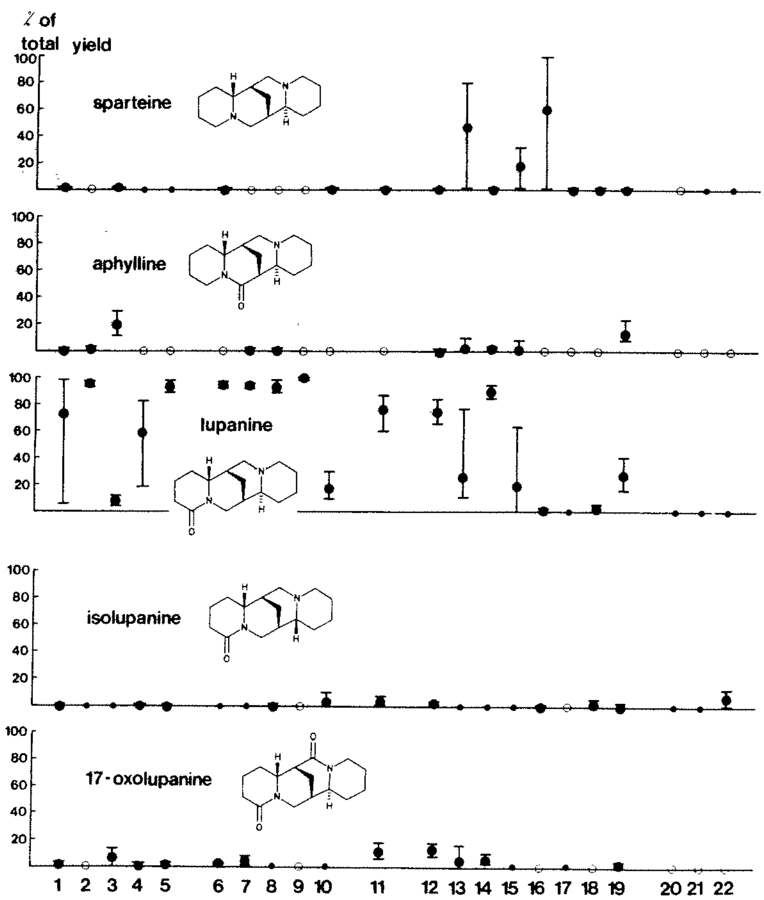

FIG. 3a. DISTRIBUTION OF SPARTEINE- AND LUPANINE-TYPE ALKALOIDS IN 96 LEAF SAMPLES FROM 22 SPECIES OF *PODALYRIA*. (The range and mean values are shown; small dots indicate trace amounts; circles indicate absence; species are numbered as in Table 1; sample size for each species as in Fig. 1.)

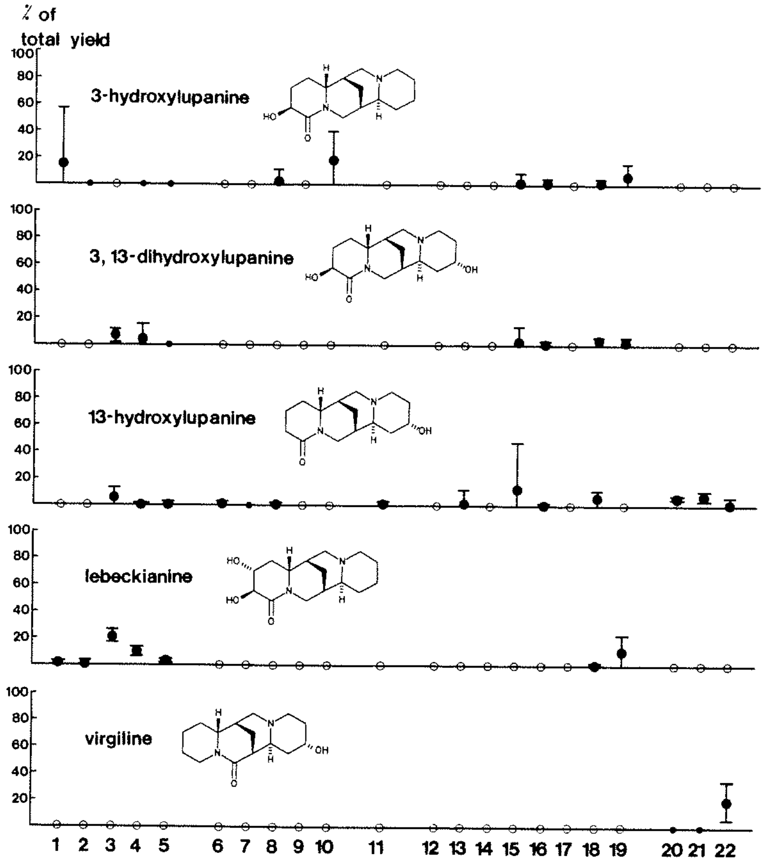

FIG. 3b. DISTRIBUTION OF HYDROXYLATED LUPANINES AND VIRGILINE IN 96 LEAF SAMPLES FROM 22 SPECIES OF *PODALYRIA*. (The range and mean values are shown; small dots indicate trace amounts; circles indicate absence; species are numbered as in Table 1; sample size for each species as in Fig. 1.)

13α-hydroxylupanine, lebeckianine, virgiline, lupanine-13α-angelate, cajanifoline, sessilifoline, pearsonine, oroboidine and virgiline-pyrrolyl-carboxylic acid ester. Major alkaloids were taken as all those which represent at least 10% of any given extract. Small quantities of ammodendrine were found in extracts from the yellow-flowered group and only rarely in other species, where it occurs at best in trace amounts. Lupanine-13α-tigliate and α-isosparteine also occur sporadically in some species, but in very low percentage yields.

Discussion

Despite considerable infraspecific variation, some species can be distinguished by their low total yields (Fig. 1). These include *P. velutina* and *P. burchellii* of the section *Villosae* and *P. leipoldtii* of the section *Sericeae*. Yields exceed 4% of dry weight in some species and these figures are amongst the highest thus far recorded in the tribes Crotalarieae, Podalyrieae and Liparieae. A comparison of yields from different plant parts (twigs, leaves, pods and seeds) showed that the highest concentrations of alkaloids occur in leaves (Fig. 2). Although there are slight trends in the relative amounts of sparteine, lupanine and lebeckianine in the various organs (Fig. 4), these are clearly insignificant compared to the large differences between species. Figure 4 shows, for example, that twigs have higher proportions of sparteine than leaves, pods

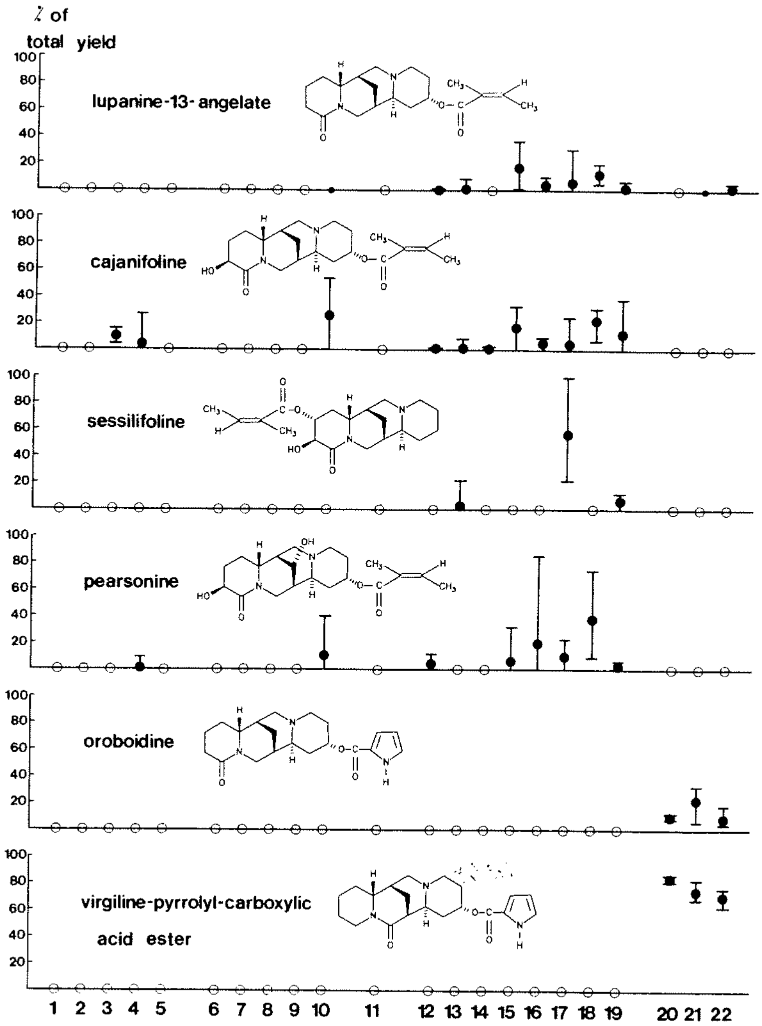

FIG. 3c. DISTRIBUTION OF VARIOUS ESTERS OF ALKALOIDS IN 96 LEAF SAMPLES FROM 22 SPECIES OF *PODALYRIA*. (The range and mean values are shown; small dots indicate trace amounts; circles indicate absence; species are numbered as in Table 1; sample size for each species as in Fig. 1.)

and seeds. In the genus *Virgilia*, branches generally also have higher concentrations of sparteine than the leaves (Greinwald *et al.*, 1989). In *Podalyria*, the differences between leaves and seeds were much smaller than in *Virgilia* (Greinwald *et al.*, 1989) and also much smaller than in various genera of the tribe Crotalarieae (Van Wyk and Verdoorn, 1991; Van Wyk and Verdoorn, in preparation), where the seeds often have a distinctive combination of alkaloids.

The 16 major alkaloids are not evenly distributed amongst the 22 species of *Podalyria* (Fig. 3a–c). It is interesting to note that species with high concentrations of lupanine (Fig. 3a) have only small amounts of hydroxylated lupanines (Fig. 3b) and small amounts of esters of alkaloids (Fig. 3c). It may be speculated that these species lack the ability to convert lupanine to other structurally related compounds, so that high concentrations are accumulated. Hydroxylation and esterification of lupanine seem to occur in most species of the section *Sericeae* (particularly in species 15–19 in

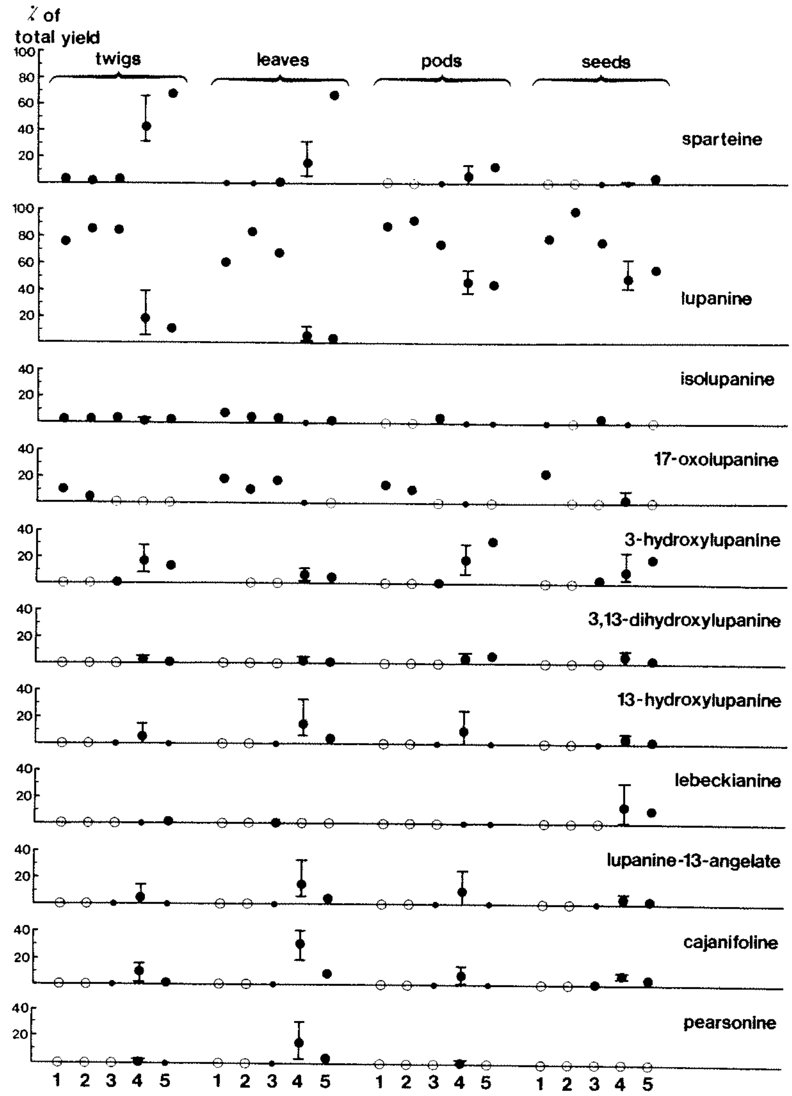

FIG. 4. DISTRIBUTION OF MAJOR ALKALOIDS IN DIFFERENT PLANT PARTS OF FIVE SPECIES OF *PODALYRIA*. Twigs, leaves, pods and seeds were taken from the same individual plants (one plant of each species except for *P. cuneifolia*, where three individuals were sampled). (The range and mean values are shown; small dots indicate trace amounts; circles indicate absence; 1 = *P. calyptrata*, 2 = *P. cordata*, 3 = *P. argentea*, 4 = *P. cuneifolia*, 5 = *P. sericea*.)

Fig. 3), and also in *P. microphylla* and *P. buxifolia* of the section *Nitidae* and in *P. burchellii* of the section *Villosae*. Some of these species are presently misplaced in their respective sections and a more natural arrangement may well be possible.

The most striking qualitative and quantitative discontinuity was found in the yellow-flowered species (group e in Fig. 1 and Table 1). All three species of this group produce large amounts of the carboxylic acid esters of 13-hydroxylupanine and virgiline. The presence of virgiline and 13-OH-lupanine as virtually the only other major alkaloids suggests that aphylline and lupanine are efficiently hydroxylated and subsequently esterified in these species. None of the other *Podalyria* species seems to have the ability to produce virgiline or carboxylic acid esters, compounds hitherto known only from the related genus *Virgilia*, some genera of the tribe Sophoreae (Van Eijk and Radema, 1976; 1977; Radema *et al.*, 1979; Asres *et al.*, 1986) and recently also reported from three species of *Priestleya* (tribe Liparieae) (Van Wyk et al., 1991).

Our results show, for the first time, a direct chemotaxonomic link between *Podalyria* and *Virgilia* and also raise doubts about the generic circumscription of *Podalyria*. The yellow-flowered species differ from the rest of the genus in more than just the colour of the flowers—the inflorescence structure, bracts and seed arils are also quite different. The unique combination of alkaloids in *P. chrysantha*, *P. tayloriana* and *P. insignis* provides convincing supportive evidence for the idea that generic delimitations in the tribe Podalyrieae will be improved if these species are excluded from *Podalyria*.

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