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Alkaloids of the genera *Aspalathus, Rafnia* and *Wiborgia* (Fabaceae – Crotalarieae)

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The presence of alkaloids in three southern African genera of the tribe Crotalarieae is reported for the first time. Sparteine, lupanine and nuttalline were detected in several species of *Aspalathus* L., *Rafnia* Thunb. and *Wiborgia* Thunb., but rarely in more than trace quantities. Except for very large quantitative differences, the alkaloids are almost identical to those found in the genus *Lebeckia* Thunb. Available evidence suggests that the three genera are more closely related to *Lebeckia* than to any other genus of the tribe. The divergence of these genera seems to be linked to an almost total loss of the ability to produce alkaloids.

Die teenwoordigheid van alkaloïede in drie Suider-Afrikaanse genera van die tribus Crotalarieae word vir die eerste keer gerapporteer. Sparteïen, lupanien en nuttallien is waargeneem in verskeie spesies van *Aspalathus* L., *Rafnia* Thunb. en *Wiborgia* Thunb. maar slegs by uitsondering in meer as spoorhoeveelhede. Afgesien van baie groot kwantitatiewe verskille, is die alkaloïede feitlik identies aan dié wat in die genus *Lebeckia* Thunb. aangetref word. Beskikbare getuienis dui daarop dat die drie genera nader verwant is aan *Lebeckia* as aan enige ander genus van die tribus. Die divergensie van hierdie genera hou skynbaar verband met 'n bykans totale verlies aan die vermoë om alkaloïede te produseer.

Keywords: *Aspalathus*, generic relationships, quinolizidine alkaloids, *Rafnia, Wiborgia*

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Introduction

The high incidence of convergence and intricate relationships amongst the Cape Crotalarieae have been discussed by Dahlgren (1963) and Polhill (1976). *Lebeckia* Thunb. is considered to be the least specialized genus of the tribe and morphological similarities with other genera of the tribe are taken as evidence of a close relationship. The distinct pattern of alkaloids observed in the genus *Lebeckia* (van Wyk & Verdoorn 1989a) indicated to us that alkaloids may provide valuable information about the generic affinities of three other genera of the tribe, namely *Aspalathus* L., *Rafnia* Thunb. and *Wiborgia* Thunb. These three genera are considered to be particularly closely related to *Lebeckia*, as is evidenced by their sequence in the latest generic and tribal revision (Polhill 1976, 1981).

An alkaloid tentatively identified as sparteine has been reported previously from one species of *Wiborgia* (van Wyk *et al.* 1988a) but, except for *Lebeckia*, no other information is available for any of the genera. Our aim with the present study was, therefore, to provide alkaloid data for a comparison of above-mentioned genera.

Materials and Methods

A total of 22 samples, representing 11 species of *Aspalathus*, 6 species of *Rafnia* and 3 species of *Wiborgia* were studied in this survey. The species, authorities for names and voucher specimens are listed in the appendix.

Methods of extraction and identification were as previously described (van Wyk *et al.* 1988a, b; van Wyk & Verdoorn 1988). Gas chromatography conditions were the same as used by van Wyk & Verdoorn (1989a). All reference samples used in analytical TLC and GC were fully authenticated by ^{1}H- and ^{13}C NMR spectroscopy and mass spectrometry. Identifications by analytical TLC and GC were confirmed by GC–MS studies of two extracts (*Aspalathus longifolia* and *Rafnia racemosa*).

Results and Discussion

The distribution of alkaloids in 20 species of *Aspalathus, Rafnia* and *Wiborgia* is shown in Table 1. Small amounts of sparteine, lupanine and nuttalline were present in several of the samples (α-isolupanine in a few of them), but rarely in more than trace quantities. We have also found some indications of the presence of ammodendrine (a piperidyl alkaloid) but this could not be confirmed. No evidence of (α-pyridone alkaloids or pyrrolizidine alkaloids were found in any of the extracts.

Yield figures were extremely low, so that relative yields are not given except for one species of *Aspalathus (A. nivea)*. The latter is a large shrub with flowers not unlike those of some species of *Lebeckia*. The almost total absence of alkaloids in *Aspalathus* (if taken to be a derived character state) indicates a more basal position for *A. nivea* than the sequence of species in Dahlgren's (1988) revision would suggest. However, Dahlgren explicitly stated that the affinities of this species are uncertain and it is interesting to note that it was placed in a monotypic infrageneric group.

Except for the large quantitative difference observed, the alkaloids of all three genera are virtually the same as those found in the genus *Lebeckia*, and the diversity is much less than expected. A comparison between various genera of the Crotalarieae is shown in Table 2. *Rothia*

Table 1 Approximate yields and distribution of alkaloids in 20 species of *Aspalathus, Rafnia* and *Wiborgia.* (Authorities for names and voucher specimen details are given in appendix 1, tr indicates trace amounts)

	Approximate yield (μg/g dry wt)	Distribution of major alkaloids (% of total yield)			
		sparteine	lupanine	isolupanine	nuttalline
Aspalathus					
A. capitata	4	tr	tr	–	–
A. carnosa	2	–	–	–	–
A. chortophila	2	tr	tr	–	–
A. cordata	20	tr	tr	–	–
A. hirta	14	tr	tr	–	–
A. juniperina	17	tr	tr	–	–
A. linearis	3	tr	–	–	–
A. longifolia	4	tr	tr	–	–
A. nivea	2587	47	45	2	1
A. perfoliata	2	tr	tr	tr	–
A. spinosa	<1	tr?	–	–	–
Rafnia					
R. angulata	3	tr	tr	–	tr
R. capensis	10	tr?	–	–	–
R. elliptica	14	tr	tr	–	tr
R. opposita	12	tr	tr	–	–
R. perfoliata	9	tr	tr	–	–
R. racemosa	4	tr	tr	–	–
Wiborgia					
W. fusca	21	tr	tr	–	tr
W. obcordata (1)	15	tr	tr	–	tr
W. obcordata (2)	31	tr	tr	–	tr
W. obcordata (3)	26	tr	tr	–	tr
W. sericea	11	tr	tr	tr?	tr

Table 2 Distribution of alkaloids reported from the genera *Lebeckia, Wiborgia, Aspalathus, Rafnia, Pearsonia, Rothia, Lotononis* and *Crotalaria.* [Data for *Lebeckia* from van Wyk & Verdoorn (1989a), *Pearsonia* from van Wyk & Verdoorn (1989b), *Rothia* from Hussain *et al.* (1988) and *Lotononis* from van Wyk & Verdoorn (1989c)]

	Lebeckia	*Wiborgia*	*Aspalathus*	*Rafnia*	*Pearsonia*	*Rothia*	*Lotononis*	*Crotalaria*
Tetracyclic quinolizidine alkaloids:								
nuttalline	+++	tr	tr	tr	tr	+	+	
sparteine	+++	tr	+	tr	+		+	
lupanine	+++	tr	+	tr	++	++	tr	
isolupanine	+	tr?	tr		+	tr	tr	
Piperidyl alkaloids:								
ammodendrine	tr?	tr?	tr?	tr?	+	++	tr	
Esters of quinolizidine alkaloids:					++	++		
Macrocyclic pyrrolizidine alkaloids:							++	++

Occurs as a major component in: +++ all species/samples, ++ most species/samples, + at least some species/samples (tr = trace amount)

Pers., *Pearsonia* Dümmer, *Lotononis* (DC.) Eckl. & Zeyh. and *Crotalaria* L. have also been included but *Argyrolobium* Eckl. & Zeyh., *Dichilus* DC., *Melolobium* Eckl. & Zeyh. and *Polhillia* Stirton, all of which contain α-pyridone alkaloids such as cytisine, *N*-methylcytisine, anagyrine and thermopsine have been excluded from the comparison. The summary of available data in Table 2 leaves little doubt that *Aspalathus, Rafnia* and *Wiborgia* are more closely related to *Lebeckia* than to any of the other genera.

The alkaloid pattern shows a striking degree of conformity with presumed evolutionary trends based on morphological evidence. A relatively recent common ancestry with *Lebeckia* is suggested, and the subsequent divergence of *Aspalathus, Rafnia* and *Wiborgia* seems to have been accompanied by the almost complete absence of alkaloids.

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Appendix 1 Plant material of *Aspalathus, Rafnia* and *Wiborgia* used for alkaloid extraction. Voucher specimens are all in the Rand Afrikaans University Herbarium (JRAU)

Aspalathus capitata L.: Top of Constantiaberg, Cape Peninsula, *Van Wyk 2754; A. carnosa* Berg.: Top of Constantiaberg, Cape Peninsula, *Van Wyk 2152; A. chortophila* Eckl. & Zeyh.: Zuurberg National Park, E. Cape, *B. & M. Van Wyk 1436; A. cordata* (L.) Dahlg.: Between Constantiaberg and Vlakkenberg, Cape Peninsula, *Van Wyk 2759; A. hirta* E. Mey. subsp. *hirta*: N. side of Garcia's Pass, S. Cape, *Van Wyk 2802; A. juniperina* Thunb. subsp. *juniperina*: Near top of Constantiaberg, Cape Peninsula, *Van Wyk 2756; A. linearis* (Burm. f.) Dahlg.: Eselbank, Cedarberg, *Van Wyk 2829; A. longifolia* Benth.: Garcia's Pass, S. Cape, *Van Wyk 2799; A. nivea* Thunb.: Kabeljous River near Humansdorp, E. Cape, *Van Wyk 2813; A. perfoliata* (Lam.) Dahlg. subsp. *perfoliata*: Jonkershoek near Stellenbosch, *Van Wyk 2786; A. spinosa* L. subsp. *spinosa*: Top of Rooiberg Pass, Oudtshoorn district, *Van Wyk 2800.*

Rafnia angulata Thunb.: Somerset West, *Van Wyk 2788; R. capensis* (L.) Druce: Near top of Constantiaberg, Cape Peninsula, *Van Wyk 2757; R. elliptica* Thunb.: Zuurberg National Park, E. Cape, *B. & M. Van Wyk 615; R. opposita* Thunb.: Garcia's Pass, S. Cape, *Van Wyk 2798; R. perfoliata* E. Mey.: Jonaskop near Villiersdorp, *Van Wyk 2067; R. racemosa* Eckl. & Zeyh.: Between Seweweekspoort and Laingsburg, Cape, *Van Wyk 2171.*

Wiborgia fusca Thunb. subsp. *fusca*: 56 km from Cape Town on West Coast Road, *Van Wyk 2686; W. obcordata* Thunb.: Near Rondeberg farm on West Coast Road, *Van Wyk 2691* (sample 1), between Paarl and Wemmershoek, *Van Wyk 2678* (sample 2), at Eilandia, between Worcester and Robertson (sample 3); *W. sericea* Thunb.: Laingsburg, SW Cape, *Van Wyk 2193.*