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Chemotaxonomic Significance of Alkaloids in the Genus *Pearsonia*

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Key Word Index—*Pearsonia*; Leguminosae; Crotalarieae; quinolizidine alkaloids; novel esters of alkaloids; chemotaxonomy; generic relationships.

Abstract—The alkaloids of six species and subspecies of *Pearsonia* have been studied to provide data for comparisons with other genera. Four different esters of tetracyclic quinolizidine alkaloids were found to be the major compounds in most of the extracts. These were lupanine-13α-angelate and three hitherto unknown esters, namely cajanifoline (lupanine-3β-hydroxy-13α-angelate), sessilifoline (lupanine-3β-hydroxy-4α-angelate) and pearsonine (lupanine-3β,8α-dihydroxy-13α-angelate). Other major alkaloids were sparteine, α-isolupanine, lupanine, nuttalline and ammodendrine. Our results strongly support the present generic concept of *Pearsonia* and provide evidence for a close taxonomic affinity with the genus *Rothia*. In *Pearsonia*, however, the major components are esters of higher oxidized quinolizidine alkaloids than those of *Rothia*. The presence of esters of alkaloids in *Pearsonia* and *Rothia* is a unique character to distinguish them from all other genera of the tribe Crotalarieae and once again confirms the chemotaxonomic value of alkaloids as a generic character.

Introduction

The concept of the genus *Pearsonia* Duemmer was broadened by Polhill [1] to include a total of eleven suffrutescent papilionoid legumes from southern tropical Africa, central Africa and Madagascar. It is distinguished from *Lotononis* (DC.) Eckl. & Zeyh. by the highly modified flowers, but otherwise the two genera are very similar. The floral features of *Pearsonia* are also present in the small genus *Rothia* Pers. and the two genera are therefore considered to be closely related.

As part of our survey of alkaloids as a generic character in the tribe Crotolarieae, we studied the alkaloids of six species and subspecies of *Pearsonia*. Data was needed to find out if the presumed affinities and generic distinctions between *Pearsonia* and other recently investigated genera (*Rothia* [2], *Lotononis* [3] and *Lebeckia* Thunb. [4]) are supported by the alkaloidal evidence.

Results

Table 1 shows the total yields and distribution of alkaloids in seven extracts from four species and two subspecies of *Pearsonia*. Four different angelate esters of quinolizidine alkaloids occurred as major constituents in most of the extracts. These were identified as lupanine-13α-angelate (13α-angeloyloxylupanine) (**1**) and three hitherto unknown esters, namely cajanifoline (lupanine-3β-hydroxy-13α-angelate) (**2**), sessilifoline (lupanine-3β-hydroxy-4α-angelate) (**3**) and pearsonine (lupanine-3β,8α-dihydroxy-13α-angelate) (**4**). The relatively high yields enabled us to isolate these compounds and fully characterize them by spectroscopic methods, details of which will be published elsewhere (Verdoorn and Van Wyk, submitted for publication in *Phytochemistry*. Sparteine (**5**), 11-epi-lupanine (α-isolupanine) (**6**), lupanine (**7**), 4α-OH-lupanine (nuttalline) (**8**) and ammodendrine (**9**) were also identified as major alkaloids of most of the species. No evidence of α-pyridone alkaloids or pyrrolizidine alkaloids was found in any of the extracts.

Discussion

The pattern of alkaloids in Table 1, particularly the presence of angelate esters in all the extracts, shows that the present generic concept of *Pearsonia* has predictive value and that the transfer of *Pleiospora* Harv. to *Pearsonia* [1] was justified. (*Pleiospora cajanifolia* Harv., now known as *Pearsonia cajanifolia*, was previously considered to be generically distinct from

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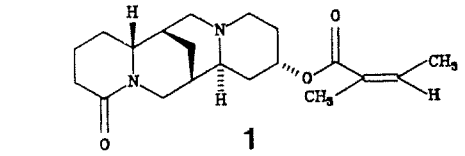
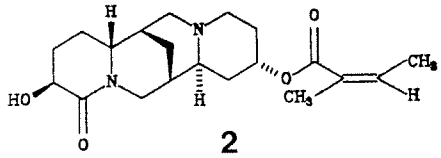


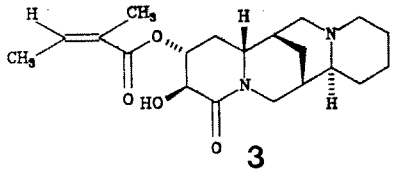
1

LUPANINE–13α–ANGELATE



2

CAJANIFOLINE



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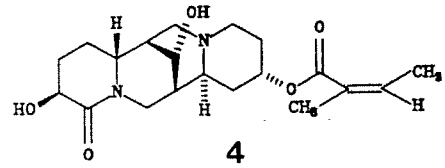
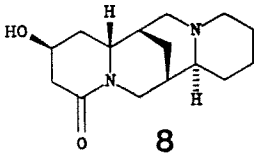
SESSILIFOLINE



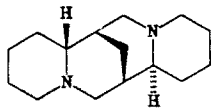
4

PEARSONINE



8

NUTTALLINE



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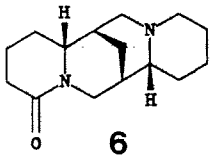
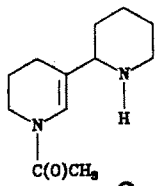
SPARTEINE



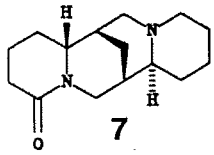
6

11–epi–LUPANINE



9

AMMODENDRINE



7

LUPANINE

Pearsonia). The relatively high yield figures indicate that a detailed study of alkaloids in the genus as a whole may provide interesting new taxonomic evidence about relationships between the species. It may also be worthwhile to study the variation in some of the species. The *Pearsonia sessilifolia* complex for example, is a variable aggregate which, until recently, comprised no less than eleven species. Large quantitative differences between the species and subspecies in Table 1 agrees with Polhill's [1] conclusion that *Pearsonia* is an exceptionally variable genus in some parts of its range.

At the generic level, the presence of esters of quinolizidine alkaloids is highly significant. These compounds, previously known only from a few genera of the tribes Sophoreae and Genisteae [5, 6], were recently also reported from the genus *Rothia* [2]. In the tribe Crotalarieae, *Rothia* and now also *Pearsonia* are therefore the only genera known to contain esters of tetracylic quinolizidine alkaloids. Esters of alkaloids were not found in *Lebeckia* [4] and those that occur in *Crotalaria* and *Lotononis* [3] are of the macrocyclic pyrrolizidine type. The idea that morphological similarities between *Pearsonia* and *Rothia* may be interpreted as indications of a common ancestry is therefore strongly supported by the alkaloidal metabolites. The major compounds of *Pearsonia* are esters of higher oxidized quinolizidine alkaloids than those of *Rothia*, suggesting that the divergence of the two genera may not have been very recent. A further difference is the apparent absence of tigliate- and other esters in *Pearsonia*.

Unfortunately, no information is available for the genus *Robynsiophyton* Wilczek. If the simi-

TABLE 1. DISTRIBUTION AND YIELDS OF MAJOR ALKALOIDS IN SIX SPECIES AND SUBSPECIES OF *PEARSONIA*

Species and subspecies	*P. aristata*	*P. cajanifolia* subsp. *cajanifolia*	*P. cajanifolia* subsp. *cryptantha*	*P. obovata*	*P. sesslilifolia* subsp. *marginata* sample 1	*P. sesslilifolia* subsp. *marginata* sample 2	*P. sessilifolia* subsp. *sessilifolia*
Total yield (mg/g dry wt)	0.728	1.691	0.908	0.547	0.488	0.472	0.850
Esters of quinolizidine alkaloids							
lupanine-13α-angelate	9	37	19	tr	12	tr	tr
cajanifoline*	—	55	40	43	tr	tr?	6
sessilifoline*	tr?	tr	11	tr?	62	tr	10
pearsonine*	—	4	28	tr?	tr	tr?	tr
Quinolizidine alkaloids							
sparteine	55	—	—	tr	tr	63	tr
α-isolupanine	3	1	tr	tr	15	tr	tr
lupanine	12	1	tr	2	tr	15	69
nuttalline	2	tr	tr	tr	4	3	tr
Piperidyl alkaloids							
ammodendrine	16	tr	tr	52	tr	2	tr

*New compounds (see Experimental section).

Figures given are percentages of the total yields as estimated from GC results. Authorities for names and voucher specimen details are given in the Experimental section.

larities with *Pearsonia* and *Rothia* [1, 7] are not merely a result of convergence, it is likely that this genus also contains lupanine-type esters. The distinct difference between the alkaloids of *Pearsonia* and those of *Lotononis* is particularly noteworthy. Although the two genera are morphologically very similar, the evidence presented here agrees with other distinctions based on floral morphology and chromosome cytology.

A summary of the differences between the above-mentioned genera of the Crotalarieae is shown in Table 2. From the distribution of major alkaloids, it may be concluded that most of the genera are related to *Lebeckia*, but that each of them has acquired a different biogenetic specialization. *Crotalaria* and *Lotononis* are distinct in the production of macrocyclic pyrrolizidine esters, while *Pearsonia* and *Rothia* share the unique ability to produce esters of quino-

TABLE 2. SUMMARY OF THE KNOWN DISTRIBUTION OF ALKALOIDS IN THE GENERA *CROTALARIA, LOTONONIS, LEBECKIA, ROTHIA* AND *PEARSONIA*

	Crotalaria	*Lotononis*	*Lebeckia*	*Rothia*	*Pearsonia*
Piperidyl alkaloids					
ammodendrine	—	tr	tr	**	*
Tetracyclic quinolizidine alkaloids					
sparteine	—	*	***	—	*
11-epi-lupanine	—	tr	*	tr	*
lupanine	—	tr	***	**	**
nuttalline	—	*	***	*	tr
Pyrrolizidine esters	**	**	—	—	—
Esters of quinolizidine alkaloids					
lupanine-13α-angelate	—	—	—	*	*
other angelate esters	—	—	—	—	**
tigliate- and various other esters	—	—	—	**	—

Occurs as a major component in: *** all species/samples, ** most species/samples, * at least some species/samples.

lizidine alkaloids. The results clearly demonstrate the chemotaxonomic value of alkaloids as a generic character in the tribe Crotalarieae.

Experimental

Plant materials. Voucher specimens representing the material used for extraction have been deposited in the Rand Afrikaans University Herbarium (JRAU). The taxa studied and voucher specimen details are given below.

Pearsonia aristata (Schinz) Duemmer: Roodepoort, near Botanical Garden, *Schutte 382*; *P. cajanifolia* (Harv.) Polhill subsp. *cajanifolia*: 26,4 km from Bronkhorstspruit on Rust De Winter Road, Van Wyk 2733; *P. cajanifolia* (Harv.) Polhill subsp. *cryptantha* (Bak.) Polhill: Magaliesberg, Scheerpoort area, *Verdoorn 3*; *P. obovata* (Schinz) Polhill: 18 km from Nelspruit on Kaapsehoop Road, Van Wyk 1864; *P. sessilifolia* (Harv.) Duemmer subsp. *marginata* (Schinz) Polhill, sample 1: Ngodwana River at intersection of N1 route, Van Wyk 2814, sample 2: 18 km from Nelspruit on Kaapsehoop Road, Van Wyk 1863; *P. sessilifolia* (Harv). Duemmer subsp. *sessilifolia*; Roadside between Bapsfontein and Bronkhorstspruit, Van Wyk 2728.

Procedures. Ground air-dried leaves and twigs were extracted by refluxing with CH_2Cl_2 for several days. Alkaloidal extracts were obtained by water phase separation [3, 4, 8] and purified by filtration through celite. Isolation of the four esters was effected by silica gel 60 column chromatography with $CHCl_3$–cyclohexane–Et_2N (14:4:1) as eluent.

Alkaloids were identified by comparative TLC, as described elsewhere [8], combined with comparative GC using authentic reference samples obtained in previous studies [3, 4, 9]. GC spectra were obtained with an SE-30 capillary glass column (25 m × 0.25 mm; N_2 as carrier gas at 0.5 kg/cm^2, column temperature 250°C isotherm; injector 300°C; FID 275°C). The identity of the major alkaloids was confirmed by GC–MS analyses of two extracts (*P. cajanifolia* subsp. *cajanifolia* and *P. sessilifolia* subsp. *marginata*, sample 2). The mass spectra of the various alkaloids were identical to those obtained in several other studies. Large-scale extractions of the following species yielded pure samples of the ester compounds: *P. cajanifolia* subsp. *cajanifolia*; 47 mg of **1** and 54 mg of **2**; *P. cajanifolia* subsp. *cryptantha*: 380 mg of **1**, 800 mg of **2**, 220 mg of **3** and 560 mg of **4**; *P. sessilifolia* subsp. *marginata* (sample 1): 17 mg of **3**. These compounds were identified by MS, ^1H and ^{13}C NMR, including various 1D and 2D experiments. The results of the NMR studies will be published elsewhere as a detailed chemical report [Verdoorn and Van Wyk, *op cit.*].

Esters of quinolizidine alkaloids. Lupanine-13α-angelate (13α-angeloyloxylupanine) (**1**): *Rt* 17.10 M^+ 346. Cajanifoline (lupanine-3β-hydroxy-13α-angelate) (**2**): *Rt* 19.50, pale yellow crystals, m.p. 87–91°C, $[\alpha]_D^{22}$—11° (c=1,4 in $CHCl_3$), ν_{max} 3400br (OH) 1640 (lactam C=O) cm^{-1}; MS *m/z* 362 (5), 277 (7), 262 (100), 246 (23), 234 (7), 205 (3), 186 (9), 165 (7), 148 (24), 134 (60), 122 (23), 108 (15), 91 (57), 69 (23), 55 (39). Sessilifoline (lupanine-3β-hydroxy-4α-angelate) (**3**): *Rt* 17.80, pale brown oil, $[\alpha]_D^{22}$—72° (c=1,6 in $CHCl_3$), ν_{max} 3400br (OH) 1640 (lactam C=O) cm^{-1}; MS *m/z* 362 (20), 279 (4), 263 (100), 245 (60), 233 (3), 221 (2), 205 (3), 191 (1), 177 (3), 163 (6), 148 (27), 136 (54), 122 (8), 110 (17), 98 (31), 84 (23), 67 (11), 55 (43). Pearsonine (lupanine-3β,8α-dihydroxy-13α-angelate) (**4**): *Rt* 20.65, pale yellow crystals, m.p. 93–96°C, $[\alpha]_D^{22}$+7°C (C=0,6 in $CHCl_3$), ν_{max} 3400br (OH) 1640 (lactam C=O) cm^{-1}; MS *m/z* 378 (25), 363 (9), 295 (6), 278 (100), 262 (29), 246 (12), 206 (6), 193 (5), 183 (19), 164 (15), 150 (28), 147 (28), 134 (24), 108 (18), 96 (20), 82 (31), 67 (21), 55 (42).

Quinolizidine alkaloids. Sparteine (**5**): *Rt* 7.45, M^+ 234; 11-epi-lupanine (α-isolupanine) (**6**): *Rt* 10,64, M^+ 248; lupanine (**7**): *Rt* 11.40, M^+ 248; nuttalline (**8**) *Rt* 12.96, M^+ 264.

Piperidyl alkaloids. Ammodendrine (**9**): *Rt* 6.85, M^+ 208.

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