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Alkaloids of the Genera *Dicraeopetalum, Platycelyphium* and *Sakoanala*

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Key Word Index—*Dicraeopetalum*; *Platycelyphium*; *Sakoanala*; Leguminosae; Sophoreae; quinolizidine alkaloids; chemotaxonomy.

Abstract—The presence of alkaloids in *Dicraeopetalum*, *Platycelyphium* and *Sakoanala* (Fabaceae, tribe Sophoreae) is reported for the first time. All three of these genera have a typical α-pyridone pattern, with *N*-methylcytisine, cytisine, *N*-formylcytisine, *N*-acetylcytisine, 5,6-dehydrolupanine, lupanine, anagyrine, baptifoline and epibaptifoline as major alkaloids. Other compounds that were identified include the bicyclic quinolizidines lupinine and epilupinine and the bipiperidyl alkaloid ammodendrine. The discovery of α-pyridone alkaloids in *Dicraeopetalum* in particular, has important taxonomic implications and casts further doubt on the monophyly of the *Cadia* group. *Dicraeopetalum* (and *Lovanafia*) may be better placed in the *Sophora* group, close to *Neoharmsia*, *Sakoanala* and *Bolusanthus*, thereby amalgamating all the Old World sophoroid genera with recaulescent bracts and α-pyridone alkaloids.

Introduction

The Sophoreae are generally regarded as one of the basal groups of papilionoid legumes (Hutchinson, 1964; Polhill, 1981), from which several independent lineages have evolved. If this is true, then much can be learnt about the evolution of quinolizidine alkaloids by studying the patterns within the Sophoreae. Many different compounds have indeed been reported from several genera of the tribe, but the data is still too meagre to allow for a rigorous comparison at the generic level. To add to the knowledge of quinolizidine alkaloid distributions in the Sophoreae, three important new generic records are given here.

Materials and Methods

Plant materials. Small samples of aerial parts were obtained from the following herbarium specimens. *Dicraeopetalum stipulare* Harms (leaves, 283 mg): *Gillet* and *Hemming 24738* (K). *Platycelyphium voense* (Engl.) Willd. (leaves, 254 mg; immature seed, 34 mg; mature seed, 258 mg): *Greenway 2046* (K). *Sakoanala villosa* R. Vig. (sample, 1, leaves, 80 mg): *Capuron 24450* (K); (sample 2, flowers, 83 mg): *Gentry 11934* (K).

Procedures. Finely ground material was extracted with 20 ml 0.05 M H_2SO_4 according to standard procedures described elsewhere (e.g. Van Wyk *et al.*, 1992), taking care to avoid all possible sources of contamination. The alkaloidal extracts were dissolved in minimum MeOH and studied by comparative GC and GC–MS. For GC studies we used 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°min $^{-1}$, 15 min isotherm; injector 230°C; PND detection 300°C; split ratio 30:1; injection volume 1 μl). The three leaf samples showed the largest diversity and were therefore chosen to be studied by GC–MS under the following conditions: DB-1 fused silica capillary column (30 m×0.32 mm i.d.; He as carrier gas; column temperature 150–300°C at 6° min $^{-1}$, split ratio 20:1; injection volume 1 μl). Authentic reference samples from several previous studies were available to us (Greinwald *et al.*, 1990a,b,c, 1991; Van Wyk *et al.*, 1988a,b,c) and comparisons with literature data (Neuner-Jehle *et al.*, 1964; Schumann *et al.*, 1968) allowed the positive identification of all the major and minor compounds by their retention indices (RI) and mass spectra. Trace quantities of some unknown alkaloids have been detected by GC–MS (see summary of results in Table 1) but due to the extremely low quantities of material, it was not possible to identify them by

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TABLE 1. DISTRIBUTION OF ALKALOIDS IN EXTRACTS FROM *DICRAEOPETALUM STIPULARE, PLATYCELYPHIUM VOENSE* AND *SAKOANALA VILLOSA*. Alkaloid distributions are given as percentages of total yield, as estimated from GC results using peak area and 4 mg ml^{-1} sparteine as external standard (– = not detected; + = present in trace amounts only, i.e. less than 0.5% of total yield)

		Dicraeopetalum stipulare	**Platycelyphium voense**			**Sakoanala villosa**	
Alkaloids	Retention index (RI)	1 leaves	2a leaves	2b immature seed	2c mature seed	3a leaves	3b flowers
epilupine	1418	**1**	–	–	–	+	+
lupanine	1420	**3**	–	–	–	–	–
sparteine	1780	+	–	–	–	–	–
β-isosparteine	1830	+	–	–	–	–	–
***N*-methylammodendrine**	1833	–	–	–	–	+	**1**
X1	1838	–	–	–	–	+	+
ammodendrine	1863	+	**2**	+	+	**73**	**39**
lusitanine	1880	+	–	–	–	–	–
X2	1907	+	+	–	+	–	–
dehydroammodendrine	1932	–	–	–	–	+	+
X3	1938	–	–	–	–	+	+
***N*-methylcytisine**	1953	**14**	**6**	**3**	**21**	**3**	**13**
X4	1968	+	+	+	–	+	+
X5	1983	+	+	+	–	+	+
cytisine	1987	**30**	**39**	**80**	**75**	**21**	**38**
X6	2035	–	–	–	–	+	+
camoensidine	2075	–	–	–	–	+	–
α-isolupanine	2100	+	**1**	+	+	+	
5,6-dehydrolupanine	2127	**6**	**3**	**5**	+	+	+
rhombifoline	2150	+	+	–	–	–	–
lupanine	2160	+	**4**	**1**	**2**	+	+
N-formylammodendrine	2206	–	–	–	–	+	+
X7	2212	–	+	–	–	–	–
***N*-formylcytisine**	2315	**7**	**6**	**7**	+	**2**	**4**
***N*-acetylcytisine**	2323	**3**	**3**	**1**	+	**1**	**2**
X8	2358	–	+	+	–	+	+
X9	2368	–	+	+	–	+	+
anagyrine	2377	**5**	**8**	**2**	**1**	+	+
X10	2560	–	+	–	–	–	–
baptifoline	2630	**31**	**5**	+	+	+	**2**
epibaptifoline	2650	+	**23**	**1**	**1**	+	**1**
estimated total yield (mg g^{-1})		**1.3**	**2.8**	**6.6**	**9.9**	**7.5**	**4.8**

spectroscopic methods. The mass spectral data of the unknown trace compounds are recorded below so as to facilitate future studies (for RI values (see Table 1).

XI (dehydroammodendrine isomer?): 206 (65), 163 (100), 121 (24), 107 (50). X2 (tetrahydrocytisine isomer?): 194 (63), 151 (15), 136 (30), 112 (22), 110 (19), 96 (38), 97 (100), 95 (67), 84 (38), 83 (50), 55 (33). X3: 208 (10), 180 (9), 150 (8), 108 (7), 98 (47), 97 (61), 84 (100). X4 (dehydrocytisine A): 188 (76), 160 (33), 148 (62), 134 (100). X5 (dehydrocytisine B): 188 (56), 173 (3), 160 (6), 147 (47), 146 (100), 134 (8), X6: 236 (83), 207 (50), 193 (42), 179 (27), 163 (100), 136 (60), 122 (50), 110 (55), 94 (35), 80 (38). X7: 244 (23), 203 (89), 146 (14), 134 (21), 122 (18), 98 (28), 82 (100). X8: 274 (3), 203 (100), 190 (2), 160 (17), 134 (10), 58 (42). X9: 274 (1), 203 (100), 160 (15), 58 (43). X10: 260 (75), 190 (14), 161 (32), 160 (17), 146 (53), 114 (100), 93 (30).

Results

The alkaloid patterns of the three genera are summarised in Table 1. All the extracts have the same basic combination of α-pyridone alkaloids structurally related to anagyrine, *N*-methylcytisine and cytisine. *Sakoanala* differs from the other two genera in the presence of ammodendrine as a second major alkaloid besides cytisine. All the extracts also have a large number of minor alkaloids such as epilupinine, lupinine, *N*-methylammodendrine, α-isolupanine, 5,6-dehydrolupanine, lupanine, *N*-

formylcytisine, *N*-acetylcytisine, anagyrine, baptifoline and epibaptifoline. Several alkaloids occur in extremely low concentration and have been detected and studied by GC and GC–MS. Mass spectral data of these trace compounds are given in the Materials and Methods section.

Discussion

Polhill (1981) called the Sophoreae "a tribe of convenience" and it seems unlikely that the group is monophyletic (Hutchinson, 1964; Yakovlev, 1972, 1975; C. H. Stirton, personal communication). A broad division of the tribe into two major lineages, the one culminating in the genistoid alliance and the other in the galegoid complex, has been proposed by Senn (1938), Turner and Fearing (1959), Mears and Mabry (1971) and Polhill (1981), based on chromosomal and chemical evidence. The data presented here suggest that the cleavage may extend further than is generally considered, namely right back to the genera without a distinct papilionoid corolla. The presence of quinolizidine alkaloids in *Dicraeopetalum* places it in the genistoid lineage, where such alkaloids are highly characteristic. The implication is that the *Cadia* group is also not monophyletic and that the homology of actinomorphic corollas should be carefully re-examined.

Dicraeopetalum is considered to be closely related to the genus *Lovanafia* (Polhill, 1981) and both have recaulescent bracts, a character which occurs elsewhere only in the first three genera of the *Sophora* group (see Polhill, 1981). The transfer of *Dicraeopetalum* (and *Lovanafia*) to the beginning of the *Sophora* group would thus amalgamate all the Afro-Madagascan genera with recaulescent bracts and α-pyridone alkaloids. In the same way, it may be sensible to remove the genus *Cadia* (and *Calpurnia*) to the base of the tribe Podalyrieae, thereby uniting all the genera with carboxylic acid esters of quinolizidine alkaloids. These rearrangements would lead to a chemically more uniform *Sophora* group. Since *Sakoanala* and *Platycelyphium* are here added to the list of genera accumulating α-pyridone alkaloids, these compounds may now be regarded as a diagnostic character for the *Sophora* and *Camoensia* groups. A recent study of the alkaloids of *Maackia tashiroi* (Ohmiya *et al.*, 1991) has shown distinct similarities with *Camoensia*, thereby further reducing the apparent isolation of *Camoensia* from the *Sophora* group.

Chemical data from alkaloidal metabolites tends to agree rather than conflict with morphological and chromosomal information and provides more and more evidence for several independent phyletic lines within the tribe Sophoreae.

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