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ALKALOID DISTRIBUTION IN SOME SPECIES OF THE PAPILIONACEOUS TRIBES SOPHOREAE, DALBERGIEAE, LOTEAE, BRONGNIARTIEAE AND BOSSIAEEAE*

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Key Word Index—Papilionoideae; tribes Sophoreae, Dalbergieae, Loteae, Brongniartieae, Bossiaeeae; Leguminosae; chemotaxonomy; quinolizidine alkaliods; 11-epileontidane; 11,12-dehydrosparteine.

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Abstract—Quinolizidine and dipiperidine alkaloid profiles have been determined for various plant parts of ten papilionaceous species in the tribes Sophoreae, Dalbergieae, Brongniartieae and Bossiaeeae. Alkaloids have been identified for the first time from species in the tribes Dalbergieae (*Dalbergia monetaria*) and Brongniartieae (*Harpalyce formosa* var. *formosa*) of Polhill's classification system of the Papilionoideae. No alkaloids were detected in seeds of several *Lotus* species (tribe Loteae). Quinolizidine–indolizidine alkaloids of the leontidine type, including 11-epileontidane, a new compound, were obtained from the leaves and stems of *Maackia amurensis*. 11,12-Dehydrosparteine, a compound which has not previously been characterized as a natural product, was observed in an extract of the stems of *Templetonia egena*.

INTRODUCTION

Quinolizidine alkaloids are considered important systematic markers for species in the more primitive tribes of the legume subfamily Papilionoideae [1–6]. There appears to be a notable increase in the complexity and number of these compounds in temperate papilionates occurring in the Northern Hemisphere, compared with their occurrence in tropical representatives of the subfamily [5, 6]. Over 120 quinolizidine alkaloids from legumes have been structurally characterized and found to occur in more than 35 genera in nine tribes of the Papilionoideae, as reclassified recently by Polhill [5, 6].

In the present contribution we have extended work performed by our group on legume quinolizidine alkaloids [6–10] to certain species in the tribes Sophoreae, Dalbergieae, Loteae, Brongniartieae and Bossiaeeae of the Papilionoideae. Plant material used in this study was either in the form of extracts from species originally collected for anticancer screening under the auspices of the National Cancer Institute, Bethesda, Maryland, or was provided as seeds from herbarium collections. Alkaloid identifications were carried out using a combination of GC/MS and TLC. GC/MS has been used in several laboratories as a precise qualitative microanalytical method for the study of legume alkaloids [8, 11–14].

RESULTS AND DISCUSSION

A total of 22 alkaloids were unambiguously identified in extracts of various plant parts of 10 papilionates in the tribes Sophoreae, Dalbergieae, Brongniartieae, and Bossiaeeae, as shown in Table 1. The genera are listed in tribes according to the scheme of Polhill [5]. Compounds are grouped into classes representative of their postulated order of biogenetic advancement [4, 15] and structural complexity as follows: (1) the dipiperidine alkaloid, ammodendrine; (2) the bicyclic quinolizidine alkaloid, epilupinine; (3) tetracyclic quinolizidine–indolizidine alkaloids of the leontidine type; (4) tetracyclic quinolizidine alkaloids of the sparteine–lupanine type; (5) tricyclic degradation products of the alkaloids in (4); (6) pyridone quinolizidine bases; (7) the quinolizidine alkaloid, matrine; and (8) pentacyclic and hexacyclic *Ormosia*-type quinolizidine alkaloids.

Altogether 47 alkaloidal identifications, not previously associated with the species listed in Table 1, were made. No attempt was made to quantitate the alkaloids identified, since much of the plant material studied was supplied in the form of extracts. Of the species and varieties listed in Table 1, alkaloid data in regard to only *Sophora microphylla* [16–18] and *Templetonia egena* [19] have appeared in the literature before, although alkaloids of *Sophora chrysophylla* [20, 21] and *Ormosia coccinea* [22] have also been studied. Our results in the main confirm these prior identifications, with the exceptions being that sophoramine was absent from the two *Sophora* species studied; pohokaline and mamanine were not observed in *S. chrysophylla* subsp. *glabrata* var. *grisea* subvar. *ovatifoliolata*, and ormosinine was not detected in *O. coccinea* var. *subsimplex*.

Compound identification was performed by comparison (GC/MS, TLC) with authentic samples obtained either by isolation from other legumes, partial synthesis, or donation from other workers. Two compounds were identified for the first time as natural products in the legume extracts under study,

*Part 1 in the series "Alkaloids of Papilionoideae".

Table 1. Quinolizidine alkaloids of some Papilionaceous species*

Tribe/species code†/ collection location and date	Plant part‡	Ammodendrine	Epilupinine	Camoensidine	11-Epileontidane	Tetrahydroleontidine§	11,12-Dehydrosparteine	Sparteine	β-Isosparteine	Lupanine	5,6-Dehydrolupanine	13-Hydroxylupanine	13-Epihydroxylupanine	13-Epimethoxylupanine	Angustifoline	Tetrahydrorhombifoline	11-Oxotetrahydrorhombifoline§	Anagyrine	Rhombifoline§	Cytisine	N-Methylcytisine	N-Formylcytisine	N-Acetylcytisine	Matrine	Ormosanine	Panamine	$C_{20}H_{33}N_3$‖	$C_{20}H_{35}N_3$‖	$C_{21}H_{33}N_3$‖	$C_{21}H_{35}N_3$‖	Unknown
		1	2	3						4					5					6				7			8				
Sophoreae																															
A, Peru, 6/72	If(F1)														+																0
A, Peru, 8/72	If									+					+					+											0
B, Sri Lanka, 4/72	Sd										+			+																	0
C, Peru, 8/72	Sb								+																						0
C, Peru, 8/72	Fr	+								+			+		+											+					3
D, Puerto Rico, 2/67	St, Lf									+		+					+									+					1

E, Maryland, 10/61	St, Lf	+		+	+	+		+	+	+				+	+	+	+	+	+			3
E, California,—	Ws, St			+												+	+					0
F, Kauai, Hawaii, 7/73	Lf, St, Fr								+	+							+			+		0
G, New Zealand, 7/72	Tw													+		+	+	+		+		0
G, New Zealand, 7/72	Fr	+												+	+	+	+	+		+		3
Dalbergieae																						
H, Peru, 8/72	Rt												+									0
H, Peru, 8/72	Sb								+		+	+	+									0
Brongniartieae																						
I, Oaxaca, Mexico, 3/66	St, Lf, Fl		+														+					2
Bossiaeeae																						
J, South Australia, 5/63	St	+	+			+	+		+	+				+		+	+	+			+	0

*Classified according to Polhill [5].

†Key to species investigated: A, *Diplotropis martiusii* Benth.; B, *Pericopsis mooniana* Thw.; C, *Ormosia coccinea* (Aubl.) G. Jacks. var. *subsimplex* (Spruce ex Benth.) Rudd; D, *O. krugii* Urban; E, *Maackia amurensis* Rupr. and Maxim.; F, *Sophora chrysophylla* (Salisb.) Seem. ssp. *glabrata* (Gray) Chock var. *grisea* (Degen. & Sherff) subvar. *ovatifoliolata* Chock; G, *S. microphylla* Ait.; H, *Dalbergia monetaria* L. fil.; I, *Harpalyce formosa* Noc. and Sesse ex DC. var. *formosa* (*H. loesneriana* Taub.); J, *Templetonia egena* (F. Muell.) Benth.

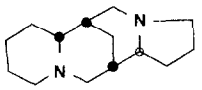
‡Key to plant parts examined: Fl, flower; Fr, fruit; If, inflorescence; Lf, leaf; Rt, root; Sb, stem bark; Sd, Seed; St, stem; Tw, twig; Ws, stem wood.

§Tentative identification.

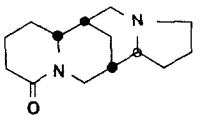
‖*Ormosia*-type quinolizidine alkaloid molecular formula.

11-epileontidane (**1**), a minor constituent of the leaves and stems of *Maackia amurensis*, and 11,12-dehydrosparteine (**5**), from the stems of *Templetonia egena*. The structure of **1**, a new compound, was confirmed by direct GC/MS and TLC comparison with the reduction product of camoensidine (**2**) using lithium aluminum hydride. Camoensidine (**2**) was found to be a major constituent of both extracts of *M. amurensis* studied, and it may be seen that compounds **1** and **2** are quinolizidine–indolizidine analogues, respectively, of the common lupine quinolizidine alkaloids, sparteine and lupanine. The trivial nomenclature we propose for **1** was chosen because its epimer, leontidane (**3**) has previously been partially synthesized from tetrahydroleontidine (**4**) [23].

The structural assignment of 11,12-dehydrosparteine (**5**) from the stems of *T. egena*, was achieved by GC/MS comparison of this constituent in the plant extract with samples of the compound partially synthesized from sparteine by reaction with both *N*-bromosuccinimide and potassium permanganate. These reagents are known to oxidize the *cis*-quinolizidine moiety (C/D ring) of sparteine, leading to the formation of several products, including sparteine-N_{16}-oxide, 17-hydroxysparteine, 17-oxosparteine, as well as 11,12-dehydrosparteine (**5**), itself [24–28]. It must, however, be pointed out **5** may be formed



1



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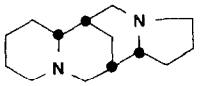

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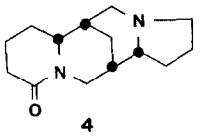

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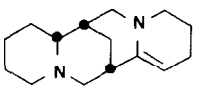

5

by thermal decomposition of sparteine-N_{16}-oxide under the GC conditions used [29, 30]. Recently, a dehydrosparteine was observed by GC/MS of an alkaloidal extract of *Lupinus polyphyllus* cell culture fed cadaverine [31]. The tentative structural assignment of this compound as 12,13-dehydrosparteine was based on the similarity of its mass spectrum with that of epiretamine (12α-hydroxysparteine) [31]. However, it may be suggested that epiretamine, on dehydration, would produce the more highly-favored enamine, **5** (11,12-dehydrosparteine) rather than the postulated olefin (12,13-dehydrosparteine) [31]. Since the dehydrosparteine in *L. polyphyllus* exhibited a mass spectrum in close correspondence to that we obtained for **5**, its tentative structural assignment [31] may be erroneous.

Three compounds for which no authentic samples were available were tentatively identified in the present study, namely, rhombifoline, 11-oxotetrahydrorhombifoline and tetrahydroleontidine (**4**). Rhombifoline was observed in extracts of *Maackia amurensis* and *Sophora chrysophylla* subsp. *glabrata* var. *grisea* subvar. *ovatifoliolata*, while 11-oxotetrahydrorhombifoline occurred in an extract of *Ormosia krugii* (Table 1). These compounds were identified on the basis of favorable comparison with published mass spectral data [32, 33]. In the case of rhombifoline, no other stereoisomers are possible, so this identification seems firm. 11-Oxotetrahydrorhombifoline has previously been recorded only once as a plant constituent, also in an *Ormosia* species [33]. A compound tentatively identified as tetrahydroleontidine (**4**) was found to co-occur with camoensidine (**2**) in a leaf-stem extract of *M. amurensis*. Both **2** and **4** exhibited identical mass spectra, with the latter alkaloid occurring in trace quantities and possessing a shorter retention time by GC/MS than camoensidine (**2**). Since it is known for lupine quinolizidine alkaloids that *cis,cis*-isomers have shorter column residence times during GC than their corresponding *cis,trans*-isomers [7, 13], it may be reasoned that tetrahydroleontidine (**4**) has a shorter retention time by GC than its C-11 epimer, camoensidine (**2**). The compound tentatively identified herein as tetrahydroleontidine (**4**) exhibited a closely comparable mass spectrum to published mass spectral data [23]. This compound does not appear to have been found as a legume constituent before, and is the C/D indolizidine analog of α-isolupanine.

Ormosia-type quinolizidine alkaloids were found in extracts of *O. coccinea* var. *subsimplex*, *O. krugii* and *Templetonia egena* (Table 1). Two representatives of this series, ormosanine and panamine, were identified in extracts by direct comparison (GC/MS, TLC) with authentic samples (Table 1). Ormosanine was differentiated from one of its stereoisomers, templetine, by GC/MS of their respective homo derivatives, prepared by reaction with formaldehyde, since it is known that such aminal derivatives are easier to separate than the parent bases [34]. The remaining *Ormosia* quinolizidine alkaloids present in these extracts are expressed in Table 1 according to the carbon skeleton represented by each alkaloid, since we have not found significant differences in fragment peak relative abundance to be apparent in *Ormosia* alkaloid stereoisomers with a common carbon skeleton [35]. Aminal *Ormosia* alkaloids with the molecular formula $C_{21}H_{33}N_3$ were detected in extracts of both *Ormosia* species under investigation. Although such compounds are heretofore unknown as natural products [1, 4, 6], paucity of plant material precluded their further study at this time.

The potential systematic value of the results expressed in Table 1 will be discussed in turn for the tribes represented. The occurrence of quinolizidine–indolizidine alkaloids of the leontidine type in *Maackia amurensis* extracts (Table 1) represents only the second identification of such compounds in the Papilionoideae, with camoensidine (**2**) and two related compounds having previously been isolated from *Camoensia maxima* [36], which is also in the tribe Sophoreae. While pyridone quinolizidine–indolizidine bases were identified in *C. maxima* [36], none was

detected in the leaf–stem extract of *M. amurensis* studied here, even though six pyridone quinolizidine bases were found to be present (Table 1). It may be noted that a clear divergence was observed in the propensity of species studied in the Sophoreae to accumulate in a mutually exclusive fashion either pyridone bases (e.g. *M. amurensis* and the two *Sophora* species studied) or non-pyridone tricyclic sparteine–lupanine degradation products (e.g. *Diplotropis martiusii* and the two *Ormosia* species studied) (Table 1). Matrine- and *Ormosia*-type quinolizidine alkaloids were restricted to species in the genera *Sophora* and *Ormosia*, respectively, in this tribe (Table 1), as observed previously [1, 6].

Alkaloids have not been identified prior to the present study in any species in the tribes Dalbergieae and Brongniartieae, as grouped in Polhill's classification system [5, 6]. The quinolizidine alkaloids listed in Table 1 in the tropical species *Dalbergia monetaria* occurred as trace constitutents in the root bark and stem bark, and were not present in other plant parts (twigs, leaves) collected at the same time and location. Alkaloids were found to be absent from other species in the genus that were also studied, namely, *D. sissoo*, *D. ecastaphyllun* and *D. variabilis*, so our positive alkaloidal identifications for *D. monetaria* appear to be unusual for the genus *Dalbergia*. The identification of quinolizidine alkaloids in *Harpalyce formosa* var. *formosa* (syn. *H. loesneriana*) (tribe Brongniartieae) is perhaps not so surprising because of the close affinity of this tribe with the tribe Bossiaeeae [37]. Species in the latter tribe are known to biosynthesize quinolizidine alkaloids [6], as exemplified further by our results in this study on *T. egena* (Table 1). It is significant that *Ormosia*-type quinolizidine alkaloids were detected in this study in a second *Templetonia* species, although (−)-templetine, originally isolated from *T. retusa* [38], was absent from the *T. egena* extract we examined.

A number of *Lotus* species (seeds) (tribe Loteae) were investigated for the presence of alkaloids in this study, in an attempt to assess a report claiming the identification of quinolizidine alkaloids in *L. aegeus* [39]. While the negative data in the present study do not invalidate the results of Mollov *et al.* [39], since *L. aegeus* was not among the species studied, it would seem that quinolizidine alkaloids are not typical constituents of species in the genus *Lotus*.

EXPERIMENTAL

^{1}H NMR: 60 MHz, $CDCl_3$; MS:70 eV; GC/MS: Varian MAT 112S, with Varian 166 data system, 70 eV, Varian 1440 gas chromatograph. TLC carried out on Si gel GHLF (Analtech, Newark, Delaware) with Dragendorff's as visualizing reagent.

Plant material. Seeds of *Pericopsis mooniana* Thw., *Lotus angustissimus* L., *L. conimbricensis* Brot., *L. cytisoides* L., *L. edulis* L., *L. peregrinus* L. and *L. uliginosus* Schkuhr were generously provided by Dr. R. M. Polhill, Royal Botanic Gardens, Kew, Surrey. All other plant materials were supplied in the form of lyophilized 80% EtOH extracts through the Developmental Therapeutics Program (Natural Products Branch) of the National Cancer Institute, formerly the Cancer Chemotherapy National Service Center, Bethesda, Maryland. Specimens representing the collection of such plant materials are deposited at the Herbarium of the National Arboretum, Agricultural Research Service, U.S. Department of Agriculture, Washington, DC.

Chromatographic methods. GC/MS was performed on a 2 m × 3 mm glass column packed with 3% OV-17 on Gas Chrom Q, according to published conditions [9]. TLC: S_1, MeOH–28% NH_4OH (131:2); S_2, $CHCl_3$–MeOH–28% NH_4OH (85:15:1); S_3, C_6H_{12}–diethylamine (7:3).

Reference alkaloids. Authentic samples of the following alkaloids, in the form of salts or free bases, were available to us, as described previously [7–9]: ammodendrine, angustifoline, anagyrine, cytisine, 5,6-dehydrolupanine, epilupinine, 13-hydroxylupanine, α-isolupanine, β-isosparteine, lupanine, lupinine, *N*-methylcytisine, sparteine, tetrahydrorhombifoline and thermopsine. Certain other reference compounds, namely, camoensidine, α-isosparteine, matrine, ormosanine, ormosinine, panamine diperchlorate and templetine were also kindly donated by other workers. Other authentic samples were generated by partial synthesis as follows:

N-Acetylcytisine and *N*-formylcytisine were prepared by refluxing cytisine with Ac_2O and 98% HCO_2H, respectively, according to published reaction conditions [40, 41]. 13-Epihydroxylupanine (jamaidine) was purified by prep. TLC in S_2 of the alkaloidal extract of *Ormosia coccinea* var. *subsimplex* (R_f 0.43); ^{1}H NMR: 1.0–3.2 (21 H, *m*), 3.55 (H, *br m*, H-13ax.), 3.87 (1H, *br s*, OH), 4.54 (1H, *br d*, $J_2 = -13$ Hz, H-10eq.). 13-Epimethoxylupanine was obtained from angustifoline by a known procedure using formaldehyde in MeOH, under acidic conditions [42]. 11-Epileontidane (**1**) was produced in low yield by refluxing camoensidine (**2**, 5 mg) with $LiAlH_4$ in dry Et_2O for 5 hr. 11,12-Dehydrosparteine (5,6-dehydro-α-isosparteine) (**5**) was produced by two procedures. Firstly, an aq. soln of sparteine sulfate was treated with $KMnO_4$ [28] for 4 hr. On work-up, **5** was obtained along with starting material and 17-oxosparteine. Secondly, **5** was generated as a low-yield reaction product by oxidation of sparteine (75 mg) with *N*-bromosuccinimide (70 mg) in CH_2Cl_2 for 3 min, with subsequent work-up [24].

Extraction of plant material and identification of alkaloids. Crude alkaloid fractions were obtained as previously described [7–9], and each was subjected without preliminary prep. TLC to GC/MS and TLC in S_1–S_3. The following compounds in the extracts (Table 1) were identified by direct comparison (RR_t to lupanine, MS, R_f) to authentic alkaloids: Dipiperidine alkaloid, ammodendrine, RR_t: 0.58; MS: *m/z*, 208 $[M]^+$ [43]; R_f: S_1–S_3 [8]. Quinolizidine alkaloids, *N*-Acetylcytisine, RR_t: 1.45; MS: *m/z*, 232 $[M]^+$ [40]; R_f: S_1 0.41, S_2 0.48. Anagyrine, RR_t: 1.36: MS; *m/z*, 244 $[M]^+$ [32]; R_f: S_1–S_3 [8]. Angustifoline, RR_t: 0.96; MS: *m/z*, 234 ($[M]^+$ missing), 193 [32]; R_f: S_1–S_2 [8]. Camoensidine (**2**), RR_t: 0.93; MS: *m/z* 234 $[M]^+$ (52), 233 (44), 149 (14), 136 (59), 135 (56), 134 (22), 122 (100), 120 (27), 110 (21), 96 (39), 84 (52), 55 (30) and 41 (45); R_f: S_1 0.16, S_2 0.31, S_3 0.39. Cytisine, RR_t: 0.96; MS: *m/z*, 190 $[M]^+$ [44]; R_f: S_1 0.32, S_2 0.42, S_3 0.07. 5,6-Dehydrolupanine, RR_t: 0.95; MS: *m/z*, 246 $[M]^+$ [32]; R_f: S_1–S_3 [8]. 11,12-Dehydrosparteine (**5**), RR_t: 0.41; MS: *m/z*, 232 $[M]^+$ (26), 175 (12), 148 (22), 137 (35), 134 (75), 98 (100), 97 (88), 96 (34), 55 (30) and 41 (68); R_f: data not obtained. 13-Epihydroxylupanine, RR_t: 1.51; MS: *m/z*, 264 $[M]^+$ (55), 247 (23), 245 (10), 166 (33), 165 (61), 152 (100), 150 (21), 114 (24), 113 (31), 112 (38) and 94 (20); R_f: S_1 0.34, S_2 0.43, S_3 0.16. 11-Epileontidane (**1**), RR_t: 0.23; MS: *m/z*, 220 $[M]^+$ (25), 179 (42), 150 (11), 137 (91), 122 (35), 110

(23), 98 (96), 96 (52), 84 (100) and 83 (75); R_f: S_1 0.05, S_2 0.07, S_3 0.67. Epilupinine, RR_t: 0.09; MS: m/z, 169 $[M]^+$ [44]; R_f: S_1–S_3 [8]. 13-Epimethoxylupanine, RR_t: 1.29; MS: m/z, 278 $[M]^+$ (35), 263 (58), 247 (72), 179 (42), 166 (81), 148 (43), 134 (43), 112 (57), 55 (100), 42 (82) and 41 (95); R_f: S_1 0.35, S_2 0.68, S_3 0.51. *N*-Formylcytisine, RR_t: 1.52; MS: m/z, 218 $[M]^+$ [41]; R_f: S_1 0.40, S_2 0.44. 13-Hydroxylupanine, RR_t: 1.51; MS: m/z, 264 $[M]^+$ [32]; R_f S_1–S_3 [8]. β-Isosparteine, RR_t: 0.38; MS: m/z, 234 $[M]^+$ [14]; R_f: S_1–S_3 [8]. Lupanine, RR_t: 1.00; MS: m/z, 248 $[M]^+$ [45]; R_f: S_1–S_3 [8]. Matrine, RR_t: 1.20; MS: m/z, 248 $[M]^+$ [46]; R_f: S_1 0.26, S_2 0.52, S_3 0.35. *N*-Methylcytisine, RR_t: 0.80; MS: m/z, 204 $[M]^+$ [45]; R_f: S_1–S_3 [8]. Ormosanine, RR_t: 1.19; MS: m/z, 317 $[M]^+$ (22), 234 (18), 233 (14), 219 (62), 151 (20), 134 (10), 98 (40), 96 (17) and 84 (100); R_f: S_1 0.06; S_2 0.08, S_3 0.76. Panamine, RR_t: 1.39; MS: m/z, 315 $[M]^+$ (20), 233 (12), 231 (11), 218 (16), 217 (100), 189 (11), 137 (5), 98 (29) 96 (9) and 84 (7); R_f: S_1 0.21, S_2 0.27, S_3 0.46. Sparteine, RR_t: 0.32; MS: m/z, 234 $[M]^+$ [47]; R_f: S_1–S_3 [8]. Tetrahydrorhombifoline, RR_t: 0.83; MS: m/z, 248 ($[M]^+$ missing), 207 [9]; R_f: S_1 0.42, S_2 0.72, S_3 0.49.

Resolution of alkaloid stereoisomers. Several pairs of diastereoisomers, isomeric at C-11, were separable by analysis of their RR_t's to lupanine under the GC/MS conditions used: anagyrine and thermopsine (RR_t 1.29); lupanine and α-isolupanine (RR_t 0.94), and sparteine and α-isosparteine (RR_t 0.27). The epimeric 13-epihydroxylupanine and 13-hydroxylupanine, although closely comparable by RR_t and R_f, were differentiated by examination of the fragment peaks in the upper region of their MS. Epilupinine was distinguished from lupinine by R_f data (lupinine, S_1 0.25, S_2 0.36).

Ormosia-*type quinolizidine alkaloid identification.* Ormosanine and templetine, two $C_{20}H_{35}N_3$ pentacyclic *Ormosia* alkaloids, were not separated by GC/MS under the conditions used in this work (templetine, RR_t: 1.20; MS: essentially identical to ormosanine). These compounds, and legume extracts containing ormosanine (Table 1), were derivatized with formaldehyde [10]. The aminal derivatives (MS, m/z, 329, $[M]^+$) so produced were separable by GC/MS [RR_t: homo-ormosanine (jamine) 1.46; homotempletine 1.37].

We have observed a general lack of success, using this GC/MS methodology, in the resolution of pentacyclic *Ormosia* alkaloid stereoisomers that are based on the same carbon skeleton [35]. Therefore, with the exception of ormosanine, only the molecular formulas of pentacyclic compounds in this series found to be present in the legume extracts studied are expressed in Table 1.

Tentative alkaloidal identifications. Three compounds in certain legume extracts were tentatively identified by comparison of MS obtained to lit. MS data (Table 1): rhombifoline [RR_t: 1.03; MS m/z 244 $[M]^+$, missing), 203 [32]]; 11-oxotetrahydrorhombifoline (RR_t: 1.53;MS: m/z, 262 $[M]^+$ (33); tetrahydroleontidine (**4**) [RR_t: 0.78; MS: identical to camoensidine (**2**), and similar to published data] [23]. No authentic samples of these compounds were available, and their partial syntheses were impractical. Quantities of extracts containing these alkaloids were insufficient to permit their isolation and identification by standard phytochemical procedures.

Plant material devoid of alkaloids. No alkaloids were detected in any of the seeds of *Lotus* species investigated. In addition, no alkaloids were found in the following lyophilized 80% EtOH extracts, supplied via the National Cancer Institute: *Dalbergia monetaria* L. fil. (twigs) (leaves), collected in Peru in August, 1972; *D. sissoo* Roxb. ex DC. (combined stems and leaves), collected in Puerto Rico in December, 1966; *D. variabilis* Vog. (combined twigs and leaves), collected in Brazil in January, 1972; and *D. ecastaphyllum* (L.) Taub. (roots), collected in Brazil in May, 1972.

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