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ALKALOIDS OF SOME ASIAN *SEDUM* SPECIES

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Key Word Index—*Sedum*; *S.* sect. *Sedum*; *S.* sect. *Aizoon*; *S.* sect. *Telephium*; pyrrolidine and piperidine alkaloids; chemotaxonomy; evolution.

Abstract—The leafy parts of 16 Asian species belonging to the three sections of *Sedum* were investigated for the presence of alkaloids. Only in seven species of *Sedum* sect. *Sedum* were alkaloids found. *Sedum bulbiferum*, *S. japonicum*, *S. lepidopodium*, *S. morrisonensis*, *S. oryzifolium*, *S. polytrichoides* and *S. sarmentosum* contain 14 pyrrolidine and piperidine alkaloids. *Sedum oryzifolium* differs significantly from the other species. It contains the typical *S. acre* alkaloids, sedamine, allosedamine and sedinone, as well as a series of monosubstituted piperidines and pyrrolidines. In addition, two new pyrrolidine alkaloids were detected in *S. oryzifolium*. i.e. both diastereoisomers of 1-phenyl-2-(2-*N*-methylpyrrolidyl)-ethanol for which the names pyrrolsedamine and pyrrolallosedamine are proposed (to express their structural relationship with sedamine and allosedamine). In five species of *Sedum* sect. *Aizoon* and four species of *S.* sect. *Telephium*, no alkaloids could be detected. The results support the hypothesis that in the family Crassulaceae, alkaloids are restricted to species of the '*Acre*' lineage.

INTRODUCTION

Most reports of alkaloids in the Crassulaceae (*ca.* 1500 species) relate to species of *Sedum* L. Of the odd 60 *Sedum* species that have been investigated for alkaloids about two-thirds were found to be positive [1–13]. Contradictory results have been reported, however, for *Sedum aizoon* L., *S. album* L., *S. crassipes* Wallich. (= *S. asiaticum* Clarcke). *S. floriferum* Praeg., *S. hybridum* L., *S. kamtschaticum* Fisch. (= *S. pallidum* Hort.), *S. lydium* Boiss., *S. middendorffianum* Maxim., *S. rupestre* L., *S. spurium* Bieb., and *S. telephium* L. *s.l.* [4, 7–12].

Of all *Sedum* species investigated for the presence of alkaloids, *S. acre* L. has received most attention and some 25 piperidine alkaloids have been reported from this species alone [5, 6, 12]. The major alkaloids of *S. acre* are the two 2-monosubstituted piperidine alkaloids, sedridine and sedamine, and the three 2,6-disubstitued *N*-methyl piperidines, sedacrine, sednine and sedinone. In addition, a number of minor alkaloids, 2-monosubstituted as well as 2,6-disubstituted, has been recorded. The alkaloids reported for the other species of *Sedum* include some 23 compounds, i.e. pelletierine, sedridine, 2-(piperidyl)-butan-2-one/ol and 2-(piperidyl)-pentan-2-one, as well as their *N*-methyl derivatives, (nor)hygrine, (nor)hygroline, 2-(piperidyl)-pentan-2-ol, (nor)sedaminon, (nor)sedamine, sedacrine, sedinine, sedinone and nicotine, some of which have also been reported for *S. acre* [2, 8–13].

In a recent survey of the distribution of alkaloids in 35 Sedoideae, the presence of alkaloids proved to be restricted to species of *Sedum* sect. *Sedum*, which belong to the '*Acre*' lineage in a phylogeny of the Crassulaceae based on chloroplast DNA restriction site analysis [12–15]. Morphologically, the species of this lineage are characterized by a reticulate or reticulo-papillose testa, except for *S. litoreum* Guss, which has a bipapillate testa [14–16]. Not surprisingly, all controversial alkaloid reports relate to species with costate seeds, which do not belong to the '*Acre*' lineage. They belong to *Sedum* sect. *Aizoon* Koch (*S. aizoon*, *S. floriferum*, *S. hybridum*, *S. kamtschaticum*, *S. middendorffianum*), *S.* sect. *Rhodiola* (*S. crassipes*), *S.* sect. *Spathulata* (Boriss.) H. Ohba (*S. spurium*), *S.* sect. *Telephium* S.F. Gray (*S. telephium s.l.*), and *S.* sect. *Sedum* (*S. album*, *S. lydium*, *S. rupestre*). The latter three species, however, appeared to be completely devoid of alkaloids on re-examination [12, 15].

The genus *Sedum s.l.* in Eastern Asia comprises *ca.* 200 species which are generally arranged in four sections, i.e. *S.* sect. *Rhodiola* (L.) Scop. (≡ *Rhodiola* L.), *S.* sect. *Telephium* (≡ Hylotelephium H. Ohba), S. sect. *Aizoon* Koch and *S.* sect. *Sedum* [17]. The species of *S.* sect. *Rhodiola*, S. sect. *Telephium* and *S.* sect. *Aizoon* are characterized by costate or bipapillate seeds, but many species of *S.* sect. *Sedum* have a reticulate or a reticulo-papillose testa [16, 18–20]. Two species of the latter group, *S. morrisonensis* and *S. sarmentosum*, were shown

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to belong to the '*Acre*' lineage [14] and, furthermore, for *S. sarmentosum* the alkaloids, *N*-methylpelletierine and *N*-methylallosedridine, have been reported [2, 21].

In the present study, we compared the alkaloid composition of 16 *Sedum* species representing three of the East Asian sections of the genus, i.e. five species of *S.* sect. *Aizoon*, four species of *S.* sect, *Telephium* and seven species with a reticulo-papillose testa of *S.* sect. *Sedum*, to test the validity of our hypothesis on alkaloid distribution in the family Crassulaceae [15].

RESULTS

In our survey of East Asian species of *Sedum* (Table 1), all seven species of *Sedum* sect. *Sedum* were found to contain alkaloids, whereas the five species of *S.* sect. *Aizoon* and the four species of *S.* sect. *Telephium* alkaloids could not be detected. A total of 14 piperidine and pyrrolidine alkaloids from species of *S.* sect. *Sedum* were found (Table 2) and identified by TLC, GC and GC-EI-mass spectrometry comparison with reference compounds (Fig. 1). The 2-monosubstituted piperidine alkaloids, pelletierine, *N*-methylpelletierine, *N*-methylsedridine and *N*-methylallosedridine, are the major alkaloids of most species of *S.* sect. *Sedum* included in the survey. In addition, *S. oryzifolium* contains significant amounts of the typical *S. acre* alkaloids, sedamine, allosedamine and sedinone.

A new alkaloid was detected in *S. oryzifolium* by GC-EI-mass spectrometry. The compound showed a mass spectrum virtually identical to that of norsedamine and its diastereoisomer ($[M]^+$ at m/z 205 and a base peak at m/z 84 representing the heterocyclic ring) but it had a significantly lower retention time than the latter piperidines. As the 2-monosubstituted *N*-methylpyrrolidines elute earlier from an apolar GC column than their piperidine isomers [12, 13], the unknown alkaloid was tentatively identified as the pyrrolidine analogue of (allo)sedamine, *viz.*, 1-phenyl-2-(2-*N*-methylpyrrolidyl)-ethanol. The structure was confirmed by GC-comparison of the extracts with synthetic 1-phenyl-2-(2-*N*-methylpyrrolidyl)-ethanol prepared from pyrrolidine and benzoyl acetate following the general procedure for the synthesis of 2-monosubstituted piperidines [22].

The synthetic pyrrolidine was separated by column chromatography on silica gel into its diastereoisomeric

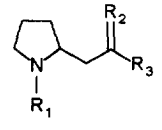
Table 1. Origin and accession number of *Sedum* plants studied

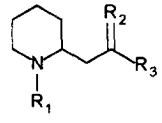
Taxon	Origin	Accession number
Sedum sect. *Sedum*		
S. bulbiferum Makino	Korea: Taejeon; Yooseong	32768
	Korea: prov. Cheonnam; Mt. Paegyang	32769
	Korea Jeju Isl., Seongsan	32795
S. japonicum Siebold	Japan: Honshu, Fukui pref.; Tohjibo	31504
S. lepidopodium Nakai	Korea: Gojae Isl. Haeogumgang	32775
S. morrisonensis Hayata	Taiwan: Mt. Yu Shan (3800 m)	26400
	Taiwan: Mt. Yu Shan (3080 n)	26402
	Taiwan: distr. Nantou; Kum Yang	31048
	Taiwan: distr. Nantou; Kum Yang	32838
S. oryzifolium Makino	Korea: Gojae Isl., Haeogumgang	32771
	Korea: Gojae Isl., Haeogumgang	32772
	Korea: Jeju Isl., Seongsan	32796
	Korea: Doek Isl.	32901
S. polytrichoides Hemsl.	Korea: prov. Chungbook; Mt. Songni	32761
	Korea: Jeju Isl., Mt. Halla, 1100 m	32797
S. sarmentosum Bunge	China: prov. Zhejiang; Hangzhou	30671
	Korea: prov. Chungbook; Mt. Songni	32762
	Korea: prov. Cheonnam; Damyang-gun	32770
	Korea: Gojae Isl., Haegumgang	32773
Sedum sect. *Aizoon*		
S. ellacombianum Praeger	China: prov. Xinjiang; Tianchi	30672
S. kamtschaticum Fisch.	Korea: prov. Kyeongbook; Mt. Chuwang	32765
	Korea: Gojae Isl., Haegumgang	32774
S. selskianum Regel & Maack.	Russia: exact prov. unknown	25461
S. takesimense Nakai	Korea: Ullung Isl., Jeodong	32902
S. zokuriense Nakai	Korea: prov. Chungbook; Mt. Songni	32763
Sedum sect. *Telephium*		
S. duckbongii Chung & Kim	Korea: prov. Kyeongbook; Mt. Chuwang	32764
S. taquetii Praeger	Korea: Jeju Isl., Mt. Halla, 1100 m	32798
S. telephium L.	Turkey: prov Bolu; Yedigoller	30867
	France: dep. Vienne; Charroux	31028
S. viviparum Maxim.	Korea: prov. Kyeongbook; Mt. Chuwang	32766

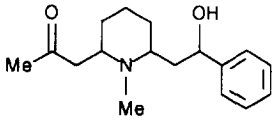
Table 2. Alkaloid profiles of some Asian *Sedum* species

Species	Coll. no.	Alkaloid pattern*													
		Pyrrolidines					Piperidines†								
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
S. oryzifolium	32771	4	–	–	–	2	16	18	–	–	–	8	3	9	39
S. oryzifolium	32772	3	–	–	–	2	18	21	–	–	–	8	4	10	34
S. oryzifolium	32796	4	‡	1	4	1	2	9	2	12	–	–	40	12	13
S. oryzifolium	32901	7	2	2	–	9	4	12	8	16	–	–	6	20	14
S. japonicum	31504	35	–	–	–	–	20	40	–	5	–	–	–	–	–
S. lepidopodium	32775	–	–	–	–	–	13	–	76	–	10	–	–	–	–
S. morrisonensis	26400	20		–	–	–	30	–	50	–	–	–	–	–	–
S. morrisonensis	26402	–	–	–	–	–	–	–	–	–	–	–	–	–	–
S. morrisonensis	31048	–	–	–	–	–	10	–	87	–	3	–	–	–	–
S. morrisonensis	32838	‡	–	–	–	–	67	4	24	–	5	–	–	–	–
S. polytrichoides	32761	–	–	–	–	–	70	30	–	–	–	–	–	–	–
S. polytrichoides	32797	6	4	‡	–	–	3	–	29	44	13	–	–	–	–
S. sarmentosum	30671	–	–	–	–	–	7	–	49	–	44	–	–	–	–
S. sarmentosum	32762	–	–	–	–	–	‡	–	21	–	78	–	–	–	–
S. sarmentosum	32770	–	–	–	–	–	6	–	36	–	58	–	–	–	–
S. sarmentosum	32773	–	–	–	–	–	3	–	31	–	66	–	–	–	–
S. bulbiferum	32768	–	–	–	–	–	100	–	–	–	–	–	–	–	–
S. bulbiferum	32769	–	–	–	–	–	100	–	–	–	–	–	–	–	–
S. bulbiferum	32795	–	–	–	–	–	100	–	–	–	–	–	–	–	–

*Abundance in percent of total alkaloids determined by GC. Signs: – = not detected, ‡ = trace amount (< 1% of total alkaloids).
†For key to alkaloid numbers see Fig. 1.







	R_1	R_2	R_3
1 norhygrine	H	O	Me
2 hygrine	Me	O	Me
3 hygroline	Me	H, OH	Me
4 pyrrolsedamine	Me	H, OH	Ph
5 pyrrol*allo*sedamine	Me	H, OH	Ph
6 pelletierine	H	O	Me
7 sedridine	H	H, OH	Me
8 *N*-methylpelletierine	Me	O	Me
9 *N*-methylsedridine	Me	H, OH	Me
10 *N*-methyl*allo*sedridine	Me	H, OH	Me
11 nor*allo*sedamine	H	H, OH	Ph
12 sedamine	Me	H, OH	Ph
13 *allo*sedamine	Me	H, OH	Ph

14 sedinone

Fig. 1. Alkaloids from some Asian *Sedum* species.

alcohols, **4** and **5**, and characterized by ^{1}H NMR comparison with sedamine, norsedamine and their diastereoisomers. Without exception, the sedamine-type alkaloids show –CH(OH)– signals at higher field than the allosedamine-type compounds [23; Dr C. Hootelé, pers. commun.]. Thus, for the sedamine-type pyrrolidine alkaloid (H-7 at 4.82 ppm) we propose the name 'pyrrolsedamine' and for the allosedamine-type pyrrolidine, 'pyrrolallosedamine' (H-7 at 5.07 ppm). The diastereoisomeric alcohols were not resolved under the GC conditions employed, but they could be (partially) separated as their trimethylsilyl ethers which allowed us to detect either of the two diastereoisomers in complex alkaloid mixtures. To this end, alkaloid extracts of *S. oryzifolium* were treated with (*bis*)-trimethylsilyl acetamide and examined by GC; mixtures of the extracts with pyrrolsedamine and pyrrolallosedamine were also chromatographed after trimethylsilylation. Pyrrolallosedamine was found in all plants of *S. oryzifolium* and, in addition, one plant of *S. oryzifolium* contained pyrrolsedamine. TLC proved to be of no help in identifying the natural pyrrolidine alkaloid because pyrrolsedamine and pyrrolallosedamine are masked by their piperidine analogues on silica gel plates.

DISCUSSION

Alkaloid patterns in Asian *Sedum* species agree with the hypothesis on the distribution of alkaloids in Crassulaceae proposed by Stevens and coworkers who stated that the occurrence of alkaloids is restricted to species of the '*Acre*' lineage which are characterized by a reticulate testa [14, 15]. Of the 16 Asian *Sedum* species investigated, only the seven species with reticulate or reticulo-papillate seeds contained alkaloids. The five species of *Sedum* sect. *Aizoon* contained no alkaloids and our results corroborate earlier negative reports for species of this section [11].

The alkaloid report for *S. kamtschaticum* could not be confirmed [10] and positive reports for other species of this section, *viz.*, *S. aizoon*, *S. floriferum*, *S. hybridum* and *S. middendorffianum* [4, 9, 11], need to be checked, especially the reports of methylisopelletierine, sedamine and sedinine in *S. aizoon* and *S. hybridum* [9]. The four species of *Sedum* sect. *Telephium* also proved to be devoid of alkaloids and our findings support the negative reports for species of this section [11]. The positive records for *S. telephium s.l.* (= *S. maximum* Suter, = *S. purpureum* Link), including reports of the occurrence of methylisopelletierine, sedamine, sedinine and sedridine in this species [8, 9], could not be confirmed and positive reports for other species of this section, i.e. *S. ewersii* Ladeb. and *S. populifolium* Pallas [9, 10], should also be checked carefully. The Asian *Sedum* species with a reticulate or reticulo-papillose testa of *Sedum* sect. *Sedum*, on the other hand, contained a wide variety of alkaloids. The occurrence of *N*-methylpelletierine and *N*-methylallosedridine in *S. sarmentosum* [2, 21], the only species of this group previously studied, could be fully confirmed (Table 1). Although, as yet only *ca.* 6% of the species of the Crassulaceae have been examined for alkaloids and *ca* 12% of the species of *Sedum*, the present results strengthen our hypothesis that in Crassulaceae, alkaloids are restricted to the '*Acre*' lineage.

Alkaloid composition varies considerably among the Asian species of *Sedum* sect. *Sedum*. Tentatively four groups can be distinguished: 1) The four plants of *S. oryzifolium* which contain a wide spectrum of alkaloids, most notably the typical *S. acre* alkaloids, sedamine and sedinone, as well as the pyrrolidines, hygrine, norhygrine and hygroline. As lysine, ornithine, and phenylalanine are the biogenetic precursors of these alkaloids [24, 25], the additional presence of the newly discovered pyrrol(allo)sedamine in *S. oryzifolium* may indicate a pathway in which phenylalanine is coupled with Δ^1-pyrrolideine, the cyclic intermediate produced from ornithine. In this respect, they differ markedly from the closely related *S. japonicum* which Ohba [26] included in *S. uniflorum* Hook.f. & Arnott, together with *S. oryzifolium* 2) The eight plants of *S. japonicum*, *S. morrisonensis*, *S. lepidopodium* and *S. polytrichoides*, in which *N*-methylpelletierine and pelletierine are the main alkaloids. In addition, these species contain varying amounts of the pyrrolidines, sedridine and *N*-methyl(allo)sedridine. 3) The four plants of *S. sarmentosum* in which the principal alkaloids are *N*-methylallosedridine and *N*-methylpelletierine. 4) The three plants of *S. bulbiferum* which contain only pelletierine, Of the seven species studied here, Berger [17] recognized only *S. japonicum*, and *S. sarmentosum*, which he classified in *S.* series *Orientalia* Berger and *S.* series *Chinensia* Berger, respectively. Fröderström [18] included six of the seven species in his study of *Sedum* (except *S. lepidopodium*) and placed these all in *S.* series *Japonica* (Max.) Fröd. Distribution patterns of alkaloids in Eurasian *Sedum* species appeared to be significantly correlated with an infrageneric classification based on biosystematic characters and chloroplast DNA RFLPs [12–14, 27]. Especially, the presence of pyrrolidines and the 2,6-disubstituted piperidines proved to be highly significant from a systematic point of view. Our results, therefore, suggest that systematic and evolutionary relationships among Asian *Sedum* species are much more intricate than present infrageneric classifications indicate. Most notably, the presence in *S. oryzifolium* of the 2,6-disubstituted piperidine (sedinone), which so far is only known from *S. acre* [12], is a valuable lead for further studies of evolutionary and systematic relationships between Asian and Eurasian species of *Sedum* sect. *Sedum*.

Infraspecific variation in the alkaloid fraction of the Asian *Sedum* species varies considerably. *Sedum bulbiferum* and *S. sarmentosum* show no or little variation, though accessions of the latter species originate from geographically very distant regions. The accessions of *S. morrisonensis*, *S. oryzifolium* and *S. polytrichoides*, on the other hand, show much more variation. In general, the variation seems to be correlated with the origin of the plant material, rather than with morphological variation. For example, the composition of the alkaloid fractions of two plants of *S. oryzifolium* from Gojae island are identical, but differ from the other two accessions. Also, the plants of *S. morrisonensis* from Kum Yang and Mt. Yu Shan differ. In this species, however, there is considerable variation among plants from the same region, most notably the complete lack of alkaloids in one of the two plants from Mt. Yu Shan. A similar variation has been observed in the European *S. sexangulare* which, like *S. morrisonensis*, is highly polyploid [13]. The composition of the alkaloid fractions of the two plants of *S. polytrichoides* differ markedly, in particular, in the presence of several pyrrolidines in the plant from Jeju island. It also differs considerably from the closely related *S. lepidopodium*. The variation in the alkaloid fraction of our accessions of *S. polytrichoides* parallels the extreme morphological and cytological variation reported for the *S. polytrichoides* species complex which comprises two continuous series of gametic chromosome numbers, $n = 11$–16 and $n = 20$–27, respectively, and the number $n = 35$ [28].

EXPERIMENTAL

Plant material. Living plants were collected in the wild and, for further study, cultivated under uniform conditions in the experimental garden at Utrecht. Origins of plants are given in Table 1. Voucher specimens are deposited in the Botanical Institute at Utrecht. The vegetative (leafy) parts of the plants were either used fresh or kept at $-18°$ prior to phytochemical analysis.

Extraction of alkaloids. Fresh (frozen) vegetative parts of plant material (20 g) were immersed in $CHCl_3$ for 15 sec to remove leaf waxes and then homogenized in 40 ml of MeOH with a food processor for 2 min. After addition of conc HCl (2.4 ml), the mixt. was left standing overnight and then centrifuged. The supernatant was concd to *ca.* 20 ml *in vacuo* at 60°. The aq. soln (plant material contained *ca* 85% moisture) was extracted with

$CHCl_3$ (1 × 20 ml, 2 × 10 ml; the comb. organic layers were discarded) and, after basification with 10 N NaOH to pH *ca* 11, extracted with $CHCl_3$ (1 × 20 ml, 2 × 10 ml) again. Separation of the layers was achieved by centrifugation if necessary. The comb. organic layers were dried (Na_2SO_4) and evapd *in vacuo* at 40°. The residue was dissolved in 1 ml of $CHCl_3$ and stored at 4° prior to chromatography.

Chromatography. TLCs were run on silica gel plates (Merck art. 5715) with $CHCl_3$–MeOH–NH_4OH (85:18:1). Spots were visualized with Dragendorff's reagent (undild) and with the *o*-toluidine reagent [29] for the specific detection of secondary amines. GC was performed on a WCOT fused silica CP Sil 5 CB column (25 m × 0.25 mm i.d., film thickness 0.12 μm) prog. from 70° to 290° at 6° min^{-1}; injector: 175°; FID: 300°; N_2 at 1 ml min^{-1}; inj. vol. 1 μl; split ratio 1:60. The GC-EIMS (70 eV) instrument was equipped with an identical column programmed from 50° to 290° at 6° min^{-1}; He 1 ml min^{-1}; inj. vol. 1–2 μl.

Reference compounds. Synthesis and/or isolation of compounds **1**–**3**. **6**–**8** and **12**–**14** is recorded in refs [12, 13]. *N*-methylsedridine **9** (also prepared by *N*-methylation of sedridine from *S. acre*) and *N*-methylallosedridine **10** were generous gifts from Dr L. Maat. Silica gel CC of synthetic 1-phenyl-2-(2-piperidyl)-ethanol gave norallosedamine **11** and norsedamine, which were identified by comparison of their ^{1}H NMR data with those reported in ref. [23].

Synthesis of 1-*phenyl*-2-(2-*N*-*methylpyrrolidyl*)-*ethanol.* The intermediate product, phenacyl-2-pyrrolidine, was prepared from pyrrolidine and ethyl benzoyl acetate according to the general procedure for the synthesis of 2-monosubstituted piperidines [22]. Phenacyl-2-pyrrolidine·HCl, mp 165.5–167°. A portion of the HCl was converted to the base. IR ν_{max} (film) cm^{-1}; 1680 (–CO–Ph); ^{1}H NMR (300 MHz, $CDCl_3$): δ8.0–7.2 (phenyl protons), 3.55 (*m*, H-5e), 3.15 (2H, *d*, ,H-6), 2.38 (N–H); EIMS (probe) *m/z* (rel. int.): 189 $[M]^+$ (72), 120 (5), 105 (78), 84 (98), 77 (100), 70 (91). *N*-Methylation and subsequent reduction [12] of the intermediate product yielded a mixt. of the diastereoisomeric alcohols of 1-phenyl-2-(2-*N*-methylpyrrolidyl)-ethanol, **4** and **5**. GC-EIMS *m/z* (rel. int.): 205 $[M]^+$ (2), 84 (100), 77 (4); R_t 17.73 min (no separation by GC).

The synthetic pyrrolidine was separated into its diastereoisomeric alcohols, **4** and **5**, by silica gel CC using increasing proportions of the TLC solvent (80–100%) in $CHCl_3$ as the eluent. Comparison of the ^{1}H NMR data with those of sedamine and allosedamine [22] allowed assignment of their structures, for which we propose the names pyrrolsedamine and pyrrolallosedamine. Pyrrolallosedamine. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.4–7.2 (5H, phenyl protons), 5.07 (1H, *dd*, *J* = 2.5 and 10.3 Hz, H-7), 3.13 (1H, *m*, H-5), 2.64 (1H, *m*, H-2), 2.40 (3H, *s*, N-Me), 2.22 (1H, *m*, H-6a); R_t TMSi ether, 17.66 min. Pyrrolsedamine. ^{1}H NMR (300 *MHz*, *CDCl*$_3$): δ7.4–7.2 (5H, phenyl protons), 4.82 (1*H*, *dd*, *J* = 2.6 and 9.9 Hz, H-7), 3.07 (1H, *m*, H-5), 2.82 (1H, *m*, H-2), 2.39 (3H, *s*, *N*-Me), 2.01 (1H, *m*, H-6a); R_t TMSi ether 17.60 min. The TMSi ethers of both diastereoisomers had identical GC-EIMS: *m/z* 277 $[M]^+$ (3), 84 (100). Trimethylsilyl ether derivatives were prepd by dissolving samples (dried with a stream of N_2) in a mixture of pyridine and (*bis*)-trimethylsilyl acetamide (1:1); the reaction mixt. was kept at 70° for 60 min prior to injn on the GC column.

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