In palinurin, the upfield chemical shifts of the 2 vinyl CH_3's at C-8 and C-18, caused by eclipsed butane non-bonded interactions[16], led us to assign E configurations for the double bonds at C-8 and C-17. Analogously the E configuration has been proposed for the double bond at C-8 of **5**. Finally, the alternative structure 7 was definitively eliminated, on the basis of known alkene chemical shift parameters[17], by the 2 low field signals in the spectrum of **1** at ppm 129.0 (C-18) and 129.3 (C-17, confirmed by selective decoupling at δ 5.25). The stereochemistry at C-21 has not been investigated.

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[2] G. Cimino, S. De Stefano, L. Minale and E. Fattorusso, Tetrahedron *28*, 333 (1972).

[3] F. Cafieri, E. Fattorusso, C. Santacroce and L. Minale, Tetrahedron *28*, 1579 (1972).

[4] D.J. Faulkner, Tetrahedron Lett. *1973*, 3821.

[5] I. Rothberg and P. Shubiar, Tetrahedron Lett. *1975*, 769.

[6] R. Kazlauskas, P.T. Murphy, R.J. Quinn and R.J. Wells, Tetrahedron Lett. *1976*, 2635.

[7] It should be noted that from a Pacific *Ircinia variabilis*, D.J. Faulkner[4] reported the isolation of variabilin (**8**).

[8] F. Pellizzoni and G. Jommi, Gazz. chim. it. *89*, 1894 (1959).

[9] W. Hofheinz and P. Schönholzer, Helv. chim. Acta *60*, 1367 (1977).

[10] ^1H-NMR of palinurin (**1**), δ ($CDCl_3$) 7.32 (H-1, bs), 7.20 (H-4, bs), 6.25 (H-2, bs), 6.15 (H-11, dd, J = 11, 14 Hz), 5.77 (H-10, d, J = 11 Hz), 5.37 (H-12, dd, J = 8, 14 Hz), 5.25 (H-17, bt, J = 7 Hz), 4.8 (H-21, bm, $W_{1/2}$ ca. 14 Hz), 1.73 (6 H, s), 1.66 (3 H, s), 0.99 (CH_3-13, d, J = 7 Hz).

[11] K. Mislowa and I.V. Steinberg, J. Am. chem. Soc. *77*, 3807 (1955).

[12] E. Wenkert, A.O. Clouse, D.W. Cochran and D. Doddrell, J. Am. chem. Soc. *91*, 6879 (1969).

[13] A. Kiewict, J. De Wit and W.D. Weringa, Org. Magn. Resonance 6, 461 (1974).

[14] H.O. House, A.V. Pradhu and W.V. Philips, J. org. Chem. *41*, 1209 (1976).

[15] C. Nishino and W.S. Bowers, Tetrahedron *32*, 2875 (1976).

[16] G.C. Levy, in: 'Topics in C-13 NMR Spectroscopy', Vol. 2, p. 84. Wiley-Interscience, New York 1976.

[17] F.W. Wehrli and T. Wirthlin, in: 'Interpretation of C-13 NMR Spectra', p. 42. Heyden, London 1976.

Baluchistine, a new bisbenzylisoquinoline alkaloid[1]

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Summary. The new phenolic bisbenzylisoquinoline alkaloid (+)-baluchistine, found in *Berberis baluchistanica* Ahrendt (Berberidaceae), has been assigned structure **1**. O-Methylation using ethereal diazomethane yields (+)-obaberine (**2**). Baluchistine is the 1 alkaloid of the oxyacanthine-berbamine group to incorporate a free phenolic function at C-6.

Chromatography of the basic extracts from 4.3 kg of dried *Berberis baluchistanica* Ahrendt (Berberidaceae) over basic alumina yielded as one of the late fractions 20 mg of the new phenolic bisbenzylisoquinoline alkaloid (+)-baluchistine (**1**), m.p. 222–224 °C (MeOH); $[\alpha]_D^{26} + 333°$ (c 0.075, MeOH); cd (c 0.095 mg/ml, MeOH) $[\theta]_{302} = 0$, $[\theta]_{294} = +3700$, $[\theta]_{287} = 0$, $[\theta]_{283} = -3700$, $[\theta]_{275} = 0$, $[\theta]_{267} = +6{,}200$, $[\theta]_{230} = +110{,}000$, and $[\theta]_{208} = 0$. The UV.-spectrum exhibited λ_{max}^{EtOH} 283 nm (log ε 3.67), with a bathochromic shift to 290 nm (log ε 3.80) upon addition of base.

Analysis by high resolution mass spectroscopy showed a molecular ion at m/e 594.2732 for $C_{36}H_{38}N_2O_6$; while low resolution measurements gave peaks at m/e 594 (M^+) (22), 487 (0.2), 382 (52), 381 (base), 367 (50), 207 (10), 192 (15), 191 (78), 174 (50), and 168 (48).

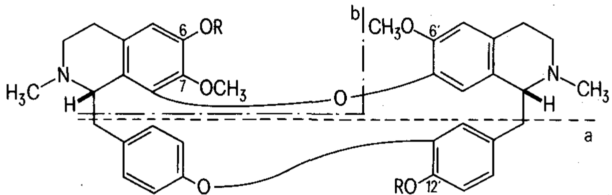
The PMR-spectrum of baluchistine at 60 MHz in $CDCl_3$ shows the presence of 2 N-methyl groups superimposed at δ 2.61, 2 O-methyl groups at δ 3.23 and 3.60, 2 hydroxyls as a broad singlet at δ 5.15, and 10 aromatic protons in a complex pattern from δ 5.43 to 7.40. An oxyacanthine type dimer was indicated because of the lack of separation between the N-methyl peaks. The peak at δ 3.23 can be assigned to the C-7 methoxyl; while the remaining methoxyl at δ 3.60 could at this stage be tentatively ascribed to C-6′, thus locating the phenolic functions at C-6 and C-12′.[3,4] By way of comparison, the critical pmr data relating to the N-methyl and methoxyl absorptions for the alkaloids obaberine, oxyacanthine, homoaromoline, aromoline and baluchistine, all of which belong to the oxyacanthine series, have been summarized in the table. In particular, it should be noted that a peak (3 H) near δ 3.20 is characteristic of a C-7 methoxyl group, while one around 3.60 is indicative of a C-6′ methoxyl. Furthermore, the position of the methoxyl peak at δ 3.60 suggested that the 2 asymmetric centers in baluchistine (**1**) possess opposite absolute configurations, since when the 2 benzylisoquinoline units have the identical chirality the C-6′ methoxyl peak is known to appear higher upfield near δ 3.35[3,4].

Returning to the low resolution mass spectrum, the following assignments can now be made for the ionic shards obtained: 487 $(M-107)^+$, 382 $(a)^+$, 381 $(382-H)^+$, 367 $(382-CH_3)^+$, 207 $(b)^+$, 192, 191 $(a)^{++}$, 174 $(a-b-H)^+$, and 168 $(a-CH_3O-CH_3)^{++}$[5].

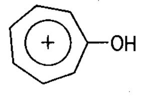
Treatment of baluchistine (**1**) with ethereal diazomethane for 2 days at near 0 °C supplied its di-O-methyl ether derivative, identical with the known (+)-obaberine (**2**).

PMR spectral data for oxyacanthine type dimers

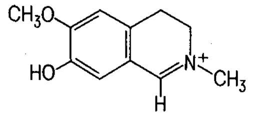
	N-CH_3	OCH_3 C-7	C-6	C-6′	C-12′
Obaberine (**2**)[3]	δ2.55, 2.65	3.20	3.79	3.60	3.90
Oxyacanthine[3] (12′-hydroxyl)	2.48	3.15	3.73	3.56	-
Homoaromoline[3] (7-hydroxyl)	2.45, 2.55	-	3.78	3.62	3.88
Aromoline[3] (7,12′-dihydroxyl)	2.49	-	3.77	3.56	-
Baluchistine	2.61	3.23	-	3.60	-



1, R = H
2, R = CH_3



m/e 107



m/e 192

Significantly, baluchistine (**1**) is different in its spectral and physical properties from the isomeric aromoline of identical absolute configuration, but in which the 2 phenolic groups are located at C-7 and C-12′.

It is worth noting that baluchistine is the 1st bisbenzylisoquinoline alkaloid within the dimeric oxyacanthine-berbamine group to incorporate a free phenolic function at C-6. It is accompanied in *B. baluchistanica* by such unusual alkaloids as the proaporphine-benzylisoquinoline pakistanamine[6], the aporphine-benzylisoquinoline pakistanine derived from the condensation of 2 N-methylcoclaurine units[6], and the isoquinolone-benzylisoquinoline baluchistanamine[7].

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[3] I.R.C. Bick, J. Harley-Mason, N. Sheppard and M.J. Vernengo, J. chem. Soc. *(1961)*, 1896.

[4] M. Shamma, in: The Isoquinoline Alkaloids, p. 149. Academic Press, New York 1972.

[5] J. Baldas, I.R.C. Bick, T. Ibuka, R.S. Kapil and Q.N. Porter, J. chem. Soc. Perkin *1*, 592 (1972).

[6] M. Shamma, J.L. Moniot, S.Y. Yao, G.A. Miana and M. Ikram, J. Am. chem. Soc. *95*, 5742 (1973).

[7] M. Shamma, J.E. Foy and G.A. Miana, J. Am. chem. Soc. *96*, 7809 (1974).

Geranyl acetate and 2-decen-1-ol in the cephalic secretion of the solitary wasp *Sceliphron caementarium* (Sphecidae; Hymenoptera)[1]

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Summary. The cephalic secretion of *Sceliphron caementarium* contains a mixture of geranyl acetate and 2-decen-1-ol; the latter has not been described previously in arthropod secretions. The secretion is orally emitted when the wasps are handled, and may serve in defense or alternatively as an aid in roosting aggregation.

Sceliphron caementarium (Drury) is a common solitary sphecid that builds its tubular clay nests on buildings and other structures. There are 4–10 cells per nest, which are provisioned with small spiders[3]. The nests are usually widely spaced due to the intraspecific agonistic behavior of the nesting females, but males and females also have been observed to roost together in aggregations on plants at night[4]. When seeking roosting aggregations, searching *S. assimile* fly slowly and repeatedly upwind until they locate a group[4]; this suggests a scent-following behavior resembling that of *Colletes* bees[5]. Although the pheromones of several of the social or solitary bees and social wasps have been identified, there are no published reports on the chemistry of the various scents produced by the many solitary nesting wasps.

For analysis, females of *S. caementarium* were collected on flowers at Beltsville, MD, and chilled immediately. During handling in the field and in the laboratory the wasps often emitted an odoriferous secretion resembling lemongrass from their mandibles. Their heads were removed, slit to expose the fragrant mandibular glands and extracted with methylene chloride. The extracts were analyzed on a combined gas chromatograph-mass spectrometer (LKB 2091) at 70 ev. on an SE-30 capillary column (0.2 mm × 25 m), a non-polar column, or alternatively on the polar SP-1000 capillary column. In both cases the columns were temperature programmed from 60 °C to 200 °C at 5 °C/min.

2 major components were detected in the mandibular exudates, and identified as geranyl acetate and 2-decen-1-ol (figure 1). On the 10% SP-1000 column geranyl acetate eluted first at 140 °C and 2-decen-1-ol immediately afterwards at 145 °C; on SE-30 the retention times were reversed. The compounds were identified by their fragmentation patterns, and their spectra and retention times compared to those of authentic standards. The mass spectrum of component 2 in the cephalic secretion, identified as 2-decen-1-ol is presented in figure 2.

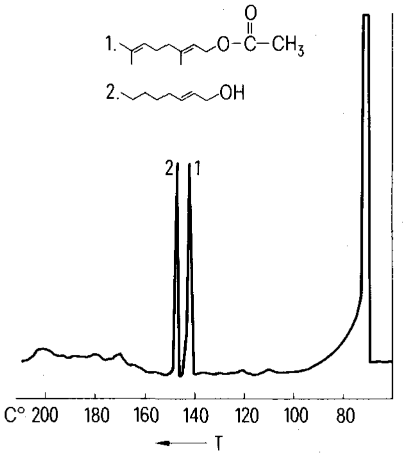

Fig. 1. Identification of geranyl acetate and 2-decen-1-ol.