5. D. Wuma-Badu, J.S.K. Ayim, T.T. Dabara, M.M. El-Azizi, P.L. Schiff Jr., D.J. Slatkin, and J.E. Knapp, *J. Nat. Prod.*, **46**, 342 (1983).
6. M.H. Abu Zarga and M. Shamma, *J. Nat. Prod.*, **45**, 471 (1982).
7. E. Sanchez and J. Comin, *Tetrahedron*, **23**, 1139 (1967).
8. N.K. Saxena and D.S. Bhakuni, *J. Indian. Chem. Soc.*, **57**, 773 (1980).
9. M.H. Abu Zarga, G.A. Miana, and M. Shamma, *Tetrahedron Lett.*, 541 (1981).
10. H.M. Fales, H.A. Lloyd, and G.W. Milane, *J. Am. Chem. Soc.*, **92**, 1590 (1970).
11. F. Bohlmann and R. Zeisberg, *Chem. Ber.*, **108**, 1043 (1975).

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PYRROLIZIDINE ALKALOIDS FROM BORAGE (*BORAGO OFFICINALIS*) SEEDS AND FLOWERS

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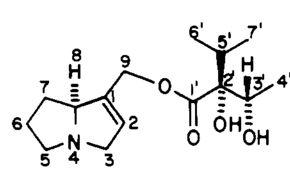
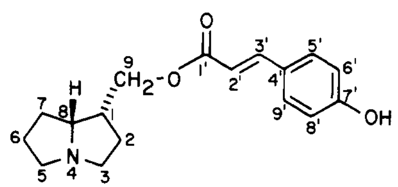
We recently reported (1) the isolation of the unsaturated pyrrolizidine alkaloid lycopsamine from leaves of borage (*Borago officinalis* L. Boraginaceae), a common garden herb used throughout the world in teas and salads. Also isolated was supinidine viridiflorate but only in trace amounts insufficient for determining optical rotation. (+)-Supinidine viridiflorate is named cynaustine; (−)-supinidine viridiflorate is amabiline (**1**) (2). Flowers of borage are used medicinally and in salads and beverages (3), while borage seed oil is known (3) to contain λ-linolenic acid and could be used as a dietary supplement. We have now analyzed seeds, seed oil, and flowers for pyrrolizidine alkaloids. The only alkaloid found in the flowers and the major seed alkaloid was thesinine (**2**), the *trans-p*-hydroxycinnamate of (+)-isoretronecanol. This is a rare pyrrolizidine, having been found only once previously (4) from *Thesium minkwitzianum*. Mature seeds were found to contain **2** and a smaller amount of the same unsaturated pyrrolizidine as the leaves (1). A sufficient amount of the latter was isolated so that an optical rotation measurement could be obtained. The alkaloid proved to be amabiline (**1**) and not cynaustine. One batch of immature seeds was also analyzed, and this material contained only thesinine. Three different samples of borage seed oil were analyzed, and no alkaloids were found. Amabiline was absent down to the 5 ppm level, but thesinine quantitation was too variable for low level determination. Unsaturated pyrrolizidines are suspect hepatotoxins (2), but saturated pyrrolizidines (such as the major seed component, thesinine) are not known to be toxic.

Because no spectral data have been published for **2** and little for **1**, ^{1}H- and ^{13}C-nmr data as well as physical properties are given below.



1



2

EXPERIMENTAL

Flowers were obtained from the previously described (1) locally grown borage. Seed was obtained from Dr. Dennis Jones, Director of Research and Quality Control, Horners' Inc., Montreal, Canada, and were grown in Europe. Seed oil was obtained from Dr. Brian Ladbrooke, POS, Saskatoon, Saskatchewan, Canada. Oil is prepared[1] by pressing the seed, which removes two-thirds of the oil. The seed is then extracted with hexane, the hexane evaporated, and the residue combined with the oil of the first pressing.

[1]B.D. Ladbrooke, private communication.

Mature borage seed yielded about 0.03% crude alkaloids via solvent extraction, followed by a differential pH distribution without a Zn reduction step. Zn reduction yielded only a small additional amount of alkaloids, and a free base to *N*-oxide ratio of 20:1 was estimated. The ratio of thesinine to amabiline was about 10:1. Immature seed yielded only thesinine by similar procedures. Similar isolations from seed oil yielded only a small residue in the "crude base" fraction, but no alkaloids were seen by tlc or by a capillary glc analysis. Standard amabiline could be detected to the 5 ppm level by this technique.

Full details of isolations are available from F.R. Stermitz.

AMABILINE (**1**).—A yellow oil (.002%), lit (2) noncrystalline; $[\alpha]^{25}D$ −9.1° (EtOH, c 0.36), lit (2) −7.1° (EtOH); tlc Rf 0.75 (KC18, Whatman, MeOH-NH_4OH, 40:1), Rf 0.22 (Si gel 60, EtOH-iPrOH-NH_4OH, 12:7:1, iodoplatinate detection); Eims *m/z* 283 (M^+), 120, 85, 83; cims (NH_3) *m/z* 284 $(M+1)^+$, 238, 220, 140, 124, 122, 120; ^1H nmr (360 MHz, $CDCl_3$) 0.89 (3H, d, 6.80 Hz, H-6′), 0.94 (3H, d, 6.86 Hz, H7′), 1.22 (3H, d, 6.05 Hz, H4′), 1.55 (1H, m, H7), 1.79 (2H, m, H6), 1.99 (1H, m, H7), 2.17 (1H, m, H5′), 2.50 (1H, m, H5), 3.15 (1H, m, H5), 3.38 (1H, br.d, H3), 3.93 (1H, br.d, H3), 4.02 (1H, q, H3′), 4.19 (1H, br.s, H8), 4.78 (2H, m, H9), 5.70 (1H, br.s, H2).

THESININE(**2**).—A yellow oil (noncrystalline solid with low melting point) (0.02%), lit (4) mp 38-40°; $[\alpha]^{25}D$ −2.6° (EtOH, c 0.77), not reported (4); tlc Rf 0.55 (KC18 Whatman, MeOH-NH_4OH, 40:1, iodoplatinate detection); eims *m/z* 287 (M^+, not visible), 124, 120, 83; cims (NH_3) *m/z* 288 (M+1), 240, 124, 120; ^{13}C nmr (67.5 MHz, $CDCl_3$) 25.7 (C7), 30.3 (C2), 31.9 (C6), 45.2 (C1), 55.5 (C5)*, 55.7 (C3)*, 65.3 (C9), 67.3 (C8), 112.5 C2′), 117.1 (C6′,C8′), 124.0 (C4′), 130.4 (C5′,C9′), 146.1 (C3′), 163.5 (C7′), 168.0 (C1′); ^1H nmr (360 MHz, $CDCl_3$) 7.55 (1H, d, 16 Hz), 7.31 (2H, d, 9 Hz), 6.77 (2H, d, 9 Hz), 6.11 (1H, d, 16 Hz), 4.47 (1H, dd, 6 Hz, 11 Hz), 4.27 (1H, dd, 6 Hz, 11 Hz), 3.67 (1H, m), 3.42 (1H, m), 3.16 (1H, m), 2.68 (4H, m), 2.00 (4H, m), 1.64 (1H, m).

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LITERATURE CITED

1. K.M. Larson, M.R. Roby, and F.R. Stermitz, *J. Nat. Prod.*, **47**, 747 (1984).
2. C.C.J. Culvenor and L.W. Smith, *Aust. J. Chem.*, **20**, 2499 (1967).
3. J.A. Duke, "Handbook of Medicinal Herbs," CRC Press, Inc., Boca Raton, Fl, 1985, pp. 81, 234.
4. A.P. Arendaruk and A.P. Skoldinov, *Zhur. Obsch. Khim.*, **30**, 489 (1960).

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METABOLITES FROM TWO SOFT CORALS FROM GUAM: *SINULARIA LEPTOCLADOS* and *SINULARIA GYROSA*

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Soft corals are well-known for their production of sesquiterpenes and diterpenes.[1] The unusual nor-diterpene lactone **1** was isolated initially from *Sinularia leptoclados* (phyllum Coelenterata, class Anthazoa, subclass Octocorallia, order Alcyonacea, family Alcyoniidea) by Australian workers (2), and subsequently, was isolated from *Sinularia foeta* by a Chinese group (3). The sesquiterpene acid **2** and closely related acids have been obtained from *Sinularia capillosa*, *Sinularia firma* (4), and also *Sinularia gonatodes* (5). In our continuing examination (6-8) of marine organisms from Guam Island, we have examined *S. leptoclados* (Ehren-

[1]For a recent review, see Faulkner (1).