

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 thesine to amabiline was about 10:1. Immature seed yielded only thesine 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 (0.002%), lit (2) noncrystalline; $[\alpha]^{25}_D -9.1^\circ$ (EtOH, *c* 0.36), lit (2) -7.1° (EtOH); tlc Rf 0.75 (KC18, Whatman, MeOH-NH₄OH, 40:1), Rf 0.22 (Si gel 60, EtOH-iPrOH-NH₄OH, 12:7:1, iodoplatinate detection); Eims *m/z* 283 (M⁺), 120, 85, 83; cims (NH₃) *m/z* 284 (M+1)⁺, 238, 220, 140, 124, 122, 120; ¹H nmr (360 MHz, CDCl₃) 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°; $[\alpha]^{25}_D -2.6^\circ$ (EtOH, *c* 0.77), not reported (4); tlc Rf 0.55 (KC18 Whatman, MeOH-NH₄OH, 40:1, iodoplatinate detection); eims *m/z* 287 (M⁺, not visible), 124, 120, 83; cims (NH₃) *m/z* 288 (M+1), 240, 124, 120; ¹³C nmr (67.5 MHz, CDCl₃) 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, CDCl₃) 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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METABOLITES FROM TWO SOFT CORALS FROM GUAM: *SINULARIA LEPTOCLADOS* and *SINULARIA GYROSA*

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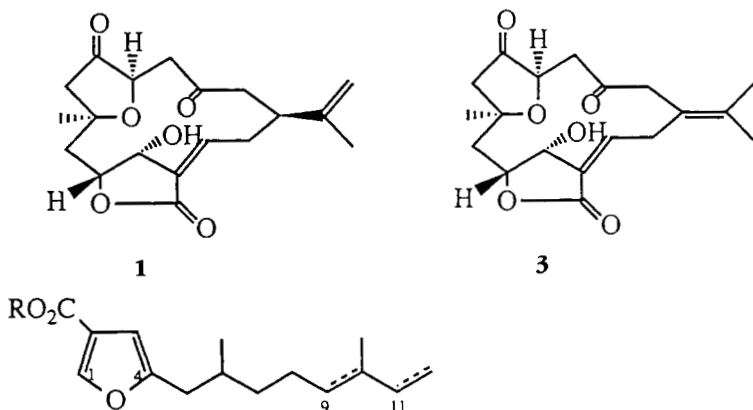
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Soft corals are well-known for their production of sesquiterpenes and diterpenes.¹ The unusual nor-diterpene lactone **1** was isolated initially from *Sinularia leptocladus* (phyllum Coelenterata, class Anthozoa, subclass Octocorallia, order Alcyonacea, family Alcyoniidae) 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. leptocladus* (Ehren-

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

berg) and have found that it contained the lactone **1**, the isomeric lactone **3**, and the sesquiterpene acid **2**. Acid **2** was further characterized by conversion to its methyl ester **4** and to the tetrahydro derivative **5**. Lactone **3** was not isolated in pure form, but its presence in small amounts (3-5% of the total lactone mixture) was detected by the presence of a second vinyl methyl signal in the ^1H -nmr spectrum at 1.56 ppm, in addition to the 1.80 ppm signal due to **1**. Lactone **3** has not been previously reported as a natural product, but has been prepared by iodine-induced isomerization of **1** (**2**). It may be artifactual in this isolation.

Only lactone **1** was obtained from *Simularia gyrosa* Klunzinger collected in Guam.



- 2** $\Delta^{9,11}$, R=H
4 $\Delta^{9,11}$, R=Me
5 9,10,11,12-tetrahydro, R=H

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—See Gunasekera and Schmitz (6).

ANIMAL COLLECTION.—*S. leptoclados* was collected in May 1979, at -15 m near the entrance to the channel at Cocos Lagoon, and *S. gyrosa* at Ana'e Island, Guam. Voucher specimens (79-GS-37 and 79-GS-45, respectively) are deposited at the University of Oklahoma.

EXTRACTION AND ISOLATION.— CHCl_3 -MeOH (1:1) extracts of frozen specimens (1 kg) of *S. gonatodes* were fractionated following a procedure described earlier (9).

Lactone 1.—From 1 kg of frozen *S. leptoclados* (200 mg); mp 233-234° [lit (2) 233° (dec)]; ir, ^1H nmr (DMSO-*d*), ms as reported for **1** (2); ^{13}C nmr ($\text{CDCl}_3 + \text{CD}_3\text{OD}$), 217.4 (s), 207.9 (s), 171.1 (s), 148.7 (s), 146, 133.7 (s), 111.6, 84.9, 80.3 (s), 76.2, 75.5, 52.2, 47.0, 44.1, 43.1, 40.6, 29.1, 27.1, 22.2 ppm.

Acid 2².—Colorless semisolid; 15 mg from 1 kg of frozen *S. leptoclados*; $[\alpha]^{25}_D$ 0.0° (0.175, CHCl_3); ir (CHCl_3) 3600-2800 (brd), 1685, cm^{-1} ; uv (EtOH) max 230 nm (7650); ^1H nmr (CDCl_3) 0.94 (3 H, d, 7 Hz) 1.31-1.75 (3 H, m), 1.78 (3 H, s, vinyl methyl), 2.20 (2 H, m), 2.56 (2 H, br t, $J=7$ Hz), 4.95, 5.08 (2 H, pr of d, $J=10, 16$, respectively), 5.46 (1 H, t, $J=6$ Hz), 6.34 (1 H, dd, $J=10, 16$ Hz), 6.37 (1 H, s, H-3), 7.98 (1 H, s, H-1), 10.06 (1 H, br, s, CO_2H); ^{13}C nmr (CDCl_3); 167.2 (s, C-13), 156.9 (s, C-4) 147.1 (d, C-11), 141.4 (d, C-1), 134.0 (s, C-10), 132.0 (d, C-9), 119.2 (s, C-2), 110.5 (t, C-12) 106.0 (d, C-3), 36.2 (t), 35.2 (t), 32.2 (d, C-6), 25.8 (t), 19.6 (q, C-15), 12.6 (q, C-14); ms (12 ev) m/z (rel. int.) 248 (m+, 21.4), 230 (80.0), 215 (24), 202 (21), 188 (16), 187 (14), 185 (21), 184 (23), 172 (17), 169 (23), 167 (16), 161 (24), 160 (100), 152 (42), 147 (39), 134 (65), 125 (45), 111 (23), 107 (17), 81 (31).

Esterification of 2.—Freshly prepared CH_2N_2 in Et_2O (5 ml) was added to 5 mg of **2** in 5 ml of Et_2O and the resultant mixture stored at 5° overnight. Evaporation of the Et_2O gave 4 mg of **4** as a sticky white solid; ir (CHCl_3) 1725 (CO_2Me), 1625, 1550 cm^{-1} ; ^1H nmr ($\text{CDCl}_3/\text{CD}_3\text{OD}$) 0.92 (3 H, $J=7$ Hz), 1.34 (3 H m), 1.80 (3 H, s, vinyl methyl), 2.20 (2 H, m), 2.56 (2 H, t, $J=7$ Hz), 3.94 (3 H, s, CO_2Me), 4.95 (1 H, d, $J=10$ Hz), 5.08 (1 H, d, $J=16$ Hz), 5.50 (1 H, t, $J=7$ Hz), 6.34 (1 H, dd, $J=10, 16$ Hz), 6.37 (1 H, s), 7.97 (1 H, s); ci ms (70 ev) m/z (rel. int), 303 ($\text{M}^+ + 41$; 3), 291 ($\text{M}^+ + 29$; 30), 263 ($\text{M}^+ + 1$;

²Discrepancies between the ^{13}C nmr data reported here and in Bowden *et al.* (2) for **2** are due to the fact that the solvent used in Bowden *et al.* (2) was CCl_4 , not CDCl_3 as reported (J. C. Coll, James Cook University, Townsville, Queensland, Australia, personal communication, 16 January 1986).

47), 244 (12), 235 (13), 232 (17), 230 (100), 207 (17), 203 (26), 193 (47), 181 (17), 175 (13), 167 (17), 161 (21), 153 (73), 148 (15), 140 (11), 139 (73), 123 (35), 115 (29).

Hydrogenation of 2.—Hydrogenation of 5 mg of **2** in MeOH in the presence of 1 mg of 5% palladium-on-carbon for 12 h (1 atom H₂) followed by filtration, and evaporation of the solvent yielded 4.5 mg of a sticky white solid (**5**); ir 3600–2500 (br), 1710 cm⁻¹; ¹H nmr (CDCl₃) 0.86 (3 H, br t, J=6 Hz), 0.92 (6 H, br d, J=7 Hz, 2 sec. Me), 1.21 (10 H, br m), 2.49 (2H, m), 6.31 (1 H, s, H-3), 7.97 (1 H, s, H-1), 10.2 (1 H, br s, -CO₂H); ms (70 ev) m/z (rel. int.) 252 (M+, 7.1), 207 (4.8), 195 (8), 181 (22), 164 (9), 157 (26), 153 (71), 139 (56), 130 (72), 126 (56), 125 (50), 113 (40), 112 (100), 109 (16), 108 (11), 107 (26), 95 (24), 87 (28), 85 (45), 84 (29), 83 (16), 81 (25), 71 (44), 69 (46), 57 (53).

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MAJOR CONSTITUENTS OF THE ESSENTIAL OILS OF THE FIJIAN DACRYDIUMS

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The leaf oils of some *Dacrydium* species, particularly *Dacrydium cupressinum* Sol. ex. Lamb. have been extensively studied, and the diterpene hydrocarbon rimuene has been the subject of a number of structural investigations (1-3).

The essential oils of the Fijian species *Dacrydium nausoriense* de Laub., whose growth is confined to restricted highland areas, and *Dacrydium nidulum* de Laub. var. *nidulum* have not, to our knowledge, been examined. However, phenolic diterpenoids were extracted from the wood of Fijian *D. nidulum* (4).

Analysis of the freshly extracted, steam-volatile oils was achieved in this study by means of capillary glc and ms. The essential oil content of six trees of *D. nidulum* var. *nidulum* and five of *D. nausoriense* was determined. The results are summarized in Table 1.

Some of the major components of the volatile oils that were identified from the *Dacrydium*s include α -pinene (up to 58%), caryophyllene, aromadendrene, viridiflorene, camphene, bicyclogermacrene, β -farnesene, and rimuene (up to 58%). The α -pinene content was significantly higher for trees obtained from the Nausori Highlands area. Twenty-one compounds were detected in *D. nidulum* var. *nidulum*, of which 19 have been identified; 32 compounds were detected in *D. nausoriense*, of which 26 have been identified. Of the compounds detected, 19 were common to both *Dacrydium* species (Table 1).