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A DITERPENE RELATED TO CLADIELLIN FROM A PACIFIC SOFT CORAL

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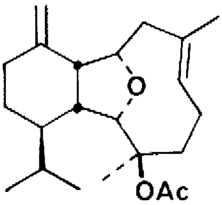
Abstract: A new diterpene 2 from a soft coral collected at Majuro Atoll has been related to cladiellin (1).

Diterpenes having the carbon skeleton of cladiellin (1) have been isolated from both soft corals (*Cladiella* sp.[1]) and gorgonians (*Eunicella* sp.[2]; *Muricella* sp.[3]). The major metabolite from an unknown soft coral[4] collected at Majuro Atoll has been identified as the simplest member of this family of diterpenoids.

Florisil chromatography of the dichloromethane soluble material from a methanol extraction of the soft coral gave the alcohol 2 (0.56% dry weight). The alcohol 2, mp 48-52°C, had the molecular formula $C_{20}H_{32}O_2$. The ^{13}C NMR spectrum[5] contained signals at δ 133.2 (d), 129.8 (d), 126.4 (s) and 121.6 (d) assigned to two olefinic groups, and at 89.9 (d), 80.9 (d) and 76.8 (s) assigned to two ether carbons and a tertiary alcohol carbon. The ^1H NMR spectrum contained signals for two olefinic protons at δ 5.53 (dd, 1H, J = 10,6Hz) and 5.40 (bs, 1H), two vinyl methyl groups at 1.82 (s, 3H) and 1.68 (s, 3H), two protons on carbons bearing oxygen at 4.09 (bd, 1H, J = 6Hz) and 3.82 (d, 1H, J = 9Hz), a methyl group at a tertiary carbon bearing oxygen



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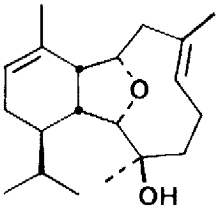

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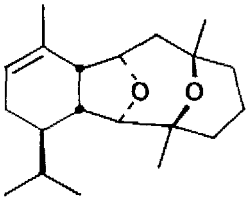
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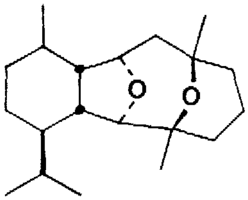
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at 1.41 (s, 3H) and for two methyl groups at 0.96 (d, 3H, J = 7Hz) and 0.87 (d, 3H, J = 7Hz). These data could be accommodated by structure 2. The chemical shifts for the methyl groups in the ^{13}C NMR spectrum, particularly the signal at δ 18.9 (q) suggested the 6E geometry.

Examination of a molecular model of alcohol 2 revealed that the alcohol oxygen was in close proximity to the $^{6}\Delta$ olefinic bond, provided that the olefinic bond had the E geometry. We were therefore able to prepare the tetracyclic di-ether 3[6] by treatment of the alcohol 2 with boron trifluoride etherate in ether at 0°C. Catalytic hydrogenation of the remaining olefinic bond in ether 3 gave a 3.5:1 mixture of the two possible diastereoisomers of ether 4.[7] Deacetylation of cladiellin (1) with lithium aluminum hydride in refluxing ether followed by the same cyclization and hydrogenation sequence gave a similar 3:1 mixture of the diastereoisomers of ether 4.

Acknowledgments

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References and Notes

1. R. Kazlauskas, P. T. Murphy, R. J. Wells and P. Schönholzer, Tetrahedron Lett. 4643 (1977).

2. O. Kennard, D. G. Watson, L. Riva di Sanserverine, B. Tursch, R. Bosmans and C. Djerassi, Tetrahedron Lett. 2879 (1968).

3. Y. Kashman, Tetrahedron Lett., 21, 879 (1980).

4. Specimen # 79-253. Collected on outer reef slope (-10 ft) at Majuro Atoll.

5. mp. 48-52°C; $[\alpha]_D$ - 22.7°(c 0.3, $CHCl_3$); IR 3500 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (d, 3H, J = 7Hz), 0.96 (d, 3H, J = 7Hz), 1.41 (s, 3H), 1.68 (bs, 3H), 1.82 (s, 3H), 3.82 (d, 1H, J = 9Hz), 4.09 (bd, 1H, J = 6Hz), 5.40 (bs, 1H), 5.53 (dd, 1H, J = 10,6Hz); ^{13}C NMR (C_6D_6) δ 132.2 (s), 129.8 (d), 126.4 (s), 121.6 (d), 89.9 (d), 80.9 (d), 76.8 (s), 47.2 (d), 44.7 (t), 40.5 (d), 38.4 (d), 37.1 (t), 29.3 (d), 27.7 (q), 23.3 (t), 23.2 (t), 22.2 (q), 21.8 (q), 20.8 (q), 18.9 (q). Mass spectrum m/e 304, 199, 179, 178; HRMS obsd. 304.2390, $C_{20}H_{32}O_2$ requires 304.2402.

6. ^{1}H NMR ($CDCl_3$) δ 0.78 (d, 3H, J = 7Hz), 0.94 (d, 3H, J = 7Hz), 1.09 (s, 3H), 1.31 (s, 3H), 1.67 (s, 3H), 3.85 (s, 1H), 4.01 (t, 1H, J = 5Hz), 5.46 (bd, 1H, J = 5Hz).

7. Major isomer: ^{1}H NMR ($CDCl_3$) δ 0.78 (d, 3H, J = 7Hz), 0.92 (d, 3H, J = 7Hz), 0.95 (d, 3H, J = 7Hz), 1.06 (s, 3H), 1.27 (s, 3H), 3.67 (s, 1H), 3.93 (bt, 1H, J = 5Hz). Mass spectrum m/e 306, 263, 246, 228, 222.

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