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LAUREACETAL-C, AN UNUSUAL SECOCHAMIGRANE SESQUITERPENE FROM THE RED ALGA LAURENCIA NIPPONICA YAMADA[1)]

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An unusual sesquiterpene α,β-unsaturated ketone, designated as laureacetal-C, has been isolated from the title alga and its structure was determined by the spectral and chemical methods.

We recently reported[2)] that Laurencia nipponica Yamada ("Ura-sozo") collected at Akkeshi and Erimo in the Pacific Coast of Hokkaido in the cold current region displayed the absence of halogenated C_{15}-nonterpenoids, the common major metabolites of this species collected in the warm current region, but the presence of prepacifenol, a chamigrane-type sesquiterpene, as the major one. Further investigations of Akkeshi's specimen have led to the isolation of several new chamigrane and secochamigrane derivatives as the minor constituents along with known halochamigranes.[3)] We wish to report herein the structure of one of three new secochamigrane derivatives, named as laureacetal-C, which contains an unusual α,β-unsaturated ketone moiety not yet encountered in the chamigrane-type metabolites of Laurencia.

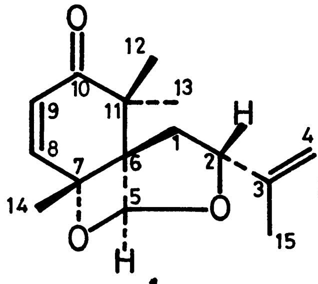
Repeated column chromatography of the methanol extracts over alumina or silica gel gave laureacetal-C (1) (0.24% of the extracts) together with laureacetal-A,[4)] laureacetal-B (2),[5)] laureacetal-D,[6)] and laureacetal-E.[6)]

Laureacetal-C (1), $C_{15}H_{20}O_3$ (m/e 248; M^+),[7)] mp 118-119°C (from isopropyl ether), $[\alpha]_D$ +9.8° (c 1.53, $CHCl_3$), possesses an α,β-unsaturated ketone moiety [UV: λ_{max}^{EtOH} 217 nm (ε 5400);[8)] IR: ν_{max}^{Nujol} 1678 cm^{-1}; ^1H NMR: δ ($CDCl_3$) 6.07 (1H, d, J=10 Hz) and 6.76 (1H, d, J=10 Hz); ^{13}C NMR: δ ($CDCl_3$) 201.6 (s), 149.0 (d), and 126.3 (d)], an isopropenyl group [δ 1.79 (3H), 4.93 (1H), and 5.10 (1H) (each br s); δ 142.6 (s), 112.5 (t), and 22.3 (q)], a $-O-\overset{|}{\underset{|}{C}}-CH_3$ grouping [δ 1.45 (3H, s); δ 73.7 (s) and 24.6

(q)], and two quaternary methyl groups (probably gem-dimethyl) [ν_{max} 1385, 1376, and 1360 cm^{-1}; δ 0.97 and 1.07 (each 3H, s); δ 17.9 (q) and 17.6 (q)].[9] Since the IR spectrum of 1 revealed the absence of hydroxyl function, the remaining two oxygen atoms in 1 were assumed to be involved as ether links, consisting of an acetal moiety which is suggested by the signals at δ 5.47 (s) and δ 105.0 (d) in the ^1H and ^{13}C NMR spectra of 1 respectively. In view of the above-mentioned data coupled with comparison of the spectral data with those of laureacetal-A and laureacetal-B, two formulas 1 and 7 could be proposed as possible structures for laureacetal-C. The structure of laureacetal-C, including the absolute configuration, was established by the following chemical derivation from laureacetal-B (2).

Treatment of 2 with LAH in ether at room temperature (2 hr) afforded debromolaureacetal-B (3),[10] $C_{15}H_{22}O_3$ (m/e 250; M^+), $[\alpha]_D$ +72.3°, in 91% yield. Jones oxidation of 3 gave α,β-unsaturated ketone (7) whose spectral properties were not consistent with those of laureacetal-C (1). On the other hand, the stereo- and regioselective epoxidation of 3 with tert-butyl hydroperoxide and vanadyl acetylacetonate in refluxing benzene (4 hr)[11] gave an epoxide (4),[10] $C_{15}H_{22}O_4$ (m/e 248; M^+-H_2O), $[\alpha]_D$ +20.3°, in 94% yield. The cis-relationship between the hydroxyl group at C-8[12] and the oxirane ring was supported by the splitting patterns of the C_8-H (dd, J=6, 6 Hz) at δ 3.97 and the hydroxyl proton (d, J=6 Hz) at δ 2.41 whose coupling (J=6 Hz) disappeared with addition of D_2O, indicating that an intramolecular hydrogen bond is present between the hydroxyl group at C-8 and the oxirane oxygen atom. Compound 4, when treated with carbon tetrabromide and triphenylphosphine in refluxing benzene (1 hr), gave the corresponding bromide (5),[10] $C_{15}H_{21}O_3Br$ (m/e 330 and 328; M^+), $[\alpha]_D$ -27.3°, in 45% yield. The stereochemistry of the bromine atom at C-8 was assigned on the basis of the reaction mechanism and the coupling constant of the bromomethine proton at C-8. Subsequently, the bromide (5) was subjected to reduction with zinc dust in acetic acid and methanol under reflux (10 min) to yield an unstable allyl alcohol (6) which was, without further purification, converted into α,β-unsaturated ketone by oxidation with Jones reagent in almost quantitative yield. This α,β-unsaturated ketone was found to be identical with natural laureacetal-C (1) by mixed mp (no depression) and comparison of the spectral properties.

Thus the structure of laureacetal-C is represented by formula 1.



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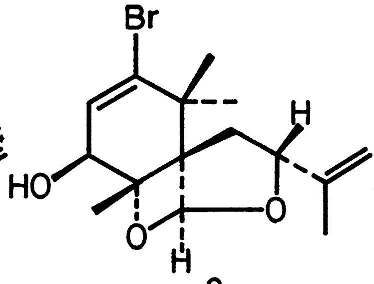

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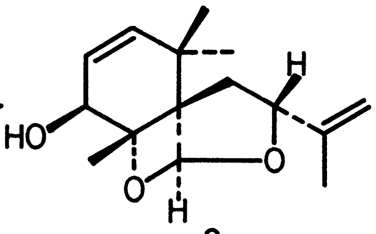

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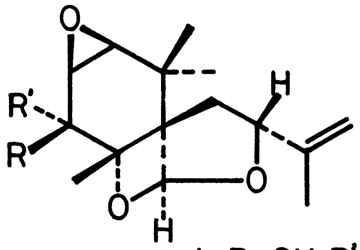
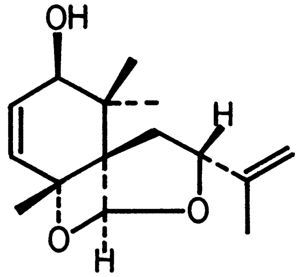


4: R=OH, R'=H
5: R=H, R'=Br



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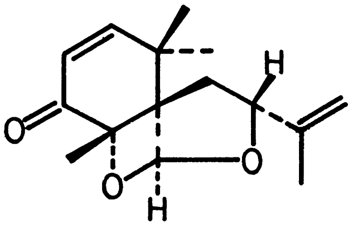

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2) K. Kurata, A. Furusaki, C. Katayama, H. Kikuchi, and T. Suzuki, Chem. Lett., 1981, 773.

3) Although no halogenated C_{15}-nonterpenoid could be detected in Akkeshi's specimen, *trans*- and *cis*-laurencenyne[13)] have been isolated from this specimen in 2.04% and 0.32% yields respectively.

4) T. Suzuki, A. Furusaki, N. Hashiba, and E. Kurosawa, Tetrahedron Lett., 1977, 3731.

5) T. Suzuki and E. Kurosawa, Chem. Lett., 1979, 301.

6) The structures of laureacetal-D and -E will be reported in the near future.

7) Molecular formula was confirmed by the high resolution mass spectral analysis; obsd m/e 248.1407, $C_{15}H_{20}O_3$ requires: 248.1410.

8) The absoption band in the UV spectrum of 1 was observed in slightly shorter wavelength than that of normal α,β-unsaturated cyclohexenone. This hypsochromic shift (about 10 nm) appears to be caused either by deformation[14)] of cyclohexenone ring in 1 or by inductive effect[15)] of the acetal oxygen atom at C-7 in 1.

9) The remaining spectral data of **1**: ν_{max}^{Nujol} 1278, 1240, 1180, 1120, 1096, 1075, 1034, 992, 928, 900, and 846; δ ca. 1.8 (1H, m), 2.28 (1H, dd, J=14, 6 Hz), 4.89 (1H, dd, J=10, 6 Hz), and 5.47 (1H, s); δ 105.0 (d), 82.4 (d), 61.1 (s), 44.3 (s), and 32.4 (t); m/e (rel. intensity) 248 (0.3; M^+), 220 (1), 159 (38), 150 (92), 135 (93), 121 (100), 105 (20), 91 (29), 43 (34), and 41 (56).

10) **3**: mp 73-75 °C; ν_{max}^{Nujol} 3370, 1650, 1110, 1090, 1028, 910, 855, and 757 cm^{-1}; δ ($CDCl_3$) 0.98, 1.03, 1.50 (each 3H, s), 1.76 (3H, br s), ca. 1.7 (1H, m: C_1-H), 2.20 (1H, dd, J=14, 6 Hz: C_1-H), 4.00 (1H, br d, J=6 Hz: C_8-H), ca. 4.9 (1H, m: C_2-H), 4.97 (1H, br s: C_4-H), 5.17 (1H, br s: C_4-H), 5.47 (1H, s: C_5-H), 5.96 (1H, d, J=10 Hz: C_{10}-H), and 6.12 (1H, dd, J=10, 6 Hz: C_9-H); m/e 250 (1: M^+), 153 (100), 137 (12), 98 (52), and 43 (92).

4: mp 78-80 °C; ν_{max}^{Nujol} ∿3500, 1654, 1112, 1060, 1048, 982, 956, 948, 896, and 864 cm^{-1}; δ ($CDCl_3$) 0.81, 1.03, 1.41 (each 3H, s), 1.78 (3H, br s), ca. 1.6 (1H, m), 2.05 (1H, dd, J=14, 6 Hz), 2.41 (1H, d, J=6 Hz: OH), 3.30 (1H, d, J=4 Hz: C_{10}-H), 3.64 (1H, dd, J=6, 4 Hz: C_9-H), 3.97 (1H, dd, J=6, 6 Hz: C_8-H), ca. 4.9 (1H, m), 4.91 (1H, br s), 5.09 (1H, br s), and 5.54 (1H, s); m/e 248 (2; M^+-H_2O), 187 (34), 159 (49), 150 (87), 135 (100), 121 (98), 43 (58), and 41 (66).

5: mp 161-163 °C; ν_{max}^{KBr} 1656, 1106, 1084, 1042, 992, 942, 918, 908, 897, and 884 cm^{-1}; δ ($CDCl_3$) 0.72, 1.14, 1.45 (each 3H, s), ca. 1.7 (1H, m), 1.76 (3H, br s), 2.08 (1H, dd, J=14, 6 Hz), 3.11 (1H, d, J=4 Hz), 3.70 (1H, dd, J=4, 3 Hz), 3.91 (1H, d, J=3 Hz), ca. 4.9 (1H, m), 4.91 (1H, br s), 5.07 (1H, br s), and 5.68 (1H, s); m/e 330, 328 (1.3; M^+), 249 (1.6), 151 (100), 109 (30), and 43 (48).

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12) The numbering system of **1** corresponds to the systems used for the members of the chamigrane derivatives.

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