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LAUREACETAL-D AND -E, TWO NEW SECOCHAMIGRANE DERIVATIVES FROM THE RED ALGA LAURENCIA NIPPONICA YAMADA[1)]

Kazuya KURATA,* Teruaki SUZUKI,† Minoru SUZUKI,† Etsuro KUROSAWA,†* Akio FURUSAKI,† and Takeshi MATSUMOTO†

Department of Industrial Chemistry, Hakodate Technical College, Hakodate 042

† Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

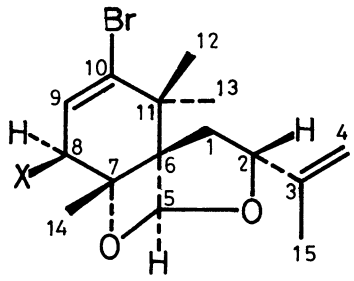
The structures of laureacetal-D and -E, new halogenated metabolites of the red alga Laurencia nipponica Yamada, were determined by the spectral properties, chemical reactions, and X-ray crystallographic analysis.

Recently we reported the structure of laureacetal-C (7) which has been isolated from the red alga Laurencia nipponica Yamada collected at Akkeshi, Hokkaido.[2)] In this paper we describe the structures of two new secochamigrane-type sesquiterpenoids, also isolated as the minor constituents of Akkeshi's specimen and designated as laureacetal-D and -E respectively.

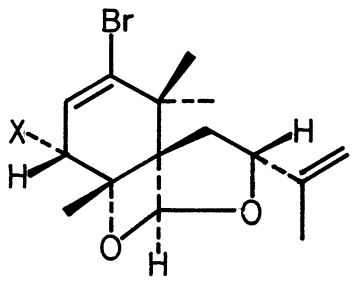
Laureacetal-D (1), $C_{15}H_{20}O_2Br_2$ (m/e 394, 392, and 390; M^+), $[\alpha]_D$ +166° (c 0.25, $CHCl_3$), and laureacetal-E (2), $C_{15}H_{20}O_2BrCl$ (m/e 350, 348, and 346; M^+), $[\alpha]_D$ +99.5° (c 0.42, $CHCl_3$), were isolated in 0.15 and 0.15% yields of the extracts, respectively. On analysis of the spectral properties[3)] of laureacetal-D (1) and -E (2), in detailed compariosn of their ^1H and ^{13}C NMR spectra with those of laureacetal-B (3)[4)] and laureacetal-A (8),[5)] formulae 1 and 9 for laureacetal-D and formulae 2 and 10 for laureacetal-E could be proposed as possible structures.

Treatment of laureacetal-B (3) with thionyl chloride in benzene at room temperature gave a chloro compound, which was identical with laureacetal-E (2), in 80% yield. Furthermore, treatment of 8-epilaureacetal-B (6)[4)] with triphenylphosphine in refluxing carbon tetrachloride yielded laureacetal-E (2) and alcohol (11)[4)] in 15 and 82% yields, respectively. On the other hand, when treated with triphenylphosphine in refluxing carbon tetrachloride, laureacetal-B (3) afforded laureacetal-E (2), epilaureacetal-E (5),[6)] and a chloro compound (10)[7)] in 11, 20, and 28% yields, respectively. Treatment of 3 with carbon tetrabromide and triphenylphosphine in refluxing benzene gave laureacetal-D (1) and epilaureacetal-D (4)[6)] in 15 and 21% yields, respectively.

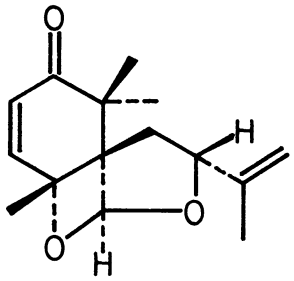
Since the possibility of rearrangement from the four-membered acetal into the five-membered acetal during the chlorination could not be completely ruled out, the choice in favour of formula 1 for laureacetal-D and formula 2 for laureacetal-E could not be made with the aid of the chemical reactions. Therefore, in order to confirm the structures, 1 and 2 were subjected to X-ray crystallographic analysis.



1: X=Br
2: X=Cl
3: X=OH



4: X=Br
5: X=Cl
6: X=OH



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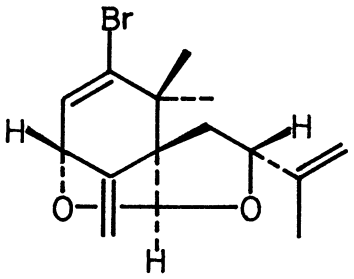

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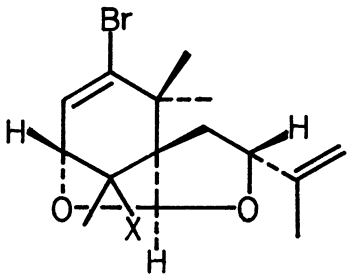
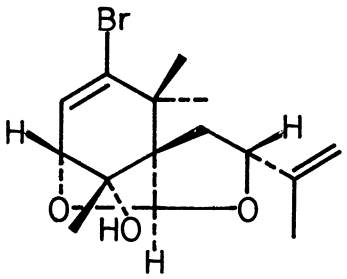


9: X=Br
10: X=Cl



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The crystal data for 1 were as follows: $C_{15}H_{20}O_2Br_2$, orthorhombic, space group $P2_12_12_1$, a=14.691(5), b=17.492(6), c=6.023(2) Å, Z=4, D_c=1.638 g cm^{-3}, μ(MoKα)=51.8 cm^{-1}. 1034 independent intensity data for 2θ<50° were collected on a Rigaku four-circle diffractometer with graphite-monochromated MoKα radiation by the use of the θ-2θ scanning technique.[8] The structure was solved by the Monte Carlo direct method,[9] using the 20 strongest reflections as the starting set. The 8th random phase set led to the correct solution; an E-map based on 447 phases revealed the locations of all the non-hydrogen atoms. After the structure had been well refined by the block-diagonal least-squares method with anisotropic temperature factors, the absolute configuration was determined by taking account of the anomalous dispersion of bromine atoms for MoKα radiation. The R ratio for the structure depicted in Fig. 1 and its antipode, 1.061, established the absolute configuration of 1 as shown in Fig. 1.[10] A difference Fourier map afforded all the hydrogen atoms. Further least-squares refinements were performed including these hydrogen atoms; the final R value was 0.072.

The crystal data for 2 were as follows: $C_{15}H_{20}O_2BrCl$, orthorhombic, space group $P2_12_12_1$, a=14.570(2), b=17.503(8), c=6.031(2) Å, Z=4, D_c=1.501 g cm^{-3}, μ(CuKα)=52.7 cm^{-1}. 1580 unique intensity data for 2θ<156° were measured on a Nonius four-circle diffractometer with Ni-filtered CuKα radiation.[11] The structure determination was accomplished in much the same manner as that of 1. The 2ndly-generated random phase set for the 20 strongest reflections led to the correct solution; an E-map calculated with 532 phases revealed the whole structure. The

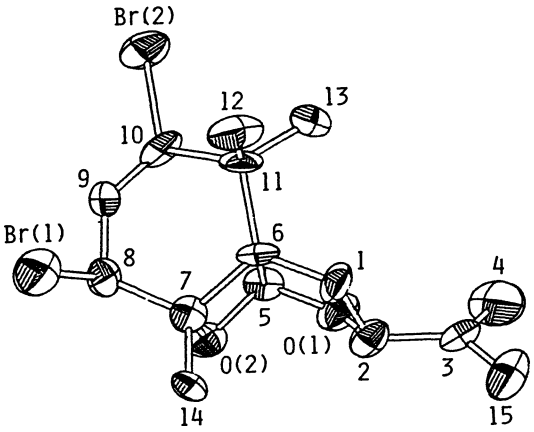
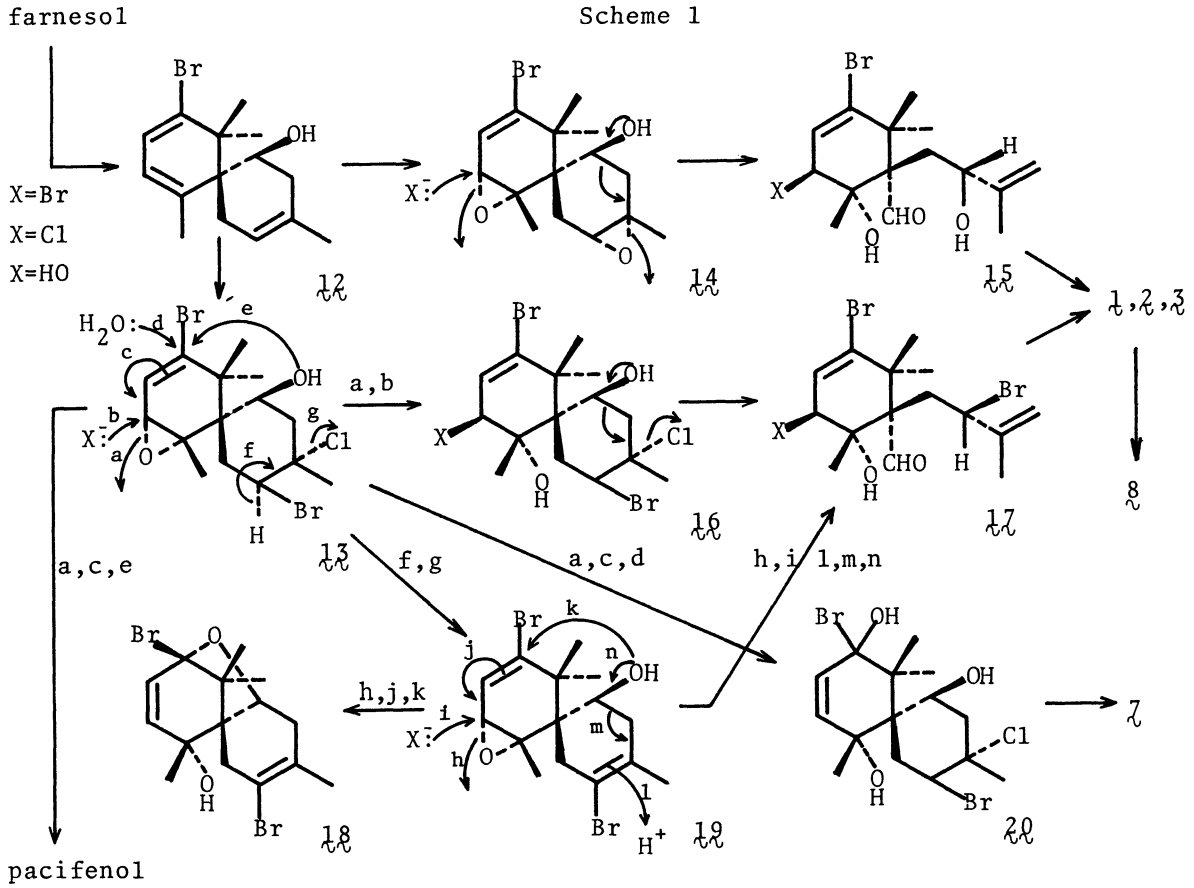


Fig. 1. A perspective view of the 1 molecule.

least-squares refinements including the anomalous dispersion effects of halogen atoms gave an R ratio of 1.036 for the two enantiomeric structures; consequently, one of them was rejected at the 99.5% confidence level.[10] After all the hydrogen atoms, except those of the isopropenyl group, had been located in a difference Fourier map, several cycles of the least-squares method were further carried out including the hydrogen atoms; the final R value was 0.065. The molecular shape of 2 thus obtained is almost identical to that of 1 given in Fig. 1.

The finding of these metabolites seems to strongly suggest that halogenated metabolites of Laurencia would biogenetically synthesized by the participation of

Scheme 1



halide ions. The biogenesis of these interesting secochamigrane derivatives can be rationalized as shown in Scheme 1, involving the possible intermediates 15 and 17 probably derived from triene (12)[12] and prepacifenol (13), respectively.

References

1) Part 53 of "Constituents of Marine Plants". Part 52; K. Kurata, T. Suzuki, M. Suzuki, E. Kurosawa, A. Furusaki, and T. Matsumoto, Chem. Lett., 1983, 299.

2) K. Kurata, T. Suzuki, M. Suzuki, and E. Kurosawa, Chem. Lett., 1983, 29.

3) 1: mp 126-127 °C (hexane-isopropyl ether); IR, ν_{max}^{Nujol} 1650, 1620, 1155, 1108, 1085, 1070, 975, 945, 900, and 855 cm^{-1}; ^1H NMR, δ ($CDCl_3$) 1.15 (6H, s; C_{12}-Me and C_{13}-Me), 1.72 (3H, s; C_{14}-Me), 1.78 (3H, br s; C_{15}-Me), 1.9 (1H, m; C_1-H), 2.24 (1H, dd, J=13, 6 Hz; C_1-H), 4.62 (1H, d, J=6 Hz; C_8-H), 4.9 (1H, m; C_2-H), 4.90 (1H, br s; C_4-H), 5.06 (1H, br s; C_4-H), 5.50 (1H, s; C_5-H), and 6.54 (1H, d, J=6 Hz; C_9-H); ^{13}C NMR, δ ($CDCl_3$) 141.8 (s), 137.9 (s), 128.6 (d), 111.2 (t), 104.8 (d), 83.8 (d), 79.6 (s), 62.5 (s), 51.5 (d), 39.5 (s), 31.9 (t), 24.9 (q), 23.6 (q), 21.1 (q), and 16.8 (q); HR-MS, m/e 391.9775 (calcd for $C_{15}H_{20}O_2{}^{79}Br^{81}Br$, 391.9810).
2: mp 119-120 °C (hexane-isopropyl ether); ν_{max}^{Nujol} 1655, 1632, 1115, 1095, 1075, 1040, 978, 948, 923, 900, 860, and 708 cm^{-1}; δ ($CDCl_3$) 1.16 (6H, s), 1.61 (3H, s), 1.78 (3H, br s), 1.9 (1H, m), 2.24 (1H, dd, J=13, 6 Hz), 4.42 (1H, d, J=6 Hz), 4.9 (1H, m), 4.90 (1H, br s), 5.06 (1H, br s), 5.50 (1H, s), and 6.50 (1H, d, J=6 Hz); δ ($CDCl_3$) 141.8 (s), 138.7 (s), 127.8 (d), 111.2 (t), 104.8 (d), 83.8 (d), 80.1 (s), 62.4 (s), 59.4 (d), 39.5 (s), 31.9 (t), 23.4 (q), 22.8 (q), 22.5 (q), and 16.8 (q); HR-MS, m/e 346.0336 (calcd for $C_{15}H_{20}O_2{}^{79}Br^{35}Cl$, 346.0336).

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

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

6) 4: $C_{15}H_{20}O_2Br_2$ (m/e 394, 392, and 390; M^+); mp 120-122 °C; $[\alpha]_D$ -37.9° (c 0.75, $CHCl_3$); δ ($CDCl_3$) 0.94 (3H, s), 1.19 (3H, s), 1.58 (3H, s), 1.80 (3H, br s), 1.9 (1H, m), 2.28 (1H, dd, J=13, 6 Hz), 4.61 (1H, d, J=2 Hz), 4.9 (1H, m), 4.94 (1H, br s), 5.10 (1H, br s), 5.57 (1H, s), and 6.53 (1H, d, J=2 Hz).
5: $C_{15}H_{20}O_2BrCl$ (m/e 350, 348, and 346; M^+); mp 127-129 °C; $[\alpha]_D$ -29.0° (c 0.92, $CHCl_3$); δ ($CDCl_3$) 0.93 (3H, s), 1.17 (3H, s), 1.55 (3H, s), 1.77 (3H, br s), 1.9 (1H, m), 2.24 (1H, dd, J=13, 6 Hz), 4.42 (1H, d, J=2 Hz), 4.9 (1H, m), 4.90 (1H, br s), 5.06 (1H, br s), 5.51 (1H, s), and 6.36 (1H, d, J=2 Hz).

7) The structure of 10 was tentatively assigned; 10: δ ($CDCl_3$) 1.15, 1.18, 1.72, 1.77 (each 3H, s), 2.25 (1H, dd, J=13, 6 Hz), 4.71 (1H, d, J=6 Hz), 4.9 (1H, m), 4.90 (1H, br s), 5.08 (1H, br s), 5.50 (1H, s), and 6.27 (1H, d, J=6 Hz).

8) The intensity measurement of 1 was done at the High Energy X-Ray Diffraction Laboratory of Hokkaido University.

9) A. Furusaki, Acta Crystallogr., Sect. A, 35, 220 (1979).

10) W. C. Hamilton, Acta Crystallogr., 18, 502 (1965).

11) We thank Dr. Takao Matsuzaki, Central Research Laboratories of Mitsubishi Chemical Industries, for the intensity measurement of 2.

12) Compounds 12 and 18 have been isolated from L. nipponica; unpublished result.

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