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LAURENCIAL, A NOVEL SESQUITERPENE α,β-UNSATURATED ALDEHYDE FROM THE RED ALGA LAURENCIA NIPPONICA YAMADA[1]

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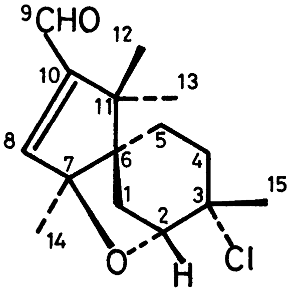
Laurencial, a novel sesquiterpene which possesses spiro[4.5]decane skeleton with α,β-unsaturated aldehyde moiety, has been isolated from the title alga and its structure was determined by X-ray crystallographic analysis.

As part of our continuing studies on the constituents of the red alga Laurencia nipponica Yamada collected in the Pacific Coast of Hokkaido, we recently reported that the specimen collected at Akkeshi have contained several chamigrane- and secochamigrane-type compounds.[2] Further investigations of the minor components of this specimen have led to the isolation of new sesquiterpene aldehyde, designated as laurencial, in 0.03% yield of the extracts. We wish to report herein the structure of laurencial (1) containing α,β-unsaturated aldehyde moiety arisen from ring contraction of chamigrane skeleton, which is unique feature not yet observed in the rearranged chamigrane-type metabolites of Laurencia.

Laurencial (1), mp 124-126 °C (hexane-isopropyl ether), $[\alpha]_D$ +11.2° (c 0.25; $CHCl_3$), was analyzed for $C_{15}H_{21}O_2Cl$ by mass spectroscopy m/e 270 and 268 (M^+); HR-MS, 268.1233 (calcd for $C_{15}H_{21}O_2{}^{35}Cl$, 268.1231). The spectral data of 1[3] indicated the presence of an α,β-unsaturated aldehyde moiety, four tertiary methyl groups, one olefinic proton, and at least one methine proton. However, because of the small quantities of material available, no chemical reaction could be performed to provide additional information of the structure. Therefore, in order to define the structure, a single crystal of 1 was subjected to X-ray crystallographic study.



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The crystal data for 1 were as follows: $C_{15}H_{21}O_2Cl$, orthorhombic, space group $P2_12_12_1$, a=8.992(3), b=23.22(1), c=6.797(3) Å, Z=4, D_c=1.258 g cm^{-3}, μ(CuKα)=23.4 cm^{-1}. 1366 unique intensity data for 2θ<130° were collected on an automated four-circle diffractometer with graphite-monochromated CuKα radiation by the use of the θ-2θ scanning technique.[4] The structure was elucidated by the Monte Carlo direct method,[5] using the 20 strongest reflections as the starting set. The 22nd random phase set led to the correct solution; an E-map calculated with 392 phases yielded all the non-hydrogen atoms. After several cycles of the least-squares refinement using the carbon atomic scattering factors for all the light atoms had been carried out, the oxygen atoms were assigned by taking account of the interatomic distances and the values of isotropic temperature factors. The structure thus obtained was refined by the block-diagonal least-squares method with anisotropic temperature factors. The absolute configuration was determined by using the anomalous dispersion effects of chlorine atoms for CuKα radiation. The R ratio for the two enantiomeric structures, 1.041, rejected one of them at the 99.5% confidence level.[6] A difference Fourier map revealed all the hydrogen atoms. Further least-squares refinements were performed including these hydrogen atoms; the final R value was 0.056. The molecular skeleton of **1** including the absolute configuration is shown in Fig. 1, while the bond distances are given in Fig. 2.

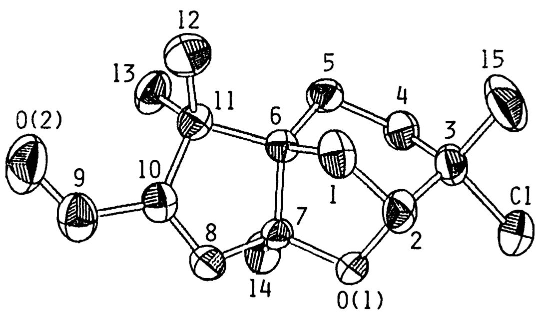

Fig. 1. A perspective view of the **1** molecule.

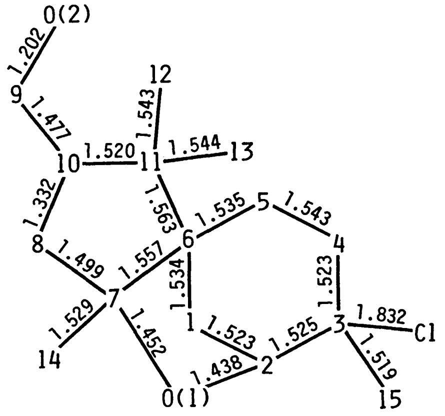

Fig. 2. Bond distances (l/Å). The e.s.d.'s are 0.004-0.008 Å.

References

1) Part 52 of "Constituents of Marine Plants". Part 51; K. Kurata, T. Suzuki, M. Suzuki, and E. Kurosawa, Chem. Lett., 1983, 29.

2) Part 51 of this series.

3) The spectral data of **1**: λ_{max} (EtOH) 227 nm (ε 10,800); ν_{max} (Nujol) 2748, 1674, 1602, 1342, 1324, 1244, 1222, 1192, 1134, 1120, 1098, 1082, 1030, 1016, 980, 906, 882, 792, 758, 720, and 650 cm^{-1}; δ ($CDCl_3$) 1.13, 1.18, 1.57, 1.58 (each 3H, s), 1.7-2.8 (6H, m), 4.11 (1H, d, J=6 Hz), 6.67 (1H, s), and 9.70 (1H, s); m/e (rel. intensity) 270, 268 (23 and 100; M^+), 255, 253 (15 and 75), 193 (15), 185 (16), 177 (18), 161 (17), 149 (17), 135 (16), 133 (19), 121 (40), 119 (17), 109 (23), 107 (20), 105 (20), 91 (28), 77 (17), and 43 (41).

4) The intensity measurement was done at the High Energy X-ray Diffraction Laboratory of Hokkaido University.

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

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

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