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ISOLAURALLENE, A NEW NONTERPENOID C_{15}-BROMOALLENE, FROM THE RED ALGA LAURENCIA NIPPONICA YAMADA[1)]

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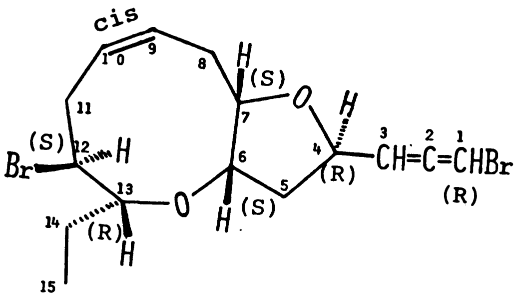
Isolaurallene ($\underset{\sim}{1}$), a new nonterpenoid C_{15}-bromoallene, was isolated from the red alga Laurencia nipponica Yamada. The structure of this compound was determined by its spectral properties and X-ray diffraction analysis.

The diversity of terpenoids and nonterpenoids biosynthesis[2)] in the red alga Laurencia nipponica Yamada has been found to be dependent upon the growth localities. In the recent paper[2m)], we reported that the halogenated C_{15}-nonterpenoid, other than the halogenated sesquiterpenoids, has not been detected from the neutral extracts from this alga collected in Akkeshi and Erimo on the Pacific Coast of Hokkaido in the cold current region. Subsequently, we also investigated the extract from this alga collected in Izumihama near Hiroo on the Pacific Coast of Hokkaido and isolated a new bromoallene, isolaurallene ($\underset{\sim}{1}$), as the main component. The present paper describes the isolation and the structure of this compound.

Isolaurallene (4.1%) was isolated from the methanol extract of the half dried alga by alumina [eluent: hexane–benzene (1:1)] and silica gel [eluent: hexane–benzene (2:1)] chromatography. Isolaurallene, $\underset{\sim}{1}$, m.p. 51–52°C (hexane), $[\alpha]_D$ -113.9° (c; 1.00, $CHCl_3$); was analyzed for $C_{15}H_{20}O_2Br_2$; M^+ m/e 394, 392, 390;



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high resolution $M^+{-}C_2H_5$ m/e 360.9462 (calcd for $C_{13}H_{15}O_2{}^{79}Br^{79}Br$, 360.9440) and showed only an end absorption in the UV-region. The absence of hydroxyl and carbonyl groups in the IR[3)] of 1 suggested that the two oxygen atoms of 1 were involved as ether linkages. Isolaurallene 1 possesses a bromoallene side chain [IR ν_{max}(KBr) 1963 cm^{-1}; ^1H-NMR[3)] ($CDCl_3$) δ 5.39(1H, dd, J=6,6 Hz) and 6.08(1H, dd, J=6,2 Hz); ^{13}C-NMR[3)] ($CDCl_3$) δ 201.5(s), 101.5(d), 73.9(d); MS m/e 287 and 285 ($M^+{-}C_3H_2Br$)] and a $\mathrm{CH_3CH_2{-}\underset{-CH-}{\underset{|}{C}}H{-}O{-}}$ moiety [δ 0.95(3H, t, J=7 Hz), 1.85(2H, dq, J=4,7 Hz), 3.37(1H, dt, J=10,4 Hz), m/e 365, 363, 361 ($M^+{-}C_2H_5$)]. Furthermore, the proton spin decoupling experiments indicated the presence of the following partial structure: $\mathrm{CH_3CH_2{-}\underset{O-}{\underset{|}{C}}H{-}\underset{X}{\underset{|}{C}}H{-}CH_2{-}CH{=}CH{-}CH_2{-}\underset{X}{\underset{|}{C}}H{-}\underset{X}{\underset{|}{C}}H{-}CH_2{-}\underset{O-}{\underset{|}{C}}H{-}CH{=}C{=}CHBr}$ (X=1 bromine atom and 2 oxygen atoms). On the basis of these facts as well as the biogenetic view point the planar structure of 1 was proposed for isolaurallene. Finally, the structure of 1 including absolute configuration was confirmed by X-ray crystallographic study as follows.

The crystal data of 1 were as follows: $C_{15}H_{20}O_2Br_2$, orthorhombic, space group $P2_12_12_1$, a=10.393(2), b=27.824(4), c=5.3968(7) Å, Z=4, D_c=1.669 g cm^{-3}, μ(MoKα)= 51.4 cm^{-1}. The intensity data were collected on a Rigaku four-circle diffractometer with graphite-monochrotomated MoKα radiation. In the range of 2θ values up to 50°, 1091 independent structure factors above the $3\sigma(F)$ level were selected for the structure determination. The structure was elucidated by the heavy-atom method. 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 located by taking account of isotropic temperature factors as well as interatomic distances. The absolute configuration was determined by using the anomalous dispersion of bromine atoms for MoKα radiations; the R ratio

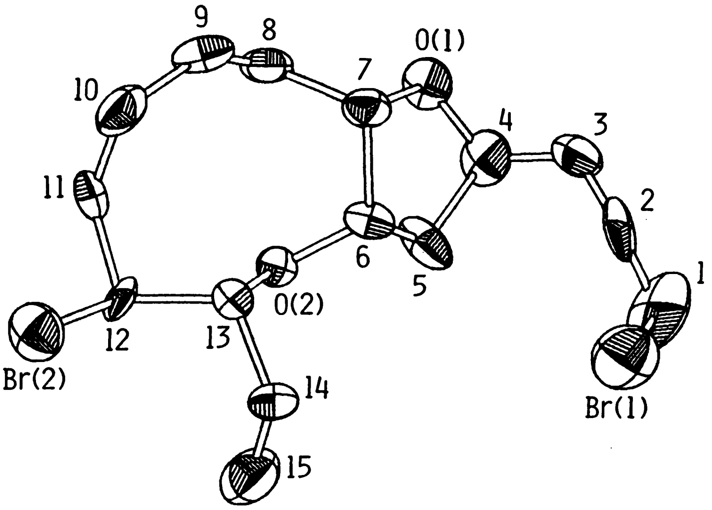

Fig. 1

for the structure drawn in Fig. 1 and its antipode, 1.045, rejected the latter at the 99.5% confidence level.[4] All the 20 hydrogen atoms were located in a difference Fourier map. The block-diagonal least-squares refinement was further repeated including these hydrogen atoms; the final R value was 0.076. The molecular skeleton of 1 thus obtained is shown in Fig. 1.

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3) IR, ^{1}H and ^{13}C NMR data for isolaurallene (**1**): ν_{max}(KBr) 3065, 3025, 1963, 1180, 1040, 890, 805, 745, and 655 cm^{-1}; δ (100 MHz, CDCl$_3$) 0.95(3H, t, J=7 Hz, H$_{15}$), 1.85(2H, dq, J=4,7 Hz, H$_{14}$), 2.13(2H, dd, J=7,6 Hz, H$_5$), 2.24–2.56(2H, m, H$_8$), 3.0–3.6(2H, m, H$_{11}$), 3.37(1H, dt, J=10,4 Hz, H$_{13}$), 3.85–4.28(3H, m, H$_6$,H$_7$, and H$_{12}$), 4.75(1H, dddd, J=7,7,6,2 Hz, H$_4$), 5.39(1H, dd, J=6,6 Hz, H$_3$), 5.72(2H, m, H$_9$ and H$_{10}$), and 6.08(1H, dd, J=6,2 Hz, H$_1$); δ (CDCl$_3$) 7.7(q), 23.8(t), 29.2(t), 32.2(t), 40.2(t), 52.4(d), 73.7(d), 73.9(d), 80.9(d), 82.3(d), 85.0(d), 101.5 (d), 126.7(d), 128.5(d), and 201.5(s).

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