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LAURINTEROL AND DEBROMOLAURINTEROL, CONSTITUENTS FROM *LAURENCIA INTERMEDIA*[1]

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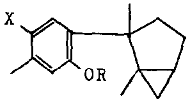
During a search of the constituents from *Laurencia* species,[2,3] a new type of sesquiterpenoid containing bromine and a corresponding debromo compound have been isolated from *L. intermedia* YAMADA. In this paper we wish to report the structures of these compounds, designated laurinterol and debromolaurinterol, are as shown in I and II, respectively, on the basis of the following experimental evidence.



(I) X = Br, R = H (Ia) X = Br, R = Ac
(II) X = R = H (IIa) X = H, R = Ac

Laurinterol[4] (I), $C_{15}H_{19}OBr$, m.p. 54 ~ 55°, mass spectrum *m/e* 296, 294, $[\alpha]_D^{15}$ +13.3° ($CHCl_3$), was obtained in ca. 0.22% yield by chromatography of ether or methanol extracts of the seaweed[5]. The U.V., I.R., and N.M.R.[6] spectra indicated the presence of a trisubstituted phenol group $[\lambda_{max}^{EtOH}$ 225, 283, and 289 mμ (ε 7100, 2200, and 2100); $\nu_{max}^{CHCl_3}$ 3600, 1610, 1495, and 1152 cm^{-1}; τ 5.14 (1H, s), 3.58 (1H, s), and 2.53 (1H, s)], an aromatic methyl group [τ 7.78 (3H, s)], two tertiary methyl groups [τ 8.66 and 8.71 (each 3H, s)], and a cyclopropane ring [$\nu_{max}^{CHCl_3}$ 3060 and 1025 cm^{-1}; τ 9.48

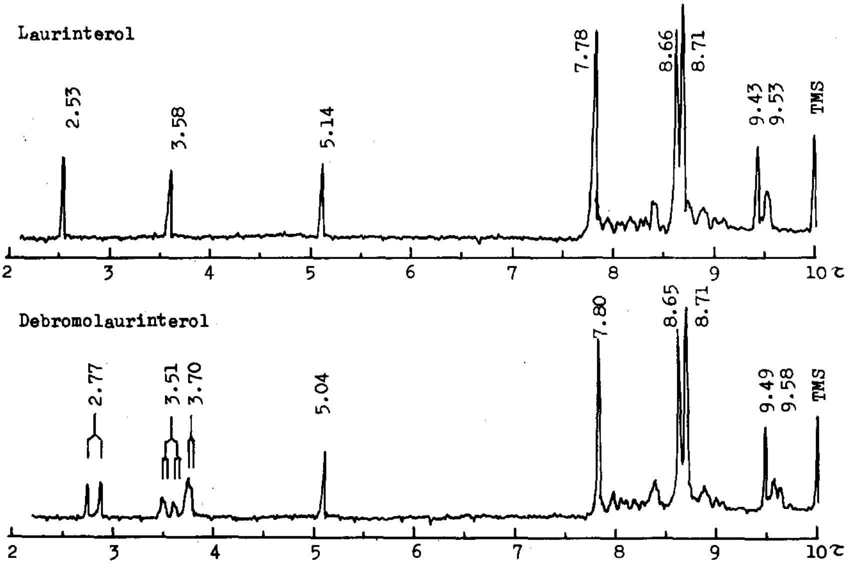
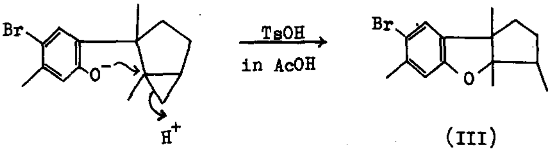


Fig. N.M.R. spectra of laurinterol (I) and debromolaurinterol (II) (in CCl_4, 60 Mc.)

(2H, d, J = 6.5 c.p.s.) and ca. 8.9 (1H, m)]. From these data and the mass spectrum, it was suggested that I would have a structure similar to aplysin (III)[7] except a hydroxyl group and a cyclopropane ring moiety. Treatment of I with *p*-toluenesulfonic acid in acetic acid[8] afforded an isomeric ether, $C_{15}H_{19}OBr$, m.p. 95°, $[\alpha]_D^{20}$ -86.1°, in good yield. This ether has now been identified as aplysin by a mixed melting point determination and by a comparison of the I.R. (Nujol) and N.M.R. spectra with those of an authentic specimen. Both this transformation and the spectral data unambiguously determine the positions of the substituents in the aromatic nucleus as well as the presence of a dimethylbicyclo [3.1.0] hexane group in laurinterol (I).



(III)

Acetylation of I yielded laurinterol acetate (Ia), $C_{17}H_{21}O_2Br$, m.p. 93 ~ 93.5°, $[\alpha]_D^{20}$ +11.1° ($CHCl_3$), λ_{max}^{EtOH} 270 and 278 mμ (ε 670 and 662), ν_{max}^{Nujol} 1765 cm^{-1}. However, acetylation of a crude sample of I followed by chromatography on silica gel led to the isolation of a new acetate (IIa), $C_{17}H_{22}O_2$, ν_{max}^{film} 3060, 1770, and 1020 cm^{-1}, in addition to Ia. Hydrolysis of IIa gave a corresponding phenol (II), $C_{15}H_{20}O$, $[\alpha]_D^{20}$ -12.2° ($CHCl_3$), $\nu_{max}^{CHCl_3}$ 3680, 3060, and 1185 cm^{-1}. Since the crude I shows no carbonyl band in the I.R. spectrum, this phenol is a naturally occurring substance. The N.M.R. spectrum of II showed the signals comparable with those of I at the higher magnetic field region, suggesting that II would have the same carbon skeleton as I. In the lower field region, however, the distinct difference was observed; i.e., in the spectrum of II, absorptions due to three aromatic protons appeared at τ 3.70 (1H, broad s), 3.51 (1H, broad d, J = 7.5 c.p.s.), and 2.77 (1H, d, J = 7.5 c.p.s.), instead of two singlets (each 1H) at τ 3.58 and 2.53 in the spectrum of I. Hence this new phenol (II) must be a debromo analog of laurinterol. This was confirmed by the reduction of I to II with lithium aluminum hydride. Thus laurinterol and debromolaurinterol should be represented by I and II, respectively.

Laurinterol may be a precursor of aplysin. Investigation is now in progress on the biogenetic relation between these compounds, laurene[3] and cuparene[9].

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3) T. Irie, Y. Yasunari, T. Suzuki, N. Imai, E. Kurosawa, and T. Masamune, ibid., 3619 (1965).
4) Satisfactory analyses were obtained for the new compounds listed in this report.
5) The seaweed was collected in August at Oshoro Bay, Hokkaido.
6) The N.M.R. spectra were measured at 60 Mc., in CCl_4, using $SiMe_4$ as an internal reference. (s = singlet, d = doublet, and m = multiplet.)
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9) C. Enzell and H. Erdtman, Tetrahedron, **4**, 361 (1958).