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Structure and Absolute Configuration of Isodictytriol, a New Diterpene from the Brown Alga *Dictyota dichotoma*

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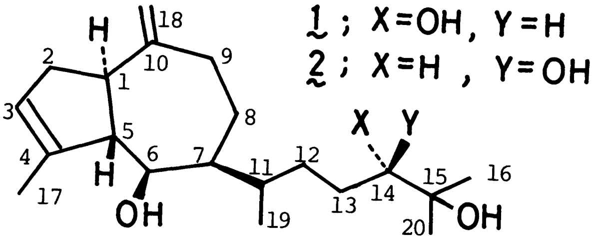
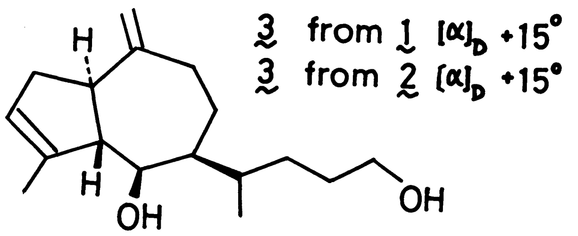
A new diterpene, isodictytriol, was isolated from the brown alga, *Dictyota dichotoma*, and its structure and absolute configuration were elucidated by means of spectral analyses and chemical transformations.

The constituents of the brown algae belonging to Dictyotaceae family have been promptly investigated because of their unique diterpenoid metabolites. In a continuing study on the components of the seaweeds,[1)] we isolated a new diterpene from the brown alga, *Dictyota dichotoma*, and the present report describes structural determination of the new compound.



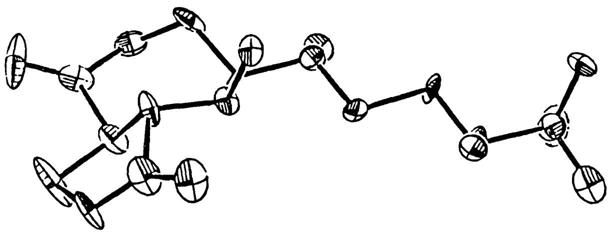


Chromatographic separation of the methanol extract of *D. dichotoma*, collected at the Yagachi beach, Okinawa, afforded a crystalline substance, designated as isodictytriol (1), mp 125-126 °C. The IR spectrum exhibited intense bands at 3300-3600 cm^{-1} (OH), and 890 cm^{-1} ($C=CH_2$). The NMR spectra suggested the presence of the following moieties: two tertiary methyls [^1H: δ 1.14 (3H, s), 1.19 (3H, s)], a secondary methyl [^1H: δ 0.97 (d, J=7 Hz)], two oxygenated tertiary carbons [^1H: δ 3.33 (dd, J=10, 2 Hz), 3.94 (dd, J=8, 3.5 Hz); ^{13}C: δ 74.4 (d), 79.7 (d)], an oxygenated quaternary carbon [^{13}C: δ 73.2 (s)], an exomethylene group [^1H: δ 4.72 (2H, s); ^{13}C: δ 107.1 (t), 152.5 (s)], and a trisubstituted olefin group [^1H: δ 5.31 (1H, bs); ^{13}C: δ 124.0 (d), 141.5 (s)]. These features are similar with those of dictytriol,[2)] the absolute configuration of which has been proposed by chemical conversion and CD measurement[2)] in the presence of a lanthanide shift reagent.[3)] Comparison of the ^{13}C-NMR data[4)] indicated that only the chemical shif of C-14 of isodictytriol was noticiably different from that of dictytriol. On the basis of this finding, the structure 1, epimeric with 2 at C-14, was tentatively assigned to isodictytriol. In order to confirm S-configuration at C-14, CD spectrum in the presence of $Eu(fod)_3$ was measured. However, the results were quite confusing:

Although dictytriol (2) showed the negative first Cotton effect as reported by Matsumoto et al.,[2] isodictytriol (1) unexpectedly showed the same negative first Cotton effect as shown in Fig. 1. These data led to the assumption that the configuration at C-14 of 1 might be R, the same as that of 2, but other asymmetric carbons of 1 might have all (or partly) reversed configurations in comparison with 2. This possibility, however, was ruled out by the following experiments: Both of 1 and 2 were converted to diol 3 by (i) oxidative cleavage of the glycol system with periodic acid, and (ii) reduction of the resulting hemiacetal with sodium borohydride. The diols (3) obtained from 1 and 2 were identical in thin layer chromatograms and ^{1}H-NMR spectra. Especially, $[\alpha]_D$ value of each diol (3) was found to be the same, which indicated that the configurations at C-1, 5, 6, 7, and 11 of 1 were the same as those of 2. To remove all ambiguity, X-ray analysis was performed for isodictytriol and the relative configuration at C-14 was elucidated to be S* (see 4), thus establishing S-configuration at the carbon.

The anomalous behavior of isodictytriol (1) in the CD spectrum can be ascribed to the occurrence of an extra hydroxy group at C-6 in addition to the vicinal glycol at C-14 and 15. The present study demomstrates that particular care should be taken in deducing the absolute configuration of a vicinal glycol system by using CD under the influence of lanthanide shift reagents when there exists an extra hydroxy group in the vicinity of the glycol system.

Acknowledgement. We are grateful to Professor Takeshi Matsumoto for his kind gift of the ^{13}C-NMR spectrum of dictytriol.



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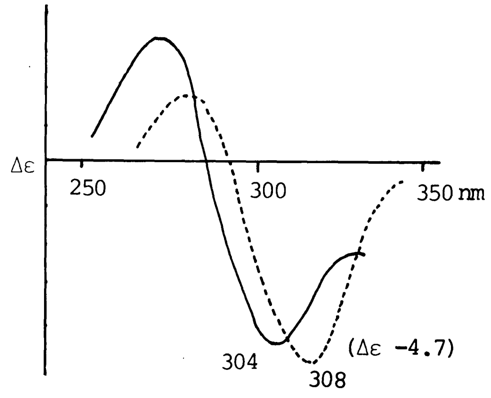

Fig. 1. CD spectra of isodictytriol (1) (···) and dictytriol (2) (—) taken with Eu(fod)3 $(CHCl_3)$.

References

1) T. Kusumi, D. M. Nkongolo, M. Goya, M. Ishitsuka, T. Iwashita, and H. Kakisawa, J. Org, Chem., 51, 384 (1986).
2) N. Enoki, R. Ishida, S. Urano, M. Ochi, T. Tokoroyama, and T. Matsumoto, Chem. Lett., 1982, 1837.
3) J. J. Partridge, V. Toome, and M. R. Uskokovic, J. Am. Chem. Soc., 98, 3739 (1976).
4) Dictytriol (2): ^{13}C-NMR (Some of the chemical shifts are erroneously reported in Ref. 2.) δ(22.5 MHz, $CDCl_3$) 16.0 (carbon number 17), 17.6(19), 23.1(16 or 20), 24.0(8), 26.5(20 or 16), 27.7(13*), 29.7(12*), 32.8(11), 33.7(2), 40.4(9), 45.8 (1°), 48.7(7°), 59.7(5), 73.0(15), 74.1(6), 76.6(14), 106.8(18), 123.6(3), 141.4 (4), 152.2(10). Isodictytriol (1): ^{13}C-NMR δ(22.5 MHz, $CDCl_3$) 16.1(17), 18.0 (19), 23.3(16 or 20), 23.9(8), 26.6(20 or 16), 29.6(13*), 31.9(12*), 34.0(2), 35.7(11), 40.5(9), 46.1(1°), 48.6(7°), 60.2(5), 73.2(15), 74.4(6), 79.7(14), 107.1 (18), 124.0(3), 141.5(4), 152.5(10): ^{1}H-NMR δ(400 MHz, $CDCl_3$) 0.97 (3H,d,J=6.3 Hz,H-19), 1.14, 1.19(each 3H,s,H-16 and 20), 1.79(3H,s,H-17), 2.31 (1H,dd,J=9, 8 Hz,H-5), 2.63(1H,q,J=9 Hz,H-1), 3.33(1H,dd,J=10.5, 2 Hz,H-14), 3.94 (1H,dd, J=8, 3.5 Hz, H-6), 4.72, 4.73(each 1H,s,H_2-18), 5.31 (s,1H.H-3).

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