Structure of Linearol, a Novel Diterpenoid from the Brown Seaweed *Dictyota linearis*

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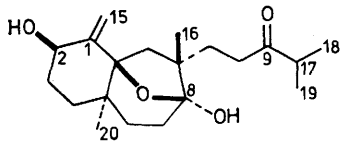
Summary The structure of linearol, a new diterpenoid isolated from the brown seaweed *Dictyota linearis*, has been determined as (**1**) with a novel secodolastane skeleton on the basis of spectral and chemical evidence.

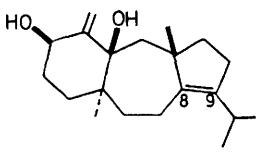
IN previous papers,[1,2] we have reported the isolation of four new diterpenoids possessing the dolastane skeleton[3] from the brown seaweed *Dictyota linearis*. Our continuing search for the constituents of this alga has now led to the isolation of a novel diterpenoid which is the first member of the secodolastane class. We now report the structure of this new compound which we have named linearol.

Linearol (**1**) was isolated from a methanol extract of the fresh alga as needles, m.p. 136·5—137·5 °C, $[\alpha]_D$ −1·9° (*c* 0·11, $CHCl_3$); ν_{max} ($CHCl_3$) 3600, 3500, 3080, 1713, 1648, and 892 cm^{-1}. The molecular formula $C_{20}H_{32}O_4$ was established by elemental analysis and ^{13}C n.m.r. data (100 MHz, $CDCl_3$)† which showed the presence of 4 CH_3 (δ 18·46, 18·49, 21·6, and 23·2), 7 CH_2 (δ 27·9, 28·6, 30·1, 31·4, 34·4, 36·4, and 41·8), 1 CH (δ 41·3) 1 CH(O) (δ 75·1), together with 3 quaternary carbon atoms (δ 37·5, 43·9, and 86·2), 1 hemiacetal (δ 106·5), 1 exo methylene (δ 113·5 and 147·1), and 1 ketonic carbon atom (δ 215·9 p.p.m.). The detailed ^1H n.m.r. analysis at 400 MHz was consistent with the 8,9-secodolastane structure (**1**): δ 5·14 and 4·90 (1H each, br s, 15-H_2), 4·34 (1H, d, *J* 10·2 Hz, 2-OH), 4·24 (1H, ddd, *J* 10·2, 3·0, and 3·0 Hz, 2-H), 2·86 (1H, s, 8-OH), 2·60 (1H, qq, *J* 6·8 and 6·8 Hz, 17-H), 1·11 and 1·10 (3H each, d, *J* 6·8 Hz, 18- and 19-H_3), and 1·03 and 0·71 (3H each, s, 16- and 20-H_3).‡ This structure would be reasonable biogenetically if we assume that linearol (**1**) is derived from a compound with the dolastane skeleton such as isoamijiol (**2**).[1]

Finally, the structure was confirmed by chemical correlation of (**1**) with (**2**). Thus, partial hydrogenation of (**2**) with $H_2/(PPh_3)_3RhCl$,[4] followed by ozonolysis, gave a hemiacetal (**3**), $C_{20}H_{34}O_4$, m.p. 126·5—127·5 °C, which was found to be identical with the compound derived from (**1**) by treatment with H_2/Pd-C.



(**1**)



(**2**)

(**3**) 1,15-dihydro-(**1**)

(*Received*, 3*rd November* 1980; *Com.* 1178.)

† The assignments will be discussed in a full paper.

‡ All the other signals were completely assigned by an extensive decoupling study and their chemical shifts and *J* values were consistent with the structure (**1**).

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[2] M. Ochi, M. Watanabe, M. Kido, Y. Ichikawa, I. Miura, and T. Tokoroyama, *Chem. Lett.*, 1980, **1233**.
[3] G. R. Pettit, R. H. Ode, C. L. Herald, R. B. Von Dreele, and C. Michel, *J. Am. Chem. Soc.*, 1976, **98**, 4677.
[4] M. Brown and L. W. Piszkiewicz, *J. Org. Chem.*, 1967, **32**, 2013.