A New Tricarbocyclic Diterpene with a Novel Carbon Skeleton from a Marine Alga

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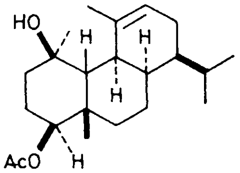
A new tricarbocyclic diterpene, chromophycadiol monoacetate (**2**), possessing a novel carbon skeleton, was isolated from a brown alga *Dictyota* sp. and its structure together with stereochemical features were determined by *X*-ray crystallography.

Although the majority of new diterpenes from brown algae of the family Dictyotaceae belong to well-established structural classes which can formally be derived by prenylation at an isopropylidene appendage of known sesquiterpenoid skeletons,[1] two exceptions to this rule have recently been discovered.[2] Initial chemical studies on algae of the genus *Dictyota* (Chromophycota, Dictyotaceae) of the Canary Islands[2a] have led to the *X*-ray structure determination of α-dictalediol monoacetate (**1**) possessing a novel ring system. Our continuing interest in these seaweeds† has resulted in the isolation and structure determination of chromophycadiol monoacetate (**2**), a further exception which also has a novel diterpenoid skeleton. Extraction of the fresh material gave a diethyl ether-soluble portion which, after chromatography, afforded (**2**) in 0.012% yield of the crude extract.

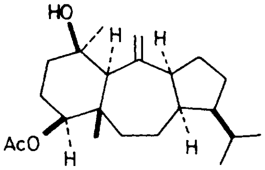
Chromophycadiol monoacetate (**2**)‡ has m.p. 137—139 °C, $[\alpha]_D$ + 26.5° (*c* 0.65, $CHCl_3$).§ Because of the limited availability of (**2**) and failure to correlate its skeletal structure with any known diterpenoid, an *X*-ray crystallographic study was carried out.¶

Figure 1 shows the structure of one of the independent molecules of (**2**) in the asymmetric unit, the other molecule being identical. The enantiomer shown is arbitrary. The six-membered ring including C(1), C(2), and C(14) is in the chair conformation and it is fused in a *trans* fashion to the seven-membered ring which is in a tub conformation. The five–seven membered ring fusion is *cis*.

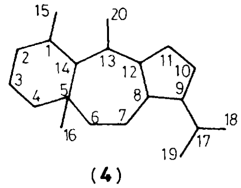
Chromophycadiol monoacetate (**2**) is the first representative of a new class of diterpenoid and the biosynthesis of such a



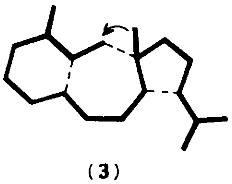
(**1**)



(**2**)



(**4**)



(**3**)

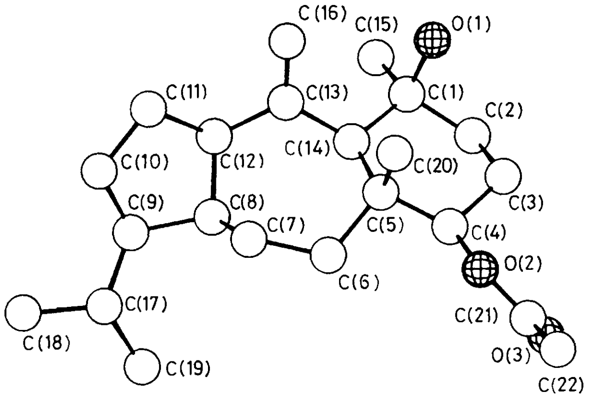


Figure 1. A computer-generated perspective drawing (PLUTO) of the final *X*-ray model of (**2**); the absolute configuration is not implied.

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† The *Dictyota* sp. was collected off Güimar, Tenerife, Canary Islands, during the summer of 1981. The best developed, large specimens were gathered in a sheltered bay with shallow water about a few metres deep.

‡ We suggest the trivial name chromophycane for the basic skeleton of this new class of diterpenes, numbered as in structure (**4**). Thus, chromophycadiol monoacetate (**2**) is (1*R**,4*S**,5*S**,8*R**,9*S**,14*S**)-4-acetoxy-1-hydroxychromophyc-13(20)-ene.

§ *Spectral data: m/z* 348.2668 (calc. for $C_{22}H_{36}O_3$ 348.2664); $\nu_{max.}$ (KBr) 3420, 1740, 1630, 1450, 1365, 1250, 1110, 1040, 970, and 910 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 0.82, 0.85 (d, *J* 6 Hz, 3H each), 1.09, 1.14, 2.02 (s, 3H each), 2.62 (m, 1H), 4.54 (dd, *J* 12, 3.5 Hz, 1H), 5.11 (s, 1H), and 5.49 (t, *J* 1.5 Hz, 1H); ^{13}C n.m.r. ($CDCl_3$): 5 × Me: δ 22.3, 22.1, 21.5, 15.5, and 15.4; 7 × CH_2: δ 113.3, 66.0, 45.9, 39.9, 28.8, 26.8, and 23.6; 6 × CH: δ 83.4, 55.4, 53.4, 52.3, 46.6, and 30.1; 4 × quaternary C: δ 171.1, 149.1, 72.6, and 40.8 (assigned using off-resonance and selective proton-noise decoupling).

¶ *Crystal data* for (**2**), monoclinic, space group *C*2, $a = 29.556(3)$, $b = 6.064(1)$, $c = 25.814(3)$ Å, $\beta = 118.11(2)°$. Density measurements indicated that two $C_{22}H_{36}O_3$ molecules formed the asymmetric unit ($Z = 8$). 3146 unique reflexions with $2\theta < 114°$ were collected using graphite-monochromated Cu-$K_{\bar{\alpha}}$ radiation ($\lambda = 1.54178$ Å) and variable speed ω-scans (1°). 2766 reflexions with $I > 3\sigma(I)$ were judged observed after correction for Lorentz, polarization, and background effects.[3] Hydrogen atoms were located on a difference Fourier synthesis following partial refinement. Block-diagonal least-squares refinement converged at $R = 0.073$. All crystallographic calculations were done on a PRIME 9950 computer, using as principal programs REDUCE and UNIQUE, M. E. Leonowicz, Cornell University, 1978; MULTAN 80, and RANTAN 80 (locally modified), P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, 1980; BLS78A, K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; BOND, K. Hirotsu and G. Van Duyne, Cornell University, 1985. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

carbon skeleton is not straightforward. We suggest that (**2**) can be accomplished formally by a single methyl shift of a dolestane type of skeleton as illustrated in structure (**3**).

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