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A NEW DITERPENOID RELATED TO EUNICELLIN AND CLADIELLIN FROM A *MURICELLA SP.*

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Abstract: The isolation and structure elucidation of a new diterpenoid from a horny-coral (Gorgonaceae) are reported. The ^{1}H and ^{13}C-NMR spectra are discussed.

Repeated silica-gel column fractionation of the petrol ether extract of freeze dried *Muricella sp.* (collected near Ophira in the Gulf of Eilat, the Red Sea), afforded in up to 0.2% dry weight a new compound, ophirin (1); m.p. 133-134°, $[\alpha]_D$- 2°, analysed for $C_{26}H_{38}O_7$. Consecutive loss of three 60 m.u. fragments from the very weak molecular ion at m/e 462 (402(24%), 342(12%) and 282(23%))[1] suggested the presence of three acetate groups. The IR spectrum[2] while confirming the presence of acetates (1730 and 1255 cm^{-1}) showed no OH-band. The ^{13}C-NMR spectrum[3] revealed three carbonyl absorptions at 170.4s, 169.9s and 167.5s in agreement with the suggested three acetate groups. Furthermore two trisubstituted double bonds (139.6s, 129.5d, 125.9s and 120.6d) and five oxygen-bearing carbons (90.2s, 87.2d, 83.7s, 80.3d and 66.3d) were revealed in the spectrum. From the latter five resonances, three belong to the carbon atoms bearing the acetate groups. The remaining resonance lines of the spectrum were located at 48.4d, 43.2d, 36.0d, 45.1t, 30.9t in addition to eight quartets at 25.4, 25.1, 22.7, 22.5, 22.0, 21.8, 21.3 and 18.3 accounting for 25 of the molecule's 26 carbon atoms[4]. The presence of three acetates was further confirmed by the ^{1}H-NMR spectrum (δ 2.01s, 2.00s and 1.95s, 3H each). Five other singlets of 3H each (δ 1.38, 1.55, 1.79, 1.80 and 1.82) could be assigned to either methyls on acetate bearing carbons or vinyl methyls. The ^{1}H-NMR spectrum also revealed five low field protons (δ 5.66, 5.44, 5.38, 4.54 and 4.38) as well as three distinct signals at δ 3.13, 2.66 and 2.51 ppm.

According to the spectral data, and based mainly on the empirical formula and the presence of five methyl groups, ophirin was suggested to be a diterpenoid possessing the following functional groups: $\underset{\underline{a}}{\text{-CH}_2\text{CH=CCH}_3}$; $\underset{\underline{b}}{\text{-CH(OAc)CH=CCH}_3}$; $\underset{\underline{c}}{(\text{CH}_3)_2\text{C(OAc)-}}$; $\underset{\underline{d}}{>\text{C(OAc)CH}_3}$; $\underset{\underline{e}}{>\text{CH-O-CH}<}$

A broad triplet at δ 5.44 and a methyl at 1.82 were attributed to a[5]. The second double bond was found to be incorporated in moiety b according to the two coupled protons at 5.66d(J=5.6Hz, H-13) and 5.38d(J=5.6Hz, H-12). The ^{13}C- and ^{1}H-NMR spectra also indicated the presence of moieties c & d. The absence of an hydroxyl or a carbonyl function, except for the 3 acetates (IR and ^{13}C-NMR) suggested the last oxygen to be part of a cyclic ether (moiety e), and the molecule was therefore tricyclic. The ether moiety was supported by the two signals at δ 4.54d (J=10Hz) and 4.38brd (J=5.9Hz) as well as the two doublets at 87.2 and 80.3 in the ^{13}C-NMR spectrum. Further structural conclusions were not possible since the various low-field protons are almost uncoupled among themselves or to other high-field protons. Combining all the above structural features (moieties a-e and additional 3 methines), it was probable that ophirin (1) was related to eunicellin[6] and the cladiellins[7], and a structure of this type could be postulated. In view of the very small quantity of material available no further chemical transformations could be carried out, and an x-ray anlaysis was undertaken to confirm ophirin's structure as 1[8]. The particular ^{1}H-NMR spectrum of ophirin, given below, can be explained in the basis of its crowded structure, thus having to maintain a particular conformation in solution.

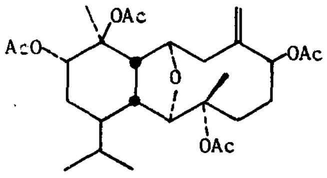
The ^{1}H-NMR data of 1[9,10] and the concluded dihedral angles (Φ):

H-13	5.66d	$J_{12,13}$=5.6,	$\Phi_{13,14} \approx 90°$	H-10	2.43d^a	$J_{1,10}$=8.5	$\Phi_{9,10} \approx 90°$
H-14	3.13s		$\Phi_{1,14} \approx 90°$	H-9	4.38brd	$J_{8\beta,9}$=5.9	$\Phi_{8\alpha,9} \approx 90°$
H-1	2.66t	$J_{1,2}$=10,$J_{1,10}$=8.5		H-8β	2.51dd	$J_{8\alpha,8\beta}$=13.5	$J_{8\beta,9}$=5.9

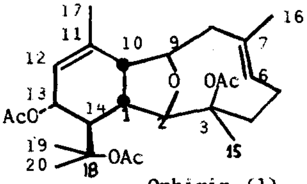
a. overlapping with H-4 and H-8α.

^{13}C-NMR studies of compound 1 suggested the following assignments:[11]

δ	90.2s	87.2d	83.7s	80.3d	66.3d	48.4d	45.1t	43.2d	36.0d	30.9t	25.4q & 25.1q	18.3q
C	3	2	18	9	13	10	8	14	1	4	iPr-Mes	16



Eunicellin



Ophirin (1)

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References and Notes.

1. The base peak in the mass spectrum appears at m/e 174 ($C_{12}H_{14}O$) and may represent the ten membered ring fragment after loss of HOAc and 2H.
2. ν_{max}^{KBr} 2940, 1730, 1530, 1375, 1255, 1135, 1070, 1025, 955, 935, 890, 860, 840 and 805 cm^{-1}.
3. The NMR spectra were recorded in $CDCl_3$ solution on a Bruker WH-90 (^{13}C) and Bruker 270MHz (^{1}H) instruments, δ-values are given in ppm from TMS; multiplicities of the ^{13}C-resonances were assigned by SFORD experiments.
4. The missing atom signal (C-5, vide infra) may overlap with one of the methyl groups in the 22-25 ppm region.
5. Extensive double irradiation experiments established the various proton relationships.
6. O. Kennard, D.G. Watson, L. Riva di Sanseverino, B. Tursch, R. Bosmans and C. Djerassi, Tetrahedron Letters, 2879 (1968).
7. R. Kazalauskas, P.T. Murphy, R.J. Wells and P. Schonholzer, ibid 4643 (1977).
8. J. Clardy and J. Finer - to be published.
9. Two other observable protons are H-5 at 2.17m and H-5' at 2.11m.
10. An LIS experiment using d_{27}-Eu(fod)$_3$ showed, according to the methyl shifts, the complexation site to be over the cyclohexene ring with the following Δδ order: H-12and14>H-2>>H-9, 13 and 6
11. The ^{13}C-NMR assignments were based on the chemical shifts and substituent effects, as well as correlations of the ^{1}H and ^{13}C-NMR spectra by SFORD experiments.

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