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Sodwanones A-C, Three New Triterpenoids From a Marine Sponge

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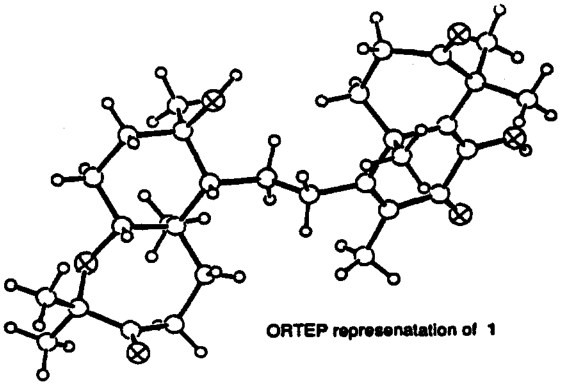
Abstract: Three new triterpenoids, sodwanones A-C (1-3) have been isolated from the sponge *Axinella weltneri*. The structure of compound 1 was unambiguously determined by X-ray diffraction studies. All ^{1}H and ^{13}C-NMR resonances of 1 were assigned by an extensive use of 1D and 2D NMR techniques. The structure of 2 and 3 were determined by comparison of their spectral data and mainly by NMR with those of 1.

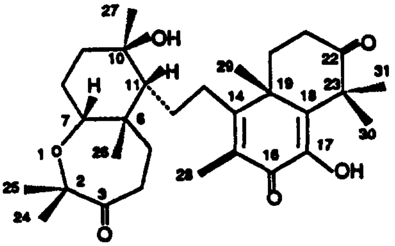
In search of biologically active marine natural products we have isolated three new triterpenoids named sodwanones A-C (1-3) from the South African purple-brown fan sponge, *Axinella weltneri*[1] and we herewith report the structure of the three. All three (1-3) were obtained by silica-gel chromatography of the ethylacetate extract[2].

Sodwanone-A (1) was isolated as optically active crystals[3]. EIMS provided m/z 500 M^+ for a molecular formula of $C_{30}H_{44}O_6$. The IR spectrum showed in addition to a broad OH stretch (3400 cm^{-1}) characteristic absorbance for a saturated and a conjugated carbonyl moiety (1700, 1613 cm^{-1}). The ^{13}C NMR spectrum[3] revealed 3 carbonyls (δ_C 218.0, 216.0, 181.5) and two double bonds (δ_C 164.7s, 128.8s and 141.8s, 137.6s), the former, mostly likely, conjugated to the high field CO-group. To fulfill the nine degrees of unsaturation four additional rings have been suggested. Close examination of the 2D-NMR spectra of 1 (COSY, TOCSY, HMQC and HMBC) proposed almost the entire planar structure of 1, namely, two bicyclic halves, one similar to the perhydrobenzoxepine of sipholenone[4] and the other a bicyclic cross conjugated dienone. The two parts being linked through an ethylene bridge. As more than one structure could have been proposed the crystals were submitted to an X-ray diffraction analysis[5].

The structure was solved by direct methods (SHELXS-86)[6], and refined by blocked-matrix least-squares (SHELX-76)[7], including the positional and anisotropic thermal parameters of the non-hydrogen atoms. The final refinement, minimizing $w(\Delta F)^2$, where $w=1/\sigma^2(F_0)$, converged at R=0.050 and wR=0.049 for 1383 observations having $I > 3\sigma(I)$.



ORTEP represenatation of 1



1 sodwanone A
2 sodwanone B, 10-deoxy
3 sodwanone C, 10,16,17-trideoxy-$\Delta^{14,16}$

Sodwanone B and C (**2**, **3**) were isolated in minute amounts only (ca. 0.01%). Compound **2**[8], $C_{30}H_{44}O_5$, m/z 484 possesses the same substituted decalin moiety as **1** but differs in the perhydrobenzoxepine system. Absence of the carbinol methyl group, Me27 δ_H 1.21s, and the appearance of a new doublet of a methyl at δ_H 1.06 suggested sodwanone B to be the 10-deoxy derivative of **1**.

The third compound, sodwanone C[9] is the less polar among the three. The EIMS provided m/z 454 for a molecular formula of $C_{30}H_{46}O_3$. The NMR data proposed unequivocally that **3** possesses the same perhydrobenzoxepine moiety as **2** and differs in the decalin portion. The only single oxygen in the latter system is a ketone which is part of the same gem-dimethylcyclohexanone as in **1**, however, instead of the hydroxy conjugated dienone of **1** compound **3** possesses a $\Delta^{14,16}$-diene (δ_c 142.0s, 131.0d, 125.2s, 124.8d). The latter moiety was established by homo COSY correlations (between Me28, H-16, 17, 18 & Me30, 31) and CH correlations ($C\underline{H}_3$ 29, 30 & 31 with C-18 (δ_c 53.4)). Related triterpenoids which contain the perhydrobenzoxepine moiety were isolated from the sponges *S. siphonella*[4] and *R. aculeata*[10].

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References and Notes

1. The sponge was collected in Sodwana Bay, South Africa.
2. Compound **1** (Rf=0.25, EtOAc-Hexane 1:1, 0.1%), **2** (Rf=0.70, 0.01%) and **3** (Rf=0.80, 0.01%).
3. Compound **1**, mp 253, $[\alpha]_D = -9^\circ$(C=0.1, $CHCl_3$), δ_H ($CDCl_3$): 7.10s (OH-17) 3.25 (ddd, J=13.5, 11.0, 2.6, H4a), 2.19 (m,H4b), 1.95 (ddd,J=11.0, 6.3, 2.2, H5a), 1.38 (m,H5b), 2.97 (dd,J=10.7, 5.1, H7), 1.62 (m, H8a), 1.58 (m, H8b), 1.76 (m, H9a), 1.48 (m, H9b), 1.13 (bdd, J=5.5, 3.4, H11), 1.55 (m, H12a), 1.45 (m, H12b), 2.62 (dd, 10.0, 2.0, H13a), 2.38 (J=13.0, 5.5, H13b), 2.48 (dd, J=13.4, 6.6, H20a), 1.75 (m, H20b), 2.74 (dd, J=18.5, 8.9, H21a), 2.60 (dd, J=9.5, 2.0), H21b), 1.31 (s, Me24), 1.25 (s,Me25), 0.95 (s, Me26), 1.21 (s, Me27), 2.02 (s, Me28), 1.09 (s, Me29), 1.56 (s, Me30), 1.46 (s, Me31); δ_c 82.0s (C2), 218.0s (C3), 35.0t (C4), 40.6t (C5), 42.0s (C6), 80.9d (C7), 24.8t (C8), 41.5t (C9), 73.5s (C10), 57.5d (C11), 28.7t (C12), 33.9t (C13), 164.7s (C14), 128.8s (C15),181.5s (C16), 141.8s (C17), 137.6s (C18), 42.9s (C19), 27.6t (C20), 32.6t (C21), 216.0s (C22), 49.0s(C23), 20.4q(C24), 26.3q(C25), 12.1q(C26), 23.6q(C27), 12.0q(C28), 21.6q(C29), 20.8q(C30), 24.3q(C31).
4. Carmely, S.; Kashman, Y.; J. Org. Chem., 1983, 48, 3517-3525.
5. The title compound crystallized as a hydrate. The X-ray diffraction measurements were carried out at room temperature (ca. 298K) on an automated CAD4 diffractometer equipped with a graphite monochromator, using MoKα (λ = 0.7107 A) radiation. Intensity data were collected out to $2\theta = 46^\circ$ by the ω-2θ scan mode with a constant scan speed of 2 deg/min and scan range of $(1.00 + 0.35 \tan\theta)^\circ$. A total of 2068 unique reflections with positive intensities were recorded.
   Crystal data: $C_{30}H_{44}O_6 \bullet H_2O$, formula weight 518.7, orthorhombic, space group $P2_12_12_1$, a=11.352(3) b= 14.579(2), c=16.964(2) A, V=2807.56 A^3, Z=4, D_{calc}=1.227g.cm^{-3}, F(000)=1128, μ(MoKα)=0.80cm^{-1}.
6. G.M. Sheldrick, SHELXS-86, in "Crystallographic Computing 3"; G.M. Sheldrick, C. Kruger and R. Goddard, Eds. Oxford University Press, 1985; pp. 175-189.
7. G.M. Sheldrick, SHELX-76. Programme for Crystal Structure Determination, University of Cambridge, England, 1976.
8. Compound **2**, glass, $[\alpha]_D = -6^\circ$(C=0.1), ν_{max} 1713, 1625 cm^{-1}. δ_H 2.01 (s, Me28), 1.55 (s, Me30), 1.52 (s, Me31), 1.35 (s, Me24), 1.30 (s, Me25), 1.15 (s,Me29), 1.06 (d, J=7.5, Me27), 1.04 (s,Me26). δ_c 218.0s, 216.0s, 181.5s, 164.5s, 141.9s, 137.2s, 129.1s, 84.9s, 81.9d, 51.3d, 48.0s, 42.7s, 41.5s, 40.5t, 35.1t, 32.5t, 31.1t, 29.9t, 28.4t, 28.2d, 26.4q, 25.8t, 25.5t, 24.4q, 21.6q, 20.8q, 20.4q, 14.7q, 13.4q, 11.9q.
9. Compound **3**, amorphous powder, $[\alpha]_D = -35^\circ$(C=0.15), ν_{max} 1715 cm^{-1}. δ_H 5.90 (dd, J=9.3, 3.2, H-16), 5.62 (dd, J=9.3, 2.7, H-17), 3.17 (dt, J=3.0, 11.3), 2.97 (dd, J=4.3, 11.6), 2.82 (dt, 5.7, 14.2), 1.78(s, Me28), 1.30 (s, Me24), 1.25 (s, Me25), 1.19 (s, Me25), 1.12 (s, Me31), 1.03 (s, Me29), 0.99 (s, Me26), 0.96 (d, J=7.5, Me27); δ_c 218.0s, 215.8s, 142.0s, 131.0d, 125.2s, 124.8d, 82.3s, 82.2d, 53.4d, 51.3d, 47.2s, 41.3s, 40.6s, 40.4t, 35.2t, 34.5t, 34.3t, 31.2t, 28.3d, 27.1t, 26.3t, 26.5q, 26.4t, 24.7q, 22.8q, 20.6q, 17.7q, 15.0q, 14.6q, 13.5q.
10. Cimino, G.; Crispino, A.; Epifanio, R.A.; Madaio, A.; Mattia, C.A.; Mazzarella, L.; Puliti, R,; Trivellone, E.; Uriz, M. Tet. 1992, 41, 9013-9022.

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