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ANADENSIN, A NEW FUSICOCCANE DITERPENOID FROM THE LIVERWORT *Anastrepta orcadensis*. CRYSTAL STRUCTURE ANALYSIS.

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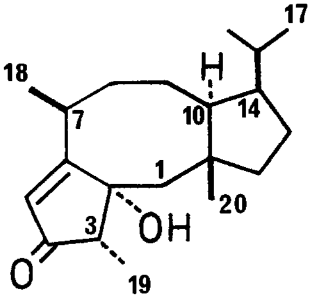
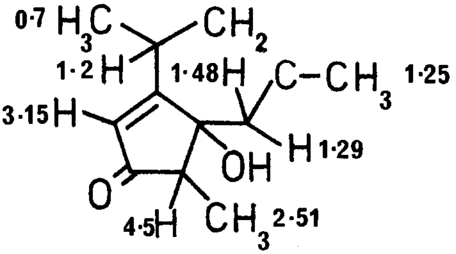
Summary. Anadensin, a new diterpenoid from the liverwort *Anastrepta orcadensis* (Hook) Schiffn., has been shown by X-ray crystallographic analysis to have the fusicoccane structure (1).

Extraction of the liverwort *Anastrepta orcadensis*, collected at the Hohne cliffs in the Harz mountains,[1] afforded a new fusicoccane diterpenoid, anadensin, which has been assigned the structure and relative configuration (1) on the basis of spectroscopic evidence and an X-ray crystal structure analysis.



(1)



Eu(fod)$_3$ Shifts

(2)

Anadensin, $C_{20}H_{32}O_2$ (m/z 304.2402; calc. 304.2402), m.p. 171-172° (ex MeOH), c.d. 322 ($\Delta\varepsilon$ −2.85), 239 ($\Delta\varepsilon$ +17.6), 206 ($\Delta\varepsilon$ −5.22), and 194 nm ($\Delta\varepsilon$ +1.63), has bands in its i.r. [(ν_{max}(CCl_4) 3598 and 1708 cm^{-1}] and u.v. [λ_{max} 227 nm (ε 10,500)] spectra consistent with the presence of a hydroxyl group and a cyclopentenone. The molecule is therefore tricarbocyclic. The ^1H and ^{13}C n.m.r. spectra[2] show that the hydroxyl group is tertiary [δ_H 1.78; δ_C 81.4 (s, C-2)] and that the enone has a trisubstituted double bond [δ_C 209.4 (s, C-4); δ_H 5.96 (s, H-5); δ_C 128.3 (d, C-5), 187.5 (s, C-6)]. In addition, there are resonances for a tertiary methyl [δ_H 0.72, δ_C 23.1 (C-20)], four secondary methyls [δ_H 0.72 and 0.86 (both d, J 7 Hz, 3H-16 and 3H-17), δ_C 18.8 and 20.2 (C-16 and C-17); δ_H 1.11 (d, J 7 Hz, 3H-18), 1.22 (d, J 7 Hz,3H-19), δ_C 23.3 (C-18) and 9.8 (C-19)] and an isolated methylene group [δ_H 2.26, 1.86 (ABq, 15 Hz, 2H-1), δ_C 51.1 (t, C-1)]. The protons splitting the two downfield methyls are clearly visible at lower field and are presumably allylic or α to the carbonyl group. One [δ_H 2.67 (q, J 7 Hz, H-3), δ_C 49.5 (d, C-3)] has no further coupling whereas the other [δ_H 2.92 (m, H-7), δ_C 29.7 (d, C-7)] has at least two further couplings. The above data, in conjunction with Eu(fod)$_3$ induced shifts ($\delta\Delta$ values for approximately 0.5 molar equivalent of shift reagent), permitted the assembly of part structure (2) which can on biogenetic grounds be readily expanded to the fusicoccane structure (1) for anadensin. Confirmation of this proposed structure was obtained by an X-ray crystal structure analysis[3] which also revealed the relative stereochemistry (see Fig. 1).

Anadensin is the first fusicoccane derivative to be reported from the Hepaticae.[4,5] Compounds with this carbon skeleton are well known in fungi e.g. the fusicoccins[6] and the cotylenins,[7] but have not yet been found in higher plants. A. orcadensis appears to exist in several chemical races.[1]

References

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2. The remaining ^{13}C resonances appear at δ_C 43.6 (s, C-11), 48.5, 48.5, and 28.3 (d), 44.1, 37.8, 23.3 and 21.5 (t).
3. Crystal data: Orthorhombic, a = 6.4717, b = 15.3706, c = 18.0354 Å, a = β = γ = 90°, Z = 4, U = 1794 Å^3, F(0,0,0) = 1212. Space group P 2_1.
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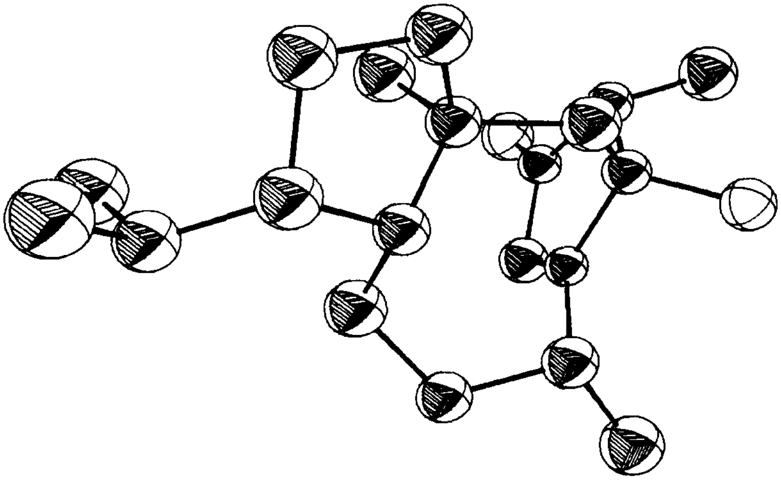

Fig. 1.

OPTEP Diagram of Anadensin

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