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HOPANOIDS FROM THE ENTOMOGENOUS FUNGUS ASCHERSONIA ALEYRODIS.

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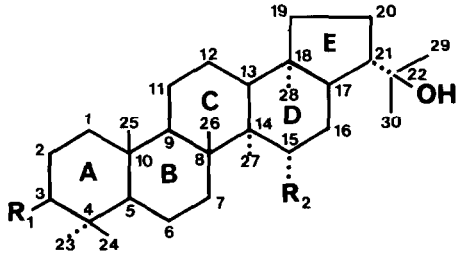
Abstract:The new triterpene triol 3β,15α,22-trihydroxyhopane, the triterpene diol dustanin (15α,22-dihydroxyhopane) and the sterol ergosterol were isolated from the entomogenous fungus Aschersonia aleyrodis.

During our study on carotenoids of the entomogenous fungus Aschersonia aleyrodis[1] CBS 541.73 we isolated an amount of white crystalline material. Separation by column chromatography (sephadex LH 20) and preparative TLC yielded the well-known fungal sterol ergosterol and two other compounds with a mass spectrometric fragmentation characteristic for pentacyclic triterpenes[2]. The molecular formula $C_{30}H_{52}O_2$ of the major compound (mp. 261-264°) was established by h.r. MS[3] (found 444.3959, calcd. 444.3967). Acetylation (Ac_2O and pyridine) gave a monoacetate and trimethylsilylation (BSA:TSIM:TMCS=3:3:2) afforded a di-TMS derivative. A search of the literature revealed a compound with the same physico-chemical data (IR, ^{1}H NMR) viz. dustanin = 15α,22-dihydroxyhopane[4]. The identification as such (1) was established by comparison with an authentic sample of dustanin isolated from an Aspergillus species[5]. There was complete agreement in all respects (^{1}H and ^{13}C NMR, GC-MS). The second minor triterpenoid (mp.>305°) showed the molecular formula $C_{30}H_{52}O_3$ (found 460.3909; calcd. 460.3916). It formed a diacetate and a tri-TMS derivative. The IR spectra of the compound and its acetate showed absorptions characteristic for equatorial C-3 hydroxyl and acetate groups respectively[6].



1	R_1 = H	R_2 = OH
2	R_1 = H	R_2 = OAc
3	R_1 = OH	R_2 = OH
4	R_1 = OAc	R_2 = OAc

^{13}C NMR chemical shifts in ppm relative to TMS (50 Mhz, solvent $CDCl_3$)

Carbon	1	2	4	Carbon	1	2	4	Carbon	1	2	4
1	40.4	40.4	38.5 t	11	20.9	20.7	20.8 t	21	50.5	50.4	50.4 d
2	18.7	18.7	26.8 t	12	24.1	23.8	23.6 t	22	73.8	73.5	73.4 s
3	42.0	41.9	80.8 d	13	49.0	49.0	49.0 d	23	33.4	33.4	28.5 t
4	33.2	33.1	37.1 s	14	47.2	45.8	45.8 s	24	21.6	22.0	21.9 q
5	55.8	55.5	54.6 d	15	74.9	76.8	76.7 d	25	15.8	15.7	15.7 q
6	18.9	21.5	21.2 t	16	32.6	28.5	28.5 t	26	15.8	15.7	15.8 q
7	36.8	35.0	34.9 t	17	50.5	50.1	50.1 d	27	11.7	12.8	12.7 q
8	43.5	43.3	43.1 s	18	44.2	43.9	43.9 t	28	17.4	17.4	16.4 q
9	50.6	50.4	50.2 d	19	40.9	40.8	40.8 t	29	28.7	28.5	27.9 q
10	37.6	37.5	37.6 s	20	26.9	26.8	23.6 t	30	31.0	31.1	31.0 q

The mass spectral base peak at m/e 207 (dustanin:base peak at m/e 191) also points to the presence of a hydroxyl at the AB rings. Refluxing in 5% ethanolic hydrochloric acid yielded a conjugated diene, showing a characteristic heteroannular diene chromophore at 243, 252 and 260 nm[7] ($C_{30}H_{48}O$, M^+ 424). This finding strongly suggested the presence of secondary hydroxyl at C-15 or C-16. The co-occurrence with dustanin made the attachment at C-15α position acceptable. Final identification as 3β,15α,22-trihydroxyhopane **3** succeeded by ^1H and ^{13}C NMR. The acetylated compound **4** showed in its ^1H n.m.r. spectrum signals at δ 4.44 (d.d., ^3J 5.7, 5.9 Hz) due to H 3α[8] and δ 4.97(d.d., ^3J 5.2, 9.9 Hz) corresponding with H 15β(for **2** at δ 4.98). The OAc signals were at δ 2.05 and δ 1.98 respectively (for **2** at δ 1.98 too). The ^{13}C NMR of **4** resembles that of **2** and fully supports the assigned structure (see table). The isolation of hopanoids from Aschersonia aleyrodis is remarkable since their presence in fungi is very rare (dustanin from Aspergillus sp. as already mentioned, and zeorin = 6α,22-dihydroxyhopane from the mycobiont of the lichen Anaptychia hypoleuca[9]).

References and footnotes

1. G.W. van Eijk, R.S. Mummery, H.J.Roeijmans and L.R.G. Valadon. Antonie van Leeuwenhoek 45, 417 (1979).
2. L. Ogunkoya. Phytochemistry 20, 121 (1981).
3. The authors are indebted to Mr. C. Versluys, Analytical Laboratory, State University of Utrecht for measuring the mass spectra.
4. Y. Tsuda and K. Isobe. Tetrahedron Letters 3337 (1965).
   R.E. Corbett and H. Young. J.Chem.Soc. (C) 1564 (1966).
5. The authors are grateful to Dr. Y.Tsuda, Shiwa College of Pharmaceutical Sciences, Tokyo, Japan for his generous gift of dustanin.
6. I.L. Allsop, A.R.H. Cole, D.E. White and R.L.S. Willix. J.Chem.Soc. 4868 (1956).
7. I. Yosioka, T. Nakanishi and I. Kitagawa. Chem. Pharm. Bull. 17, 279 (1969).
8. M. Shamma, R.E. Glick and R.O. Mumma. J. Org. Chem. 27, 4512 (1962).
   W.-H. Hui and M.-M. Li. J. Chem. Soc. Perkin Trans. I, 897 (1977).
9. H. Ejiri and S. Shibata. Phytochemistry 13, 2871 (1974).

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