SUMMARY

By x-ray structural analysis, the structure of chimganidin has been refined and its stereochemistry has been established unambiguously; it is 6α-hydroxy-8β-vanilloyloxy-germacra-1(10),4(5)-diene.

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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS Silene.

XI. 2-DEOXY-α-ECDYSONE 3-ACETATE FROM Silene scabrifolia

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From the epigeal organs of Silene scabrifolia Kom. has been isolated the new phytoecdysteroid 2-deoxy-α-ecdysone 3-acetate (II) (0.0011%), $C_{29}H_{46}O_6$, mp 216-218°, $[\alpha]_D^{20}$ +131.9° (methanol). The enzymatic hydrolysis of (II) led to 2-deoxy-α-ecdysone (I). The acetylation of 2-deoxy-α-ecdysone (I) yielded (II) and the 22-monoacetate (III) and 3,22-diacetate (IV) of 2-deoxy-α-ecdysone, which have been described previously. Details of the IR, UV, CD, mass, and NMR spectra are given for (I) and of the IR, mass, and NMR spectra for (III).

We are continuing a study of the ecdysteroids of Silene scabrifolia Kom. (family Caryophyllaceae) [1]. Additional chromatography which isolated 2-deoxy-α-ecdysone and ecdysterone 22-O-benzoate produced mother liquors which contained a new ecdysteroid (II) with the composition $C_{29}H_{46}O_6$.

The α,β-unsaturated keto grouping that is characteristic for ecdysteroids was shown in the UV spectrum of compound (II) by a maximum at 245 nm (log ε 4.00) and in the UV spectrum by a band at 1665 cm^{-1}. In addition, absorption in the IR spectrum at 1735 and 1250 cm^{-1} and the presence in the PMR spectrum of a three-proton singlet at 1.85 ppm showed that ecdysteroid (II) contained one acetyl group.

The enzymatic hydrolysis of compound (II) performed with the combined enzymes isolated from bakers' yeast [2] led to 2-deoxy-α-ecdysone [1]. The peak of an ion with m/z 374 (cleavage of the C-20—C-22 bond), its derivatives with m/z 356 and 341, and also a fragment with m/z 326 (cleavage of the C-17—C-20 bond) observed in the mass spectrum of the acetate (II) made it possible to assume that the acetyl group was located in the steroid nucleus [3, 4].

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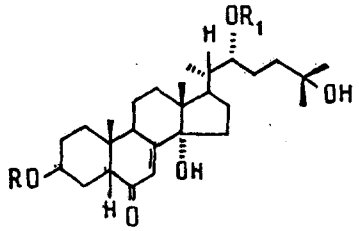

I. R = R_1 = H
II. R = Ac; R_1 = H
III. R = H; R_1 = Ac
IV. R = R_1 = Ac

The downfield shift of the resonance lines of the proton at C-3 in the PMR spectrum of the acetate (II) as compared with that for 2-deoxy-α-ecdysone (I) (4.87 and 4.00 ppm, respectively) showed that the acetyl group was located on this particular carbon atom.

Thus, the ecdysteroid (II) was 2-deoxy-α-ecdysone 3-acetate.

We subjected 2-dexoy-α-ecdysone (I) to acetylation with acetic anhydride in pyridine. From the reaction mixture, in addition to the known 22-monoacetate (III) [4] and 3,22-diacetate (IV) [3] of 2-deoxy-α-ecdysone, we isolated a compound identical with the ecdysteroid (II).

EXPERIMENTAL

PMR spectra were taken on a C-60-H instrument (C_5D_5N, ppm, 0 – MDS). For other details see [5].

2-Deoxy-α-ecdysone 3-acetate (II). The mother liquors accumulated in the isolation of 2-deoxy-α-ecdysone and ecdysterone 22-O-benzoate [1] from 15 kg of Silene scabrifolia were rechromatographed repeatedly on a column of silica gel in the chloroform–methanol (25:1) system. After recrystallization from aqueous ethanol, 175 mg (yield 0.0011% calculated on the air-dry raw material) of the ecdysteroid (II) was isolated; $C_{29}H_{46}O_6$, mp 216-218°, $[\alpha]_D^{20}$ +131.9 ± 2° (c 0.90; methanol), $\lambda_{max}^{C_2H_5OH}$: 245 nm (log ε 4.00), ν_{max}^{KBr} (cm^{-1}): 3340-3475, 1665, 1735, 1250, CD (c 0.12; methanol): Δε = −2.30 (253 nm); Δε = +2.11 (330).

Mass spectrum, m/z (%): 490 (M^+; 0.2), 473 (2), 454 (27), 444 (2), 439 (2), 412 (3), 397 (2), 384 (3), 379 (4), 374 (25), 356 (27), 341 (31), 327 (27), 326 (34), 305 (27), 281 (7), 276 (8), 275 (6), 267 (7), 266 (7), 251 (27), 217 (27), 216 (27), 215 (17), 99 (100), 81 (65).

PMR spectrum (δ, ppm): 0.57 (3H at C-18, s); 0.87 (3H at C-19, s); 1.12 (3H at C-21, d, J = 6 Hz); 1.25 (6H at C-26 and C-27, s); 1.85 (3H, $OCOCH_3$, s); 3.25 (H at C-9, m); 4.00 (H at C-22, m); 4.87 (H at C-3, m); 6.00 (H at C-7, broadened singlet).

Enzymatic Hydrolysis of the Ecdysteroid (II). To 5 ml of a freshly prepared aqueous extract from 1 g of bakers' yeast was added 25 mg of the ecdysteroid (II) and 2-3 drops of ethanol. After being kept at 36°C for 15 days, the reaction mixture was diluted with 15 ml of water and extracted with ethyl acetate (3 × 10 ml). The solvent was evaporated off and the residue was chromatographed on a column of silica gel. Elution with the chloroform–methanol (15:1) system yielded 10 mg of 2-deoxy-α-ecdysone (I) with mp 235-236°C from aqueous ethanol), $[\alpha]_D^{20}$ +93.2 ± 2° (c 1.0; methanol), identified by comparison with an authentic sample [3].

Acetylation of 2-Deoxy-α-ecdysone (I). The acetylation of 227 mg of ecdysteroid (I) was carried out in 10 ml of pyridine with 0.4 ml of acetic anhydride at room temperature for 2 days. Then the reaction mixture was diluted with water and extracted with ethyl acetate. The ethyl acetate fraction was evaporated to dryness and the residue was chromatographed on a column of silica gel. Elution with chloroform–methanol (15:1) yielded 47 mg of 2-deoxy-α-ecdysone 3,22-diacetate (IV), $C_{31}H_{48}O_7$, mp 245-246°C (from chloroform–ethanol), $[\alpha]_D^{24}$ +39.0 ± 3° (c 0.22; methanol). The diacetate was identified by comparison with an authentic sample [3] by the usual methods.

When the elution of the column with the same solvent mixture was continued, 32 mg of a compound with mp 216-218°C (aqueous ethanol) $[\alpha]_D^{20}$ +132 ± 2° (c 0.94; methanol) was isolated which was found to be identical by direct comparison in TLC and from spectral characteristics with 2-deoxy-α-ecdysone 3-acetate (II).

The further elution of the column with the same solvent mixture led to 50 mg of 2-deoxy-α-ecdysone 22-monoacetate (III) [4], $C_{29}H_{46}O_6$, mp 146-148° (aqueous methanol), $[\alpha]_D^{20}$ +50.2 ± 2° (c 0.15; methanol); ν_{max}^{KBr} (cm^{-1}): 3445, 1665, 1730, 1255.

Mass spectrum, m/z (%): 490 (M^+; 21), 472 (11), 462 (14), 457 (31), 454 (42), 444 (20), 430 (14), 412 (22), 403 (13), 397 (36), 394 (35), 384 (36), 379 (16), 331 (14), 314 (14), 313 (13), 303 (14), 302 (14), 285 (46), 284 (100), 269 (25), 251 (25), 234 (91), 233 (90), 109 (46), 99 (46), 81 (48), 69 (46).

PMR spectrum (δ, ppm): 0.62 (3H at C-18, s); 0.90 (3H at C-19, s); 1.01 (3H at C-21, d, J = 6 Hz); 1.20 (6H at C-26 and C-27, s); 1.95 (3H, $OCOCH_3$, s); 3.30 (H at C-9, m); 3.93 (H at C-3, m); 5.14 (H at C-22, m); 6.02 (H at C-7, broadened singlet).

Subsequent elution with the same mixture of solvents gave 82 mg of the initial 2-deoxy-α-ecdysone (I).

SUMMARY

A new ecdysteroid, 2-deoxy-α-ecdysone 3-acetate, has been isolated from the epigeal organs of Silene scabrifolia Kom.

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STEROID COMPOUNDS OF MARINE SPONGES.

VII. PREPARATION OF DERIVATIVES OF SOKOTRASTEROL AND HALISTANOL SULFATES AND STRUCTURE-ACTIVITY INTERRELATIONSHIPS AMONG THESE COMPOUNDS

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Five new sulfated derivatives of sokotrasterol and halistanol have been obtained: 24-nor-5α-cholane-2β,3α,6α,23-tetraol 2β,3α,6α-tri(sodium sulfate); 24-nor-5α-cholane-2β,3α,6α,23-tetraol 2β,3α,6α-tri(sodium sulfate) 23-palmitate; 24ε,25-dimethyl-5α-cholestane-2β,3α,6α-triol 3α-(sodium sulfate); 24ε,25-dimethyl-5α-cholestane-2β,3α,6α-triol 6α-(sodium sulfate); and 24ε,25-dimethyl-5α-cholestane-2β,3α,6α-triol 2β,6α-di(sodium sulfate). The inhibiting and membranolytic properties of the polysulfated steroids from sponges and their derivatives have been studied. It has been shown that physiological activity in this series of compounds depends on biphilicity.

Sulfated steroid polyols from sponges of the family Halichondriidae – halistanol sulfate (1) [1] and sokotrasterol sulfate (2) [2] – possess cytotoxic properties and disturb membrane permeability.

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