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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Silene*
XX. INTEGRISTERONE A 25-ACETATE FROM *Silene brahuica*.

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A new ecdysteroid — integristerone A 25-acetate — has been isolated from the roots of Silene brahuica *Boiss. Its structure has been determined on the basis of chemical transformations and spectral characteristics.*

Continuing a study of phytoecdysteroids from the roots of *Silene brahuica* Boiss., in addition to the ecdysteroids found earlier [1], we have isolated a new one — integristerone A 25-acetate (**1**), with the composition $C_{29}H_{46}O_9$.

In the IR spectrum of compound (**1**), in addition to the absorption due to hydroxy groups (3200 cm^{-1}) and to an α,β-unsaturated keto grouping (1655 cm^{-1}), there were absorption bands at 1730 and 1244 cm^{-1} showing the presence of an ester residue. A three-proton singlet at 1.96 in the PMR spectrum of ecdysteroid (**1**) showed that this compound contained an acetate group.

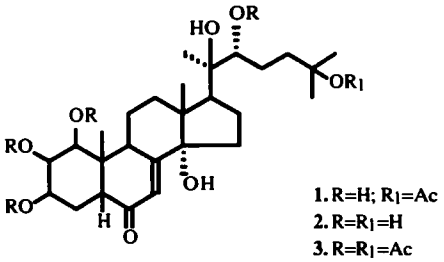
The alkaline saponification of ecdysteroid (**1**) led to integristerone A (**2**) [2].

In the mass spectrum of ecdysteroid (**1**) the peak of an ion with *m/z* 379 (cleavage of the C-20—C-22 bond) and its derivatives with *m/z* 361, 343, and 325 permitted the assumption that the acetyl group was located in the side-chain and not in the steroid nucleus [3—6].

In a comparison of the PMR spectra of the ecdysteroid (**1**) and of integristerone A (**2**) the only significant difference was in the position of the signals of the 26/27 methyls, which were shifted downfield. An analogous downfield shift has also been observed for viticosterone E [1, 7]. This fact showed that in ecdysteroid (**1**) the acetyl group was attached to the hydroxy group at C-25.

Acetylation of ecdysteroid (**1**) gave a pentaacetate (**3**). In the PMR spectrum of the pentaacetate (**3**) the CH_3-26 and CH_3-27 signals had scarcely changed.

On the basis of what has been said above, it may be concluded that the ecdysteroid (**1**) was integristerone A 25-acetate.



1. R=H; R_1=Ac
2. R=R_1=H
3. R=R_1=Ac

EXPERIMENTAL

General Information. For eluting columns we used the systems chloroform—methanol: 1) 4:1; 2) 50:1. For other details, see [1].

Integristerone A 25-Acetate (1). The enriched fractions obtained in the isolation of sileneoside G [1], 5α-sileneoside E [8], and sileneoside F [9] were chromatographed on a column of silica gel in system 2. This permitted the isolation of 50 mg of ecdysteroid (**1**), $C_{29}H_{46}O_9$, mp 198—200°C (methanol).

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IR spectrum (KBr, γ, cm^{-1}): 3400 (OH), 1655 (7-ene-6-keto grouping), 1730, 1244 (ester group).

Mass spectrum, m/z(%): 442 (M^+ -CH_3COOH+2H_2O; 5), 427 (3.5), 424 (3.5), 409 (3.5), 391 (4), 379 (23), 361 (100), 343 (60), 325 (41), 283 (39), 143 (41), 125 (44), 99 (44), 81 (96).

PMR spectrum (C_5D_5N, δ, ppm, TMS, 400 MHz): 1.26 (3H, CH_3-19, s), 1.43 (3H, CH_3-19, s), 1.44 and 1.50 (6H, CH_3-26 and CH_3-27, s), 1.63 (3H, CH_3-21, s), 1.96 (3H, $OCOCH_3$, s), 3.00 (1H, H-17, t, J = 9.1 Hz), 3.60 (1H, H-9, m), 3.87 (1H, H-22, d, J = 9.4 Hz), 4.30-4.38 (3H, H-1, H-2 and H-3, s), 6.30 (1H, H-7, s).

Alkaline Hydrolysis. A reaction mixture formed by adding 20 mg of the ecdysteroid (**1**) to 5 ml of a 0.5% aqueous methanolic solution of $KHCO_3$ was left at room temperature for two days. It was then diluted with water and neutralized with acetic acid, and the reaction product was extracted with ethyl acetate. After the solvent had been distilled off, the residue was chromatographed on a column of silica gel. Elution with system 2 yielded 13 mg of integristerone A (**2**), $C_{27}H_{44}O_8$, mp 246—248°C (from methanol—ethyl acetate) identical with an authentic specimen according to its R_f value in TLC (system 1) and its IR spectrum [2].

Acetylation of Integristerone A Acetate. The acetylation of 20 mg of ecdysteroid (**1**) was carried out in 2 ml of dry pyridine with 2 ml of acetic anhydride at room temperature for a day. Then the reaction mixture was diluted with water and extracted with ethyl acetate. After elimination of the solvent, the dry residue was chromatographed on a column of silica gel. Elution with system 2 yielded 17 mg of the pentaacetate of integristerone A (**3**), $C_{37}H_{54}O_{13}$, mp 156—158°C (methanol).

IR spectrum (KBr, γ, cm^{-1}): 3495 (OH), 1661 (7-ene-6-keto group), 1743, 1244 (ester group).

Mass spectrum, m/z(%): 646 (M^+ -CH_3COOH; 0.8), 628 (0.9), 587 (3.5), 586 (3.5), 568 (17), 550 (16), 505 (97), 487 (95), 462 (80), 445 (61), 427 (40), 403 (17), 392 (100), 385 (44), 343 (50), 325 (22), 307 (17), 99 (15), 81 (21), 69 (18).

PMR spectrum (C_5D_5N, δ, ppm, TMS): 1.46 (6H, CH_3-18 and CH_3-19, s), 1.45 and 1.46 (6H, CH_3-26 and CH_3-27, s), 1.62 (3H, CH_3-21, s), 1.98 (6H, 2×$OCOCH_3$, s), 2.08 (9H, 3×$OCOCH_3$, s), 3.62 (H, H-9, m), 5.03 (H, H-22, m), 5.60 (2H, H-1 and H-2, m), 5.85 (H, H-1, m), 6.12 (H, H-7, s).

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