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PHYTOECDYSTEROIDS OF PLANTS OF THE *Silene* GENUS.
XVIII. TOMENTESTERONE FROM *Silene tomentella*

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A new ecdysteroid — tomentesterone B — has been isolated from the epigeal part of Silene tomentella. *Its structure has been established by chemical transformations and spectral investigations.*

On continuing a study of the ecdyteroids of *Silene tomentella* Schischk. (fam. Caryophyllaceae) [1], we isolated the new ecdysteroid (**1**) from the epigeal part of this plant.

The IR spectrum of (**1**) showed a broad absorption band at 3429 cm^{-1} (OH) and also a maximum at 1662 cm^{-1} corresponding to the absorption frequency of a keto group conjugated with a double bond. Absorption bands at 1712 and 1292 cm^{-1} and at 1643, 1584, and 713 cm^{-1} corresponded to an ester group and a benzene ring, respectively. These facts, and also intense peaks of ions in the mass spectrum with *m/z* 122 ($C_7H_6O_2$) (100%), 105 (C_7H_5O), and 77 (C_6H_5) indicated that ecdysteroid (**1**) contained a benzoic acid residue. The signals of five aromatic protons at (ppm) 8.22 (2H) and 7.49 (3H) in the PMR spectrum showed the presence of one benzoyl group (Table 1).

In the neutral fraction of the products of the alkaline saponification of ecdysteroid (**1**) we identified 5α-2-deoxyecdysone (**2**) [1-3], and in the acid fraction of the hydrolysate the presence of benzoic acid was detected.

The acetylation of ecdysteroid (**1**) gave an acetyl derivative. In its mass spectrum we observed intense peaks of ions with *m/z* 374 ($C_{23}H_{34}O_4$) and 276 ($C_{17}H_{24}O_3$) [4], showing that the benzoic acid residue was present in the side-chain of the ecdysteroid. In actual fact, on comparing the characteristics of the PMR spectra of ecdysteroid (**1**) and of 5α-2-deoxyecdysone (**2**) a considerable downfield shift of the resonance lines of the 26/27 methyl groups in the spectrum of the former was observed (see Table 1). We have observed an analogous shift previously in the spectrum of tomentesterone A [1]. This fact permitted the assumption that in compound (**1**) the hydroxy group at C-25 was esterified by benzoic acid.

To confirm the structure of ecdysteroid (**1**), we saponified the diacetate (**3**) with 0.5% aqueous methanolic potassium bicarbonate. As was to be expected, under these conditions the acetate group at C-22 remained unaffected, and the physicochemical constants (R_f, IR and mass spectra) of the reaction product coincided with those of tomentosterone A (**4**) [1].

The facts presented showed that the benzene residue was indeed attached to the hydroxy group at C-25. Thus, ecdysteroid (**1**) is 5α-2-deoxyecdysone 25-O-benzoate. (See scheme on following page.)

EXPERIMENTAL

For methods of isolation, instruments, and conditions for chromatography, see [1].

Tomentesterone B (1), $C_{34}H_{48}O_6$, mp 145-147°C (from the methanol—water system). IR spectrum (KBr, ν, cm^{-1}): 3429 (OH), 1662 (Δ^7-6-keto grouping), 1712, 1292 (ester group), 1584, 713 (benzene ring).

Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 430 (M^+ — 122; 24), 415 (24), 412 (44), 397 (24), 379 (24), 332 (44), 284 (84), 234 (82), 122 (100), 105 (66), 99 (32), 77 (42).

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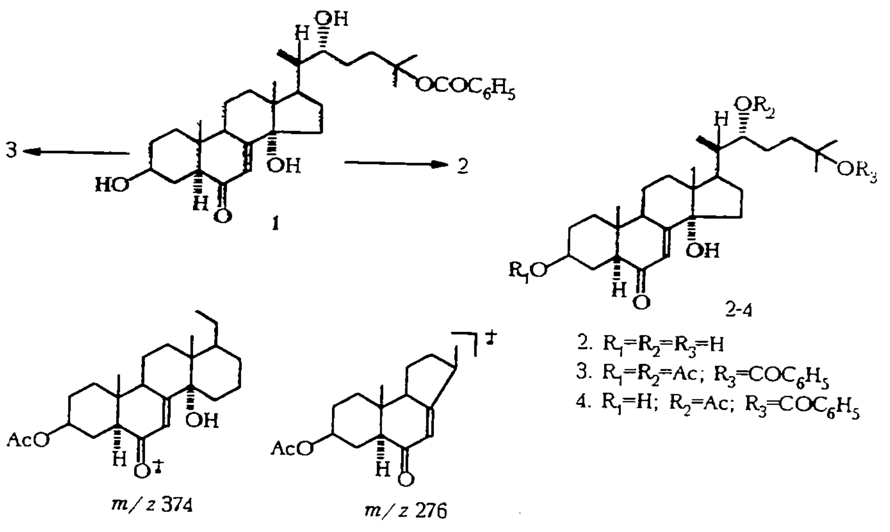
TABLE 1. Chemical Shifts (δ, ppm) and SSCCs (J) of the Protons of Tomentesterone B (**1**), 5α-2-Deoxyecdysone (**2**), Tomentesterone B 3,22-Diacetate (**3**), and Tomentesterone A (**4**)

Protons	Compound			
	1	**2**	**3**	**4**[1]
H-3	4.09	4.05	4.71	4.10
H-22	4.09	4.05	4.91	5.34
H-7	6.16 J=3 Hz	6.18 J=3 Hz	5.91 J=3 Hz	6.19 J=2.5 Hz
CH_3-18	0.71	0.73	0.67	0.74
CH_3-19	0.89	0.93	0.87	0.89
CH_3-21	1.30 J=6 Hz	1.27 J=6 Hz	0.84 J=6 Hz	1.13 J=6.5 Hz
CH_3-26/27	1.65	1.41	1.59/1.61	1.60
Ar-H	7.49(3H) 8.22(2H)	-	7.47(3H) 8.01(2H)	7.48(3H) 8.18(2H)
OAc	-	-	2.04(3H) 2.06(3H)	2.14(3H)

Note. The spectra of compounds (**1**), (**2**), and (**4**) were taken in C_5D_5N, and that of (**3**) in $CDCl_3$; chemical shifts were determined relative to the internal standard TMS. The signal of the CH_3-21 group was a doublet and those of the other methyl groups were singlets. The H-7 protons appeared in the form of a doublet, while the other signals were broadened multiplets.



2. $R_1=R_2=R_3=H$
3. $R_1=R_2=Ac$; $R_3=COC_6H_5$
4. $R_1=H$; $R_2=Ac$; $R_3=COC_6H_5$

Alkaline Hydrolysis of Tomentesterone B (1). To 5 mg of ecdysteroid (**1**) in 5 ml of methanol was added 3 ml of a 0.5% aqueous solution of potassium bicarbonate. The reaction mixture was kept in a thermostat at 37°C for 3 days. Then it was diluted with water and neutralized, and the methanol was evaporated off in vacuum. The aqueous solution was extracted with ethyl acetate, the solvent was distilled off to dryness, and the residue was recrystallized from aqueous methanol to give 2 mg of the ecdysteroid (**2**) with mp 225-227°C, identical, according to its IR spectrum [(KBr, ν, cm^{-1}): 3440 (OH), 1645 (7-ene-6-keto grouping)], with 5α-2-deoxyecdysone [1-3].

When the aqueous residue was acidified with dilute (1:1) hydrochloric acid and extracted with ethyl acetate, benzoic acid was obtained.

Tomentesterone B 3,22-Diacetate (3). In solution in 3 ml of pyridine, 20 mg of tomentesterone B was acetylated with 3 ml of acetic anhydride at room temperature for 24 h. After the solvent had been distilled off in vacuum, the residue was chromatographed on a column of silica gel. Elution of the column with chloroform—methanol (15:1) yielded 10 mg of the diacetate (**3**), $C_{38}H_{52}O_8$.

IR spectrum (KBr, ν, cm^{-1}): 3420 (OH), 1650 (Δ^7-6-keto grouping), 1720, 1730, 1290, 1250, 1225 (ester group), 1610, 1590, 715 (benzene ring).

Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 618 (M^+ — H_2O; 0.2), 514 (8), 496 (22), 486 (33), 454 (66), 430 (66), 426 (36), 374 (27), 373 (60), 327 (72), 326 (60), 313 (72), 276 (60), 275 (71), 216 (66), 215 (97), 122 (100), 105 (98), 81 (78), 77 (96).

Tomentesterone A (4) from Tomentesterone B 3,22-Diacetate (3). The diacetate (3) was dissolved in 5 ml of a 0.5% aqueous methanolic solution of $KHCO_3$. The reaction mixture was left at room temperature for 4 h, after which it was diluted with water and neutralized with acetic acid, and the reaction product was extracted with ethyl acetate. The solvent was distilled off, and the residue was chromatographed on a column of silica gel. Elution of the column as decribed in the preceding paragraph gave 3 mg of tomentesterone A (**4**) with mp 139-140°C (from MeOH—H_2O), identified by a TLC and IR-spectral comparison with an authentic specimen of tomentesterone A [1].

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