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PHYTOECDYSTEROIDS OF PLANTS OF THE *Silene* GENUS. 2-DEOXYECDYSTERONE-25-ACETATE FROM *Silene wallichiana*

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The new ecdysteroid 2-deoxyecdysterone-25-acetate was isolated from roots of Silene wallichiana *Klotzsch.*

Key words: ecdysteroids, 2-deoxyecdysterone, 2-deoxyecdysterone-25-acetate, 5α-2-deoxyecdysterone.

In continuation of the study of ecdysteroids of *Silene wallichiana* Klotzsch [*Oberna wallichiana* (Klotzsch) Ikonn., Caryophyllaceae] [1], we isolated a new ecdysteroid (**1**) from its roots.

The IR spectrum of **1** has absorption bands for hydroxyls (3378 cm^{-1}) and an α,β-unsaturated ketone (1640 cm^{-1}) in addition to bands at 1721 and 1255 cm^{-1}, which are indicative of an ester. This is supported by the presence in the PMR spectrum of **1** of a 3H singlet at δ 1.95 ppm (Table 1).

The mass spectrum of **1** lacks a peak for the molecular ion M^+ at *m*/*z* 506 and contains peaks for products of successive dehydration of the molecular ion at 410, 395, 392, and 377 together with fragments at 332, 285, 284 (fragments of the steroid core), 144, 99, 81, and 69 (fragments of the side chain). This indicates that **1** is a 2-deoxyecdysteroid with an acetyl in the side chain [2].

Base hydrolysis of **1** gives 2-deoxyecdysterone (**2**) and ecdysteroid **3**, which was identified as 5α-2-deoxyecdysterone [1].

Enzymatic hydrolysis of **1** using total enzymes from Baker's yeast [3] gave 2-deoxyecdysterone (**2**) [4].

Comparison of the PMR spectra of **1** and **2** show a significant difference only for the positions of signals for the 26/27 methyls, which shift to weak field. The ^{13}C NMR spectra of **1** and **2** are practically identical with the exception of the signals for C-24, C-26, and C-27, which are observed at weaker field for the former, and the signal for C-25, at strong field (Table 1) [5].

The spectral data (IR, ^1H and ^{13}C NMR) indicate that the acetyl is located on the C-25 hydroxyl [6].

An analogous weak-field shift occurs for viticosterol E [7] and integristerone A 25-acetate [8].

Therefore, we conclude that **1** is 2-deoxyecdysterone-25-O-acetate.

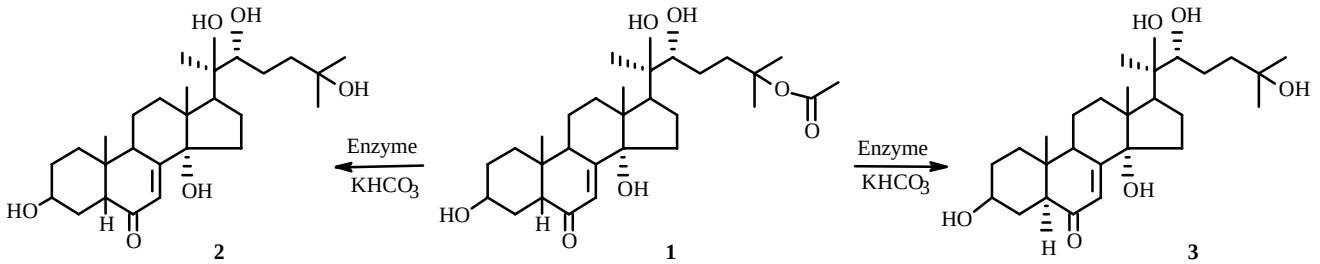

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TABLE 1. Chemical Shifts of the ^{13}C Signals of 2-Deoxyecdysterone-25-acetate (**1**) and 2-Deoxyecdysterone (**2**) (C_5D_5N, 0 = TMS, δ, ppm)

Atom	Compound	
	1	2
1	29.19	28.8
2	29.51	29.3
3	64.18	64.1
4	32.40	32.9
5	51.85	51.9
6	203.41	203.5
7	121.63	121.3
8	166.42	166.4
9	33.32	34.2
10	37.09	36.8
11	21.61	21.4
12	31.67	31.3
13	46.73	48.4
14	84.43	84.5
15	32.01	32.1
16	21.70	21.4
17	50.29	50.0
18	17.97	17.7
19	24.47	24.2
20	76.91	76.9
21	22.33	21.4
22	77.53	77.5
23	27.00	27.2
24	39.42	42.2
25	82.44	69.8
26	26.21	29.8
27	26.38	29.8
CH_3COO	170.0	
	21.21	

EXPERIMENTAL

General comments have been published [1].

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 instrument at working frequencies 500.13 and 125.27 MHz, respectively, in deuteropyridine at 30°C with TMS standard. Two-dimensional spectra were recorded using standard Bruker methods. The delay time for TOCSY and ROESY spectra was 0.2 sec. The measurement accuracy of the chemical shifts for ^1H and ^{13}C was 0.01 ppm; SSCC $^1H/^1H$, 0.2 Hz.

Isolation of 2-Deoxyecdysterone-25-acetate (1). Mother liquors (150 mg) obtained from recrystallization of 2-deoxyecdysterone were chromatographed repeatedly over a silica-gel column with elution by CCl_3—CH_3OH (15:1) to give a mixture of two compounds. Rechromatography of the eluates using $CHCl_3$—CH_3OH (25:1) gave **1** (25 mg, 0.001% calculated for air-dried mass), $C_{29}H_{46}O_7$, mp 192-196°C (methanol—water). IR spectrum (KBr, ν, cm^{-1}): 3378 (OH), 1640 (Δ^7-6-ketone), 1721, 1255 (ester).

Mass spectrum, *m/z* 506 $[M - CH_3COOH - 2H_2O]^+$, 395, 392, 377, 336, 332, 331, 318, 287, 286, 285, 284, 237, 185, 144, 143, 99, 81, and 69.

PMR spectrum (C_5D_5N, TMS, δ, ppm): 1.08 (3H, CH_3-19, s), 1.27 (3H, CH_3-18, s), 1.44 and 1.51 (6H, CH_3-26 and

CH_3-27, s), 1.95 (3H, $OCOCH_3$, s), 3.56 (H, H-9, m), 3.85 (H, H-22, m), 4.15 (H, H-3, m), 6.20 (H, H-7, s).

^{13}C NMR spectra are listed in Table 1.

Base Hydrolysis of 2-Deoxyecdysterone-25-acetate (1). A solution of **1** (15 mg) in methanol (2 mL) was treated with $KHCO_3$ solution (0.5%). The reaction mixture was left for 24 h and neutralized with acetic acid. The methanol was evaporated. Water was added. The mixture was extracted with ethylacetate. The extract was evaporated to dryness. The solid was chromatographed over a silica-gel column with elution by $CHCl_3$—CH_3OH (50:1) to give **3** (8 mg), $C_{27}H_{44}O_6$, mp 235-237°C (methanol—water), identical with an authentic sample (by TLC and IR spectrum) [1].

PMR spectrum (C_5D_5N, TMS, δ, ppm): 0.92 (3H, CH_3-19, s), 1.20 (3H, CH_3-18, s), 1.38 (6H, CH_3-26 and CH_3-27, s), 1.58 (3H, CH_3-21, s), 3.83 (2H, H-3 and H-22, m), 3.59 (H, H-9, m), 6.11 (H, H-7, s).

Further elution of the column with the same solvent system afforded **2** (4 mg), mp 254-255°C (aqueous ethanol), identical to an authentic sample [1, 3] by TLC and mixed melting point.

PMR spectrum (C_5D_5N, δ, ppm, TMS): 1.05 (3H, CH_3-19, s), 1.22 (3H, CH_3-18, s), 1.38 (6H, CH_3-26 and CH_3-27, s), 1.58 (3H, CH_3-21, s), 3.54 (H, H-9, m), 3.86 (H, H-22, m), 4.12 (H, H-3, m), 6.23 (H, H-7, s).

^{13}C NMR spectra are listed in Table 1.

Enzymatic Hydrolysis of 1. Freshly prepared aqueous extract (2 mL) of Baker's yeast (0.5 g) was treated with **1** (5 mg) and one drop of alcohol, left for 15 days at 37°C, diluted with water (8 mL), and extracted with ethylacetate (4×5 mL). The solvent was evaporated. The solid was chromatographed over a silica-gel column with elution by $CHCl_3$—CH_3OH (50:1) to give **2** (4 mg) that was identical to an authentic sample [1, 3].

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