Letters to the Editor

A new phytoecdysteroid

V. N. Odinokov,[a]* *I. V. Galyautdinov,*[a] *A. A. Fatykhov,*[b] *and L. M. Khalilov*[a]

[a]*Institute of Petrochemistry and Catalysis, Bashkortostan Republic Academy of Sciences*
and Ufa Research Center of the Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347 2) 31 2750. E-mail: ink@anrb.ru
[b]*Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences,*
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066. E-mail: chemorg@anrb.ru

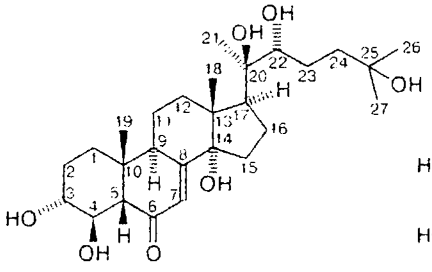
A new phytoecdysteroid, *viz.*, 2-deoxy-3-*epi*-4β,20-dihydroxyecdysone ((20*R*,22*R*)-3α,4β,14α,20,22,25-hexahydroxy-5β-cholest-7-en-6-one), named coronatasterone, was isolated from *Serratula coronata* and identified by NMR spectroscopy.

Key words: *Serratula coronata*, phytosteroid, 20-hydroxyecdysone, 2-deoxy-3-*epi*-4β,20-dihydroxyecdysone (coronatasterone), ^{1}H and ^{13}C NMR spectra.

A new phytoecdysteroid, *viz.*, 2-deoxy-3-*epi*-4β,20-dihydroxyecdysone (**1**), named by us coronatasterone, was isolated by extraction with ethyl acetate from the sap of the aerial part of the freshly gathered plant *Serratula coronata* and purified by HPLC. The structure of **1** was established from one- and two-dimensional ^{1}H and ^{13}C NMR experiments (JMOD CH, NOE DIFF, COSY, CH CORR, NOESY) and selective proton double resonance.

Table 1. Comparison of chemical shifts (δ) of the C(1)—C(5) atoms in the ^{13}C NMR spectra of compounds **1** and **2**

Atom	δ	
	1	**2**
C(1)	33.62 (t)	37.46 (t)
C(2)	42.98 (t)	68.72 (d)
C(3)	72.10 (d)	68.54 (d)
C(4)	75.31 (d)	32.81 (t)
C(5)	57.40 (d)	51.78 (d)



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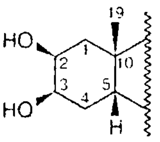

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Comparison of the ^{13}C NMR spectra of compound **1** and the main component, 20-hydroxyecdysterone (**2**), whose structure has been established previously,[1] shows the substantial distinctions in position and multiplicity of the signals (obtained in the JMOD mode) for the C(1)—C(5) atoms of the ring *A* of molecules **1** and **2**[2] (Table 1), whereas other signals of the C atoms of both compounds are close to each other.

The upfield shift (Δδ = 3.84) of the signal for C(1) and the downfield shift (Δδ = 5.62) of that for C(5)

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indicate that molecule **1** contains no hydroxy group at C(4). Therefore, the triplet signal at δ 42.98 belongs to C(2), whereas the doublet at δ 75.31 corresponds to the C(4) atom.

The signal for the proton at δ 3.31 in the ^{1}H NMR spectrum was assigned to H(4) because it has cross peaks with H(3) (δ 3.63) in the homonuclear HH COSY experiment and with C(4) (δ 75.31) in the heteronuclear CH CORR experiment. The configuration of the hydroxy groups at the C(3) and C(4) atoms of compound **1** was found from the NOE DIFF experiment and selective proton double resonance. Presaturation of the signal for the axial H(2) atom (δ 1.09, the position of the signal was established from two-dimensional spectroscopy) resulted in the nuclear Overhauser effect at the H(4) and H(9) atoms, and not at H(3). This indicates that the $H_a(2)$, H(4), and H(9) atoms are close to each other, occupy the axial positions, and have α-orientations. The vicinal spin-spin coupling constants $J_{\text{H-3,H-4}}$ and $J_{\text{H-3,H}_a\text{-2}}$ found by the double resonance method and equal to 9.8 and 9.7 Hz, respectively, unambiguously confirm the axial arrangement of the H(3) and H(4) atoms. Therefore, the hydroxy group at C(3) has α-orientation, whereas OH(4) corresponds to the β-configuration.

2-Deoxy-3-*epi*-4β,20-dihydroxyecdysone ((20*R*,22*R*)-3α,4β,14α,20,22,25-hexahydroxy-5β-cholest-7-en-6-one) (1). m.p. 215—216 °C, $[\alpha]_D^{15}$ +61.5° (*c* 0.88, MeOH). IR (KBr), ν/cm^{-1}: 1610 (C=C); 1655 (C=O); 3420 (OH). UV (EtOH), $\lambda_{\max}$/nm (ε): 240 (13600). ^{1}H NMR (CD$_3$OD, 300.13 MHz), δ: 0.89 (s, 3 H, H(18)); 0.96 (s, 3 H, H(19)); 1.09 (m, 1 H, $H_a(2)$); 1.19 (s, 3 H, H(21)); 1.20 (s, 6 H, H(26), H(27)); 1.06—2.02 (m, 14 H, CH, CH$_2$); 2.04—2.18 (m, 2 H, $H_e(2)$, H(5)); 2.40 (m, 1 H, H(17)); 3.17 (m, 1 H, H(9)); 3.31 (m, 1 H, H(4)); 3.36 (m, 1 H, H(22)); 3.63 (ddd, 1 H, H(3), $J_{3,4}$ = 9.8 Hz, $J_{3,2a}$ = 9.7 Hz, $J_{3,2e}$ = 4.3 Hz); 5.83 (d, 1 H, H(7), J = 2.2 Hz). ^{13}C NMR (CD$_3$OD, 75 MHz), δ: 18.1 (q, C(18)); 21.1 (q, C(21)); 21.5 (t, C(11), C(16)); 23.9 (q, C(19)); 27.3 (t, C(23)); 29.0 (q, C(26)); 29.7 (q, C(27)); 31.8 (t, C(15)); 32.5 (t, C(12)); 33.6 (t, C(1)); 36.0 (d, C(9)); 39.6 (s, C(10)); 42.4 (t, C(24)); 43.0 (t, C(2)); 48.5 (s, C(13)); 50.5 (d, C(17)); 57.4 (d, C(5)); 71.4 (s, C(25)); 72.1 (d, C(3)); 75.3 (d, C(4)); 78.0 (s, C(20)); 78.5 (d, C(22)); 85.2 (s, C(14)); 122.0 (d, C(7)); 166.2 (s, C(8)); 204.8 (s, C(6)).

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