PHYTOECDYSONES OF Ajuga turkestanica. II

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The isolation from the leaves of A. turkestanica (Rgl.) Briq. (family Labiatae) of cyasterone and ecdysterone has been reported previously [1]. Continuing a study of the phytoecdysones, we have investigated the roots of this plant.

The comminuted roots (2 kg) were extracted with methanol, the extract was concentrated to a volume of 800 ml and diluted with a double amount of water, and the hydrophobic compounds were extracted with petroleum ether. The aqueous methanolic fraction after additional removal of methanol by vacuum distillation was extracted with ethyl acetate. The ethyl acetate extract, by chromatography on alumina and rechromatography on silica gel [eluted with chloroform–methanol (9 : 1) and (4 : 1)] gave, in addition to cyasterone (175 mg) and ecdysterone (625 mg), 860 mg (0.043%) of an amorphous compound (I), $C_{27}H_{44}O_8$, with R_f 0.15 [SiO_2/gypsum; chloroform–methanol (4 : 1)].

The phytoecdysone obtained had $[\alpha]_D^{20}+52.0°$ (c 1.46; methanol), $\lambda_{max}^{C_2H_5OH}$ 244 nm (log ε 3.95); ν_{max}^{KBr} 3300-3500 (OH): 1660 cm^{-1} (CO–CH=C<). The mass spectrum of (I) (MKh-1303; 170°C; 40 eV) showed peaks of ions with m/e 460 (M–2 H_2O), 442 (M–3H_2O), 424 (M–4H_2O), corresponding to dehydration processes, and also peaks with m/e 379 and 361 and m/e 343 and 325, which are characteristic of phytoecdysones containing four hydroxy groups in the steroid nucleus [2-4]. Decomposition of the side chain is characterized by intense ions with m/e 99 and 81, which are typical for fragmentation of the side chain of ecdysterone [5].

NMR spectrum of (I) (C_5D_5N, 100 MHz, internal standard HMDS, δ, ppm): 1.12 (3 H at C_{18}, s); 1.18 (3 H at C_{19}, s); 1.24 (6 H at C_{26} and C_{27}, s); 1.45 (3 H at C_{21}, s); 6.12 (H at C_7).

On acetylation, compound (I) gave a mixture of amorphous 2,3,11,22-tetraacetate (II), $C_{35}H_{52}O_{12}$, with $\alpha_D^{20}+81.7°$ (1.86; methanol) and amorphous 2,3,11,22,25-pentaacetate (III), $C_{37}H_{54}O_{13}$.

NMR spectrum of (II) ($CDCl_3$): 0.85 ppm (3 H at C_{18}, s); 1.05 (3 H at C_{29}, s); 1.13 and 1.18 (6 H at C_{26} and C_{27}); 1.21 (3 H at C_{21}, s); and 5.85 (H at C_7).

The facts given permit the assumption that the substance that we isolated is a new phytoecdysone which has provisionally been called turkesterone. The results of a comparison of the chemical shifts of the C_{18} and C_{19} methyl groups of (I) with those of ajugasterone C and of (II) with the tetraacetate of ajugasterone C [2] show that turkesterone has a steroid skeleton with hydroxyls in the 2β, 3β, 11α, and 14α positions. The side chain of the new ecdysone, from the positions of the chemical shifts of the C_{26} and C_{27} methyls, corresponds to the 25-hydroxyecdysones [5]. The presence of four hydroxy groups in the steroid nucleus and a fifth at C_{25} of the side chain, as has been shown above, is confirmed by the fragments of mass-spectrometric decomposition. It is most likely that turkesterone is 25-hydroxyajugasterone C.

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