STEROID SAPONINS AND SAPOGENINS OF Allium

VII. THE STRUCTURE OF NEOAGIGENIN AND AGIGENIN

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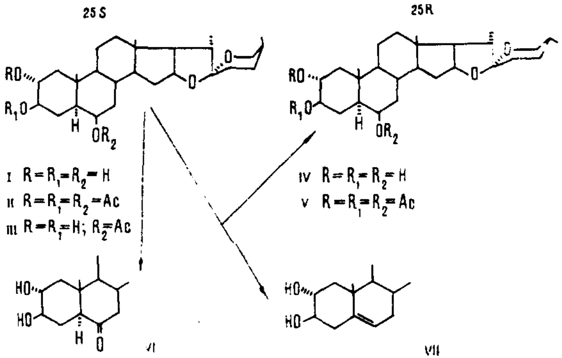
As reported previously [1], from the skins of the bulbs of Allium giganteum Rgl. (family Alliaceae) we have isolated a new steroid sapogenin – neoagigenin, $C_{27}H_{44}O_5$, mp 269-270°C (from methanol), $[\alpha]^{20}_{D}$ −76.0° (c 1.45; chloroform). The acetylation of (I) gave tri-O-acetylneoagigenin (II), $C_{33}H_{50}O_8$, mp 143-146°C (from methanol), $[\alpha]^{20}_{D}$ −177.3° (c 1.76; chloroform). The NMR spectrum of the sapongenin (I) [0.74 – 3 H at C_{18}, s; 0.96 – 3 H at C_{27}, d, J = 6 Hz; 1.02 – 3 H at C_{21}, d, J = 7 Hz; 1.28 – 3 H at C_{19}, s; 3.25 – H at C_{26}, m; 3.97 – 4 H at C_2, C_3, C_6, and C_{26}, m; 4.40 – H at C_{16}, m] confirms its assignment to the 25S series [2, 3].

The consumption of one mole of sodium periodate in the oxidation of neoagigenin (I) shows the presence of a diol grouping in its molecule.

As a result of the isomerization [4] of the genin (I) we isolated compounds (IV) and (VII). The sapogenin (IV) has the composition $C_{27}H_{44}O_5$, M^+ 448, mp 265-267°C (from methanol), $[\alpha]^{25}_{D}$ −74.2° (c 1.33; chloroform). ν^{KBr}_{max} 3300-3500 (OH), 872, 905 > 927, 965 cm^{-1} (spiroketal chain of the 25R series) [5]. NMR spectrum of (IV): 0.53 – 3 H at C_{27}, d, J = 5 Hz; 0.74 – 3 H at C_{18}, s; 0.98 – 3 H at C_{21}, d, J = 6 Hz; 1.27 – 3 H at C_{19}, s; 3.35 – 2 H at C_{26}, m; 3.90 – 3 H at C_2, C_3, and C_6, m; 4.35 – H at C_{16}, m. Thus, the genin (IV), which we have called agigenin, is the 25R isomer of neoagigenin (I). By the acetylation of agigenin (IV) we obtained the triacetate (V), $C_{33}H_{50}O_8$, with a double mp of 126-130°C and 195-197°C (from methanol), $[\alpha]^{25}_{D}$ −110.5° (c 1.26; chloroform). The sapogenin (VII), with M^+ 430 and mp 238-241°C (from methanol), $[\alpha]^{25}_{D}$ −115.2° (c 1.69; chloroform) was identified as yuccagenin [6]. The formation of yuccagenin (VII) shows the position of the hydroxy groups in the molecule of neoagigenin in positions 2α, 3β, and 6.

The selective oxidation of (I) by N-bromosuccinimide [7] gave the ketone (VI), $C_{27}H_{42}O_5$ with mp 240-242°C (from methanol), $[\alpha]^{22}_{D}$ −102.2° (c 1.60; chloroform). The nature of the optical rotatory dispersion curve of compound (VI) with a negative Cotton effect (c 0.072; methanol; $[M]_{309}$ −4030, $[M]_{271}$ +1340) shows the trans linkage of rings A/B [8].

The selective saponification with a 0.5% methanolic solution of KOH of the triacetate (II) enabled us to obtain the monoacetate (III), $C_{29}H_{46}O_6$, with mp 199-202°C (from methanol), $[\alpha]^{25}_{D}$ −69.9° (c 1.61; chloroform). In the NMR spectrum of (III) the proton geminal to the acetate group resonates in the 5.00 ppm region with $W_{1/2}$ ≈8 Hz, which shows the axial arrangement of the acetyl group at C_6. Thus, neoagigenin (I) is (25S)-5α-spirostan-2α,3β,6β-triol, and agigenin (IV) is (25R)-5α-spirostan-2α,3β,6β-triol.



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From the total steroid genins obtained from the florescences of A. giganteum we isolated β-chlorogenin with mp 228-231°C (from benzene), $[\alpha]_D^{25} -70.3°$ (c 1.75; chloroform) [9], and also a mixture of the genins (I) and (IV). The latter were separated by chromatographing their acetates on silica gel.

The NMR spectra were taken on a JNM-4H-100/100 MHz instrument (C_5D_5N, HMDS, δ, ppm).

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*In the Consultants Bureau translation of this article, neoagigenin was erroneously called neoapigenin — Publisher.