STEROID SAPONINS AND SAPOGENINS OF Allium

VI. THE 3-O-β-D-GLUCOPYRANOSIDE OF KARATAVIGENIN B

F. S. Khristulas, M. B. Gorovits,
and N. K. Abubakirov

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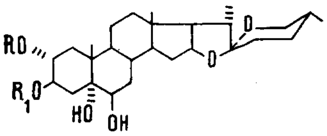
We have continued a study of all the extracted substances of steroid nature isolated previously [1] from the bulbs of Allium karataviense Rgl. (family Alliaceae). By chromatography of the extract on SiO_2 [with elution by chloroform–methanol (25 : 1)] we have isolated 0.33% (on the air-dry weight of the raw material) of a glycoside (IV), $C_{40}H_{58}O_{12}$, mp 294-296°C (ethyl acetate); $[\alpha]_D^{20} - 98.1 \pm 2°$ (c 1.64; pyridine); $\lambda_{\max}^{C_2H_5OH}$ 230 nm (log ε 4.20); $\nu_{\max}^{\text{kBr}}$ 3400-3580 (OH); 1710, 1280 (ester group); 870, 900 > 930, 995 (spiroketal chain, R series) [2, 3]; 1605, 1585, and 720 cm^{-1} (benzene ring).

The alkaline hydrolysis of compound (IV) in a 1% methanolic solution of KOH gave a glucoside (II) identified as alliogenin glucopyranoside [1, 4]. Benzoic acid was found in the hydrolyzate by TLC. The acid hydrolysis of (IV) with 5% of HCl in methanol at the boil for 2.5 h led to the production of a mixture of genins (I) and (III) separated by chromatography on silica gel. Elution by chloroform–methanol (100 : 1) gave the genin (III), which we have called karatavigenin B, $C_{34}H_{48}O_7$, mp 301-303°C (methanol), $[\alpha]_D^{20} - 84.7 \pm 2°$ (c 1.18 pyridine); $\lambda_{\max}^{C_2H_5OH}$ 230 nm (log ε 4.14); $\lambda_{\max}^{\text{KBr}}$ 3400-3500 (OH); 1695, 1280 (ester grouping); 870, 903 > 930; 990 (spiroketal chain R series); 1603, 1590, 720 cm^{-1} (benzene ring). In the mass spectrum of karatavigenin B (170°C, 40 eV), in addition to the molecular ion with m/e 568 and the peaks of ions with m/e 509, 499, 496, 454, 439, 42 ,*139, and 115, which are characteristic for the fragmentation of steroid sapogenins [5], there were fragments of benzoic acid with m/e 122 ($C_7H_6O_2$) and 105 (C_7H_5O).

The genin (I), eluted with chloroform–methanol (20 : 1), was identified as alliogenin [4].



I $R = R_1 = H$
II $R = H$; $R_1 = C_6H_{11}O_5$ (D-glucose residue)
III $R = C_6H_5CO$; $R_1 = H$.
IV $R = C_6H_5CO$; $R_1 = C_6H_{11}O_5$ (D-glucose residue)
V $R = H$; $R_1 = C_6H_5CO$.

The combination of facts given shows that karatavigenin B is alliogenin benzoate. Since in the NMR spectrum of (IV) in the 5.95-ppm region there is a broad ($W_{1/2} \approx 20$ Hz) signal of an axial proton geminal to a benzoate group, and the alkaline hydrolysis of this glycoside forms alliogenin pyranoside (II), it follows that the benzoic acid must esterify the hydroxyl at C_2. Thus, karatavigenin B is alliogenin 2-O-benzoate, and the glycoside (IV) is its 3-O-β-D-glucopyranoside. Alliogenin 3-O-benzoate (V) has been isolated pre-

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* Digit is omitted in Russian original – Publisher.

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viously from the same plant [1], and now, in order to distinguish the two isomeric benzoates, it is desirable to call this karatavigenin A.

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