STEROID SAPONINS AND SAPOGENINS OF *Allium*.

VIII. STRUCTURE OF GANTOGENIN

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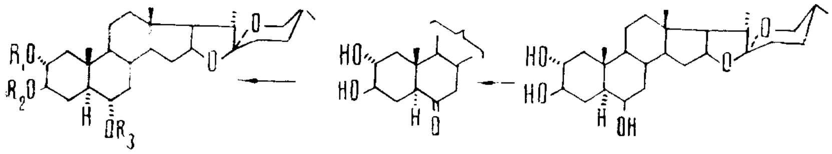
We have continued the study of the total steroid sapogenins isolated previously from the skins of the bulbs of *Allium giganteum* Rgl. (family Alliaceae) [1, 2]. By chromatographing the mixture of genins on a column of Al_2O_3 [elution with chloroform—methanol (20:1)] we have obtained a new steroid sapogenin which we have called gantogenin (I) (yield 0.008% calculated on the air-dry raw material), $C_{27}H_{44}O_5$, mp 265-268°C (methanol), $[\alpha]_D^{20}$ —49.1° (c 1.01; chloroform), γ_{max}^{KBr} 3300-3500 cm^{-1} (OH), 872, 907 > 925, 985 cm^{-1} (spiroketal chain, 25R series) [3]. The peak of the molecular ion of sapogenin (I) with m/e 448, and also the peaks of ions with m/e 305, 139, and 115 show that heptagenin is a trihydroxy sapogenin with the hydroxy groups in the androstane part of the molecule [4].

The acetylation of gantogenin (I) under the usual conditions gave the triacetate (II), $C_{33}H_{50}O_8$, M^+ 574, mp 236-239°C (methanol), $[\alpha]_D^{22}$—102.4° (c 1.15; chloroform). NMR spectrum of (I) (C_5D_5N, 100 MHz, HMDS, δ, ppm): 0.53 (3H at C_{27}, d, J = 5 Hz); 0.71 (3H at C_{19}, s); 0.81 (3H at C_{18}, s); 0.98 (3H at C_{21}, d, J = 6 Hz); 3.40 (2H at C_{26}, m); 3.88 (3H at C_2, C_3, and C_6, m); 4.40 (H at C_{16}, m)] confirms its assigment to the 25R series [5, 6]. The results of a comparison of the chemical shifts of the C_{18} and C_{19} methyl groups of the sapogenin (I) with the chemical shifts of these groups calculated [7] for (25R)-5α-spirostan-2α,3β,6α-triol permitted the conclusion that the hydroxy groups of gaptogenin (I) have a similar configuration.

For confirmation, we performed a partial synthesis of gaptogenin (I) from agigenin (IV). The selective oxidation of (I) with N-bromosuccinimide [2, 8] in aqueous dioxane gave the 6-ketosapogenin (III) $C_{27}H_{42}O_5$, M^+ 446, mp 242-244°C (methanol), $[\alpha]_D^{23}$ —86,8° (c 1.39; chloroform); γ_{max}^{KBr} 3300-3500 cm^{-1} (OH), 1712 cm^{-1} (C=O), 872, 907 > 929, 985 cm^{-1} (spiroketal chain of the 25R series).

The reduction of the ketone (III) with sodium in absolute ethanol [9] gave (25R)-5α-spirostan-2α,3β,6α-triol with mp 267-269°C (methanol), $[\alpha]_D^{23}$—51.8° (c 1.23; chloroform), which was identified by a mixed melting point. The IR, NMR, and mass spectra of the compounds compared coincided. The acetylation of compound (I) gave the triacetate (II) with mp 238-240°C (methanol) which proved to be identical in its physicochemical properties with gantogenin triacetate.



I $R_1=R_2=R_3=H$
II $R_1=R_2=R_3=Ac$

III

IV

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LITERATURE CITED

1. A. N. Kel'ginbaev, M. B. Gorovits, S. A. Hamidkhodzhaev, and N. K. Abubakirov, Khim. Prirodn. Soedin., 438 (1973).
2. A. N. Kel'ginbaev, M. B. Gorovits, and N. K. Abubakirov, Khim. Prirodn. Soedin., 801 (1974).
3. M. E. Wall, C. R. Eddy, M. L. McClennan, and M. E. Klump, Anal. Chem., 24, 1337 (1952).
4. H. Budzikiewicz, J. M. Wilson, and C. Djerassi, Monatsh. Chem., 93, 1033 (1962).
5. W. E. Rosen, J. B. Liegler, A. C. Shabica, and J. N. Schoolery, J. Amer. Chem. Soc., 81, 1687 (1959).
6. J. R. Kitney, Steroids, 2, 225 (1963).
7. K. Tori and K. Aono, Ann. Rept. Shionodi Res. Lab., 14, 136 (1964).
8. L. F. Fieser and S. Rajagopalan,J. Amer. Chem. Soc., 71, 3938 (1949).
9. T. Okanishi, A. Akahori, and F. Vasuda, Chem. Pharm. Bull., 13, 545 (1965).