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STEROID SAPOGENINS OF YUCCA GLORIOSA

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We have previously reported [1] that the hydrolysis of the leaves of Yucca gloriosa L. gives a considerable amount of tigogenin and a small amount of dihydroxysapogenins.

It is known [2] that tigogenin is one of the steroid sapogenins that can be used for the synthesis of hormones.

We obtained the yucca leaves from the Nikitskii, Sukhum, and Baku botanical gardens and also from the Kobuletskaya zonal station of the All-Union Institute of Medicinal Plants. The sapogenins were isolated by hydrolysis of the raw material by a modification of Rothrock's method [3, 4]. When the leaves were hydrolyzed without preliminary extraction with chloroform or dichloroethane, together with the sapogenins the petroleum ether extracted about 40% of amorphous substance [Sannié et al. have also reported the amorphous substances accompanying the sapogenins in Yucca gloriosa growing in France]. After a second extraction with petroleum ether and then recrystallization from methanol, about 1% of tigogenin was obtained. The methanolic filtrate deposited a crystalline substance with mp 257-259° C with a characteristic Sannié reaction for steroid sapogenins [6]. Its IR spectrum, taken on a IKS-14 spectrometer in paraffin oil, had the four absorption bands characteristic for steroid sapogenins: 983, 918, 900, and 864 cm^{-1}; bands characterizing carbonyl bonds were absent.

On the basis of the IR spectra, this sapogenin was assigned to the D-series. By elementary analysis, the compound and its acetate corresponded to a dihydroxy-sapogenin, but its constants were dissimilar to those of any sapogenins described in the literature. The study of its structure is continuing.

The benzene filtrate, by chromatography on a column of alumina, also yielded smilagenin and gitogenin.

In the cleavage of tigogenin acetate to form the acetate of 3β-hydroxyallopregn-16-en-20-one we used a method developed in the hormone laboratory of the All-Union Chemical and Pharmaceutical Scientific-Research Institute for converting diosgenin acetate into the acetate of 3β-hydroxypregna-5,16-dien-20-one [7]. This gave 44% of the pure acetate of 3β-hydroxyallopregnen-20-one with mp 163-167° C.

Experimental

Isolation of tigogenin. Hydrolysis of the previously purified leaves. 1) In a Soxhlet apparatus, 100 g of the air-dry comminuted leaves of Yucca gloriosa obtained from the Baku botanical gardens were exhaustively extracted with chloroform or dichloroethane and the material was then hydrolyzed by boiling in a water bath, with stirring, with one *l* of 2 N hydrochloric acid containing 5% of butanol for 4.5 hr. The remaining plant material, containing the sapogenins, was filtered off, washed with water and 5% sodium bicarbonate solution until the acid reaction had disappeared, and dried at 80° C. The dry residue (43 g) was extracted in a Soxhlet apparatus with petroleum ether for 6 hr. The solvent was driven off, and the residue (2.06 g) was recrystallized from methanol (1 : 70) and dried at 80° C. This yielded 1.05 g of a residue with mp 200-202° C, $[\alpha]_D^{20}$ −62.31° (c 1.0; chloroform), identified as tigogenin.

2) The purified leaves (100 g) were hydrolyzed with 4 N sulfuric acid for 3 hr and worked up as in Exp. 1. The yield of unpurified sapogenins was 1.88 g, and after recrystallization from methanol the yield of tigogenin was 1.01 g with mp 198-200° C, $[\alpha]_D^{20}$ −69.24°.

Hydrolysis without previous purification of the leaves was carried out under the conditions of Exp. 1. The total unpurified sapogenins isolated from 1.6 kg of the leaves (40.12 g) were treated with petroleum ether for 2-3 hr, which removed about 40% of a waxy substance containing some tigogenin. The remaining sapogenin (20.35 g) was recrystallized from methanol (1 : 70). This gave 12.75 g of tigogenin with mp 204-206° C, $[\alpha]_D^{20}$ − 60.33° (c 1.0; chloroform).

Tigogenin acetate. A mixture of 5 g of tigogenin and 20 ml of acetic anhydride was boiled for 30 min. The precipitate that deposited on cooling was washed with cold acetic anhydride and with water and was recrystallized from methanol. This gave tigogenin acetate with mp 204-206.5° C, $[\alpha]_D^{20}$ −71.29° (c 1.0; chloroform), which corresponds to literature data [8-10].

Isolation of the other genins present. After the separation of the tigogenin, the solvent was distilled off completely from the methanolic filtrate and the 5.55 g of residue (R_f 0.69 and two small spots in the region of dihydroxy sapogenins) was dissolved in 80 ml of benzene with heating. The insoluble fraction of the residue was filtered off and recrystallized from ethanol twice to give 0.15 g of a substance (0.01% with respect to the weight of the raw material) with mp 257-259°

C, $[\alpha]_D^{20}$ −36.35° (c 1.0; chloroform), R_f 0.23 [Sannié's second system: petroleum ether—chloroform—acetic acid (100 : 40 : 4)]. The reaction with tetranitromethane was negative.

Found, %: C 75.12, 74.73; H 10.33, H 10.25. Calculated for $C_{27}H_{44}O_4$, %: C 74.96; H 10.25.

The benzene filtrate after the separation of the dihydroxysapogenins was chromoatographed on alumina. Elution was begun with benzene and was continued with more polar solvents. The 7-th–10-th benzene fractions yielded 0.14 g of a crystalline substance. After recrystallization from acetone, it melted at 183° C, R_f 0.76 (Sannié's first system), and was identical with a sample of smilagenin. The subsequent benzene eluates gave 3.2 g of tigogenin with mp 205–206° C (from methanol), R_f 0.69. Ethyl acetate—acetone (1 : 1) eluates yielded 0.11 g of a crystalline substance with R_f 0.21 (unknown dihydroxysapogenin) and 0.18 g of a compound with R_f 0.42 (Sannié's second system) which coincides completely with the R_f value of gitogenin.

The sapogenin acetate with mp 257–259° C. 0.06 g of the sapogenin was boiled with 2 ml of acetic anhydride for 10 min. The precipitate that deposited was filtered off, washed with water, and dried in vacuum at 60° C. After recrystallization from hexane, mp 155–157° C.

Found, %: C 71.88, 71.35; H 9.00, 9.18. Calculated for $C_{31}H_{48}O_6$, %: C 72.05; H 9.36.

Acetate of 3β-hydroxyallopregn-16-en-20-one from the tigogenin isolated from Yucca gloriosa. Three grams of tigogenin acetate and 6 ml of a mixture of acetic anhydride and acetic acid (3 : 1) was heated with vigorous stirring in a glass tube in an electric thermostat at 180° C for 5 hr. The conversion of the acetate into pseudotigogenin was followed by paper chromatography in the β-phenoxyethanol—heptane system. The spots were revealed with Sannié's reagent. The reaction mixture was diluted with 22 ml of acetic acid and then, with stirring, a solution of 1.42 g of dichromate in 10 ml of acetic acid was rapidly poured in. After 10 min, 0.32 g of sodium sulfite and 4 ml of acetic anhydride were added and the reaction mixture was boiled for 3 hr. After cooling, 30 ml of water was gradually added (the acetic acid content in the solution must be about 45–50%). The precipitate that deposited was filtered off and was washed with 45% acetic acid and then with water to neutrality. After drying in the air, 2.09 g of a resinous substance was obtained which was recrystallized from 4 ml of ethanol and washed with a small amount of ethyl ether. On recrystallization from 15 ml of methanol with carbon, 1.04 g of a precipitate with mp 163–164° C (44%) was obtained. A mixture with the acetate of 3β-hydroxyallopregn-16-en-20-one (mp 163–164° C) obtained in VNIKhFI [All-Union Chemical and Pharmaceutical Scientific-Research Institute] from tomatidine gave no depression of the melting point.

Conclusions

It has been shown that the leaves of Yucca gloriosa L. yield about 1% of pure tigogenin and about 0.01% of a saturated dihydroxysapogenin with the composition $C_{27}H_{44}O_4$ of unknown structure; smilagenin and gitogenin are present as impurities.

REFERENCES

1. O. S. Madaeva and T. A. Pkheidze, Sbornik trudov TNIKhFI, Tbilisi, **9**, 13, 1960.
2. R. Marker, R. Wagner, P. Ulshafer, et. al., J. Am. Chem. Soc., **69**, 2167, 1947.
3. J. Rothrock, P. Hammes, and W. McAleer, Industr. Eng. Chem., 49, 186, 1957.
4. L. S. Chetverikova and O. S. Madaeva, Med. prom. SSSR, **8**, 28, 1958.
5. Ch. Sannie and H. Lapin, Bull. Soc. Chim. Fr., **11–12**, 1083, 1952.
6. S. Heitz, H. S. Lapin, Ch. Sannie, and P. Burschewitz, Bull. Soc. Chim. Biolog., **36**, 227, 1954.
7. V. I. Maksimov, F. A. Lur'i, and L. A. Morozova, USSR patent no. 136 380, 19 January 1961; USSR 14 309, 23 February 1962.
8. M. E. Wall, H. E. Kenney, and E. S. Rothman, J. Am. Chem. Soc., 77, 5665, 1955.
9. M. E. Wall, C. R. Eddy, and M. L. McClemann, Analyt. Chem., 24, 1337, 1952.
10. L. Fieser and M. Fieser, Steroids, N.Y., 830, 1959.

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