as carried out above, there was obtained: 5 g. of unreacted diol, 3.5 g. of the unsaturated hydrocarbon A, and 0.6 g. of an unsaturated liquid boiling at 145–165°. The last fraction is probably identical with a similar material obtained by Bourguel, which he believed to be the intermediate dehydration product, 2,5-dimethyl-3,5-hexadiene-2-ol. Our material polymerized rapidly on standing, and on heating at atmospheric pressure decomposed with formation of the unsaturated hydrocarbon A and polymers.

Summary

The configurations of the *cis–trans* isomers of 2,5-dimethyl-3-hexene-2,5-diol have been established, and their behavior toward sulfuric and hydrochloric acids has been studied.

The *cis*-isomer undergoes dehydration readily with either reagent to give 2,2,5,5-tetramethyltetrahydrofuran. The structure of this dehydration product has been definitely established.

The *trans*-isomer undergoes dehydration with sulfuric acid to yield an unsaturated hydrocarbon which is probably the *trans*-form of 2,5-dimethyl-1,3,5-hexatriene. A higher boiling fraction was obtained which is a dimer of the triene. The *trans*-isomer is merely converted to a dichloride by the action of cold hydrochloric acid.

These results show a very clear cut difference in the behavior of the isomeric *cis-trans* diols on dehydration. Neither form undergoes rearrangement of the pinacol–pinacolone type.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Sterols. CVII. Steroidal Sapogenins of Aletris, Asparagus and Lilium*

BY RUSSELL E. MARKER, D. L. TURNER, ANTONY C. SHABICA, ELDON M. JONES, JOHN KRUEGER AND J. D. SURMATIS

Steroidal sapogenins have been obtained by the hydrolysis of saponins from plants belonging to the families *Liliaceae*, *Dioscoreaceae* and *Scrophulariaceae*.[1,2]

We have investigated about thirty plants of these families and have now obtained steroidal sapogenins from three of them. The method of isolation was essentially identical with that described previously.[2]

From the roots of *Aletris farinosa* (L.) (*Liliaceae*) a sapogenin was obtained. The analysis of the genin and its acetate and mixed melting point determinations showed that it was diosgenin.

The roots of *Asparagus officinalis* (L.) (*Liliaceae*) gave sarsasapogenin, which gave no depression in melting point with a sample from sarsaparilla root. The identification was confirmed with the acetate.

Japanese lily bulbs purchased from Charles E. Meyer, Inc., New York City, under the name "*Lilium rubrum magnificum*" also gave a sapogenin. The formation of an insoluble digitonide indicated that the substance was steroidal with a hydroxyl group at the 3-position. However, it is not identical with any of the sapogenins which have been described previously. Elementary analysis showed that it was isomeric with gitogenin. It formed a diacetate. Mild oxidation of the new sapogenin with chromic acid gave only acid products. This indicates that the substance has adjacent hydroxyl groups which probably are 2,3 or 3,4. If the hydroxyl groups are 2,3 it may be a structural isomer of gitogenin with the coprostane configuration at C-5 or it may differ from gitogenin in the configuration of the side-chain as sarsasapogenin differs from isosarsasapogenin.[3] It has been shown that gitogenin has the iso-configuration of the side-chain.[4] We propose the name "liligenin" for the new sapogenin.

We are grateful to Parke, Davis and Company for their generous assistance.

Experimental Part

Diosgenin from *Aletris farinosa* **(L.).**—Dried and powdered aletris roots (25 pounds) were treated as described previously,[2] for *Trillium erectum*, except that the final hydrolysis mixture was extracted with ether. The ethereal solution was washed with water. The residue from the evaporation of the ether was refluxed with hot methanolic potassium hydroxide for fifteen minutes. The alcoholic solution was poured into water and the sapogenin was taken up in ether. The ether was washed with water. The solvent was removed and the residue was refluxed for thirty minutes with 20 cc. of acetic anhydride. The genin separated as the acetate from the cooled solution.

(*) Previous paper, THIS JOURNAL, **62**, 2548 (1940).

(1) Fieser, "Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1937.

(2) Marker, Turner and Ulshafer, THIS JOURNAL, **62**, 2542 (1940).

(3) Marker and Rohrmann, *ibid*, **61**, 846 (1939).

(4) Marker and Rohrmann, *ibid*., **61**, 2724 (1939).

It was washed with methanol and recrystallized from a mixture of methanol and ethyl acetate; m. p. 196–199°. A mixture with diosgenin acetate, m. p. 199–200°, melted at 198–200°, and a mixture with tigogenin acetate, m. p. 202°, melted at 185–191°.

Anal. Calcd. for $C_{29}H_{44}O_4$: C, 76.3; H, 9.7. Found: C, 76.5, 76.5; H, 9.7, 9.8.

A solution of 200 mg. of the acetate and 150 mg. of potassium hydroxide in 15 cc. of ethanol was boiled for thirty minutes, poured into water, and filtered. The solid was washed with water and dried. After recrystallization from aqueous acetone the product melted at 208–209°. A mixture with diosgenin, m. p. 207–209°, melted at 208–209°.

Anal. Calcd. for $C_{27}H_{42}O_3$: C, 78.2; H, 10.2. Found: C, 77.9, 77.9; H, 10.2, 10.2.

Sarsasapogenin from *Asparagus officinalis* (L.).—The dried and powdered root (25 lb.) was treated as described above under *Aletris*.

The crude genin from the ether extract of the hydrolysis mixture was not acetylated but was recrystallized directly from ethanol. It melted at 203–205°. When mixed with diosgenin or with tigogenin the melting point was depressed 20°. When mixed with sarsasapogenin, m. p. 203–205°, the melting point was 203–205°.

The acetate was prepared by refluxing with acetic anhydride and melted at 142° after recrystallization from ethyl acetate. When mixed with sarsasapogenin acetate, m. p. 142°, the melting point was 142°.

Anal. Calcd. for $C_{29}H_{46}O_4$: C, 75.9; H, 10.1. Found: C, 75.9; H, 10.2.

Liligenin from *Lilium rubrum magnificum*.—The wet lily bulbs (36 lb.) were ground in a food chopper and extracted with ethanol. The procedure followed that given above for asparagus root. The ether extract from the hydrolysis mixture was washed with 2 *N* sodium hydroxide solution and water. On evaporation of the ether 1.1 g. of sapogenin was obtained. After recrystallization from ethanol the product had a m. p. 245–246°.

Anal. Calcd. for $C_{27}H_{44}O_4$: C, 74.95; H, 10.25. Found: C, 75.1; H, 10.1.

When a solution of the substance in ethanol was treated with a solution of digitonin in ethanol, there was immediately formed a heavy white precipitate of the digitonide. It was saturated to bromine.

The acetate was prepared by refluxing with acetic anhydride, followed by crystallization from methanol, m. p. 158°.

Anal. Calcd. for $C_{31}H_{48}O_6$: C, 72.06; H, 9.36. Found: C, 72.33; H, 9.16.

To a solution of 400 mg. of liligenin in 30 cc. of glacial acetic acid at 25° was added a solution of 600 mg. of chromic anhydride in 10 cc. of 80% acetic acid. The mixture stood for thirty minutes at room temperature. It was poured into water and extracted with ether. The ethereal solution was washed with dilute sodium carbonate and the acidic material precipitated with dilute hydrochloric acid. The acid could not be crystallized. There was no neutral fraction left in the ether after extraction with sodium carbonate.

Summary

Diosgenin and sarsasapogenin have been obtained from the roots of *Aletris farinosa* (L.) and *Asparagus officinalis* (L.), respectively. A new steroidal sapogenin has been obtained from bulbs of a Japanese lily.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Sterols. CVIII. The Preparation of Dihydroandrosterone and Related Compounds from Diosgenin and Tigogenin

BY RUSSELL E. MARKER

Androsterone has the *epi* configuration of the C-3 hydroxyl group and is of the *allo* series.[1] We have shown[2,3] that the oxidation of 20-keto-pregnane compounds with Caro's acid is a convenient method of preparing androstanol-17 compounds. By this method androstanol-17(α), *etio*-cholanediol-3(α),17(α), Δ^5-androstenediol-3,17 and testosterone have been prepared.[3]

In order to apply the same procedure to the preparation of dihydroandrosterone, *allo*-pregnanol-3(α)-one-20 was required. This was made by the method of Marker and Rohrmann.[4] Tigogenone, obtained by the oxidation of tigogenin from diosgenin, was reduced with aluminum isopropylate and the tigogenin in the product was separated as the digitonide. The residual product was *epi*-tigogenin. It gave an acetate and was reconverted to tigogenone on oxidation with chromic acid.

When *epi*-tigogenin was heated with acetic anhydride at 200° it gave pseudo-*epi*-tigogenin, a substance analogous to the other pseudo sapogenins previously reported from this Laboratory.

(1) Ruzicka, Goldberg, Meyer, Brunnger and Eichenberger, *Helv. Chim. Acta*, **17**, 1395 (1934).

(2) Marker), Rohrmann, Wittle, Crooks and Jones, THIS JOURNAL, **62**, 650 (1940).

(3) Marker, *ibid.*, **62**, 2543 (1940).

(4) Marker and Rohrmann, *ibid.*, **62**, 518 (1940).