the theoretical amount of hydrogen for one double bond was absorbed. Shaking was continued for eight hours, but apparently no additional hydrogen was absorbed. The solution was filtered and the solvent was evaporated *in vacuo*. The residue was refluxed for thirty minutes with a 3% alcoholic potassium hydroxide solution. The 22,23-dihydroneoergosterol was crystallized from ethyl alcohol, m. p. 146–148°; yield, 7 g.

Anal. Calcd. for $C_{27}H_{42}O$: C, 84.7; H, 11.1. Found: C, 84.6; H, 11.2.

When the reduction was carried out in ether, or in alcohol containing hydrochloric acid, the same product was obtained.

When refluxed with acetic anhydride, it gave an acetate which was crystallized from ethyl alcohol, m. p. 120.5–121.5°.

Anal. Calcd. for $C_{29}H_{44}O_2$: C, 82.0; H, 10.5. Found: C, 81.7; H, 10.5.

The catalytic hydrogenation of the acetate of neoergosterol gave the same product as above.

Hydrogenation of Dehydroneoergosterol.—A mixture of 500 mg. of dehydroneoergosterol, 120 mg. of platinum oxide catalyst, 150 cc. of 95% alcohol and 2 cc. of concentrated hydrochloric acid was shaken with hydrogen at room temperature and 45 pounds pressure for four hours. The solution was filtered, vacuum distilled and the residue was dissolved in 5 cc. of alcohol. An oily product which came out was separated and crystallized from alcohol, m. p. 64–65°. Reduction in acetic acid gave the same product. This is apparently the same product as that obtained from neoergosterol acetate.[4]

Anal. Calcd. for $C_{27}H_{42}$: C, 88.4; H, 11.6. Found: C, 88.1; H, 11.8.

Oxidation of Neoergosterol. (a) With Aluminum Isopropylate.—A mixture of 500 mg. of neoergosterol, 1 g. of aluminum isopropylate, 8 cc. of cyclohexanone and 30 cc. of dry toluene was refluxed for two and one-half hours. The product was diluted with ether, washed with water and dilute acid and the solvent was removed. The residue was steam distilled until no more odor of cyclohexanone derivatives came over. The solution was extracted with ether, washed with water and the solvent was removed. The residue was treated with Girard's reagent in alcohol to separate the ketonic fraction. This was hydrolyzed with hydrochloric acid, extracted with ether and crystallized from aqueous acetone, m. p. 120.5–122.5°.

(b) **With Copper Powder.**—A mixture of 1.5 g. of epineoergosterol and 1.5 g. of copper powder was slowly distilled. The distillate was treated in alcohol with norite, filtered and crystallized from aqueous acetone, m. p. 121–122.5°. Mixed with the above product, there was no depression in melting point.

Anal. Calcd. for $C_{27}H_{38}O$: C, 85.6; H, 10.1. Found: C, 85.5; H, 10.0.

The above product gave a semicarbazone which was purified by refluxing with water, alcohol and with ether. It did not melt below 295°.

Anal. Calcd. for $C_{28}H_{41}ON_3$: C, 77.2; H, 9.5. Found: C, 77.3; H, 9.3.

(c) **Oxidation of Dihydro-neoergosterol with Chromic Anhydride.**—A mixture of 3.5 g. of dihydro-neoergosterol in 35 cc. of acetic acid was cooled and to it was added a solution of 1.2 g. of chromic anhydride in 6 cc. of acetic acid and 2 cc. of water. It was allowed to stand over night, poured into water and extracted with ether. The acidic fraction was removed from the ether by washing with sodium carbonate solution. The ether was removed and the residue was crystallized from alcohol, m. p. 145–146°. It gave no depression in melting point when mixed with the starting material, dihydro-neoergosterol. When a larger amount of chromic anhydride was used, only acidic products were obtained.

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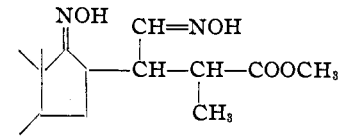
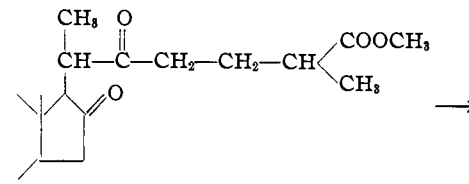
Sterols. CXXXV. Sapogenins. LVI. Sarsasapogenoic Acid

BY RUSSELL E. MARKER AND ANTHONY C. SHABICA

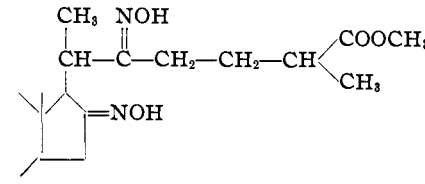
Fieser and Jacobsen[1] treated sarsasapogenoic methyl ester with hydroxylamine at 130° under the conditions used to obtain the dioxime of sarsasapogenoic acid and claim that the product they obtained had lost three carbon atoms. They assigned formula I to the product. We have repeated this work and have obtained a product in



I. Fieser and Jacobsen



II. Sarsasapogenoic Methyl Ester (Marker and Rohrmann)



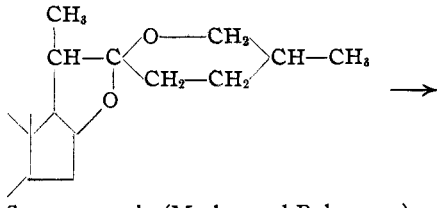
III. Our formulation of the dioxime

good yield which checks the melting point of that obtained by the above authors. Analysis shows that the dioxime is formed in the normal manner without the loss of carbon atoms, giving the product of formula III.

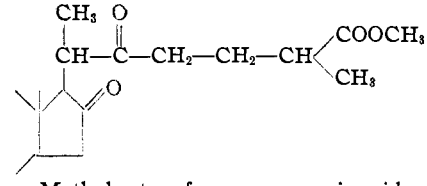
Marker and Rohrmann[2] obtained by the oxidation of the monoacetate of dihydrosarsasapogenin

(1) Fieser and Jacobsen, THIS JOURNAL, **60**, 2753 (1938).
(2) Marker and Rohrmann, *ibid.*, **61**, 846 (1939).

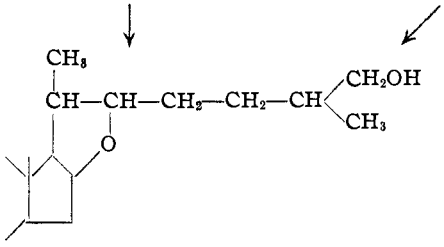
an acid, which after hydrolysis gave a product melting at 187°. According to our structure of the sapogenin side-chain this acid should be identical with anhydrotetrahydrosarsasapogenoic acid, obtained by Fieser and Jacobsen[1] by the reduction of sarsasapogenoic acid. Although no direct comparisons were made, Fieser, Fry and Jones[3] have indicated that the acids prepared by these two methods are different because "their acid (Marker and Rohrmann) is stated to melt at 187° and forms a crystalline methyl ester. Our acid (Fieser and Jacobsen) melts over a characteristi-



Sarsasapogenin (Marker and Rohrmann)



Methyl ester of sarsasapogenoic acid



Dihydrosarsasapogenin

cally long range (174–184°) and gives a liquid ester." We have made a direct comparison[4] of the two acids and their esters and find them to be identical. As additional proof of the identity of the two acids, we have now reduced the methyl ester of sarsasapogenoic acid with sodium and alcohol and have obtained dihydrosarsasapogenin which was identified by mixed melting points with a sample obtained by the catalytic hydrogenation of sarsasapogenin. Their acetates are also identical.

We wish to thank Parke, Davis and Company for their assistance.

Experimental

Methyl Ester of Sarsasapogenoic Acid.—To 4 g. of pure sarsasapogenoic acid in 250 cc. of ether was added a cold ethereal solution of diazomethane in ether. After standing for twenty-four hours at room temperature the solvent was evaporated and the residue was crystallized from methanol as flat plates, m. p. 132–134°.

Anal. Calcd. for $C_{28}H_{44}O_5$: C, 72.9; H, 9.6. Found: C, 72.7; H, 9.8.

Oxime of the Methyl Ester of Sarsasapogenoic Acid.—A mixture of 1.0 g. of the methyl ester of sarsasapogenoic acid, 0.7 g. of hydroxylamine hydrochloride, 1.0 g. of potassium acetate and 70 cc. of methanol was heated in a bomb tube at 130° for three hours. The solution was diluted with water, extracted with ether and the solvent removed. The residue was crystallized from aqueous methanol as small white needles, m. p. 169–171°.

Anal. Calcd. for $C_{28}H_{46}O_5N_2$: C, 68.5; H, 9.45; N, 5.7. Found: C, 68.6; H, 9.6; N, 5.6.

Reduction of the Methyl Ester of Sarsasapogenoic Acid.—To a boiling solution of 800 mg. of the methyl ester of sarsasapogenoic acid in 250 cc. of absolute ethanol was added 20 g. of sodium over a period of two hours. The solution was cooled, diluted with water and the precipitated solid was extracted with ether. The ethereal extract was washed with water, evaporated and the residue was crystallized from acetone in needles, m. p. 163–165°. This gave no depression in melting point when mixed with dihydrosarsasapogenin, prepared by the catalytic reduction of sarsasapogenin. A yield of 150 mg. of pure product was obtained.

Anal. Calcd. for $C_{27}H_{46}O_3$: C, 77.4; H, 11.1. Found: C, 77.7; H, 11.2.

When refluxed with acetic anhydride it yielded a diacetate which crystallized from ether–pentane in white prisms, m. p. 116–118°. When mixed with an authentic sample of the diacetate of dihydrosarsasapogenin there was no depression in melting point.

Anal. Calcd. for $C_{31}H_{50}O_5$: C, 74.0; H, 10.0. Found: C, 74.1; H, 10.0.

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(3) Fieser, Fry and Jones, THIS JOURNAL, **61**, 1849 (1939).
(4) Marker and Rohrmann, *ibid.*, **61**, 2072 (1939).

On the Structure of Hydrogen Cyanide

BY C. R. MCCROSKY, F. W. BERGSTROM AND G. WAITKINS

Many arguments have been advanced in support of the hypothesis that hydrogen cyanide is a mixture of tautomers; hydrogen cyanide proper and hydrogen isocyanide. In connection with the recent study of the synthesis of thiocyanates by the reaction of sulfur with organic cyanides,[1] it occurred to us that the presence of any isocyanide might be detected by treatment of ordinary hydrogen cyanide with sulfur, since it was known[2]

(1) McCrosky, Bergstrom and Waitkins, THIS JOURNAL, **62**, 2031 (1940).
(2) Nef, *Ann.*, **270**, 312, 328 (1892); **280**, 296 (1894); **287**, 325 (1895).