stannous ion is about 30% hydrolyzed to $SnOH^+$. Obviously these figures of Prytz cannot be correct.

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An Oxidation Product of $\Delta^{9,10}$-Octalin

BY G. CHRIS HARRIS

In a recent communication[1] the preparation of an unsaturated octalone-1 by selenium dioxide oxidation was reported. On the basis of the maximum at 243 mμ in the ultraviolet absorption spectrum of this substance, the suggestion was made that the double bond should be written at 8,9 instead of the previously postulated 9,10-position. It was pointed out,[2] however, that all of the α,β-unsaturated ketones whose spectra had been determined had an exocyclic double bond (as $\Delta^{8,9}$-octalone) and none of the $\Delta^{9,10}$-octalone type had been measured. This evidence, therefore, could not be considered conclusive until further data were available.

We now have some evidence of a different nature which favors the 9,10-position for the double bond. Kharasch and Tawney[3] reported the 1,4-addition of methylmagnesium chloride to isophorone in 82.5% yield when 1.0 mole per cent. of cuprous chloride is present. This reaction was repeated successfully and then was tried under the same conditions on the unsaturated octalone. No oxime-forming material was found in the reaction mixture. The distilled product of the reaction readily absorbed bromine in carbon tetrachloride solution without the evolution of hydrogen bromide.

The failure to obtain a ketone in this reaction indicates that no 1,4-addition took place. The reaction of the product with bromine is indicative of the unsaturated alcohol or hydrocarbon formed by 1,2-addition rather than the saturated ketone which would result from the 1,4-addition. It is more difficult to explain the lack of 1,4-addition if the octalone is the $\Delta^{8,9}$-isomer since the double bond appears to be less hindered.

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(1) W. P. Campbell and G. C. Harris, THIS JOURNAL, **63**, 2721 (1941).
(2) Robert Burns Woodward, *ibid.*, **64**, 72, 76 (1942).
(3) Kharasch and Tawney, *ibid.*, **63**, 2308 (1941).

Sterols. CXXXIV. Some Observations on the Structure of Ouabain

BY RUSSELL E. MARKER, D. L. TURNER, THOMAS S. OAKWOOD, EWALD ROHRMANN AND PAUL R. ULSHAFER

When heptaacetyldesoxydihydroouabain is subjected to acetolysis it loses the sugar residue and three acetoxy groups. One carbon atom is also eliminated as formaldehyde.[1,2] To explain this reaction Fieser[3] assumed that ring B had become aromatic. On this basis he assigned provisional formulas to ouabain and its derivatives. A careful study of the existing literature and some new experiments with neoergosterol and related compounds convince us that these formulas cannot be correct. The pertinent facts both old and new are given in Table I.

TABLE I

Neoergosterol (has ring B aromatic)	Acetolysis product from ouabain
Readily dehydrogenated	Cannot be dehydrogenated
Cannot be hydrogenated	Hydrogenated in acetic acid
Cannot be oxidized to a ketone with chromic anhydride	Oxidized to a ketone with chromic anhydride
5,7,9-Estratrienol-17 (has ring B aromatic, cannot be hydrogenated	
Equilenin (has rings A and B both aromatic), ring A hydrogenated in acetic acid; ring B cannot be hydrogenated	
Theelin (has ring A aromatic), ring A is reduced in acetic acid	
Trianhydrostrophanthidin (has ring B aromatic), ring B cannot be reduced	
Dehydroneoergosterol (has rings A and B aromatic), only ring A is reduced in acetic acid	

All of these facts indicate that ring A in the acetolysis product and not ring B has become aromatic. It thus seems improbable that Fieser's formulas for ouabain and its derivatives can be correct. At present there is not sufficient evidence available to determine the structure of ouabain.

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

Experimental

Hydrogenation of Neoergosterol.[4]—A mixture of 10 g. of neoergosterol, 500 cc. of glacial acetic acid and 2 g. of platinum oxide catalyst was shaken with hydrogen at room temperature and 45 pounds. After about thirty minutes,

(1) Jacobs and Bigelow, *J. Biol. Chem.*, **96**, 647 (1932).
(2) Jacobs and Bigelow, *ibid.*, **101**, 15 (1933).
(3) Fieser and Newman, *ibid.*, **114**, 705 (1936).
(4) *Cf.* Bonstedt, *Z. physiol. Chem.*, **185**, 165 (1929).

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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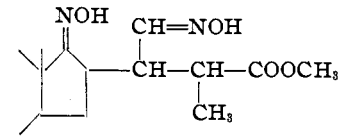
STATE COLLEGE, PENNA. RECEIVED JULY 11, 1941

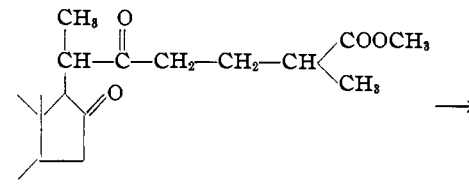
Sterols. CXXXV. Sapogenins. LVI. Sarsasapogenoic Acid

BY RUSSELL E. MARKER AND ANTHONY C. SHABICA

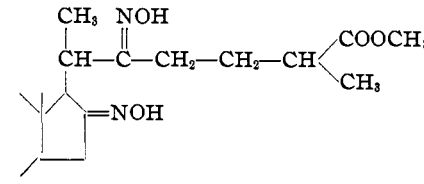
Fieser and Jacobsen[1] treated sarsasapogenoic methyl ester with hydroxylamine at 130° under the conditions used to obtain the dioxime of sarsasapogenoic acid and claim that the product they obtained had lost three carbon atoms. They assigned formula I to the product. We have repeated this work and have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