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).