therefore +4.27°. An additional double bond in the 3,4-position in cholestene or in the 6,7-position in coprostene effects a considerable increase in levorotation.

$\Delta^{4,6}$-Cholestadiene was found to be rearranged to $\Delta^{3,5}$-cholestadiene by treatment with dry hydrogen chloride in chloroform.

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[CONTRIBUTION FROM THE G & A LABORATORIES, INC.]

On the Dehydration of 22-Dihydrostigmasterol and Cholesterol with Iodine

BY TORSTEN HASSELSTROM AND BURT L. HAMPTON

The catalytic dehydration with iodine of secondary alcohols yields in most cases unsaturated hydrocarbons. Hibbert,[1] suggests that the action of iodine on alcohols proceeds with the formation of alkyl iodide and hypoiodite, which may react together to cause the formation of an ether and free iodine. While such a reaction apparently does not occur with ordinary monobasic secondary alcohols as a normal course of reaction, we have observed that such an ether formation takes place in the sterol series, without apparent formation of the expected unsaturated hydrocarbons.

Cholesterol and 22-dihydrostigmasterol were heated at an elevated temperature with about 5% of iodine, yielding di-cholesterol ether and di-22-dihydrostigmasterol ether, respectively, together with iodides of apparently the same type as Montignie[2] obtained on treating cholesterol at 100° with about 20% of iodine in benzene solution. The 22-dihydrostigmasterol used in this work was prepared from sulfate pulp tallol; the di-22-dihydrostigmasterol ether and dicholesterol ether obtained were identified, respectively, by their tetrabromides.

Acknowledgment.—Thanks are due to Professor Marston T. Bogert of Columbia University, New York City, for permitting us to study his notes on the catalytic action of iodine on organic compounds.

Experimental

Dicholesterol Ether.—The cholesterol used was obtained by the hydrolysis with alcoholic potassium hydroxide of cholesteryl acetate with subsequent recrystallization; m. p. 150–151° (cor.); $(\alpha)_D$ −38.8° (in chloroform).

Ten grams of cholesterol was heated for two hours at 170–180° with 5% of iodine, the iodine being added slowly during the first ten minutes of heating. After three extractions of the reaction mass with boiling ethanol, from which 2.3 g. of cholesterol was recovered, the residue was dissolved in hot ethyl acetate and the solution allowed to stand overnight whereupon a white crystalline material separated out. After four recrystallizations from ethyl acetate, the material melted constantly at 198–199° (cor.); $(\alpha)_D$ −52° (in chloroform); yield 0.8 g. or 8.5%.

Anal. Calcd. for $C_{54}H_{90}O$: C, 85.93; H, 12.02. Found: C, 85.65; H, 12.07.[3]

The mother liquor from the first ethyl acetate crystallization was evaporated to dryness leaving six grams of a red oil which would not crystallize. This oil contained iodine as shown by a sodium fusion, and apparently was identical with the oil obtained by Montignie[2] by the action of iodine on cholesterol in benzene solution.

Tetrabromide of Dicholesterol Ether.—0.20 gram of dicholesterol ether was dissolved in 15 ml. of chloroform and 0.5 g. of bromine dissolved in 10 ml. of chloroform added. The solution was allowed to stand for thirty minutes, the chloroform and excess bromine removed *in vacuo*, and the resulting solid recrystallized from ethyl acetate containing a little benzene, m. p. 178–179° (cor.).

Anal. Calcd. for $C_{54}H_{90}Br_4O$: C, 60.36; H, 8.44. Found: C, 60.60; H, 8.56.

22-Dihydrostigmasterol.—The procedure followed is an improvement of the method described by Hasselstrom[4] for the separation of fatty and resin acids of tallol.

1000 grams of crude sulfate pulp tallol, 1000 cc. of methanol and 100 cc. of concentrated sulfuric acid (sp. gr. 1.84), were refluxed for one hour, then cooled and shaken with two liters of 10% salt solution and 2000 cc. of benzene. The benzene layer was separated and shaken with an excess of 1% sodium hydroxide solution until the resin acids were removed. The benzene solution was washed with water, the benzene removed by distillation at ordinary temperature and the residue fractionated in vacuum; yield 438 g. of methyl ester of fatty acids of tallol, b. p. 192–210° at 6 mm. pressure, and 290 g. of residue.

256 grams of the above residue was saponified for one and one-half hours with 1300 cc. of a 10% potassium hydroxide solution. The alkaline solution was extracted three times with ether, the ether solution was washed with water and finally dried over anhydrous sodium sulfate. After evaporation of the ether, there was obtained a semi-solid residue which after two recrystallizations from ethanol melted at 123–128° (uncor.), yield 14.5 g. After several crystallizations from ethanol, the melting point of the 22-

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[1] Hibbert, THIS JOURNAL, **37**, 1748 (1915).

[2] Montignie, *Bull. soc. chim.*, **53**, 1412 (1933).

[3] All analyses by Mr. S. Gottlieb, Columbia University, New York City.

[4] Hasselstrom, *Paper Trade J.*, **83** [2], 60 (1926).

dihydrostigmasterol remained constant at 137.5–138.5° (cor.); (α)D −21.5 (in chloroform).

For further identification the above material was converted into the 3,5-dinitrobenzoate in pyridine solution in the usual manner. The 22-dihydrostigmasterol-3,5-dinitrobenzoate melted at 208.5–209.5° (cor.). This melting point agrees with the figures given by Bengtsson.[5]

The 22-dihydrostigmasterol, recovered from its *m*-dinitrobenzoate derivative, melted at 138–139°.

22-Dihydrostigmasterol Ether.—Four grams of 22-dihydrostigmasterol of melting point 136–137° (cor.), (α)D −21.5° (in chloroform), was heated for three hours at 160–170° with 5% of iodine, the iodine being added slowly over a period of ten minutes. The reaction mixture was then extracted three times with boiling alcohol from which 1.3 g. of 22-dihydrostigmasterol was recovered, being identified as the dinitrobenzoate, m. p. 211–212° (cor.), obtained in the usual way. The residue was dissolved in boiling ethyl acetate which deposited crystals of 22-dihydrostigmasterol ether on cooling; yield 0.18 g. or 4.7%. After three recrystallizations from ethyl acetate, the ether melted constantly at 182–183° (cor.), (α)D −23° (in chloroform).

Anal. Calcd. for $C_{58}H_{98}O$: C, 85.85; H, 12.17. Found: C, 85.70; H, 12.17.

The ethyl acetate mother liquor from the first extraction of the original reaction mass was evaporated to dryness leaving 2 g. of a red oil which could not be crystallized. This oil contained iodine, as shown by a sodium fusion, and apparently was similar to the oil obtained by Montignie[2] by the action of iodine on cholesterol.

Tetrabromide of 22-Dihydrostigmasterol Ether.—0.022 gram of the 22-dihydrostigmasterol ether was allowed to stand for thirty minutes in chloroform solution with 0.04 g. of bromine. After removal of the chloroform and excess bromine *in vacuo*, the resulting solid was recrystallized from ethyl acetate to a constant melting point of 164–166° (cor.).

Anal. Calcd. for $C_{58}H_{98}OBr_4$: C, 61.59; H, 8.73. Found: C, 61.73; H, 8.77.

Summary

Dehydration by iodine of cholesterol and 22-dihydrostigmasterol does not result in unsaturated hydrocarbons but yields instead dicholesterol ether and di-22-dihydrostigmasterol ether and as byproducts unidentified iodides.

The result thus confirms the theory by Hibbert in 1915, regarding the use of iodine as a dehydrating catalyst.

SAVANNAH, GEORGIA RECEIVED OCTOBER 10, 1940

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(5) Bengtsson, *Z. physiol. Chem.*, **237**, 46 (1935).

[CONTRIBUTION FROM FOREST PRODUCTS LABORATORY,[1] FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

The Reaction of Methyl Hypochlorite with Lignin[2]

BY ELWIN E. HARRIS AND LYLE J. LOFDAHL

Lignin reacts with chlorine in methanol solution to give a product containing a higher methoxyl content than would be expected if the methanol did not enter the reaction. Since some methyl hypochlorite will be formed by the action of chlorine on methanol, it was thought that methyl hypochlorite, which is known to add to ethylenic linkages,[3,4] had added to ethylenic linkages in lignin. If this reaction were quantitative, it might be used to determine the number of ethylenic linkages in lignin.

This paper covers a study of the reaction of lignin with methyl hypochlorite prepared by different methods.

Experimental

Chlorination of Lignin in Methanol.—Five grams of dried lignin was suspended in dried methanol, the mixture was cooled to and maintained at 10°; dried chlorine was introduced until no further change in the color of the resulting product was evident. During the reaction lignin, which was not previously dissolved, went into solution. The mixture was poured on crushed ice and washed with ice water until the wash water gave no test with starch-iodide paper. The product was dried in a vacuum at room temperature. Table I shows the composition of various lignins which have been treated with chlorine in methanol; yield approximately 6.5 g.

TABLE I

COMPOSITION OF LIGNIN CHLORINATED IN METHANOL AT 10°

Material	Before treatment	After treatment		
	Methoxyl, %	Methoxyl, %	Chlorine, %	Approx. ratio of groups MeO/Cl
Maple lignin[a]	20.6	16.6	33.4	8/14
Methanol maple lignin[b]	27.0	21.3	32.0	10/14
Spruce lignin[a]	17.0	16.8	34.1	8/14
Methanol spruce lignin[c]	20.4	17.1	33.8	8/14

[a] Prepared by sulfuric acid method. [b] The most soluble fraction of methanol lignin. [c] The less soluble fraction of methanol lignin.

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(1) Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

(2) Presented before the American Chemical Society, Detroit, Mich., Sept. 9–13, 1940.

(3) P. D. Bartlett and D. S. Tarbell, THIS JOURNAL, **58**, 466 (1936).

(4) E. L. Jackson, *ibid.*, **56**, 977 (1934).