TABLE II

Compound	Molecular formula	M. p., [a] °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
3,4-bis-(*m*-Methyl-*p*-hydroxyphenyl)-2,4-hexadiene	$C_{20}H_{22}O_2$	187–189	81.60	81.73	7.53	7.41
Diacetate	$C_{24}H_{26}O_4$	166–168	76.16	76.30	6.93	6.96
Dipropionate	$C_{26}H_{30}O_4$	138–139	76.82	76.78	7.44	7.56
Dibutyrate	$C_{28}H_{34}O_4$	123–124	77.39	77.40	7.89	8.05
Dipalmitate	$C_{52}H_{82}O_4$	69–70	80.98	80.70	10.72	10.66
Dibenzoate	$C_{34}H_{30}O_4$	207–208	81.25	81.26	6.02	6.06
Dimethocarbonate	$C_{24}H_{26}O_6$	171–172	70.22	70.20	6.38	6.61
Diethocarbonate	$C_{26}H_{30}O_6$	150–151	71.21	71.19	6.90	7.17
Diacid succinate	$C_{28}H_{30}O_8$	193	68.00	68.03	6.11	6.35
Di-*m'*-sulfobenzoate (disodium salt)	$C_{34}H_{28}O_{10}Na_2S_2$	[b]	S, 9.07	8.79	Na, 6.51	6.41
3,4-bis-(*m*-Methyl-*p*-hydroxyphenyl)-hexane	$C_{20}H_{26}O_2$	145	80.50	80.89	8.78	8.44
Diacetate	$C_{24}H_{30}O_4$	132	75.36	75.21	7.91	7.82
Dipropionate	$C_{26}H_{34}O_4$	115	76.06	76.09	8.35	8.28
Dibutyrate	$C_{28}H_{38}O_4$	100–101	76.67	77.32	8.73	8.76
Dipalmitate	$C_{52}H_{86}O_4$	68–69	80.56	80.67	11.18	10.77
Dibenzoate	$C_{34}H_{34}O_4$	199–200	80.60	80.54	6.61	6.56
Dimethocarbonate	$C_{24}H_{30}O_6$	148–149	69.54	69.34	7.30	7.24
Diethocarbonate	$C_{26}H_{34}O_6$	138	70.56	70.69	7.74	7.28
Diacid succinate	$C_{28}H_{34}O_8$	198–200	67.45	67.60	6.87	6.91
Di-*m'*-sulfobenzoate (disodium salt)	$C_{34}H_{32}O_{10}Na_2S_2$	[b]	S, 9.02	8.98	Na, 6.47	6.62

[a] All melting points are uncorrected. [b] Melts with decomposition at about 300°.

search, under whose guidance all determinations of estrogenic potency and toxicity on experimental animals have been conducted.

Summary

3,4-bis-(*m*-Methyl-*p*-hydroxyphenyl)-2,4-hexadiene, 3,4-bis-(*m*-methyl-*p*-hydroxyphenyl)-hexane and some of their organic esters have been prepared. Many of these compounds are active estrogens.

JERSEY CITY, N. J. RECEIVED AUGUST 11, 1947

[CONTRIBUTION FROM THE RESEARCH DIVISION, THE UPJOHN COMPANY]

Steroid Acids and their Transformation Products. I. Thiol Esters[1a]

BY ROBERT H. LEVIN, A. VERN MCINTOSH, JR., GEORGE B. SPERO, DOUGLAS E. RAYMAN AND ELIZABETH M. MEINZER

The use of Raney nickel catalyst for the desulfurization and reduction of sulfur compounds has recently been extended to the preparation of aldehydes[1] and alcohols[2] from carboxylic acids via the corresponding thiol compounds. Among the acids used by Jeger and co-workers[2a] were 3β-acetoxy-*etio-allo*-cholanic acid and 3β-acetoxy-Δ^5-*etio*-cholenic acid. For the broader use of the thiol esters as starting materials for the side chain degradation of steroids we have prepared a number of these previously unreported esters.

The steroid thiol esters were prepared by two methods:[3] (A) reaction of the acid chloride with an excess of mercaptan in pyridine; and (B) treatment of the acid chloride with a suspension of lead mercaptide[4] in ether. Generally speaking method A gave slightly better yields of crystalline thiol ester, but the products from B were easier to purify to constant m. p. Table I summarizes our data. Several of these compounds were chromatographed over alumina. It was found that the acetoxy thiol esters could be readily purified in this way. However, a number of the crystalline formoxy compounds became oily when put over the column, probably because of deformylation at the 3-position.

Ethyl 3α-hydroxy-12α-acetoxy-*nor*-thiolcholanate (III) was obtained from 3α-hydroxy-12α-acetoxy-*nor*-cholanic acid (II)[5] using method A. This involves the interesting preparation of a non-aromatic hydroxy acid chloride by the use of thi-

(1a) Presented before the Division of Medicinal Chemistry, 112th A. C. S. Meeting, New York, N. Y., September 17, 1947.

(1) M. L. Wolfrom and J. V. Karabinos, THIS JOURNAL, **68**, 1455 (1946).

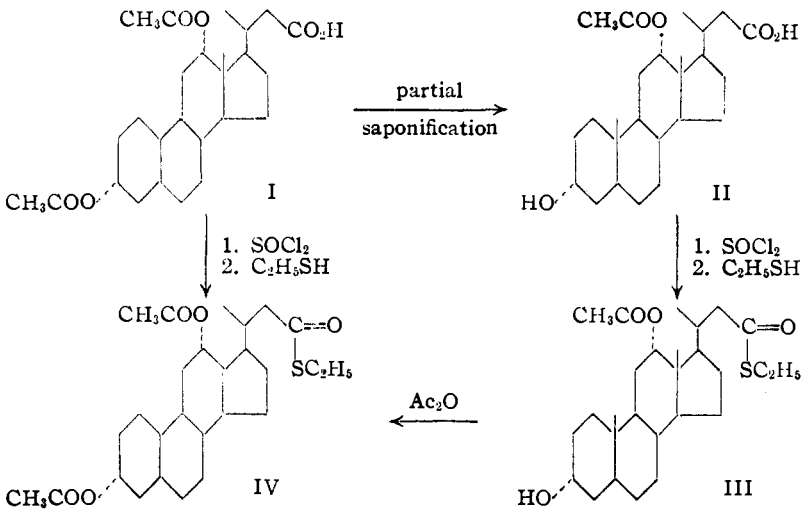
(2) (a) V. Prelog, J. Norymberski and O. Jeger, *Helv. Chim. Acta*, **28**, 360 (1946). (b) O. Jeger, J. Norymberski, S. Szpilfogel and V. Prelog, *ibid.*, **28**, 684 (1946). (c) L. Ruzicka, S. Szpilfogel and O. Jeger, *ibid.*, **29**, 1520 (1946).

(3) A. W. Ralston, E. W. Segebrecht and S. T. Bower, *J. Org. Chem.*, **4**, 502 (1939), have reviewed the literature.

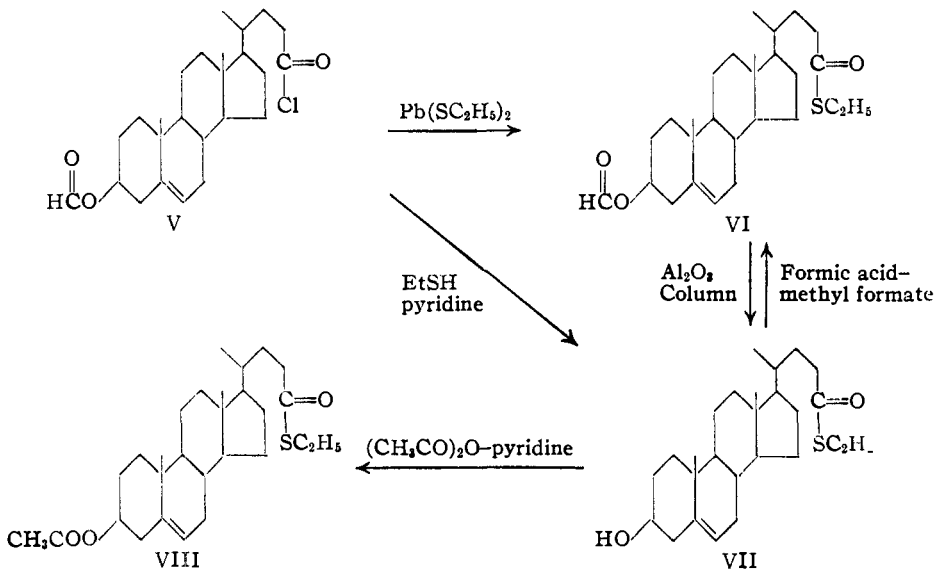
(4) P. Borgstrom, L. M. Ellis, Jr., and E. E. Reid, THIS JOURNAL **51**, 3649 (1929).

(5) Byron Riegel and A. Vern McIntosh, Jr., *ibid.*, **66**, 1102 (1944).

onyl chloride without protection of the hydroxyl group.[6] Compound III was isolated as an oil which did not crystallize after chromatography. However, on acetylation with acetic anhydride and pyridine, ethyl 3α,12α-diacetoxy-*nor*-thiol cholanate (IV) was formed and proved to be identical with the compound similarly prepared from 3α,12α-diacetoxy-*nor*-cholanic acid (I).



The lability of the 3-formoxy group is illustrated by reactions in the 3β-hydroxy-Δ⁵-cholenic acid series. When 3β-formoxy-Δ⁵-cholenyl chloride (V) was treated with lead ethyl mercaptide, ethyl



3β-formoxy-Δ⁵-thiolcholenate (VI), m. p. 80–82°, was formed. Esterification of the acid chloride (V) with ethyl mercaptan and pyridine produced a compound, m. p. 108.5–109.5°, which was characterized as 3β-hydroxy-Δ⁵-thiolcholenate (VII) by the reactions shown.

When 3β-formoxy-Δ⁵-thiolcholenate (VI) was chromatographed over alumina, the hydroxy compound was obtained as the main fraction. Reformylation of VII with formic acid and methyl formate produced VI. Acetylation of the hydroxy compound (VII) gave 3β-acetoxy-Δ⁵-thiolcholenate (VIII), identical with the compound produced by esterification of 3β-acetoxy-Δ⁵-cholenic acid by methods A or B. The acetoxy thiol ester (VIII) was recovered unchanged after passage over the alumina column. When 3β-hydroxy-Δ⁵-cholenic acid was treated with thionyl chloride and then ethyl mercaptan and pyridine, ethyl 3-chloro-Δ⁵-thiolcholenate was formed in good yield and readily purified over an alumina column.

The treatment of these steroid thiol esters with Raney nickel will be discussed in a future paper.

We wish to acknowledge the technical assistance of Jeane F. DeWitt in part of this work.

Experimental

Preparation of Thiol Esters.—An example of each method will be given in detail.

Method A. Benzyl 3α,12α - diacetoxy - *nor* - thiolcholanate.—To 1.5 g. (0.0033 mole) of 3α,12α-diacetoxy-*nor*-cholanic acid was added 6 ml. (9.8 g., 0.082 mole) of purified thionyl chloride.[7] The acid dissolved within five minutes and the solution was allowed to stand, with occasional swirling, at room temperature for one hour. Twenty milliliters of a 1:1 mixture of anhydrous benzene and ether was then added and the whole was evaporated to dryness *in vacuo* at 40°. This process of treatment with benzene–ether was repeated twice in order to ensure the complete removal of excess thionyl chloride.

To the resulting acid chloride dissolved in 10 ml. of anhydrous benzene was added 0.4 ml. (0.005 mole) of dry pyridine and 2 ml. (1.12 g., 0.009 mole) of benzyl mercaptan. A precipitate formed. After standing for

(6) One of us (A. V. M.) while working in the laboratory of Professor Byron Riegel, had previously prepared this acid chloride and converted it quantitatively with concentrated aqueous ammonia into 3α-hydroxy-12-α-acetoxy-nor-cholanic acid amide, m. p. 198–199°, [α]D +111.3° (in absolute ethanol). A Beilstein halogen test on the amide was negative. *Anal.* (By Dr. T. S. Ma) Calcd. for $C_{25}H_{41}O_4N$: N, 3.38. Found: N, 3.18.

(7) Fieser, "Experiments in Organic Chemistry," Part II, D. C. Heath and Co., New York, N. Y., 1941, p. 381.

TABLE I

THIOL ESTERS OF STEROID ACIDS

Compound	M. p., °C.[a]	Rotation[b] $[\alpha]_D$ deg.	Method of prepn.	Yield,[u] %	Molecular formula	Analyses,[p] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found
Ethyl 3β-hydroxy-Δ⁵-thiolcholenate	108.5-109.5	−38.5[c]	A[q]	71	$C_{26}H_{42}O_2S$	74.59	74.64	10.11	10.07	7.66	7.79
Ethyl 3β-formoxy-Δ⁵-thiolcholenate	81-82	−47.5[d]	B	63	$C_{27}H_{42}O_3S$	72.60	72.07[e]	9.48	9.61	7.18	7.01[e]
Ethyl 3β-acetoxy-Δ⁵-thiolcholenate	101.5-103.5	−40.9[e]	A	73	$C_{28}H_{44}O_3S$	72.99	72.92[e]	9.63	9.69	6.98	7.36[e]
			B	71							
Isopropyl 3β-acetoxy-Δ⁵-thiolcholenate	131-133	−40.4[f]	A	74	$C_{29}H_{46}O_3S$	73.37	73.39	9.77	9.55	6.75	6.81
t-Butyl 3β-acetoxy-Δ⁵-thiolcholenate	169.5-171	−39.8[g]	A	75	$C_{30}H_{48}O_3S$	73.72	74.07	9.90	9.96	6.56	6.71
n-Hexyl 3β-acetoxy-Δ⁵-thiolcholenate	77.5-79.5	−35.4[h]	A	66	$C_{34}H_{56}O_3S$	74.37	74.70[e]	10.14	10.00	6.20	6.60
Ethyl 3-chloro-Δ⁵-thiolcholenate	103.5-105	−30.4[i]	A	51	$C_{28}H_{41}OSCl$	71.44	71.51[k]	9.46	9.58	8.11	8.75[i]
Ethyl 3β-acetoxy-5-chloro-*nor*-thiolcholanate	165-168	.....	B	18	$C_{28}H_{42}O_3SCl$	...	....	...	...	6.45	6.32
Ethyl 3β-acetoxy-Δ⁵-*bisnor*-thiolcholenate	132-133	−38.0[l]	B	81	$C_{28}H_{40}O_3S$	72.18	72.50	9.32	9.13	7.41	7.44
Ethyl 3α,12α-diformoxy thiolcholanate[r]	111-112	+92.1[k]	A	62	$C_{28}H_{44}O_4S$	68.25	68.39	9.00	8.89	6.51	6.51
			B	53							
Ethyl 3α-formoxy thiolcholanate	81-82	+41.3[l]	A	82	$C_{27}H_{44}O_2S$	72.27	72.53	9.88	9.74	7.14	7.23
			B	73							
Ethyl 3α,12α-diacetoxy-*nor*-thiolcholanate	91-91.5	+96.0[m]	A	89	$C_{28}H_{44}O_4S$	68.76	69.07	9.15	9.47	6.33	6.37
			B	79							
Benzyl 3α,12α-diacetoxy-*nor*-thiolcholanate	154-156	+95.5[n]	A	73	$C_{34}H_{48}O_4S$	71.79	71.56	8.51	8.79	5.64	5.66
Phenyl 3α,12α-diacetoxy-*nor*-thiolcholanate	146-147	+99.7[o]	A	80	$C_{33}H_{46}O_4S$	71.44	71.30	8.36	8.04	5.78	5.64

[a] All m. p.'s corrected. [b] Rotations taken in chloroform with a 1 dm. tube. [c] 207.8 mg. in 20 ml., $\alpha^{24.5}D$ −0.40°. [d] 139.0 mg. in 10 ml., $\alpha^{25}D$ −0.66°. [e] 200.3 mg. in 10 ml., $\alpha^{25}D$ −0.82°. [f] 198.0 mg. in 10 ml., $\alpha^{24.5}D$ −0.80°. [g] 198.6 mg. in 10 ml., $\alpha^{25}D$ −0.79°. [h] 201.2 mg. in 10 ml., $\alpha^{25}D$ −0.71°. [i] 69.0 mg. in 10 ml., $\alpha^{25}D$ −0.21°. [j] 100.0 mg. in 10 ml., $\alpha^{25}D$ −0.38°. [k] 203.0 mg. in 10 ml., $\alpha^{25}D$ +1.87°. [l] 186.1 mg. in 10 ml., $\alpha^{25}D$ +0.77°. [m] 100 mg. in 10 ml., $\alpha^{25}D$ +0.96°. [n] 200 mg. in 10 ml., $\alpha^{25}D$ +1.91°. [o] 199.0 mg. in 10 m., $\alpha^{25}D$ +1.98°. [p] Analyses and rotations by the Upjohn microanalytical group unless otherwise indicated. [q] Starting with the 3-formoxy compound. [r] Desoxycholic acid is formulated as 3α,12α- according to the latest evidence (*Ann. Rev. Biochem.*, 15, 162 (1946)). [s] Analysis by Oakwold Laboratories, Alexandria, Virginia. [t] Chlorine analysis. [u] These over-all yields have been calculated from starting acid. Varying amounts of unreacted acid were recovered, which would raise actual yield.

twenty-four hours at room temperature the mixture was diluted with 15 ml. of water and 15 ml. of ether. The precipitate dissolved and the ether–benzene phase was separated. The aqueous portion was extracted with two 15-ml. portions of ether and the combined ether–benzene layer was washed with 30-ml. portions of water, 1% sodium hydroxide, 1% hydrochloric acid and finally with water again. The neutral fraction was dried over anhydrous sodium sulfate and the solvent evaporated to dryness *in vacuo*. The residual oil was crystallized from 50 ml. of 95% alcohol to give 1.38 g. (73%) of product, m. p. 147–152°. After three recrystallizations from alcohol 1.23 g. (65.5%) of benzyl thiol ester with a constant m. p. of 154–156° (cor.) was obtained.

Method B. **Ethyl 3α,12α-Diformoxythiolcholanate.**—The acid chloride (prepared from 4.5 g. (0.01 mole) of 3,12-diformoxydesoxycholic acid in the manner described under A) was dissolved in 30 ml. of anydrous ether and added to 1.8 g. (0.0055 mole) of lead ethyl mercaptide covered with 20 ml. of anhydrous ether. The mixture was allowed to stand at room temperature with occasional swirling. The yellow lead mercaptide was gradually replaced by white lead chloride. After twenty-four hours the solution was filtered and the precipitate washed with 50 ml. of ether. The combined ether filtrate was washed with 100 ml. of 1% sodium hydroxide and 300 ml. of water, then dried over anhydrous sodium sulfate and evaporated to dryness *in vacuo* on the steam-bath. The residual oil was dissolved in 50 ml. of hot alcohol and 10 ml. of water was added. On cooling under the water tap an oil separated, taking with it all the color in the solution. Crystallization then took place in the clear colorless solution, giving 2.2 g. of material. An additional 0.32 g. of crystals was obtained by crystallizing the oil from alcohol. The total yield was 2.6 g. (53% of the theoretical), m. p. 105–110°. After three recrystallizations the m. p. was constant at 111–112° (cor.).

Ethyl 3α-Hydroxy-12α-acetoxy-*nor*-thiolcholanate, (III).—A solution of 2.1 g. of 3α-hydroxy-12α-acetoxy-*nor*-cholanic acid[5] in 8 ml. of thionyl chloride was allowed to stand an hour at room temperature. After removal of the thionyl chloride, the 3α-hydroxy-12α-acetoxy-*nor*-cholanyl chloride was dissolved in 10 ml. of benzene by warming. The solution was cooled and 0.6 ml. of pyridine, then 1.9 ml. of ethyl mercaptan added. The reaction mixture was allowed to stand a day at room temperature, then diluted with 100 ml. of ether and washed successively with water, 1% sodium hydroxide, dilute hydrochloric acid and water. After drying of the ether and evaporation, the residue weighed 2.3 g. (96% of theoretical). Attempts to crystallize the thiol ester from various solvents failed. On chromatography over alumina[8] 81% of the recovered material was eluted in the main fraction, but could not be crystallized.

Ethyl 3α,12α-Diacetoxy-*nor*-thiolcholanate (IV).—A solution of 501 mg. of ethyl 3α-hydroxy-12α-acetoxy-*nor*-thiolcholanate in 10 ml. of acetic anhydride and 10 ml. of pyridine was heated on the steam-bath for one and one-half hours and the solvent was then distilled *in vacuo*. The residue was partly crystalline. It was chromatographed and the fractions eluted with benzene were combined and crystallized from alcohol and water, giving a yield of 120

(8) The alumina used in our chromatographic work was "Fisher Adsorption Alumina" obtained from the Fisher Scientific Company and used without further treatment.

mg., m. p. 85–87°. Recrystallization gave a product, m. p. 90–91°, identical with that obtained by esterifying 3α,12α-diacetoxy-*nor*-cholanic acid.

Ethyl 3β-Hydroxy-Δ⁵-thiolcholenate (VII).—The acid chloride prepared from 30.0 g. (0.075 mole) of 3 β-formoxy-Δ⁵-cholenic acid was dissolved in 200 ml. of benzene and treated with 37 ml. (0.50 mole) of ethyl mercaptan and 10 ml. of pyridine. After standing overnight at room temperature the reaction mixture was diluted with 250 ml. of water and extracted with 250 ml. of ether in portions. The ether layer was washed with 1% sodium hydroxide, 1% hydrochloric acid and water. After drying the ether was distilled and the residue crystallized from 300 ml. of alcohol and 50 ml. of water, giving 23 g. (72%) of ethyl 3β-hydroxy-Δ⁵-thiolcholenate, m. p. 98–100°. Several recrystallizations from hexane–benzene raised the m. p. to 108.5–109.5°.

Deformylation of Ethyl 3β-Formoxy-Δ⁵-thiolcholenate (VI) over Alumina.—Two hundred mg. of ethyl 3β-formoxy-Δ⁵-thiolcholenate, m. p. 78.5–81.5°, was dissolved in 8 ml. of benzene and passed through a 10-g. alumina[8] column. The column was eluted, using the free flow method, with 8-cc. portions of benzene, benzene + 0.4% methanol, benzene + 1% methanol, benzene + 2% methanol, benzene + 4% methanol, benzene + 8% methanol and methanol. The benzene eluate contained 35 mg.% of crystalline material of m. p. 78–82° (starting material). The methanol fraction contained 135 mg. of crystalline material of m. p. 95–100°. After several recrystallizations from 3A alcohol[9] and from hexane (Skellysolve "B") the m. p. became constant at 105–108°. An admixture with a sample of ethyl 3β-hydroxy-Δ⁵-thiolcholenate, m. p. 108.5–110°, melted at 108–110°. An admixture with starting material melted at 63–100°.

Formylation of Ethyl 3β-Hydroxy-Δ⁵-thiolcholenate (VII).—A mixture of 710 mg. of ethyl 3β-hydroxy-Δ⁵-thiolcholenate, m. p. 108–109.5°, 25 ml. of formic acid (87%) and 12.5 ml. of methyl formate was heated under reflux on the steam-bath for two and one-half hours; then the reaction mixture was evaporated *in vacuo* and the residue dissolved in ether. The ether solution was washed with 0.5% sodium hydroxide, then with water, and was dried over sodium sulfate. Evaporation *in vacuo* gave 452 mg. of ethyl 3β-formoxy-Δ⁵-thiolcholenate (VI), m. p. 78–79.5.° Several recrystallizations from methanol, water and from alcohol brought the m. p. up to 80–82°. A mixture m. p. with authentic formoxy ester was not depressed.

Acetylation of Ethyl 3β-Hydroxy-Δ⁵-thiolcholenate.—Three hundred mg. of ethyl 3β-hydroxy-Δ⁵-thiolcholenate, m. p. 108–109.5°, was mixed with 5 ml. of acetic anhydride and 5 ml. of pyridine. After refluxing for two and one-half hours the mixture was evaporated to dryness on the steam-bath *in vacuo*. The residue was taken up in alcohol. The alcohol solution was diluted with water and extracted with ether. After washing with 1% sodium hydroxide and water the ether solution was dried over sodium sulfate and evaporated to dryness. The residue was crystallized from 3A alcohol to yield 290 mg. of ethyl 3β-acetoxy-Δ⁵-thiolcholenate (VIII), m. p. 101–104°. After several recrystallizations, the melting point became constant at 101–102.5°. An admixture with a sample of authentic ethyl 3β-acetoxy-Δ⁵-thiolcholenate, m. p. 101–103°, showed no melting point depression. An admixture with starting material melted at 79–82°.

Hydrolysis of 300 mg. of the thiol ester (VIII) with 1 g. of sodium hydroxide in 2.5 ml. of water and 15 ml. of alcohol gave an almost quantitative yield of 3β-hydroxy-Δ⁵-cholenic acid.

(9) 3A alcohol is commercial 95% alcohol denatured by the addition of 5% methanol.

Summary

A number of thiol esters of steroid acids have been prepared and characterized using ethyl, isopropyl, *t*-butyl, *n*-hexyl, benzyl and phenyl mercaptans; and the following acids: 3β-hydroxy-Δ⁵-cholenic, 3β-hydroxy-5-chloro-*nor*-cholenic, 3-β-hydroxy-Δ⁵-*bisnor*-cholenic, desoxycholic, *nor*-desoxycholic and lithocholic.

KALAMAZOO, MICHIGAN RECEIVED SEPTEMBER 2, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Chemical Interactions of Amino Compounds and Sugars. III.[1] The Conversion of D-Glucose to 5-(Hydroxymethyl)-2-furaldehyde[2]

BY M. L. WOLFROM, R. D. SCHUETZ[3] AND LIEBE F. CAVALIERI[3]

It is well established that D-glucose and other hexoses are converted to 5-(hydroxymethyl)-2-furaldehyde on heating with acids.[4] Scallet and Gardner[5] have previously demonstrated that 5-(hydroxymethyl)-2-furaldehyde is formed from D-glucose on refluxing in water alone.

The purpose of the work herein reported was to determine whether ultraviolet spectroscopy would give any insight into the mechanism and intermediates in the conversion of D-glucose to 5-(hydroxymethyl)-2-furaldehyde. Hydrochloric acid was the catalyst chosen for these studies.

When an aqueous solution (initial *p*H 6.5) of D-glucose was prepared from triply distilled water and refluxed, a series of changes could be detected in the ultraviolet absorption spectrum; these are shown in Figs. 1 and 2. After three and one-half hours (curve 1, Fig. 1) a distinct band with a maximum at 228 mμ was evident. After eight hours of

(1) Previous communication in this series: M. L. Wolfrom, L. F. Cavalieri and Doris K. Cavalieri, THIS JOURNAL, **69**, 2411 (1947).

(2) The subject matter of this paper has been undertaken in coöperation with the Committee on Food Research of the Quartermaster Food and Container Institute for the Armed Forces under a contract (W11-009-Q-M-70183 and W44-109-QM-1027) with The Ohio State University Research Foundation. The opinions or conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or indorsement of the War Department.

(3) Research Associate of The Ohio State University Research Foundation, Projects 278 and 238, respectively.

(4) G. Düll, *Chem. Ztg.*, **19**, 216 (1895); J. Kiermayer, *ibid.*, 1003; W. Alberda van Ekenstein and J. J. Blanksma, *Chem. Weekblad*, **6**, 217 (1909); *Ber.*, **43**, 2355 (1910); W. N. Haworth and W. G. N. Jones, *J. Chem. Soc.*, 667 (1944); B. Singh, G. R. Dean and S. M. Cantor, THIS JOURNAL, **70**, 517 (1948).

(5) B. L. Scallet with J. H. Gardner, THIS JOURNAL, **67**, 1934 (1945).