addition of Norite, gave 6.5 g. (88%) of the phenol, m. p. 177.5–179.5°, which produced no color with ferric chloride. *Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.54; H, 7.53. Found: C, 80.56, 80.54; H, 7.41, 7.20.

1,2-bis-(*p*-Acetoxyphenyl)-cyclohexane, m. p. 114.8–116.2° (micro), was prepared and purified just as described for the corresponding unsaturated compounds. *Anal.* Calcd. for $C_{22}H_{24}O_4$: C, 74.96; H, 6.88. Found: C, 74.88, 75.00; H, 6.81, 6.75.

Physiological Activity.—On subcutaneous injection into rats[22] of an oil solution, bis-(*p*-hydroxyphenyl)-cyclohexene, Ib, showed 300 I. U./mg.; bis-(*p*-hydroxyphenyl)-cyclohexene, IIb, 150 I. U./mg.; and 1,2-bis-(*p*-hydroxyphenyl)-cyclohexane, 200 I. U./mg. of estrogenic activity.

(22) We are grateful to Parke Davis and Company, Detroit, Michigan, for testing these compounds.

Summary

1,2-bis-(*p*-Hydroxyphenyl)-cyclohexane and two intermediate cyclohexenes together with their methyl and acetyl derivatives have been prepared. The phenols have moderate estrogenic activity. The hindrance to ring closure of 1,6-diarylhexamethylene derivatives has been indicated and the formation of a polypinacol discussed.

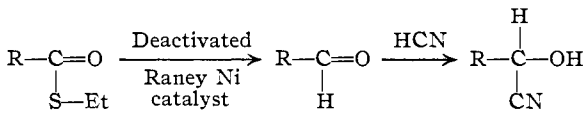
KNOXVILLE, TENNESSEE RECEIVED APRIL 4, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UPJOHN COMPANY]

Steroid Acids and their Transformation Products. VI. Some New Aldehydes and Their Derived Cyanohydrins

BY A. VERN MCINTOSH, ANNA MAE SEARCY, ELIZABETH M. MEINZER AND ROBERT H. LEVIN

Preparation of steroid aldehydes by the desulfurization of thiol esters of 3β-hydroxy-5-cholenic acid, 3β-hydroxybisnor-5-cholenic acid and desoxycholic acid with acetone deactivated W-1[1] Raney nickel catalyst has been reported in previous papers of this series.[2] We have now prepared aldehydes starting with the thiol esters of nor-desoxycholic acid, lithocholic acid, 12α-hydroxycholanic acid, and 3α-hydroxy-11-cholenic acid, in yields of 39 to 78%. These aldehydes have been converted to cyanohydrins in excellent yields, completing the sequence of reactions



Ethyl 3α,12α-diacetoxynorthiolcholanate has been used as a model for the study of variations in the desulfurization procedure. The information gained from the experiments on the desulfurization of this compound is summarized very briefly below, excluding data which have been previously reported in this series.

A number of attempts were made to prepare 3α,12α-diacetoxynorcholan-23-al from the thiol ester without deactivation of the nickel. It was found that five parts of W-4 Raney nickel, or twenty parts of W-1 or commercial active Raney nickel, would reduce the thiol ester in alcohol quantitatively to 3α,12α-diacetoxynorcholan-23-ol at either room temperature or at reflux. When ten parts of W-1 Raney catalyst was heated with one part of ester in alcohol solution, a mixture of 3α,12α-diacetoxynorcholan-23-ol and ethyl 3α,12α-diacetoxynorthiolcholanate was obtained, besides about a 1% yield of aldehyde isolated as the semicarbazone.

Next, an experiment was devised to analyze the products obtained by use of Raney nickel which had been deactivated by reaction with the thiol ester. A mixture of Raney nickel and Celite filter-aid was placed in a chromatogram column and a solution of the thiol ester was filtered through and collected in portions. When 10 g. of W-4 Raney nickel was used, 2.1 g. of very pure 3α,12α-diacetoxynorcholan-23-ol was obtained in the first several fractions, then alcohol–ester mixtures followed. The time of contact of the solution in the column was about a minute, indicating a very rapid reaction at room temperature. Using W-1 Raney nickel, a little less than half the yield of alcohol given by the W-4 nickel was obtained, followed by some gummy mixtures, then the pure thiol ester. A very small amount of aldehyde semicarbazone was obtained on working up the mixtures, besides both alcohol and ester.

Without deactivation of the Raney nickel before the reaction with the thiol ester not more than 1% of aldehyde was obtained, isolated as the semicarbazone. Pretreatment of the Raney nickel in acetone under reflux proved by far the most suitable of the methods of deactivation tried.[2] When deactivated with acetone W-1 and W-4 Raney nickels, prepared in this Laboratory, and a commercial active Raney nickel[3] were used successfully as desulfurizing agents. A commercial pelleted Raney catalyst was found to be entirely inactive. Within experimental error the yields obtained when the commercial active Raney nickel was used were the same as were obtained with the W-1 catalyst. The W-4 catalyst gave consistently lower yields of aldehyde although different deactivation and reaction times were tried. However, for reduction of thiol esters to alcohols the W-4 nickel was best, giving nearly quantitative

(1) Adkins and Pavlic, THIS JOURNAL, **69**, 3039 (1947).

(2) (a) Spero, McIntosh and Levin, *ibid.*, **70**, 1907 (1948); (b) McIntosh, Meinzer and Levin, *ibid.*, **70**, 2955 (1948).

(3) Raney Active Nickel Catalyst, in water, obtained from the Gilman Paint and Varnish Co., Chattanooga, Tenn. This catalyst is analogous to W-1 or W-2 catalysts in activity.

TABLE I

THIOL ESTERS OF STEROID ACIDS

Compound, ethyl	M. p., °C.[b]	Rotation[c] $[\alpha]_D$ deg.	Yield, %	Molecular formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found
3α-Acetoxythiolcholanate	97–102	+36[d]	76	$C_{28}H_{46}O_3S$	72.68	72.39	10.02	9.79	6.93	7.05
3α-Hydroxythiolcholanate[a]	81–82	+20[e]	..[a]	$C_{26}H_{44}O_2S$	74.23	74.04	10.54	10.08	7.62	7.22
3α-Acetoxy-11-thiolcholenate	81–82.5	...	74	$C_{28}H_{44}O_3S$	72.99	73.05	9.63	9.39	6.98	7.09
12α-Acetoxythiolcholanate	.....[h]	+66[f]	65	$C_{28}H_{46}O_3S$	72.68	72.81	10.02	9.78	6.93	7.04
12α-Formoxythiolcholanate	.....[h]	+69[g]	88	$C_{27}H_{44}O_3S$	72.27	72.15	9.89	9.74	7.15	7.45
3β-Methoxybisnor-5-thiolcholenate	86–90	...	40	$C_{25}H_{40}O_2S$	74.20	74.11	9.96	9.65	7.92	8.18

[a] Prepared in 80% yield by passing ethyl 3α-formoxythiolcholanate over alumina. [b] All melting points taken on the Fisher–Johns block and corrected. [c] Rotations taken in chloroform with a 1-dm. tube. [d] 42.96 mg. in 10 ml. α_D +0.156°. [e] 106.6 mg. in 10 ml., α_D +0.21°. [f] 80.2 mg. in 10 ml., α_D +0.532°. [g] 69.4 mg. in 10 ml., α_D +0.480°. [h] Not crystalline.

TABLE II

STEROID ALDEHYDES AND DERIVATIVES

Compound	M. p., °C.[a]	Rotation[b] $[\alpha]_D$ deg.	Yield, %	Molecular formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
3α-Acetoxycholan-24-al	113.5–115.5	+42[c]	39	$C_{26}H_{42}O_3$	77.56	77.34	10.52	10.20
2,4-Dinitrophenylhydrazone	201.5–202.5			$C_{32}H_{46}O_6N_4$[k]	65.95	65.88	7.96	7.73
3α-Formoxycholan-24-al	98–100	+47[d]	78	$C_{25}H_{40}O_3$	77.27	77.17	10.38	10.60
2,4-Dinitrophenylhydrazone	162.5–164.5			$C_{31}H_{44}O_6N_4$[l]	65.47	65.82	7.80	7.65
3α-Hydroxycholan-24-al	146–148	+20[e]	[i]	$C_{24}H_{40}O_2$	79.94	80.07	11.18	10.98
Semicarbazone	226–229			$C_{25}H_{43}O_2N_3$[m]	71.90	71.70	10.38	9.94
12α-Acetoxycholan-24-al	112–115	+64[f]	60	$C_{26}H_{42}O_3$	77.56	77.62	10.52	10.46
3α,12α-Diacetoxynorcholan-23-al	128–131	+88[g]	69	$C_{27}H_{42}O_5$	72.61	72.49	9.48	9.37
Semicarbazone	237–240			$C_{28}H_{45}O_5N_3$[n]	66.77	66.65	9.01	8.91
3α-Acetoxy-11-cholen-24-al	115–117.5	+49[h]	53	$C_{26}H_{44}O_3$	77.95	77.75	10.07	10.21
3α-Formoxy-5-cholen-24-al	130–134	−76[i]	78	$C_{25}H_{38}O_3$	77.70	77.60	9.91	9.97

[a] All melting points taken on the Fisher–Johns block and corrected. [b] Rotations taken in chloroform with a 1-dm. tube. [c] 112.51 mg. in 10 ml., α_D 0.473°. [d] 124.82 mg. in 10 ml., α_D +0.59°. [e] 82.54 mg. in 10 ml., α_D +0.161°. [f] 205.8 mg. in 10 ml., α_D +1.326°. [g] 156.27 mg. in 10 ml., α_D +1.38°. [h] 100.3 mg. in 10 ml., α_D +0.486°. [i] 66.1 mg. in 10 ml., α_D −0.50°. [j] Prepared from 3α-formoxycholan-24-al by hydrolysis in 2% methanolic potassium hydroxide for three hours at room temperature; yield 47%. [k] Calcd.: N, 9.62. Found: N, 9.55. [l] Calcd.: N, 9.85. Found: N, 9.7. [m] Calcd.: N, 10.06. Found: N, 9.81. [n] Calcd.: N, 8.34. Found: N, 8.53.

TABLE III

CYANOHYDRINS

Aldehyde	M. p., °C.[a]	Rotation[b] $[\alpha]_D$ deg.	Yield, %	Molecular formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
3α-Acetoxycholan-24-al	154.5–156	...	89	$C_{27}H_{43}O_3N$	75.48	75.47	10.09	10.05	3.26	3.39
3α-Hydroxycholan-24-al	146–149	+28[c]	95	$C_{25}H_{41}O_2N$	77.47	77.86	10.66	10.48	3.61	3.46
12α-Acetoxycholan-24-al	153–156	+71[d]	98	$C_{27}H_{43}O_3N$	75.48	75.56	10.09	9.96	3.26	3.38
3α,12α-Diacetoxynorcholan-23-al	164–165.5	+99[e]	97	$C_{28}H_{43}O_5N$	71.00	71.10	9.15	8.93	2.96	2.92
3β-Acetoxy-5-cholen-24-al	154–157	−55[f]	100	$C_{27}H_{41}O_3N$	75.83	75.97	9.67	9.58	3.28	3.11
3β-Formoxy-5-cholen-24-al	137–143	−53[g]	82	$C_{26}H_{39}O_3N$	75.50	75.43	9.50	9.24	3.39	3.57
3α-Acetoxy-11-cholen-24-al	162–163.5	+45[h]	100	$C_{27}H_{41}O_3N$	75.83	75.64	9.67	9.50	3.28	3.42

[a] All melting points taken on the Fisher–Johns block and corrected. [b] Rotations taken in chloroform in a 1-dm. tube. [c] 122.0 mg. in 10 ml., α_D +0.344°. [d] 89.8 mg. in 10 ml., α_D +0.641°. [e] 100.0 mg. in 10 ml., α_D +0.988°. [f] 158.47 mg. in 10 ml., α_D −0.872°. [g] 100.0 mg. in 10 ml., α_D −0.529°. [h] 89.3 mg. in 10 ml., α_D +0.404°.

yields in a few minutes at room temperature with alcohol or ether as the solvent.

In several less thorough series of experiments with thiol esters of other steroid acids the results were similar to those outlined above.

Commercial active Raney nickel[3] has been used in the desulfurization of most of the thiol esters reported in this series of articles,[2] in every case successfully. The conditions were those reported for ethyl 3α,12α-diacetoxynorthiolcholanate in the experimental section of this paper. Variation of the amount of catalyst used by about 20% in some cases slightly improved the yield. When the thiol ester is not sufficiently soluble in aqueous acetone[4] it may be added in dry acetone or dioxane.

Two examples of the separation of the aldehyde

(4) The water is not necessary for the reaction, but makes the reaction mixture easier to work up.

from the by-products of the reaction through formation of the sodium bisulfite complex[5] are given in the experimental section. Bisulfites of some steroid aldehydes, especially those containing free hydroxyl groups, tend to be both water soluble and relatively difficult to decompose with aqueous sodium carbonate. This is the case with 3α,12α-diacetoxynorcholan-23-al. When the complex is highly insoluble, *e. g.*, with 3α-formoxycholan-24-al, the aldehyde is more easily worked up.

The steroid aldehydes not previously reported are listed in Table II. Semicarbazones and 2,4-dinitrophenylhydrazones are included in the same table.

Cyanohydrins were prepared from the aldehydes described in this paper, as well as from several aldehydes reported previously.[2] These are listed in Table III. Three methods of preparation were investigated. In one the aldehyde bisulfite was suspended in excess 1.25% aqueous potassium cyanide and heated on the steam-bath five to ten minutes, then stirred for an hour and extracted with ether to obtain the product.[6] In a second the aldehyde was dissolved in a mixture of alcohol and acetic acid and treated with excess potassium cyanide at 0°.[7] The first method gave a good yield of cyanohydrin from 3β-acetoxy-5-cholen-24-al, but did not work well with 3α,12α-diacetoxynorcholan-23-al. Using the second method these results were reversed. In a third variation the aldehyde was dissolved in a small amount of dioxane and stirred with 40% aqueous sodium bisulfite, then excess solid potassium cyanide was added and the mixture was heated five minutes on the steam-bath, allowed to cool, and poured into water. This method gave good results with all the steroid aldehydes used, and is described in the experimental section.

3α,12α-Diacetoxynorcholan-23-al cyanohydrin and 3β-acetoxy-5-cholen-24-al cyanohydrin were found to be stable when chromatographed over alumina. This contrasts with the behavior of 20-ketosteroid cyanohydrins which Sarett[1] found to be dehydrated or split by passage over alumina columns.

A number of new steroid thiol esters prepared in the course of this research are listed in Table I.

Experimental[8]

Thiol Esters.—Six new thiol esters are listed in Table I. These were prepared by treating the corresponding steroid acid chlorides with ethyl mercaptan in the presence of pyridine,[9] with the exception of ethyl 3α-hydroxythiolcholanate which was obtained by passing ethyl 3α-formoxythiolcholanate[9] over Fisher adsorption alumina.[9,10]

12α-Formoxy- and 12α-acetoxycholanic acids, used as starting materials, have not been reported previously. These were prepared from 12α-hydroxycholanic acid[11] by formylation following Moffett's procedure[12] and by acetylation in acetic anhydride–acetic acid mixture using anhydrous perchloric acid as a catalyst.[13]

12α-Formoxycholanic acid was crystallized from 1-1 dioxane–formic acid mixture, m. p. 145–147°; $[\alpha]^{21}D$ +75° (203.7 mg. in 10 ml. of chloroform, *l*, 1 dm.; αD +1.53).

Anal. Calcd. for $C_{25}H_{40}O_4$: C, 74.22; H, 9.97. Found: C, 73.91; H, 10.08.

12α-Acetoxycholanic acid melted at 214–215° after crystallization from glacial acetic acid; $[\alpha]^{25}D$ + 71° (233.9 mg. in 10 ml. of chloroform, *l* 1 dm.; αD + 1.67°).

Anal. Calcd. for $C_{26}H_{42}O_4$: C, 74.60; H, 10.12. Found: C, 74.70; H, 10.16.

The Desulfurization Reaction.—The aldehydes prepared by treatment of steroid thiol esters with deactivated Raney nickel are listed in Table II. Two examples of the method are given below.

3α,12α-Diacetoxynorcholan-23-al.—A suspension of 30 g. of commercial active Raney nickel (washed alkali free) in 90 ml. of acetone was stirred and heated under reflux an hour, then 30 ml. of water was added, followed by a solution of 3.0 g. of ethyl 3α,12α-diacetoxynorthiolcholanate in 60 ml. of acetone. The reaction mixture was heated an hour, then was filtered hot. The Raney nickel was washed with hot acetone and the filtrate and washings concentrated *in vacuo* till a heavy precipitate formed. The precipitate (2.67 g.) was dissolved in a mixture of 45 ml. of ether and 40 ml. of methanol, then 100 ml. of 40% aqueous sodium bisulfite was added and the mixture was shaken for ten minutes. On standing three layers separated (some water may be required). The aldehyde bisulfite complex was richest in the middle layer. The two lower layers combined were brought to *p*H 10 by addition of saturated aqueous sodium carbonate and extracted with ether to give 1.76 g. of crystalline aldehyde. The ether layer, extracted a second time with bisulfite, gave 0.36 g. of aldehyde. A residue of 0.61 g. remained after evaporation of the ether. The crude aldehyde was crystallized from aqueous acetic acid to give 1.82 g. (69%) of 3α,12α-diacetoxynorcholan-23-al, m. p. 115–121°. After crystallization from Skellysolve "B" the aldehyde melted at 128–131°.

3α-Formoxycholan-24-al.—Desulfurization of 2.7 g. of ethyl 3α-formoxythiolcholanate with 30 g. of Raney nickel was carried out as described above. The acetone solution of the aldehyde was concentrated *in vacuo* to less than 30 ml. An oil separated. Water was added and the mixture was extracted with ether. The ether solution was concentrated to 30 ml., then 30 ml. of methanol and 75 ml. of saturated aqueous sodium bisulfite were added and the mixture was shaken ten minutes. A white precipitate formed, and was separated by centrifuging. The precipitate was shaken with ether and ice water and again centrifuged, then was suspended in 10% aqueous sodium carbonate under ether and agitated thirty minutes with a stream of nitrogen. The ether layer was washed with water, dried, and evaporated under nitrogen to give 1.50 g. (62%) of 3α-formoxycholan-24-al, m. p. 95–98°. After crystallization from Skellysolve "B," then aqueous acetic acid, the m. p. was 98–100°.

3α,12α-Diacetoxynorcholan-23-ol and Derivatives.—In the desulfurization of ethyl 3α,12α-diacetoxynorthiolcholanate the material remaining in the ether solution after extraction with aqueous sodium bisulfite was dissolved in benzene and passed over Fisher adsorption alumina. The fraction eluted with benzene consisted of ethyl 3α,12α-diacetoxynorthiolcholanate; a second fraction eluted with 2% methanol in benzene consisted of 3α,12α-diacetoxynorcholan-23-ol. When the yield of alde-

(5) Centolella, Heyl and Herr, THIS JOURNAL, **70**, 2953 (1948).

(6) Heyl and Herr, personal communication, have previously prepared the cyanohydrin of 3β-acetoxybisnor-5-cholen-22-al by this method in high yield.

(7) Sarett, THIS JOURNAL, **70**, 1454 (1948).

(8) All m. p.'s taken on the Fisher–Johns block and corrected. Analyses and rotations by the Upjohn microanalytical and physics groups.

(9) Levin, McIntosh, Spero, Rayman and Meinzer, THIS JOURNAL, **70**, 511 (1948).

(10) Levin, McIntosh and Spero, *Science*, **108**, 82 (1948).

(11) Wieland and Schlichting, *Z. physiol. Chem.*, **150**, 267 (1925).

(12) Hoehn and Moffett, THIS JOURNAL, **67**, 740 (1945).

(13) Whitman and Schwenk, *ibid.*, **68**, 1865 (1946).

hyde was highest the proportion of the two by-products was roughly equal, but even when the Raney nickel–ester ratios were varied from 5-1 to 20-1 both products were present.

The identity of the alcohol was checked by preparation of 3α,12α-diacetoxynorcholan-23-ol by direct reduction of ethyl 3α,12α-diacetoxynorthiolcholanate with W-4 Raney nickel in alcohol at room temperature.[2] The two alcohols were identical. The compound was crystallized both from aqueous alcohol and chloroform–hexane mixture; m. p. 148.5–151°; $[\alpha]^{26}D$ + 110° (100.0 mg. in 10 ml. of $CHCl_3$, *l* 1 dm.; αD +1.10°).

Anal. Calcd. for $C_{27}H_{44}O_5$: C, 72.30; H, 9.89. Found: C, 72.49; H, 9.95.

3α,12α-Diacetoxynorcholan-23-ol refluxed for two hours in 1-1 pyridine-acetic anhydride gave a 70% yield of 3α,-12α,23-triacetoxynorcholane, m. p. 108–110° from aqueous acetic acid.

Anal. Calcd. for $C_{29}H_{46}O_6$: C, 70.98; H, 9.45. Found: C, 71.05; H, 9.38.

3α,12α-Diacetoxynorcholan-23-ol was allowed to stand seven hours in a 5% solution of potassium hydroxide in 80% alcohol at room temperature. The product was precipitated by the addition of water, chromatographed and crystallized from aqueous alcohol to give a 70% yield of 3α,23-dihydroxy-12-acetoxynorcholane, m. p. 181.5–182°.

Anal. Calcd. for $C_{25}H_{42}O_4$: C, 73.85; H, 10.41. Found: C, 73.89; H, 10.32.

Hydrolysis of 3α,12α-diacetoxynorcholan-23-ol in 10% alcoholic potassium hydroxide under reflux for three hours gave 83% of 3α,12α,23-trihydroxynorcholane, m. p. 194–200°. On recrystallization from ethanol the compound melted at 209.5–211°.

Anal. Calcd. for $C_{23}H_{40}O_3$: C, 75.77; H, 11.06. Found: C, 75.67; H, 10.96.

The dinitrophenylhydrazones and semicarbazones reported in Table II were prepared as described in previous papers in this series.[2]

Cyanohydrins.—The preparation of the steroid aldehyde cyanohydrins listed in Table III is illustrated by the method used for **3α-acetoxycholan-24-al cyanohydrin.** A mixture of 0.500 g. of 3α-acetoxycholan-24-al, 1.5 ml. of dioxane, and 3 ml. of saturated aqueous sodium bisulfite was stirred at room temperature for thirty minutes, then 0.5 g. of solid potassium cyanide was added and the mixture was heated for five minutes on the steam-bath, then allowed to cool to room temperature for thirty minutes, with occasional stirring. The reaction mixture was poured into 50 ml. of water giving a gummy precipitate. This was crystallized from aqueous acetic acid to give 0.476 g. (85%) of crystals melting at 148–152°. After several crystallizations from aqueous acetic acid the m. p. was 154.5–156°.

Summary

3α-Hydroxycholan-24-al, its 3-acetyl and 3-formyl derivatives, 12α-acetoxycholan-24-al, 3α,-12α-diacetoxynorcholan-23-al, 3α-acetoxy-11-cholen-24-al, and 3β-formoxy-5-cholen-24-al have been prepared by the desulfurization of the corresponding thiol esters with acetone deactivated Raney nickel catalyst.

The cyanohydrins have been obtained by treating these aldehydes with sodium bisulfite and potassium cyanide in dioxane–water.

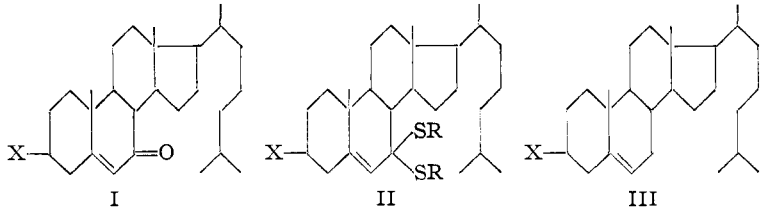
KALAMAZOO, MICHIGAN RECEIVED APRIL 28, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Addition of Mercaptans to Unsaturated Steroid Ketones

BY JACK W. RALLS,[1] R. M. DODSON[2] AND BYRON RIEGEL

Cholesterol that has been labeled with isotopic carbon in the nucleus would be useful for many biological investigations. A method for the introduction of the carbon isotopes into ring B of cholesterol (III-C) involves the intermediate 7-ketocholesterol (I-C). The final step would be the reduction of the 7-keto group to give the labelled cholesterol. This critical step was studied in some detail. Classical methods of reduction require strongly acid or basic conditions, which will cause the elimination of the group at the 3-position[3] with the formation of a second conjugated ethylenic linkage. Reduction of a carbonyl group without the simultaneous reduction of the α,β-unsaturation limits the methods that may be employed. The Wolff–Kishner reduction is unsatisfactory.



I II III

X A AcO—
B Cl—
C HO—

Recently Hauptmann[4] has prepared 4-cholestene from cholestenone by desulfurizing the dibenzyl mercaptole derivative. This method has also been used for the reduction of saturated steroid ketones[5] where the carbonyl group occupies the 3, 7, 12 and 17 positions.

The mercaptoles of 7-ketocholesteryl acetate (II-A) do not form readily. The best yield (40%) was obtained using ethanedithiol in

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(3) (a) H. Stavely and W. Bergmann, *J. Org. Chem.*, **1**, 567 (1936); (b) R. Marker, O. Kamm, G. Fleming, A. Popkin and E. Wittle, THIS JOURNAL, **59**, 619 (1937); (c) O. Wintersteiner and S. Bergstrom, *J. Biol. Chem.*, **137**, 785 (1941).

(4) H. Hauptmann, THIS JOURNAL, **69**, 562 (1947).

(5) (a) S. Bernstein and L. Dorfmann, *ibid.*, **68**, 1152 (1946); (b) L. Norymberska, J. Norymberski and A. Olade, *ibid.*, **70**, 1256 (1948); (c) R. H. Levin and J. L. Thompson, *ibid.*, **70**, 3140 (1948).