[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE AND THE PARKE, DAVIS AND COMPANY RESEARCH LABORATORY]

Sterols. XXX. The Structure of Pregnanetriol-B

BY RUSSELL E. MARKER, OLIVER KAMM, EUGENE L. WITTLE, THOMAS S. OAKWOOD AND ELMER J. LAWSON

A compound which appeared to be related to pregnanediol but with a greater oxygen content was isolated from mares' pregnancy urine by Haslewood, Marrian and Smith,[1] who suggested the formula $C_{21}H_{33}(OH)_3$ and advanced the interesting hypothesis that it might have been formed by the hydroxylation of pregnanediol. The same compound was subsequently obtained by us[2] together with a new triol from which it could be separated by crystallization of the triacetates. It was designated provisionally as pregnanetriol-B and the work reported in this paper is concerned with the elucidation of its structure which is postulated to be that shown in (I) having hydroxyl groups at C_3, C_4 and C_{20} and belonging to the pregnane series. Some evidence is presented also for the configurations of the hydroxyl groups.

In an attempt to prepare the chloride of pregnanetriol-B with phosphorus pentachloride a mixture was obtained from which no definite compounds could be separated by crystallization. These chlorides were reduced with sodium in alcohol and the hydrocarbons which were formed were found to be unsaturated. They were reduced catalytically to give a mixture from which the hydrocarbon pregnane, identical with the known compound, could be isolated. The formation of this hydrocarbon shows that the triol contains the same basic ring structure as the pregnanediols, as was suggested by Haslewood, Marrian and Smith and would indicate that it belongs to the pregnane series. It will be shown, however, that under suitable conditions the hydrocarbon *allo*-pregnane also may be obtained from pregnanetriol-B.

Partial hydrolysis of the triol triacetate with the removal of one acetyl group, followed by oxidation, gave a keto diacetate. The position of the ketone group is not known but probably it is not at C_3, since treatment with aluminum isopropylate gave no substances which precipitated with digitonin. It does not give the Zimmermann[3] test for a C_3 ketone but this reaction is questionable with these compounds since the diacetate of pregnanediol-4,20-one-3[4] gave no reaction. With the view of obtaining a diol, the keto diacetate was treated with zinc and hydrochloric acid, and unexpectedly was found to give the hydrocarbon *allo*-pregnane in good yield. This unusual reaction involving the removal of two hydroxyl groups may be explained by postulating that the ketone group is at C_{20}. This group would be removed on reduction and the glycol formed by hydrolysis of the diacetate might undergo dehydration to yield a C_3 or C_4 ketone which then could be reduced to a hydrocarbon. A similar reaction of 4-hydroxycholesterol has been reported by Rosenheim and Starling.[5] The formation of a C_4 ketone could give rise to inversion at C_5 into the *allo*-form.[6]

The formation of pregnane and *allo*-pregnane from pregnanetriol-B shows an unusual lability at position C_5 which could only be caused by the proximity of a hydroxyl group. Treatment of *allo*-pregnanediol diacetate in the same manner gave *allo*-pregnanediol as the only compound that could be isolated. That none of the three hydroxyl groups is tertiary in character is shown by the fact that the triol readily forms a triacetate or a tribenzoate. That at least two of these hydroxyl groups are in close proximity is indicated by the ready oxidation of this compound and by the fact that Haslewood, Marrian and Smith[1] were unable to obtain any triketone on mild oxidation. We also were unable to obtain a triketone, a result which is in striking contrast to that obtained in our oxidation of pregnanetriol-A. On the other hand, we have found that mild oxidation with a limited amount of chromium trioxide gives a mixture of keto hydroxy compounds, while large quantities of chromium trioxide lead to the formation of carboxylic acids. Since the mixture of hydroxy ketones formed by mild oxidation would be expected to contain some

(1) Haslewood, Marrian and Smith, *Biochem. J.*, **28**, 1316 (1934).

(2) Marker, Kamm, Crooks, Oakwood, Wittle and Lawson, THIS JOURNAL, **60**, 210 (1938).

(3) Zimmermann, *Z. physiol. Chem.*, **233**, 257 (1935).

(4) Marker, Kamm and Jones, THIS JOURNAL, **59**, 1595 (1937).

(5) Rosenheim and Starling, *J. Chem. Soc.*, 377 (1937).

(6) Windaus, *Ann.*, **447**, 233 (1926).

α-ketol (III) we subjected this mixture to the reaction of Kling.[7] *allo*-Pregnanedione was obtained readily by oxidation of the resulting product.

The formation of *allo*-pregnanedione locates two of the hydroxyl groups, one at C_3 and the other at C_{20}, and the removal of the third hydroxyl group in the Kling reaction shows that it is adjacent to one of the other hydroxyl groups. Evidence that this third hydroxyl group is not at position C_{21} was obtained by treatment of the triol with periodic acid in which reaction no formaldehyde could be obtained and also by the fact that no 3-keto-aetio-*allo*-cholanic acid or 3-keto-aetiocholanic acid, products which would be expected to form readily from $C_{20}-C_{21}$ glycols, could be obtained on mild oxidation. The lability of the hydrogen at C_5 as shown by the tendency of the triol to isomerize during the Clemmensen

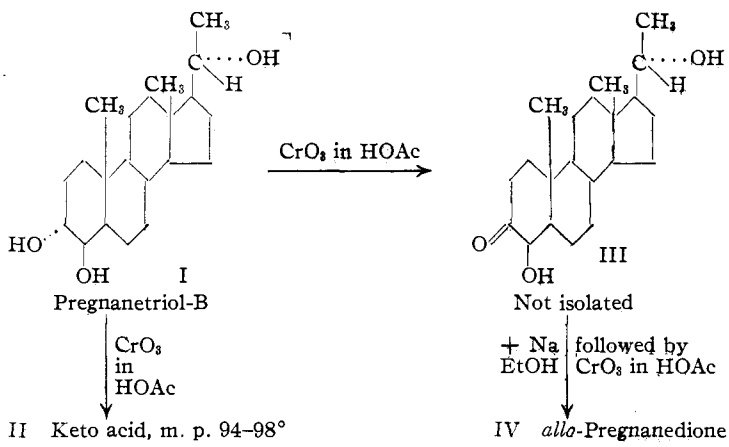

Fig. 1.

and Kling reactions indicates that the third hydroxyl group may be at C_4. More positive proof that the third hydroxyl group occupies position C_4 is shown by oxidation reactions. The triol on treatment with chromium trioxide at 25° gives a good yield of a keto acid which is water soluble. The acid exists in two forms, one a yellow oil which separates from organic solvents and the other a white solid which crystallizes from water solution. It can be dissolved completely in water and precipitated by evaporation of the water. The methyl ester formed with diazomethane was obtained only as a yellow oil. Titration shows the acid to be monobasic with a molecular weight of 360. Since the acid cannot be crystallized from organic solvents the difficulty of obtaining a pure sample is at once apparent.

At this time we are unable to assign a definite structure to this keto acid (II). It is a monocarboxylic acid containing two ketone groups, one of which can take part (in the form of an enol) in lactone formation. It yields a definite monosemicarbazone and a dioxime. Its molecular weight is not consistent with empirical formulas based upon the analyses of the free acid or its derivatives, which indicate the loss of five carbon atoms in the oxidation process. It is probable that the titration value is in error due to partial lactone formation. That a characteristic derivative is involved is shown by the fact that the identical product has been obtained in four independent oxidation experiments. Moreover, we have obtained this same acid from a compound of known structure. The diacetate of pregnanone-3-diol-4,20[4] was reduced catalytically and the resulting substance was hydrolyzed to give a mixture of epimeric triols which on oxidation gave the same acid as that obtained from pregnanetriol-B. It formed a semicarbazone and oxime with the same properties as that of the acid from pregnanetriol-B. This fact provides our best evidence that the third hydroxyl group is at position C_4 and has led us to postulate the structure as that of (I). Since the triol does not precipitate digitonin but on isomerization with sodium and xylene gives only a small amount of a digitonide, the configuration of the hydroxyl group at C_3 is *epi* or alpha. The hydroxyl group at C_{20} probably would have the same configuration as that of the pregnanediols (alpha); in fact, natural products have not been found to have the beta configuration at C_{20}. Pregnanetriol-B is not affected by treatment with lead tetraacetate under conditions that lead to oxidation of 4-hydroxycholestanol.[8] This indicates that the glycol has the *trans* configuration.[9] Oxidation of *cis-allo* diols[8] results in splitting of the glycol to form dibasic acids and the formation of this keto acid, in which more extensive destruction of the molecule has taken place, is additional evidence for the *trans* and pregnane structures of the original triol.

(7) Kling, *Compt. rend.*, **140**, 313, 1456 (1905); *Ann. chim. phys.*, [8] **5**, 551 (1905); *Bull. soc. chim.*, [3] **35**, 214 (1906); [3] **33**, 326 (1905).

(8) Marker, Kamm and Wittle, THIS JOURNAL, **60**, 1071 (1938).

(9) Criegee, Kraft and Rank, *Ann.*, **507**, 159 (1933).

We do not feel justified at this time in speculating about the formation of 3,4,20-trihydroxypregnane (pregnanetriol-B) in the animal body. Is it formed by the oxidation of pregnanediol or is it an intermediate resulting from the biological inactivation of progesterone? Such questions must be left for the future. We can report, however, that it does not appear to be a precursor of progesterone since it exhibits no progestational effect in the Corner rabbit test when administered in several times the effective dose of progesterone.

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Experimental Part

The Preparation of Pregnanetriol-B Benzoate.—A solution of 1 g. of pregnanetriol-B and 5 cc. of benzoyl chloride in 10 cc. of pyridine was allowed to stand at 20° for twenty-four hours. It was then poured into 500 cc. of water, shaken vigorously for several minutes and extracted with 200 cc. of ether. The ether solution after being washed with dilute hydrochloric acid and then with water was evaporated to dryness, leaving a white solid which on crystallization from ethyl acetate and methyl alcohol yielded 1.5 g. of pregnanetriol tribenzoate (m. p. 218°). A sample of this benzoate was distilled in a molecular still at 250° bath temperature during three hours in an attempt to eliminate benzoic acid but the compound was recovered unchanged.

Anal. Calcd. for $C_{42}H_{48}O_6$: C, 77.8; H, 7.5; mol. wt., 648. Found: C, 77.9; H, 7.8; mol. wt., 641.

The Partial Hydrolysis of Pregnanetriol-B Triacetate.—To a solution of 6 g. of triol triacetate in two liters of methyl alcohol at 20° was added 10.5 cc. of a solution of 1.24 *N* potassium hydroxide in methyl alcohol and 5 cc. of water. The solution was shaken vigorously and allowed to stand at 20° for seventy hours after which time it was treated with 12 cc. of 1.03 *N* sulfuric acid and concentrated on a steam-bath to 200 cc. This solution was diluted with a liter of water and the gelatinous solid which precipitated was filtered off and dried at 100°. It was oxidized by dissolving it in 500 cc. of acetic acid, cooling the solution to 20° and slowly adding a solution of 1.8 g. of chromium trioxide in 25 cc. of 90% acetic acid with vigorous shaking. The solution was allowed to stand at 20° for one hour, diluted with 25 cc. of methyl alcohol and evaporated to dryness *in vacuo*. The resulting solid was dissolved in 500 cc. of ether, the solution being washed with water and dilute sodium carbonate solution to remove acids and then evaporated to dryness. The resulting solid was dissolved in 200 cc. of ethyl alcohol, boiled for fifteen minutes with 8 g. of Girard's reagent and then poured into 300 cc. of water. The aqueous alcoholic solution was extracted with three 100-cc. portions of ether, acidified with 100 cc. of concd. hydrochloric acid and allowed to stand overnight. The white solid which precipitated was filtered off and crystallized from aqueous methyl alcohol and from acetone. From the former solvent it crystallized in the form of needles melting at 188° and from the latter in cubic crystals melting at 170°; yield, 2 g.

Anal. Calcd. for $C_{25}H_{38}O_5$: C, 71.6; H, 9.2. Found: C, 71.4; H, 9.8.

The compound is a keto diacetate. Its semicarbazone did not melt below 315°. An attempt to prepare a phenylhydrazone using sulfuric acid gave a mixture. It did not give the Zimmermann test for a ketone at position C_3. On reduction with aluminum isopropylate in dry isopropyl alcohol it gave a product which showed no precipitation with digitonin.

***allo*-Pregnane.**—The above keto diacetate was reduced by the method of Clemmensen by dissolving 0.5 g. in 50 cc. of acetic acid and 50 cc. of concd. hydrochloric acid and refluxing the solution with 20 g. of amalgamated zinc for one and one-half hours. Oil formed on the surface of the solution after one-half hour. The solution was poured into 500 cc. of water and the product was extracted with 200 cc. of ether. The ether solution was washed with water and dilute sodium carbonate solution and evaporated to dryness to leave a white oil which was soluble in acetone and only slightly soluble in methyl alcohol. It did not crystallize readily and so was refluxed with a solution of 100 cc. of ethyl alcohol and 0.5 g. of potassium hydroxide. It dissolved very slowly in alcohol and was recovered by pouring the solution into 500 cc. of water and extracting with ether. After standing overnight in acetone, the mixture gave crystals of *allo*-pregnane which were recrystallized from acetone–methyl alcohol (m. p. 80–81°). It gave no depression with *allo*-pregnane (m. p. 84°) prepared by the reduction of *allo*-pregnanedione, but gave a marked depression with pregnane prepared from pregnanedione. The yield was 100 mg.

Pregnane.—A mixture of 1 g. of pregnanetriol-B and 2 g. of phosphorus pentachloride was ground in a mortar for fifteen minutes and the viscous oil was then poured into 200 cc. of water and extracted with 100 cc. of ether. The ether solution after washing with water and dilute sodium carbonate solution was evaporated to leave a yellow oil which would not crystallize. It was reduced by dissolving it in 200 cc. of absolute ethyl alcohol and treating the refluxing solution with 5 g. of sodium over a period of one hour. The solution was poured into 500 cc. of water and extracted with 200 cc. of ether. The ether solution was washed with water, evaporated to dryness and the oil which remained was distilled in a molecular still. The clear oil which distilled at 90° bath temperature gave tests for unsaturation with bromine and so was hydrogenated by subjecting it in a solution of 100 cc. of ether, 10 cc. of acetic acid and 0.5 g. of platinum oxide catalyst to hydrogen at 3 atmospheres pressure during two hours. The solution was filtered from the catalyst and evaporated to dryness leaving an oil which with some difficulty was finally crystallized from an acetone–methyl alcohol mixture. The product melted at 78° and was obtained in a yield of 50 mg. It gave no depression in melting point when mixed with pregnane prepared from pregnanedione but gave a marked depression when mixed with *allo*-pregnane.

Conversion of Pregnanetriol-B to *allo*-Pregnanedione.—A solution of 0.8 g. of chromium trioxide in 10 cc. of 90%

acetic acid was added in small portions to a solution of 2 g. of triol in 100 cc. of acetic acid at 25° and the mixture was allowed to stand for one-half hour. The solution was diluted with 300 cc. of water and extracted with 200 cc. of ether. The ether solution was washed with water and then with dilute potassium hydroxide solution to remove the small quantity of by-product acid. It was then evaporated to dryness to leave a white solid which was dissolved in 150 cc. of ethyl alcohol and treated with 10 g. of sodium over a period of one-half hour. This solution was diluted with 500 cc. of water and extracted with ether. The ether solution was washed with water and evaporated to dryness. The yellow solid which remained was dissolved in 100 cc. of acetic acid and treated with 1.5 g. of chromium trioxide at 25° for fifteen minutes. The solution was diluted with 300 cc. of water and extracted with ether. The ether extract was washed with water and then with dilute sodium carbonate solution and evaporated to dryness. The residue was distilled in a molecular still and the fraction distilling at 120–150° which was a white solid (m. p. 185–196°) was crystallized from acetone and methyl alcohol to yield 200 mg. of *allo*-pregnanedione, m. p. 197–199° (IV). It gave no depression in melting point when mixed with *allo*-pregnanedione.

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.7; H, 10.2. Found: C, 79.4; H, 10.4.

Oxidation of Pregnanetriol-B.—To a stirred solution of 2 g. of triol in 200 cc. of acetic acid at 20° was added dropwise over a period of one hour a solution of 2.5 g. of chromium trioxide in 25 cc. of 95% acetic acid and the solution was allowed to stand at 20° overnight. It was then diluted with 25 cc. of methyl alcohol and evaporated to dryness *in vacuo* to give a solid residue which was dissolved in 500 cc. of water and 200 cc. of ether. The ether layer was washed with water and then extracted with dilute sodium carbonate and the sodium carbonate solution, after extraction with ether, was acidified with hydrochloric acid to give a finely divided precipitate which on standing overnight formed white fiber clusters which were filtered off and dried. The yield was 0.9 g. of a product melting at 94–98° (II). Attempts to crystallize this acid from organic solvents were unsuccessful. It dissolves readily in acetone, alcohol and acetic acid to give yellow solutions from which it is precipitated with water only as a yellow oil. It dissolves in benzene less rapidly to give a yellow solution and is precipitated as a yellow oil by the addition of pentane. It dissolves in ether quite slowly, giving a yellow solution. It is thus capable of existing in two forms and seems to be mainly yellow in organic solutions. It can be removed from water-immiscible organic solvents by extraction with sodium carbonate solution and is precipitated as a white solid when such alkaline solutions are acidified. Tests for halogens were negative.

The acid is sparingly soluble in water (100 mg. dissolves in about 300 cc. of hot water) but readily forms supersaturated solutions. It does not crystallize on cooling and partial evaporation of the solution is necessary in order to recover the product which, however, shows no essential change in melting point. On drying at room temperature at 2–3 mm., during which the acid remained white, it gave the following analyses: C, 66.7; H, 8.6; and C, 66.9; H, 8.7. At 50° and 2–3 mm. the samples became tinged yellow but gave results differing only slightly, specifically, C, 67.3; H, 8.3 and C, 67.21; H, 8.6. Titration showed the acid to be monobasic, with an equivalent weight of approximately 350.

The acid reacts with ketone reagents to form derivatives fairly soluble in most solvents so that they do not separate readily. The semicarbazone melted with decomposition at 190°. *Anal.* C, 63.9; H, 8.1; N, 12.8. The oxime melted at 181–183°. *Anal.* C, 64.6; H, 8.33; N. 9.1.

Reactions of the Keto Acid (II).—The acid reacts with diazomethane to form an ester as was shown by the fact that the reaction product no longer was acidic. The derivative, however, was obtained only as a yellow oil which resisted efforts at crystallization.

A specimen (100 mg.) was heated at 200° for one hour, at which time all effervescence had ceased. The residue was dissolved in 100 cc. of ether and extracted with sodium carbonate solution. The alkaline solution after acidification yielded, on standing for a day, 50 mg. of a slightly yellow crystalline acid, m. p. 90–94°, which gave no depression in melting point when mixed with the unheated acid. Only a trace of neutral material was left in the ether.

The acid showed no reduction with alkaline silver nitrate. It was non-reactive also to hydrogen peroxide. A solution of 100 mg. in 5 cc. of 50% acetic acid was treated with 2 cc. of 30% hydrogen peroxide and heated on the steam-bath during twenty-four hours. The solution was diluted with 25 cc. of water and after standing for several days yielded crystals of the original acid melting at 94–98°.

Preparation of the Keto Acid (II) from the Diace ate of Pregnanone-3-diol-4,20.—A solution of 0.7 g. of the diacetate of pregnanone-3-diol-4,20, m. p. 247°, in 100 cc. of acetic acid was treated with 0.2 g. of platinum oxide catalyst and reduced with hydrogen under 3 atm. pressure for two hours. The solution was filtered to remove the catalyst and the filtrate was evaporated to dryness. The solid was dissolved in 100 cc. of ethyl alcohol and refluxed with 0.7 g. of potassium hydroxide in ethyl alcohol for one hour. The solution was diluted with water and extracted with ether. After washing, the ether solution was evaporated to dryness and the residue (0.5 g.) was dissolved in 100 cc. of acetic acid and cooled to 20°. A solution of 0.7 g. of chromium trioxide in 50 cc. of 95% acetic acid was added with stirring over a period of one hour. The solution was allowed to stand at 20° overnight and then evaporated to dryness *in vacuo* after the addition of 10 cc. of methyl alcohol. The solid was dissolved in 200 cc. of water and extracted with 200 cc. of ether. The ether layer was washed well with water and then extracted with 5% sodium carbonate. The sodium carbonate solution was extracted with ether and then made distinctly acid with hydrochloric acid. The solution became milky white; and after standing at room temperature overnight gave needles of acid which were filtered off; yield 0.15 g.; m. p. 95–97°. This material turned yellow when melted. It gave no depression in melting point when mixed with acid II from pregnanetriol-B.

The semicarbazone of this acid softens at 180°, liberates a gas at 190°, and though remaining solid it turns slightly brown at 250°. A mixture with the semicarbazone of the acid from triol-B behaved analogously.

Anal. C, 63.4; H, 8.3; N, 12.8.

Similar to acid II, it gave an oxime which crystallized in fiber clusters from methyl alcohol and water, m. p. and mixed m. p. 181–182°.

Anal. N, 9.17.

Treatment of Pregnanetriol-B with Periodic Acid.—To a solution of 0.67 g. of pregnanetriol-B in 250 cc. of alcohol was added a solution of 100 cc. of 0.01 *M* periodic acid and 3 cc. of 5 *N* sulfuric acid. After standing for fifteen hours the mixture was distilled into 0.7 g. of Dimedon (dimethyldihydroxyresorcinol) in 50 cc. of alcohol. When most of the water and alcohol had been removed, 300 cc. of water was added to the residue and the distillation was repeated. The distillate was concentrated to 150 cc. to remove the alcohol, but no precipitate of the formaldehyde derivative was obtained. Pregnanetriol-B was recovered substantially unchanged from the residual solution.

Isomerization of Pregnanetriol-B.—A solution of 0.5 g. of triol-B in 200 cc. of dry xylene and 3 g. of sodium was refluxed for six hours and then 50 cc. of amyl alcohol was added to dissolve the sodium. The solution was washed thoroughly with water, steam distilled, and the remaining water solution filtered. The solid was dissolved in 250 cc. of ethyl alcohol and treated with 2 g. of digitonin in 200 cc. of ethyl alcohol to yield 400 mg. of digitonide.

Treatment of Pregnanetriol-B with Lead Tetraacetate.—To a solution of 2 g. of lead tetraacetate in 200 cc. of acetic acid was added 0.5 g. of triol-B. It dissolved readily with shaking and the solution was allowed to stand at 25° for three days. It was then diluted with one liter of water and washed with 300-cc. portions of ether. The ether solution was evaporated and the residue was dissolved in 25 cc. of hot acetic acid and treated with 5 cc. of 30% hydrogen peroxide over a period of four hours on the steam-bath. The solution was diluted with ether and after washing with water was extracted with sodium carbonate. No acid was obtained on acidifying the carbonate solution and the triol was recovered in the ether solution. This procedure gave a good yield of Diels saturated acid from 4-hydroxycholestanol.

Summary

Pregnanetriol-B, a trihydroxy steroid occurring in mares' pregnancy urine, has been identified as 3(α),4(β),20(α)-trihydroxypregnane.

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Sterols. XXXI. Oxidation of Sitosterol by Selenium Oxide

BY RUSSELL E. MARKER, OLIVER KAMM AND EUGENE L. WITTLE

In the preceding article in this series[1] we reported that the structure of one of the triols (pregnanetriol-B) obtained from mares' pregnancy urine is quite probably that of a glycol having hydroxyl groups at positions C_3 and C_4 of the pregnane nucleus. Since it represents the first compound of this type which has been isolated from urine and is probably closely related to the sex hormones, we have decided to prepare similar compounds from readily available materials to learn more of the chemistry of these glycols and also as a possible means for the synthesis of pregnanetriol-B.[1] This paper reports such work on sitosterol.

Oxidation of sitosteryl acetate by selenium dioxide has been found to take place very readily following a course similar to that with cholesterol,[2] giving 4-hydroxysitosteryl acetate and 6-hydroxysitosteryl acetate. The two oxidation products were separated readily through their diacetates, the 4-hydroxy derivative being obtained by direct crystallization whereas 6-hydroxysitosterol was isolated from the acetic anhydride mother liquors after hydrolysis.

Catalytic reduction of the diacetate of 4-hydroxysitosterol gave the corresponding derivative of 4-hydroxysitostanol which was hydrolyzed to the saturated diol. Oxidation of this 4-hydroxysitostanol with chromium trioxide in acetic acid took place very readily, yielding a dibasic acid which was characterized by its dimethyl ester. We have found also that the oxidation of 4-hydroxycholestanol with chromium trioxide in acetic acid gives Diels' saturated acid which is identical with the compound prepared from the diol by oxidation with lead tetraacetate and hydrogen peroxide. It is apparent that C_3—C_4 diols of the *allo* series (β-configuration at C_5) on oxidation with chromium trioxide undergo splitting to yield C_3—C_4 dibasic acids. This is in marked contrast to the oxidation of C_3—C_4 glycols of the pregnane series,[1] which yield a monobasic acid of unknown structure.

When 4-hydroxysitosterol is heated with alcoholic hydrochloric acid it undergoes dehydration and rearrangement to form sitostenone.

(1) Marker, Kamm, Wittle, Oakwood and Lawson, THIS JOURNAL, **60**, 000 (1938).

(2) Rosenheim and Starling, *J. Chem. Soc.*, 377 (1937); Butenandt and Hausmann, *Ber.*, [5] **70**, 1154 (1937).