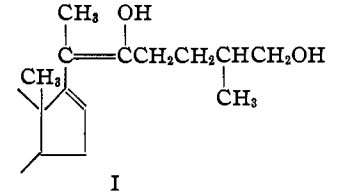
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

# Sterols. LXXXIX. Reactions of Pseudosarsasapogenin

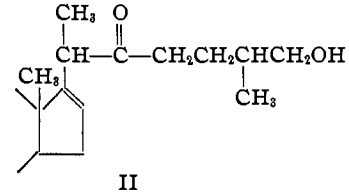
BY RUSSELL E. MARKER AND EWALD ROHRMANN

Of the many reactions which are peculiar to sarsasapogenin,[1] probably the most interesting and certainly the most significant from the standpoint of elucidating the relationship existing between this sapogenin and the sterols is the isomerization by acid anhydrides[2] to yield pseudosarsasapogenin. This isomeric substance is of great significance because of the ease with which it is converted into $\Delta^{16,17}$-pregnenedione-3,20 by mild oxidation with chromic anhydride.

All of our evidence, which is derived largely from oxidation and reduction studies seems to indicate that pseudosarsasapogenin is best represented by structure I or possibly by one of its equivalents, II or III.



I



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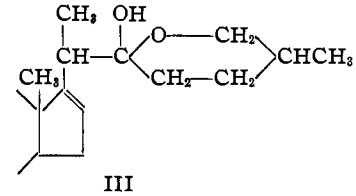


III

Pseudosarsasapogenin (suggested formulations)

As discussed in previous work,[2] pseudosarsasapogenin upon mild oxidation with chromic anhydride yields $\Delta^{16,17}$-pregnenedione-3,20 (VII) and 3-keto-*etio*-bilianic acid. Pseudosarsasapogenin upon acetylation with hot acetic anhydride gives a non-crystalline product which upon mild oxidation with chromic anhydride yields $\Delta^{16,17}$-pregnenol-3($\beta$)-one-20 acetate (VI) and 3($\beta$)-hydroxy-*etio*-bilianic acid (V).[3] Further oxidation of $\Delta^{16,17}$-pregnenol-3($\beta$)-one-20 acetate yielded 3($\beta$)-hydroxy-*etio*-bilianic acid. The oxidation of acetylated pseudosarsasapogenin at elevated temperatures gives largely the bilianic acid. Neither pseudosarsasapogenin nor the acetylated product reacts with semicarbazide acetate under the usual conditions.

Pseudosarsasapogenin upon hydrogenation with Adams catalyst in acetic acid, ethanol or acidic ethanol yields dihydropseudosarsasapogenin. This substance yields a diacetate and a di-*p*-nitrobenzoate. It is of interest that acetylated pseudosarsasapogenin upon hydrogenation with Adams catalyst yields a substance identical with the diacetate of dihydropseudosarsasapogenin. This fact does not appear to be in accordance with structure III for pseudosarsasapogenin.

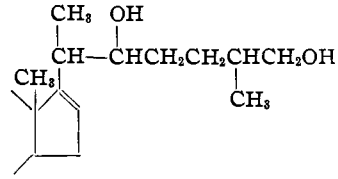
Dihydropseudosarsasapogenin upon oxidation at 15° with chromic anhydride readily yields $\Delta^{16,17}$-pregnenedione-3,20 and a diketo acid (VIII) of the composition $C_{27}H_{42}O_4$. This acid forms a disemicarbazone and a methyl ester and on further oxidation with chromic anhydride yields $\Delta^{16,17}$-pregnenedione-3,20. The fact that this acid readily forms a disemicarbazone while pseudosarsasapogenin does not react with semicarbazide acetate does not seem to be in accordance with structure II for pseudosarsasapogenin.

Dihydropseudosarsasapogenin diacetate upon oxidation with chromic anhydride at 90° gives a good yield of 3-($\beta$)-hydroxy-*etio*-bilianic acid. No neutral product was obtained. Oxidation of the diacetate at 25–30° yields 3-($\beta$)-hydroxy-*etio*-bilianic acid and a neutral fraction consisting of $\Delta^{16,17}$-pregnenol-3($\beta$)-one-20 acetate and a mixture of neutral products which were not separated. When the diacetate was oxidized at 15° it was recovered largely unchanged which is in contrast to the analogous oxidation of the free dihydro compound. Evidently the presence of an acetoxy group at C-27 hinders the oxidation of a reactive group at C-22.

The ease of formation of $\Delta^{16,17}$-pregnenedione-3,20 from both pseudosarsasapogenin and dihydropseudosarsasapogenin suggests that both of these substances contain a non-reducible ethylenic linkage at C-16, C-17 and a reactive group at C-22.

(1) Marker and Rohrmann, THIS JOURNAL, **61**, 846 (1939).
(2) Marker and Rohrmann, *ibid.*, **62**, 518 (1940).
(3) Marker and Rohrmann, *ibid.*, **61**, 2722 (1939).

The occurrence of non-reducible ethylenic linkages in sterol compounds is of course not unusual, apocholic acid[4] being a notable example. Inspection of the three suggested formulations (I, II, and III) for pseudosarsasapogenin indicates that all of these should yield the same dihydro compound on reduction and that dihydropseudosarsasapogenin is probably best represented by structure IV.

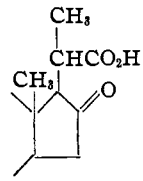


IV. Dihydropseudosarsasapogenin (suggested)

It seems peculiar that pseudosarsasapogenin and dihydropseudosarsasapogenin form *bis* rather than the expected *tris* derivatives. This is possibly due to hindrance at the C-22 position.

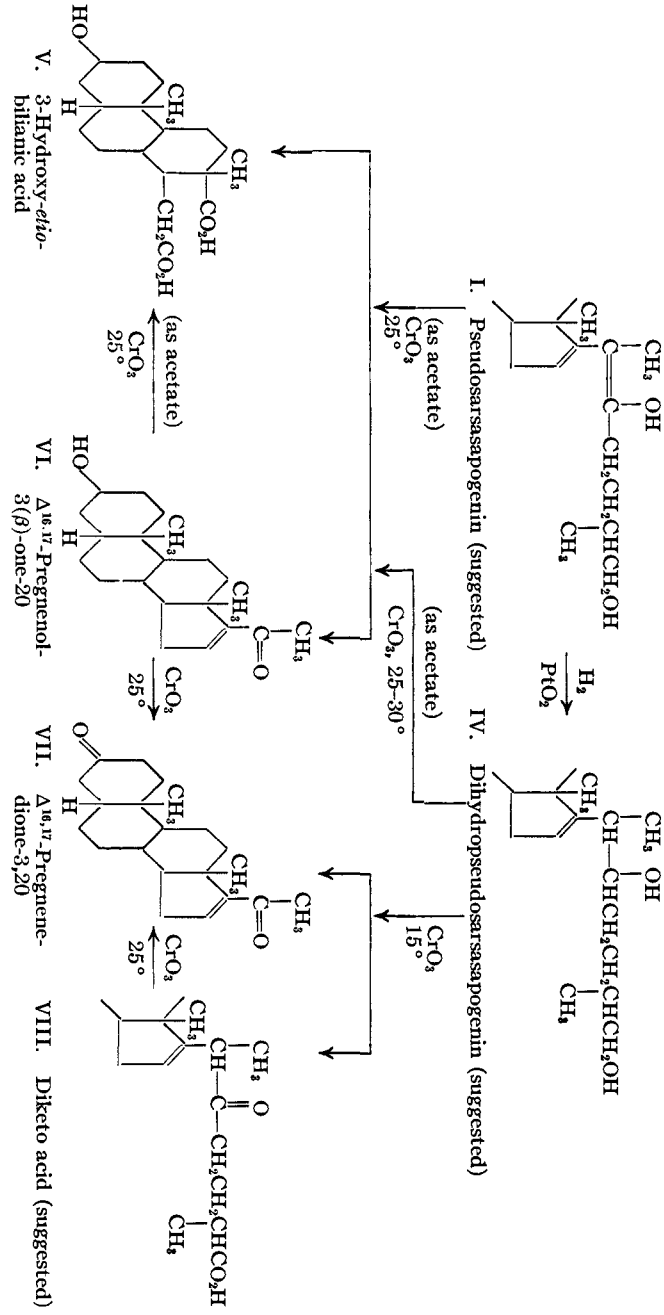
It is of interest that in the oxidation of the diacetates of pseudosarsasapogenin and dihydropseudosarsasapogenin an appreciable amount of the 3-($\beta$)-hydroxy-*etio*-bilianic acid apparently is formed as the anhydride and occurs as such in the neutral fraction of the oxidations. This is in accordance with observations on the analogous oxidation of *allo*-pregnanetriol-3,16,20 to 3-keto-*etio-allo*-bilianic acid.[5]

In all of the oxidation studies of the pseudo and dihydropseudo diacetates it is significant that none of the $C_{22}$ keto acid[6] (IX) was encountered. This is in accordance with suggested structures of the pseudo and dihydropseudo compounds.



IX. $C_{22}$ Keto Acid

The $\Delta^{16,17}$-pregnenol-3($\beta$)-one-20 acetate obtained in the oxidation of acetylated pseudosarsasapogenin and dihydropseudosarsasapogenin was characterized by a study of its reduction products. With sodium and ethanol it yields pregnanediol-3-($\beta$),20($\alpha$). Hydrogenation with Adams catalyst and subsequent oxidation with chromic anhydride yielded the acetate of pregnanol-3($\beta$)-one-20. These transformations are in accordance with previous postulations concerning the configuration of the C-3 hydroxyl group in sarsasapogenin.[7,8] $\Delta^{16,17}$-Pregnenol-3($\beta$)-one-20 acetate on alkaline hydrolysis and subsequent mild oxidation with chromic anhydride readily yields $\Delta^{16,17}$-pregnenedione-3,20.




(4) Wieland and Dane, *Z. physiol. Chem.*, **212**, 263 (1932).
(5) Marker and Wittle, THIS JOURNAL, **61**, 855 (1939).
(6) Marker and Rohrmann, *ibid.*, **61**, 1285 (1939).
(7) Farmer and Kon, *J. Chem. Soc.*, 414 (1937).
(8) Marker and Rohrmann, THIS JOURNAL, **61**, 943 (1939).

We wish to thank Parke, Davis and Company for their generous help and assistance in the various phases of this work.

## Experimental Part[9]

**Pseudosarsasapogenin.**—This was prepared as described in previous work. Pseudosarsasapogenin is very readily oxidized by selenium dioxide, a reaction which we have not investigated further as yet. It reacts readily with bromine but at present we have not isolated any definite crystalline products from this reaction. Pseudosarsasapogenin does not react with semicarbazide acetate under the usual conditions. The acetylated product is likewise unreactive.

**Oxidation of Acetylated Pseudosarsasapogenin. (a) at 90°.**—Pseudosarsasapogenin (2.5 g.) was refluxed for thirty minutes with 15 cc. of acetic anhydride. The acetic anhydride was evaporated *in vacuo* and the residual sirup dissolved in 60 cc. of acetic acid. The solution was heated on a steam-bath while 5 g. of chromic anhydride in 50 cc. of 80% acetic acid was added over a period of one hour. Ethanol (10 cc.) was then added and the solution evaporated *in vacuo* to a volume of about 50 cc. Water was added and the precipitated solid taken up in ether and the ethereal extract washed with 3% sodium hydroxide solution and water. The sodium hydroxide washing was heated on the steam-bath for twenty minutes to complete hydrolysis. The solution was then cooled, acidified with hydrochloric acid and the precipitated solid was taken up in ether and crystallized from chloroform to give 600 mg. of white crystals, m. p. 221–223°. This gave no depression with a sample of 3-hydroxy-*etio*-bilianic acid, m. p. 220–222°.

*Anal.* Calcd. for $C_{19}H_{30}O_5$: C, 67.4; H, 8.9. Found: C, 67.3; H, 8.9.

With hot acetic anhydride the acid gave an *acetate anhydride* which crystallized from aqueous acetone as flat white needles, m. p. 204.5–206.5°. This gave no depression with a sample of the acetate anhydride of 3-hydroxy-*etio*-bilianic acid, m. p. 205–207°.

*Anal.* Calcd. for $C_{21}H_{30}O_5$: C, 69.6; H, 8.3. Found: C, 69.5; H, 8.3.

The ethereal solution containing the material not extracted with alkali was evaporated and the residual sirup hydrolyzed with ethanolic potassium hydroxide. Water and dilute hydrochloric acid were added and the precipitate taken up in ether and crystallized from ether to give 30 mg. of small white crystals, m. p. 284–287°. This product has not been investigated further.

*Anal.* Calcd. for $C_{22}H_{34}O_4$: C, 72.9; H, 9.5; neut. equiv., 362. Found: C, 73.1, 73.1; H, 9.3, 9.5; neut. equiv., 358.

The filtrate from this acid was evaporated and crystallized from chloroform to give white crystals, m. p. 220–222°. This gave no depression with a sample of 3-hydroxy-*etio*-bilianic acid, m. p. 220–222°.

**(b) At Room Temperature.**—Pseudosarsasapogenin (3 g.) was treated with acetic anhydride as before and the residual sirup dissolved in 100 cc. of acetic acid. To this solution was added 3 g. of chromic anhydride in 30 cc. of 80% acetic acid. The mixture was allowed to stand at room temperature for one hour. Water was added and the precipitated solid taken up in ether. The ethereal extract was washed with water and 3% sodium hydroxide solution.

The alkaline water layer was acidified with hydrochloric acid and the precipitated acid was taken up in ether and crystallized from chloroform to give white crystals, m. p. 220–222°. This gave no depression with a sample of 3-hydroxy-*etio*-bilianic acid, m. p. 220–222°.

*Anal.* Calcd. for $C_{19}H_{30}O_5$: C, 67.4; H, 8.9. Found: C, 67.0; H, 8.8.

The neutral fraction was crystallized from aqueous methanol to give white plates, m. p. 144–146°. This product is the *acetate* of $\Delta^{16,17}$-pregnenol-3($\beta$)-one-20.

*Anal.* Calcd. for $C_{23}H_{34}O_3$: C, 77.0; H, 9.6. Found: C, 76.8, 77.0; H, 9.5, 9.4.

When treated with semicarbazide acetate under the usual conditions the product gave a *semicarbazone* which crystallized from aqueous ethanol, m. p. 250–252°.

*Anal.* Calcd. for $C_{24}H_{37}O_3N_3$: C, 69.35; H, 9.0. Found: C, 69.2; H, 8.8.

The filtrate remaining after removal of most of the $\Delta^{16,17}$-pregnenol-3($\beta$)-one-20 acetate upon hydrolysis with ethanolic potassium hydroxide yielded an acid which crystallized from chloroform as white crystals, m. p. 219–222°. This gave no depression with a sample of 3-hydroxy-*etio*-bilianic acid, m. p. 220–222°. This indicates that some of the 3-hydroxy-*etio*-bilianic acid is present in the oxidation mixture as the anhydride.

**3-($\beta$)-Hydroxy-*etio*-bilianic Acid from $\Delta^{16,17}$-Pregnenol-3($\beta$)-one-20 Acetate.**—The acetate of $\Delta^{16,17}$-pregnenol-3($\beta$)-one-20 was oxidized in acetic acid solution with chromic anhydride for sixteen hours at room temperature. The acid fraction after alkaline hydrolysis was crystallized from chloroform to give small white plates, m. p. 221–223°. This gave no depression with a sample of 3($\beta$)-hydroxy-*etio*-bilianic acid, m. p. 220–222°.

*Anal.* Calcd. for $C_{19}H_{30}O_5$: C, 67.4; H, 8.9. Found: C, 67.3; H, 8.9.

**$\Delta^{16,17}$-Pregnenedione-3,20 from $\Delta^{16,17}$-Pregnenol-3($\beta$)-one-20 Acetate.**—The acetate of $\Delta^{16,17}$-pregnenol-3($\beta$)-one-20 was hydrolyzed by refluxing for ten minutes with ethanolic potassium hydroxide solution. The product was crystallized from ethanol as white needles, m. p. 207–209°. The product evidently contains a molecule of ethanol, as indicated by the analysis.

*Anal.* Calcd. for $C_{23}H_{32}O_3$: C, 76.2; H, 10.6. Found: C, 76.2, 76.2; H, 10.6, 10.6.

When treated with semicarbazide acetate under the usual conditions the product gave a *semicarbazone* which crystallized from ethanol, m. p. 240° dec.

*Anal.* Calcd. for $C_{22}H_{35}O_2N_3$: C, 70.7; H, 9.5. Found: C, 70.6; H, 9.5.

Treatment with boiling acetic anhydride gave the acetate, m. p. 143–145°, which gave no depression with the original acetate, m. p. 144–146°.

To a solution of 150 mg. of the hydrolyzed product in 10 cc. of acetic acid was added 100 mg. of chromic an-

(9) Microanalyses by Dr. John R. Adams, Jr., of this Laboratory.

hydride in 5 cc. of 80% acetic acid. After standing for twenty minutes at room temperature, water was added and the products taken up in ether, and washed free from acid with sodium hydroxide. The neutral material was crystallized from acetone to give white plates, m. p. 199–201°. This gave no depression with a sample of $\Delta^{16,17}$-pregnenedione-3,20, m. p. 200–202°.

*Anal.* Calcd. for $C_{21}H_{30}O_2$: C, 80.2; H, 9.6. Found: C, 80.3; H, 9.5.

**Reduction of $\Delta^{16,17}$-Pregnenol-3($\beta$)-one-20 Acetate. (a) With Sodium and Ethanol.**—To a boiling solution of 500 mg. of the acetate of $\Delta^{16,17}$-pregnenol-3($\beta$)-one-20 in 100 cc. of absolute ethanol was added 6 g. of sodium over a period of one hour. The solution was diluted with water and extracted with ether. The product was crystallized from ether and finally from acetone to give compact white crystals, m. p. 180–183°. This gave no depression with a sample of pregnanediol-3($\beta$),20($\alpha$), m. p. 182–184°.

Acetylation with hot acetic anhydride yielded an acetate which crystallized from aqueous ethanol as white needles, m. p. 138–140°. This gave no depression with a sample of the diacetate of pregnanediol-3($\beta$),20($\alpha$), m. p. 139–141°.

**(b) With Adams Catalyst.**—A mixture of 300 mg. of $\Delta^{16,17}$-pregnenol-3($\beta$)-one-20 acetate, 300 mg. of Adams catalyst and 120 cc. of absolute ethanol was shaken with hydrogen at 3 atm. at room temperature for three hours. No definite crystalline product was isolated. The entire product was oxidized in acetic acid (20 cc.) at room temperature with 300 mg. of chromic anhydride for one hour. The product was crystallized from aqueous ethanol as compact white crystals, m. p. 118–119.5°. This gave no depression with a sample of pregnanedione-3,20, m. p. 118–120°.

*Anal.* Calcd. for $C_{21}H_{32}O_2$: C, 79.7; H, 10.2. Found: C, 79.6; H, 10.2.

In another experiment the acetate of $\Delta^{16,17}$-pregnenol-3-($\beta$)-one-20 (800 mg.) was reduced as above. The catalyst and solvent were removed and the residue dissolved in 25 cc. of acetic acid. To this solution was added a solution of 500 mg. of chromic anhydride in 10 cc. of 80% acetic acid. After standing for thirty minutes at room temperature, water was added and the precipitated solid taken up in ether and freed from acids by washing with water and sodium carbonate solution. The product was crystallized from aqueous ethanol as thick white needles, m. p. 116–118°. This gave no depression with a sample of pregnanol-3($\beta$)-one-20 acetate, m. p. 118–120°.

*Anal.* Calcd. for $C_{23}H_{36}O_3$: C, 76.6; H, 10.1. Found: C, 76.6; H, 10.1.

**Dihydropseudosarsasapogenin.**—A mixture of 1 g. of pseudosarsasapogenin, 500 mg. of Adams catalyst and 120 cc. of acetic acid was shaken with hydrogen at 3 atm. at room temperature for fifteen hours. The catalyst was filtered and the filtrate evaporated *in vacuo*. The residual sirup was hydrolyzed with ethanolic potassium hydroxide and crystallized from acetone as small white plates, m. p. 168–170°. The mixture with the original pseudosarsasapogenin (m. p. 171–173°) melted at 150–155° and that with dihydrosarsasapogenin (m. p. 165–166°) at 154–162°. Similar results were obtained when the reduction was carried out in ethanol or in ethanol acidified with hydrochloric acid.

*Anal.* Calcd. for $C_{27}H_{46}O_3$: C, 77.4; H, 11.1. Found: C, 77.3; H, 10.9.

With boiling acetic anhydride the substance gave a **diacetate** which crystallized from pentane as white needles, m. p. 95–97°.

*Anal.* Calcd. for $C_{31}H_{50}O_5$: C, 74.1; H, 10.0. Found: C, 74.0, 74.1; H, 9.9, 10.0.

With *p*-nitrobenzoyl chloride in pyridine at 60° a **di-*p*-nitrobenzoate** was formed which crystallized from ethyl acetate as white needles, m. p. 196–197.5°.

*Anal.* Calcd. for $C_{41}H_{52}O_9N_2$: C, 68.7; H, 7.3. Found: C, 68.7; H, 7.1.

Dihydropseudosarsasapogenin does not react noticeably with selenium dioxide. It absorbs bromine slowly in acetic acid solution.

**Reduction of Acetylated Pseudosarsasapogenin.**—Pseudosarsasapogenin (2 g.) was refluxed with an excess of acetic anhydride and the anhydride evaporated *in vacuo*. The residual sirup was reëvaporated several times with acetic acid and finally dissolved in a mixture of 50 cc. of acetic acid and 75 cc. of absolute ethanol. The solution was shaken with 1 g. of Adams catalyst and hydrogen at 3 atm. pressure at room temperature for twelve hours. The catalyst was removed and the acetic acid evaporated *in vacuo*. The residue was crystallized from pentane as white needles, m. p. 95–97°. This gave no depression with a sample of the diacetate of dihydropseudosarsasapogenin, m. p. 95–97°.

*Anal.* Calcd. for $C_{31}H_{50}O_5$: C, 74.1; H, 10.0. Found: C, 74.2; H, 9.9.

**Oxidation of Dihydropseudosarsasapogenin.**—To a solution of 4 g. of dihydropseudosarsasapogenin in 200 cc. of acetic acid was added 6 g. of chromic anhydride in 50 cc. of 80% acetic acid. After standing at 15–18° for ninety minutes a large volume of water was added and the mixture shaken with ether. The ethereal solution was washed with water and 3% sodium hydroxide solution. The aqueous alkaline layer was acidified with hydrochloric acid and the precipitated acid taken up with ether and crystallized from acetone as small white needles, m. p. 233–236°. This is a diketo acid (VIII).

*Anal.* Calcd. for $C_{27}H_{42}O_4$: C, 75.3; H, 9.6. Found: C, 75.3, 75.1; H, 9.4, 9.6.

With semicarbazide acetate in the usual manner, the acid gave a **disemicarbazone** which crystallized from ethanol as small white crystals, m. p. 209° dec.

*Anal.* Calcd. for $C_{29}H_{48}O_4N_6$: C, 63.9; H, 8.9. Found: C, 63.7; H, 8.5.

With diazomethane in ether–methanol solution the acid gave a **methyl ester** which crystallized from pentane as white needles, m. p. 85–87°.

*Anal.* Calcd. for $C_{29}H_{44}O_4$: C, 75.6; H, 10.0. Found: C, 75.4; H, 9.8.

The ethereal extract containing the neutral fraction was evaporated and the residue crystallized from acetone to give $\Delta^{16,17}$-pregnenedione-3,20 as white plates, m. p. 199–201°. This gave no depression with an authentic sample of $\Delta^{16,17}$-pregnenedione-3,20, m. p. 200–202°.

*Anal.* Calcd. for $C_{21}H_{30}O_2$: C, 80.2; H, 9.6. Found: C, 80.3; H, 9.6.

**$\Delta^{16,17}$-Pregnenedione-3,20 from Diketo Acid (VIII).**—To a solution of 250 mg. of diketo acid in 20 cc. of acetic acid was added a solution of 250 mg. of chromic anhydride in 5 cc. of 80% acetic acid. After standing at 25° for seventy-five minutes water was added and the precipitated solid taken up in ether and washed with water and potassium hydroxide solution. Evaporation of the ether gave a product which crystallized from acetone as white plates, m. p. 199–201°. This gave no depression with a sample of $\Delta^{16,17}$-pregnenedione-3,20, m. p. 200–202°.

*Anal.* Calcd. for $C_{21}H_{30}O_2$: C, 80.2; H, 9.6. Found: C, 80.1; H, 9.5.

The acidic fraction yielded some unchanged diketo acid.

**Oxidation of Diacetate of Dihydropseudosarsasapogenin.** (a) **At 90°.**—To a solution of 4 g. of dihydropseudosarsasapogenin diacetate in 100 cc. of acetic acid heated at 90° was added with stirring over a course of one hour 8 g. of chromic anhydride in 40 cc. of 80% acetic acid. The mixture was heated for an additional hour after which ethanol was added and the mixture evaporated *in vacuo* to a volume of about 75 cc. Water was added and the precipitated solids taken up in ether. The ethereal solution was washed with water and 3% sodium hydroxide. The aqueous alkaline layer was heated on the steam-bath for twenty minutes and the acids precipitated with hydrochloric acid. The acidic product was crystallized from chloroform as white crystals, m. p. 220–223°. This gave no depression with an authentic sample of 3-hydroxy-*etio*-bilianic acid, m. p. 220–222°. The yield was 1.4 g.

*Anal.* Calcd. for $C_{19}H_{30}O_5$: C, 67.4; H, 8.9. Found: C, 67.3; H, 8.8.

Hydrolysis of the "neutral fraction" gave only additional amounts of the above bilianic acid. There was no noticeable neutral material.

(b) **At Room Temperature.**—To a solution of 2 g. of dihydropseudosarsasapogenin diacetate in 100 cc. of acetic acid was added 2 g. of chromic anhydride in 20 cc. of 80% acetic acid. After standing at 25–28° for two hours, water was added and the precipitated solid taken up in ether. The ethereal solution was washed with water and 3% sodium hydroxide solution. The acidic fraction was hydrolyzed and worked up as under (a). The product crystallized from chloroform as small white crystals, m. p. 219–222°. This gave no depression with a sample of 3-hydroxy-*etio*-bilianic acid, m. p. 220–222°.

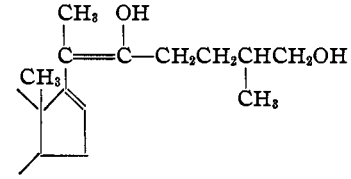
The neutral fraction was crystallized from aqueous methanol to give white plates, m. p. 143–145°. This gave no depression with a sample of pregnenol-3-($\beta$)-one-20 acetate, m. p. 144–146°.

*Anal.* Calcd. for $C_{23}H_{34}O_3$: C, 77.0; H, 9.6. Found: C, 76.7; H, 9.4.

When the reaction was carried out below 20° the only neutral product which could be isolated (after alkaline hydrolysis) was dihydropseudosarsasapogenin.

## Summary

Evidence has been presented indicating that pseudosarsasapogenin probably has the structure (or one of its equivalents)





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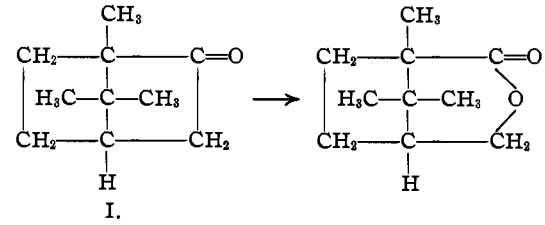
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

# Sterols. XC. Oxidation Products of Sarsasapogenin. Pregnanetriol-3,16,20

BY RUSSELL E. MARKER, EWALD ROHRMANN, HARRY M. CROOKS, EUGENE L. WITTLE, ELDON M. JONES AND D. L. TURNER

In a recent publication the conversion of sarsasapogenin to pregnane derivatives was described.[1] This degradation involved the isomerization of sarsasapogenin to pseudosarsasapogenin, the oxidation of this substance to $\Delta^{16,17}$-pregnenedione-3,20 and the subsequent reduction of this to pregnanedione-3,20 and the various pregnanediols.

The fact that sarsasapogenin (III) appears to have a potential ketone group which is very reactive in the presence of acids[2] suggested a method of directly converting the substance to a pregnane derivative in one step, namely, by a persulfate oxidation. It is well known that persulfates in the presence of sulfuric acid readily react with polycyclic ketones to yield lactones. A typical example of this type of oxidation is the conversion of camphor (I) to $\alpha$-campholide (II).[3] Ruzicka and Stoll[4] carried out similar oxidations in a lig-



I.

(1) Marker and Rohrmann, THIS JOURNAL, **62**, 518 (1940).
(2) Marker and Rohrmann, *ibid.*, **61**, 846 (1939).
(3) Baeyer and Villiger, *Ber.*, **32**, 3630 (1899).
(4) Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).