

Anal. Calcd. for $C_{27}H_{42}O_3$: C, 78.2; H, 10.2. Found: C, 78.5; H, 10.2.

Summary

The preparation of $\Delta^{4,5}$ -bromosarsasapogenone is described.

$\Delta^{4,5}$ -Bromosarsasapogenone upon reduction with sodium and ethanol yields neotigogenin, indicating that tigogenin, chlorogenin and diosgenin differ from sarsasapogenin in the side chain configurations.

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

Sterols. XCIII. *epi*-Pseudosarsasapogenin, Pseudosarsasapogenone and Pseudo-chlorogenin

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In continuation of our study of the pseudosapogenins^{1,2,3,4} we have extended the acetic anhydride isomerization to *epi*-sarsasapogenin, sarsasapogenone, isosarsasapogenin and chlorogenin. All of these substances are thus isomerized to give pseudo compounds.

As in the case with pseudosarsasapogenin³ both *epi*-pseudosarsasapogenin and pseudo-chlorogenin take up a mole of hydrogen in the presence of Adams catalyst to yield dihydropseudosapogenins. Dihydropseudo-chlorogenin forms a triacetate and *epi*-dihydropseudosarsasapogenin a di-*p*-nitrobenzoate. Pseudosarsasapogenone forms a mono-semicarbazone.

As would be expected from the previous results with pseudosarsasapogenin^{1,2,3} both *epi*-pseudosarsasapogenin and pseudosarsasapogenone yield $\Delta^{16,17}$ -pregnenedione-3,20 on mild oxidation with chromic anhydride.

From the suggested structures of sarsasapogenin⁵ and isosarsasapogenin⁵ one might expect these substances to yield the same pseudo compound, which was found to be the case. It is a significant fact that dihydrosarsasapogenin⁵ was unaffected by treatment with acetic anhydride.

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Experimental Part⁶

Reduction of Sarsasapogenone with Sodium and Ethanol.—To a boiling solution of 6 g. of sarsasapogenone in 800 cc. of absolute ethanol was added 25 g. of sodium over a period of two hours. Water was added and the precipi-

tated solid taken up in ether, washed with water and crystallized from acetone as white needles, m. p. 205–207°, yield 5.1 g. This gave no depression with a sample of *epi*-sarsasapogenin, m. p. 205–207°.

With hot acetic anhydride the product gave an acetate which crystallized from acetone as white plates, m. p. 191–193°.

Anal. Calcd. for $C_{29}H_{46}O_4$: C, 75.9; H, 10.1. Found: C, 75.8; H, 10.0.

***epi*-Pseudosarsasapogenin.**—A mixture of 2 g. of *epi*-sarsasapogenin acetate and 20 cc. of acetic anhydride was heated at 200° for ten hours in a sealed tube. The acetic anhydride was evaporated *in vacuo* and the residue hydrolyzed with hot ethanolic potassium hydroxide. The neutral fraction was crystallized from acetone as white needles, m. p. 211–213°. This gave a large depression with both *epi*-sarsasapogenin, m. p. 205–207°, and sarsasapogenin, m. p. 199–201°.

Anal. Calcd. for $C_{27}H_{44}O_3$: C, 77.8; H, 10.6. Found: C, 77.6; H, 10.6.

***epi*-Dihydropseudosarsasapogenin.**—A mixture of 1.5 g. of *epi*-pseudosarsasapogenin, 1 g. of Adams catalyst and 150 cc. of acetic acid was shaken with hydrogen at 3 atm. pressure at room temperature for seventeen hours. After removal of the catalyst, concentration *in vacuo* gave a residue which was saponified for five minutes with ethanolic potassium hydroxide. The product was crystallized from acetone to give white needles, m. p. 135–137°.

Anal. Calcd. for $C_{27}H_{46}O_3$: C, 77.4; H, 11.1. Found: C, 77.3; H, 11.0.

With *p*-nitrobenzoyl chloride in pyridine at 60° the product gave a di-*p*-nitrobenzoate which crystallized from acetone as white needles, m. p. 207–209°.

Anal. Calcd. for $C_{41}H_{52}O_2N_2$: C, 68.7; H, 7.3. Found: C, 68.6; H, 7.3.

$\Delta^{16,17}$ -Pregnenedione-3,20 from *epi*-Pseudosarsasapogenin.—To a solution of 100 mg. of *epi*-pseudosarsasapogenin in 10 cc. of acetic acid was added a solution of 300 mg. of chromic anhydride in 8 cc. of 80% acetic acid. After standing at room temperature for one hour, water was added and the precipitate taken up in ether and washed free from acids with a solution of sodium hydroxide. The neutral fraction crystallized from acetone as white

(1) Marker and Rohrmann, *THIS JOURNAL*, **61**, 3592 (1939).

(2) Marker and Rohrmann, *ibid.*, **62**, 518 (1940).

(3) Marker and Rohrmann, *ibid.*, **62**, 521 (1940).

(4) Marker and Rohrmann, *ibid.*, **62**, 647 (1940).

(5) Marker and Rohrmann, *ibid.*, **61**, 846 (1939).

(6) Microanalyses by Dr. John R. Adam, Jr., of this Laboratory.

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, 79.9; H, 9.5.

Pseudosarsasapogenone.—A mixture of 4 g. of sarsasapogenone and 30 cc. of acetic anhydride was heated in a sealed tube at 200° for ten hours. The product was worked up as described for *epi*-pseudosarsasapogenin. The neutral fraction after treatment with Norite in methanol was crystallized from aqueous acetone to give white needles, m. p. 165–166°.

Anal. Calcd. for $C_{27}H_{42}O_3$: C, 78.2; H, 10.2. Found: C, 78.2; H, 10.3.

With semicarbazide acetate under the usual conditions the product gave a semicarbazone which was crystallized from aqueous ethanol, m. p. 215–216°, dec.

Anal. Calcd. for $C_{25}H_{40}O_3N_3$: C, 71.3; H, 9.6. Found: C, 71.1; H, 9.5.

$\Delta^{16,17}$ -Pregnenedione-3,20 from Pseudosarsasapogenone.—To a solution of 1.5 g. of pseudosarsasapogenin in 50 cc. of acetic acid was added a solution of 1.5 g. of chromic anhydride in 25 cc. of 80% acetic acid. After standing at room temperature for ninety minutes water was added and the precipitated solids taken up in ether and freed from acids with 5% sodium hydroxide. The neutral fraction 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°.

Reaction of Isosarsasapogenin with Acetic Anhydride.—A mixture of 3.3 g. of isosarsasapogenin acetate, m. p. 149–151°, and 25 cc. of acetic anhydride was heated at 195° for nine hours and worked up as described in previous reactions. The neutral fraction was crystallized from acetone to give 1.7 g. of fine white needles, m. p. 169–172°. This gave no depression with a sample of pseudosarsasapogenin.

Dihydrosarsasapogenin when treated with acetic anhydride as in previous experiments was recovered unchanged.

Pseudochlorogenin.—A mixture of 2.5 g. of chlorogenin and 30 cc. of acetic anhydride was heated at 200° for ten hours. The acetic anhydride was evaporated *in vacuo*

and the non-crystalline residue hydrolyzed with hot ethanolic potassium hydroxide. Small crystals which separated from the saponification mixture were collected and washed well with ethanol. The product was recrystallized from methanol in a Soxhlet extractor to give a product of m. p. 268–270°, yield 1.4 g. This gave a depression of 30° with a sample of chlorogenin, m. p. 265–268°. The substance is very sparingly soluble in nearly all solvents.

Anal. Calcd. for $C_{27}H_{44}O_4$: C, 74.9; H, 10.2. Found: C, 74.5; H, 10.2.

Dihydropseudochlorogenin.—A mixture of 1 g. of pseudochlorogenin, 300 cc. of absolute ethanol, 50 cc. of acetic acid and 800 mg. of Adams catalyst was shaken at 3 atm. pressure of hydrogen at room temperature for twenty hours. Crystalline material had separated at the end of this time. This was dissolved by the addition of 75 cc. of hot acetic acid and the catalyst filtered. The filtrate was evaporated to a volume of 125 cc., diluted with water and the precipitated solid taken up in chloroform and crystallized from methanol as fine white needles, m. p. 269–272°. This gave a 20° depression with the starting material. It also gave a large depression with chlorogenin.

Anal. Calcd. for $C_{27}H_{46}O_4$: C, 74.6; H, 10.7. Found: C, 74.8; H, 10.7.

With boiling acetic anhydride this yielded a triacetate which crystallized from aqueous acetone as fine white needles, m. p. 149–152°, and gave a 20° depression with a sample of chlorogenin diacetate, m. p. 149–151°.

Anal. Calcd. for $C_{33}H_{52}O_7$: C, 70.7; H, 9.35. Found: C, 70.3; H, 9.2.

Summary

epi-Pseudosarsasapogenin and pseudosarsasapogenone have been prepared. Oxidation of these products with chromic anhydride yields $\Delta^{16,17}$ -pregnenedione-3,20.

Isosarsasapogenin reacts with acetic anhydride to give pseudosarsasapogenin.

Pseudochlorogenin has been prepared.

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