plants of *Maguey cacaya* and their structures determined. Old plants gave manogenin, gitogenin, chlorogenin and tigogenin.

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[CONTRIBUTION FROM THE LABORATORY OF BOTANICA-MEX., S. A.]

Steroidal Sapogenins. No. 170. The Position of the Double Bond in Yuccagenin and Kammogenin

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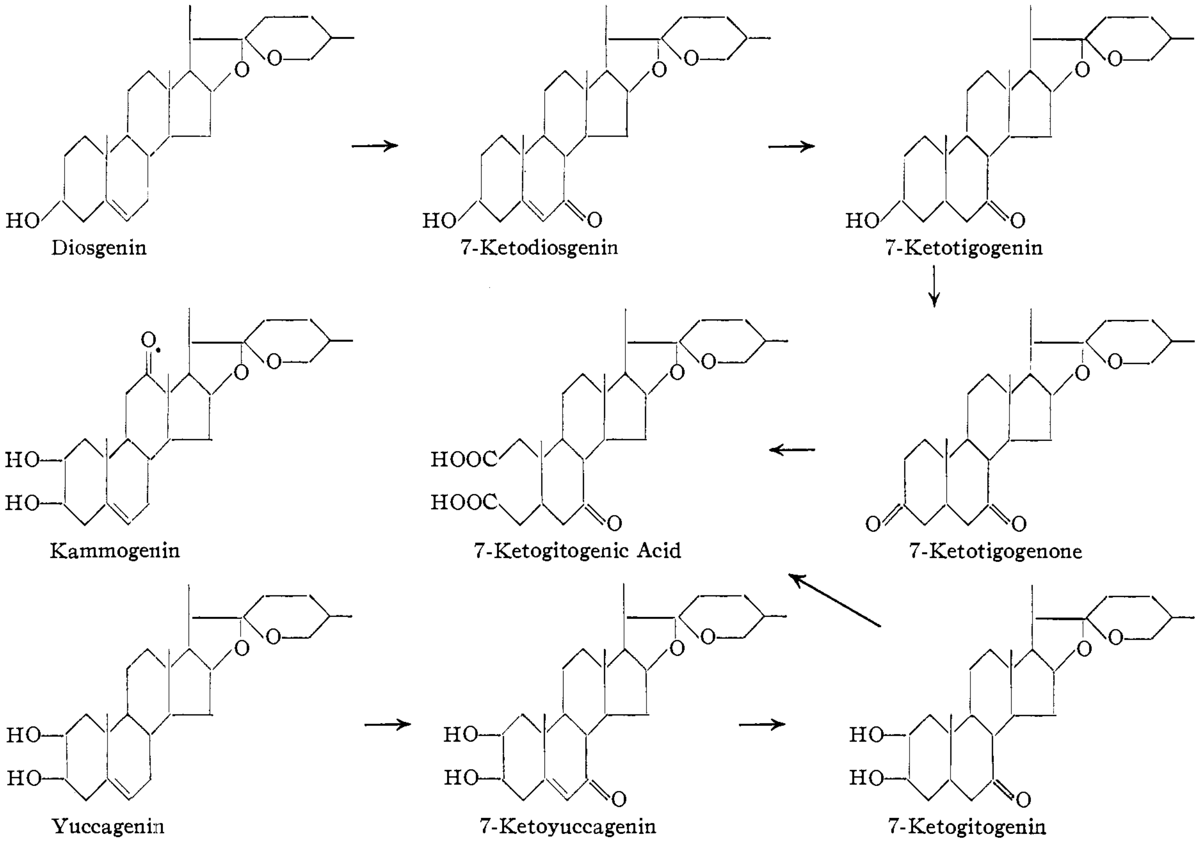
Reduction of the ketone group of kammogenin gives yuccagenin,[2] both of which compounds have been isolated as naturally occurring steroidal sapogenins. The position of the double bond in these compounds is shown by the reactions



Oxidation of diosgenin acetate gave 7-ketodiosgenin acetate[3] which upon reduction with palladium catalyst gave 7-ketotigogenin. Mild oxidation of the latter gave 7-ketotigogenone, which upon further oxidation gave 7-ketogitogenic acid.

Likewise, oxidation of yuccagenin diacetate gave 7-ketoyuccagenin diacetate, which upon reduction and hydrolysis gave 7-ketogitogenin. Oxidation of the 7-ketogitogenin gave 7-ketogitogenic acid which was identical with the product prepared from diosgenin. As the oxidation produces a ketone group adjacent to the double bond the only position that this can have is identical with that in diosgenin or the 5,6-position in the molecule.

The ketonic steroidal sapogenins, manogenin, hecogenin, kammogenin, etc., contain the ketone group in the same position in the molecule.[2] Oxidation of hecogenin gave hecogenone which is not identical with 7-ketotigogenone, nor with 6-ketotigogenone (chlorogenone). This furnishes direct proof that the ketonic group in these sapogenins is not in the 6 or 7 positions in the molecule. As a further proof, oxidation of manogenin or hecogenin gives hecogenic acid with cleavage at the 2,3-position. This acid is not identical with either 6-ketogitogenic acid (chlorogenonic acid) or with 7-ketogitogenic acid.

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[1] Present address: Hotel Geneve, Mexico City.

[2] Marker and Lopez, THIS JOURNAL, **69**, 2375 (1947).

[3] Marker and Turner, *ibid.*, **63**, 767 (1941).

Experimental Part

Hecogenone.—To a solution of 1 g. of hecogenin in 250 cc. of acetic acid was added a mixture of 1 g. of chromic anhydride in 50 cc. of 80% acetic acid at room temperature. After standing for thirty minutes, water was added and the product was extracted with ether. The solvent was removed to a small volume and the product was cooled in a refrigerator for crystallization. It was recrystallized from ether; m. p. 240°. A mixture with chlorogenone, m. p. 237° melted 227–230°.

Anal. Calcd. for $C_{27}H_{40}O_4$: C, 75.7; H, 9.4. Found: C, 75.5; H, 9.4.

Hecogenic Acid from Hecogenone.—To a solution of 5 g. of hecogenone in 250 cc. of glacial acetic acid was added a solution of 4 g. of chromic anhydride in 40 cc. of 80% acetic acid. The mixture was heated to 50° for three hours, water was added and the product was extracted with ether. The ethereal solution was washed well with water, followed by alkali. The alkaline solution was acidified with hydrochloric acid and extracted with ether. Upon evaporation of the solvent to a small volume and cooling the product crystallized, m. p. 268° dec.

Anal. Calcd. for $C_{27}H_{40}O_7$: C, 68.0; H, 8.5. Found: C, 68.2; H, 8.7.

7-Ketotigogenin.—A solution of 5 g. of 7-ketodiosgenin acetate[1] in 500 cc. of ether was shaken with 5 g. of palladium–barium sulfate catalyst and hydrogen at three atm. for one hour. The solution was filtered and concentrated to a small volume. Upon standing the product crystallized. It was recrystallized from ether, m. p. 218°; yield 4.0 g. A mixture with hecogenin acetate melted 210–214°.

Anal. Calcd. for $C_{29}H_{44}O_5$: C, 73.7; H, 9.4. Found: C, 73.9; H, 9.6.

Hydrolysis of the above acetate with alcoholic potassium hydroxide gave 7-ketotigogenin, which was crystallized from ether, m. p. 216°.

Anal Calcd. for $C_{27}H_{42}O_4$: C, 75.3; H, 9.8 Found: C, 75.0; H, 10.0.

7-Ketotigogenone—To a solution of 1 g. of 7-ketotigogenin in 200 cc. of acetic acid was added 1 g. of chromic anhydride in 50 cc. of 90% acetic acid. The mixture was allowed to stand at room temperature for thirty minutes, water was added and the product was extracted with ether. The ethereal solution was washed with water and with sodium carbonate solution. Upon evaporation of the ether the product crystallized. It was recrystallized from ether, m. p. 242°. A mixture with hecogenone, 240°, melted 215–220°; a mixture with chlorogenone, 237°, melted 225–230°.

Anal. Calcd. for $C_{27}H_{40}O_4$: C, 75.7; H, 9.4. Found: C, 75.8; H, 9.3.

7-Ketogitogenic Acid from 7-Ketotigogenin.—To a solution of 5 g. of 7-ketotigogenin in 500 cc. of glacial acetic acid was added a solution of 5 g. of chromic anhydride in 50 cc. of 90% acetic acid. The mixture was kept at 55° for two hours. The product was extracted with ether and washed well with water and with sodium hydroxide solution. The alkaline solution was acidified with hydrochloric acid and extracted with ether. The product was crystallized from ether, m. p. 294° dec.; mixing with hecogenic acid gave a depression to 252–257° dec.

Anal. Calcd. for $C_{27}H_{40}O_7$: C, 68.0; H, 8.5. Found: C, 67.9; H, 8.7.

7-Ketoyuccagenin Diacetate.—To a solution of 10 g. of yuccagenin diacetate in 500 cc. of acetic acid with stirring at 55°, was slowly added a solution of 7 g. of chromic anhydride in 100 cc. of 90% acetic acid over a period of one hour. The product was stirred for an additional three hours, and then stirred for fifteen minutes with 10 g. of zinc dust. The solution was filtered and the solvent was removed *in vacuo*. The residue was extracted with ether and the ethereal solution was washed with water and with sodium hydroxide solution. The solvent was removed and the residue was crystallized from methanol, m. p. 240°. A mixture with kammogenin diacetate, 260°, melted at 228–232°.

Anal. Calcd. for $C_{31}H_{44}O_7$: C, 70.4; H, 8.4. Found: C, 70.2; H, 8.6.

7-Ketogitogenin.—A solution of 3 g. of 7-ketoyuccagenin diacetate in 500 cc. of ether was shaken with 5 g. of palladium–barium sulfate catalyst and hydrogen at 40 pounds pressure for one hour. The solution was filtered and the ether was evaporated to a small volume. The diacetate was recrystallized from ether, m. p. 282°.

Anal. Calcd. for $C_{31}H_{46}O_7$: C, 70.2; H, 8.7. Found: C, 70.4; H, 8.8.

A solution of 1 g. of the above diacetate was hydrolyzed with alcoholic potassium hydroxide. The product was crystallized from ether, m. p. 262°.

Anal. Calcd. for $C_{27}H_{42}O_5$: C, 72.6; H, 9.5. Found: C, 72.9; H, 9.8.

7-Ketogitogenic Acid from 7-Ketogitogenin.—To a solution of 1 g. of 7-ketogitogenin in 100 cc. of glacial acetic acid was added a solution of 1 g. of chromic anhydride in 25 cc. of 90% acetic acid. The reaction mixture was allowed to stand at room temperature for thirty minutes, water was added and the product was extracted with ether. The solution was washed well with water and finally with sodium hydroxide solution. The alkaline solution was acidified and the crude acid was crystallized from ether, m. p. 295° dec. A mixture with 7-ketogitogenic acid prepared from 7-ketotigogenin gave no depression.

Anal. Calcd. for $C_{27}H_{40}O_7$: C, 68.0; H, 8.5. Found: C, 68.3; H, 8.6.

Summary

The double bond in kammogenin and yuccagenin has been shown to be in the 5,6-position in the molecule.

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