for six hours, allowed to cool down, the crystals filtered and recrystallized from ether–petroleum ether, m. p. 219°. A mixed melting point with the ester showed no depression. Attempted saponification of the acetyl compound with alcoholic potassium hydroxide gave no crystalline product.

Summary

A dicarboxylic acid, which yields a lactone on heating above its melting point, has been isolated from the bark of the root of *Ceanothus Americanus*. From it a crystalline lactone and dimethyl ester, and from the latter a crystalline acetyl derivative, have been prepared. Examination of the acid and these derivatives points to the formula, $C_{29}H_{44}O_5$ for the former, which it is proposed to call ceanothic acid.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF SCHERING CORPORATION]

Preparation of *epi-allo*-Pregnanol-3-one-20

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Marker, *et al.*[1] isolated *epi-allo*-pregnanol-3-one-20 from the urine of pregnant women and have prepared this substance both from 3-chloro-*allo*-cholanic acid[2] and from *allo*-pregnanediol.[3] We have prepared this substance from pregnenolone, which is now made on a technical scale. Thus larger amounts of *epi-allo*-pregnanolone may be secured easily. Our substance had a higher melting point and lower rotation than that originally reported by Marker and co-workers.[1]

Experimental

Preparation of *allo*-Pregnanedione.—Pregnenolone was reduced with platinum oxide and hydrogen in alcoholic solution to *allo*-pregnanolone, and this oxidized with chromic acid in acetic acid solution to *allo*-pregnanedione in the known manner.[4]

Preparation of *epi-allo*-Pregnanolone.—Platinum oxide (0.5 g.) in 15 cc. of acetic acid was reduced to platinum black, a hot solution of 6.75 g. of *allo*-pregnanedione in 40 cc. of acetic acid and 0.55 cc. of 48% hydrobromic acid were added, and the whole was shaken with hydrogen, while being heated. During one and one-half hours one mol of hydrogen had been taken up. After filtering from the catalyst, the solution was poured into water and taken up in ether, and the extract was washed with sodium hydroxide and water. After the ether had been distilled, the residue was boiled with 25 cc. of 2% potassium hydroxide in methanol for two hours to hydrolyze any acetate which was formed during reduction, and then poured into water. The white precipitate was filtered off, washed with water, dried, and dissolved in 300 cc. of 90% alcohol, and a solution of 10 g. of digitonin in 1 l. of 90% alcohol was added. After standing for one-half hour a precipitate settled, and this was collected, washed thoroughly with alcohol, and dried; yield, 7.8 g. (corresponding to 1.6 g. of *allo*-pregnanolone). The alcoholic solution was evaporated to a very small volume, mixed with water, and the *epi-allo*-pregnanolone extracted with ether. The undissolved digitonin was filtered off and washed thoroughly with ether; dry weight, 3.8 g. The ether was washed twice with water, then evaporated. On crystallizing the crude material from alcohol, 3 g. of crude *epi-allo*-pregnanolone was obtained, having a melting point of 147–152°, $[\alpha]D$ +58° in absolute ethanol. After several recrystallizations, the melting point was constant at 176–178°;[5] $[\alpha]D$ +87.7° in absolute ethanol.

Anal. Calcd. for $C_{21}H_{34}O_2$: C, 79.18; H, 10.77. Found: C, 78.92; H, 10.77.

Acetate of *epi-allo*-Pregnanolone.—*epi-allo*-Pregnanolone (100 mg.) was boiled with acetic anhydride (2 cc.) for thirty minutes, anhydride was then evaporated *in vacuo*, and the product recrystallized several times from petroleum ether and aqueous alcohol. The melting point was 141–142°, its rotation $[\alpha]^{22}D$ + 94.5° in absolute ethanol.

Anal. Calcd. for $C_{23}H_{36}O_3$: C, 76.61; H, 10.07. Found: C, 76.72; H, 10.01.

Splitting of the Digitonide.—The 7.8 g. of digitonide was dissolved in 125 cc. of dried pyridine and, while stirring, 1.3 l. of dry ether was dropped in during one hour. The digitonin was filtered off (dry weight 6 g.), and the filtrate was slightly acidified, washed, dried and the ether evaporated. The residue was *allo*-pregnanolone[6] (1.5 g.), m. p. 178–185°. After several recrystallizations the substance melted at 194°; $[\alpha]^{22}D$ +90.5° in absolute ethanol.

Acetate of *allo*-Pregnanolone.—*allo*-Pregnanolone, acetylated in the usual manner, gave material melting at 144° (uncorr.); $[\alpha]^{22}D$ +79.8° in absolute ethanol.

Anal. Calcd. for $C_{23}H_{36}O_3$: C, 76.61; H, 10.07. Found: C, 76.71; H, 10.11.

Summary

The preparation of *epi-allo*-pregnanol-3-one-20 from pregnenolone is described. *allo*-Pregnanolone was obtained as a by-product.

BLOOMFIELD, N. J. RECEIVED NOVEMBER 16, 1937

(1) Marker, Kamm and McGrew, THIS JOURNAL, **59**, 616 (1937).

(2) Marker, *et al.*, *ibid.*, **59**, 1367 (1937).

(3) Marker, *etal.*, *ibid.*, **59**, 1595 (1937).

(4) A. Butenandt and G. Fleischer, *Ber.*, **68**, 2094 (1935).

(5) We wish to thank Dr. Marker for the kindness of having made a mixed melting point determination of our substance and his own *epi-allo*-pregnanolone. There was no depression. Dr. Marker now finds also the higher melting point for his own preparation.

(6) A. Butenandt and L. Mamoli, *Ber.*, **67**, 1897 (1934).