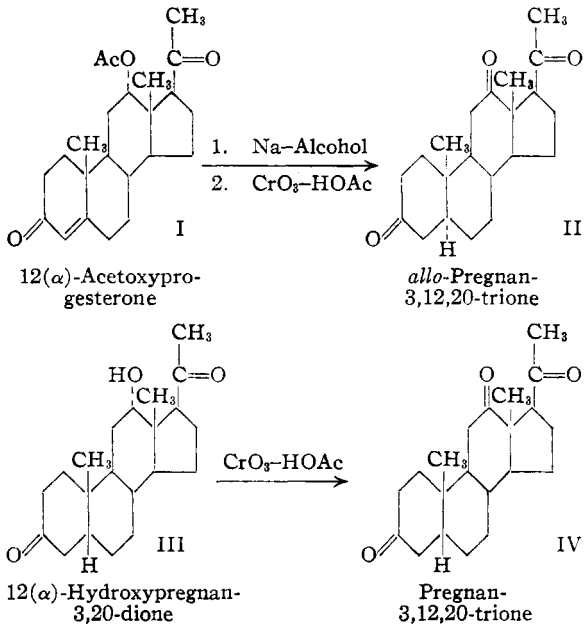

12(α)-Acetoxyprogesterone — *allo*-Pregnan-3,12,20-trione

12(α)-Hydroxypregnan-3,20-dione — Pregnan-3,12,20-trione

to lead to the *allo*-configuration at C-5. Nevertheless, we have prepared the corresponding isomer, pregnan-3,12,20-trione (IV), by the mild oxidation of an authentic sample of 12(α)-hydroxypregnan-3,20-dione (III). It had the following properties: m.p. 204–206°, $[\alpha]^{26}D$ +181°, $[\alpha]^{26}_{5461}$ +225° (chloroform). *Anal.* Calcd. for $C_{21}H_{30}O_3$: C, 76.3; H, 9.2. Found: C, 76.0; H, 9.1. Reichstein and von Arx[5] report for pregnan-3,12,20-trione: m.p. 201–202°; $[\alpha]^{17}D$ +182 ± 7, $[\alpha]^{17}_{5461}$ +219 ± 8 (ethanol). A mixture of IV with II showed a melting point depression of 36°. The melting point of each of these compounds was depressed 10–20° by the trione from hecogenin.

Since the properties of *allo*-pregnan-3,12,20-trione (II) are different from those of the samples derived from hecogenin and botogenin, some doubt must be entertained as to the structures of the degradation products from both of these sapogenins.

We thank Parke, Davis and Company for their help.

(5) Reichstein and von Arx, *Helv. Chim. Acta*, **23**, 747 (1940).

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RECEIVED OCTOBER 10, 1949

SYNTHESES IN THE DIRECTION OF MORPHINE. I. 7-METHOXY- AND 7,8-DIMETHOXY-2-TETRALONE.

Sir:

We wish to report the synthesis of 7,8-dimethoxy-2-tetralone, which may serve as a useful intermediate for elaboration in the direction of morphine and certain of its degradation products,[1] and may open a way for the preparation of physiologically active substances oxygenated at points corresponding to the 3 and 4 positions in morphine. 7-Methoxy-2-tetralone may serve in the syntheses of substances similarly substituted in the 3 position; and is of particular interest in view of the recent report that 3-hydroxymorphinane is a powerful analgesic surpassing morphine in clinical tests[2].

1,2,7-Trimethoxynaphthalene,[3] m.p. 38.5–39.5°, b.p. 133° at 1 mm. (picrate[3], m.p. 113°), gave by reduction[4] with sodium and alcohol, the crystalline ketone, m.p. 76° (*anal.* calcd. for $C_{10}H_8O(OCH_3)_2$: OCH_3, 30.1. Found: OCH_3, 29.5, 29.3), characterized as the semicarbazone, m.p. 191–191.5°, and the 2,4-dinitrophenylhydrazone, m.p. 167° dec. (*anal.* calcd. for $C_{18}H_{18}O_8N_4$: C, 56.0; H, 4.7; N, 14.5. Found: C, 55.7; H, 4.6; N, 15.0, 14.8). The structure of the ketone was shown by oxidation, with alkaline permanganate, to hemipinic acid, identified by its m.p.[6] (177–179°) and by the m.p.[6] (166–167°) and characteristic fluorescence[6] of the pure anhydride.

2,7-Dimethoxynaphthalene similarly[4] gave on reduction 7-methoxy-2-tetralone, m.p. 27–28°, b.p. 124–126° (1.5 mm.); semicarbazone, m.p. 174–176° (*anal.* calcd. for $C_{12}H_{15}O_2N_3$: C, 61.8; H, 6.5. Found: C, 62.1, 62.1; H, 6.4, 6.4); 2,4-dinitrophenylhydrazone m.p. 177–181° (*anal.* calcd. for $C_{17}H_{16}N_4O_5$: C, 57.3; H, 4.5. Found: C, 57.2, 57.5; H, 4.4, 4.6).

(2) Schnider and Grussner, *Helv. Chim. Acta*, **32**, 821 (1939).
(3) Chakravarti and Pasupati, *J. Chem. Soc.*, 1859 (1937).
(4) Cornforth, Cornforth and Robinson, *ibid.*, 689 (1942).
(5) Perkin, *ibid.*, **109**, 922 (1916).
(6) Dobbie and Lauder, *ibid.*, **67**, 19 (1895).

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DEGRADATION OF GLYCOGEN TO ISOMALTOSE

Sir:

Methylation studies[1] have indicated that the glycogen molecule has a highly ramified structure composed of α-D-glucopyranosyl units joined 1,4 with branching at C6 on one out of twelve units. As additional evidence in support of this structure we report the isolation of crystalline 6-α-D-glucopyranosyl-β-D-glucopyranose octaacetate (β-D-isomaltose octaacetate)[2] from an acetylated acid hydrolysate of glycogen.

Animal (rabbit liver) glycogen (5.00 g., $[\alpha]^{25}D$ +200°, *c* 0.92, water) in 2% concentration was hydrolyzed at 100° in 0.05 *N* sulfuric acid for nine hours (degree of hydrolysis *ca.* 75%). After acid neutralization with barium carbonate and ion removal with exchange resins (Amberlite IR-100 and IR-4), the amorphous solid obtained on solvent removal was acetylated with hot acetic anhydride and sodium acetate. The resultant sugar acetate mixture (6.08 g.) was chromatographed[2] on Magnesol–Celite under such developmental conditions that monosaccharides were removed from the column. β-D-Glucose pentaacetate was identified,

(1) W. N. Haworth and E. G. W. Percival, *J. Chem. Soc.*, 2277 (1931); W. N. Haworth, E. L. Hirst and F. Smith, *ibid.*, 1914 (1939).
(2) M. L. Wolfrom, L. W. Georges and I. L. Miller, THIS JOURNAL, **69**, 473 (1947); **71**, 125 (1949).

(1) Fieser and Holmes, THIS JOURNAL, **60**, 2548 (1938); **58**, 2319 (1936); Cahn, *J. Chem. Soc.*, 2565 (1926).