



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°, $[\alpha]^{20D} + 181$, $[\alpha]^{26_{461}} + 225$ ° (chloroform). *Anal.* Calcd. for C₂₁H₃₀O₃: C, 76.3; H, 9.2. Found: C, 76.0; H, 9.1. Reichstein and von Arx² report for pregnan-3,12,20-trione: m.p. 201–202°; $[\alpha]^{17D} + 182 \pm 7$, $[\alpha]^{17_{461}} + 219 \pm 8$ (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

(1) Fieser and Holmes, *THIS JOURNAL*, **60**, 2548 (1938); **58**, 2819 (1936); *Cahn. J. Chem. Soc.*, 2565 (1936).

powerful analgesic surpassing morphine in clinical tests².

1,2,7-Trimethoxynaphthalene,³ m.p. 38.5–39.5°, b.p. 133° at 1 mm. (picrate³, m.p. 113°), gave by reduction⁴ with sodium and alcohol, the crystalline ketone, m.p. 76° (*anal.* calcd. for C₁₀H₈O(OCH₃)₂: OCH₃, 30.1. Found: OCH₃, 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 C₁₈H₁₈O₈N₄: 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 fluorescence⁶ of the pure anhydride.

2,7-Dimethoxynaphthalene similarly⁴ 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 C₁₂H₁₅O₂N₃: 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 C₁₇H₁₈N₄O₅: C, 57.3; H, 4.5. Found: C, 57.2, 57.5; H, 4.4, 4.6).

(2) Schneider 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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RECEIVED OCTOBER 19, 1949

DEGRADATION OF GLYCOGEN TO ISOMALTOSE

Sir:

Methylation studies¹ 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., $[\alpha]^{25D} + 200$, *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 chromatographed² 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*, **60**, 473 (1947); **71**, 125 (1949).