

Chf., $\lambda_{\text{Max}}^{\text{Chf}}$ 5.77, 5.85 μ . Anal. C₂₆H₄₀O₅: C, 72.19; H, 9.32; OCH₃, 14.34. Found: C, 72.21; H, 9.05; OCH₃, 13.99. Thioethyl derivative (VI, RSH-HBr-HOAc), m. p. 67.2–68.5°, $[\alpha]^{22\text{D}} +100^\circ$ Chf. Anal. C₂₇H₄₂O₄S: C, 70.08; H, 9.15; S, 6.93. Found: C, 70.24; H, 9.32; S, 6.76. Desulfuration of VI with Raney nickel and hydrolysis afforded 3 α ,9 α -oxido-11-ketocholanic acid,⁶ m. p. 174.9–175.6°, $[\alpha]^{25\text{D}} +88.1^\circ$ Chf.; no depression in mixed m. p. Wolff-Kishner reduction of III gave $\Delta^9(11)$ -cholenic acid, m. p. 139.4–140.8°, $[\alpha]^{21\text{D}} +40.2^\circ$ Chf., methyl ester,⁷ m. p. 67.4–68.2°, $[\alpha]^{22\text{D}} +42.8^\circ$ Chf.; Clemmensen reduction gave 11-ketocholanic acid, methyl ester,⁷ m. p. 89.4–90.5°, $[\alpha]^{20\text{D}} +48.1^\circ$ An.⁴ In acetic acid over platinum the hemiketal absorbed two moles of hydrogen and afforded two triol esters (V), isolated as the monoacetates. Methyl 3 α -acetoxy-9 α ,11 β -dihydroxycholanate, m. p. 166–167°, $[\alpha]^{20\text{D}} +55.1^\circ$ Chf., $\lambda_{\text{Max}}^{\text{Chf}}$ 2.86, 5.88 μ . Anal. C₂₇H₄₄O₆: C, 69.79; H, 9.54. Found: C, 70.22; H, 9.81. The 3 β -epimer, m. p. 171.2–172.4°, $[\alpha]^{21\text{D}} +33.6^\circ$ Chf., $\lambda_{\text{Max}}^{\text{Chf}}$ 2.86, 5.85 μ . Found: C, 69.99; H, 9.75. Chromic acid oxidation of the triol monoacetates with chromic acid gave the 11-ketones: 3 α , m. p. 149–150.4°, $[\alpha]^{22\text{D}} +83.4^\circ$ Chf. Anal. C₂₇H₄₂O₆: C, 70.10; H, 9.15. Found: C, 70.25; H, 9.16; 3 β , m. p. 134–135.5° and 143.6–144.6°, $[\alpha]^{21\text{D}} +58.2^\circ$ Chf., $\lambda_{\text{Max}}^{\text{Chf}}$ 2.87, 5.89–5.94 μ . Clemmensen reduction of methyl 3 α -acetoxy-9 α -hydroxy-11-ketocholanate, followed by esterification and acetylation gave methyl 3 α -acetoxy-11-ketocholanate,⁸ m. p. 129.4–131.8°, $[\alpha]^{22\text{D}} +59.4 \pm 5^\circ$, not depressed by an authentic sample.

The 9,11-oxide I is at present available only from methyl $\Delta^9(11)$ -lithocholanic acid, obtainable in moderate yield from desoxycholic acid, but a way is now open for utilization of such an intermediate for the synthesis of cortisone and a satisfactory

(6) Turner, Mattox, Engel, McKenzie and Kendall, *J. Biol. Chem.*, **166**, 345 (1946).

(7) Reich and Reichstein, *Helv. Chim. Acta*, **26**, 562 (1943).

(8) Lardon and Reichstein, *ibid.*, **20**, 586 (1943).

method of preparation from other sources is being sought.

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COMPOSITION OF SYNTHETIC LIQUID FUELS. I. PRODUCT DISTRIBUTION AND ANALYSIS OF C₅-C₈ PARAFFIN ISOMERS FROM COBALT CATALYST

Sir:

We wish to call attention to the following diagram which was unfortunately omitted from our recent paper entitled "Composition of Synthetic Liquid Fuels. I. Product Distribution and Analysis of C₅-C₈ Paraffin Isomers from Cobalt Catalyst," THIS JOURNAL, **72**, 1212 (1950).

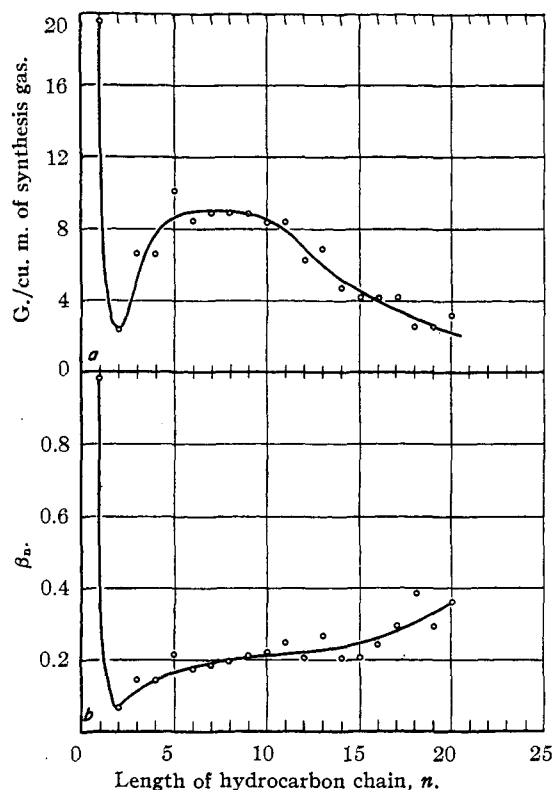


Fig. 1.—Part a is the distribution of hydrocarbon products from atmospheric pressure tests of cobalt catalysts at about 190°C. Part b is a plot of Herington's term β_n against n , where β_n is the probability that a hydrocarbon radical on the surface will appear as product of chain length n rather than grow to higher molecular weight.

These graphs are necessary for a complete understanding of the discussion presented in that paper.

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