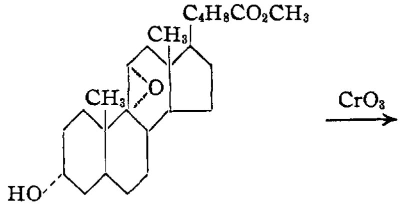

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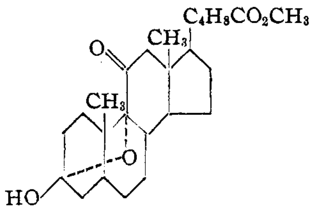

III

Chf., $\lambda_{\text{Max}}^{\text{Chf}}$ 5.77, 5.85μ. *Anal.* $C_{26}H_{40}O_5$: C, 72.19; H, 9.32; OCH_3, 14.34. Found: C, 72.21; H, 9.05; OCH_3, 13.99. Thioethyl derivative (VI, RSH–HBr–HOAc), m. p. 67.2–68.5°, $[\alpha]^{22}\text{D}$ +100° Chf. *Anal.* $C_{27}H_{42}O_4S$: 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 3α,9α-oxido-11-ketocholanic acid,[6] m. p. 174.9–175.6°, $[\alpha]^{25}\text{D}$ +88.1° 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° Chf., methyl ester,[7] m. p. 67.4–68.2°, $[\alpha]^{22}\text{D}$ +42.8° Chf.; Clemmensen reduction gave 11-ketocholanic acid, methyl ester,[7] m. p. 89.4–90.5°, $[\alpha]^{20}\text{D}$ +48.1° 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 3α-acetoxy-9α,11β-dihydroxycholanate, m. p. 166–167°, $[\alpha]^{20}\text{D}$ +55.1° Chf., $\lambda_{\text{Max}}^{\text{Chf}}$ 2.86, 5.88μ. *Anal.* $C_{27}H_{44}O_6$: C, 69.79; H, 9.54. Found: C, 70.22; H, 9.81. The 3β-epimer, m. p. 171.2–172.4°, $[\alpha]^{21}\text{D}$ +33.6° Chf., $\lambda_{\text{Max}}^{\text{Chf}}$ 2.86, 5.85μ. Found: C, 69.99; H, 9.75. Chromic acid oxidation of the triol monoacetates with chromic acid gave the 11-ketones: 3α, m. p. 149–150.4°, $[\alpha]^{22}\text{D}$ +83.4° Chf. *Anal.* $C_{27}H_{42}O_6$: C, 70.10; H, 9.15. Found: C, 70.25; H, 9.16; 3β, m. p. 134–135.5° and 143.6–144.6°, $[\alpha]^{21}\text{D}$ +58.2° Chf., $\lambda_{\text{Max}}^{\text{Chf}}$ 2.87, 5.89–5.94μ. Clemmensen reduction of methyl 3α-acetoxy-9α-hydroxy-11-ketocholanate, followed by esterification and acetylation gave methyl 3α-acetoxy-11-ketocholanate,[8] m. p. 129.4–131.8°, $[\alpha]^{22}\text{D}$ +59.4 ± 5°, not depressed by an authentic sample.

The 9,11-oxide I is at present available only from methyl $\Delta^{9(11)}$-lithocholenate, 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 method of preparation from other sources is being sought.

CONVERSE MEMORIAL LABORATORY LOUIS F. FIESER
HARVARD UNIVERSITY HANS HEYMANN
CAMBRIDGE 38, MASS. SRINIVASA RAJAGOPALAN

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[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).

COMPOSITION OF SYNTHETIC LIQUID FUELS. I. PRODUCT DISTRIBUTION AND ANALYSIS OF C_5–C_8 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 C_5–C_8 Paraffin Isomers from Cobalt Catalyst," THIS JOURNAL, **72**, 1212 (1950).

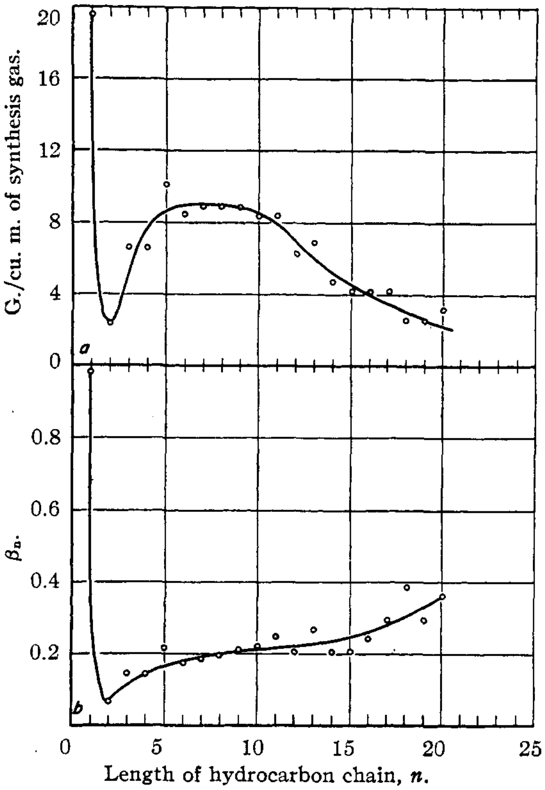

Fig. 1.—Part **a** is the distribution of hydrocarbon products from atmospheric pressure tests of cobalt catalysts at about 190°C. Part **b** is a plot of Herington's term β_n against *n*, where β_n is the probability that a hydrocarbon radical on the surface will appear as product of chain length *n*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

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

CENTRAL EXPERIMENT STATION
BUREAU OF MINES R. A. FRIEDEL
PITTSBURGH, PENNSYLVANIA R. B. ANDERSON

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[1] Manuscript originally received January 12, 1949.