each of the steps leading to the formation of aminobutyric acid from acetaldehyde and animal livers appears to contain enzymes which can catalyze these same reactions. The enzyme reported by Vilenkina[2] should catalyze reactions (1) and Lien and Greenberg[5] have reported conversion of threonine to aminobutyric acid, apparently by reactions (2) and (3) in rat livers. Though this synthetic pathway may not be used by animals it may be of importance in some organisms.

(5) O. G. Lien, Jr., and D. M. Greenberg, *J. Biol. Chem.*, **200**, 367 (1953).

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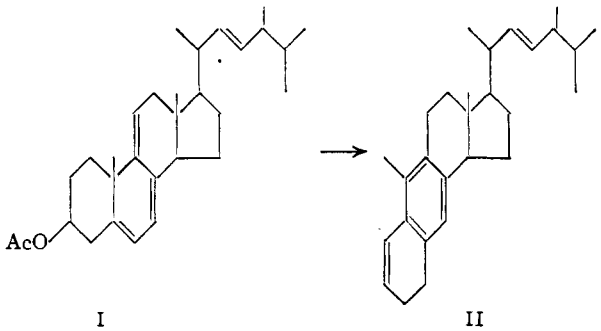
THE REARRANGEMENT OF DEHYDROERGOSTERYL ACETATE TO A *s*-OCTAHYDROANTHRACENE DERIVATIVE

Sir:

On treatment of a chloroform solution of dehydroergosteryl acetate (I) with catalytic amounts of hydrogen chloride at room temperature a skeletal rearrangement of the steroid takes place. The pure product (II) obtained in a yield of about 30% lacks an oxygen function and shows an ultraviolet absorption spectrum characteristic of an aromatic ring with one conjugated double bond, $\lambda_{max.}$ (isooctane) 222, 227, 266, 296, and 308 mμ. (ε 26,100, 27,100, 18,600, 2,760, 2,220, respectively); $\lambda_{max.}$ (CS_2) 968 cm.$^{-1}$; m.p. 105–107°; $[\alpha]^{20}D$ −70° ($CHCl_3$); *Anal.* Calcd. for $C_{28}H_{40}$: C, 89.29; H, 10.70. Found: C, 88.96; H, 10.74. It is proposed that, by the rupture of the C_1–C_{10} bond and reattachment of C_1 to C_6, 1,2,3,4,7,8-hexahydro-3′-(5,6-dimethyl-3-heptenyl-2)-2,10-dimethyl-1,2-cyclopentanthracene (II) is formed. (Positions 7,8 and 3,4 for the conjugated double bond have not been ruled out experimentally.) Kinetic measurements by ultraviolet spectrophotometry show that this rearrangement is first order in steroid and approximately second order (1.85) in hydrogen chloride. The reaction rate constant is equal to 0.146 ± 0.003 liter^2 moles^{-2} sec.$^{-1}$ at 20°.



I II

By catalytic hydrogenation (PtO_2, ethyl acetate–acetic acid) the double bond in the side chain and the conjugated olefinic double bond are saturated to give the corresponding *s*-octahydroanthracene derivative (III), m.p. 106–107°; $[\alpha]^{20}D$ +21° ($CHCl_3$); $\lambda_{max.}$ (isoöctane) 273, 278 and 282 mμ (ε 670, 550 and 695 respectively), $\lambda_{min.}$ 247 mμ (ε 95); *Anal.* Calcd. for $C_{28}H_{44}$: C, 88.34; H, 11.65. Found: C, 88.42; H, 11.47. Oxidation of II with 70% nitric acid and subsequent esterification of the resulting compound with diazomethane leads to 1-methyl-2,3,5,6-tetracarbomethoxybenzene (IV), m.p. 121–123°; *Anal.* Calcd. for $C_{15}H_{16}O_8$: C, 55.55; H, 4.97. Found: C, 55.43; H, 5.06. The structure of IV was confirmed by its comparison with a sample obtained by an analogous oxidation of 9-methyl-*s*-octahydroanthracene. Compound IV, incidentally, was found to be identical with the methyl tetracarbomethoxybenzene obtainable by the nitric acid oxidation of various steroids.[1] From the analogous oxidation of 9-methyl-*s*-octahydrophenanthrene we obtained pentacarbomethoxybenzene instead of the expected, unknown 1-methyl-2,3,4,5-tetracarbomethoxybenzene (V).

We are considering the possibility that this type of facile rearrangement, *i.e.*, the transformation of steroids into anthracene derivatives, is involved in spontaneous carcinogenesis.

(1) (a) H. H. Inhoffen, *Ann.*, **494**, 122 (1932); (b) A. Windaus and G. Zühlsdorff, *ibid.*, **536**, 204 (1938); (c) M. Müller, *Z. physiol. Chem.*, **233**, 223 (1935).

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ENZYMES OF THE FATTY ACID CYCLE. II. ETHYLENE REDUCTASE[1]

Sirs:

We have recently reported on the identification and isolation of β-keto thiolase and β-keto reductase.[2] Similar results have been obtained in other laboratories.[3,4,5] Through the combined action of these two enzymes the cell elongates the chain of the CoA thioester derivatives of fatty acids by the addition of a C_2 carbon chain from acetyl-S-CoA forming the corresponding β-hydroxy-CoA-thioester derivatives. In this way β-hydroxy-butyryl-S-CoA is formed from acetyl-S-CoA (Reactions 1 and 2).

$$2CH_3—CO—S—CoA \rightleftharpoons CH_3—CO—CH_2—CO—S—CoA + HS—CoA \quad (1)$$

$$CH_3—CO—CH_2—CO—S—CoA + DPNH + H^+ \rightleftharpoons CH_3—CHOH—CH_2—CO—S—CoA + DPN^+ \quad (2)$$

$$CH_3—CHOH—CH_2—CO—S—CoA \rightleftharpoons CH_3—CH=CH—CO—S—CoA + H_2O \quad (3)$$

$$\text{Leuco-safranine} + CH_3—CH=CH—CO—S—CoA \longrightarrow \text{Safranine} + CH_3—CH_2—CH_2—CO—S—CoA \quad (4)$$

(1) This work was supported in part by a grant from the Research Foundation of Germany. The following abbreviations are used: Coenzyme A, CoA–SH; acyl coenzyme A derivatives, acyl-S-CoA; oxidized and reduced diphosphopyridine nucleotide, DPN^+ and DPNH; reduced triphosphopyridine nucleotide, TPNH; flavinadenine dinucleotide, FAD; micromoles, μM.

(2) F. Lynen, L. Wessely, O. Wieland and L. Rueff, *Angew. Chem.*, **64**, 687 (1952).

(3) J. R. Stern, M. J. Coon and A. del Campillo, THIS JOURNAL, **75**, 1517 (1953).

(4) A. L. Lehninger and G. D. Greville, *ibid.*, **75**, 1515 (1953).

(5) D. E. Green and S. Mii, *Federation Proc.*, **12**, 211 (1953).