Conversion of V to VI.—Desoxysmilagenin (V), 10.0 g., was dissolved in 1 liter of refluxing 95% alcohol to which was added a solution of 670 ml. of 95% ethanol and 300 ml. of concentrated hydrochloric acid. After refluxing 72 hours an additional 135 ml. of hydrochloric acid was added followed by 24 hours further heating. The usual work-up and chromatography on Florosil gave 5.57 g. of V and 1.0 g. of VI, the two components being cleanly separated as described previously.

Conversion of VI to V.—Desoxysarsasapogenin (VI) was relatively insoluble in 85% ethanol. In one experiment carried out using this solvent in the usual manner the conversion of VI to V was only 50%. Use of isopropyl alcohol overcame solubility problems. Thus, 0.6 g. of VI in 120 ml. of refluxing isopropyl alcohol to which were added 130 ml. of isopropyl alcohol and 45 ml. of concentrated hydrochloric acid was refluxed 72 hours. Aliquots were removed at various time intervals. The proportion of desoxysmilagenin (V) and of desoxysarsasapogenin (VI) was calculated from the ratios of the corrected absorbancies 900 $cm.^{-1}$/920 $cm.^{-1}$. A standard curve was prepared from known mixtures of V and VI from which the proportions present in various unknown samples could be calculated. A similar experiment starting with VI was carried out under anhydrous conditions. VI, 0.75 g., was refluxed in 250 ml. of absolute ethanol containing dry hydrogen chloride (2 *N*). The results for both the aqueous and anhydrous experiments are shown below.

Time, hr.	Desoxysarsasapogenin, % Aqueous	Anhyd.	Time, hr.	Desoxysarsasapogenin, % Aqueous	Anhyd.
0.5	100	100	12	..	40
1	95	95	24	20	30
3	85	75	48	10	30
5	70	60	72	5	25
8	50	55	120	5	..

Acknowledgment.—We should like to acknowledge the assistance of H. W. Jones, R. F. Mininger, C. S. Fenske and D. R. Killen in various phases of this investigation. Infrared spectroscopy was under the direction of C. R. Eddy. The plant samples from which various sapogenins were prepared were collected by D. S. Correll and H. S. Gentry, Plant Introduction Section, Horticultural Crops Research Branch, Beltsville, Maryland.

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[CONTRIBUTION FROM THE PHARMACEUTICAL INSTITUTE, MEDICAL FACULTY, UNIVERSITY OF KYUSHU]

Cholesterol and Related Compounds. III. Conversion of Phenanthrene to Anthracene Ring System in $\Delta^{5,7}$-, $\Delta^{6,8(9)}$- and $\Delta^{5,8(9)}$-Cholestadienol

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RECEIVED JULY 7, 1954

The irradiation of alcoholic solutions of 7-dehydrocholesterol (I), isodehydrocholesterol (II) and $\Delta^{5,8(9)}$-cholestadienol (III) with mercuric acetate and *p*-toluenesulfonic acid, in a nitrogen stream, yielded the same substance IV in each case; the ultraviolet absorption spectrum of IV showed the bands of a benzenoid type compound. The structure of IV was established by nitric acid oxidation to methylpyromellitic acid and by selenium dehydrogenation which yielded a hydrocarbon VI. The latter showed the ultraviolet absorption curve typical of anthracene hydrocarbons.

When 7-dehydrocholesterol and ergosterol are irradiated with visible light, peroxide is formed in the presence of oxygen and bis-(ergostadienol) in the absence of oxygen.[2] In the present experiments, the irradiation of mixtures of a sterol (7-dehydrocholesterol (I), isodehydrocholesterol (II) or $\Delta^{5,8(9)}$-cholestadienol (III)[3]) *p*-toluenesulfonic acid and mercuric acetate with a mercury and an incandescent lamp, in the absence of air, yielded a common product (IV) with a cyclopentanoanthracene nucleus. This product (m.p. 153–154°) is a trienol with the empirical formula $C_{27}H_{42}O$; the ultraviolet absorption data suggest that it has a benzenoid structure.

Crystals of m.p. 153–154° also were obtained by the irradiation of III (in acetic anhydride and *p*-toluenesulfonic acid) with sunlight under somewhat different conditions in the absence of mercuric acetate. This method is superior to the general procedure described above in that chromatography is unnecessary for the purification of the desired product (IV) which precipitates as the acetate and is pure after one recrystallization. However, we found that this reaction proceeds satisfactorily only in the summer in the presence of strong sunlight.

When the common product (m.p. 153–154°) was oxidized with nitric acid and the resulting acid methylated, an ester (V) was obtained which was identical with the tetramethyl methylpyromellitate[3,4] obtained by the nitric acid oxidation and subsequent methylation of 7-dehydrocholesterol or $\Delta^{5,8(9)}$-cholestadienol. The product of the skeletal conversion reaction was, therefore, tentatively assigned the structure represented by formula IV.

The following results furnished confirmatory evidence: The selenium dehydrogenation of IV give a hydrocarbon, $C_{19}H_{18}$, the melting point of which was difficult to determine. The picrate was identical with the picrate of the hydrocarbon, $C_{19}H_{18}$, obtained by the selenium dehydrogenation of the phenol formed by the dienone–phenol rearrangement of 7-keto-$\Delta^{5,8(9)}$-cholestadienol.[3] As was pointed out previously,[3] this hydrocarbon, $C_{19}H_{18}$, shows an ultraviolet absorption curve which is characteristic of anthracene rather than phenanthrene compounds. These facts can be explained if formula IV is assigned to the reaction product of the skeletal conversion and formula VI, 3′-methyl-1,2-cyclopentano-10-methylanthracene, to the hydrocarbon.

The nitric acid oxidation of a steroid possessing two double bonds in the B-ring results in the forma-

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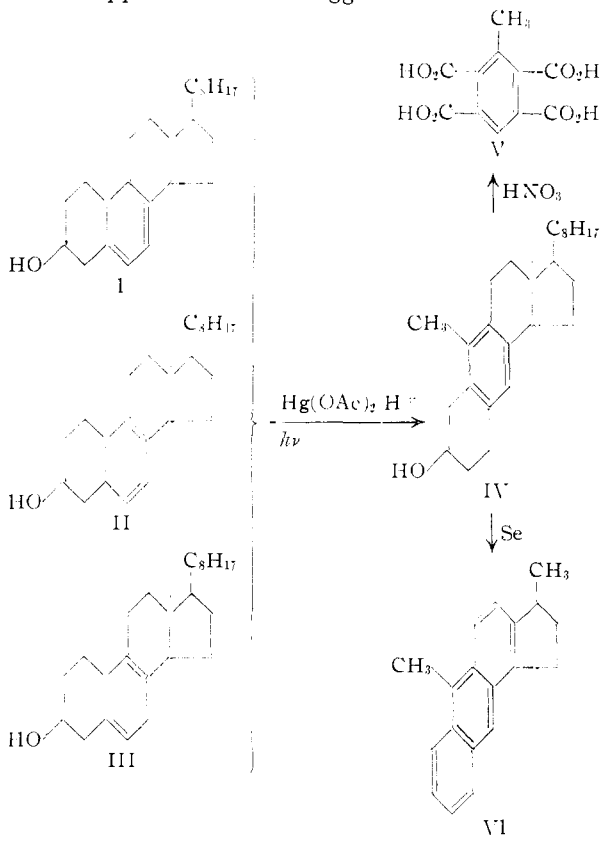
(2) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, p. 163.

(3) K. Tsuda, K. Arima and R. Hayatsu, THIS JOURNAL, **76**, 2933 (1954).

(4) Reference 2, p. 169.

tion of pyromellitic acid.[3-5] Alder's[6] assumption that an anthracene compound is an intermediate in this reaction recently was confirmed experimentally by Nes and Mosettig.[7] Our results furnish additional support for Alder's suggestion.



Experimental

Skeletal Conversion of Sterols. (A) I, II and III.—*p*-Toluenesulfonic acid (3.5 g.) and 0.5 g. of mercuric acetate were added to a mixture of 5 g. of the sterol and 300 ml. of ethanol in a 1-liter flask. Nitrogen was introduced and the flask suspended in a box, lined with aluminum foil, 15 cm. from the bottom and 30 cm. from the sides. The flask was irradiated for 24 hours in a nitrogen stream by a mercury lamp (Mazda SHL-100UV) and an incandescent lamp (100 volts, 350 watts) placed 15 cm. away. The temperature rose to 35–40°. After the reaction was complete, the precipitated gray solid was collected and washed thoroughly with ether. The combined filtrate and washings was evaporated under reduced pressure and extracted with ether. The ethereal extract was washed with water and evaporated under reduced pressure. The resulting oil solidified when dried in a desiccator.

This material, in 60 ml. of petroleum ether–benzene (1:1), was chromatographed on a column of aluminum oxide (80 g., Brockmann Grade II). The column was developed with 600 ml. of the same solvent and the effluent fractionated in 60-ml. portions. All three sterols yielded IV,[8] m.p. 153–154°, $\lambda_{max}^{Et_2O}$ 272 mμ (*E* 1200), 278 (820), 280 (1060), $\alpha^{19}D$ −10.3° (1.16% chf.). *Anal.* Calcd. for $C_{27}H_{42}O$: C, 84.81; H, 10.99. Found: C, 84.94; H, 11.22.

The *m*-dinitrobenzoate of IV melted at 179–180° dec. *Anal.* Calcd. for $C_{34}H_{44}N_2O_6$: C, 70.83; H, 7.5; N, 4.86. Found: C, 70.43; H, 7.17; N, 5.06.

(B) III.—A mixture of 2 g. of III, 0.6 g. of *p*-toluenesulfonic acid and 100 ml. of acetic anhydride was allowed to react at 100° for 27 hours under a stream of nitrogen in the sunlight. The cooled reaction mixture was poured into ice-water and filtered. The solid was recrystallized from acetone; m.p. 152–153°, $\lambda_{max}^{Et_2O}$ 269 mμ. This substance, the acetate of IV, was heated with 5% ethanolic potassium hydroxide and poured into water; the resulting solid was recrystallized from ethanol as plates of IV, m.p. 153–154°, yield 22.5%.

Mixtures of the various samples of IV with the sample prepared from III by procedure A gave no depression of the melting point.

Ergosterol.—Ergosterol (2 g.) in 300 ml. of ethanol and 100 ml. of benzene was treated as described above with 2 g. of *p*-toluenesulfonic acid and 0.2 g. of mercuric acetate. The crude product, chromatographed as in A, yielded crystals, m.p. 183–184°, yield 7.2%, $\alpha^{19}D$ −24.4° (1.31% chf.); $\lambda_{max}^{Et_2O}$ 232 mμ (*E* 1080), 268 (520), 277 (460), 281 (510).

Anal. Calcd. for $C_{28}H_{42}O$: C, 85.29; H, 10.66. Found: C, 84.89; H, 10.72.

Selenium Dehydrogenation of IV.—A mixture of 7 g. of IV and 10 g. of selenium was heated at 290–300° for 2 hours and at 330–340° for 32 hours. The cooled mixture was extracted with benzene and filtered. The filtrate was evaporated under reduced pressure. The residual oil (1.2 g.) was distilled at 170–200° at 0.002 mm., dissolved in 100 ml. of petroleum ether–benzene (1:1) and passed through a column containing 80 g. of aluminum oxide (Brockmann Grade II/III). The column was developed with 200 ml. of the same solvent and the effluent fractionated in 40-ml. portions. The oil from fractions 3–5, dissolved in 30 ml. of petroleum ether, was passed through 30 g. of aluminum oxide. The column was developed with 50 ml. of petroleum ether and the effluent fractionated in 20-ml. portions.

Fractions 1–3 yielded a colorless oil which was dissolved in dry benzene, and a benzene solution of picric acid was added. After the mixture had stood at 0° for 24 hours, orange needles (m.p. 127–130°) precipitated. A benzene solution of these crystals was chromatographed and the resulting colorless oil again converted to the picrate. When this procedure was repeated, the picrate was obtained as orange needles, m.p. 133.5–134°, yield 90 mg.

Anal. Calcd. for $C_{19}H_{18}\cdot C_6H_3N_3O_7$: C, 63.15; H, 4.4; N, 8.8. Found: C, 63.00; H, 4.89; N, 9.01.

This picrate showed no depression of m.p. when mixed with the picrate (m.p. 133.5–134°) of the hydrocarbon, $C_{19}H_{18}$, prepared from 7-keto-$\Delta^{5,8(9)}$-cholestadienol.[3]

The hydrocarbon, $C_{19}H_{18}$, solidified on standing at 0°; $\lambda_{max}^{Et_2O}$ 262 (*E* 123,600), 303 (790), 328 (3170), 341 (4150), 358 (4000), 372 (2980) and 388 (710).

Anal. Calcd. for $C_{19}H_{18}$: C, 92.7; H, 7.3. Found: C, 92.77; H, 7.24.

Nitric Acid Oxidation of IV.—A mixture of 4.5 g. of IV and 30 ml. of nitric acid (sp. gr. 1.32) was heated at 100° for 30 hours. Most of the nitric acid was removed by vacuum distillation and the residue was dried in a desiccator. The yellow solid was added to 10 volumes of an ether solution of diazomethane, the mixture was allowed to stand overnight, and the ether evaporated under reduced pressure. The residual oil was recrystallized from ethanol; m.p. 122–123°, yield 85 mg. No depression of the melting point occurred on admixture of these samples with tetramethyl methylpyromellitate (m.p. 122–123°) obtained by the nitric acid oxidation of 7-dehydrocholesterol and $\Delta^{5,8(9)}$-cholestadienol.

Anal. Calcd. for $C_{15}H_{16}O_8$: C, 55.5; H, 4.9. Found: C, 55.35; H, 4.96.

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(5) H. H. Inhoffen, *Naturwissenschaften*, **40**, 455 (1953).

(6) K. Alder and B. Krüger, *Ber.*, **86**, 985 (1953).

(7) W. R. Nes and E. Mosettig, THIS JOURNAL, **76**, 3182, 3186 (1954).

(8) II also yielded crystals (m.p. 112–114°) containing 84.39% C and 10.60% H, $\lambda_{max}^{Et_2O}$ 307 mμ (*E* 3200), yield 1.8%. III gave two additional crystalline products: (1) m.p. 121–122°, yield 18%, containing 84.46% C and 11.32% H, $\lambda_{max}^{Et_2O}$ 305 mμ (*E* 4470); and (2) m.p. 148–149°, yield 8%, containing 84.12% C and 10.89% H, $\lambda_{max}^{Et_2O}$ 261 (*E* 8700) and 275 mμ (*E* 11480).