

The Photochemical Dehydrogenation of 7-Dehydrocholesterol and the Pyrolysis of the Product.

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In a preliminary note⁽¹⁾ the authors reported that the photochemical dehydrogenation of 7-dehydrocholesterol (I) yielded a dimolecular derivative ("pinacone") analogous to ergopinacone from ergosterol. Nearly at the same time F. Schenck, K. Buchholz, and O. Wiese⁽²⁾ published a paper on the studies of 7-dehydrocholesterol, in which they described "7-dehydrocholesterol-pinacone" obtained from 7-dehydrocholesterol by a method similar to, but not identical with, that by which the present authors dehydrogenated 7-dehydrocholesterol (see the experimental part). However, the "pinacone" of the German investigators melted at 196–197°, higher by about 10° than the present authors' "pinacone". The German investigators gave to their "pinacone" a formula with one and a half molecules of water: $C_{54}H_{86}O_2 + 1\frac{1}{2}H_2O$.

The present authors repeated the dehydrogenation of 7-dehydrocholesterol by the same method as before and obtained the same results. The "pinacone", recrystallized from benzene-alcohol, had formula $C_{54}H_{86}O_2 + H_2O$ and melted at 184–185° (corr.) with decomposition. The substance dried in vacuum at 110° had formula $C_{54}H_{86}O_2$ and melted at 185.5–186° (corr.) with decomposition.

The "pinacone" was subjected to pyrolytic decomposition followed by distillation in high vacuum. The distillate obtained in a yield of 70–78% was a viscous greenish yellow oil which crystallized with difficulty. Recrystallized from methanol, the substance formed small long plates melting at 110–111° (corr.). Its 3,5-dinitrobenzoate formed light-yellow small plates melting at 210.5–211° (corr.). Analyses showed the substance was 10-desmethyl-cholestatrienol-(3) (II), analogous to neoergosterol from ergopinacone.

Schenck and co-workers, by boiling their "pinacone" with acetic anhydride and saponifying the uncrystallizable product with potash in

(1) Y. Urushibara and T. Ando, this Bulletin, **11** (1936), 802.

(2) *Ber.*, **69** (1936), 2696.

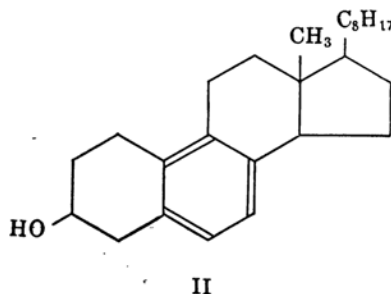
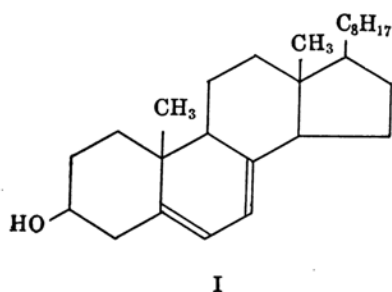
methanol, obtained "norsterol" melting at 111°. Its 3,5-dinitrobenzoate melted at 207° with decomposition.

As indicated in the accompanying table, the substances obtained by the present authors and the corresponding substances described by the German investigators show similar properties except the melting points of the "pinacone". However, it cannot be decided whether or not they are identical each with each.

Schenck, Buchholz, and Wiese			Urushibara and Ando		
Substance	Melting point	$[\alpha]_D$	Substance	Melting point	$[\alpha]_D$
"Pinacone" $C_{54}H_{86}O_2 + 1\frac{1}{2}H_2O$	196-197°	-181.6°(22°) in C_5H_5N	"Pinacone" $C_{54}H_{86}O_2 + H_2O$ $C_{54}H_{86}O_2$	184-185° (corr.) 185.5-186° (corr.)	-171°(18°) in C_5H_5N
Norsterol	111°	+1.6°(22°) in $CHCl_3$	10-Desmethyl- cholesta- trienol-(3)	110-111° (corr.)	Nearly null in $CHCl_3$
3,5-Dinitro- benzoate of the above	207°	-2.5°(22°) in $CHCl_3$	3,5-Dinitro- benzoate of the above	210.5-211° (corr.)	-3.8°(17°) in $CHCl_3$

Dehydrogenation of 7-dehydrocholesteryl benzoate by the same method yielded the dibenzoate of the "pinacone", $C_{68}H_{94}O_4$, which, re-crystallized from benzene-alcohol, formed colourless needles melting at 183-183.5° (corr.) with gas evolution. On mixing it with the free "pinacone" a depression of the melting point was observed.

While the free "pinacone" does not keep long, its dibenzoate is so stable that no change was observed in six months.



Experimental.

7-Dehydrocholesterol. Prepared according to the directions of A. Windaus, H. Lettré and F. Schenck.⁽³⁾ Recrystallized from ether-methanol, colourless needles, m.p. 143–146.5° (corr.). The 3,5-dinitrobenzoate, recrystallized from chloroform-acetone, formed yellow needles, m.p. 212–212.5° (corr.) with decomposition⁽⁴⁾ (Found for the dinitrobenzoate dried over phosphorus pentoxide in vacuum at 110°: C, 70.68; H, 8.28; N, 4.76. Calculated for $C_{31}H_{46}O_6N_2$: C, 70.55; H, 8.02; N, 4.84%).

"Pinacone" from 7-dehydrocholesterol. 7-Dehydrocholesterol was dehydrogenated according to the directions of H. H. Inhoffen⁽⁵⁾ for the preparation of ergopinacone from ergosterol: 7-Dehydrocholesterol and an equal amount of eosin (Eosin, spirit-löslich, Dr. G. Grübler and Co., Leipzig) were dissolved in a mixture of 95% alcohol and a small amount of benzene. The solution was boiled thoroughly to remove air,⁽⁶⁾ and exposed to the sun for two weeks in exclusion of air. The crystalline precipitate was collected, boiled with alcohol, and recrystallized from benzene-alcohol. Colourless thin needles, m.p. 180.5–181.5° (uncorr.) or 184–185° (corr.) with decomposition (Found: C, 82.19; H, 11.04. Calculated for $C_{54}H_{86}O_2 + H_2O$: C, 82.58; H, 11.31%). On being dried over phosphorus pentoxide in vacuum at 110°, the substance gave up the combined water (Found: H_2O , 2.06. Calculated for $C_{54}H_{86}O_2 + H_2O$: H_2O , 2.29%). The dried substance melted at 185.5–186° (corr.) with decomposition (Found: C, 84.37; H, 11.29. Calculated for $C_{54}H_{86}O_2$: C, 84.53; H, 11.31%). $[\alpha]_D^{25} = -171^\circ$ (9.2 mg. of the dried substance in 1 c.c. pyridine solution, $l = 1$ dm., $\alpha_D^{150} = -1.57^\circ$).

The "pinacone" was decomposed by keeping.

10-Desmethyl-cholestatrienol-(3) and its 3,5-dinitrobenzoate. The "pinacone" was heated at 175° under the pressure of 0.28 mm. for 15 minutes, and immediately distilled at 210–250° under 0.004–0.0015 mm. The distillate (yield 70%), forming a viscous greenish yellow oil, was heated for 30 minutes with 3,5-dinitrobenzoyl chloride and pyridine. The crystals separating out on adding water to the reaction mixture were washed with dilute acetic acid and with water, boiled with dilute acetone, and recrystallized repeatedly from benzene-methanol. Glittering light-yellow small plates, m.p. 206.5–207° (uncorr.) or 210.5–211° (corr.) (Found: C, 70.66; H, 7.42; N, 4.94. Calculated for $C_{33}H_{42}O_6N_2$: C, 70.44; H, 7.53; N, 4.98%). $[\alpha]_D^{25} = -3.8^\circ$ (13.3 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{170} = -0.05^\circ$).

In another experiment of pyrolysis, the "pinacone" was heated at 185°, 0.25 mm., for 20 minutes, and distilled at 210–260°, 0.0035–0.0008 mm., in the course of 10

(3) *Ann.*, **520** (1935), 98.

(4) Windaus and co-workers give m.p. 207°.

(5) *Ann.*, **497** (1932), 130.

(6) Schenck and co-workers removed air from the alcoholic solution (with no benzene) of 7-dehydrocholesterol and eosin by passing carbon dioxide.

minutes. The distillate (78%) forming a viscous light greenish yellow oil solidified to an opaque yellowish mass. It was collected with ether, the ether was evaporated, and the residue was brought to crystallization by rubbing with methanol. The substance was recrystallized repeatedly from methanol. Colourless glittering small long plates, m.p. 109–110° (uncorr.) or 110–111° (corr.). $[\alpha]_D^{15} =$ nearly null (6.7 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{15} = \pm 0.01^\circ$). For analysis the substance was dried over phosphorus pentoxide in vacuum at 76° (Found: C, 84.60; H, 10.86. Calculated for $C_{20}H_{40}O$: C, 84.72; H, 10.95%).

The 3,5-dinitrobenzoate prepared from the purified 10-desmethyl compound was identical with the above specimen obtained from the crude oily distillate.

The dibenzoate of the "pinacone" from 7-dehydrocholesteryl benzoate. 7-Dehydrocholesteryl benzoate (m.p. 141–142.5°, clear at 187°, corr.) was dehydrogenated in the same manner as described above. The product depositing in needles was collected, boiled with alcohol, and recrystallized from benzene-alcohol. Colourless needles, m.p. 183–183.5° (corr.) with gas evolution (Found: C, 84.03; H, 10.01. Calculated for $C_{68}H_{94}O_4$: C, 83.70; H, 9.72%). $[\alpha]_D^{17} = -114^\circ$ (11.9 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{17} = -1.36^\circ$). In admixture with the free "pinacone" the dibenzoate showed a depression of the melting point. The substance is stable in air, no change being observed in six months.

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