

### Isolation of 22-Dehydrocholesterol from *Hypnea japonica*

In the course of investigations on the sterols of the seaweeds, 22-dehydrocholesterol was isolated as an unsaponifiable matter from a red alga of *Hypnea japonica* TANAKA. It was purified by chromatography of the *p*-phenylazobenzoyl ester on silicic acid-Celite according to the method of Idler, *et al.*<sup>1)</sup>

The sterol (m.p. 134.5~135.5°,  $[\alpha]_D -56.9^\circ$ ), analyzed for  $C_{27}H_{44}O$ ,\*<sup>1</sup> formed a monoacetate ( $C_{29}H_{46}O_2$ , m.p. 127~128°,  $[\alpha]_D -61.1^\circ$ ) and a monobenzoate ( $C_{34}H_{46}O_2$ : m.p. 145~146°,  $[\alpha]_D -29.0^\circ$ ). The steryl acetate afforded on treatment with bromine a tetrabromide ( $C_{29}H_{46}O_2Br_4$ , m.p. 186~187°(decomp.)), and on hydrogenation over platinum oxide in acetic acid at 20-lb. pressure gave a saturated acetate of m.p. 109~110°, which was proved to be identical with cholestanyl acetate by mixed melting point and infrared spectra.

Oppenauer oxidation of the sterol gave a stenone ( $C_{27}H_{42}O$ , m.p. 67~70°) absorbing at 240.5 m $\mu$  ( $\epsilon$  18,000) in ultraviolet region, and on treatment with ozone the steryl acetate yielded isovaleraldehyde, whose 2,4-dinitrophenylhydrazone (m.p. 121~123°) was identified with an authentic sample. The presence of double bonds at C-5 and C-22 was thus clearly shown and this was also supported from the infrared absorption bands at 798, 840 ( $\Delta^5$ ), and 970  $cm^{-1}$  ( $\Delta^{22}$ ).<sup>2)</sup>

From these results the sterol of *Hypnea japonica* was established to be 22-dehydrocholesterol, which was already synthesized by Bergmann and Dusza on expecting its natural occurrence on biogenetic grounds.<sup>3)</sup> The physical properties of synthetic and natural sterols and some of their derivatives are in good agreement.

The isolation of cholesterol analog from a species of red algae is of considerable biogenetic interest, since it has been found that cholesterol itself occurs without exception in all fifteen species of red algae so far examined in these laboratories.<sup>4)</sup>

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\*<sup>1</sup> All substances described in this report gave correct analyses and their optical rotations were measured in chloroform solution.

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