The Identity of Hitodesterol with α-Spinasterol

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Hitodesterol was first separated from star-fish by one of the authors, T. Matsumoto, and Y. Toyama[1]. Recently, the authors re-examined this sterol with the results that they found that this sterol accords with α-spinasterol in its properties[2].

The present study affords a further evidence for the identity of this sterol with α-spinasterol. A volatile aldehyde was separated from the products of ozonolysis of hitodesteryl acetate as its 2,4-dinitrophenyl hydrazone which was identified as 2,4-dinitrophenyl hydrazone of *l*-ethylisopropylacetaldehyde by its melting point and mixed melting point.

Hence, hitodesterol is identified with α-spinasterol. This is the first instance of the occurrence of α-spinasterol in the animal kingdom.

Experimental

Hitedesteryl acetate was prepared by repeated recrystallizations of steryl acetate mixture of star-fish "*Asterias amurensis Lütken*" from ethanol.

The purified product had m.p. 182°C, $[\alpha]_D = -3°$ (in chloroform) and saponification value 124.2 (calcd. for $C_{31}H_{50}O_2$: 123.4). It showed no depression of melting point when mixed with α-spinasteryl acetate.

Hitodesteryl acetate (0.10 g.) was suspended in glacial acetic acid, and ozonized oxygen (ozone 3%) was passed through the solution for 1.5 hours. Zinc dust and a few drops of silver nitrate solution were then added to the solution. The mixture was diluted with water, and then distilled. The volatile substances were caught in a trap containing a 0.2% solution of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid. The solution in the trap was allowed to stand for some time, and then the precipitate formed was collected, yield 10 mg. On recrystallization from ethanol, it showed a constant m.p. 116°C and $[\alpha]_D = -3.6°$. It showed no depression of melting point when mixed with a specimen of 2,4-dinitrophenylhydrazone of ethylisopropylacetaldehyde, m.p. 117–118.5°C and $[\alpha]_D = -7°$, prepared from stigmasteryl acetate, while the mixed melting point with a specimen of 2,4-dinitrophenylhydrazone of methylisopropylacetaldehyde, m.p. 121–122°C and $[\alpha]_D = -40°$, prepared from ergosteryl acetate was 112–114°C. Found: C, 53.18; H, 6.10; N, 18.11; Mol. wt. (Rast method), 301. Calcd. for $C_{13}H_{18}N_4O_4$: C, 53.05; H, 6.16; N, 19.04; Mol. wt., 294.3.

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1) Taro Matsumoto and Yoshiyuki Toyama, *J. Chem. Soc. Japan*, **64**, 326 (1943).
2) Taro Matsumoto and Toru Wainai, *J. Chem. Soc. Japan*, Pure Chem. Sec., **75**, 1147 (1954).
Melting point is uncorrected.

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