Communications to the Editor

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Sargasterol from *Sargassum Ringgoldianum* HARVEY

In the course of our investigation on algal sterols, we have isolated a new sterol from *Sargassum Ringgoldianum* HARVEY and named it sargasterol.

Physical constants of sargasterol (I), $C_{29}H_{48}O$, its acetate, and benzoate are, respectively, m.p. 129~130.5°, $[\alpha]_D$ −47.5°; 138~139°, $[\alpha]_D$ −52.9°; 114~115°, $[\alpha]_D$ −22.5°. Catalytic reduction of (I) with PtO_2 in neutral medium afforded 5,6-dihydrosargatserol (II), m.p. 138~139°, $[\alpha]_D$ −13°(*Anal.* Calcd for $C_{31}H_{52}O_2$(Acetate) : C, 81.52; H, 11.48. Found: C, 81.40; H, 11.20), absorbing 1 mol. equivalent hydrogen, while Pd-C reduction in neutral medium yielded 24,28-dihydrosterol (III), m.p. 138~139°, $[\alpha]_D$ −44.6°(*Anal.* Calcd. for $C_{31}H_{52}O_2$(Acetate) : C, 81.52; H, 11.48. Found : C, 81.16; H, 11.19). Both (II) and (III) afforded the same stanol (IV), m.p. 131~132°, $[\alpha]_D$ +6.5°, by PtO_2-reduction in acidic medium.

Ozonolysis of the acetate of (I) yielded acetaldehyde and a 24-oxosteryl acetate (Va), m.p. 115~117°, $[\alpha]_D$ −25.0°, which was obviously different in physical constants from the 24-oxocholesteryl acetate derived from fucosteryl acetate.

Oppenauer oxidation of (I) afforded an α,β-unsaturated ketone (VI), m.p, 109~111.5°, $[\alpha]_D$ +84.7°; λ_{max}^{EtOH} 240 mμ(ε 16,700) (*Anal.* Calcd. for $C_{29}H_{46}O$: C, 84.81; H, 11.29. Found, C, 84.67; H, 11.07). Treatment of (VI) with N-bromosuccinimide and subsequent dehydrobromination yielded a trienone (VII) and its ozonolysis gave 3-oxo-20-iso-bisnorcholest-4-en-22-al (VIII), m.p. 139~140°, $[\alpha]_D$ +102.9°(*Anal.* Calcd. for $C_{22}H_{32}O_2$: C, 80.44; H, 9.83. Found : C, 80.63; H, 10.12), which was identical with that reported by Herr, *et al.*[1] (Va) was converted by the Wolff-Kishner reduction to a sterol (IX), m.p. 134.5°, $[\alpha]_D$ −43°(*Anal.* Calcd. for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found : C, 84.24; H, 12.30), which seems to be 20-isocholesterol.

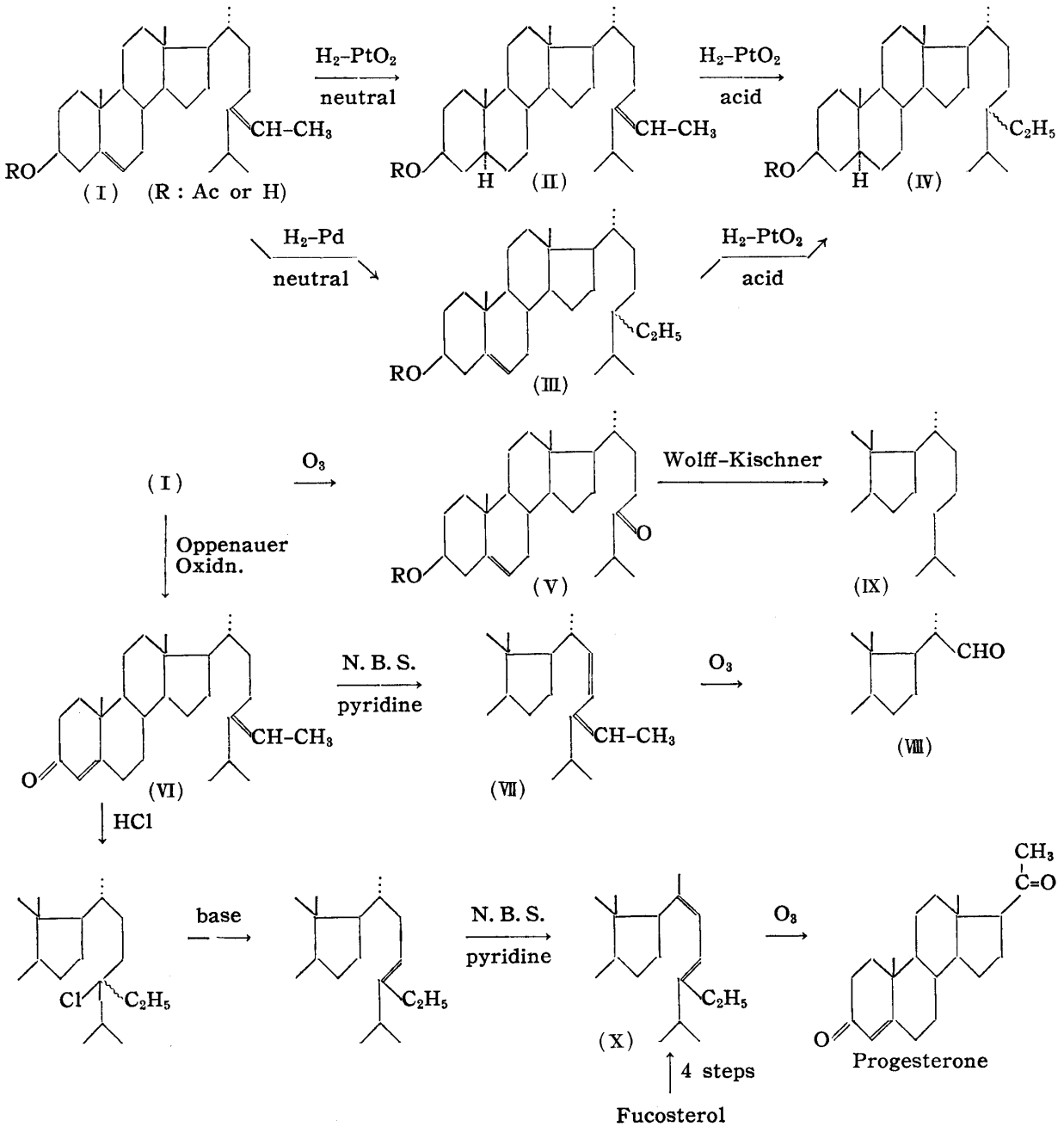
Addition of hydrogen chloride to (VI) and subsequent dehydrochlorination resulted in the migration of the double bond to 23—24. This compound was treated with N-bromosuccinimide and subsequent dehydrobromination afforded a compound (X) from which progesterone was formed by ozonolysis. While (X) was also made in four steps from fucosterol, sargasterol would be identical with fucosterol if the asymmetric carbon at 20 disappears.

The discrepancies of the M_D values of the two pairs; sargasterol (M_D −195) and 20-isocholesterol (M_D −168), and fucosterol (M_D −168) and cholesterol (M_D −151) are both negative (−27 and −17).

All of the above observations would favor the assumption that sargasterol is 20-isofucosterol. Haliclona- and palysterol were reported[2] as C_{20}-iso-series but the configurations were only supported by the molecular rotational concept. Therefore, sargasterol is the first example of C_{20}-isosterol that was proved chemically.

In addition, we wish to report that we also isolated fucosterol[3] from brown algae (Phaeophyceae) : *Eisenia bicyclis* (KJELLMAN) SETCHELL, *Cystophyllum hakodatenese* YENDO, *Fucus evanescens* AGARDH, *Pelvetia wrightii* (HARVEY) YENDO, and *Costaria costata* GREY. Identification of all samples with fucosterol was made by ozonolysis and Oppenauer oxidation.

1) M. E. Herr, F. W. Heyl : J. Am. Chem. Soc., **74**, 3627(1952).
2) W. Bergmann, R. J. Feeney, A. N. Swift : J. Org. Chem., **16**, 1337(1951).
3) I. M. Heilbron, R. F. Phipers, H. R. Wright : J. Chem. Soc. **1934**, 1572.



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