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ACETYLPINNASTEROL AND PINNASTEROL, ECDYSONE-LIKE METABOLITES, FROM THE MARINE RED ALGA LAURENCIA PINNATA YAMADA

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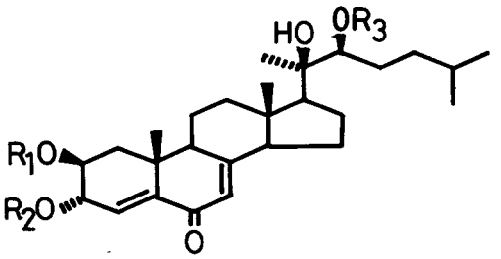
Abstract The structures of two sterols, isolated from the title alga and designated as acetylpinnasterol and pinnasterol, were determined on the basis of the X-ray crystallography. These metabolites are the first marine phytosterols with ecdysone-like structures and biological activity as moulting hormones.

In a continuing study,[1] on components of the red alga Laurencia pinnata Yamada, we have isolated two sterols, designated as acetylpinnasterol and pinnasterol, respectively. These sterols are characterized by structures closely related to crustecdysones[2a] and callinecdysones.[2b] We report herein the structures of the sterols.

Methanol extracts (10.4 g) of the alga (wet 4 kg), collected at Motsuta point, Hokkaido, in early July, was separated by repeated chromatography over silica gel and by fractional recrystallization to yield acetylpinnasterol (1) (42 mg) and pinnasterol (2) (19 mg) as comparatively polar components.

Acetylpinnasterol (1), mp 105-107 °C and $[\alpha]_D$ +64 (MeOH), had molecular formula $C_{29}H_{44}O_6$ [MS, 488 (M^+)] and gave its diacetate (3), $[\alpha]_D$ +93, on acetylation. The UV, IR, ^1H (400 MHz)[3] and ^{13}C NMR spectra,[4] coupled with spin-decoupling experiments on the ^1H NMR spectrum, indicated the presence of the following structural units: $-CH_2-CH(OAc)-CH(OH)-CH=(\dot{C})-\dot{C}(=O)-CH=(C)<^{CH-}_{\dot{C}H-}$; $CH_3(\dot{C})(OH)-$; $-CH(OH)-$; $-CH(CH_3)_2$; 2 × $-(\dot{C})-CH_3$; 6 × $-CH_2-$; 1 × $-\dot{C}H-$. While the structural moieties suggested that 1 would possess a steroid skeleton, the whole structure was elucidated by the X-ray crystallography.[5]



1 R_1=Ac, R_2=R_3=H
2 R_1=R_2=R_3=H
3 R_1=R_2=R_3=Ac

The X-ray experiment was carried out at about -20 °C. The crystal data for the acetone solvate of 1 were as follows: $C_{29}H_{44}O_6 \cdot (CH_3)_2CO$, triclinic, space group P1, a = 11.030(2), b = 13.000(2), c = 5.886(1) Å, α = 95.05(1), β = 100.52(1), γ = 104.97(1)°, Z = 1, D_c = 1.144 g cm^{-3}. 2670 unique intensity data for 2θ < 130° were collected on automatic, four-circle diffractometer with graphite-monochromated CuKα radiation. The structure was solved by the Monte Carlo direct method,[6] and refined by the block-diagonal least-squares method. The final R value was 0.035. The molecular framework of 1 is shown in Fig. 1.

Pinnasterol (2), mp 198-201 °C and $[\alpha]_D$ +37, had molecular formula $C_{27}H_{42}O_5$ [MS, m/e 446 (M^+)], and displayed the UV, IR, and ^1H NMR (400 MHz) spectra[4] suggesting that 2 would be a deacetyl derivative of 1. In fact, 2 gave its triacetate, which was identical with the diacetate (3) in all respects. This correlation confirms that pinnasterol is represented by formula 2.

These sterols are the first marine phytosterols with ecdysone-like structures and show the biological activity as moulting hormones by a Sarcophaga method[7] (kindly carried out by Dr. T. Ohtaki, Kanazawa University).

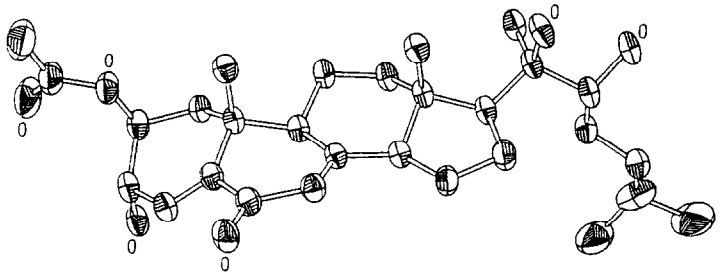


Fig. 1

References and Notes

1. A. Fukuzawa and T. Masamune, Tetrahedron Lett. (the preceding paper).
2. a) D. H. S. Horn, E. J. Middleton, J. A. Wunderlich, J. Chem. Soc., Chem. Commun., 1966, 339; M. N. Galbraith, D. H. S. Horn, E. J. Middleton, and R. J. Hackney, ibid., 1968, 63. b) A. Faust, D. H. S. Horn, E. J. Middleton, H. M. Fales, and M. E. Love, J. Chem. Soc., Chem. Commun., 1969, 175.
3. δ (C_5D_5N) 0.97 and 0.98 (each 3H, d, J = 7; 26- and 27-H), 1.05, 1.14, and 1.51 (each 3H, s; 19-, 18-, and 21-H), 1.26 (1H, dt, J = 12 and 5), 1.86 and 1.89 (each 1H, t, J = 10), 2.05 (3H, s, $OCOCH_3$), 2.21 (1H, dt, J = 12 and 2; 14-H), 2.34 (2H, m), 2.54 (1H, ddd, J = 12, 7, and 2; 9-H), 3.74 (1H, d, J = 9; 22-H), 4.71 (1H, dd, J = 7 and 2; 3-H), 5.00 (3H, br s, OH), 5.34 (1H, ddd, J = 10.5, 7, and 3.5; 2-H), 6.03 (1H, t, J = 2; 7-H), and 6.82 (1H, d, J = 2; 4-H).
4. All new compounds gave satisfactory spectral data (MS, IR, ^1H and ^{13}C NMR).
5. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center.
6. A. Furusaki, Acta Crystallogr., Sect. A, 35, 220 (1979).
7. T. Ohtaki, R. D. Milkman, and C. M. Williams, Biol. Bull., 135, 322 (1968).

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