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Litophynin C, a New Insect Growth Inhibitory Diterpenoid from a Soft Coral Litophyton sp.

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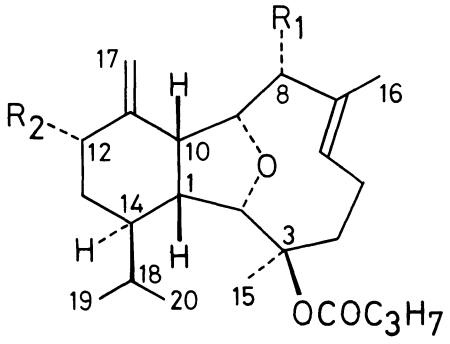
A new diterpenoid, litophynin C, which exhibits insect growth inhibitory activity against the silkworm, Bombyx mori L., has been isolated from a soft coral Litophyton sp., and its structure including the absolute configuration established on the basis of spectral and chemical evidence.

In the previous paper,[1] we have described the isolation of two new diterpenoids, litophynin A (1) and B (2), from the soft coral Litophyton sp. Our continuing search for the biologically active constituents of the same animal has now led to the isolation of an additional congener, named litophynin C, which exhibits insect growth inhibitory activity against the silkworm, Bombyx mori L.[2] The present paper deals with the structural determination of this new compound.

The dichloromethane soluble material from the methanol extract of frozen specimens was chromatographed over Sephadex LH-20 (MeOH) and silica gel (hexane - EtOAc), and then purified by HPLC (TSK-GEL LS-410KG column, MeOH - H_2O 9:1) to obtain litophynin C (3) (0.00013%, wet weight) as an optically active colorless oil, $[\alpha]_D^{24}$ -2.3° (c 0.90, $CHCl_3$). The molecular formula, $C_{24}H_{38}O_4$, was deduced by high resolution mass spectrum (m/z 390.2799, M^+, Δ +2.9 mmu). It had IR absorptions indicative of hydroxyl (3560 and 3380 cm^{-1}) and carbonyl (1715 cm^{-1}) groups, and formed a monoacetate 4, $C_{26}H_{40}O_5$, colorless oil, on acetylation with pyridine - acetic anhydride. The close similarity between the acetate 4 and litophynin A (1) was showed by the comparison of their spectral data.[1,3] The ^{13}C NMR data of 4 included twenty signals compatible with the carbon frame work of 1.



1 $R_1 = R_2 = H$

2 $R_1 = OCOC_3H_7$, $R_2 = H$

3 $R_1 = H$, $R_2 = OH$

4 $R_1 = H$, $R_2 = OAc$

Variances noted were in observations of signals attributable to an additional secondary acetoxyl group [δ_C 21.50, 73.63, and 170.02]. The detailed ^{1}H NMR analysis of 4 at 400 MHz were consistent with the structure 4. The secondary acetoxyl group of 4 was probably located at C-12α judging from the chemical shift and the coupling pattern of ^{1}H NMR signal due to its carbinyl proton [H_{12}: δ 5.49 (t, J=3.0 Hz)]. This was also supported by the appearance of exocyclic methylene proton signals at lower fields (δ 5.24 and 5.06) as compared with those of 1 (δ 4.79 and 4.74).

The absolute configuration of 3 was determined by the CD spectrum of the p-bromobenzoate 5, which was derived from 3 by treatment with p-bromobenzoyl chloride - pyridine, based on the exciton chirality method of allylic alcohol benzoate.[4] The UV spectrum of 5 showed a p-bromobenzoate Π→Π* transition at 244 nm (ε 20800), in which region the CD spectrum showed a positive Cotton effect, λ_{ext} 249 nm, Δε +1.6 in ethanol, indicating a clockwise relationship between the exocyclic double bond and p-bromobenzoate chromophores as shown in Fig. 1. The absolute configuration of litophynin C was thus found to be as shown in structure 3.

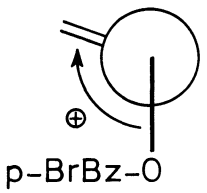
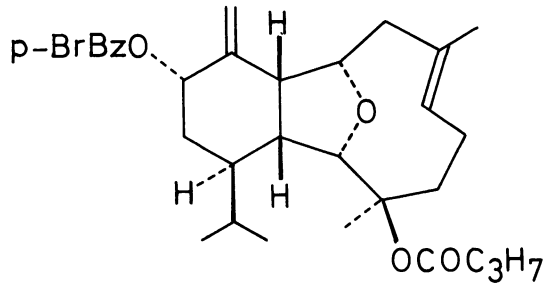


Fig. 1.



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References

1) M. Ochi, K. Futatsugi, H. Kotsuki, M. Ishii, and K. Shibata, Chem. Lett., 1987, 2207.

2) The ED_{50}-value, the effective dose for 50% growth inhibition, of litophynin C against the second instar larvae of the silkworm was 25 ppm.

3) 4: IR (CCl_4) 3070, 1735, 1640, 1235, and 890 cm^{-1}; MS m/z 432 (M^+, 8%), 372 (M^+ - AcOH, 4), (M^+ - $C_3H_7CO_2H$, 26), 276 (54), 177 (42), 71 (79), and 43 (100); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 and 0.95 (3H each, d, J=6.8 Hz, 19- and 20-H_3), 0.94 (3H, t, J=7.3 Hz, 4'-H_3), 1.55 (3H, br s, 15-H_3), 1.61 (2H, sext, J=7.3 Hz, 3'-H_2), 1.81 (3H, s, 16-H_3), 1.85 (1H, m, 18-H), 2.02 (3H, s, Ac), 2.03 (1H, d, J=14.0 Hz, 8β-H), 2.14 (1H, dd, J=11.8 and 6.7 Hz, 1-H), 2.21 (2H, t, J=7.3 Hz, 2'-H_2), 2.45 (1H, dd, J=14.0 and 5.0 Hz, 8α-H), 2.83 (1H, m, 10-H), 3.84 (1H, s, 2-H), 4.32 (1H, dd, J=9.8 and 5.0 Hz, 9-H), 5.06 (1H, d, J=1.2 Hz, 17-H), 5.24 (1H, d, J=1.7 Hz, 17-H), 5.49 (1H, br t, J=3.0 Hz, 12-H), and 5.55 (1H, m, 6-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.61 (4'), 15.45 (20), 18.62 (3'), 21.01 (16), 21.50 (Ac), 21.70 (19), 24.01 (15), 25.15 (5), 27.38 (18), 29.32 (13), 35.74 (4), 37.61 (2'), 38.12 (8), 45.67 (14), 46.04 (1), 46.45 (10), 73.63 (12), 81.75 (9), 87.19 (3), 91.38 (2), 117.71 (17), 124.89 (7), 131.96 (6), 142.31 (11), 170.02 (Ac), and 172.59 (1').

4) N. Harada, Y. Yokota, J. Iwabuchi, H. Uda, and M. Ochi, J. Chem. Soc., Chem. Commun., 1984, 1220.

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