

PINNATAZANE, A BRIDGED CYCLIC ETHER SESQUITERPENE FROM *LAURENCIA PINNATIFIDA*

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Key Word Index—*Laurencia pinnatifida*; Rhodomelaceae; sesquiterpene; bridged cyclic ether; Pinnatazane; X-ray analysis.

Abstract—Pinnatazane, a bridged cyclic ether sesquiterpene, has been isolated from *Laurencia pinnatifida* and structurally characterized with X-ray crystallographic and spectroscopic techniques.

INTRODUCTION

Marine red algae of the genus *Laurencia* have been a prolific source of unusual terpenoid and nonterpenoid C_{15} metabolites [1–3]. Our recent studies on the constituents of *L. pinnatifida* Lamouroux have resulted in the isolation of pinnatazane (1), a bridged cyclic ether sesquiterpene.

RESULTS AND DISCUSSION

Pinnatazane (1) was isolated from a petrol extract using chromatography on silica gel. Crystallization from methanol gave rod-like crystals, mp 190–192°, $[\alpha]_D = 4.34^\circ$ ($CHCl_3$; c 0.230). The structure was established by single crystal X-ray diffraction. Crystals formed in the orthorhombic space group $P2_12_12_1$ with $a = 10.147(2)$, $b = 11.938(2)$ and $c = 12.531(14)$ Å. All unique diffraction maxima with $2\theta \leq 114^\circ$ were collected using $1^\circ \omega$ -scans with graphite monochromated $CuK\alpha$ radiation (1.54178 Å). Of the 1194 unique reflections, 1078 (91%) had $|F_o| \geq 3\sigma(F_o)$ and were judged observed. The structure was solved uneventfully by standard heavy atom techniques and refined by block-diagonal least-squares to a final discrepancy index of 0.066 for the observed data. A computer generated drawing of the final X-ray model is given in Fig. 1.

Spectroscopic data were completely consistent with formula 1 for pinnatazane. The mass spectrum did not show a parent ion; the highest observable peaks were m/z 289, 291, and 293 (4:6:1). The ^{13}C NMR (75 MHz,

$CDCl_3$) showed signals for 15 carbon atoms. DEPT experiments established that four of these were quaternary carbons (δ 70.31, 61.32, 49.27, 47.02). Three were oxygen containing methine carbons (δ 83.47, 77.13, 57.41), one halogen containing methine carbon (δ 59.88), three methylene carbons (δ 42.81, 34.28, 31.47) and four were

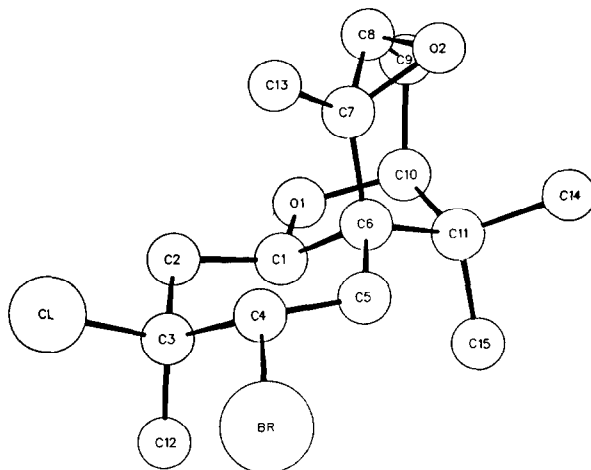
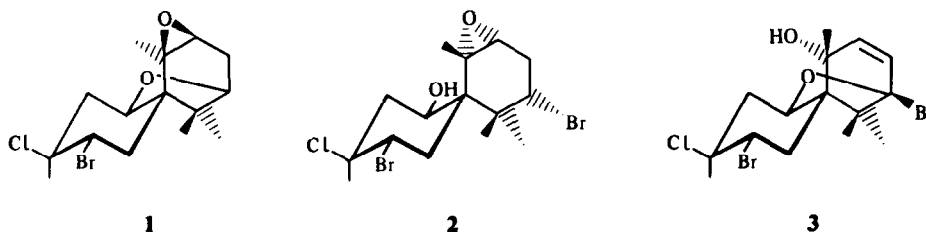


Fig. 1. A computer generated perspective drawing of the final X-ray model. Hydrogens are omitted for clarity and the absolute configuration is assumed.



methyl carbons (δ 21.81, 28.24, 29.06, 29.41). The ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR assignments were made by comparison with related compounds [1–3]. COSY-45 and ^1H – ^{13}C hetero COSY spectra supported the structural assignments.

Pinnatazane is related to previously discovered chamigranes from *Laurencia* such as pacifenol (3) [4] and the recently discovered icthyotoxin 2 [3].

EXPERIMENTAL

Ms m/z : 289, 291 and 293 (2:3:0.5) 209, 211 (6:2), 174 (10), 159 (30), 114 (60), 79 (20, and 60 (10); IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 850, 980, 1045, 1380, 1430, 1480, 2900, 2925 and 3000; ^1H NMR (300 MHz, CDCl_3): δ 4.01 (*dd*, $J_{1,2e} = 4.55$, $J_{1,2a} = 13.74$ Hz, H1), 2.59 (*dd*, $J_{2e,1} = 4.35$, $J_{2e,2a} = 12.69$ Hz, H2e), 2.68 (*dd*, $J_{2a,1} = 13.74$, $J_{2a,2e} = 12.69$ Hz, H2a), 5.06 (*dd*, $J_{4,5e} = 6.27$, $J_{4,5a} = 12.54$ Hz, H4), 2.06 (*dd*, $J_{5e,4} = 6.27$, $J_{5e,5a} = 14.31$ Hz, H5e), 2.50 (*dd*, $J_{5a,4} = 12.54$, $J_{5a,5e} = 14.31$ Hz, H5a), 2.77 (*dd*, $J_{8,9e} = 2.1$, $J_{8,9a}$

$= 4.59$ Hz, H8), 1.98–2.05 (*m*, H9), 3.74 (*dd*, $J_{10,9a} = 5.0$, $J_{10,9e} = 2.0$ Hz, H10), 1.27 (*s*, H12), 1.11 (*s*, H13), 1.58 (*s*, H14), and 1.85 (*s*, H15). Tables containing the final fractional co-ordinates, thermal parameters, bond distances and bond angles have been deposited at the Cambridge Crystallographic Data Centre, U.K.

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