# Callydiyne, a New Diacetylenic Hydrocarbon from the Sponge Callyspongia flammea

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# CALLYDIYNE, A NEW DIACETYLENIC HYDROCARBON FROM THE SPONGE *CALLYSPONGIA FLAMMEA*

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ABSTRACT.—Callydiyne [**1**], a new symmetrical diacetylenic hydrocarbon, has been isolated from the marine sponge *Callyspongia flammea*.

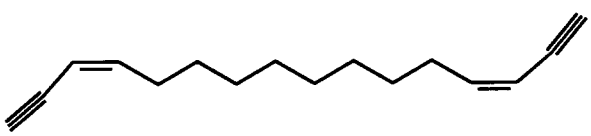
Marine sponges frequently contain polyacetylenic metabolites (1). As part of our ongoing chemical studies of sponges collected in Papua, New Guinea (2), we have discovered that MeOH extracts of *Callyspongia flammea* Desqueyrox (Callyspongiidae) contain one major secondary metabolite, callydiyne [**1**], a symmetrical diacetylenic hydrocarbon.

Callydiyne [**1**] gave a parent ion in the hreims at *m/z* 214.1713 Da appropriate for a molecular formula of $C_{16}H_{22}$ (6 unsaturations). The $^{13}$C-nmr spectrum of **1** contained only eight resonances (see Experimental), and the $^{1}$H-nmr spectrum contained resonances that integrated for a total of eleven hydrogen atoms, suggesting that callydiyne possessed a twofold element of symmetry. Terminal alkyne [ir 3302 $cm^{-1}$; $^{13}$C nmr δ 80.3 (s), 81.2 (d); $^{1}$H nmr δ 3.06] and disubstituted alkene [$^{13}$C nmr δ 107.9 (d), 146.2 (d); $^{1}$H nmr δ 5.44, 5.99] functionalities were readily identified from the nmr data. The COSY spectrum of **1** showed correlations that linked the terminal alkyne to the disubstituted olefin (δ 5.44 and 5.99 correlated to δ 3.06), and it also established that the second alkene substituent contained at least three contiguous methylenes (observed correlations: δ 5.99 to 2.32, 2.32 to 1.40, 1.40 to 1.30). APT data ($4 \times CH_2$) showed that the remaining two protons at δ 1.30 were attached to a methylene carbon, which then had to be connected to the terminus of the three-carbon methylene chain. Because callydiyne [**1**] was symmetrical, it had to be the dimer of the $C_8H_{11}$ hydrocarbon fragment identified from the nmr data. Observation of an nOe between the two olefinic protons (δ 5.44 and 5.99) established the *Z* configuration.

Callydiyne [**1**] has not been previously reported from either natural sources or synthesis.

## EXPERIMENTAL

Specimens of *C. flammea* (195 g wet wt) were collected by hand using SCUBA on reefs off Madang, Papua, New Guinea. A voucher sample of *C. flammea* has been deposited at the Zoological Museum of Amsterdam (voucher # ZMA POR. 8435). Freshly collected sponge material was quick-frozen on site and transported to UBC on dry ice. Thawed sponge tissue was homogenized in a Waring blender with MeOH. Filtration of the homogenate gave an aqueous MeOH filtrate that was concentrated in vacuo to give a gummy residue. The residue was suspended in $H_2O$ and extracted sequentially with hexanes, $CH_2Cl_2$, and EtOAc. The hexane-soluble materials were fractionated by sequential application of LH20 [eluent MeOH-$CH_2Cl_2$ (1:1)] and Si gel coumn (eluent hexane) chromatographies to give pure



**1**

callydiyne [**1**] (41 mg): colorless oil; ir (neat) 3302, 3022, 2926, 2855, 2097, 1698, 1616, 1463, 1441, 1216 $cm^{-1}$; $^1H$ nmr (400 MHz, $CDCl_3$) (integrations are relative values only) δ 1.30 (bs, 4H, 1.40 (m, 2H), 2.32 (dq, $J$ = 1.4, 7.4 Hz, 2H), 3.06 (dd, $J$ = 1.4, 0.8 Hz, 1H), 5.44 (ddt, $J$ = 10.6, 2.3, 1.4 Hz, 1H), 5.99 (ddt, $J$ = 10.6, 0.8, 7.5 Hz, 1H); $^{13}C$ nmr (75 MHz, $CDCl_3$) δ 28.7 ($CH_2$), 29.1 ($CH_2$), 29.3 ($CH_2$), 30.2 ($CH_2$), 80.3 (C), 81.2 (CH), 107.9 (CH), 146.2 (CH); hreims *m/z* $[M]^+$ 214.1713 ($C_{16}H_{22}$ ΔM −0.9 mmu); lreims *m/z* (rel. int.) 214 (0.9), 199 (1), 185 (2), 171 (7), 157 (11), 143 (31), 129 (64), 117 (82), 91 (100), 79 (77), 77 (58), 67 (59), 65 (66).

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