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Ginamallene, a New Norditerpene with Allene Functionality from Four Gorgonians of the Genus Acalycigorgia

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A bioactive metabolite, ginamallene, has been isolated from four species of Acalycigorgia and shown to be a xenicin-type norditerpene having a terminal allene functionality.

Acalycixeniolide B (**1**), a norditerpene containing a terminal allene, has recently been reported by the Tokyo group from the gorgonian Acalycigorgia inermis collected in Suruga Bay.[1] On the other hand, the Okinawa group isolated a new related compound, ginamallene (**2**), as a bioactive constituent of a species of the same genus collected at Ginama, Okinawa.[2] Subsequently, the latter group found in Okinawa two additional species of Acalycigorgia yielding the same compound. More recently, the Tokyo group also isolated a compound identical with **2** from another species found in Suruga Bay. In this paper we report the isolation and structure of ginamallene (**2**), a xenicin-type norditerpene with a rare terminal allene.

A Ginama collection (200 g) of Acalycigorgia sp. was extracted by steeping in acetone. The ethyl acetate soluble portion (0.63 g) was chromatographed on silica gel (hexane-acetone) and a Lobar Si-60 column (hexane-EtOAc) and finally purified by HPLC (silica gel, hexane-EtOAc) to give 40 mg of ginamallene (**2**) as colorless oil, $[\alpha]_D$ +48.2° (c 1.56, $CHCl_3$). The FABMS showed a weak parent ion at m/z 387 [$(M+H)^+$, 10%] and two prominent peaks at m/z 327 (-AcOH, 75%) and 267 (-2AcOH, 86%). These together with ^{13}C and ^1H NMR data (Table 1) established the molecular formula as $C_{23}H_{30}O_5$. In addition to two acetoxy groups (1735, 1230 cm^{-1}; δ 2.01s, 2.02s; δ 170.2s, 169.5s) the presence of a terminal allene was shown by IR (1960,

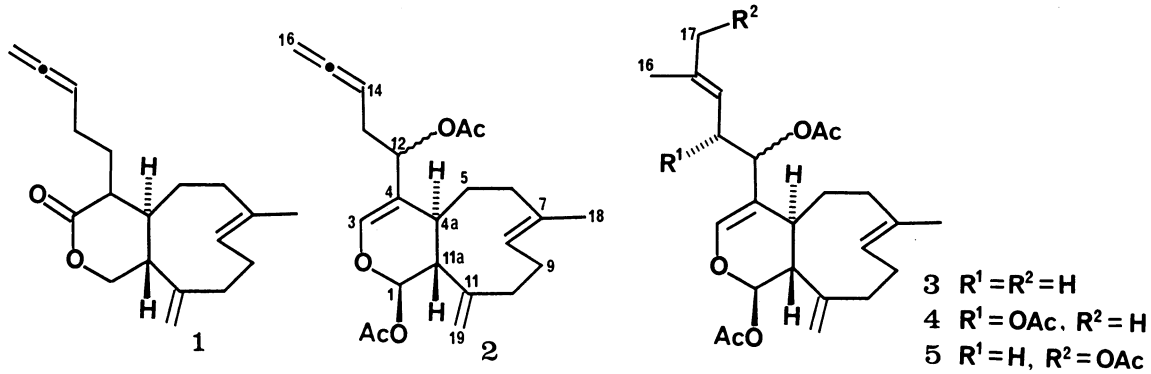

Table 1. Comparison of NMR data ($CDCl_3$) for ginamallene (**2**) and compound **3**[a)]

C No.	2 δ_H	2 δ_C	3 δ_H	3 δ_C	C No.	2 δ_H	2 δ_C	3 δ_H	3 δ_C
1	5.86d	91.8d	5.87d	91.8d	11		151.2s		151.2s
3	6.50d	141.0d	6.49d	140.7d	11a	1.95bs	49.3d		49.3d
4		115.6s		115.9s	12	5.33t	74.2d	5.28t	74.9d
4a	2.17m	36.6d		36.7d	13	2.37m	31.8t		31.3t
5	1.96m	30.5t		30.5t	14	4.97tt	85.3d	4.99bt	119.0d
	1.52m				15		209.5s		134.3s[b)]
6	2.04m	39.9t		40.0t	16	4.67dd	75.3t	1.68bs	18.1q
7		135.8s		135.8s[b)]		4.68dd			
8	5.37bt	124.4d	5.36bt	124.3d	17			1.66bs	25.7q
9	2.45m	25.1t		25.0t	18	1.65s	16.8q	1.65bs	16.7q
	2.10m				19	4.80s	113.2t	4.79s	113.1t
10	2.25m	35.5t		35.4t		4.87s		4.87s	

$J_{H,H}$(Hz) for **2**: 1,11a=1.8, 3,4a=1.9, 8,9=8.3, 12,13=7.5, 13,14=7.7, 14,16=6.6, 16,16'=3.1

a) Taken from Ref. 3b. b) Reversed from the original assignment.

845 cm^{-1}) and ^{13}C NMR data (δ209.5s, 85.3d, 75.3t). Inspection of the spectral data suggested that ginamallene (**2**) was a norditerpene of xenicin-type.[3)] As shown in Table 1, almost identical ^{13}C NMR data for the ring portion with those of 9-deacetoxy-14,15-deepoxyxeniculin (**3**),[3b)] 9-deacetoxyxenicin (**4**),[3c)] and waixenicin-A (**5**)[3d)] clearly demonstrate that **2** has the same ring structure including stereochemistry with these compounds and differs only at the side chain. The relative stereochemistry for the ring portion was confirmed by NOE difference spectroscopy. Allene functionality has been known from some marine carotenoids[4)] and C_{15} acetogenins of Laurencia,[5)] in which biogenesis of the allene bonding can be envisioned as derived from an enyne precursor, while that of **1** and **2** must involve oxidative fission of a methyl group.

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