

PGF_{2α}-9-O-ACETATE METHYL ESTER, A MINOR NATURALLY OCCURRING PROSTAGLANDIN FROM THE GORGONIAN CORAL *PLEXAURA HOMOMALLA*AMIRAM GROWEISS¹ and WILLIAM FENICAL*

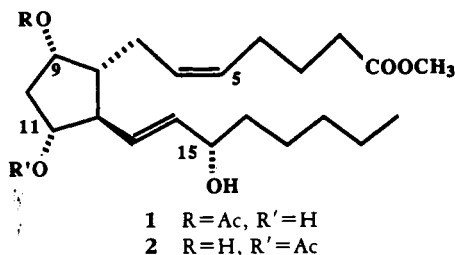
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ABSTRACT.—PGF_{2α}-9-O-acetate methyl ester [**1**] has been found as a natural product in extracts of the gorgonian coral *Plexaura homomalla* collected in the Bahama islands. The structure of this prostaglandin derivative was assigned on the basis of spectral analysis.

In 1968, Weinheimer and Spraggins (1) discovered that the Caribbean gorgonian *Plexaura homomalla* (Esper.) (Plexauridae) contained remarkable quantities (in excess of 2% dry wt) of 15-*epi* and 15-normal prostaglandin PGA₂. Smaller quantities of PGB₂ and PGE₂ were also reported from this source. In subsequent work, prostaglandin derivatives have also been reported from other marine organisms, including red algae (2,3), and other soft corals (4-6).

As part of our interest in the potential natural functions of these compounds (7,8), we have reinvestigated extracts of *P. homomalla* collected in the Bahama islands. We report here the isolation of another simple prostaglandin derivative, PGF_{2α}-9-O-acetate methyl ester, from the latter source. PGF_{2α}-11-O-acetate methyl ester [**2**], an acetate positional isomer of **1**, has been isolated as a natural product from the Red Sea soft coral *Lobophytum depressum* (9).

The structure of the prostaglandin derivative **1** was deduced by consideration



of its combined spectral data. Prostaglandin **1** was isolated as a viscous oil that analyzed for C₂₃H₃₈O₆ by combined hrms and ¹³C-nmr methods. The compound showed its spectral characteristics for multiple ester linkages (1750 br) and hydroxyl functionalities (3450 br). Consideration of ¹³C- and ¹H-nmr data, and specifically the results of COSY analysis (Table 1), allowed the complete structure of **1** to be assigned. The 5 and 15.2 Hz coupling constants are typical values for the Δ⁵Z and Δ¹³E olefin functionalities. Also, the *J* values for H-9-H-10 and H-10-H-11 of 6 and 8 Hz, respectively, are typical for the C-9β and C-11β proton configurations (9). The 15-*S* configuration in **1** was assigned based upon

TABLE 1. Selected ¹H-nmr Assignments for Prostaglandin **1**.^a

Proton	δ	<i>m</i>	<i>J</i>
H-2	2.29	t	7
H-5	5.33	t	5
H-6	5.33	t	5
H-9	5.08	dt	2, 6
H-10	2.53	ddd	14, 8, 6
	1.6	<i>m</i>	
H-11	3.86	dt	6, 8
H-12	2.34	<i>m</i>	
H-13	5.42	dd	15.2, 9.2
H-14	5.59	dd	15.2, 7.5
H-15	4.06	ddd	7.5
H-20	0.88	t	6.8
OAc(Me)	2.05	s	
COOMe	3.66	s	

^aSpectra were recorded at 360 MHz in CDCl₃ solution. Assignments are on the basis of COSY experiments.

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the similar ^{13}C -nmr shifts of C-13–C-17 in comparison with those reported from compound **2**.

A careful literature survey revealed that **1** has been prepared as a synthetic intermediate (10). To the best of our knowledge, this is the first report of the ester occurring as a natural product.

EXPERIMENTAL

GENERAL PROCEDURES AND ISOLATION.— Instrumental parameters and methods employed in this study have been summarized elsewhere (11). *P. homomalla* was collected on 3 August 1983, at 80-ft depth at Acklins Island, Bahamas. The animal was immediately frozen, later freeze-dried, and then immediately extracted with CHCl_3 . The combined CHCl_3 extracts were chromatographed over tlc grade Si gel, using vacuum flash methods, to yield 30 fractions containing mainly various prostaglandin (PGA) derivatives. Several of the most polar fractions (eluted with 100% EtOAc) were combined and rechromatographed by hplc (LiChroprep-60 column, 100% EtOAc) to yield 237 mg (0.6% extract) of purified $\text{PGF}_{2\alpha}$ -9-*O*-acetate methyl ester.

$\text{PGF}_{2\alpha}$ -9-*O*-ACETATE METHYL ESTER [**1**].— Compound **1** (9 α -acetyloxy-11 α ,15 δ -dihydroxyprosta-5 Z ,13 E -dienoic acid methyl ester) was isolated as a viscous oil that showed the following spectral characteristics: ir (film) 3450 (br), 1750 (br), 1430, 1240, 970 cm^{-1} ; eims m/z 332.2388 for $\text{C}_{21}\text{H}_{32}\text{O}_3$ [$\text{M} - \text{H}_2\text{O} - \text{HOAc}$] $^+$; ^{13}C nmr (25 MHz, CDCl_3) 174.0 (C-1), 170.6 (OAc), 136.6 (C-14), 132.7 (C-13), 129.6 (C-5), 128.3 (C-6), 76.0 (C-9), 74.0 (C-11), 73.3 (C-15), 55.6 (C-12), 51.5 (OMe), 47.1 (C-8), 40.8 (C-10), 37.1, 33.4, 31.8, 26.6, 25.3, 25.1, 24.8, 22.7 (8 unassigned CH_2 groups), 21.2 (OAc Me), 14.0 (C-20).

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