(**6a**), mp 25–35°, was obtained from **3a** in 60% yield and was converted to its tris(hydroxymethyl)aminomethane (THAM) salt,[12] mp 100–101°. Both $PGF_{2\alpha}$ and its THAM salt were identical with authentic materials.

Utilization of the (15*R*)-PGA_2 diester (**1b**) from coral as a precursor of PGE_2 and $PGF_{2\alpha}$ requires an inversion of configuration at C-15.[11] For the synthesis of $PGF_{2\alpha}$, **1b** was carried through the same sequence as above giving the corresponding intermediates **2b**, **3b**, and **5b**. On hydrolysis **5b** gave **6b**, the 15-epimer of $PGF_{2\alpha}$.

Selective oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[13] gave ketone **7** (λ_{max} 234 nm (ϵ 11,850)) which was reduced by zinc borohydride in dimethoxyethane[14] after temporary protection of the hydroxyl groups by trimethylsilylation, giving a 73:27 ratio of $PGF_{2\alpha}$ (**6a**) and its 15-epimer **6b**.

(15*R*)-PGA_2 methyl ester (**8b**), also available from coral, was treated with methanesulfonyl chloride in pyridine and the resulting crude 15-mesylate was solvolyzed in acetone–water to give modest yields of the C_{15} inverted product, (15*S*)-PGA_2 methyl ester (**8a**), along with some **8b** and several other products. Acetylation of **8a** in acetic anhydride–pyridine gave **1a** and thus ultimately PGE_2 and $PGF_{2\alpha}$.

Plexaura homomalla, var. (*R*) and var. (*S*), are thus both suitable sources of (coral) prostaglandins useful in the synthesis of PGE_2 and $PGF_{2\alpha}$. From the (*S*) variety, PGE_2 can be obtained in three steps and $PGF_{2\alpha}$ in four steps.

(12) This crystalline salt of $PGF_{2\alpha}$ was first prepared by W. Morozowich, The Upjohn Co.

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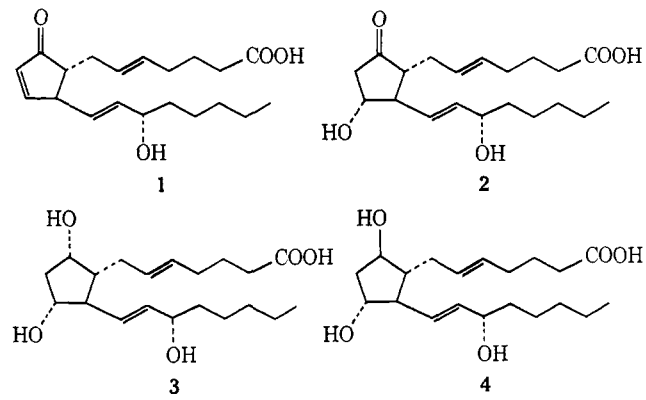
Received December 27, 1971

Isolation of a New Naturally Occurring Prostaglandin, 5-*trans*-PGA_2. Synthesis of 5-*trans*-PGE_2 and 5-*trans*-$PGF_{2\alpha}$

Sir:

During the chromatographic purification of (15*S*)-PGA_2 obtained from the gorgonian *Plexaura homomalla* var. (*S*),[1] a new natural prostaglandin was detected which was chromatographically less polar than PGA_2 on silver nitrate impregnated silica gel. We report here the purification of this material, its structure elucidation, and confirmation of the structure by chemical transformations.

Column chromatography of crude (15*S*)-PGA_2 on Amberlyst-15 Ag^+ form[2] or on silver nitrate impregnated silica gel gave a minor component to which the structure (15*S*)-15-hydroxy-9-oxo-5-*trans*,10,13-*trans*-prostatrienoic acid (5-*trans*-PGA_2) (**1**) is assigned. Content of the trans isomer usually ranged between 5 and 15% of the PGA_2 present. 5-*trans*-PGA_2 is an oil [λ_{max} 217 nm (ϵ 9050); $[\alpha]D$ +128° ($CHCl_3$); molecular ion at 478.2998 for TMS derivative (calcd for $C_{26}H_{46}O_4Si_2$, 478.2932); mass spectrum identical with that of PGA_2]. Conversion of **1** to the β-ketol was effected by a modification of the epoxidation–reduction sequence[3] to give (15*S*)-11α,15-dihydroxy-9-oxo-5-*trans*,13-*trans*-prostadienoic acid (5-*trans*-PGE_2) (**2**)[4] together with the 11β isomer. 5-*trans*-PGE_2 was crystalline: mp 76–77° (*Anal.* Found: C, 68.52; H, 9.23); $[\alpha]D$ −66° (*c* 0.983, ethanol); mass spectrum identical with PGE_2. After conversion to a trimethylsilyl (TMS) derivative, reduction of **2** with sodium borohydride[5] and hydrolysis gave a mixture of (15*S*)-9α,11α,15-trihydroxy-5-*trans*,13-*trans*-prostadienoic acid (5-*trans*-$PGF_{2\alpha}$) (**3**) and (15*S*)-9β,11α,15-trihydroxy-5-*trans*,13-*trans*-prostadienoic acid (5-*trans*-$PGF_{2\beta}$) (**4**),



which were separated by silica gel chromatography. 5-*trans*-$PGF_{2\alpha}$ was crystalline: mp 94.8–95.8° (*Anal.* Found: C, 67.99; H, 9.64); $[\alpha]D$ +9° (ethanol); mass spectrum *m/e* at 354 (M^+), 336, 318, 264, 247, 191, 137. 5-*trans*-$PGF_{2\beta}$ was also crystalline: mp 68–69° (*Anal.* Found: C, 67.89; H, 9.78); $[\alpha]D$ −8° (ethanol).

Irradiation of prostaglandin E_2 in oxygen-free benzene–methanol solution with 3500-Å light for 24 hr in a Rayonet photochemical reactor in the presence of diphenyl sulfide[6,7] gave, after careful chromatography on acid-washed silica gel, a 22% yield of 5-*trans*-PGE_2, mp 75–77°, which was identical with the material derived from *P. homomalla*. In a similar fashion and in similar yield, crystalline 5-*trans*-$PGF_{2\beta}$ and 5-*trans*-$PGF_{2\alpha}$ were prepared from the corresponding 5-*cis*-prostaglandins and were also identical with the coral-derived compounds.

A reexamination of the extracts of *P. homomalla* var. (*S*) prior to hydrolysis shows that, while small amounts of the free acids are present, the 5-trans isomer is predominantly in the form of its 15-acetate methyl ester. It is not clear at this time whether the presence of this isomer represents biosynthetic formation from 5-*trans*-arachidonic acid endogenous to *P. homomalla*, or a subsequent transformation product of 5-*cis*-PGA_2.

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Received December 27, 1971