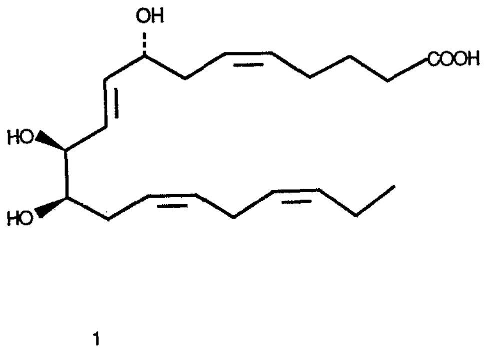

1

2, 17(18)-dihydro

lowed us to propose the gross structure of 8,11,12-trihydroxyeicosa-5,9,14,17-tetraenoic acid.

The trans geometry of the Δ^9 double bond was verified by a ^{1}H NMR study of the acetonide of **1**. This derivative was prepared by stirring 1 mg of **1** at room temperature for 4 h with 2,2-dimethoxypropane (0,5 ml) and few milligrams of the resin Dowex 50 WX2. The mixture was centrifuged, then evaporated in vacuo, and the residue was analyzed by FAB-MS, m/z 391 $(M-H)^-$ and ^{1}H NMR in CD_3OD at 250 MHz. The C-9 and C-10 protons were clearly doublets of doublets (J = 15, 5.8 Hz) at δ 5.77 and 5.65 ppm, coupled respectively with the triplet at δ 4.65 assigned to H-11 and with the 2H multiplet at δ 4.15 assigned to H-8, and H-12, which coincidentally overlap. The *cis* geometry of the remaining double bonds was assigned by analogy with 8-HETE and comparison of their ^{1}H NMR spectra.

The chemical shifts of the two geminal methyl groups in the ^{1}H NMR spectrum of the acetonide of **1** were quite different (δ 1.37 and 1.50), and this means that the substituents were *cis* to each other on the acetonide ring. On the basis of the data above, compound **1** is an erythro 8,11,12-trihydroxyeicosa-5,14,17(Z),9(E)-tetraenoic acid. We assume the 8R stereochemistry by analogy with 8-(R)-HETE. Moreover, of the two possible configurations, 8(R), 11(R), 12(S) and 8(R), 11(S), 12(R), we prefer the latter, because the ^{1}H NMR signals for the C-8/C-13 substructure are very similar to those reported for the analogous substructure of malyngic acid, 9(S), 12(R), 13(S)-trihydroxyoctadeca-10(E), 15(Z)-dienoic acid (same relative configuration as **1**), isolated from *Lyngbya majuscula*[5].

The 8,11,12-trihydroxyeicosa-5,9,14,17-tetraenoic acid has been previously described, and named trioxilin A_4, as a hydrolysis product of the epoxilin A_4 (i.e. 8-hydroxy-11,12-epoxyeicosa-5,14,17(Z),9(E)-tetraenoic acid), which is obtained by treatment of 12-hydroperoxyeicosa-5,8,10,14,17-pentaenoic acid with bovine emine[6].

The second trihydroxylated eicosanoic acid (**2**) from starfishes was characterized as the 17(18)-dihydroderivative of **1**, on the basis of FAB mass spectrometry, m/z 353 $(M-H)^-$, ^{1}H NMR (table 2) and comparison with **1**. The biological role of these trihydroxylated eicosanoic acids in starfishes remains to be discovered.

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