

OPHIOXANTHIN, A NEW MARINE CAROTENOID SULPHATE FROM THE OPHIUROID OPHIODERMA LONGICAUDUM

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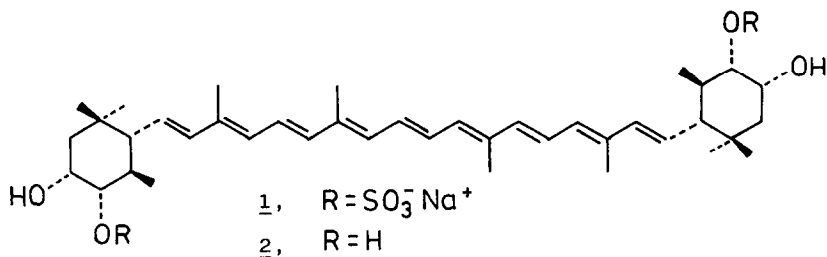
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Abstract.- A new carotenoid sulphate, Ophioxanthin, has been isolated from the ophiuroid Ophioderma longicaudum; ophioxanthin is the second known naturally occurring carotenoid sulphate and was shown to be 5,6,5',6'-tetrahydro- $\beta,\beta$ -carotene-3,4,3',4'-tetraol 4,4'-disulphate (1).

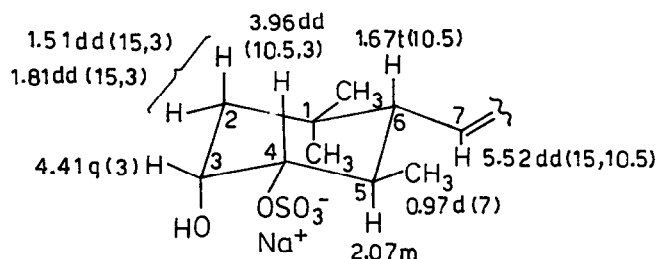
Marine species have been a rich source for discovery of carotenoids with novel structures <sup>1,2</sup>. Recently Liaanen-Jensen and co-workers have reported the occurrence of a new sponge carotenoid, bastaxanthin, from Ianthella basta, identified as carotenoid sulphate.<sup>3</sup>

Continuing with our investigation of active metabolites from echinoderms we have isolated a novel carotenoid sulphate from the ophiuroid Ophioderma longicaudum, which was designated as ophioxanthin. This compound is the second known naturally occurring carotenoid sulphate, and has the novel structure, 5,6,5',6'-tetrahydro- $\beta,\beta$ -carotene-3,4,3',4'-tetraol 4,4'-disulphate (1).

The methanol extract of O.longicaudum (collected at Naples bay, Italy, in June 1984) was fractionated chromatographically on a column of Sephadex LH-20 (CH<sub>3</sub>OH as eluting solvent), giving a polar yellow fraction. Fractionation was continued by HPLC on a column of Waters C-18  $\mu$ -bondapak (30 % H<sub>2</sub>O in methanol) to give ophioxanthin (0.002 % yield on wet weight basis).



The presence of a sulphate function in ophioxanthin was indicated by its polarity, strong IR absorption at 1240 cm<sup>-1</sup> and micro sulphur analysis ( Found: S, 7.9 %, Calcd: S, 8.4 %) Upon mild acid hydrolysis (0.2 N-HCl/CH<sub>3</sub>OH, room temperature, 3 h) ophioxanthin (1) was desulphated to ophioxanthol (2) of lower polarity, whose mass spectrum revealed a molecular weight of 604, compatible with C<sub>40</sub>H<sub>60</sub>O<sub>4</sub>. Finally <sup>1</sup>H and <sup>13</sup>C NMR spectra of the native ophioxanthin (1) in comparison with those of ophioxanthol (2) are compatible with a sulphate function (Fig. 1). The electronic spectrum of ophioxanthin,  $\lambda_{\max}$  (CH<sub>3</sub>OH) 415 ( $\epsilon$  =46,640), 435 ( $\epsilon$  =56,320) and 465 ( $\epsilon$  = 48,960) nm, is consistent with the all-trans nonaene chromophore assigned<sup>4</sup>.

<sup>13</sup>C-NMR shifts (62.7 MHz CD<sub>3</sub>OD)

	<u>1</u>	<u>2</u>
C-1	34.5	34.4
C-2	45.4	46.2
C-3	<u>69.1</u>	<u>71.4</u>
C-4	<u>86.5</u>	<u>78.4</u>
C-5	<u>32.7</u>	<u>34.6</u>
C-6	59.3	59.0
1-Me's	32.4-24.1	32.5-24.1
5-Me	17.2	17.2

Other signals:  $\delta$  6.05-6.75 (olefinic H's),  
 0.835-1.095 (1-Me's), 1.955-2.005 (9-,13-Me's);  
 in 2 3- and 4-H have shifted upfield to  $\delta$  4.04 and 3.18.

Fig. 1 - Assignment of <sup>1</sup>H and <sup>13</sup>C NMR signals (CD<sub>3</sub>OD) of ophioxanthin (1) and ophioxanthol (2).  
<sup>1</sup>H shift assignments were based on double resonance experiments at 500 MHz; <sup>13</sup>C shift assignments were determined by J-modulated spin-echo, DEPT at 90° (only CH groups) and selective decoupling experiments at 62.7 MHz.

Table 1. - <sup>13</sup>C NMR shifts (62.7 MHz, CD<sub>3</sub>OD) for in-chain carbons of 1 in ppm<sup>a)</sup>

7,7'	8,8'	9,9'	10,10'	11,11'	12,12'	13,13'	14,14'	15,15'	9,9'-Me's	13,13'-Me's
130.9	138.5	136.2	131.7	126.2	138.5	137.5	133.5	131.2	13.1	12.8

a) Tentative assignments based on those reported for  $\beta$ -carotene<sup>5</sup>.

Also compatible with the nonaene structure was the <sup>13</sup>C NMR spectrum (Table 1). <sup>13</sup>C NMR showed a total of 20 carbon resonances indicating a symmetrical structure. <sup>1</sup>H NMR also revealed identical chemical shifts of the two end groups. The <sup>1</sup>H NMR of 1 contained one double doublet ( $J = 10.5$ , 3 Hz) at  $\delta$  3.96 and one quartet ( $J = 3$  Hz) at  $\delta$  4.41, coupled each to the other by 3 Hz. These data lead to a structural element with cis-vicinal secondary hydroxy and sulphonyl groups, one adjacent to a carbon bearing one proton and the other to one bearing two protons, i.e. a cis-3,4-glycol arrangement in a 5,6-dihydro- $\beta$ -ring. In <sup>13</sup>C NMR spectrum the carbons- 3,3' and -4,4' were observed at 69.1 and 86.5 ppm. Selective decouplings delineated the <sup>13</sup>C, <sup>1</sup>H correlation and established C-4,4' to be the sites of sulphation. Proton-proton decoupling delineated the correlation of all the protons in the end groups and suggested the relative stereochemistry as shown (Fig.1).

Compound 1 is the first representative of a novel group of carotenoids that incorporate a 5,6-dihydro- $\beta$ -end group.

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