Dehydroophioxanthin, a New Acetylenic Carotenoid Sulfate from the Ophiuroid Ophiocomina nigra

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DEHYDROOPHIOXANTHIN, A NEW ACETYLENIC CAROTENOID SULFATE FROM THE OPHIUROID *OPHIOCOMINA NIGRA*

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ABSTRACT.—A new carotenoid, designated as dehydroophioxanthin [**2**], has been isolated from the ophiuroid *Ophiocomina nigra*. The structure has been determined as 7′,8′-didehydro-5,6,5′,6′-tetrahydro-β,β-carotene-3,4,3′,4′-tetraol 4,4′ disulfate, which is related to the previous ophioxanthin from *Ophioderma longicaudum*.

Recently we reported the occurrence of a new carotenoid sulfate, ophioxanthin [**1**], with a new 3,4-dihydroxy-5,6-dihydro-β-end group 4-sulfated from the Mediterranean ophiuroid *Ophioderma longicaudum* (1). Carotenoid sulfates have been previously encountered from natural sources only in bastaxanthins, isolated from the marine sponge *Ianthella basta* (2,3).

Continuing with our work on active metabolites from echinoderms, we have now isolated from the ophiuroid *Ophiocomina nigra* Abildgaard (Ophiuroidea) a new minor carotenoid sulfate (0.5 mg from 1.8 kg of fresh animal), designated as dehydroophioxanthin [**2**], co-occuring with ophioxanthin [**1**].

The uv spectrum of dehydroophioxanthin showed bands at 410, 432, 461 nm; the fabms spectrum (negative ion mode) exhibited molecular ion species peaks at *m/z* 761, 783 (major), and 799, corresponding to $[M(SO_3H)SO_3]^-$, $[M(SO_3Na)SO_3]^-$, and $[M(SO_3K)SO_3]^-$, respectively. Intense fragmentation peaks at *m/z* 681 and 663 were interpreted as due to monosulfated ions. The presence of sulfate functions was confirmed by its polarity, the strong ir absorption at 1231 cm^{-1}, and conversion on mild acid hydrolysis (0.2 N HCl/MeOH, room temperature, 3 h) to dehydroophioxanthol of lower polarity, whose eims spectrum revealed a molecular ion at *m/z* 602, compatible with the molecular formula $C_{40}H_{58}O_4$, two mass units lower than ophioxanthol obtained by desulfating ophioxanthin [**1**]. Thus the new carotenid **2** must possess a further unsaturation with respect to ophioxanthin. The ^{1}H-nmr spectrum of **2** showed signals ascribable to two end groups, whereas ophioxanthin showed only half of the signals because of its symmetrical structure. One group of signals in **2** was superimposable with those assigned to the end groups of ophioxanthin; the second group of signals was very close to the previous ones except the methyl signals, which were observed significantly shifted downfield relative to ophioxanthin, as expected upon introduction of a triple bond in the 7,8 position (4). The signal for one in-chain methyl group was observed at δ 2.00, which is a further support for a 7,8-location of the triple bond (5). Thus, the structure of **2** has been determined to be 7′,8′-didehydro-5,6,5′,6′-tetrahydro-β,β-carotene-3,4,3′,4′-tetraol 4,4′ disulfate. The relative stereochemistry is based on proton-proton decoupling experiments and comparison with ophioxanthin [**1**].

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—For instruments used, see Riccio *et al.* (6).

EXTRACTION AND CAROTENOID ISOLATION.—*O. nigra* (1.8 kg fresh wt) was collected in December 1987, along the coasts of Galicia, Spain. A voucher specimen is preserved at the Departamento de Quimica Organica, University, Santiago de Compostela, Spain. The animals were

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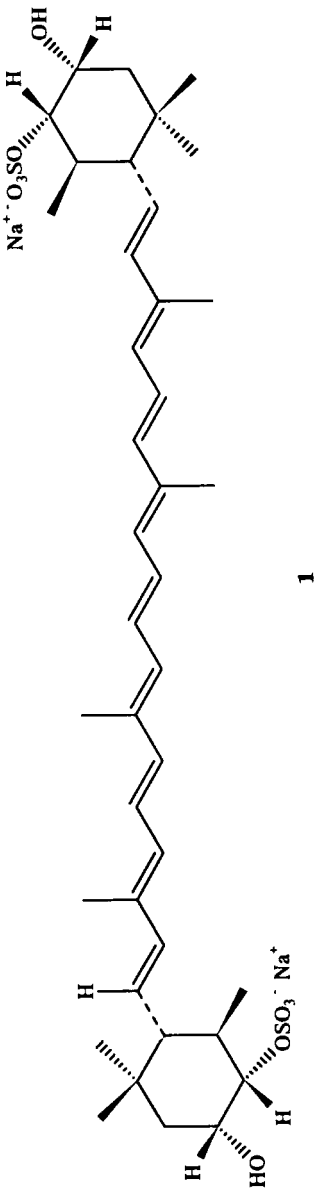
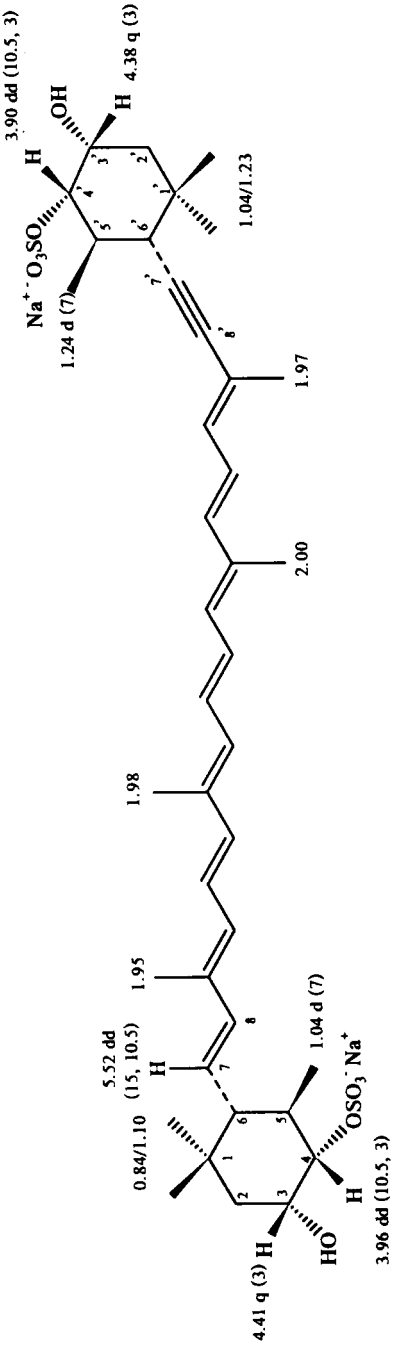

OH
H
H
$Na^+ \cdot O_3SO$
H
$OSO_3^- Na^+$
H
HO
H

1


3.90 dd (10.5, 3)
4.38 q (3)
OH
H
$Na^+ \cdot O_3SO$
1.24 d (7)
1.04/1.23
1.97
2.00
1.98
1.95
5.52 dd
(15, 10.5)
H
0.84/1.10
1.04 d (7)
$OSO_3^- Na^+$
H
HO
4.41 q (3)
H
3.96 dd (10.5, 3)

2

extracted by soaking in MeOH (3 liters × 3). Removal of solvent under reduced pressure left a residue which was partitioned between H_2O and EtOAc (100 ml × 3). The aqueous residues were then extracted with *n*-BuOH (3 × 100 ml). The *n*-BuOH extract (3.6 g) was applied in two runs to a column (2 × 60 cm) of Sephadex LH-20 using MeOH as eluent. Fractions of 7 ml were collected and checked by tlc on Si gel with *n*-BuOH–HOAc–H_2O (12:3:5). Fractions 117–122 contained carotenoid sulfates. These were subjected to preparative reversed-phase hplc on a Waters C_{18} μ-Bondapak column (7.8 mm i.d. × 30 cm) with MeOH-H_2O (65:35) as eluent (flow rate 5 ml/min) to give pure ophioxanthin [**1**] (0.8 mg, Rt = 8.0 min) and pure dehydroophioxanthin [**2**] (0.5 mg, Rt = 6 min): vis (MeOH) λ max 461, 432, 410; Ft-ir (KBr) cm^{-1} 3440, 2930, 1550, 1231, 1065, 965; ^1H nmr (CD_3OD, 250 MHz) see **2**, other signals δ 1.67 (1H, t, J = 10.5 Hz, H-6), 2.08 (2H, m, H-5, -5′), 6.05–6.70 (11H, conj. olefinic); fabms (negative ion) *m/z* 799, 783, 761.

ACID HYDROLYSIS OF DEHYDROOPHIXANTHIN.—Compound **2** (0.3 mg) was treated with 0.2 N HCl/MeOH for 3 h to give dehydroophioxanthol: vis (MeOH) λ max 452, 433; eims *m/z* $[M]^+$ 602.

ACKNOWLEDGMENTS

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