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SIDNYAXANTHIN, A NEW CAROTENOID FROM THE TUNICATE, *SIDNYUM ARGUS.*

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Summary : *A new carotenoid, Sidnyaxanthin, was isolated from the Tunicate : Sidnyum argus. The structure was elucidated by spectral analysis and chemical transformation*

Sidnyum argus is a bright orange colonial tunicate we collected near Roscoff (Brittany). The animals (15 kg, wet weight) were homogeneized in acetone. After the acetone was distilled off, the aqueous residue was extracted by hexane. Hexane extract was submitted to the successive chromatographic separations : a) silicagel 60 (C_6H_6-EtOAc, 85/15), b) LH 20 Sephalex (MeOH-$CHCl_3$, 50/50), c) silicagel 60 H ($CHCl_3$-Et_2O, 85/15) which allowed us to obtain, among many other carotenes, sidnyaxanthin, 1, 28 mg, as dark reddish cristals from ether, m. p. 88-89°C, $[\alpha]_D$ +1.6° (c 0.9, $CHCl_3$). The infrared spectrum (neat) showed absorption bands at $\nu_{max}(cm^{-1})$ 3350 (OH), 2150 (C≡C) and 1645 (conjugated carbonyl). Its visible light absorption spectrum (hexane) showed absorption maximum at 468 nm (ε 29500), similar to absorption given for isomytiloxanthin 3 (λ 459 nm, hexane) (1) suggesting the same end group, which was further confirmed by NMR.

The ^1H-NMR spectrum ($CDCl_3$) (table 1) contained signals for : one ethylenic proton β to a carbonyl (doublet at δ 7.03) and one α to a carbonyl (δ 5.83), one proton at a carbon of a secondary alcohol (δ 4.08) and two isolated methines with two AB systems centered respectively at δ 2.99 (3.06 d, 2.93 d) and δ 2.41 (2.48 d, 2.34 d). The chemical shifts for methyl signals were consistent with the presence of six vinylic methyl groups and four *gem*-dimethyl groups ; the signals at δ 1.91, 1.26, 1.09 are reminiscent of those given for Me-5' and Me-1' of isomytiloxanthin 3 (1.90, 1.20, 1.14) (1).

The ^{13}C-NMR spectrum carried out using a GASPE sequence (2,3) (table 2) exhibits besides expected ethylenic carbons, peaks for two ketonic carbonyls (δ -203.4 and -197.6), two acetylenic (-98.6 and -95.2), one tertiary alcohol (-78.57), a secondary one (+64.88) and six quaternary or CH_2 carbons.

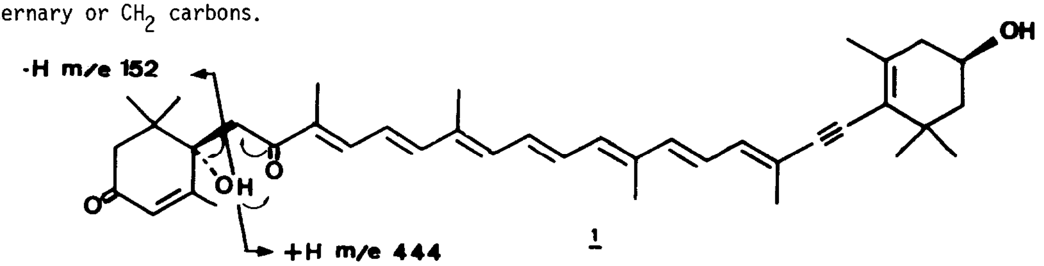

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Table 1 - ^{1}H-NMR data of sidnyaxanthin 1 ($CDCl_3$)* and abscisic acid 2 (Me_2CO)**,(δ ppm, J Hz).

			1		2				1	2
7.03	1H	d	(J=10.5)	H-10		2.02	3H	s	CH_3-5	2.04
6.93-6.23	9H	m		ethylenic H		1.99	9H	s	CH_3-9,13,13'	
5.83	1H	s		H-4	5.78	1.93	3H	s	CH_3-9'	
4.08	1H	m		H-3'		1.91	3H	s	CH_3-5'	
3.06	1H	d	(J=15)	CH_2-7		1.26	3H	s	CH_3-1'	
2.93	1H	d	(J=15)			1.09	3H	s		
2.48	1H	d	(J=18)	CH_2-2	2.42 (J=20)	1.20	3H	s	CH_3-1	1.12
2.34	1H	d	(J=18)		2.37 (J=20)	1.06	3H	s		1.03

* 400 MHz ** 80 MHz

Table 2 - ^{13}C-NMR data of sidnyaxanthin 1 ($CDCl_3$) and abscisic acid 2 ($(CD_3)_2CO$),(20.35 MHz).

1		2	1		2	1		2
-203.44	C-3	206.51	133.22	*c* C-14'		-42.05	C-4'	
-197.60	C-8		132.94	*d* C-15		-41.59	C-1	41.66
-167.90	C-5	166.78	132.49	*d* C-15'		-38.78	C-7	
147.11	C-10		129.63	*e* C-11		-36.63	C-1'	
-138.71	C-9'		129.36	*e* C-11'		30.53	Me-1'	
-138.46	*a* C-13'		123.03	C-4	126.36	28.90	Me-1	23.01
138.04	*b* C-12		-121.06	C-5'		28.83	Me-1'	
-137.89	*a* C-13		- 98.6	C-7'		24.88	Me-1	24.19
136.74	*b* C-12'		- 95.2	C-8'		22.58	Me-9	
-135.23	C-9		- 78.57	C-6	79.31	20.73	Me-5	20.72
135.16	C-10'		64.88	C-3'		12.84	Me-13	
-134.96	C-6'		- 49.78	C-2	49.85	12.68	Me-13'	
133.30	*c* C-14		- 46.75	C-2'		11.64	Me-9'	

a,*b*,*c*,*d*,*e* : Assignments may be reversed.

The electron impact mass spectrum shows no molecular ion in the expected 600 mass range, but only two predominent ions at *m/e* 444 ($C_{31}H_{40}O_2$) and 152 ($C_9H_{12}O_2$) (4). Careful reduction of this carotene with KBH_4 (ether, 0°C, 30 min) allowed us to obtain a tetrahydro-derivative which shows a molecular ion at M^+ 600. We therefore deduced the empirical formula of 1 as $C_{40}H_{56}O_4$. Thus, carotene 1 undergoes a cleavage following a McLafferty-type rearrangement which gives the two fragments *m/e* 444 and 152, and this allowed us to localize one carbonyl function at the 8-position, and a hydroxyl at C-6 position.

In view of all these elements, the formula of sidnyaxanthin can be formulated as 1.

To our knowledge, ring A has never been reported until now, despite the large number of known carotenoids of marine or terrestrial origin.

However, this ring is present in abscisic acid 2 an important plant hormone (which acts in plant growth, in stomate closure of plants exposed to dryness and in seed dormancy).

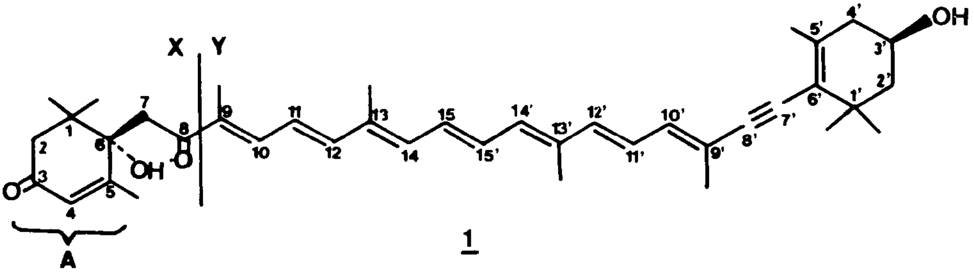
As proof of the proposed structure for sidnyaxanthin, we compared ^{13}C- and ^{1}H-NMR data of our product with those of abscisic acid. Except for slight differences which may be due to a solvent effect, since abscisic acid was not soluble in $CDCl_3$, all chemical shifts are comparable, and what is more, comparison of these values helped us in the assignment of some NMR data of 1 (tables 1 & 2) ; assignments of typical values for carotenoid carbons were attributed according to (5).

Futhermore, in order to establish the configuration at 6-position we performed the CD spectrum of 1 and observed a negative Cotton effect with a maximum at 242 nm and a slight positive Cotton effect with a maximum at 284 nm These values are similar to those reported for natural abscisic acid (6) which was determined to have the *S* configuration (7) (table 3). We then deduced the configuration at C-6 to be *S* in 1.

Table 3 - Cotton effect parameters

Compound	λ nm (Δε)	λ nm (Δε)
Sidnyaxanthin 1	242 (-117)	285 (+19)
(*S*)-(+)-Abscisic acid	246 (-190)	289 (+58)
(*R*)-(-)-Abscisic acid	246 (+190)	289 (-65)

Other closely related carotenoids have been recently reported : isomytiloxanthin 3 (1) isolated from *Mytilus edulis* and halocynthiaxanthin 4 (8) from a tunicate : *Halocynthia roretzi*, and we can observe that all these carotenoids have the same configuration at C-6.



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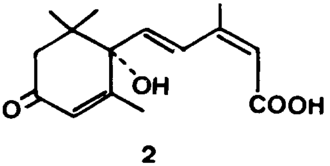

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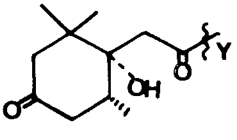

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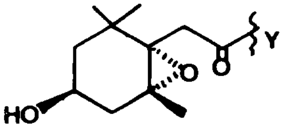

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From the biogenetic point of view, the hypothesis pointed out than abscisic acid came from mevalonic acid *via* carotenoids such as violaxanthin (9,10). This hypothesis was supported by *in vitro* experiments in which, after UV irradiation of carotenoids, if abscisic acid was not isolated, abscisic acid-like activity was observed.

In conclusion, it is rather surprising than no carotene containing ring A was isolated in terrestrial plants, where it can be useful, leading eventually to abscisic acid, instead of having been isolated from a marine animal.

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