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VITIXANTHIN AND DIHYDROVITIXANTHIN - NEW UNUSUAL 7'-APOCAROTENOIC ACIDS FROM *COCHLOSPERMUM VITIFOLIUM*

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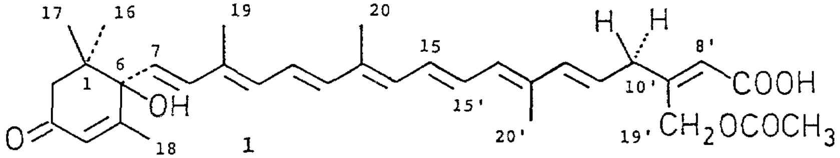
Abstract - The title compounds **1** and **2** from the American *Cochlospermum vitifolium* represent new 7'-apocarotenoic acids with unusual structural features.

The root of *Cochlospermum vitifolium* Willdenow (Sprengel) is used as a remedy against jaundice in Middle American folk medicine and as a dye (1). Repeated column chromatography of methanolic root extracts on organic gels yielded two major coloured fractions, which - upon methylation - were further separated using hplc. One of these fractions consisted of the methyl esters of the 8'-apocarotenoids cochloxanthin and dihydrocochloxanthin, two pigments already known from African *Cochlospermum* species (2,3); the second fraction gave the methyl esters of the new pigments vitixanthin (**1**) ($[\alpha]_D^{20}$ -558° ($CHCl_3$)) and dihydrovitixanthin (**2**) ($[\alpha]_D^{20}$ -82° ($CHCl_3$)).



1

2 : 4,5-dihydro-**1**

The ei-ms of both compounds exhibit strong molecular ions at m/z 548.3136 (for **1**) and 550.3297 (for **2**), respectively; the only significant fragment ions occur at m/z 43.

The electronic spectra show maxima (MeOH) at 422, 398, 377 and 359 (sh) nm, which indicate a carotenoid heptaene chromophor.

Most characteristic features in the ^1H- and ^{13}C-nmr spectra (Tab. 1) are the signals of an isolated methylene group at $\delta_C = 38.1$ and $\delta_H = 3.05$ ppm within the double bond system and of a CH_3-CO-O-CH_2 unit. Homo- and heteronuclear COSY experiments establish structural details, which resemble cochloxanthin and dihydrocochloxanthin as far as the iononering and part of the carotenoid polyene chain are concerned (2,3). CD-measurements show that the absolute configuration of **1** is contrary to that of cochloxanthin (3).

C1: 41.6	C7 : 126.7	C13 : 136.1	C12': 131.5	C16 : 23.0	C19': 62.5
C2: 49.8	C8 : 138.8	C14 : 133.4^a	C11': 124.1	C17 : 24.2	$COO\underline{C}H_3$: 51.3
C3: 198.1	C9 : 133.6	C15 : 130.1^b	C10': 38.1	C18 : 19.1	$\underline{C}OCH_3$: 170.5
C4: 127.4	C10: 133.0^a	C15': 129.9^b	C9' : 155.1	C19 : 13.1^c	$CO\underline{C}H_3$: 20.7
C5: 163.1	C11: 124.3	C14': 138.3	C8' : 118.4	C20 : 12.8^c	
C6: 79.8	C12: 135.4	C13': 135.3	C7' : 166.0	C20': 12.7^c	

Tab. 1: ^{13}C-nmr resonances of vitixanthin methyl ester (a,b,c: assignments may be interchanged).

The all-E configuration of the heptaene system is indicated by the absence of any cis-peaks in the electronic spectra (4); the Z-configuration at the 8',9'-double bond is the result of nuclear Overhauser experiments.

1 and **2** belong to the rare group of 7'-apocarotenoids (5); the known members of this group are exclusively methyl-ketones with the carotenoid polyene system in conjugation to the ketonic carbonyl. An "isolated" methylene within the polyene system and, thereby, the separation of an α,β-unsaturated terminal carbonyl group (carboxylic acid function) from the other conjugated double bonds is unprecedented among natural carotenoids.

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