13C NMR EVIDENCE FOR THE CENTRAL MONO-*CIS* STEREOCHEMISTRY OF A NATURALLY OCCURRING VIOLAXANTHIN ISOMER

Lajos Radics, Péter Molnár* and József Szabolcs*

NMR Laboratory, Central Research Institute for Chemistry, H-1525 Budapest, Hungary, *University Medical School of Pécs, H-7643 Pécs, Hungary

Abstract—The geometrical configuration of central-mono-*cis*-violaxanthin has been confirmed by 13C NMR analysis

INTRODUCTION

We have recently described the isolation of a new mono-cis isomer of (3S,5R,6S,3'S,5'R,6'S)-violaxanthin (1) from the blossoms of *Viola tricolor* L [1] On the basis of its electron spectrum, the isomer was tentatively assigned C-15-(central)-mono-*cis* geometry (2) 13C NMR spectral comparison of **2** with all-*trans* **1** has now provided conclusive evidence for this structure

1
2 = 15-*cis*
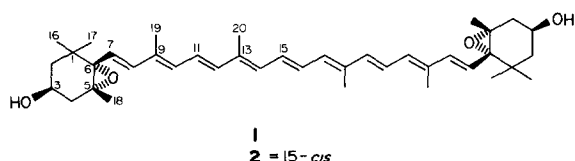
RESULTS AND DISCUSSION

The 13C NMR data of compounds **1** and **2** are summarized in Table 1 together with the respective *trans–cis* differential shieldings The assignment of resonances to individual carbon atoms was based on our earlier studies on **1** and on related isomeric mono-*cis* carotenoids [2, 3, Szabolcs, J *et al*, unpublished results]

The data shows that the overall symmetry of the all-*trans* molecule (**1**) (i e 20 resonances for 40 carbon atoms) remained unaffected by the isomerism in **2** and the resonances most influenced by changes in the stereochemistry are due to C-14 (C-14') and C-15 (C-15') According to well-established chemical shift rules for carotenoid systems [4], these observations are in complete agreement with the proposed C-15-mono-*cis* geometry of **2**

EXPERIMENTAL

Pigments **1** and **2** were isolated as previously described [1] The 13C NMR spectra were recorded in a disk-augmented Varian XL-100/15 FT

Table 1 13C NMR data of pigments 1 and 2 (25 16 MHz, pyridine-d_5, TMS as int standard)

Carbon No	1	2	Δ*
1(1')	35 49	35 51	+0 02
2(2')	47 93	47 95	+0 02
3(3')	63 19	63 24	+0 05
4(4')	41 86	41 85	−0 01
5(5')	67 19	67 24	+0 05
6(6')	70 55	70 59	+0 04
7(7')	125 51	125 85	+0 34
8(8')	137 52	137 47	−0 05
9(9')	134 86	135 16	+0 30
10(10')	132 70	132 60	−0 10
11(11')	125 45	125 75	+0 30
12(12')	138 62	138 78	+0 16
13(13')	136 85	137 65	+0 80
14(14')	133 56	126 49	−7 07
15(15')	130 94	128 11	−2 83
16(16')	25 45	25 45	0 00
17(17')	29 76	29 77	+0 01
18(18')	20 39	20 39	0 00
19(19')	13 07	13 10	+0 03
20(20')	12 86	12 58	−0 28

*Δ = δ cis − δ all-trans

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