

It is interesting that compounds (II), (III), (VI), and (VII) are widely represented in the genus *Cerasus* [2]. In our opinion, it is impossible to exclude the probability that compounds (IV) was an artefact arising in the course of isolation of the substances, since ethanol was used at the stage of extracting the raw material.

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#### CAROTENOIDS OF THE SEA BUCKTHORN, VARIETY OBIL'NAYA

S. E. Kudritskaya, L. M. Zagorodskaya,  
and E. E. Shishkina

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The aim of the present investigation was a study of the carotenoid complex of the fruit of the sea buckthorn, variety Obil'naya, bred by the M. A. Lisavenko Scientific-Research Institute of Siberian Horticulture.

The carotenoids were extracted with petroleum ether and ethanol [1]. To separate the carotenoids we used not only column chromatography but also thin-layer chromatography which considerably expands the possibilities of the isolation of zones containing small amounts of carotenoids. The carotenoids, obtained were identified with the aid of a spectrophotometer, the colors and positions of the zones on the chromatograms, and color reactions [2, 3]. The amounts of carotenoids were examined by using the extinction values and the results of spectrophotometric measurements. The fresh fruit investigated contained 16.5 mg of carotenoids per 100 g. The results of the investigation are given in Table 1.

It follows from Table 1 that the carotenoids possessing provitamin A activity ( $\beta$ -carotene,  $\beta$ -zeacarotene,  $\gamma$ -carotene, cryptoxanthin, and sintexanthin) make up 48% of the total. Of them more than half consists of the most biologically active carotenoids -  $\beta$ -carotene and cryptoxanthin.

TABLE 1

Number in order of position on the column	Carotenoid	Maxima of the absorption spectra, nm		Amount, % of the total carotenoids
		hexane	benzene	
1	$\beta$ -Carotene	424, 453, 483	435, 462, 486	15,8
2	$\beta$ -Zeacarotene	406, 426, 454	—	7,3
3	$\gamma$ -Carotene	435, 462, 490	447, 476, 509	2,4
4	Prolycopene	434, 470, —	455, 481, —	3,2
5	Lycopane	447, 471, 502	454, 487, 520	6,0
6	Mutatochrome	404, 426, 450	414, 436, 463	1,8
7	$\beta$ -Cryptoxanthin	425, 446, 477	—	18,4
8	Taraxanthin	418, 443, 470	430, 454, 484	12,4
9	Sintexanthin	425, 448, 474	436, 462, 484	4,1
10	Lutein	420, 444, 475	433, 453, 485	14,2
11	Lycophyll	446, 473, 502	456, 487, 520	0,7
12	Escholtzanthin	444, 472, 500	458, 485, 515	0,9
13	Flavoxanthin	400, 420, 450	—	0,8
14	Luteoxanthin	—	408, 431, 458	0,4
15	cis-Luteoxanthin	—	305, 318, 406	0,4
16	Capsanthin	450, 475, 504	— 430, 458	0,5
17	Autoxanthin	380, 401, 425	459, 483, 516	5,8
18	Trollichrome	—	431, 457, —	4,9

D. S. Korotchenko Kiev Institute of the National Economy. Translated from *Khimiya Prirodnikh Soedinenii*, Vol. 6, pp. 852-853. November-December, 1989. Original article submitted February 6, 1989; revision submitted May 4, 1989.

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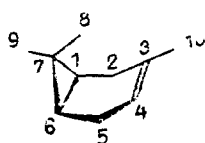
## $^{13}\text{C}$ - $^{13}\text{C}$ SPIN-SPIN COUPLING CONSTANTS IN 3-CARENE

A. Yu. Denisov, A. V. Tkachev,  
and V. I. Mamatyuk

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The  $n\text{JCC}$  constants provide unique information for establishing the structure and investigating the spatial arrangement of natural compounds [1, 2]. Considerable interest is presented by the coupling constants of nuclei through several chemical bonds [3, 4]; however, the measurement of these parameters of  $^{13}\text{C}$  NMR spectra for compounds with the natural content of the  $^{13}\text{C}$  isotope is usually associated with considerable experimental difficulties. In order to study indirect  $^{13}\text{C}$ - $^{13}\text{C}$  SSCs in natural compounds we have measured  $n\text{JCC}$  values in (+)-3-carene for the first time ( $\pm 0.1$  Hz; other  $n\text{JCC}$  constants less than 1.5 Hz):

	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
C-1	43.5	2.6	5.3	1.7	11.3	14.0	—	—	3.4
C-2	—	40.6	—	5.1	1.8	—	3.0	—	4.3
C-3	—	—	75.4	—	6.0	—	—	—	44.2
C-4	—	—	—	41.8	3.2	—	—	—	3.0
C-5	—	—	—	—	43.1	—	3.0	—	4.2
C-6	—	—	—	—	—	14.0	—	—	—
C-7	—	—	—	—	—	—	44.7	43.9	—
C-8	—	—	—	—	—	—	—	2.5	—
C-9	—	—	—	—	—	—	—	—	—



As a result, all the  $^1\text{JCC}$  constants and seven each of the indirect constants  $^2\text{JCC}$  and  $^3\text{JCC}$  were determined; the sign of  $^2\text{JCC}$  may be negative. On the whole, the vicinal constants  $^3\text{JCC}$  depend on the dihedral angle  $\vartheta$  between bonds [5]:  $\vartheta_{2,8} = \vartheta_{5,9} = 1^\circ$ ;  $\vartheta_{1,10} = 175^\circ$  and  $\vartheta_{5,10} = 179^\circ$ ; while  $\vartheta_{3,7} = \vartheta_{4,7} = 65^\circ$  and  $\vartheta_{2,9} = \vartheta_{5,9} = 145^\circ$  (the angle  $\vartheta$  were calculated by the method of molecular mechanics using the MM2 program [6]). For a more detailed analysis it is necessary to take into account the possibility of the transfer of an interaction over several routes, valence angles, types of chemical bonds, and other factors. The values of  $^3\text{J}_{1,4}$ ,  $^3\text{J}_{3,6}$ , and  $^3\text{J}_{2,5}$  are greater than the values for the other  $^3\text{JCC}$  constants since they include interactions by two routes through three carbon bonds ( $\vartheta_{1,4} = \vartheta_{3,6} = 6^\circ$  and  $\vartheta_{2,5} = 0^\circ$ ). The measurement of  $^{13}\text{C}$ - $^{13}\text{C}$  shifts in 3-carene (70% by volume in acetone- $d_6$ ,  $^2\text{D}_{\text{CD}_3} = 29.80$  ppm): 19.36; 25.46; 131.54; 120.17; 21.46; 17.55; 17.25; 13.64; 28.88, and 24.02 ppm, respectively, for C-1, C-2, ..., C-10 (the opposite assignment of C-1 and C-6 is assumed in the literature [7]). Bruker AM-400 and WP-200 SY spectrometers were used for the measurements, and  $^{13}\text{C}$ - $^{13}\text{C}$  SSCs were determined by the INADEQUATE method [8], including its elective version [9] which we applied to the measurement of the indirect  $n\text{JCC}$  constants.

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Novosibirsk Institute of Organic Chemistry, Siberian Branch, USSR Academy of Sciences.  
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