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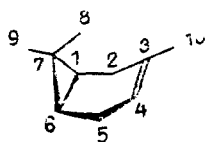
 ^{13}C - ^{13}C SPIN-SPIN COUPLING CONSTANTS IN 3-CARENE

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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}C NMR spectra for compounds with the natural content of the ^{13}C isotope is usually associated with considerable experimental difficulties. In order to study indirect ^{13}C - ^{13}C SSCCs in natural compounds we have measured $n\text{JCC}$ values in (+)-3-carene for the first time (± 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 ^1JCC constants and seven each of the indirect constants ^2JCC and ^3JCC were determined; the sign of ^2JCC may be negative. On the whole, the vicinal constants ^3JCC depend on the dihedral angle ϑ between bonds [5]: $\vartheta_{2,8} = \vartheta_{5,8} = 1^\circ$; $\vartheta_{1,10} = 175^\circ$ 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 ϑ 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 ^3JCC 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}C - ^{13}C shifts in 3-carene (70% by volume in acetone- d_6 , $^{20}\text{CD}_3 = 29.80$ 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}C - ^{13}C SSCCs 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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ANALYSIS OF MENTHYL ESTERS OF FATTY ACIDS IN THE PRESENCE OF MENTHOL

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The desirability of the analysis of menthyl esters of fatty acids in the presence of methanol is due to at least two factors: in the first place, to evaluate the state of the methanol in natural materials and, in the second place, to solve applied problems of the enzymatic separation of racemic mixtures of menthol [1, 2]. In the first case, we isolated the essential oil fraction from peppermint by Ginzburg's method [3]. It was dissolved in diethyl ether (the total volume was 1.0 ml) and was analyzed for its total content of menthol by a modified method [4] consisting in the addition of 0.4 ml of the given fraction to a test-tube, followed by 2 ml of a 1% solution of vanillin in concentrated sulfuric acid and, after stirring, by 2 ml of water. After 20 min, the optical density at 597 nm was measured and the menthol content was determined from a calibration curve. For 100 g of the dry mint it amounted to 0.81 mg. The qualitative characteristics of the essential oils of the mint were determined by the TLC method in the presence of markers, and it was established that peppermint contains menthol and menthyl isovalerate. To estimate the ratio of the concentrations of mentanol in the two forms, an aliquot of the essential oil fraction was subjected to TLC as shown previously. The menthol on the plate was located with the aid of a control band, and it was cut out and extracted with ethyl alcohol. After the performance of quantitative determination it was shown that 100 g of the dry mint contained 0.33 mg of menthol in the free form and 0.24 mg in form of a fatty acid ester.

The amounts of menthyl esters in the products of the enzymatic esterification of menthol with various fatty acids is given below:

Fatty acid	Amount of menthol taking part in the reaction, mg	Calculated amount, mg fatty acid taking part in the reaction	menthyl esters synthesized
Butyric	11.96	6.75	18.71
Isobutyric	9.78	5.52	15.30
Valeric	14.23	9.31	23.54
Isovaleric	6.84	4.47	11.58
Caproic	5.92	4.41	10.33
Caprylic	205.60	190.05	335.65
Palmitic	18.71	30.75	49.46
Cinnamic	12.80	12.16	24.96

Reaction conditions: 10 g (64 mmole) of racemic menthol, 20 ml of isooctane, 0.1 ml of Triton X-100, 0.1 ml of 1 M CaCl₂, 0.4 ml of 0.2 M borate buffer, pH 8.0, 60 mg of lipoorizin (Biotehnologiya Scientific Production Combine) and 64 mmole of each of the fatty acids. The reaction was carried out at 20°C for 200 h.

As we established, the quantitative determination of menthyl esters is not affected by the presence in the medium of diethyl ether, alkanes, carboxylic acids, and aliphatic alcohols or by water-soluble biopolymers, which can be eliminated by preliminary extraction.

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