The stilbene solution was prepared by dissolving 0.05 g of stilbene (TU [Technical Specifications] 6-09-4489–77) in ethanol in a 200 ml measuring flask and diluting 1 ml of the resulting solution to 50 ml with ethanol in a measuring flask.

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INDIRECT ^{13}C–^{1}H SPIN–SPIN COUPLING CONSTANTS IN 3-CARENE

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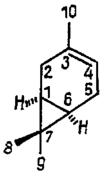
The potential value of the indirect constants $^{n}J_{CH}$ (n ≥ 2) as powerful tools in the investigation of the compositions and spatial structures of organic compounds is generally known [1, 2], but the usual procedures for their measurement from proton-linked ^{13}C NMR spectra are ineffective in the case of terpenoid compounds in view of the complex multiplet structures of the signals. On the other hand, the determination of these constants is considerably more attractive from the point of view of the sensitivity of the NMR method than the ^{13}C–^{13}C SSCCs that we have obtained previously [3]. In the present paper, using (+)-3-carene as an example, the possibility is demonstrated of measuring the complete set of indirect ^{13}C–^{1}H SSCCs with the aid of two-dimensional J-resolved ^{13}C NMR with selective excitation of protons [4] (using the DANTE Procedure [5]). The values of the constants are given below [±0.1 Hz, apart from $^{1}J_{CH}$ (±1 Hz)], the other values of $^{n}J_{CH}$ being ≤0.3 Hz)



	H-1	H-2β	H-2α	H-4	H-5β	H-5α	H-6	Me-8	Me-9	Me-10
C-1	160	5,0	4,0	—	4,4	0,6	3,0	3,3	4,5	0,6
C-2	1,3	125	125	7,1	2,4	1,2	1,7	—	0,4	4,2
C-3	4,9	7,1	8,0	—	5,1	6,0	0,6	—	—	6,2
C-4	0,6	4,2	5,1	153	7,3	8,3	5,2	—	—	5,8
C-5	1,7	2,2	1,1	4,7	125	125	1,4	—	0,4	0,4
C-6	3,1	4,2	0,6	6,5	5,2	4,2	160	3,3	4,5	—
C-7	2,2	4,5	6,2	—	4,4	6,1	2,2	5,1	4,8	—
C-8	1,8	—	—	—	—	—	1,8	125	4,0	—
C-9	5,7	—	—	—	—	—	5,7	4,5	125	—
C-10	0,5	2,2	2,1	7,0	1,4	1,5	0,5	—	—	125

The signs of the $^{n}J_{CH}$ (n = 2 or ≥4) constants may be negative [1]. The qualitative analysis of the vicinal constants $^{3}J_{CH}$ showed that their values obeyed a Karplus-type dependence on dihedral angles [2], except for cases of the transmission of interaction through a path with a double bond (C=C–C–H). For a more detailed investigation of the dependence of the indirect constants $^{n}J_{CH}$ on structural and spatial factors a further expansion of the volume of experimental results on the constants is necessary.

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For measuring the constants we used Bruker AM-400 and AC-200 spectrometers, a 50%-by-volume solution of 3-carene in acetone-d_6, and a 5 mm ampul. The assignment of the signals in the ^{13}C and ^1H NMR spectra was taken from the literature [3, 6].

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STRUCTURE OF ARGRACIN — A NEW SESQUITERPENE LACTONE FROM Artemesia gracilescens

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Continuing a chemical study of the epigeal part of Artemisia gracilescens Krasch. et Iljin., gathered in the valley of the R. Tundyk, Karaganda province, Kazakhstan [1-3], by the chromatographic separation of an acetone extract with elution of the column by benzene–ether (9:1) we have isolated a colorless crystalline substance with the composition $C_{17}H_{22}O_4$, mp 210-212°C (ethanol; decomp.) — a new sesquiterpene lactone, which we have called agracin. Its IR spectrum contained bands at (cm^{-1}) 1760 (carbonyl of a γ-lactone); 1725, 1250 (ester group); and 1670 (C=C).

In the PMR spectrum (Bruker WP 200 SY; $CDCl_3$; 0 — TMS) singlets at (ppm) 1.45 and 1.71 (3 H each) characterized the presence of methyl groups at double bonds. A doublet at 4.63 (1 H; J = 10 Hz) and a multiplet with its center at 5.19 ppm (1 H) was assigned to olefinic protons, and doublets at 5.54 and 6.27 (1 H each, with J = 3 and 3.5 Hz, respectively) to the protons of an exomethylene group conjugated with the carbonyl of a γ-lactone. Consequently, there are three double bonds in the argracin molecule. A comparison of the chemical shifts of its PMR spectrum with those of germacranolides of the costunolide series (11,13-dihydrocostunolide, dihydronovanin, tulipinolide, epitulipinolide, herbolide B, and tamaulipin B acetate) [4-8] permitted a germacra-trans-1,trans-5-dienolide structure to be proposed for argracin.

A doublet of doublets at 4.50 ppm could be assigned to the lactone proton (H-6) interacting with H-5 (J = 10 Hz) and H-7 (J = 8.5 Hz). Such a value of the SSCC showed the trans-linkage of the lactone ring in relation to the main carbon skeleton.

A singlet at 2.04 ppm (3 H) indicated the presence of an acetyl group in the structure of argracin, while the signal of a gem-acyl proton — a doublet of doublets at 5.19 ppm with J = 10.5 and 3 Hz — showed its interaction with two vicinal protons located on one and the same carbon atom. The chemical shift of the gem-acyl proton and its SSCC enabled us to consider the possibility of the location of the acetyl group at C-3 or at C-9. A correlation of the chemical shift of the gen-acyl proton in the spectrum of argracin with the literature [9] showed its identity with that of haagenolide acetate; i.e., the acetoxy group was present at C-9.

Thus the argracin molecule has the structure 9β-acetoxy 6β, 7α(H)-germacr-1(10), 4(5), 11(13)-trien-6, 12-olide (I).

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