COMPOSITION OF THE NEUTRAL FRACTION OF THE OLEORESIN OF PINUS SIBIRICA

IV. Structure of the Sesquiterpene Hydrocarbon Sibirene

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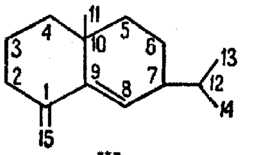
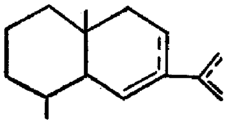
In studying the sesquiterpenes of the oleoresin of Pinus sibirica R. Mayr.(Siberian cedar), Pentegova, Motl, and Herout [1] isolated a previously undescribed bicyclic sesquiterpene hydrocarbon sibirene.

As was established [1], sibirene contains two double bonds, one of which, according to the IR spectrum, may relate to a trisubstituted double bond and the other to a methylene double bond. The UV spectra that we have taken of this compound, with λ_{max} 246 mμ (log ε 2.5), indicates that they are conjugated. The presence of a methylene bond is confirmed by ozonization by Naves's method [2].

The dehydrogenation of sibirene with selenium gave 1-methyl-7-isopropyl-naphthalene (II) [3]. On the basis of the results obtained, the following structures (III) and (IIIa) may be considered as established for sibirene:



III



IIIa

Structure (III) agrees with the IR spectrum (1174, 1380, and 1385 cm^{-1}, isopropyl group) and the mass spectrum m/e 161 (M−43).

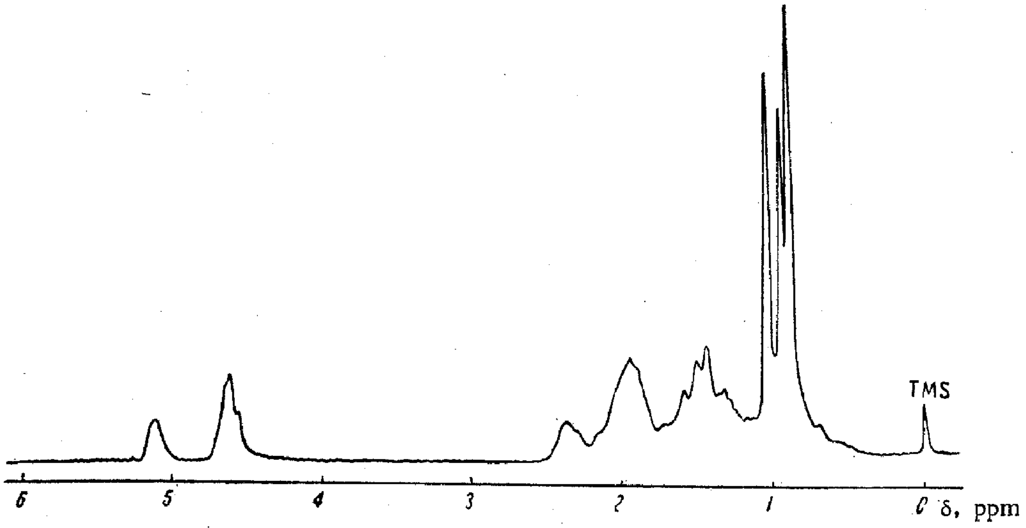
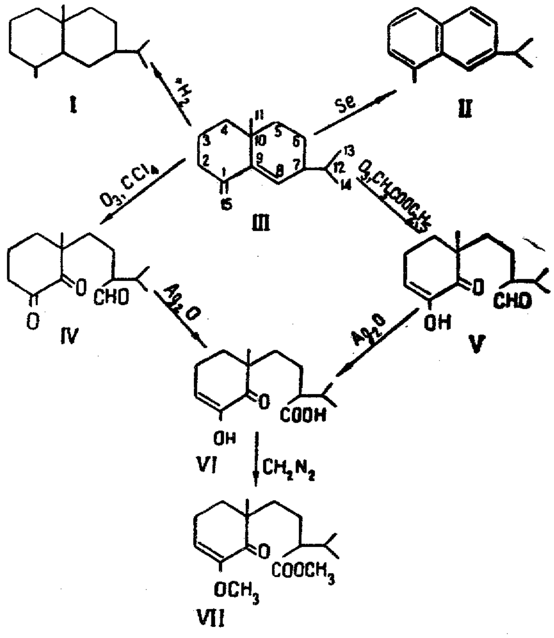


Fig. 1. NMR spectrum of sibirene.

The NMR spectrum of sibirene (Fig. 1) also confirms structure (III). In the weak-field region there are two signals: at 5.12 and 4.62 ppm relative to TMS. The ratio of the areas of these signals was found to be 1:2. The signal at 5.12 ppm corresponds to a proton on a double bond at C_8 and the signal at 4.62 ppm with a relative intensity of 2 to a methylene group with a double bond. This agrees well with Jackman's data [4]. The signal at 2.36 ppm, the relative intensity of which is 1, with an unresolved fine structure, is due to the proton at C_7, and the bands with a complex structure at 1.95 and 1.47 ppm relate to saturated methylene groups. The signal of the proton of an isopropyl group also falls in the 1.4 ppm region. In the strong-field region there is an isolated signal at 1.03 ppm and a doublet at 0.93 ppm. The singlet at 1.03 ppm is assigned to an angular methyl group and the doublet at 0.93 ppm with a spin-spin interaction constant of 2 Hz is due to the methyl of an isopropyl group [5].



The ozonization of sibirene in carbon tetrachloride at 0° C led to a mixture consisting of two components. A product $C_{14}H_{22}O_3$ (IV) was isolated by thin-layer chromatography on silica gel, its IR spectrum having absorption bands at 1658 and 1720 cm^{-1} (carbonyl groups). The data of the UV spectrum, $\lambda_{max}^{n\text{-heptane}}$ 296–298 mμ (log ε 2.4), permit the assumption that the carbonyl compound contains two keto groups in the α-position. The high extinction coefficient of the compound obtained (log ε 2.1) [6] can be explained by the presence of an aldehyde group (log ε 1.3) in the compound [7]. The NMR spectrum of the carbonyl compound (IV) lacks the signals at 5.12 and 4.62 ppm but a signal appears at 9.59 ppm which is characteristic for an aldehyde proton. In the strong field there is a doublet due to the methyl of an isopropyl group, and also the single line of an angular methyl group. The signal at 2.36 ppm, previously assigned to the proton at C_7, has undergone a displacement of 1 ppm towards weaker fields. The NMR spectrum of the carbonyl compound also does not contradict the structure proposed.

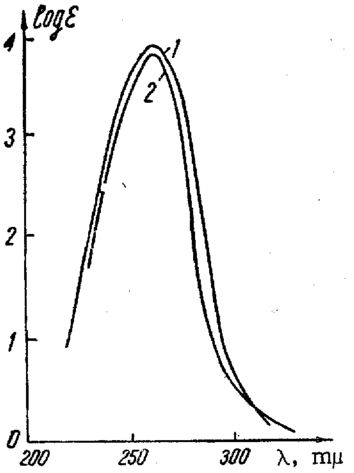


Fig. 2. Additive UV spectrum of propionaldehyde + cyclohexane-1, 2, -dione in the enolic form (1) and the UV spectrum of compound (V) (2).

As mentioned above, the ozonization of sibirene in carbon tetrachloride at 0° C gave a mixture consisting of two components. The substance forming the impurity in the α-diketoaldehyde (IV), compound (V), was obtained as the main product when sibirene was ozonized in ethyl acetate at −70°C. The IR spectrum of compound (V) has absorption bands at 1720 cm^{-1} (carbonyl) and 3600 cm^{-1} (hydroxyl). The appearance in the IR spectrum of bands due to a hydroxy group is explained by the enolic form of the compound. The curve of the UV spectrum of compound (V) agrees with the additive curve of the UV spectra of propionaldehyde and the enolic form of cyclohexane-1,2-dione, which also points to the enolic form of compound (V) (Fig. 2).

The oxidation of compounds (IV) and (V) with silver oxide in alcoholic alkali gave an acid (VI). The UV spectrum of this acid, $\lambda_{max}^{n\text{-heptane}}$ 264 mμ (log ε 3.86), confirms the enolic form of compound (VI). The formation of the acid (VI) from the α-diketoaldehyde (IV) must be due to the previous enolization of (IV) into (V) under the action of the alcoholic alkali [7]. The possibility of the enolization of compound (IV) was shown by a special experiment.

When the acid (VI) was methylated with diazomethane, compound (VII) was obtained, the quantitative analysis of which shows that a hydroxy group was methylated as well as the carboxy group [9].

On the basis of what has been said, we have come to the conclusion that sibirene belongs to the selinane group and has the structure (III). A large number of compounds of the selinane type is known in the literature [10, 11], and of these the isomer closest to sibirene is selinanediene, obtained by the dehydration of the sesquiterpene alcohol junenol [3, 10].

Experimental

Isolation of sibirene. The sesquiterpene compounds (230 g) isolated from the oleoresin of Pinus sibirica by the previously reported method [1] were percolated through alkaline alumina (activity grades I, II, in a ratio of 1 : 10). The hydrocarbons (150 g) were eluted with petroleum ether and were then subjected to distillation in a fractionating column with 70 theoretical plates at a residual pressure of 8 mm. The fractions enriched in sibirene were selected by means of gas-liquid chromatography ["Khrom 1", column (170 × 0.6 cm) filled with poly-(ethylene glycol adipate) (16.7%) on washed acid INZ-600 brick (280–400 μ), 150° C, carrier gas nitrogen (24 ml/min), flame-ionization detector] and by analytical thin-layer chromatography on silica gel impregnated with silver nitrate [KSK silica gel (70) + $AgNO_3$ (15%); solvent: petroleum ether–benzene (3 : 1); revealing agent: $SbCl_3$ in chloroform; plates activated for 2 hr at 120° C] [12]. Selected fractions were chromatographed on a column containing silica gel impregnated with silver nitrate [KSK silica gel (140) + $AgNO_3$ (10%); sorbent activated for 8 hr at 120° C; ratio of substance and sorbent 1 : 30] [13]. A mixture of petroleum ether and benzene (9 : 1) eluted sibirene with $[\alpha]_D^{20}$ + 120°; n_D^{20} 1.4972. The NMR spectrum of sibirene has proton resonance signals at 5.12, 4.62, 2.36, 1.95, and 1.03 and a doublet at 0.93 (in ppm from TMS). The NMR spectrum was taken on a JNM-3 (4b MGU) instrument.

Found, %: C 88.11; H 11.89; mol. wt. 204 (mass spectrometry). Calculated for $C_{15}H_{24}$, %: C 88.24; H 11.76; mol. wt. 204.

Hydrogenation of sibirene. Sibirene (670 mg) was hydrogenated in glacial acetic acid in the presence of platinum oxide. The consumption of hydrogen was 149.2 ml (0° C, 760 mm), which corresponds to two double bonds (theoretical consumption of hydrogen for two double bonds, 147 ml). The saturated hydrocarbon (I) was purified by chromatography on silica gel impregnated with silver nitrate [ratio of substance to sorbent 1 : 100, solvent, petroleum ether]. The yield of product was 400 mg, n_D^{20} 1.4770.

Quantitative determination of the methylene double bonds [2]. Sibirene (2.5 mg) in solution in propionic acid (3 ml) was ozonized at −20° C for 2 min. The amount of formaldehyde liberated (0.32 mg) corresponded to one methylene double bond (theoretical amount of formaldehyde for one methylene bond, 0.37 mg).

Dehydrogenation of sibirene. Sibirene (1 g) and selenium (1.2 g) were heated at 220–230° C for 3 hr. The dehydrogenation product was chromatographed on alkaline alumina (activity grades I, II). The aromatic hydrocarbon (0.7 g) was eluted with petroleum ether. A picrate with mp 91–92° C and a styphnate with mp 119°–120° C were prepared. The mixtures of the picrate and the styphnate of the aromatic hydrocarbon (II) with authentic samples of the picrate and styphnate of 1-methyl-7-isopropylnaphthalene gave no depression of the melting point (the melting points were determined on a Kofler apparatus).

Ozonization of sibirene. Sibirene (2 g) was ozonized in carbon tetrachloride (60 ml) at 0° C for 6 hr. The ozonides were decomposed with water at 120° C for 7 hr. The ozonization product was extracted with ether and was washed with a saturated solution of sodium hydrogen carbonate and then with water until neutral. The mixture isolated (1.5 g) was separated by preparative thin-layer chromatography on silica gel in a fixed layer (solvent, chloroform) into compounds (IV) and (V). The main compound (IV) (1 g) consisted of an intensely yellow viscous liquid. Compound (V), a liquid with a faint yellow coloration, was isolated in small amount (0.05 g).

Preparation of the semicarbazone of compound (IV). A methanolic solution of compound (IV) (0.5 g) was treated with a methanolic solution of semicarbazide hydrochloride (0.52 g) and sodium acetate (0.85 g). The semicarbazone obtained (0.35 g) was purified by chromatography on neutral alumina (activity grades III and IV, ratio 1 : 120). Elution was carried out with the solvents petroleum ether–benzene (1 : 1), benzene, and ethanol. Ethanol eluted a semicarbazone with mp 153°–154° C (from ethanol).

Found, %: C 50.02; H 7.68; N 30.36. Calculated for $C_{17}H_{31}O_3N_9$, %: C 49.80; H 7.58; N 30.86.

Oxidation of diketoaldehyde (IV) [14]. A solution of caustic soda (0.72 g) in ethanol (120 ml) was added in drops to a mixture of the carbonyl compound (IV) (0.47 g) and silver nitrate (1.3 g) in absolute ethanol (12 ml). The oxidation product (0.3 g), which was isolated by the usual method, consisted of a viscous liquid (VI). The acid (VI) was methylated with diazomethane in ethereal solution. A crystalline product (VII) with mp 43°–44° C (from methanol) was isolated.

Found, %: C 68.35; H 9.33. Calculated for $C_{16}H_{26}O_4$, %: C 68.05; H 9.28.

Ozonization of sibirene in ethyl acetate. Sibirene (1.5 g) was ozonized in ethyl acetate at −70° C for 6 hr. The ozonization product, isolated by the method described above, was separated by preparative thin-layer chromatography on silica gel in a fixed layer into two components. The main product (0.9 g), a viscous liquid, was identical with respect to its IR and UV spectra with compound (V). Present as a small impurity in compound (V) was a liquid (0.04 g) identical with respect to its IR and UV spectra with compound (IV).

Preparation of the semicarbazone of compound (IV). A methanolic solution of semicarbazide hydrochloride (0.42 g) and sodium acetate (0.68 g) was added to a methanolic solution of compound (V) (0.4 g). The semicarbazone, purified by the method described above, had mp 107°-108° C (from ethanol).

Found, %: C 54.46; H 8.20; N 23.30. Calculated for $C_{16}H_{28}O_3N_6$, %: C 54.52; H 8.01; N 23.85.

Oxidation of compound (V). Compound (V) (0.4 g) and silver nitrate (1.1 g) were dissolved in absolute ethanol (11 ml), and, in drops, a solution of caustic soda (0.61 g) in ethanol (17 ml) was added. The product which separated out was identical with respect to its IR and UV spectra with the acid (VI). This acid was methylated in ethereal solution with diazomethane. A crystalline product with mp 43°-44° C (from methanol) was isolated. A mixture of the methyl esters of the acids obtained by the oxidation of compounds (IV) and (V) gave no depression of the melting points.

Conversion of compound (IV) into (V). The α-diketoaldehyde (IV) (100 mg) was dissolved in absolute ethanol (2 ml), and a solution of caustic soda (0.15 g) in ethanol (5 ml) was added. The mixture was kept for 24 hr at room temperature and was then extracted with ether, and the ethereal extract was washed with water until neutral. The compound isolated (70 mg), purified by thin-layer chromatography on silica gel (solvent, chloroform), consisted of a liquid identical with respect to IR and UV spectra with compound (V).

The mass spectrum of sibirene was taken on a MKh-1303 mass spectrometer. The IR spectra were determined on a UR-10 spectrophotometer and the UV spectra on a SF-4 instrument.

The gas-liquid chromatography was carried out by L. N. Vol'skii. V. A. Koptyug gave advice on the interpretation of the spectra. The elementary analyses were carried out in the analytical laboratory of the Novosibirsk Institute of Organic Chemistry.

Summary

It has been established that sibirene (isolated from the oleoresin of Pinus sibirica R. Mayr. has the structure 10-methyl-1-methylene-7-isopropyldecal-8-ene.

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