PRESENCE OF MONOTERPENES OF THE SYLVESTRENE SERIES IN THE TURPENTINE OIL FROM THE OLEORESIN OF Pinus silvestris

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The question of the presence of sylvestrene (m-mentha-6,8-diene) in the turpentine oils isolated from the oleoresin of various species of conifers has so far been disputed in the literature [1-3]. The presence of this hydrocarbon in Swedish turpentine oil from the oleoresin of Pinus silvestris was first shown by the fact that sylvestrene dihydrochloride was obtained from a fraction (bp 173-175°C, d^{20} 0.8612, $[\alpha]_D + 19.5°$) of this oil [4, 5]. Subsequently, the presence of sylvestrene in other turpentine oils [6-8] and essential oils [9] from this species of conifer was confirmed by this method.

Wallach [10] discovered a qualitative reaction for sylvestrene which consisted in the fact that a dilute solution of sylvestrene in acetic anhydride or in glacial acetic acid with the addition to it of a drop of concentrated H_2SO_4 acquired an intense blue coloration. This reaction was used to demonstrate the presence of sylvestrene in many turpentines and essential oils of conifers.

Later [10-12] it was shown that the hydrocarbon regenerated from sylvestrene dihydrochloride boiled at a temperature 3-5°C higher than the fraction of the oil from which this dihydrochloride was obtained. Furthermore, the "sylvestrene" fractions of oils frequently did not give the characteristic coloration with the Wallach reagent. It was assumed that the sylvestrene dihydrochloride was formed not from sylvestrene but from another terpene isomeric with it, present in natural oils [13]. In actual fact, it was soon shown that sylvestrene dihydrochloride is formed from Δ^3- and Δ^4-carenes [14], that the "sylvestrene" fractions of turpentine and conifer essential oils contained not sylvestrene but Δ^3-carene, and that pure samples of sylvestrene do not give a coloration in the presence of the Wallach reagent, this reaction being characteristic for m-mentha-1,3(8)-diene [15].

On the basis of this information, it was assumed that sylvestrene and other hydrocarbons of the m-menthane series were not present at all in natural turpentine oil and essential oils [1-3].

We have shown that sylvestrene and m-mentha-1,3(8)-diene are components of the industrial turpentine oil obtained from the oleoresin of Pinus silvestris.

EXPERIMENTAL

The α pinene was distilled off under industrial conditions from the turpentine oil of the oleoresin of P. silvestris. The residue (35%, Table 1, Figure 1) was distilled through a column with 20 theoretical plates at a reflux number of 10. The fractions containing sylvestrene (I) and m-mentha-1,3(8)-diene (II) amounted to 20 and 3% of the weight of the turpentine oil, respectively.

Gas–liquid chromatography was performed on a LKhM-7A instrument in a capillary column (40,000 × 0.25 mm) with tricresyl phosphate at a rate of flow of H_2 of 30 ml/min and of hydrogen of 300 ml/min at 130°C.

Sylvestrene. The sylvestrene fraction (I) (5000 g) was twice fractionally distilled at 20 mm Hg in a column with an efficiency of 120 theoretical plates at a reflux number of 100. This gave fractions (Ia) (500 g) and (Ib) (15 g) (see Table 1 and Fig. 1), containing, respectively, 3% and 45% of sylvestrene. Even traces

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TABLE 1. Properties of the Fractions and of the Sylvestrene and the m-Mentha-1,3(8)-diene Isolated from Them

Fractions and hydrocarbons	Amt. of the desired hydrocarbon	n_D^{20}	d_4^{20}	$[\alpha]_D^{20}$, deg
Residue	—	1,4780	0,8738	— 12,0
Sylvestrene fraction (I)	0,4	1,4755	0,8420	— 54,8
Sylvestrene fraction (Ia)	3,0	1,4772	0,8517	— 50,5
Sylvestrene fraction (Ib)	45,0	1,4760	0,8489	+ 37,2
Sylvestrene	98,5	1,4740	0,8448	+111,7
Sylvestrene [17]	100	1,4744	0,8446	+121,0
m-Mentha-1,3(8)-diene fraction (II)	0,5	1,5130	0,9180	— 9,5
m-Mentha-1,3(8)-diene fraction (IIa)	5,0	1,4949	0,9057	— 0,8
m-Mentha-1,3(8)-diene fraction (IIb)	34,7	1,5030	0,8630	0
m-Mentha-1,3(8)-diene	100	1,5140	0,8669	0
m-Mentha-1,3(8)-diene [17]	100	1,5140	0,8658	0

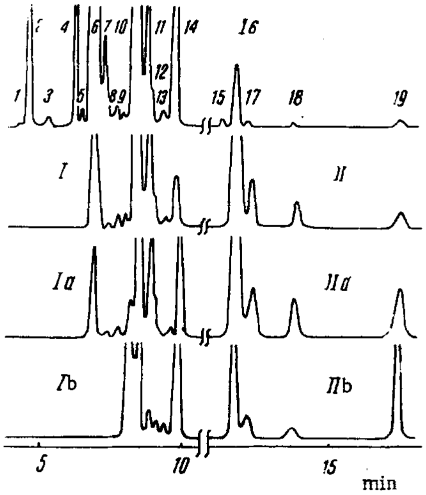

Fig. 1. GLC of the residue from the distillation of the turpentine oil; sylvestrene fractions (I-Ib) and m-mentha-1,3(8)-diene fractions (II-IIb): peaks (%): 1) tricyclene (traces); 2) α pinene (8.1); 3) camphene (0.2); 4) β pinene (3.8); 5) myrcene (0.4); 6) Δ^3-carene (43.4); 7) α-terpinene (1.5); 8) component X_1 (0.2); 9) sylvestrene (0.1); 10) limonene and dipentene (32.1); 11) β phellandrene (2.7); 12) component X_2 (0.3); 13) γ terpinene (0.1); 14) p-cymene (5.7); 15) component X_3 (0.1); 16) terpinolene (1.2); 17) component X_4 (traces); 18) component X_5 (traces); 19) m-mentha-1,3(8)-diene (0.1).

of Δ^3-carene were absent from fraction (Ib). It must be mentioned that sylvestrene and limonene are extremely difficult to separate both by fractional distillation and by preparative GLC.

Fraction (Ib) (2.2 g) was vigorously shaken with 50% aqueous $AgNO_3$ for 30 min [16]. The mixture was cooled to −5°C, and, after 2 h, the sylvestrene adduct ($C_{10}H_{16} \cdot 2AgNO_3$) was filtered off and washed with diethyl ether. The adduct (yield 69.2% of the theoretical amount), with mp 210.5-211.5°C (decomp) was decomposed with water at 60-70°C. Sylvestrene was obtained (yield 71.4%), its structure being confirmed by elementary analysis and by UV and IR spectroscopy. The dihydrochloride of this hydrocarbon (yield 79.7%) had mp 72.5-73°C and $[\alpha]_D^{20}$ +26.6° (c 4.5; chloroform) [17, 18]; nitrosochloride (yield 37.4%), mp 113.5-114°C and $[\alpha]_D^{20}$ +326° (c 0.46; chloroform) [19]; tetrabromide (yield 72%), mp 137.5-138.5°C and $[\alpha]_D^{20}$ +62.6° (c 0.48; chloroform) [18].

The sylvestrene did not show the characteristic coloration with the Wallach reagent [15].

m-Mentha-1,3(8)-diene. Fraction (II) (4000 g) containing 0.5% of m-mentha-1,3(8)-diene was twice redistilled at 10 mm Hg through a column with an efficiency of 120 theoretical plates at a reflux number of 80. Fractions (IIa) and (IIb) (see Table 1 and Fig. 1) containing, respectively, 5% and 34.7% of m-mentha-1,3 (8)-diene were obtained.

Fraction (IIb) was purified on a PAKhN-03 preparative chromatograph with a column (8000 × 4 mm) filled with deactivated Inza diatomite brick (grain size 0.25-0.5 mm) impregnated with diethyleneglycol azelate (30%); rate of flow of helium 20 ml/min at 125°C. This gave m-mentha-1,3(8)-diene with its characteristic properties (see Table 1). With the Wallach reagent it gave an intense blue coloration [15]. UV spectrum: log ε 4.22 at 244 nm [20]. The elementary analysis and IR spectrum confirmed the structure as that of m-mentha-1,3(8)-diene [17, 20]. From the terpine, carvestrene dihydrochloride with mp 50.5-51.5°C [21] was isolated (yield 21.7%).

On being heated with maleic anhydride, the m-mentha-1,3(8)-diene isomerized into m-mentha-1,3-diene which formed an adduct (yield 47%) with mp 308-309°C (decomp) [19].

CONCLUSIONS

It has been shown that an industrial sample of the turpentine oil from the oleoresin of Pinus silvestris contains, in addition to monoterpenes of the p-menthane series, monoterpenes of the m-menthane series: m-mentha-6,8-diene and m-mentha-1,3(8)-diene.

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