molar amounts of quercetin with mp 317 (pentaacetate with mp 194–195° C) and rhamnose (osazone with mp 180.5–182° C), and methylation with dimethyl sulfate and subsequent splitting off of the carbohydrate part of the molecule led to 3-hydroxy-5,7,-3',4'-tetramethoxyflavone with mp 193–194° C. On the basis of the chemical reactions mentioned and the IR spectra and R_f values of the substance in several systems of solvents, it was identified as quercetin 3-rhamnoside (quercitrin). A mixture of quercitrin and the derivatives obtained with authentic samples [1] gave no depression of the melting points.

The evaporated ethereal fraction was chromatographed on polyamide, and 30% ethanol eluted 0.02% of a colorless crystalline substance with mp 227–229° C. It gave positive reactions for flavones with alkali, sodium borohydride in an acid medium [2], with Mg + HCl (crimson), with Zn + HCl (transient crimson), $FeCl_3$ (brown), and with concentrated HNO_3 (red). The substance was soluble in aqueous Na_2CO_3, which shows the presence of acid phenolic groups in it (for example 7-OH). The compound underwent no change on acid hydrolysis, but alkaline degradation yielded products differing from the products of the decomposition of hesperetin. Microanalysis showed that its molecule contained one CH_3O group. Its IR spectrum showed absorption bands of hydroxyl groups at 3440 (sharp), 3320 (unsharp), 3140 (broad) cm^{-1}, the carbonyl of a γ-pyrone probably bound by a hydrogen bond with the 5-OH [3] at 1633 cm^{-1}, and also bands at 843 and 817 cm^{-1} characteristic for CH– with a 3',4'-substituted B ring. Evidently one OH group is methylated, since the difference in the intensities of these bands is marked [4]. The IR spectrum is characteristic for flavanones or isoflavanones [5] and, in contrast to those of the flavones, has one strong and one ill-defined maximum: λ_{max} 292, 331 mμ (log 4.30, 3.69, respectively). The bathochromic shift of the short-wave maximum under the influence of sodium acetate (λ_{max} 328 mμ, log ε 4.46), sodium ethoxide (λ_{max} 328 mμ, log ε 4.47), and aluminum chloride (λ_{max} 312 mμ, log ε 4.43) permits the compound isolated to be assigned to the flavanones having free OH groups in positions 5 and 7 [5]. The study of the compound isolated is continuing with the aim of elucidating the position of the substituents in ring B.

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THE PRESENCE OF α-TERPINENE IN THE TURPENTINES OF VARIOUS CONIFERS

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We have previously [1] reported that the Δ^3-carene fraction of the turpentines from Pinus silvestris L. (Scotch pine) [1], and also the turpentines of other conifers, contain a monoterpene of unknown structure the relative retention time of which in GLC corresponds to α-terpinene (p-mentha-1,3-diene).

In the present investigation, we have shown that this monoterpene is in fact α-terpinene.

The α-pinene and part of Δ^3-carene were distilled off from the oleoresin turpentine of Pinus silvestris L. through a column with an efficiency of 18 theoretical plates at a reflux number (R. No.) of 20. From the distillation residue (Fig. 1, a)* by rectification with a column of 50 theoretical plates at a R. No. of 50 was isolated the α-terpinene fraction

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*The analysis of the turpentines and their fractions was carried out on KhV-2 instrument with a column (6000 × 4 mm) filled with Inza deactivated diatomite brick impregnated with tricresyl phosphate (10%) with hydrogen as carrier gas.

(Fig. 1, b), which was then purified on a PAKhV-03 preparative chromatograph at 126° C in a column (6000 × 8 mm) filled with Inza deactivated diatomite brick (grain size 0.25–0.50 mm) impregnated with diethyleneglycol azelate (30%). The carrier gas was nitrogen.

The sample of α-terpinene (Fig. 1, c) had d_4^{20} 0.8442; n_D^{20} 1.4780; $[\alpha]_D^{20}$ −0.8°. UV spectrum: λ_{max} (in isooctane) 265 mμ (log ε 3.81).

Pure α-terpinene [2] has d_4^{20} 0.8409; n_D^{20} 1.4778; UV spectrum: λ_{max} (in isooctane) 265 mμ (log ε 3.81). The IR spectrum of our sample of α-terpinene (Fig. 2) was in complete agreement with literature data [3].

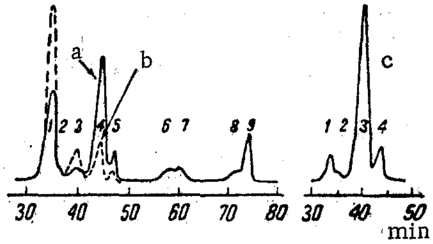

Fig. 1. Chromatograms of the residue (a) obtained after the distillation of α-pinene and Δ^3-carene from pine oleroresin turpentine; α-terpine fraction (b) obtained after reretification; and a sample of the α-terpinene purified on a PAKhV-03 instrument (c). Peaks: 1) Δ^3-carene; 2) substance of undetermined structure; 3) α-terpinene; 4) *l* + d, *l*-limonene; 5) β-phellandrene; 6) γ-terpinene; 7) p-cymene; 8) substance of undetermined structure; 9) terpinolene.

Chemical derivatives characteristic for α-terpinene were obtained with the constants appropriate to them: nitrosite 154–155° C [4]; adduct with maleic anhydride, mp 61–64° C [4].

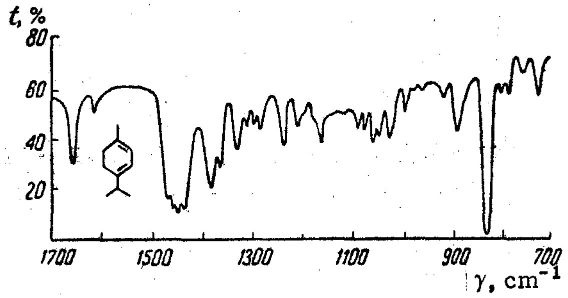

Fig. 2. IR spectrum of the α-terpinene isolated from the turpentine of Pinus silvestris L.

We have also shown by preparative and analytical GLC that other turpentines contain α-terpinene in the following amounts (%) from Pinus silvestris L. —oleoresin, 0.1; extraction, 0.5; dry-distillation, 2.2; oleoresin turpentines from the pines P. silvestris L. subspecies lapponica Fries (Lapland Scotch pine), 0.9; P. silvestris L. subspecies sibirica Ldb. (Siberian pine), 2.2; P. silvestris L., subspecies Kulundensis Sukaczew (Kulundian pine), 0.4; P. Pallasiana Lamb. (Crimean pine), < 0.1; P. austriaca Höss (Austrian pine), < 0.1; P. sibirica Ldb. (Siberian cedar), 0.2; Abies sibirica Ldb. (Siberian fir), 0.1; Larix sibirica Mayr. (Siberian larch), 0.1; Picea excelsa Link. (Norway spruce), < 0.1.

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