raised according to a linear program from 70 to 220°C at the rate of 4 deg/min. The temperature of the detector was 250°C and that of the evaporator 285°C. The rate of flow of helium was 120 ml/min.

CONCLUSION

1. It has been established that the accumulation of essential oil in the litter of the Siberian larch takes place up to the end of the vegetation season.

2. It has been shown that during the vegetation period not only the amount but also the composition of the essential oil from the litter of the Siberian larch changes.

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TERPENOIDS OF THE OLEORESIN OF *Pinus kochiana*

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The chemical composition of the oleoresin of Koch's pine growing in the Caucasus has been studied. It has been shown that, with respect to the composition of the monoterpenes and the resin acids, the oleoresin of this species does not differ from oleoresins of the subgenus *Diploxylon* studied previously. Predominating among the sesquiterpenes is germacrene D, which has not previously been found in the resins of the conifers of the USSR. The diterpenoids are represented by tricyclic compounds (pimarinol, isopimarinol, and methyl 15-hydroxydehydroabietate and the hydrocarbons corresponding to them).

The pines (genus *Pinus*) growing in the USSR are subdivided into two subgenera *Haploxylon* and *Diploxylon*. At the present time, the chemical compositions of the oleoresins of pines of the subgenus *Haploresin* have been studied, and for these a considerable content of labdane and cembrane diterpenoids is characteristic [1-4]. Of the pines of the subgenus *Diploxylon*, the oleoresin of only one species has been studied — the Scots pine. It has been established that tricyclic compounds of the pimarane and dehydroabietane types predominate in it [5].

In the present paper we give the results of a study of the terpenoids of the oleoresin of *Pinus kochiana* Koch. (Koch's pine). The name of this species is a disputed question: in the literature eight species names and seventeen in units of lower rank have been given [6, 7]. In the book "Flora Gruzii" ["The Flora of Georgia"], the pine growing in the Borzhomi gorge is named *Pinus sosnovskii* Nakai (syn. *Pinus hamata* Stev.) [6, 8]. On the basis of recent literature information [7], we shall use for this species the name *Pinus kochiana* Koch.

The compositions of the turpentine and of the resin acids of this species have been studied [9-11], but no information is available on the sesqui- and diterpenoids.

We have isolated the neutral and acid components from the oleoresin of the pine by a method described previously [4]. The neutral substances were separated by adsorption chromatogtaphy into hydrocarbons and oxygen-containing compounds, and these were fractionated by vacuum distillation into narrow groups.

The composition of the monoterpene hydrocarbons was determined by gas-liquid chromatography (GLC). α- and β-pinenes (46.7% and 46.3%, respectively) were identified as the main

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components, which is in harmony with the results for the composition of the turpentine of *Pinus sylvestris* ssp. *hamata* Stev. [9].

In the fraction of oxygen-containing monoterpenoids methylchavicol, methyleugenol, pinocarveol, α-terpineol, and α-terpenyl acetate were identified. The main component of this group of compounds was methyleugenol, which has not been found previously in the oxygen-containing compound fraction of the oleoresin turpentine of *Pinus hamata* [10].

The main sesquiterpene hydrocarbons-germacrene D, α- and γ-murolenes and the minor components-β-copaene, α-ylangene, and α-copaene- were isolated by adsorption chromatography and preparative GLC.

A feature of the oleoresin of *Pinus kochiana* is the high content of germacrene D, which has been detected previously only in the oleoresins of *Pinus edulis* and *Pinus monophylia* growing in North America [12].

Diterpene hydrocarbons were represented by compounds of the abietane and pimarane type, the main ones being abietadiene, isopimaradiene, and pimaradiene. The neutral oxygen-containing compounds consisted mainly of diterpenoids, and these were studied by adsorption chromatography. We isolated methyl abietate, methyl dehydroabietate, methyl isopimarate, pimarinol, and methyl 15-hydroxydehydroabietate and identified, from spectral characteristics, pimarinal, and methyl 15-hydroxyabietate.

The resin acids were studied by the GLC method. It was established that the set of acids is characteristic for conifer resins, the components present in largest amount being palustric (levopimaric) and dehydroabietic acids [11].

Thus, the results of the investigation have shown that the composition of the oleoresin of Koch's pine is close to that of the oleoresin of Scots pine with respect to the amounts of mono- and diterpenes. The presence of tricyclic compounds of the pimarane type is probably characteristic for the diterpenoids of pines (subgenus *Diploxylon*) [5, 13]. The composition of the monoterpenes and resin acids does not differ fundamentally from the results obtained previously for pines of this subgenus [9, 11]. At the same time, there are marked differences in the compositions of the sesquiterpenes of the oleoresin of Koch's pine and the oleoresin of the Scots pine [14] with a high content of germacrene D.

EXPERIMENTAL

IR spectra were taken on a UR-20 instrument. PMR spectra were recorded in CCl_4 on a Varian A 56/60 A instrument with HMDS as internal standard (δ scale), its chemical shift being taken as δ 0.05 ppm. Mass spectra were recorded on a MS-902 instrument with a glass inlet system (70 eV, 120°C).

The analytical GLC of the sesquiterpene hydrocarbons was carried out in capillary columns with OV-17 and OV-225 on a Khrom-4 instrument with 50 m × 0.2 mm columns at a rate of flow of carrier gas (nitrogen) of 6 ml/min, the column temperature being raised from 100 to 220°C at 2°C per minute.

The pine oleoresin was collected in June, 1979, in the region of the Bordzhomula River (Georgia).

Treatment of the Oleoresin. When 500 g of the oleoresin was treated by a known method [4], 300 g of a mixture of resin acids, 45.3 g of monoterpene hydrocarbons, 5 g of sesquiterpene hydrocarbons, 0.9 g of diterpene hydrocarbons, and 1.5 g and 24 g of mono- and diterpenoid oxygen-containing compounds, respectively, were obtained.

Monoterpene Hydrocarbons. The qualitative and quantitative analysis of the monoterpenes was carried out by GLC using a method described in the literature [15]. The following were identified through their relative retention times: α-pinene (46.7%), camphene (0.5%), β-pinene (46.3%), Δ^3-carene (1.6%), myrcene (0.5%), limonene (2.6%), β-phellandrene (1.3%), and terpinolene (0.5%).

Sesquiterpene Hydrocarbons. The mixture of sesquiterpene hydrocarbons (5 g) was chromatographed on silica gel (125 g). Gradient elution (petroleum ether—diethyl ether) yielded six fractions: A (0.19 g), B (0.45 g), C (0.6 g), D (2 g), E (0.74 g), and F (0.9 g).

γ-Murolene (0.2 g) was isolated by the chromatography of fraction G on $SiO_2/AgNO_3$ (40 g). According to the results of TLC and of IR, UV, and PMR spectroscopy, fraction D contained pure germacrene D $[\alpha]_D^{20}$ −350° (c 2.5; $CHCl_3$).

By preparative GLC, fraction A yielded a mixture of α-ylangene and α-copaene, fraction B β-copaene, and fraction C α-murolene with $[\alpha]_D^{20}$ −46.7° (without solvent), n_D^{20} 1.5048. The individuality of the compounds isolated was confirmed by comparing their PMR spectra with those of authentic samples.

Longicyclene, longifolene, δ-cadinene, and ε-murolene were identified through their relative retention times (GLC).

The amounts of the following sesquiterpenes were determined by analytical GLC in capillary columns: germacrene D (64.9%), α-murolene (11.1%), γ-murolene (5.2%), longicyclene (3.3%), α-copaene (4.9%), α-ylangene (4.9%), ε-murolene (2.7%), δ-cadinene (2.3%), longifolene (2.2%), and β-copaene (2.0%).

Oxygen-Containing Monoterpenoids. The fraction of oxidized monoterpenoids (1.5 g) was chromatographed on silica gel (45 g). Petroleum ether with increasing amounts of diethyl ether eluted methylchavicol (0.06 g), a mixture of methylchavicol and α-terpenyl acetate (0.16 g), a mixture of α-terpenyl acetate and methyleugenol (0.13 g), methyleugenol (0.2 g), pinocarveol (0.07 g), and α-terpineol (0.06 g). The compounds isolated were identified by their PMR spectra.

Diterpene Hydrocarbons. The fraction of diterpene hydrocarbons (0.9 g) was separated by chromatography on silica gel (72 g) with petroleum ether into two fractions, A (0.54 g) and B (0.26 g). The chromatography of fraction A on $SiO_2/AgNO_3$, 5% (22 g) (petroleum ether—1% of diethyl ether) yielded abietadiene (0.08 g) with $[\alpha]_D^{20}$ +10.3° (c 3.6; $CHCl_3$), n_D^{20} 1.5022; isopimaradiene (0.12 g) with $[\alpha]_D^{20}$ −31.6° (c 4.5; $CHCl_3$, n_D^{20} 1.5185; and pimaradiene (0.04 g) with n_D^{20} 1.5190.

According to GLC, fraction B contained paraffinic hydrocarbons from C_{24} to C_{36}.

Oxygen-Containing Diterpenoids. The oxygen-containing diterpenoids (5 g) were chromatographed on silica gel (100 g), and petroleum ether with increasing concentrations of diethyl ether (from 0 to 25%) eluted seven fractions: A (0.65 g), B (0.4 g), C (0.82 g), D (0.85 g), E (0.2 g), F (0.81 g), and G (0.92 g).

According to the results of TLC, GLC, and IR and PMR spectroscopy, fraction A contained pimarinal and isopimarinal (a comparison was made with authentic samples).

Fraction B consisted of the dimethyl ether of pinosylvin and the methyl esters of abietic, dihydroabietic, pimaric, and isopimaric acids (identified by GLC), and fraction C consisted of methyleuginol (identical with an authentic sample). By chromatography on $SiO_2/AgNO_3$ (16 g), fraction D yielded pimarinol (0.12 g, with $[\alpha]_D^{20}$ +65.5° (c 4.0; $CHCl_3$, n_D^{20} 1.5262, the IR and PMR spectra of which were identical with those of the authentic sample.

Fraction B,* eluted by a mixture of petroleum ether and diethyl ether (80:20) contained methyl 15-hydroxydehydroabietate and methyl 15-hydroxyabietate in a ratio of 2:1 (checked by GLC). The presence of methyl 15-hydroxyabietate was confirmed by spectral characteristics (UV spectrum λ_{max} 238, 241 nm: PMR spectrum, 5.73 ppm (1 H, singlet), 5.35 ppm (1 H, broadened triplet). The methyl 15-hydroxydehydroabietate with mp 81-83°C gave no depression of melting point with an authentic sample.

The most polar fraction G consisted of a mixture of methyl 15-hydroxydehydroabietate and polyfunctional compounds which have not been investigated.

Resin Acids. The acids (1 g) were dissolved in diethyl ether and treated with diazomethane. After the elimination of the solvent, the methyl esters of the resin acids were analyzed by GLC as described previously [15].

The mixture was found to contain abietic acid (9%), neoabietic acid (9%), dehydroabietic acid (16%), pimaric acid (6%), palustric/levopimaric acid (59%), and, in small amounts, isopimaric and sandaracopimaric acids.

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*As in Russian original — Publisher.

CONCLUSION

1. The chemical composition of the oleoresin of Koch's pine growing in the Caucasus has been studied.

2. It has been shown that the main components of the sesquiterpene fraction is germacrene D.

3. The diterpenoids are represented by tricyclic compounds of the pimaric and isopimaric types. Methyl 15-hydroxydehydroabietate and 15-hydroxyabietate have been found in pine oleoresin for the first time.

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