SUMMARY

A new germacranolide – shonachalin C with the composition $C_{15}H_{22}O_4$, mp 203-205°C – has been isolated from Artemisia fragrans.

A structure has been proposed for shonachalin C.

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CHEMICAL COMPOSITION OF THE OLEORESIN OF *Larix kamtschatica*

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The chemical composition of the oleoresin of the Kamchatka larch has been studied. Mono-, sesqui-, and diterpenoids have been found in it. The monoterpenes were represented by nine components (the main one being 3-carene), and among the sesquiterpene hydrocarbons γ-element, longifolene, and germacrene D predominated. The main oxygen-containing diterpenoid was larixyl acetate. Seven resin acids were determined, the main one being isopimaric and palustric and/or levopimaric.

Continuing a study of the oleoresin of larches growing in the Far East, we have investigated the chemical composition of the oleoresin of *Larix kamtschatica* (Rupr.) var. *kurilensis* (Kamchatkan or Kurile Dahurian larch) growing on the Kurile Islands [1, 2].

After the initial oleoresin had been treated by the usual method, about 60% of neutral and 40% of acidic compounds were obtained. The neutral fraction consisted of a mixture of mono-, sesqui-, and diterpene hydrocarbons and their oxygen-containing derivatives. The hydrocarbons (30%) and the oxygen-containing compounds (70%) were separated by the chromatography of the neutral fraction on alumina. The hydrocarbons were separated by vacuum distillation into monoterpenes (24% on the neutral fraction), sesquiterpenes (2.1%), and diterpenes (1.7%).

The monoterpene hydrocarbons were analyzed by the GLC method. Of the nine compounds found – camphene, α- and β-pinenes, 3-carene, limonene, myrcene, β-phellandrene, γ-terpinene, and terpinolene – the main component was 3-carene (78%).

Chromatography of the sesquiterpene fraction on SiO_2 and $SiO_2 + AgNO_3$ led to the isolation of γ-elemene, longifolene, germacrene D, α-, γ-, and δ-cadinenes, and α- and γ-muurolenes. Another 15 hydrocarbons were identified by their retention times in the GLC method. Only three components – germacrene D (25.9%), longifolene (21.8%), and γ-elemene (13.4%) were found in considerable amounts.

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It must be mentioned that, with increasing times of storage of the oleoresin or of the hydrocarbon fraction, and also the GLC conditions, the amount of germacrene D decreases, but the amount of bicyclic hydrocarbons of the muurolane-cadinane group increases. A similar phenomenon has been observed for the oleoresin of the Amur and Dahurian larches (L. amurensis and L. dahurica) [3].

The composition of the diterpenoids was studied mainly by adsorption chromatography using a sorbent with added silver nitrate.

The diterpene hydrocarbons contained dehydroabietane, abietadiene, and isopimaradiene.

The oxygen-containing diterpenoids forming the basis of the neutral fraction were represented by primary and tertiary alcohols. The sum of the primary alcohols was investigated in the form of acetates by the GLC method with the addition of authentic samples. The acetates of palustrol, isoprimarinol, dehydroabietinol, abietinol, and neoabietinol were identified, and among them the acetates of dehydroabietinol and of palustrol predominated (33% and 21.4%, respectively). In the oleoresin investigated the amounts of epimanool (10%) and larixol (6%) were low, and the amine component was larixyl acetate (57%).

The acid fraction of the oleoresin was analyzed in the form of methyl esters by gas-liquid chromatography. Among the seven resin acids – sandaracopimaric, palustric, levopimaric, isopimaric, dehydroadietic, neoabietic, and abietic – isopimaric acid predominated (56.3%), which is characteristic for larch oleoresins [4, 5].

The study of the chemical composition of the oleoresin of the Kamchatkan larch revealed its common and its distinguishing features in relation to other Far Eastern species of larch: Dahurian and Amur [3], Korean Dahurian (L. olgensis) [5], and Cajander's (L. cajanderi) [6]. Characteristic features of the oleoresin of the Kamchatkan larch include a high content of 3-carene and of germacrene D and also the absence of oxygen-containing mono- and sesquiterpinoids. In other larches, the main monoterpene is α-pinene, and only in the Korean Dahurian larch does the amount of 3-carene reach 50%. In the last-mentioned larch, likewise, no oxygen-containing mono- and sesquiterpenoids are found. The group distribution of the sesquiterpenoids according to the types of cyclization of the precursor [7] – farnesyl pyrophosphate – is approximately the same for all species of larch.

No diterpene aldehydes and esters were found in the oleoresin of the given species. Among the resin acids pimaric and communic acids were absent, and we may mention that the presence of communic acid is characteristic only for certain species of larch [8].

EXPERIMENTAL

The oleoresin of the Kamchatkan larch was collected on the island of Iturup in August, 1983.

Treatment of the Oleoresin. The oleoresin (430 g) was treated with a 1% aqueous solution of caustic soda (3 liters). The neutral compounds (260 g) were isolated by extraction with diethyl ether. Part of the sodium salts was treated with 5% hydrochloric acid and the products were then extracted with diethyl ether. After the solvent had been driven off, a mixture of acids (50 g) was obtained.

Separation of the Neutral Fraction. The neutral compounds (150 g) were chromatographed on alumina (activity grade I-II; ratio 1:10). Petroleum ether eluted hydrocarbons (45 g) and ethanol eluted oxygen-containing compounds (105 g).

The hydrocarbon fraction (45 g) was separated by vacuum distillation into monoterpenes (36.8 g, 60-110°C/10 mm), sesquiterpenes, (3.2 g, 80-130°C/0.1 mm), and diterpenes (2.5 g, still residue).

The Monoterpene Hydrocarbons. Analysis of this fraction was performed by the GLC method under conditions given previously [3]. It was established that the main component was 3-carene (78.0%). The following were identified from their relative retention times: camphene (traces), α-pinene (13.4%), β-pinene (5.4%), limonene (1.0%), myrcene (traces), β-phellandrene (1.0%), β-terpinene (0.5%), and terpinolene (0.6%).

The Sesquiterpene Hydrocarbons. The sesquiterpene fraction (1.5 g) was chromatographed on silica gel (60 g, 0.100-0.160 mm), giving a mixture of longifolene and α-longipinene (0.06 g, 2:1, PMR), longifolene (0.16 g), a mixture mainly of bicyclic sesquiterpenes of the cadalene series (0.53 g), γ-elemene (0.14 g), and germacrene D (0.27 g).

Rechromatography of the combined bicyclic sesquiterpenes (0.53 g) on silica gel with silver nitrate (20%) led to the isolation of longifolene (0.06 g), δ-cadinene (0.11 g), α-muurolene (0.04 g), α-cadinene (0.1 g), and γ-muurolene (0.06 g).

All the hydrocarbons isolated were identified from their PMR spectra.

The qualitative and quantitative compositions of the combined sesquiterpenes were determined from their relative retention times and by the method of additives on a capillary column containing OV-101 with programming of the temperature from 120 to 180°C (2°C per minute): β-farnesene (0.8%), ar-curcumene (4.4%), germacrene D (25.9%), α-muurolene (1.6%), γ-muurolene (1.9%), ε-muurolene (1.3%), δ-cadinene (6.2%), γ-cadinene (5.1%), α-cadinene (1.8%), α-calacorene (1.0%), α-ylangene, (1.3%), α-copaene (2.5%), β-copaene (1.0%), cyclosativene (traces), longifolene (21.8%), α-longipinene (1.3%), longicyclene (0.5%), γ-elemene (13.4), sibirene (traces), α- and β-selinenes (4.1%), α-humulene (1.5%), and caryophyllene (1.0%).

The Diterpene Hydrocarbons. The diterpenes (0.85 g) were chromatographed on silica gel with silver nitrate (5%). Petroleum ether–diethyl ether (99:1) eluted 0.15 g of a mixture of dehydroabietane and abietadiene (1:1.5, GLC, PMR). Petroleum ether–diethyl ether (97:3) yielded isopimaradiene (0.1%) with n_D^{22} 1.5220 and $[\alpha]_D^{22}$–28.1° (c 3.2; $CHCl_3$) (according to the literature [9]: $[\alpha]_D^{22}$–31.3°); the IR and PMR spectra of the hydrocarbons isolated were identical with those of isopimaradiene.

The Oxygen-Containing Diterpenoids. The ethanolic fraction (2 g) was chromatographed on silica gel (ratio 1:20). Petroleum ether–diethyl ether (95:5) eluted epimanool (0.22 g) with n_D^{22} 1.5180 and $[\alpha]_D^{22}$ + 38° (c 7.3; $CHCl_3$); the IR and PMR spectra were identical with those of an authentic sample.

The same system eluted a fraction of primary alcohols (0.34 g), which was acetylated with acetic anhydride in pyridine. After the usual working up of the reaction mixture, a mixture of acetates was obtained which was analyzed by GLC. Recording conditions: Chrom 41 instrument, 2.5 × 3 mm glass column, stationary phase 5% of XE-60 on Chromaton 0.125-0.160 mm; column temperature 210°C; evaporator temperature 250°C; carrier gas nitrogen at a rate of flow of 30 ml/min. Acetates of the following alcohols were identified by the additive method: palustrol (21.4%), isopimarinol (18%), dehydroabietinol (33%), abietinol (12.5%), and neoabietinol (9.4%), and there was an unidentified compound (4.7%).

Petroleum ether–diethyl ether (90:10) yielded larixyl acetate (1.14 g) with mp 78-80°C and $[\alpha]_D^{22}$ + 68.2° (C 1.7; $CHCl_3$) (according to the literature [10]: mp 80°C, $[\alpha]_D$ +67°).

The most polar compound (0.12 g) was eluted by the (80:20) system. Crytaliine substance with mp 98-99°C, $[\alpha]_D^{22}$ +52.3°, identical in its physical constants and spectral characteristic with larixol (according to the literature [10], mp 101°C $[\alpha]_D$ + 57°).

The Resin Acids. The acids (10 g) were dissolved in diethyl ether and treated with an ethereal solution of diazomethane. After the solvent had been eliminated, the methyl esters of the acids were chromatographed on silica gel. Petroleum ether–diethyl ether (95:5) yielded methyl esters of the resin acids (7.2 g), and diethyl ether eluted esters of polyfunctional resin acids (2.7 g). The following composition of the methyl eters of the resin acids was established by the GLC method under the conditions given in [11]: sandaracopimaric (3.4%), palustric and/or levopimaric (19.1%), isopimaric (56.3%), dehydroabietic (7.7%), abietic (9.7%), and neoabietic (3.8%).

SUMMARY

1. The chemical composition of the oleoresin of the Kamchatkan larch growing in the Kurile islands has been studied.

2. It has been shown that the oleoresin of this species differs from those of other Far Eastern species of larch by its high levels of 3-carene and germacrene D and by the absence from it of oxygen-containing mono- and sesquiterpenoids and diterpene aldehydes and esters, and also of pimaric and communic acids.

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CYCLIZATION AND REARRANGEMENT OF DITERPENOIDS.

IV. SYNTHESIS OF Δ^{12}- AND $\Delta^{13(14)}$-ISO-20-DEOXYLUTEONES

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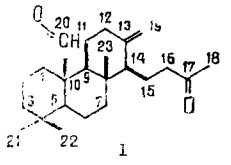
Δ^{12}- and $\Delta^{13(14)}$-Iso-20-deoxyluteones have been synthesized from 13E- and 13Z-bicyclogeranylgeranylacetones. The latter were reduced to the corresponding alcohols, which were acetylated, and the acetates obtained were cyclized with fluorosulfonic acid in nitropropane. The reaction product was saponified to a mixture of tricyclic alcohols which were oxidized with the chromium trioxide-pyridine complex to a mixture of Δ^{12}- and $\Delta^{13(14)}$-iso-20-deoxyluteones and this was separated chromatographically.

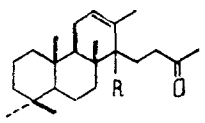
Recently, a binorsesterterpene ketone of the cheilanhane series, luteone (I), possessing a pleasant fruity aroma, has been isolated from the nudibranchiate mollusc Cadlina luteomarginata [1, 2].

In view of this, and also considering the fact that luteone and ketones related to it may serve as intermediates in the synthesis of certain sesterterpenes, we decided to perform the synthesis of its 20-deoxo analogs starting from readily available labdanoids.

In the present communication we describe the synthesis of Δ^{12}- and $\Delta^{13(14)}$-iso-20-deoxoluteones (II-IV) from sclareol (V) and manool (VI).



I



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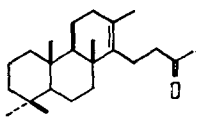
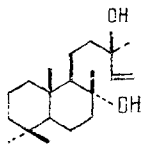
III. R=βH



IV



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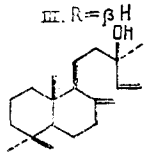
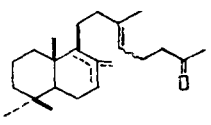


VI



VII

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