MONO- AND SESQUITERPENOIDS OF THE OLEORESIN OF *Pinus koraiensis* AND *P. pumila.*

CRYSTAL STRUCTURE OF 1β,4αH,7αH,10βH-GUAIANE-5α,14-DIOL

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The composition of the mono- and sesquiterpenoids of the oleoresin of two species of conifers of the *Pinaceae* family has been studied. In the oleoresin of *Pinus koraiensis* Sieb. et Zucc. 10 oxidized monoterpenoids, 18 sesquiterpene hydrocarbons, and six sesquiterpene alcohols have been identified. In the oleoresin of *Pinus pumila* (Pall.) Rgl. 10 monoterpenoid hydrocarbons, six oxidized monoterpenoids, 14 sesquiterpene hydrocarbons, and four sesquiterpene alcohols have been found. The structure of 1β,4αH,7αH,10βH-guaiane-5α,14-diol, one of the hydroboration-oxidation products of an unidentified sesquiterpene alcohol isolated from both oleoresins, has been determined by x-ray structural analysis.

We have previously reported the composition of the mono- and sesquiterpene hydrocarbons of the oleoresins of the Korean pine (*Pinus koraiensis* Sieb. et Zucc.) [1] and the Japanese stone pine (*Pinus pumila* (Pall.) Rgl., island of Sakhalin) [2]. In the present communication we consider the results of an investigation of the mono- and sesquiterpenoids of the oleoresins of the Korean and Japanese stone pines growing on the northern shores of Lake Baikal.

In the oleoresin of the Korean pine, in addition to the a-longipinene, longifolene, caryophyllene, a-humulene, γ-cadiene, γ-murolene, and cadalene isolated previously, we have identified δ-cadiene, a-murolene, β-farnesene, γ-elemene, γ-amorphone, α-cadinene, ε-murolene, β-bisabolene, cyclosativene, calamenene, and calacorene. The main components of the sesquiterpene hydrocarbon fractions are caryophyllene (25%), β-bisabolene (15%), and longifolene (14%).

Of the oxidized mono- and sesquiterpenoids in the oleoresin of the Korean pine we have identified a-terpineol, terpineol-4, borneol, linalool, pinocamphone, pinocarveol, pinan-l-ol, sabinene hydrate, a-terpenyl acetate, bornyl acetate, δ-cardinol, bisabolol, cubebol, epicubebol, and epicubenol, and also korairol (1) — a sesquiterpene alcohol with a new type of carbon skeleton. The structure of the last-mentioned compound has been determined by x-ray structural analysis [3]. Bisabolol is the main component of the fraction of oxidized mono- and sesquiterpenoids. Gas-liquid chromatography and thin-layer chromatography showed the presence of small amounts of several more alcohols, of which we isolated three unidentified sesquiterpene alcohols denoted by the letters A, B, and C.

Alcohol A is a labile sesquiterpene compound (mol. wt. 220) with two double bonds: trisubstituted (5.56 ppm, 1 H) and exocyclic (4.72 ppm, 2 H; ν = 890, 3080 cm⁻¹). The spectral characteristics indicate the presence of a tertiary hydroxyl (3605 cm⁻¹) and of three methyl groups (1.0 ppm, doublet, J = 8 Hz, 6H; 1.22 ppm, 3 H). The hydroboration-oxidation of alcohol A gave a mixture of products from which we separated by chromatography previously undescribed 1β,4αH,7αH,10βH-guaiane-5α,14-diol. The structure (2) and the conformation (Fig. 1) of this diol were determined by x-ray structural analysis.

![Diagram](image-url)
Alcohol B also belongs to the group of sesquiterpene alcohols (mol. wt. 222). The IR and PMR spectra show the presence of a tertiary hydroxyl (3610 cm\(^{-1}\)) and of a secondary methyl group (0.82 ppm, 3 H, doublet, \(J = 5.5\) Hz), of a \(\text{CH}_3-\text{C}-\text{OH}\) fragment (1.18 ppm, 3 H), and of an exocyclic double bond (4.61 ppm, 2 H, \(\nu = 890, 3080\) cm\(^{-1}\)).

Alcohol C (mol. wt. 220) contains two exocyclic double bonds (4.75 ppm, 2 H; 4.92 ppm, 1 H; 5.02 ppm, 1 H; \(\nu = 890, 910, 3080\) cm\(^{-1}\)), geminal methyl groups (1.0 ppm, 6 H; 1360, 1374 cm\(^{-1}\)), and a tertiary hydroxy group (3610 cm\(^{-1}\)).

The oleoresin of the Japanese stone pine from the northern shores of Lake Baikal differs in relation to the composition of the mono- and sesquiterpene hydrocarbons from the oleoresin of this species of pine that we investigated previously, which was collected on the island of Sakhalin [2]. Thus, the new oleoresin lacks \(\alpha\)-thujene and contains considerably less \(\beta\)-phellandrene while the content of \(\alpha\)-pinene, the dominating component of the monoterpen hydrocarbon fraction, has increased somewhat.

The sesquiterpene hydrocarbons of these oleoresins differ mainly by the presence of \(\alpha\)-bisabolene in the oleoresin under investigation. Furthermore, in this fraction we identified cyclosativene, longicyclene, longifolene, sibirene, caryophyllene, \(\gamma\)-elemene, \(\alpha\)-humulene, \(\alpha\)-muurolene, \(\delta\)- and \(\gamma\)-cedinene, \(\beta\)-bisabolene, ar-curcumene, and calacorene. The main components of the sesquiterpene hydrocarbons are longifolene (34%), \(\alpha\)-bisabolene (30%), and \(\beta\)-bisabolene (14%).

In the fraction of oxidized mono- and sesquiterpenoids, bisabolol predominates (42%), and together with this we have found cubebol and epicubebol, koraol, the unidentified alcohol A, \(\alpha\)-terpineol, terpineol-4, borneol, bornyl acetate, sabine hydrate, and linalool. This fraction was also found to contain a labile alcohol which, on chromatography, gave as decomposition products a mixture of \(\delta\)- and \(\gamma\)-cadinenes.

The dominating position of compounds of the bisabolane series (\(\alpha\) and \(\beta\)-bisabolenes, bisabolol) among the sesquiterpenoids of the oleoresin of the Japanese stone pine from Lake Baikal must be noted.

**EXPERIMENTAL**

For instruments and methods, see the literature [4].

The oleoresin of the Korean pine was collected in 1976 in Khabarovsky territory, and the oleoresin of the Japanese stone pine was obtained from open resin blazes on the north eastern shores of Lake Baikal, also in 1976.

For chromatography we used air-dry silica gel or silica gel impregnated with 10% AgNO\(_3\) (SiO\(_2\) + AgNO\(_3\)) activated at 100°C for 3 h. The eluent for the chromatography of the hydrocarbons on SiO\(_2\) was petroleum ether, and on SiO\(_2\) + AgNO\(_3\) petroleum ether with the addition of 2-10% of diethyl ether.