

THE CHEMICAL COMPOSITION OF THE OLEORESIN
OF THE GENUS *Picea* DITERPENOIDS OF THE OLEORESIN
OF *Picea obovata*

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We have previously reported a study of the monoterpene and sesquiterpene compounds of the oleoresin of *Picea obovata* Ledb. (Siberian spruce) [1, 2].

The present paper gives the results of an investigation of the high-boiling neutral fraction of the oleoresin, no information on the chemical composition of which exists. The diterpene compounds were isolated from the spruce oleoresin (Krasnoyarsk region, 400 g) by the usual method [3]. Then the diterpenoids (51.7 g) were separated chromatographically into hydrocarbons (15 g) and oxygen-containing compounds (31.0 g).

Among the hydrocarbons we found cembrene, mp 59–60°C, $[\alpha]_D^{20} + 234^\circ$ (c 2.0; chloroform), λ_{\max} 246, nm (log ϵ 4.8) (literature data [4]: mp 59–60°C; $[\alpha]_D^{20} + 238^\circ$, λ_{\max} 245 nm, ϵ 17,000) and a new diterpene – neocembrene with $[\alpha]_D^{20} - 20^\circ$ (c 0.1; n-heptane), n_D^{20} 1.5110, the determination of the structure of which has been reported separately (see page 705).

By chromatography of the oxygen-containing compounds we isolated four diterpenoids: isocembrol with $[\alpha]_D^{20} + 78.4^\circ$ (c 2.0; chloroform), n_D^{20} 1.5020 (literature data [5]; $[\alpha]_D^{20} + 80.1^\circ$ (c 3.2), n_D^{20} 1.5035); epimanoyl oxide, mp 97–98°C, $[\alpha]_D^{20} + 35.7^\circ$ (c 2.1; chloroform) (literature data [3]: mp 99–101°C, $[\alpha]_D^{20} + 36.8^\circ$ (c 2.5; chloroform); neoabienol, $[\alpha]_D^{20} + 13.3^\circ$ (c 1.7; chloroform), n_D^{20} 1.5240, λ_{\max} 238 nm (log ϵ 4.38) (literature data [6]: $[\alpha]_D^{20} + 12.95^\circ$ (c 3.85; chloroform), n_D^{20} 1.5266, λ_{\max} 238 nm (log ϵ 4.46), and dehydroabietinol, $[\alpha]_D^{20} + 50.1^\circ$ (c 2.2; chloroform), n_D^{20} 1.5305, 3,5-dinitrobenzoate with mp 123–124°C (literature data [7]: bp 177°C, $[\alpha]_D^{25} + 53^\circ$ (absolute ethanol); 3,5-dinitrobenzoate with mp 123–124°C).

Dehydroabietinol is rarely found in the native state [8] and has not been found at all in the oleoresins of the genus *Picea*.

Of the compounds mentioned, cembrene, isocembrol, neoabienol, and dehydroabietinol are the main components of the neutral fraction of the oleoresin.

The investigation performed shows that the compositions of the diterpenoids of the oleoresin of *Picea obovata* Ledb. and *P. ajanensis* Fisch. differ markedly [3]. In the latter, the predominating components are tetracyclic compounds of the phyllocladane type, which were not found in the oleoresin of the Siberian spruce. The study of the minor components of the spruce oleoresin is continuing.

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