EXTRACTIVE SUBSTANCES IN THE BARK OF Larix dahurica

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The Dahurian larch, Larix dahurica Ledb., occupies an enormous territory on Eastern Siberia [1] and is actively subjected to felling and processing. Only the wood is used, and the bark has found no practical application.

In order to determine possible methods for the utilization and complex processing of the bark we have studied the composition of a gasoline extract of the bark of the Dahurian larch growing in the region of Ust-'Ilima. The air-dry ground larch bark (600 g) was extracted with "Kalosha" gasoline in a Soxhlet apparatus for 6 h. The yield of extractive substances changes over the height of the trunk (top – 1.8%; middle – 1.7%; butt – 2.5%). The extract obtained was evaporated, giving 12 g of product (yield 1.5-2.5%, varying with the time of storage of the bark). The extract was separated by the usual method into acid (45%) and neutral (55%) substances [2].

The free acids of the extract were treated with urea in order to separate the saturated fatty acids [3]. The ratio of saturated and unsaturated acids was 1:1.5. Then the acids were methylated with diazomethane and the resulting methyl esters were analyzed by GLC. The main components of the mixture of saturated fatty acids were palmitic (4.5%), arachidic (4.2%), behenic (20.0%), and lignoceric (51.2%).

The sum of the unsaturated fatty and resin acids consisted of the following components (%): oleic (2.6), linoleic (1.6), linolenic (1.1), pimaric (3.0), levopimaric/palustric (2.7), isopimaric (35.9), abietic (7.6), dehydroabietic (16.3), and neoabietic (2.8).

The neutral part of the extract (analysis by absorption chromatography on silica gel) contained hydrocarbons (4.5% of the neutral fraction), aldehydes (10%), esters (22.5%), alcohols (terpenic – 10%; aliphatic – 15%), alkyl ferulates (12%), diols (15%), and polyfunctional polar compounds (10%), which were not investigated.

Hydrocarbons (according to GLC) were represented by n-alkanes (%): C_{13} (1.4), C_{14} (13.5), C_{15} (6.9), C_{16} (1.3), C_{17} (1.2), C_{18} (1.9), C_{20} (12.9), C_{21} (1.8), C_{22} (2.6), C_{23} (1.7), C_{24} (1.7), C_{25} (2.1), C_{26} (0.7), C_{27} (1.0), and C_{28} (0.6%), and unidentified unsaturated compounds.

The identification of individual components of the neutral fraction of the extract was made by a comparison with authentic specimens with respect to physical constants and spectral characteristics. The main compounds were pimarinal, isopimarinal, dehydroabietinal, epimanool, docosanol, tetracosanol, larixyl acetate, epitorulosol acetate, larixol, epitorulosol, and β-sitosterol. Esters of ferulic acid and aliphatic alcohols were isolated: Their saponification gave $C_{22}H_{46}O$ and $C_{24}H_{50}O$ alcohols and free ferulic acid with mp 168-169°C [4].

An aliquot of the neutral fraction of the extract (4.2 g) was treated with a 5% methanolic solution of caustic soda in a current of nitrogen and, after the working up of the reaction mixture, 1.3 g of "bound" acid and 2.7 g of neutral unsaponifiable substances were obtained. The acids were methylated and analyzed by GLC: They included myristic, palmitic, and arachidic, but the main ones were behenic (19.2%), lignoceric (25.8%), and oleic (22.3%).

The composition of the neutral unsaponifiable substances was distinguished by a large amount of fatty alcohols (~40%), among which the main ones were docosanol and tetracosanol.

Thus, the composition of the extractive substances of the bark of the Dahurian larch is close to that of the bark of the Siberian larch [5] but is distinguished by the presence of diterpene aldehydes and of larixol and its acetate.

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FLAVONOIDS OF Lagochilus platycalyx

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The genus Lagochilus, family Lamiaceae consists of 44 species, 33 of which grow in Central Asia [1].

Lagochilus platycalyx is a fairly widespread mountain species of the flora of Uzbekistan [2]. It has been found pharmacologically that an infusion of this plant possesses sedative and hypotensive properties, and there have been no indications whatever that it possesses a toxic action [3].

The comminuted air-dry leaves, gathered in the period of mass flowering at the beginning of June, 1988, in the outskirts of the village of Brichmulla, Bostanlykskii region, Tashkent province, were subjected to extraction with chloroform and then with 50% aqueous acetone. The aqueous acetone extract was concentrated to small volume and the flavonoids were extracted with ethyl acetate–ethanol (9:1). Their composition was analyzed by chromatography on Filtrak No. 11 paper and on Silufol plates in the n-butyl alcohol–acetic acid–water (4:1:5) and chloroform–methanol–ethyl acetate (3.5:1.5:0.5) systems. Seven substances of phenolic nature were detected.

The separation and isolation of individual compounds was achieved by column chromatography on polyamide. On elution with water, aqueous alcohol (9:1), and the ethyl acetate–methanol (9:1) system, four substances of flavonoid nature were isolated. They were identified on the basis of physicochemical constants, the results of IR spectroscopy with diagnostic reagents, chromatographic comparison with authentic markers, and a study of the products of acid hydrolysis and alkaline degradation.

Substance (I) – pale yellow crystals with the composition $C_{27}H_{30}O_{16}$, mp 191-192°C – formed on acid hydrolysis the aglycon quercetin and the sugars glucose and rhamnose. On the basis of physicochemical constants, IR and UV spectra, and a comparison with an authentic sample, substance (I) was identified as quercetin 3-O-[6-O-(α-L-rhamnopyranosyl)-β-D-glucopyranoside], which is known in the literature as rutin [4].

Substance (II) – bright yellow crystals with the composition $C_{15}H_{10}O_7$, mp 305-307°C – corresponded in its physicochemical constants to myricetin.

Substance (III) – yellow crystals with the composition $C_{15}H_{10}O_8$, mp 360°C – corresponded in its physicochemical constants to myricetin.

Substance (IV) – pale yellow crystals with the composition $C_{15}H_{10}O_6$, mp 272-274°C – corresponding in its physicochemical constants to kaempferol.

It had been shown previously by chromatography that the epigeal part of L. platycalyx contains rutin [5]. For a reliable identification we isolated it in the crystalline state and made a complete study of its physicochemical properties. We are the first to have isolated quercetin, kaempferol, and myricetin from the plant under investigation.

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