

EXTRACTIVE SUBSTANCES OF THE BARK OF *Larix sibirica* GROWING IN THE ALTAI

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A study of the chemical composition of the neutral fraction of a petroleum extract of the bark of the larch *Larix sibirica* L. growing in Krasnoyarsk territory has been published previously [1]. In the present paper we give the composition of a petroleum extract of the bark of the Siberian larch of the Altai population*. The yield of extract amounted to 1.5% of the weight of the air-dry bark.

When the extract was treated with aqueous alkali for its separation into acid and neutral components a voluminous flocculent precipitate (12% of the weight of the extract) deposited. Analysis of the precipitate showed that it mainly contained a known component of the bark — the natural polymer suberin [2] — and also phenolic acid esters, waxes, and fatty alcohols. Saponification of the precipitate with alcoholic alkali gave 45% of unsaponifiable substances and 30% of acids. The following fatty acids of normal structure were identified in the acid fraction (GLC, % by weight): 20:0 — 3.1; 22:0 — 29.0; 24:0 — 27.0; and also ferulic and p-coumaric acids — 20.0 and 15.0, respectively. The unsaponifiable substances contained the following aliphatic alcohols (GLC, % by weight): C₁₈ — 12.6; C₂₀ — 15.7; C₂₂ — 41.8; and C₂₄ — 5.9; and also β -sitosterol and campesterol — 11.2 and 1.6, respectively.

It is known that considerable amounts of esters of phenolic acids, particularly alkyl ferulates, are present in larch bark [3], but alkyl coumarates have not been detected in the extractive substances. Phenolic acids in the free form have been isolated previously from larch bark on its extraction with polar solvents and have been studied in detail [3–5]; when the bark was extracted with petroleum ether an insignificant amount of free phenolic acids was obtained.

The free acids made up about 60% of the extract and were represented by saturated and unsaturated fatty, resin, and aromatic acids. The composition of the free acids was as follows (analyzed by GLC in the form of methyl esters, % by weight): 16:0 — 5.6; X — 2.7; 18:1 — 6.3; 18:2 — 1.1; 18:3 — 2.0; 22:0 — 22.9; methyl pimarate — 3.3; 24:0 — 34.1; methyl isopimarate — 2.1; methyl abietate — 4.2; methyl dehydroabietate — 13.6; compare with the figures in [6].

The phenolic acids made up 3% of the total free acids and consisted of ferulic, coumaric, and caffeic acids.

The composition of the neutral fraction (n.f.) of the extract corresponded almost completely to the results obtained previously [1], but quantitative differences were observed. Thus, the neutral fraction contained larger amounts of fatty alcohols (about 25% of the weight of the n.f.) and esters. Saponification of the esters (15% of the weight of the n.f.) gave the unsaponifiable substances and acids, the latter mainly containing saturated components (GLC, %): 16:0 — 0.5; 18:0 — 2.3; 20:0 — 4.8; 22:0 — 69.0; 24:0 — 17.9.

According to GLC, the unsaponifiables contained docosanol (65%), tetracosanol (16%), β -sitosterol (10%) and campesterol (5%).

Saponification of the phenolic acid esters (12% on the weight of the n.f.) gave ferulic, p-coumaric, and caffeic acids, which were identified from their IR spectra and by comparison with authentic specimens. The alcohols docosanol and tetracosanol were identified among the unsaponifiable substances.

Phenolic acid esters are frequently found in extracts of various natural materials [7, 8] and have been well studied; recently, interest in them has increased in view of their biological activity [9].

In the neutral fraction of the extract we also identified the following substances from their spectral characteristics and by comparison with authentic specimens: epimanol (6%), β -sitosterol (20%), epitorulosol acetate (5%), and epitorulosol (10%). The hydrocarbons (totalling about 2%) and the polar substances (about 8%) were not investigated.

*The larch bark was collected in the Altai in the region of Lake Chemal in July, 1990.

REFERENCES

1. G. F. Chernenko and É. N. Shmidt, *Khim. Prir. Soedin.*, No. 6, 833 (1990).
2. É. D. Levin, O. B. Denisov, and R. Z. Pek, *The Complex Processing of the Larch* [in Russian], *Lesnaya Prom.*, Moscow (1978), p. 224.
3. K. I. Lapteva, N. A. Tyukavkina, and L. A. Ostroukhova, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, No. 4, 161 (1974).
4. T. K. Chumbalov, L. G. Pashinina, and Z. A. Leiman, *Khim. Prir. Soedin.*, 284 (1973).
5. M. L. Laver and H. H. L. Fang, *J. Agric. Food Chem.*, **37**, 114 (1989).
6. L. M. Levina and É. D. Levin, *Khim. Drev.*, No. 1, 88 (1975).
7. M. Boll, M. Hald, Y. S. Parmar, O. D. Tyagi, N. K. Sharma, and S. Hansen, *Phytochemistry*, **31**, No. 3, 1035 (1992).
8. T. Norin and B. Winell, *Acta Chem. Scand.*, **26**, 2289 (1972).
9. A. M. Balde, M. Claeys, L. A. Pieter, V. Wray, and A. J. Vlietnik, *Phytochemistry*, **30**, No. 3, 1024 (1991).