NEUTRAL EXTRACTIVE SUBSTANCES FROM THE BARK OF Larix sibirica

G. F. Chernenko and É. N. Shmidt

UDC 634.866:547.914

The larch, being the main forest-forming species of the Union, is widely used in the national economy, but this leads to the formation of a large amount of bark wastes. The literature contains reports on the chemical composition of the bark [1-6] and its complex processing [7]; but there is inadequately complete information on the composition of the neutral resinous substances of the bark. In the present communication we give the results of an investigation of the composition of the neutral fraction of a petroleum ether extract of the bark of the Siberian larch Larix sibirica Ledeb.*

The total yield of extract ranged from 2.5 to 4%, depending on the time of storage of the bark. The extract was treated with an aqueous solution of alkali to separate it into acid and neutral substances, which were then investigated separately. Information on the composition of the acid fraction of the extract has been given in [5-7].

The neutral substances of the extract (55%) were separated into individual components by absorption chromatography. It was established that the neutral fraction contained 50% of fatty aliphatic compounds and the same amount of terpenoids. Among the aliphatic compounds, saturated linear alcohols of the composition C_{22} and C_{24} (docosanol and tetracosanol) predominated (10%), the main one being docosanol. The alcohols were identified from their spectral characteristics and by GLC with the introduction of authentic samples; this fraction also contained the esters of these alcohols with fatty acids of the C_{20}–C_{22}–C_{24} composition (15%) and esters of ferulic acid with docosanol-tetracosanol (10%).

The hydrocarbon fraction (15%) consisted of paraffinic hydrocarbons with the composition C_{16}–C_{24} with straight and branched chains, which were identified by the GLC method in comparison with a standard mixture of individual hydrocarbons.

Among the terpenoids we detected epimanool (5%), shown to be identical with an authentic sample by TLC, GLC, and IR and PMR spectroscopies; epitorulosol (9%) with mp 112-114°C; a mixture containing epitorulosol and its epimer at the primary hydroxy group (35% of the epimer, according to its PMR spectrum); and epitorulosol acetate (7%). The compounds isolated were identified by the melting points, spectral characteristics, and GLC and TLC with authentic samples [8]. Larixol and larixyl acetate were not detected in the neutral part of the extract.

The sterol fraction (20%) contained β-sitosterol, with mp 130-135°C; campesterol (according to TLC); and a new triterpenoid — the methyl ester of 3α-hydroxy-24S, 25R-epoxylanost-9(11)-en-27-oic acid, the structure of which has been established by x-ray structural analysis [9].

All the compounds mentioned were isolated in the individual form and were identified by direct comparison with authentic samples. The extract also contained unidentified polar compounds (9%).

LITERATURE CITED

1. N. D. Barabash and É. D. Levin, Khim. Prir. Soedin., 386 (1970).
2. É. N. Gvozdeva, I. S. Artem'eva, and V. P. Levanova, Khim. Prir. Soedin., 100 (1979).
3. T. K. Chumbalov, L. T. Pashinina, and Z. A. Leiman, Khim. Prir. Soedin., 478 (1970).
4. T. K. Chumbalov, L. T. Pashinina, and Z. A. Leiman, Khim. Prir. Soedin., 763 (1970).
5. L. P. Rubchevskaya and É. D. Levin, Khim. Prir. Soedin., 103 (1986).
6. L. P. Rubchevskaya and É. D. Levin, Khim. Prir. Soedin., 109 (1982).

*The bark of the Siberian larch was collected in Krasnoyarsk Territory in 1988.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 833-834, November-December, 1990. Original article submitted November 27, 1989; revision submitted May 28, 1990.

 0009-3130/90/2606-0714$12.50

7. É. D. Levin, B. Denisov, and R. Z. Pen, The Complex Processing of the Larch, [in Russian], Lesnaya Prom-st', Moscow (1978), p. 224,
8. Hnadbook of Terpenoids, CRC Press, Boca Raton, Florida, Vol. 11 (1985), p. 158.
9. G. F. Chernenko, I. Yu. Bagryanskaya, and É. N. Shmidt, Khim. Prir. Soedin., No. 5, 641 (1990).

LAMIIDE FROM Phlomis cancellata

G. A. Fokina and T. V. Bukreeva

UDC 547.918:547.192

We have detected compound (I) of iridoid nature, in the epigeal part of the plant Phlomis cancellata Bunge (family Lamiaceae) collected in April, 1988 in the south-western Kopet Dagh.

The air-dry comminuted raw material (1.2 kg) was extracted at room temperature with 70% ethanol until extraction was complete. The concentrated extract (1 liter) was freed from lipophilic substances with diethyl ether (3 × 1 liter) and chloroform (3 × 1 liter) and then, to eliminate the phenolic compounds, was passed through a column of neutral alumina that had previously been washed with water. The column was eluted with water until the reaction for iridoid glycosides was negative, and the aqueous eluate ws evaporated under reduced pressure. Ground activated carbon (750 g) was added to the concentrated extract until the iridoid glycosides had been adsorbed completely. The resulting suspension was placed in a column and was washed with water (15 liters) and then with aqueous alcoholic mixtures with increasing concentrations of ethanol.

The fraction containing 20% of ethanol afforded an individual compound (I) (yield on the air-dry raw material 1.5%) in the form of a white amorphous substance $C_{17}H_{26}O_{12}$, $[\alpha]_D^{25}$–122°(c 1.0, CH_3OH), $\lambda_{max}^{CH_3OH}$ nm: 230 (log 4.15); ν_{max}, cm^{-1}: 1700 (C=O); 1635 (C=C); ^{13}CNMR (50.33 MHz, D_2O); 94.46 (C-1), 152.67 (C-3), 114.21 (C-4), 68.71 (C-5), 45.80 (C-6), 77.14 (C-7), 79.14 (C-8), 56.86 (C-9), 19.60 (C-10), 169.00 (C-11), 99.14 (C-1'), 52.61 (CH_3O).

Substance (I) (0.3 g) was acetylated with acetic anhydride at room temperature for a month. The reaction products were chromatographed on a column of silica gel with elution by the chloroform–methanol (9:1) system. This gave 180 mg of the pentaacetate (II) $C_{27}H_{36}O_{17}$, mp 186-188°C (from ethanol), $[\alpha]_D^{25}$–76° (c 0.5; $CHCL_3$) and 75 mg of the hexaacetate (III), $C_{29}H_{38}O_{18}$ mp 203-204°C (ethanol), $[\alpha]_D^{25}$ –54° (c 1.0; $CHCl_3$).

From the physicochemical constants and spectral characteristics of substance (I) and its derivatives (II) and (III), the compound isolated from Phlomis cancellata was identified as lamiide, an iridoid glucoside of the loganin group [1, 2].

LITERATURE CITED

1. M. L. Scarpati and M. Guiso, Gazz. Chim. Ital., 99, 1150 (1969).
2. A. Bianco, P. Caciola, M. Guiso, C. Iavarone, and C. Trogolo, Gazz, Chim. Ital., 111, 201 (1981).

Botanical Institute, Academy of Sciences of the USSR, Leningrad. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 834-835, November-December, 1990. Original article submitted March 15, 1990.

0009-3130/90/2606-0715$12.50