extract with petroleum ether gave A, and on extraction with chloroform the other substances (C, D, E, and F) passed into the organic phase and were separated on silica gel (stationary phase – formamide; mobile phase – chloroform) to give substances C, D, and E.

Substance A (psoralen), $C_{11}H_6O_3$, mp 164–165° C, fluoresced on the paper chromatogram in UV light. Before treatment with alkali it was pale blue, and after treatment golden yellow.

On the basis of its $R_f$ values in various solvent systems, IR spectra, and mixed melting points, substance A proved to be identical with psoralen (furo [6, 7: 2', 3'] coumarin).

Substance B (daphnoretin), $C_{19}H_{12}O_7$, mp 254–256° C, fluoresced on a paper chromatogram in UV light. Before treatment with alkali it was pale blue and after treatment the fluorescence disappeared almost completely. The substance formed a monoacetyl derivative ($C_{21}H_{14}O_8$, mp 240–242° C) and a methyl derivative ($C_{20}H_{14}O_7$, mp 239–241° C). On decomposition in a current of hydrogen [2], it was converted into umbelliferone and scopoletin.

From its physicochemical properties and conversion products, the substance under investigation was identified as daphnoretin (6-methoxy-7-hydroxy-3, 7'-dicoumaryl ether) [2].

Substance D (scopoletin), $C_{10}H_8O_4$, mp 200–202° C, fluoresced on the paper chromatogram in UV light pale blue both before and after spraying with alkali. From its physicochemical properties and $R_f$ values this substance was identified as scopoletin (6-methoxy-7-hydroxycoumarin) [3].

Substance E (umbelliferone), $C_9H_6O_3$, mp 223–224° C. The methylation of this compound gave a substance with composition $C_{10}H_8O_3$ and mp 117–118° C, identical with herniarin (7-methoxycoumarin).

From the physicochemical properties of the starting material and its derivatives, it was identified as umbelliferone (7-hydroxycoumarin) [4].

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# FLAVONOIDS OF LARIX DAHURICA. I

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The heartwood of Larix dahurica (Dahurian larch) ground to dust (28.5 kg with a moisture content of 24.94%), taken from two trees 128 and 156 years old in the Chita Oblast was exhaustively extracted with acetone. The dry extract (1.16 kg) was treated successively with absolute acetone, ether, and benzene. The substances insoluble in ether (699.09 g or 3.2% of the dry wood) and in benzene (150.65 g or 0.75%) were taken for study. From the results of ascending paper chromatography [Leningrad slow paper, formic acid–acetic acid–water (10: 2: 3) system] and thin-layer chromatography on Kapron [methanol–$CCl_4$ (15: 85) system], these two fractions were similar in the number and qualitative composition of the flavonoid components.

Individual substances were isolated by preparative chromatography on Kapron powder. The ratio of adsorbent to total substances chromatographed was 30: 1, and the process was monitored by thin-layer chromatography. The concentration of methanol was increased from 15 to 50 vol. %. The flavonoids, recrystallized from aqueous ethanol, were identified by their melting points, elemental compositions, and chromatographic behaviour in the presence of reference samples (the authors are grateful to E. Rudloff (Canada) for kindly providing samples of dihydroquercetin and dihydrokaempferol). The samples obtained were dried at 110° C and a residual pressure of $10^{-3}$–$10^{-4}$ mm Hg for 20–22 hr.

The IR spectra of the substances themselves and of mixtures with ionizing and complex-forming additives confirmed the presence in them of quercetin, dihydroquercetin, and dihydrokaempferol [1]. The IR spectra contained characteristic absorption bands: 1645–1655 (C = O), 1600–1615 (=), 1590 ($C_6H_5$–), 3300–3500 $cm^{-1}$ (OH) [2].

From quercetin and dihydroquercetin were obtained the pentaacetates [3] which were characterized by their melting points and IR and UV spectra. In addition, the mutual interconversion of quercetin and dihydroquercetin was carried out [4] and the reaction products were identified chromatographically. The dihydroquercetin was optically active, $[\alpha]_D^{20}$ + 42.1° [acetone–water (1:1].

Thus, Larix dahurica, like other species of the family Larix [5] contains not only flavonols but also their reduced forms–flavanols.

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# FLAVONOLS OF RHODODENDRON LUTEUM AND RH. DAHURICUM

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We have studied the flavonoid composition of Rh. luteum (pontic azalea) collected in the flowering period in the Teberda reserve (northern Caucasus) and Rh. dahuricum (Dahurian rhododendron) collected in the budding period at the village of Elabuga (Khabarovsk territory). The total flavonoids were isolated from an ethanol–water extract of the leaves of the two rhododendrons after treatment with ethyl acetate and precipitation with chloroform.

Two-dimensional paper chromatography in systems 1) water and 2) butanol–acetic acid–water (4: 1: 2) showed that the leaves of Dahurian rhododendron contain three compounds of flavonol nature. The total flavonols were separated by fractional recrystallization from alcohol with subsequent purification on a column of polyamide sorbent.

A study of the UV and IR spectra and the products of acid and enzymatic hydrolysis show that one of the substances – $C_{21}H_{20}O_{12}$ with mp 236–239° C – is hyperoside (quercetin 3-β-D-galactopyranoside), a second – $C_{20}H_{18}O_{11}$ with mp 208–211° C – is avicularin (quercetin 3-α-L-arabinoside) [1, 2], and a third – $C_{16}H_{12}O_7$, with mp 300–303° C – is azaleatin (quercetin 5-methyl ether) [3].

Five compounds were found in the leaves of the pontic azalea, three of which were identical with those given above, while the fourth, of composition $C_{21}H_{20}O_{12}$ with mp 196–199° C, proved to be myricitrin and the fifth – $C_{15}H_{10}O_7$ with mp 309–312° C – quercetin.

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