FLAVONOLS OF THE NEEDLES OF *Larix sibirica*

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The needles (10.0 kg), collected in August, 1970, with a moisture content of 55.6%, were exhaustively extracted with methanol by steeping at room temperature. The methanolic extract was concentrated in a film evaporator at 55-60°C. On standing, the extract deposited the bulk of the chlorophyll. The remaining chlorophyll and wax were eliminated by repeated washing with petroleum ether. Then the extract was evaporated to dryness in a rotary evaporator and was treated repeatedly with absolute acetone. The acetone extract (180.2 g) was chromatographed on polyamide powder. Elution was performed successively with water, aqueous methanol, and methanol.

From the results of paper chromatography [acetic acid–formic acid–water (10 : 2 : 3)] and thin-layer chromatography in polyamide [methanol–chloroform (3 : 7)], the methanolic eluate (2.48 g) contained four flavonoid aglycones. Preparative chromatography on polyamide with elution by chloroform–methanol mixtures (with increasing proportions of methanol) gave the individual components (I)-(IV).

The PMR spectra of the silyl ethers of the first three compounds each had two doublets in the δ 5.93 and 6.23 ppm regions with $J = 2$ Hz (meta substitution), due to the protons at C_6 and C_8 of ring A. While the positions of the substituents in ring A of the three compounds obtained did not differ from one another, the structures of ring B in them differed. Thus, for compound (III) in the weaker-field region there was only one singlet at δ 6.9 ppm (2H), due to $H_{2'}$, and $H_{6'}$, of ring B, and for compound (I) there were two doublets at δ 6.72 ppm (2H) and 7.82 ppm (2H) with $J = 8$ Hz (ortho substitution) due to $H_{3'}$, $H_{5'}$ and $H_{2'}$, $H_{6'}$, respectively. The NMR spectrum of compound (II) had signals at δ 6.77 ppm (doublet, $J = 8$ Hz) of a proton at $C_{5'}$, a multiplet with its center at δ 7.43 ppm of a proton at $C_{6'}$, and a singlet at δ 7.6 ppm (1H) of a proton at $C_{2'}$. A singlet at δ 3.82 ppm (3H) corresponded to a methoxy group.

The positions of the hydroxy groups were confirmed by the UV spectra with ionizing and complex-forming additives. These compounds were also characterized by their IR spectra, elementary compositions, melting points, and chromatographic behavior with authentic samples. In this way compound (I) was identified as kaempferol, (II) as isorhamnetin, and (III) as myricetin.

The presence of kaempferol in the needles of Pseudolarix kaempferi and Larix kaempferi has been reported previously [1]. We are the first to have found isorhamnetin and myricetin in the needles of the genus Larix.

LITERATURE CITED

1. M. Takahachi, I. Tokuzo, M. Akihiko, and I. Koichiro, J. Pharm. Soc. Japan, 80, 1488 (1960).

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