

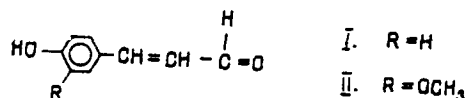
PHENYLPROPANOIC ALDEHYDES IN PROPOLIS AND ITS SOURCES

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Earlier, in a study of the composition of the axillary buds of European aspen, *Populus tremula*, and of propolis of the "aspen" type we isolated a number of new natural compounds - conjugates of hydroxycinnamic acids [1] and of trans-coniferyl alcohol [2, 3].

In a further study of the chemical composition of aspen axillary buds and of propolis of the "aspen" type we have isolated and identified two aromatic aldehydes - p-coumaraldehyde (I) and trans-coniferaldehyde (II).



Compounds (I) and (II) were detected on Silufol plates in the form of blue-green spots after the plates had been sprayed with concentrated sulfuric acid. These compounds were isolated by the use of column chromatography on alumina and silica gel [2]. An enriched fraction containing the desired compounds was additionally separated on a column (2 x 200 cm) filled with silica gel. The separation was monitored by the TLC method in the benzene-acetone (9:1) system. The fractions containing compound (I) (R_f 0.20) and II (R_f 0.24) were finally purified by the preparative TLC (PTLC) method on silica gel.

The mass spectra of the compounds isolated in this way contained intense peaks of molecular ions with m/z 148, $\text{C}_9\text{H}_8\text{O}_2$ (calc. 148.0524; meas. 148.0524) and 178, $\text{C}_{10}\text{H}_{10}\text{O}_3$ (calc. 178.0680; meas. 178.0680), and also a number of peaks of characteristic ions with m/z 177, 147, and 119. As we have demonstrated previously [2], the presence in the mass spectrum of (I) of the peak of an ion with m/z 147 having the maximum intensity value showed that the molecules of (I) and (II) contained fragments of p-coumaric and ferulic acids, respectively.

NMR results satisfactorily confirmed those of the mass-spectrometric analysis. The spectra of (I) and (II) each contained the signal of a phenylpropanoid grouping with the trans arrangement of the protons at the double bond ($J = 16$ Hz). The presence of an aldehyde grouping in each of the molecules (I) and (II) was confirmed by the presence in their NMR spectra of one-proton doublets at 9.66 and 9.70 ppm, respectively, with $J = 8$ Hz.

The results obtained, taken together, permitted the compounds isolated to be determined as (I) and (II). This is the first time that these compounds have been described in aspen axillary buds and propolis of the "aspen" type. The p-coumaraldehyde and trans-coniferaldehyde that we have identified, together with the conjugates of trans-coniferyl alcohol that we have described and isolated previously [2, 3], are characteristic components of propolis of the "aspen" type and can therefore be used for the standardization of samples of propolis.

LITERATURE CITED

1. S. A. Popravko, I. V. Sokolov, and I. V. Torgov, *Khim. Prir. Soedin.*, 169 (1982).
2. S. A. Popravko, I. V. Sokolov, and I. V. Torgov, *Khim. Prir. Soedin.*, 152 (1984).
3. I. V. Sokolov and I. V. Torgov, *Khim. Prir. Soedin.*, 319 (1989).

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