CATECHIN 7-RHAMNOSIDE FROM *Spiraea hypericifolia*

T. K. Chumbalov, L. T. Pashinina,
and N. D. Storozhenko

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The detection of a (+)-catechin rhamnoside in the stems of *Spiraea hypericifolia* has been reported previously [1]. The present paper gives information on the determination of the structure of this glycoside.

The glycoside consists of a white powder with the composition $C_{21}H_{24}O_{10}$, mp 146-148°C, $[\alpha]_D^{20}$ −86.2° (c 3.48; acetone). A heptaacetyl derivative, $C_{35}H_{36}O_{17}$, was obtained in the form of plates with mp 103-105°C, R_f 0.31 [TLC in system 1 — benzene—acetone (9:1)], $[\alpha]_D^{20}$ −45.6° (c 1.99; acetone).

The trimethyl derivative, $C_{24}H_{30}O_{10}$, formed plates with mp 108-109°C, R_f 0.30 (TLC in system 1), $[\alpha]_D^{20}$ −107.8° (c 1.4; acetone).

The rhamnose is substituted in the phenolic hydroxyl, since in the NMR spectrum of the heptaacetyl derivative there are three, and not four, aromatic acetyl groups (nine-proton singlet at 2.24 ppm) and four three-proton singlets (δ 2.11, 2.00, 1.94, 1.92) of aliphatic acetyl groups, three of which belong to the rhamnose and the fourth to an alcoholic hydroxyl at C_3. The position of the sugar in the phenolic hydroxyl is also confirmed by the formation of a tri- and not a tetramethyl ether on methylation with diazomethane. The formation of such a derivative was shown by elementary analysis, NMR spectroscopy (three-proton singlet at 3.70 ppm and six-proton singlet at 3.81 ppm), and the mass number M^+ 646 corresponding to that calculated for a tetraacetyl-trimethyl derivative $C_{32}H_{38}O_{14}$.

The sugar does not glycosidate the phenolic groups of ring B, since the o-dihydroxy grouping of this ring forms a colored complex with iron salts and in the mass spectrum of the trimethyl—tetraacetyl derivative of the glycoside there are fragments with m/e 222, 180, and 151 which are characteristic for ring B of methylated catechins [2].

The position of the sugar in position 5 or position 7 of ring A was shown by comparing the trimethyl ether of (+)-catechin, obtained on acid hydrolysis of the glycoside, with the synthesized methyl ethers of (+)-catechin. The methyl ether isolated from the hydrolyzate corresponded in its melting point (256-257°C) and position on TLC with the 3',4',5-trimethyl ether of (+)-catechin. In addition, the synthetic methyl ethers and the methyl ethers obtained by hydrolysis were oxidized to the corresponding anthocyanidins by potassium persulfate. For the anthocyanidin obtained from the glycoside under investigation and its synthetic analog the ratio of the intensities of the absorption of light at 440 nm to the intensity of the visible maximum was 14%, which corresponds to the replacement of the hydroxyl at C_5 by a methoxy group [3]. Consequently, the sugar is present in position 7 of the catechin molecule. The pyranose form of the ring and the α-configuration of the anomeric center were determined by a Klyne analysis of molecular rotations, by enzymatic hydrolysis with rhamnodiastase, by the IR spectrum (1040, 1055, 1070 cm^{-1}), and by the NMR spectrum ($CDCl_3$; one-proton doublet with J = 2 Hz at 5.35 ppm).

Thus, the glycoside isolated has the structure of (+)-catechin 7-O-α-L-rhamnopyranoside. No such compound has been described previously.

LITERATURE CITED

1. T. K. Chumbalov, L. T. Pashinina, and N. D. Storozhenko, Khim. Prirodn. Soedin.,523 (1974).

S. M. Kirov Kazakh State University, Alma-Ata. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 258-259, March-April, 1976. Original article submitted July 21, 1975.

2. A. Pelter, P. Stainton, A. P. Johnson, and M. Barber, J. Heterocyc. Chem., 2, 256 (1965).
3. J. B. Harborne, Comparative Biochemistry of the Flavonoids, Academic Press, New York (1967), pp. 1-36.

ESTERS OF PHENOLIC ACIDS OF THE BARK OF *Picea ajanensis*, *P. koraiensis*, AND *P. obovata*

A. S. Gromova, V. I. Lutskii, T. V. Rykova, and N. A. Tyukavkina

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There is information in the literature on the isolation from the bark of coniferous plants of a phenolic wax consisting of esters of phenolic acids and n-aliphatic alcohols. Thus, from the bark of some species of spruce [1a], fir [2], broad-leaved trees [3, 4], and pines [1b, 2, 5] esters of ferulic acid have been isolated, and from the bark of the Norway spruce esters of p-coumaric acid, in addition [1a].

On studying the phenolic compounds of the bark of *Picea ajanensis* Fisch. (Yeddo spruce), *P. koraiensis* Nakai (Korean spruce), and *P. obovata* Ledeb. (Siberian spruce) [6, 7], from a benzene extract by treatment with solvents [1, 5] and by column chromatography on silica gel [chloroform–methanol (99:1)], we obtained a phenolic wax fraction. By preparative thin-layer chromatography on Silufol in the same system, from the phenolic waxes of *P. koraiensis* and *P. obovata* we isolated alkyl coumarates and alkyl ferulates, and from *P. ajanensis* only alkyl ferulates.

From the point of view of chemotaxonomy, it is interesting that alkyl coumarates are found only in the bark of species of *Picea* belonging to the section Morinda (Norway, Korean, and Siberian spruces).

In the products of the alkaline hydrolysis [2] of the alkyl ferulates and alkyl coumarates we identified ferulic and coumaric acids, respectively, in the form of their TMS derivatives [8] by GLC.

The neutral fraction of the esters consisted of a homogeneous series of C_{16}–C_{25} n-aliphatic alcohols, those with odd numbers of carbon atoms being present in trace amounts. The predominating alcohols were C_{22} and C_{24} (see Table 1).

The alcohols were analyzed by the GLC method on a "Khrom-4" chromatograph with a flame-ionization detector using as stationary phase 5% of SE-30 on Chromaton N-AW-HMDS, column

TABLE 1. Neutral Fraction in the Esters of Coumaric and Ferulic Acids

Alcohol	Elution temperature, °C	Amount of alcohols,* C_{16}-C_{25} fraction, %				
		P. koraiensis		P. obovata		P. ajanensis
		coumarates	ferulates	coumarates	ferulates	ferulates
C_{16}	194	+†	+	+	+	+
C_{18}	216	+	9	4	17	4
C_{20}	230	+	+	+	+	+
C_{22}	246	17	43	43	33	37
C_{24}	261	64	32	34	30	38

*Calculation by the method of internal normalization.
†Amount less than 4%.

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