

UV spectroscopy and acid hydrolysis it may be concluded that the rhamnose in substance (I) is attached at position 3, and the only possible site of attachment of the glucose is position 8. On the basis of the results obtained we propose for substance (I) the structure of 7-methylgossypetin 8- $\beta$ -D-glucopyranoside 3-O- $\alpha$ -L-rhamnopyranoside, and for (II) 7-methylgossypetin 8- $\beta$ -D-glucopyranoside.

V. I. Sheichenko and L. P. Smirnova took part in the recording of the NMR spectra of the substances obtained.

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#### C-GLYCOSIDES OF *Ajania fastigiata*

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A methanolic extract from the epigeal mass of *Ajania fastigiata* family Compositae, was concentrated, and the chlorophyll was precipitated with water. The aqueous methanolic solution was distributed in organic solvents. From an ethereal extract, in addition to quercetin and luteolin [1], by preparative chromatography on paper we isolated a substance (I) with the composition  $C_{15}H_{10}O_5$ , mp 343-345°C (aqueous methanol), which proved to be apigenin, as was confirmed by the melting point of the acetyl derivative, the products of alkaline fusion, and the results of IR and UV spectroscopy.

The residual aqueous methanolic solution was chromatographed on Kapron. Elution with 20% methanol gave the total C-diglycosides [substances (II) and (III)], which were purified on a column of cellulose. Similar glycosides have previously been separated by preparative chromatography on paper [2]. We propose the use of Sephadex LH-20, which considerably shortens the time of separation and gives substances of higher purity.

The Sephadex was swollen in water, and water was also used for dissolving the substances and for elution from the columns.

Substances (II) and (III) had mp 228-230°C and 236-238°C (aqueous ethanol). The action of 5% HCl led to their mutual isomerization with the appearance of two new isomers, which is characteristic for C-diglycosides [3].

Compounds (II) and (III) did not undergo enzymatic hydrolysis [4]. On acid hydrolysis by Kiliani's method, apigenin, D-glucose, and traces of D-arabinose were detected [5].

IR spectrum of the C-glycosides,  $cm^{-1}$ : 3300-3400, 1650, 1620, 1570, 1520, 1450, 1075, 1045, 1020, 910.

UV spectrum [ $\lambda_{max}$  (absolute ethanol)] of substance (II): 332 and 280 nm ( $\log \epsilon$  3.93; 3.89); substance III: 336 and 276 nm ( $\log \epsilon$  3.91; 3.88). The ratios of the intensities of the absorption maxima in the long-wave region of the spectra of (II) and (III) were 35 and 32% of the intensity of the absorption maximum of the aglycone [6]. A reduced bathchromic shift with zirconyl chloride was observed:  $\Delta\lambda + 23$  nm (II) and  $+ 20$  nm (III) [7];  $[\alpha]_D^{22} + 55^\circ$  (II) and  $+ 99^\circ$  (III) (c 0.5%; dimethylformamide) [2];  $[M]_D \cdot K_p = + 153.5$  (II) and  $+ 276.3$  (III) [8].

Substance (II) was identified as apigenin 6,8-di-C- $\beta$ -D-glucopyranoside and (III) as a rotational isomer of (II).

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# A FLAVONOL GLYCOSIDE FROM PLANTS OF THE GENUS Phellodendron

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A glycoside with the composition  $C_{26}H_{32}O_{12}$ , mp 205°C,  $\lambda_{\max}$  290, 345 nm has previously been isolated from *Phellodendron amurense* Rupr. (Amur cork tree) and has been named phellamurin. It has the structure of noricarin 7-O- $\beta$ -D-glycoside. A glycoside with the composition  $C_{26}H_{32}O_{12}$ , mp 154-156°C, has been isolated from *P. japonicum* Maxim (Japanese cork tree) and *P. amurense*, and this has been assigned the structure of  $\beta$ -anhydronoricarin 3-O- $\beta$ -D-glucoside and the name phellodendroside [2]. From the same plant has been isolated a glycoside with the composition  $C_{32}H_{42}O_{17}$ , mp 152-153°C,  $\lambda_{\max}$  225, 290, 345 nm having the structure of dihydronoricarin 7, $\gamma$ -di-O- $\beta$ -glucopyranoside which has been called dihydrophelloside [3]. From *P. lavalleyi* Dode. (Lavalley cork tree) and *P. amurense* a glycoside has been isolated with the composition  $C_{26}H_{32}O_{12}$ , mp 151-153°C,  $\lambda_{\max}$  290, 345 nm, for which the structure of isonicarin 7-O- $\beta$ -D-glucopyranoside and the name phellavin have been proposed [4].

Phellodendroside, dehydrophelloside, and phellavin have similar constants and are the main flavonol glycosides of the materials investigated. To compare their flavonol compositions, we studied six species of cork tree the constants of the substances obtained being given below. The initial material consisted of the leaves of the plants collected in Maritime Territory (*P. amurense*) and in the botanical garden of the Academy of Sciences of the Uzbek SSSR in Tashkent (the other plants):

Plant	Composition	mp, °C	$\lambda_{\max}$ (CH <sub>3</sub> OH)
Phellodendron amurense Rupr.	$\{C_{26}H_{32}O_{12}$ $C_{26}H_{32}O_{12}$	200-203 151-154	220, 291, 346 220, 291, 346
<i>P. japonicum</i> Maxim	$C_{26}H_{32}O_{12}$	150-155	220, 291, 348
<i>P. chinense</i> Schneid.	$C_{26}H_{32}O_{12} \cdot 1H_2O$	150-153	220, 291, 346
<i>P. Lavalleyi</i> Dode.	$C_{26}H_{32}O_{12}$	150-152	220, 291, 346
<i>P. sacchalinense</i> (Fr. Schmidt) Sarg.	$C_{26}H_{32}O_{12} \cdot 1/2H_2O$	150-152	220, 291, 346
<i>P. piriforme</i> E. Wolf.	$C_{26}H_{32}O_{12} \cdot 1/2H_2O$	150-154	220, 291, 346

From the Amur cork tree together with the main glycoside (mp 151-154°C) we isolated a glycoside with the composition  $C_{26}H_{32}O_{12}$ , mp 200-203°C, which is probably phellamurin.

The glycosides from *R. japonicum*, *P. chinense* Schneid. (Chinese cork tree), *P. sacchalinense* (Fr. Schmidt.) Sarg. (Sakhalin cork tree), and *P. piriforme* E. Wolf (pearfruit cork tree) proved from their chromatographic mobilities [Silufol UV-254, chloroform-ethyl acetate-formic acid (6:6:3) system], melting points,

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