FLAVONOIDS OF *Campanula patula*

L. S. Teslov

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Continuing a study of the flavonoid complex of *Campanula patula* L. [1-3], by means of column chromatography on polyamide and cellulose we have isolated another five glycosides present in very small amounts. In this paper we give the results of a proof of the structures of two of them.

Glycoside (I), composition $C_{26}H_{28}O_{15}$, in the form of light yellow needles with mp 224-226°C (methanol), $[\alpha]_D^{22}$ −127.2° [c 0.28; ethanol—DMFA (3:1)], λ_{max} 256, 267 sh, and 355 nm (log ε 4.49, 4.45, and 4.51), is a bioside. In the products of acid hydrolysis of (I) (2% HCl, 100°C, 3 h), we found luteolin and two sugars: D-glucose and D-apiose. Heating with the same acid for 10 min gave a monoglycoside with the composition $C_{21}H_{20}O_{11}$, mp 258-259°C, $[\alpha]_D^{20}$ −75.3° [c 0.5; ethanol—DMFA (1:1)], which was identical with luteolin 7-O-β-D-glucopyranoside (cynaroside), and in the hydrolyzate we found apiose by PC.

A comparison of the UV spectra of the bioside and its aglycone in the presence of additives showed that the carbohydrate moiety is attached to C_7. The glycoside was stable to the action of rhamnodiastase and emulsin, which excludes the possibility that the sugars are linked to one another by 1→6 or 1→4 bonds. Likewise, it did not undergo alkaline hydrolysis, which shows the probability of a 1→2 bond between them. Such a linkage of glucose and apiose exists in known glycosides: apiin [4] and likuraside [5]. The difference between the molecular rotations of the bioside under investigation and the monoglycoside enables us to suggest a β bond for the apiose according to a calculation by Klyne's rule.

Thus, glycoside (I) most probably has the structure of luteolin 7-O-[β-(D or L)-apiofuranosyl-(2→1)-β-D-glucopyranoside. The luteolin 7-apioglucoside described in the literature (graveobioside A) from *Apium graveolens* L. [6] has mp 251-254°C and has not been characterized in more detail.

Glycoside (II), in the form of yellow prismatic crystals with mp 233-235°C, $[\alpha]_D^{22}$ −100° [c 0.32; ethanol—DMFA (1:1)], R_f 0.77 [BAW (4:1:2)], proved to be a new flavonoid bioside, which we have called *campanoside*. UV spectrum: λ_{max} (ethanol) 256, 267 sh., and 352 nm (log ε 4.39, 4.33, and 4.42).

The glycoside is unstable in acid and alkaline media. After its treatment with 5% hydrochloric acid for 10 min in the boiling-water bath, we detected the presence of luteolin and two carbohydrate residues: D-xylose and D-apiose. Under milder conditions (0.5% HCl, 10 min), hydrolysis led to an intermediate compound the physicochemical properties of which showed that it was identical with patuloside (luteolin 7-xyloside) [1].

The IR spectrum of (II) showed an absorption band at 1745 cm^{-1}, which is characteristic for an ester grouping.

On alkaline saponification (0.1% KOH, 5 min, 100°C, N_2), an acetic acid residue was split off and a new intermediate compound was formed with R_f 0.61, which we have called deacetylcampanoside (III). This could not be obtained in the crystalline form. The acetic acid was detected by the hydroxylaminolysis reaction [7]. The acethydroxamic acid obtained was identified by PC and by TLC on silica gel in the presence of markers.

Complete acid hydrolysis of (III) gave luteolin, xylose, and apiose and its stepwise hydrolysis gave patuloside and apiose.

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Spectral investigations in the UV region showed that in the molecules of (II) and (III) the hydroxyls in position 3', 4', and 5 are free, and the 7-OH group is substituted by a carbohydrate residue.

Consequently, campanoside is an acylated luteolin 7-apioxyloside the acetyl group of which is present in the carbohydrate part of the molecule. This is the first time that a glycoside with such a combination of sugars has been found. The study of its structure is continuing.

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CHEMICAL COMPOSITION OF THE MONOTERPENES AND RESIN ACIDS OF THE OLEORESIN OF FAR-EASTERN SPECIES OF FIR

E. N. Shmidt, Zh. V. Subovenko,
Yu. G. Tagil'tsev, and V. A. Pentegova

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There is almost no systematic information in the literature on the physicochemical properties and component compositions of the oleoresins of Far-Eastern species of fir. Only the compositions of the turpentine of the Sakhalin fir and of the acids of the Khingan fir have been reported previously [1, 2].

We have studied the composition of the oleoresin of *Abies nephrolepis* Maxim. (Khingan fir, the specimen being obtained from the Lazo region, Khabarovsk territory), *A. mayriana* Miyabe et Kudo (Mayr's fir), and *A. sachalinensis* Schmidt (Sakhalin fir, collected in the Korsakov and Poronai regions of the Sakhalin oblast).

The physicochemical properties of the fir oleoresins were investigated in accordance with GOST [State Standard] 10271-62:

Index	Khingan fir	Mayr's fir	Sakhalin fir
Refractive index, n_D^{20}	1.5254	1,5270	1,5271
Specific rotation, $[\alpha]_D^{20}$, deg	+12.9	+15.4	+13,4
Acid No.	62	60	63
Content, %: of			
ballast substances	0.8	0,04	0.8
moisture	0,94	3.38	3.49
turpentine	22.9	25,1	23.5
resin acids	62.2	63.3	63,0

The qualitative and quantitative compositions of the turpentine were analyzed by the GLC method (TCEP, 37 m × 3 mm, 74°C). The monoterpene hydrocarbons detected and their amounts are given below (%):

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