

Luteolin 7- β -rutinoside coincides in its R_f values with scolimoside (a sample of scolimoside was kindly provided by L. I. Dranik) but has a different melting point and a different specific rotation [5].

Among the luteolin 7-diglucosides described in the literature a complete structure is given only for luteolin 7- β -laminariobioside [6]. This is the first time that luteolin 7- β -gentiobioside has been reported.

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FLAVONES AND THEIR O-GLYCOSIDES FROM THE EPIGEAL PART OF *Dianthus deltoides*

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The flavonoids of *Dianthus deltoides* L. (maiden pink) family Caryophyllaceae were isolated from the epigeal part collected in the flowering phase (June-July, 1974, environs of the village of Shelud'kovka, Khar'kov oblast). By chromatography on paper, the aqueous acetone (9:1) extracts were found to contain not less than five substances of flavonoid nature. They were separated by the chromatography of aqueous extracts on columns of polyamide (eluents—water and aqueous ethanol), and substances (I-IV) were obtained in the individual state.

Substance (I), $C_{15}H_{10}O_6$, mp 328–330°C, λ_{\max} in methanol 255, 265 sh., 350 nm; with sodium acetate 390 nm (here and below differential spectra as described previously [1, 2]); with alkali 405 nm; with sodium acetate and boric acid 385 nm; with zirconyl chloride 415 nm. Substance (I) was identified as luteolin.

Substance (II), $C_{21}H_{20}O_{11}$, mp 180–182°C $[\alpha]_D^{20} + 4.0^\circ$ (c 0.2; ethanol) λ_{\max} in methanol 245 sh., 270, 295 sh., 335 nm; with sodium acetate 385 nm; with alkali 395 nm; with zirconyl chloride 395 nm; with boric acid and sodium acetate there were no changes in the UV spectrum. The acid hydrolysis of (II) (10% sulfuric acid in 50% methanol, 100°C, 2 h) led to the isolation of (I) and D-glucose in equimolar ratio. Enzymatic cleavage with emulsin took place with difficulty. From the IR-spectroscopic results it is assumed that the carbohydrate residue substitutes the 4'-hydroxy group, since free 3'-, 5-, and 7-hydroxy groups are found in the glycoside, and the longwave maximum of the aglycone (350 nm) is shifted in the glycoside to the 335-nm region.

Thus, (II) is characterized as luteolin 4'-O- β -D-glucopyranoside.

Substance (III), $C_{16}H_{12}O_6$, mp 319–322°C, λ_{\max} in methanol 245, 270, 345 nm; with sodium acetate 395 nm; with alkali 405 nm; with zirconyl chloride 400 nm; with boric acid and sodium acetate no changes were observed. The triacetate of (III) has mp 220–222°C.

Substance (IV), $C_{22}H_{22}O_{11}$, mp 262–266°C (decomp.) $[\alpha]_D^{20} + 28.0^\circ$ (c 0.2; ethanol); λ_{\max} 245 sh., 335 nm; with sodium acetate 335 nm; with alkali 400 nm; with zirconyl chloride 395 nm; with sodium acetate and boric acid no changes in the spectrum were observed. The acid hydrolysis of (IV) [as described for (II)] led to the liberation of (III) and D-glucose in equimolar ratio. Enzymatic hydrolysis with emulsin scarcely took place, probably because of steric hindrance.

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From the results of PMR spectroscopy, the aglycone was shown to be identical with the previously known chrysoeriol. The proton at C-1" (glycosidic center) gives a signal in the form of an unsymmetrical doublet at 4.90 ppm ($J = 7$ Hz), which is characteristic of flavone β -D-glycopyranosides [3]. A singlet in the 3.92-ppm region (3 H) for (III) and (IV) shows the presence of a methoxy group at C-3'. In the acetate of (IV) two acetyl groups were detected—at C-5 (2.42 ppm) and at C-7 (2.33 ppm)—in the aglycone moiety and four in the carbohydrate moiety: a nine-proton singlet at 2.08 ppm for acetyl groups at C-2", -3", and -4" and a three-proton singlet at 2.04 ppm for an acetyl group at C-6". Thus, (IV) has been characterized as chrysoeriol 4'-O- β -D-glucopyranoside. Both flavonoid 4'-glycosides appear on chromatograms in filtered UV light in the form of dark spots the color of which changes little with zirconyl chloride and ammonia vapor, which corresponds to B-unsubstituted flavones [4]. This is the first time that substances (II), and (III), and (IV) have been isolated from plants of the family Caryophyllaceae [5], and (IV) is a new glycoside.

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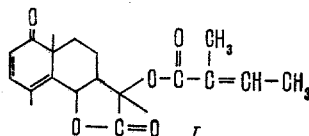
THE STRUCTURE OF SEMOPODIN AND A HYDROXYLACTONE FROM *Ferula oopoda*

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We have previously reported the new sesquiterpene lactones semopodin [1] and a hydroxylactone [2] isolated from *Ferula oopoda* Boiss.

Semopodin contains a γ -lactone ring (1785 cm^{-1}), an α, β -unsaturated ester group (1710 cm^{-1}), a conjugated ketone group (1660 cm^{-1} , 232 nm , $\log \epsilon 4.3$), and double bonds ($1640, 1610\text{ cm}^{-1}$). The spin-spin coupling constant of the olefinic protons of the secondary-secondary double bond conjugated with the ketone group (doublets with centers at 6.30 and 6.81 ppm) is 10 Hz. This value is characteristic for six-membered rings and shows that semopodin belongs to the group of sesquiterpene lactones of the eudesmane (selinane) series [3].



The choice between the possible variants of the structure of the main skeleton was made by comparing the value of the chemical shift of the angular methyl group of semopodin (1.30 ppm) with those for taurin (1.33 ppm) [4], artemin (0.89 ppm) [5], erevanin (0.80 ppm) [6], tauremisin (1.20 ppm) [7], artesisin (1.02 ppm) [8], and others. The frequency of the lactone carbonyl (1785 cm^{-1}) in the IR spectrum of semopodin is somewhat high, which shows that it is connected with a vinyl ester group [9, 10]. On the basis of what has been said, we consider structure (I) to be likely for semopodin.

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