

GLYCOSIDES OF DAPHNE JULIA

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Daphne Julia is a relict evergreen shrub growing in the Kursk Oblast, family Hymelaeacea [1].

The substances dissolved by water from a dry methanolic extract of the bark of the branches were chromatographed on alumina impregnated with a 50% aqueous solution of dimethylformamide. Elution with a mixture of chloroform and acetone (1:1) gave 1.85% of a substance with the composition $C_{15}H_{16}O_9$ having mp 191-193° C, $[\alpha]_D^{17} + 22^\circ$ (c 1.0; methanol) with a bright pale blue fluorescence. The R_f on paper impregnated with a 10% methanolic solution of dimethylformamide in the system 1-butanol-acetic acid-water (4:1:5) was 0.43-0.44.

Further elution of the column with methanol gave 0.1% of another substance having the composition $C_{15}H_{16}O_9$, with mp 215-217° C, $[\alpha]_D^{17} -106^\circ$ (c 1.0; methanol), R_f 0.40, with a weak yellow-green fluorescence.

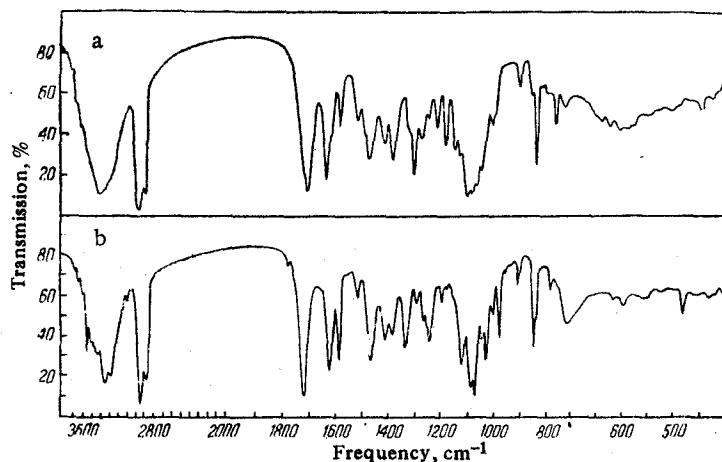


Fig. 1. IR spectra of daphnin (a) and 8-β-glucosidyl-7-hydroxycoumarin (b).

From their chemical properties, both substances are coumarin glycosides, and on acid hydrolysis they formed 7,8-dihydroxycoumarin (daphnetin) which was identified from its IR spectrum and by a mixed melting point test. The second of them corresponds in its physicochemical constants to 7-β-glucosidyl-8-hydroxycoumarin (daphnin), which was also confirmed by the data of UV and IR spectroscopy. The first compound differed in its constants and IR spectrum from known hydroxycoumarins (Fig. 1). The position of the sugar residue was established on the basis of a study of its UV spectrum in weakly acid (pH 4) and weakly alkaline (pH 11) media (solutions in 95% ethanol).

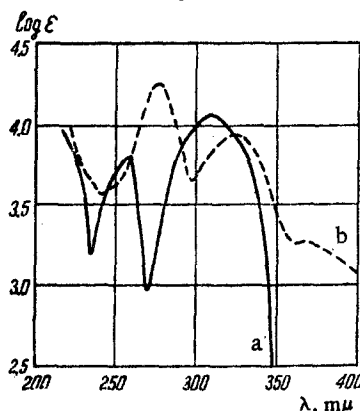


Fig. 2. UV spectra of daphnin in a weakly acid (a) and a weakly alkaline (b) medium.

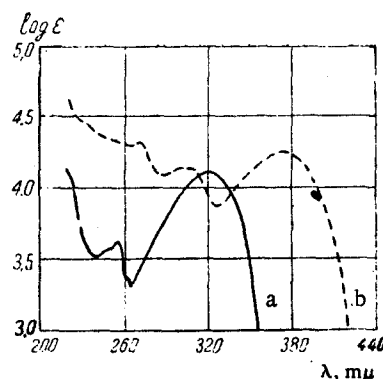


Fig. 3. UV spectrum of 8-β-glucosidyl-7-hydroxycoumarin in a weakly acid (a) and a weakly alkaline (b) medium.

On considering the UV spectra of the glycosides isolated (Fig. 2) it can be seen that in the case of daphnin, passage to the anion gives a picture typical for 8-hydroxycoumarins [2]. In the case of the other glycoside (Fig. 3) the UV spectrum of the anion shows an increase in the intensity of the long-wave band and a shift of it to the red region by 52 mμ, which demonstrates the presence of a free hydroxy group in position 7. Consequently, this substance is 8-glucosidyl-7-

hydroxycoumarin. Judging from the cleavage of the glucoside with emulsin, we assume that it is the β -anomer.

8- β -Glucosidyl-7-hydroxycoumarin has been isolated previously [3] from *Gnidia polycephala*, but this sample differed from ours in optical activity and melting point because of contamination with daphnin. We are the first to have isolated 8- β -glucosidyl-7-hydroxycoumarin as a natural compound in the pure state.

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ERICININE — A NEW ALKALOID FROM *VINCA ERECTA*

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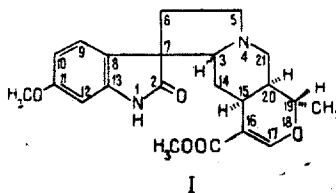
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Continuing our separation of the mixture of alkaloids of the epigeal part of *Vinca erecta* Rgl. et Schmalh [1], collected on the 30th April 1963 in the Osh Oblast, we have isolated a base with the composition $C_{21}H_{26}O_5N_2$ with mp 206–207° C (methanol), $[\alpha]_D^{18} +43.8^\circ$ (acetone), which we have called ericinine (I). This forms a crystalline hydrobromide with mp 237–238° C (methanol). The UV spectrum has an absorption maximum at 220 m μ (log ϵ 4.68). The IR spectrum

has the following vibrational bands: 3295 cm $^{-1}$ (=NH), 1610 and 1730 cm $^{-1}$ (the grouping $H_3COOC-\overset{|}{C}=\overset{|}{C}-O-$), 1670 cm $^{-1}$ (amide carbonyl group). The UV and IR absorption spectra of ericinine show that it belongs to the hydroxyindole group of alkaloids [2]. On the basis of the data given, the alkaloid has the following developed formula:



On acetylation with acetic anhydride, ericinine forms a N-acetyl derivative, $C_{24}H_{28}O_6N_2$, mp 158–159° C (methanol), $[\alpha]_D^{18} -98^\circ$ (acetone). N-Acetylericinine was shown to be identical with N-acetylvinerine [3]. When ericinine was heated in pyridine, in addition to the initial base an isomerization product with mp 200–201° C (diethyl ether), $[\alpha]_D^{20} -98^\circ$ (acetone) was isolated. The latter proved to be identical with hydroxyindole reserpinine [3]. Consequently, ericinine is a base isomeric with vinerine and vineridine and has the following configuration: $C_{15}-\alpha$; $C_{20}-\alpha$; $C_{19}-\beta$. The configurations at the C_3 and C_7 centers remain undetermined.



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