crimson with cyanidin, crimson with zinc + HCl, pink with concentrated H_2SO_4.

The results of acid hydrolysis carried out under various conditions exclude the possibility that the compounds studied exist in the form of O- and C-glycosides.

The results obtained permit the conclusion that the flavonoid composition of the fruit of S. marianum consists mainly of flavonols of a nonglycosidic nature.

The IR spectra of the compounds isolated were interpreted by I. P. Kovalev (Kharkov Chemical and Pharmaceutical Scientific-Research Institute).

REFERENCES

1. B. Janiak and R. Hänsel, Planta Med., 8, 71-84, 1960.
2. H. Wagner, L. Hörhammer, and R. Münster, Naturwiss., 52, No. 11, 1965.

11 July 1967

Kharkov Chemical and
Pharmaceutical Scientific-Research
Institute

UDC 547.972

ISOMYRICITRIN FROM EUPHORBIA STEPPOSA

O. M. Sotnikova and V. I. Litvinenko

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 1, p. 50, 1968

From the herb Euphorbia stepposa Zoz flavonol glycosides have been isolated, in addition to flavonones. One of the glycosides has the composition $C_{21}H_{20}O_{13}$, mp 275-277° C (from 50% ethanol), $[\alpha]_D^{20}$ − 36° (c 0.1; dimethylformamide), λmax 260, 310 and 362 mμ ($E_{1cm}^{1\%}$ 320, 130 and 350). R_f 0.53 [BAW*(4:1:2)], 0.40 (15% acetic acid). The substance gives a positive cyanidin reaction and the pigment so formed is not extracted by octanol, which characterizes the glycoside as a flavonoid compound. The ratio of the maxima (bands I and II) is 100%, as is generally observed in flavones or flavonols. Acid hydrolysis gave D-glucose and an aglycone $C_{15}H_{10}O_8$ with mp 358-360° C from 70% ethanol, λ_{max} 255, 305, 370 mμ ($E_{1cm}^{1\%}$ 690, 275 and 750 resp.), R_f 0.44 [BAW (4:1:2)] and 0.30 [benzene-ethyl acetate-acetic acid-formamide (24.5:73.5:2.1)]. Alkaline cleavage of the aglycone under nitrogen led to the isolation of phloroglucinol and gallic acid.

The further investigation of the functional groups of the glycoside and the aglycone was carried out by spectroscopic methods in the UV region with diagnostic reagents, with the following results: for the glycoside-$\lambda_{max}^{\text{sodium acetate}}$ 272, 327, 380 mμ ($\Delta\lambda_I$ 18 mμ); $\lambda_{max}^{\text{sodium ethoxide}}$ 270, 315, 405 mμ ($\Delta\lambda_I$ 43 mμ); $\lambda_{max}^{\text{zirconyl ion}}$ 270, 425 mμ ($\Delta\lambda_I$ 63 mμ); and for the aglycone-$\lambda_{max}^{\text{sodium acetate}}$ 255, 335 mμ ($\Delta\lambda_I$ 35 mμ); $\lambda_{max}^{\text{hexamethylenetetramine}}$ 255, 300, 380 mμ ($\Delta\lambda_I$ 10 mμ); $\lambda_{max}^{\text{sodium ethoxide}}$ 265, 310 mμ ($\Delta\lambda_I$ 60 mμ); $\lambda_{max}^{\text{zirconyl ion}}$ 275, 480 mμ ($\Delta\lambda_I$ 110 mμ); $\lambda_{max}^{\text{zirconyl ion+citric acid}}$ 260, 420 mμ ($\Delta\lambda_I$ 50 mμ).

The spectroscopic results show the presence in the glycoside of free 7-, 5-, and 4'-hydroxy groups, and in the products of the alkaline hydrolysis of the aglycone and the glycoside hydroxy groups in positions 3' and 5', as well. A spectroscopic study of the aglycone showed that sodium acetate causes not a bathochromic shift but a hypsochromic shift of maximum I by 35 mμ, which is not indicative of a 7-hydroxy group.

This phenomenon can probably be explained by the ready oxidizability of an aglycone with a free 3', 4', 5'-trihydroxy grouping even in a weakly alkaline medium. Consequently, to decrease the alkalinity the ionizing reagent used was hexamethylenetetramine, causing a bathochromic shift of the long-wave maximum by 10 mμ, which is characteristic for 7-hydroxyflavonols.

On the basis of its chromatographic behavior, spectroscopic properties, and the absence of a depression of the melting point in a mixture with the authentic material, the aglycone was shown to be identical with myricetin.

The ratio of the intensities of the absorption maxima of the glycoside and the aglycone permits the assumption that the glycoside contains one molecule of D-glucose.

It was found by polarimetric analysis that the D-glucose has the pyranose form and the β-configuration of the glycosidic bond.

*BAW-1-butanol-acetic acid-water.

Thus, the glycoside of E-stepposa can be characterized as myricetin 3-β-D-glucopyranoside. This is the first time that this myricetin glycoside has been isolated, and by analogy with quercetin 3-glucoside (isoquercitrin) we have called it isomyricitrin.

20 July 1967

Kharkov Pharmaceutical Institute,
Kharkov Chemical and Pharmaceutical
Scientific-Research Institute

UDC 547.972

STRUCTURE OF A FLAVONOID GLYCOSIDE FROM ADONIS VERNALIS

V. T. Chernobai, N. F. Komissarenko, and V. I. Litvinenko

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 1, p. 51, 1968

We have previously isolated from the herb adonis, and studied, a flavonoid glycoside which is, according to our data, a monoxyloside of homoorientin [1].

We have also studied the flavonoid composition of the herb spring adonis. After the elimination of the total cardiac glycosides by chromatography on a polyamide sorbent of the aqueous residue of an extract, we obtained a flavonoid glycoside. This substance gave a positive cyanidin reaction (orange red). The pigment so obtained did not dissolve in octanol, which shows the glycosidic nature of the flavonoid compound. Its melting point was 202–205° C (decomp.), $[\alpha]_D^{20}$ $-22\pm2°$ (c 1,00; in ethanol). UV spectra: λ_{max} 257, 268, 350 mμ; $\lambda_{max}^{CH_3COONa}$ 268, 380 mμ; $\lambda_{max}^{H_3BO_3 + CH_3COONa}$ 270, 385 mμ; $\lambda_{max}^{C_5H_5ONa}$ 270, 410 mμ; $\lambda_{max}^{ZrO(NO_3)_2}$ 280, 330, 395, mμ; $\lambda_{max}^{ZrO(NO_3)_2 + \text{citric acid}}$ 258, 269, 350 mμ; from the UV spectrum the glycoside has free 5-, 7-, 3'-, and 4'-hydroxy groups.

On severe hydrolysis (boiling for 2 hr with 10% hydrochloric acid), the sugar D-xylose was obtained and identified, together with two flavonoid substances which were shown by paper chromatography in the 15% acetic acid and 1-butanol–acetic acid–water (4:1:5) systems and also by spectroscopic data to be identical with authentic samples of orientin and homoorientin [2]. After hydrolysis, homoorientin and somewhat less orientin are formed.

To answer the question of the structure on which the glycoside is based, homoorientin or orientin, mild hydrolysis of the glycoside was carried out (by boiling for 5 min with 5% HCl), which gave only orientin. The latter was also formed when the xylose was split off by an enzyme preparation from the fungus Aspergillus oryzae.

The ratio of the specific intensities [3] at the absorption maximum at 350 mμ of the glycoside to orientin was 0.6, which characterizes it as a monoxyloside of orientin.

The results of spectroscopic studies of the glycoside and orientin show that the xylose is attached to the carbohydrate moiety of the orientin molecule. On polarimetric analysis [4] in comparison with the corresponding phenyl and methyl glycosides the bond was found to have the β-configuration and the xylose to be in the pyranose form.

Thus, the flavonoid glycoside studied, unlike adonivernitol [1], is a derivative of orientin and can be represented as 5, 7, 3', 4'-tetrahydroxyflavone 8-C-(β-D-glucopyranosyl-6-β-D-xylopyranoside).

REFERENCES

1. L. L. Hörhammer, H. Wagner, and W. Leeb, Arch. Pharm. 293, 264, 1960.
2. A. I. Tikhonov, P. E. Krivenchuk, V. I. Litvinenko, and I. P. Kovalev, Farm. zh., no. 3, 53, 1965.
3. V. I. Litvinenko, Rastit. resury, 2, no. 4, 451, 1966.
4. I. P. Kovalev and V. I. Litvinenko, KhPS [Chemistry of Natural Compounds], 233, 1965.

1 August 1967

Kharkov Chemical and
Pharmaceutical Scientific-
Research Institute