PEUCEDANIN FROM THE ROOTS OF PEUCEDANUM LUXURIANS

G. K. Nikonov and M. G. Pimenov

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 1, pp. 48–49, 1968

In a paper-chromatographic study of P. Luxurians Tamamsch, collected in Armenia between Idzhevan and Berd, we have established in it the presence of substances with the same R_f values as those in P. morisonii and similar species. By the method described previously [1], we have isolated from the roots of these plants a furocoumarin $C_{15}H_{16}O_4$ with mp 99–101° C (from carbon tetrachloride) which was found by mixed melting point and IR spectrum to be identical with peucedanin. Yield about 3%.

Peucadanin has previously been found in five species of Umbelliferae [1–4] belonging, like P. luxurians, to the section Peucedanum [5]. The presence of this substance in the section Peucedanum can be regarded as its chemical characteristic.

REFERENCES

1. G. K. Nikonov, Tr. VILAR, No. 11, 180, 1959.
2. C. H. Schlatter, Ann. Pharm., 5, 201, 1833.
3. G. K. Nikonov and A. A. Ivashenko, ZhOKh, 33, No. 8, 2740, 1963.
4. D. I. Baranauskaite and G. K. Nikonov, Apt. delo, No. 1, 25, 1965.
5. Flora of the USSR [in Russian], 17, 173, Moscow, 1951.

1 July 1967

All-Union Scientific-Research Institute
for Medicinal Plants

UDC 547.972

FLAVONOIDS OF THE FRUIT OF SILYBUM MARIANUM

L. I. Dranik and V. T. Chernobai

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 1, pp. 49–50, 1968

Two flavonoid compounds have been isolated from the fruit of Silybum marianum (L) Gaertn., but their structure has not been definitively established at the present time [1, 2]. By means of two-dimensional paper chromatography, we have found about five compounds of a flavonoid nature in an ethanolic extract of the fruit. By using chromatography on a polyamide sorbent and cellulose, we have isolated two crystalline flavonoids, I and II, and one in the amorphous state, III.

Substance I, mp 234–237° C, $[\alpha]_D^{22} + 34.5°$ (c 0.2; dimethylformamide; electric spectropolarimeter). UV spectrum: λ_{max} 288, (325); $\lambda_{max}^{CH_3COONa}$ 288, 327; $\lambda_{max}^{H_3BO_3+CH_3COONa}$ 288, 328; $\lambda_{max}^{C_2H_5ONa}$ 255, (288), 325; $\lambda_{max}^{AlCl_3}$(290), 315, 370 mμ; IR spectrum: 1647 (C=O, joined by a hydrogen bond to the 5-OH and the 3-OH); 1170, 1070, and 1035 (C–O–H); 3300–3440 (phenolic and alcoholic OH groups) cm^{-1}. In the solvent systems 1) ethyl acetate–benzene–acetic acid (73:24.5:2.5) and 2) 25% acetic acid, I had R_f 0.36 and 0.57, respectively. Red orange color reaction with sodium borohydride, crimson with cyanidin, crimson with zinc + HCl, and yellow with concentrated H_2SO_4. The acetyl derivative has mp 118–120° C. In many of its properties, the substance obtained is similar to substance E_6 (silybin) previously obtained from S. marianum but differs from it in its optical activity and melting point [1, 2].

Substance II, mp 173–175° C, $[\alpha]_D^{20} + 150°$ (c 0.2; dimethylformamide). UV spectrum: λ_{max} 288, (325); $\lambda_{max}^{C_2H_5ONa}$ 245, 325; $\lambda_{max}^{CH_3COONa}$ (288), 325; $\lambda_{max}^{H_3BO_3+CH_3COONa}$ 288 (325); $\lambda_{max}^{AlCl_3}$ (288), 315 mμ. IR spectrum: 1644 (OH in position 5 of a flavonoid); 1745 (C=O of an ester or a five-membered lactone); 3200–3300 (phenolic OH groups); 3460 (alcoholic OH groups) cm^{-1}. In system 1 R_f 0.63; in system 2, R_f 0.51. Red orange color reaction with sodium borohydride, yellow with cyanidin, yellow with zinc + HCl, and dark red with concentrated H_2SO_4. The acetate has mp 182–185° C. II is identical with substance E_5 previously isolated from S. marianum, but has a different melting point and optical activity.

Substance III. UV spectrum: λ_{max} 285, (340); $\lambda_{max}^{C_2H_5ONa}$ (295), 325; $\lambda_{max}^{CH_3COONa}$ 288, (325); $\lambda_{max}^{H_3BO_3+CH_3COONa}$ 288, 340; $\lambda_{max}^{AlCl_3}$ (280), 315 mμ. In system 1, R_f 0.79; in system 2, R_f, 0.07. Orange color reaction with sodium borohydride,

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.