hyperoside, 0.01; and rutin, 0.001 (on the weight of the absolutely dry raw material).

REFERENCES

1. T. K. Chumbalov and L. T. Pashinina, Uchenye zapiski KazGU, ser. khim., 44, 87, 1958.
2. T. K. Chumbalov and L. T. Pashinina, Biokhim., 27, 693, 1962.
3. V. A. Bandyukova, Rast. resursy, 1, 591, 1965.
4. L. Jurd and T. A. Geissman, J. Org. Chem., 21, 1395, 1956.
5. L. Jurd and R. M. Horowitz, J. Org. Chem., 22, 1618, 1957.

2 July 1968

Kirov Kazakh State University

UDC 547.913

4',5,6,7-TETRAMETHOXYFLAVONE FROM MARRUBIUM PEREGRINUM

L. A. Salei, D. P. Popa, and G. V. Lazur'evskii

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, pp. 182–183, 1969

We have previously isolated from Marrubium peregrinum [1] in high yield a substance $C_{19}H_{18}O_6$ with two forms of crystals from ethanol and mp 141–142° C, 161–162° C, $[\alpha]_D \pm 0°$, M^+ 342.

On a thin layer of alumina (activity grade III) in the benzene–ethanol (9 : 1) system the substance had a R_f value of 0.65 (spot revealed in UV light or by the action of iodine); in silica gel containing gypsum in the benzene–acetone (9 : 1) system, R_f = 0.5 (the same blue fluorescence in UV light or a yellow coloration on spraying with concentrated H_2SO_4).

This paper gives information enabling the structure of this compound to be established.

The substance has four methoxyl groups and no free hydroxyl groups. It is not hydrogenated under the usual conditions on catalysts and readily forms bright yellow salts with strong acids. These results, and also the features of the UV spectrum [λ_{max} (ethanol) 265 and 370 mμ (log ε 4.23, 4.50)] and the IR spectrum (KBr; 2820, 1643, 1633, 1516 cm^{-1}) give grounds for assigning the substance to the flavone group.

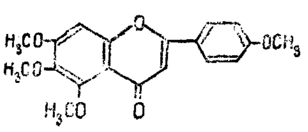
When the compound was oxidized by Jones' method [2] with heating to 80° C, an acid $C_8H_8O_3$ was obtained. The mass spectrum of the latter had the peak M^+ 152, an intense ion with m/e 135 (M −17) and a fragment with m/e 107 (m^* 85) formed from it. This shows the stepwise elimination of a carboxyl group.

The splitting off of formaldehyde from the fragment with m/e 107 leads to the appearance of a phenyl ion with m/e 77 (m^* 55.5) which shows that the acid is a methoxybenzoic acid. By comparing the melting point of the acid (173–175° C) and its methyl ester (48° C) with literature data, it can be stated that it is p-methoxybenzoic (anisic acid).

Consequently, the natural flavone contains one methoxyl group in position 4' of ring B.

On the basis of information that the family Labiatae usually contains 5,6,7- or 5,7,8-trihydroxyflavones [3], and also of the results of a comparison of the UV spectra of the substance and those of various substituted flavones, it was concluded that the native product is 4',5,6,7-tetramethoxyflavone (I) identical with tetramethylscutellarein [4], which has not previously been found in plants.

This was definitely confirmed by the IR spectrum, thin-layer chromatography, and the absence of a depression of the melting point of a mixture with an authentic sample of 4',5,6,7-tetramethoxyflavone which was kindly given to us by Ya. Streletskii (Budapest, Hungary). The mass spectrometric measurements of the samples was carried out by Dr. L. Doleiš (Prague).



REFERENCES

1. L. A. Salei, D. P. Popa, and G. V. Lazur'evskii, KhPS [Chemistry of Natural Compounds], 2, 249, 1966.
2. R. G. Curtis, I. Heilbron, E. R. H. Jones, and G. F. Woods, J. Chem. Soc., 457, 1953.
3. The Biochemistry of Phenolic Compounds [in Russian], Moscow, p. 79, 1968.
4. Dictionary of Organic Compounds [Russian translation], Moscow, vol. III, p. 622, 1949.

10 December 1968

Institute of Chemistry, AS Moldavian SSR

UDC 547.9

PHENOLIC GLYCOSIDES OF SALIX PENTANDROIDES

V. A. Kompantsev

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, p. 183, 1969

We have studied the phenolic compounds of the leaves of Salix pentandroides A. Skv. (the raw material was collected in the Teberda reserve). By two-dimensional paper chromatography with the subsequent use of qualitative reactions, we established the presence in the leaves of seven compounds of phenolic nature, of which three were obtained in the pure state. The dried leaves (1.8 kg) were exhaustively extracted with 70% ethanol. The ethanolic extracts were concentrated under vacuum, diluted with water, and treated with chloroform. The purified aqueous fraction was extracted with ethyl acetate. The ethyl acetate extract deposited hyperoside (quercetin 3-O-β-D-galacetopyranoside), $C_{21}H_{20}O_{12}$, in the crystalline form with mp 232–235° C (from ethanol), $[\alpha]_D^{20}$ −59° (c 0.5; ethanol), λ_{max} 362, 259 mμ [1].

After the treatment of the aqueous fraction with ethyl acetate, extraction was continued with a mixture of ethyl acetate and ethanol (3 : 1). Fractional recrystallization yielded the phenol glycoside salicin (saligenin O-β-D-glucopyranoside), $C_{13}H_{18}O_7$, with mp 201–203° C (from ethyl acetate saturated with water), $[\alpha]_D^{20}$ −63° (c 1.22; water). Melting point of the acetyl derivative, 131–134° C (chloroform), $[\alpha]_D^{20}$ −21° (c 1.08; chloroform [2]).

After the separation of the salicin, the mother liquor was deposited on a Kapron column and was eluted first with water and then with ethanol of various concentrations. The 30% ethanol fraction yielded quercimeritrin (quercetin 7-O-β-D-glucopyranoside), $C_{21}H_{20}O_{12}$, with mp 256–259° C (from acetone), $[\alpha]_D^{20}$ −58° [c 0.24; methanol–pyridine (5 : 1)], λ_{max} 371, 258 mμ; mp of the acetyl derivative 210–212° C (chloroform–petroleum ether) [3].

REFERENCES

1. E. T. Oganesyan, V. A. Bandyukova, and A. L. Shinkarenko, Rast. resursy, 4, 2, 240, 1968.
2. H. Thieme, Die Pharmazie, 7, 471, 1964.
3. L. Attree and A. Perkin, J. Chem. Soc., 234, 1927.

20 December 1968

Pyatigorsk Pharmaceutical Institute

UDC 661.715, 668.53

THE PRESENCE OF ALLOOCIMENE IN THE TURPENTINE FROM PINUS SILVESTRIS

I. I. Bardyshev and E. P. Dontsova

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, pp. 183–184, 1969

Alloocimene (2,6-dimethylocta-2,4,6-triene) has been found previously in the dry-distillation turpentine of the pine stumps that have been present in peat beds for 1000 years [1].

We have shown the presence of this hydrocarbon in commercial samples of Russian turpentines from P. silvestris L. (Scotch pine).