FLAVONOIDS OF LESPEDEZA BICOLOR

V. I. Glyzin, A. I. Ban'kovskii, O. V. Zhurba, and V. I. Sheichenko

Khimiya Prirodnykh Soedinenii, Vol. 6, No. 4, pp. 473–474, 1970

UDC 547.972

We have found no less than 12 substances of a flavonoid nature in Lespedeza bicolor Turez. (shrub lespedeza) by the two-dimensional paper chromatography of an ethanolic extract.

The combined flavonoids were obtained from the ethanolic extract purified with chloroform in a yield of 0.5%. When the flavonoids were separated on a column of polyamide sorbent by using repeated rechromatography of the individual fractions, six substances were isolated and identified.

Quercetin, $C_{15}H_{10}O_7$, mp 307–312° C (pentaacetate with mp 198–199° C). It was identified by direct comparison with a sample of quercetin.

Kaempferol, $C_{15}H_{10}O_6$, mp 278–281° C (tetraacetate with mp 185–186° C). It was identified by direct comparison with a sample of kaempferol.

Trifolin, $C_{21}H_{22}O_{11} \cdot 2H_2O$, mp 229–231° C, $[\alpha]_D$ –46° (c 0.16, ethanol), λ_{max} 267 and 354 mμ. The substance was identified on the basis of its IR and UV spectra and by direct comparison with a sample isolated from Sorbaria sorbifolia [1].

Isoquercitrin, $C_{21}H_{20}O_{12}$, mp 220–222° C, λ_{max} 256–359 mμ. The substance was identified by a direct comparison with a sample of isoquercitrin from Nardosmia laevigata [2].

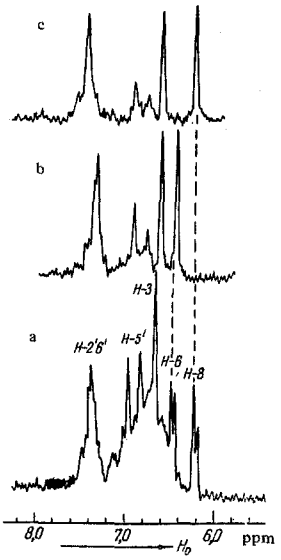
Homoorientin, $C_{21}H_{22}O_{11} \cdot H_2O$, mp 229–231° C, $[\alpha]_D$ +40° (c 0.1, ethanol), λ_{max} 261 and 355 mμ. The substance is not hydrolyzed under the usual conditions. On hydrolysis with hydriodic acid in phenol, the aglycone $C_{15}H_{10}O_6$ was obtained with mp above 300° C, λ_{max} 268 and 352 mμ; acetate with mp 224–226° C, identical with luteolin.

In the NMR spectrum of luteolin taken in dimethyl sulfoxide, the signal with δ 7.38 ppm corresponds to the H-2' and H-6' protons, the doublet at δ 6.91 ppm to H-5', the singlet with δ 6.68 to H-3, and the doublets with δ 6.48 ppm and 6.21 ppm to H-8 and H-6, respectively. Since opinions vary concerning the position of the hydroxyl substituent in homoorientin and other C-glycosides [3], we recorded the NMR spectrum of homoorientin under conditions similar to those for luteolin (parts a and c of the figure). The NMR spectrum of homoorientin lacks the signal of the H-6 proton, which shows that the glucose is attached at this position. Thus, homoorientin is 6-C-β-D-glucopyranosyl-5, 7, 3', 4'-tetrahydroxyflavone.

Orientin, $C_{21}H_{22}O_{11}$, mp 258–261° C, $[\alpha]_D$ +20.5° (c 0.3, dimethylformamide), λ_{max} 272 and 355 mμ. It was obtained by the preparative separation of the fraction on chromatographic paper. Hydrolysis with hydriodic acid yielded luteolin and D-glucose. The position of the glucose in orientin was established on the basis of its NMR spectrum (part b of the figure), in which the signal of the H-8 proton is absent and there is a singlet with δ 6.21 ppm corresponding to the proton in position 6. Consequently, orientin is 8-C-β-D-glucopyranosyl-5, 7, 3', 4'-tetrahydroxyflavone.

REFERENCES

1. L. A. Kruglii and V. I. Glyzin, KhPS [Chemistry of Natural Compounds], **4**, 379, 1968.
2. V. I. Glyzin, Tr. Khabarovskogo med. in-ta, Khabarovsk, 79–80, 1965.
3. V. I. Litvinenko and V. N. Darmograi, DAN URSR [Ukrainian], no. 7, 639, 1968.



NMR spectra of a) luteolin, b) orientin, and c) homoorientin.

20 April 1970

All-Union Scientific-Research Institute of Medicinal Plants