Substance (III) formed yellow acicular crystals with mp 237-238°C, $C_{21}H_{20}O_{12}$, the acid hydrolysis of which formed quercetin and D-galactose. It gave a positive cyanidin reaction but a negative Bryant reaction. Substance (III) was characterized as quercetin 3-O-β-D-galactoside, or hyperoside.

LITERATURE CITED

1. N. P. Maksyutina and V. I. Litvinenko, Phenolic Compounds and Their Biological Functions [in Russian], Moscow (1968), p. 7.
2. N. P. Maksyutina and D. G. Kolesnikov, Med. Prom. SSSR, No. 3, 41 (1964).
3. E. F. Bryant, J. Am. Pharm. Assoc., Sci. Ed., 39, 480 (1950).

FLAVONOIDS OF *Stachys inflata*

N. F. Komissarenko, A. I. Derkach,
I. P. Sheremet, I. P. Kovalev,
V. G. Gordienko, and D. A. Pakaln

UDC 547.918

The isolation from the epigeal part of *Stachys inflata* Benth. of stachyflaside has been reported previously [1].

In continuing investigations of the flavonoids of this plant we have isolated the total substances, which could not be separated by chromatography on paper in various systems. To establish the nature of the aglycones we hydrolyzed the combined glycosides with 5% sulfuric acid. The aglycones that deposited were separated on a column of polyamide sorbent (ratio of sorbent and mixture being separated 10:1) using as eluents chloroform–ethanol (98:2 and 80:2 by volume).

As a result, we obtained three aglycones: isoscutellarein ($C_{15}H_{10}O_6$, mp 252-256°C; for PMR spectrum, see below), scutellarein ($C_{15}H_{10}O_6$, mp 340-343°C), which was identified by comparison with that isolated previously [2] and 4'-O-methylisoscutellarein ($C_{16}H_{12}O_6$, mp 275-278°C) the structure of which was shown by comparison of the PMR spectra of the complete and 5-OH trimethylsilyl ethers [3], and also by the demethylation of the initial substance to isoscutellarein.

The spectrum of the TMS ether of 4'-O-methylisoscutellarein has the following signals: 7.80 ppm (H-2', H-6'), J = 8.5 Hz, 6.89 ppm (H-3', H-5'), J = 8.5 Hz, 6.39 ppm (H-3), 6.12 ppm (H-6), and 3.83 ppm (OCH_3-4'). The position of attachment of the methoxy group was shown by the production of 4-methoxybenzoic acid after alkaline degradation of the initial genin.

In the separation of the combined flavonoid glycosides under the same conditions as in the case of the aglycones, in addition to stachyflaside we isolated a substance with the composition $C_{27}H_{30}O_{16}$, mp 158-163°C; $[\alpha]_D^{20}$ −62° (c 0.1; ethanol), which we have called isostachyflaside. Like stachyflaside it is stable to enzymatic and alkaline hydrolysis [4, 5]. It was cleaved by 5% sulfuric acid into D-glucose, D-mannose, and an aglycone which on paper chromatography showed up in UV light before treatment with alkalis in the form of a dark spot. This shows the absence of a free OH group at C_3 of the flavonoid nucleus.

After treatment of the chromatogram with alkalis for 2-3 min, the spot of the aglycone began to fluoresce blue. In absolute ethanol with the addition of sodium ethanolate, both the glycoside and its genin formed no green coloration, and therefore it may be assumed that ring A does not have three free vicinal hydroxy groups.

As the PMR spectra showed, the genin forms a tetraacetyl derivative — signals with chemical shifts of 2.42 ppm (AcO at C_5) and 2.33 ppm (AcO — $C_{4',7,8}$), and signals of the chemical shifts of aromatic protons at 7.74 ppm (H-2', H-6'), J = 8.5 Hz, 7.26 ppm (H-3', H-5'), J = 8.5 Hz, 6.59 ppm (H-3), and 6.97 ppm (H-6), which shows the 4',5,7,8- type of substitution

Khar'kov Scientific-Research Institute of Pharmaceutical Chemistry. Ukrainian Zonal Experimental Station of Medicinal Plants of the All-Union Scientific-Research Institute of Medicinal Plants.

Translated from Khimiya Prirodnykh Soedinenii, No. 4, p. 521, July-August, 1978. Original article submitted March 21, 1978.

0009-3130/78/1404-0445$07.50

of the 2-phenylbenzo-γ-pyrone nucleus. The substitution of the lateral phenyl radical by the carbohydrate component at position 4' was confirmed by the methylation of the glycoside followed by the hydrolysis and alkaline degradation of the resulting methylated genin, which formed p-hydroxybenzoic acid.

On the basis of the facts given, the structure of the aglycone can be represented as 4',5,7,8-tetrahydroxyflavone (isoscutellarein), with the sugar component attached at position 4'. The order of attachment of the D-mannose and D-glucose in the bioside, and also the configurations of the glycosidic bonds were determined as described for stachyflaside [2], since the sugar components of these compounds were identical.

Thus, the structure of isostachyflaside can be represented as 4'-O-[O-β-D-mannopyranosyl-(1→2)-β-D-glucopyranosyl-5,7,8-trihydroxyflavone.

LITERATURE CITED

1. N. F. Komissarenko, I. P. Sheremet, A. I. Derkach, and D. A. Pakaln, Khim. Prirodn. Soedin., 98 (1976).
2. I. P. Sheremet and N. F. Komissarenko, Khim. Prirodn. Soedin., 721 (1971).
3. T. I. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of the Flavonoids, Springer, New York (1970), p. 262.
4. V. I. Litvinenko and V. A. Makarov, Khim. Prirodn. Soedin., 366 (1969).
5. M. D. Alaniya, Khim. Prirodn. Soedin., 646 (1977).

POLYPHENOLS OF *Lonicera microphylla*

T. K. Chumbalov, O. V. Fadeeva, and E. I. Chesnokova

UDC 547.972

We have studied the leaves of *Lonicera microphylla* for their polyphenol content. The air-dry raw material subjected to preliminary treatment with benzene was extracted with 80% methanol and ethyl acetate. Seven individual substances were isolated from the ethyl acetate extract by column chromatography.

By a comparison of physicochemical constants and spectral characteristics, substances (I) and (II) were identified as luteolin and quercetin, respectively. A substance with the composition $C_{21}H_{20}O_{11}$, mp 240-242°C, R_f 0.22-0.24, λ_{max} 352, 256 nm, $[\alpha]_D^{20}$ −84.6° (c 0.3; methanol) was split by hydrolysis with 10% sulfuric acid into luteoline and galactose in a molar ratio of 1:1.

Spectral investigations in the UV region showed that the sugar in substance (III) was located at C_7 [1]. The results of a comparison of the $[M]_D$ value of the glycoside under investigation with that of phenyl galactoside showed the presence of a furanose ring and of the β linkage of the galactose [2]. These results were confirmed by those of differential spectroscopy in the IR region (890, 1030, 1069 cm^{-1}), and of the NMR spectrum of the TMS ether in CCl_4: δ = 4.70 ppm (1 H, J = 7 Hz) [3]. Thus, flavonoid (III) is 3',4',5,7-tetrahydroxyflavone 7-O-β-D-galactofuranoside.

By qualitative reactions and the results of chromatography with known materials, substances (IV-VII) were identified as p-hydroxybenzoic, protocatechuic, vanillic, and p-coumaric acids [4].

LITERATURE CITED

1. V. I. Litvinenko and N. P. Maksyutina, Khim. Prirodn. Soedin., 420 (1965).
2. J. Canchie, G. A. Levvi, and C. A. Marsh, Adv. Carbohydrate Chem., 12, 157 (1957).
3. T. J. Mabry, K. B. Markham, and M. B. Thomas, The Systematic Identification of the Flavonoids, Springer, New York (1970).

S. M. Kirov Kazakh State University, Alma-Ata.

Translated from Khimia Prirodnykh Soedinenii, No. 4, p. 522, July-August, 1978. Original article submitted March 29, 1978.

0009-3130/78/1404-0446$07.50