STACHYFLASIDE – A FLAVONE GLYCOSIDE FROM Stachys annua

I. P. Sheremet and N. F. Komissarenko

UDC 547.972

As we have reported previously [1], the herb Stachys annua L. has yielded in the individual state four compounds, which have been denoted by A (stachannin), B (stachannoside), C, and D. The structures of stachannin and stachannoside have been established. The present paper gives the results of a chemical study of substance D, which we have called stachyflaside.

On acid hydrolysis, stachyflaside was cleaved to form D-glucose, D-mannose, and an aglycone which, on acetylation, formed a tetraacetyl derivative. On paper chromatography, the aglycone, like the glycoside, appeared in UV light in the form of a dark brown spot, which shows the absence in it of a free hydroxy group in position 3. A positive Bargellini reaction [2] gave grounds for assuming that the genin contains three vicinal hydroxy groups. Alkaline cleavage led to p-hydroxybenzoic acid, while no ring A fragment was detected, probably because of its degradation due to the presence in the substance of the three free OH groups that have been mentioned. On the basis of the facts given, the structure of the aglycone corresponds to that of scutellarein [3]. A comparison of the UV and IR spectra, R_f in various systems, and a mixed melting point have shown the identity of the aglycone of stachyflaside with scutellarein (4',5,6,7-tetrahydroxyflavone) [3].

The position of attachment of the sugar residue to the aglycone was determined from the UV spectrum of the glycoside. The absence of a pronounced shift in stachyflaside on the addition of sodium acetate showed the substitution of position 7 in scutellarein, as is also confirmed by the Bargellini reaction.

The structure of the sugar component was determined in a similar manner to that of stachannoside [1]. It was established that they were identical. Thus, stachyflaside is scutellarein 7-[O-β-D-mannopyranosyl-(1→2)-β-D-glucopyranoside].

EXPERIMENTAL

The isolation of stachyflaside D has been described previously [1]. The melting point of the glycoside was 220-224°C, $[\alpha]_D^{20}$ −60° (c 0.1; methanol). Its solution in anhydrous ethanol containing sodium ethoxide was yellow (negative Bargellini reaction).

IR spectrum: 3420 cm^{-1} (carbohydrate OH); 2940 cm^{-1} (carbohydrate CH); 1670 cm^{-1} (γ-pyrone C = O), and 1620, 1590, 1512, and 1460 cm^{-1} (C = C of an aromatic system). UV spectra: $\lambda_{max}^{CH_3OH}$ 330, 278 nm; λ_{max}^{+AcONa} 332, 275 nm; $\lambda_{max}^{+CH_3ONa}$ 385, 275 nm; $\lambda_{max}^{+AlCl_3}$ 352, 280 nm.

Found %: C 53.11; 53.18; H 4.84; 4.92. $C_{27}H_{30}O_{16}$. Calculated %: C 53.12; H 4.9.

Acid Hydrolysis of Stachyflaside. The glycoside (500 mg) was hydrolyzed in the same way as stachannin [1].

Aglycone of Stachyflaside. The hydrolysis gave 180 mg of the aglycone, which melted at 340-343°C and gave a green coloration in ethanolic solution containing sodium ethoxide (positive Bargellini reaction).

IR spectrum: 3400, 3300, 2960 cm^{-1} (phenolic OH groups), 1670 cm^{-1} (γ-pyrone C = O), and 1590, 1520, 1460 cm^{-1} (C = C of an aromatic system).

Khar'kov Chemical and Pharmaceutical Scientific-Research Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 721-723, November-December, 1971. Original article submitted June 25, 1971.

UV spectra: $\lambda_{max}^{CH_3OH}$ 330, 280 nm; λ_{max}^{+AcONa} 356, 278 nm; $\lambda_{max}^{+CH_3ONa}$ 370, 310 nm; $\lambda_{max}^{+AlCl_3}$ 375, 292 nm.

The acetate of the aglycone, obtained in the usual way, had mp 234-236°C. It was found [4] to contain four acetyl residues.

The alkaline degradation of the aglycone was performed as described previously [3]. The products of alkaline degradation were shown by paper chromatography in the butan-1-ol–benzene–acetic acid–water (2 : 10 : 2 : 1) system to contain p-hydroxybenzoic acid.

From a comparison of the IR and UV spectra, of the R_f values in the benzene–ethyl acetate–acetic acid (23.5 : 74.5 : 2) system, and a mixed melting point it was found that the aglycone of stachyflaside was identical with scutellarein.

The Sugar Component. After the separation of the aglycone, the aqueous alcoholic filtrate was neutralized with AV-17 ion-exchange resin and purified with activated carbon. The hydrolysis products were shown by paper chromatography in the liquid phenol system to contain D-glucose and D-mannose. The purified solution of sugars was evaporated to a syrupy residue, and from this an osazone was prepared [5] with mp 204-205°C, identified by its R_f values in the chloroform–formamide and benzene–methyl ethyl ketone (2 : 1)–water (35%) systems and by a mixed melting point as D-glucose phenylosazone.

The oxidative cleavage of the biose in the glycoside-periodate oxidation, stepwise acid hydrolysis with formic acid, and alkaline degradation were performed as described in a previous paper [1]. The results obtained show the identity of the sugar component of stachyflaside with that of the stachannoside described previously [1].

CONCLUSIONS

It has been established that stachyflaside, obtained from the herb Stachys annua L. is a new flavonoglycoside which has the structure of scutellarein 7-[O-β-D-mannopyranosyl-(1 → 2)-β-D-glucopyranoside].

LITERATURE CITED

1. I. P. Sheremet and N. F. Komissarenko, Khim. Prirodn. Soedin., 7, 373 (1971).
2. G. Bargellini, Gazz. Chim. Ital., 49, 47 (1919).
3. V. G. Zaitsev, G. V. Makarova, and N. F. Komissarenko, Khim. Prirodn. Soedin., 5, 504 (1969).
4. Houben-Weyl, Methoden der organischen Chemie, Georg Thieme Verlag, Berlin.
5. N. K. Richtmyer, "Phenylosazones," in: Methods in Carbohydrate Chemistry, Academic Press, Vol. 2 (1963), p. 132.