A STUDY OF THE HERB Aerva lanata

IV. FLAVONOID GLYCOSIDES

L. N. Pervykh, B. S. Karasartov, and G. G. Zapesochnaya

UDC 615.322.582.663.547.972

Eight nitrogen-containing substances [1, 2] and a whole series of phenolic compounds, among which a special place is occupied by flavonoid acylglycosides [3], have previously been isolated from the herb Aerva lanata. It was shown that kaempferol derivatives (tiliroside and coumaroyltiliroside) dominated among the acylglycosides, while their isorhamnetin analgoues were present in minor amounts [3].

The chemical standardization of this plant raw material is based on the qualitative and quantitative determination of flavonoids. In particular, the main flavonoids of the plant – tiliroside, coumaryltiliroside, and the isorhamnetin glycosides described in the present paper (I and II) – are clearly determined by TLC on Silufol.

The preparative isolation of compounds (I) and (II) proved to be extremely laborious, which was due to their high polarity and lability. For their extraction we used hot water or aqueous alcohol, treatment of the evaporated extract with butanol, and many-times-repeated chromatography of the butanolic and aqueous fractions with an alternation of sorbents (silica gel, polyamide, Sephadex LH-20) using chloroform–methanol as eluent.

We used chemical and spectral methods to study the structures of the flavonoids (I and II) isolated.

Compound (I), yellow crystals from ethanol, $C_{28}H_{32}O_{16}$, mp 174-176°C, $[\alpha]_{546}^{22}$ + 12.0° (0.83, water), λ_{max}^{MeOH} 257, 268, 357 nm. ^{1}H NMR spectrum in D_2O (200 MHz), δ: 7.60 (d, 9 Hz, H-5'), 7.32 (d, 2 Hz, H-2'), 7.18 (dd, 2 and 9 Hz, H-6'), 6.68 (d, 2 Hz, H-8), 6.60 (d, 2 Hz, H-6), 5.86 (d, 7 Hz, H-1"), 4.45 (d, 2 Hz, H-1'"), 3.70 (s, CH_3O), 3.1-3.8 (m, 10H of sugars), 1.07 (d, 6 Hz, CH_3 of rhamnose).

^{1}H NMR spectrum of the nonacetate of (I) ($CDCl_3$), δ: 8.08 (H-5'), 7.88 (H-2'), 7.60 (H-6'), 7.30 (H-8), 6.80 (H-6), 3.97 (CH_3O), 3.1-5.4 (m, 12H of sugars), 2.45 (3H), 2.34 (3H), 2.32 (3H) – singlets of three arom. Ac, 1.93-2.17 (singlets of 6 aliph. Ac.), 1.09 (CH_3 of rhamnoses).

Compound (II), yellow crystals from ethanol, $C_{34}H_{42}O_{20}$, mp 185-188°C, $[\alpha]_{546}^{22}$ + 20.0° (2.6 water), λ_{max}^{MeOH} 256, 268, 355 nm. ^{1}H NMR spectrum in D_2O (200 MHz) δ: 7.63 (H-5'), 7.38 (H-2'), 7.23 (H-6'), 6.76 (H-8), 6.68 (H-6), 5.82 (d, 7 Hz, H-1"), 5.35 (d, 2 Hz, H-1""), 4.42 (d, 2 Hz, H-1'"), 3.1-4.3 (m, 14H of sugars), 1.28 (d, 6 Hz, CH_3 of rhamnose), 1.02 (d, 6 Hz, CH_3 of rhamnose).

^{1}H NMR spectrum of the undecaacetate of (II) ($CDCl_3$), δ: 8.07 (H-5'), 7.82 (H-2'), 7.62 (H-6'), 7.30 (H-8), 6.83 (H-6), 3.1-5.5 (m, 17H of sugars), 2.48 (3H), 2.34 (3H), 2.31 (3H) – singlets of three arom. Ac, 1.92-2.14 (singlets of 8 aliph. Ac) 1.06 (CH_3), 0.94 (CH_3).

On acid hydrolysis (2% HCl, 100°C, 1 h) compounds (I) and (II) gave the same aglycon, isorhamnetin: $C_{16}H_{12}O_7$, M^+ 316, λ_{max}^{MeOH} 257, 267 sh., 367 nm. The carbohydrate fragments of both compounds were represented by glucose and rhamnose.

Compound (I) was hydrolyzed by the enzyme rhamnodiastase, which permitted the conclusion that a rutinose residue was present in this glycoside. Compound (II) was not hydrolyzed under analogous conditions.

The NMR spectrum of compound (I) did not differ from that of isorhamnetin 3-rutinoside [5], while in the spectrum of compound (II) there were the additional signals of a second

All-Union Scientific-Research Institute of Medicinal Plants Scientific-Production Association, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 581-583, September-October, 1992. Original article submitted January 2, 1992.

0009-3130/92/2805-0509$12.50

rhamnose residues: a characteristic doublet of the CH_3 group (δ 1.28, J = 6 Hz) and the anomeric proton (δ 5.35, J = 2 Hz).

To establish the sequence of attachment of the sugar residues in substance (II) we used partial acid hydrolysis (20% AcOH, 100°C, 1 h), which gave narcissin (I) and rhamnose. In the NMR spectra of the full acetates of compounds (I) and (II) the signals of triacetylisorhamnetin were identical, and the difference in the spectra according to the numbers of aliphatic acetoxy groups (6 and 8, respectivey) confirmed the 3-glycosylation of the isorhamnetin triglycoside in substnace (II).

Thus, the comparison of the NMR spectra of the initial substances and their acetates permitted compound (I) to be identified as narcissin (isorhamnetin 3-rutinoside) and compound (II) as isorhamnetin 3-rhamnosylrutinoside. It must be mentioned that the literature includes descriptions of a series of rhamnosylrutinosides with various aglycons [5, 6], including isorhamnetin [5], but the structures of the carbohydrate moieties remained unclear and no constants are given, apart from R_f values.

In view of the fact that among rhamnosylglucosides the most common are two bioses – rutinose (6-α-L-rhamnosyl-D-glucose) and neohesperidose (2-α-L-rhamnosyl-D-glucose), in our opinion the attachment of the second rhamnose residue to the 2-OH group of the glucose residue in the trioside (II), which we have called aervitrin, is most likely. A similar structure of the carbohydrate moiety has been established for glycosides of kaempferol and quercetin [7, 8].

This is the first time that compounds (I) and (II) have been isolated from the herb Aerva lanata.

LITERATURE CITED

1. G. G. Zapesochnaya, V. A. Kurkin, and L. N. Pervykh, Khim. Prir. Soedin., No. 5, 694 (1990).
2. G. G. Zapesochnaya, L. N. Pervykh, and V. A. Kurkin, Khim. Prir. Soedin., No. 3, 388 (1991).
3. A. M. Zadorozhnyi, G. G. Zapesochnaya, L. N. Pervykh, A. N. Shavlinskii, L. S. Kovtun, and N. V. Svanidze, Khim.-farm. Zh., No. 7, 855 (1986).
4. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970).
5. W. H. Parker and B. A. Bohm, Phytochemistry, 14, No. 2, 553 (1975).
6. J. B. Harborne, The Flavonoids: Advances in Research since 1980, Chapman and Hall, London (1988).
7. B. R. Buttery and R. I. Buzzell, Can. J. Bot., 53, No. 2, 219 (1975).
8. A. Sakishima, S. Nishibe, and S. Hisada, Phytochemistry, 19, No. 4, 712 (1980).