FLAVONOLS OF THE FRUIT OF VARIOUS SEEDS OF THE GENUS *Amelanchier*

V. V. Vereskovskii, D. K. Shapiro, and T. I. Narizhnaya

UDC 581.19+634.1/7:634.741

Continuing a study of the fruit of four species of serviceberry *Amelanchier* Medic., family *Rosaceae* [1, 2], we have investigated the flavonol glycosides.

The dry comminuted fruit of *Amelanchier spicata* (Lam.)C. Koch, *A. alnifolia* Nutt., *A. oligocarpa* Roem., and *A. sanguinea* DC. (10 g of each species) was extracted with 80% ethanol four times in the hot water bath at 80°C in a flask with a reflux condenser. Each combined extract, after filtration, was evaporated to dryness and the residue was dissolved in 20 ml of the same solvent. The solution was used for hydrolysis and the identification of the phenolic compounds.

The phenolic substances were separated with the aid of two-dimensional chromatography on Filtrak FN-1 paper in the following solvent systems: 1) butan-1-ol–acetic acid–water (3:1:1), and 2) 15% acetic acid (in the second direction). It was established that the main qualitative compositions of the flavonoids of the fruit of the species of serviceberry mentioned were the same, comprising four glycosides, one aglycone, and three caffeic acid esters.

The individual components of the flavonoids were obtained by the preparative paper chromatography of ethanolic extracts of systems 1 and 2 (more than 50 chromatograms). The substances were eluted from the chromatograms with methanol. The results of Bryant's cyanidin reaction showed the glycosidic nature of substances (1-4) and the aglycone nature of substance (7). The structure of the glycosides and their aglycones were established by UV spectroscopy with diagnostic reagents [3, 4]. A free hydroxy group at C_7 in the flavonoid glycosides and aglycones was detected from the bathochromism of the second band (on the addition of sodium acetate) by 4-23 nm, and a 3,4-dihydroxy grouping from the bathochromism of the first band by 15-25 nm on the addition of sodium acetate and boric acid. A free hydroxy group in the C_5 position was detected from the bathochromism of the first band on the addition of the aluminum chloride. The freeing of the 3-hydroxy group in flavonols causes an increase in the shift by 75-90 nm. The attachment of the carbohydrate moiety in the C_3 position was established from the bathochromism of the first band by 40-60 nm with aluminum chloride and hydrochloric acid.

The acid hydrolysis of substances 1-4 liberated the aglycone quercetin and the following sugars: D-glucose and L-rhamnose (from substance (2)); D-galactose (from substance 3); and L-arabinose (from substance (4)). The hydrolysis was performed in the boiling water bath with 2 N HCl in a flask with a reflux condenser for 2 h. The flavonoid aglycones were extracted with diethyl ether [5], and the carbohydrate components were identified from the results of paper chromatography in system 3) butan-1-ol–acetate–water (6:4:3) with marker sugars. The hydrolysates were first neutralized with Dowex 1 × 8 21/50 mesh ion-exchange resin in the HCO_3^- form.

Thus, on the basis of the results of spectral analysis in the UV region with diagnostic reagents, the colors of the spots on the chromatograms in visible and UV light, mobilities in paper chromatography with various solvent systems, the products of acid hydrolysis, and also direct comparison with authentic samples and comparison with literature information [3, 4], it has been established that substance (2) is quercetin 3-rutinoside (rutin), (3) is quercetin 3-galactoside (hyperoside), (4) is quercetin 3-arabinoside (avicularin), and (7) is quercetin. Substance (1) is a quercetin derivative the structure of which has not yet been possible definitively to establish.

Central Botanical Garden, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Khimiya Prirodnykh Soedinenii, No. 2, p. 257, March-April, 1982. Original article submitted December 25, 1981.

0009-3130/82/1802-0239$07.50

LITERATURE CITED

1. N. V. Sergeeva, D. F. Shapiro, V. A. Bandyukova, L. V. Anikhimovskaya, and T. I. Narizhnaya, Khim. Prir. Soedin., 98 (1979).
2. N. V. Sergeeva, V. A. Bandyukova, D. K. Shapiro, T. I. Narizhnaya, and L. V. Anikhimovskaya, Khim. Prir. Soedin., 726 (1980).
3. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970), p. 354.
4. K. L. Klyshev, V. A. Bandyukova, and L. S. Alyukina, Plant Flavonoids [in Russian], Alma-Ata (1978), p. 219.
5. V. V. Vereskovskii, Khimiya Prir. Soedin., 723 (1979).

A NEW XANTHONE COMPOUND FROM *Centaurium erythraea*

N. M. Neshta, G. G. Nikolaeva,
V. I. Sheichenko, and A. V. Patudin

UDC 547.972

Previously, hexasubstituted xanthones with the 1,3,5,6,7,8- type of substitution such as 1,3,5,6,7,8-hexamethoxyxanthone and 1-hydroxy-3,5,6,7,8-pentamethoxyxanthone have been isolated from the roots of *Canscora decussata* Schult. [1, 2]. We have isolated another new compound with this arrangement of constituents.

The epigeal part of *Centaurium erythraea* Rafn. was extracted with 96% ethanol. The ethanolic extracts were evaporated in vacuum and were treated with hot water, and the aqueous extract exhaustively re-extracted with chloroform. From the chloroform extract by chromatography on silica gel in the petroleum ether–chloroform (7:3) system a yellow crystalline substance of xanthone nature was isolated with the formula $C_{16}H_{14}O_8$, M^+ 334, mp 213-215°C (from FeOH).

The UV spectrum of the substance showed three absorption maxima (nm): λ_{max}^{MeOH} 235, 254, 335; + NaOAc 254, 270, 388; + NaOAc/H_3BO_3 254, 270, 378; + $AlCl_3$ 235, 273, 355 sh. 372; + $AlCl_3$/HCl 235, 273, 335 sh, 372; + NaOME 242, 256, 372.

The PMR spectrum ($CDCl_3$) showed the signals of two protons at 6.8 and 6.51 ppm (d, J = 3.5 Hz, 1 H) due to H-2 and H-4, respectively. There were no other signals of aromatic protons. Consequently, ring B is completely substituted. There were the signals of three methoxy groups: 4.01, 3.91, and 3.82 ppm (s, 3 H each).

Thus, it follows from the results of UV, mass, and PMR spectroscopy that the compound is a hexasubstituted xanthone containing three —OH and three —OCH_3 groups. Two of the OH groups are present in the α-positions to a carbonyl, as is confirmed by the PMR spectrum [DMSO, 11.78 and 11.62 ppm (s, 1 H, OH groups in positions 1 and 8)], and by the spectrum of the acetyl derivatives [$CDCl_3$, signal at 2.5 ppm (s, 6 H)], and also the UV spectrum [bathochromic shift with $AlCl_3$]. The third hydroxy group is present in position 3 or 6 of the xanthone—bathochromic shift with NaOAc [3].

To establish the positions of the OH groups, we employed a chemical shift reagent, making use of the fact that an OCH_3 group in a benzene ring in the ortho position to which there are no substituents does not form a complex with the chemical shift reagent. On the other hand, if there is an ortho substituent the methoxy group departs from conjugation with the benzene ring and forms a complex with the chemical shift reagent [4]. As the experiment showed, the signal of the protons of the methoxy group did not change its position with an increase in the concentration of the paramagnetic shift reagent $Eu(fod)_3$. Such behavior may be expected for a —OCH_3 group present in position 3.

On the basis of the facts given above, it may be concluded that the substance has the structure of 1,6,8-trihydroxy-3,5,7-trimethoxyxanthone and is a new xanthone compound

Tyumen' State Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 2, p. 258, March-April, 1982. Original article submitted November 13, 1981.

 0009-3130/82/1802-0240$07.50