FLAVONOIDS OF Atraphaxis pyrifolia. IV

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In the present communication we give information on the structure of a flavonol diglycoside from the leaves of Atraphaxis pyrifolia.

A methanolic extract evaporated to small volume was treated successively with chloroform, ether, ethyl acetate, and n-butanol. The ethereal extract was found to contain p-hydroxybenzoic, protocatechuic, p-coumaric, and caffeic acids. We have previously reported the isolation from an ethyl acetate extract of three flavonol rhamnosides. Repeated chromatography of the butanol extract on polyamide and purification on Sephadex LH-20 yielded a substance (I). On acid hydrolysis (0.1% formic acid, 1 h at 80°C) [1], in addition to the initial substance we detected the formation of a substance (II); boiling for 2 h yielded substances (II), (III), rhamnose, and glucose. Substance (I) was hydrolyzed completely by being boiled with hydrochloric acid for 2 h. This gave substance (III), rhamnose, and glucose (1 : 1 : 1).

Substance (II) was isolated from the products of incomplete acid hydrolysis of substance (I) by chromatography on Sephadex [substance (I) was eluted with water, and (II) with 30% aqueous acetone]. Its acid hydrolysis led to the formation of substance (III) and glucose (1 : 1). The same products were obtained by enzymatic hydrolysis with β-glucosidase. The physicochemical constants of the flavonoids of the leaves of A. pyrifolia were as follows:

Substance	mp, °C	$[\alpha]_D^{22}$	R_f(BAW 4 : 1.5)	R_f (CH_3COOH, 15%)	Fluorescence in UV light
I	186-188	−24.0	0.30	0.85	Brown
II	228-230	−67.7	0.30	0.31	Yellow
III	315-316	–	0.53	0.05	Brown

Below we give details of IR spectroscopy with ionizing and complex-forming reagents (λ_{max} nm):

Substance	C_2H_5OH	C_2H_5OH + CH_3COONa	C_2H_5ONa	C_2H_5OH, CH_3COONa H_3BO_3	C_2H_5OH, zirconyl chloride
I	240, 262 358	262, 358	268, 394	264, 378	268, 394
II	258, 384	258, 382	decomposes	264, 396	280, 330, 424
III	260, 278 344, 384	264, 278 382	decomposes	266, 406	280, 418

The NMR spectra of the trimethylsilyl ethers of the substances in CCl_4 show the signals of three protons characteristic for ring B substituted in position 3' and 4', the protons of a methoxy group (δ 3.88 ppm), and the signals of a proton having the same chemical shift in all cases at δ 6.20 ppm. In addition to these, the NMR spectrum of the TMS ether of substance (II) showed the signals of the protons of glucose protons present in the β form, and the spectrum of (I) the signals of glucose and rhamnose protons.

UV spectroscopy with diagnostic reagents showed the presence of free hydroxy groups in the following positions: for substance (I) in positions 3', 4', and 5, and for substances (II) and (III) in positions 3, 3', 4', and 5. Substance (III) which is the aglycone of (I) and (II), gave a positive gossypetin reaction and coincided in its physicochemical properties with the 7-methylgossypetin that we isolated previously [2]. From the results of

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UV spectroscopy and acid hydrolysis it may be concluded that the rhamnose in substance (I) is attached at position 3, and the only possible site of attachment of the glucose is position 8. On the basis of the results obtained we propose for substance (I) the structure of 7-methylgossypetin 8-β-D-glucopyranoside 3-O-α-L-rhamnopyranoside, and for (II) 7-methylgossypetin 8-β-D-glucopyranoside.

V. I. Sheichenko and L. P. Smirnova took part in the recording of the NMR spectra of the substances obtained.

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C-GLYCOSIDES OF Ajania fastigiata

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A methanolic extract from the epigeal mass of Ajania fastigiata family Compositae, was concentrated, and the chlorophyll was precipitated with water. The aqueous methanolic solution was distributed in organic solvents. From an ethereal extract, in addition to quercetin and luteolin [1], by preparative chromatography on paper we isolated a substance (I) with the composition $C_{15}H_{10}O_5$, mp 343-345°C (aqueous methanol), which proved to be apigenin, as was confirmed by the melting point of the acetyl derivative, the products of alkaline fusion, and the results of IR and UV spectroscopy.

The residual aqueous methanolic solution was chromatographed on Kapron. Elution with 20% methanol gave the total C-diglycosides [substances (II) and (III)], which were purified on a column of cellulose. Similar glycosides have previously been separated by preparative chromatography on paper [2]. We propose the use of Sephadex LH-20, which considerably shortens the time of separation and gives substances of higher purity.

The Sephadex was swollen in water, and water was also used for dissolving the substances and for elution from the columns.

Substances (II) and (III) had mp 228-230°C and 236-238°C (aqueous ethanol). The action of 5% HCl led to their mutual isomerization with the appearance of two new isomers, which is characteristic for C-diglycosides [3].

Compounds (II) and (III) did not undergo enzymatic hydrolysis [4]. On acid hydrolysis by Kiliani's method, apigenin, D-glucose, and traces of D-arabinose were detected [5].

IR spectrum of the C-glycosides, cm^{-1}: 3300-3400, 1650, 1620, 1570, 1520, 1450, 1075, 1045, 1020, 910.

UV spectrum [λ_{max} (absolute ethanol)] of substance (II): 332 and 280 nm (log ε 3.93; 3.89); substance III: 336 and 276 nm (log ε 3.91; 3.88). The ratios of the intensities of the absorption maxima in the long-wave region of the spectra of (II) and (III) were 35 and 32% of the intensity of the absorption maximum of the aglycone [6]. A reduced bathchromic shift with zirconyl chloride was observed: Δλ + 23 nm (II) and + 20 nm (III) [7]; $[\alpha]_D^{22}$ + 55° (II) and + 99° (III) (c 0.5%; dimethylformamide) [2]; $[M]_D \cdot K_p$ = + 153.5 (II) and + 276.3 (III) [8].

Substance (II) was identified as apigenin 6,8-di-C-β-D-glucopyranoside and (III) as a rotational isomer of (II).

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