FLAVONOIDS OF Achillea cartilaginea II

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In a further study of Achillea cartilaginea [1], from an ethyl acetate extract of the leaves by chromatography on polyamide with elution by 40-50% aqueous ethanol we have isolated substances (I), (II), (III), and (IV), and from an aqueous eluate (V) (Table 1).

From the flower heads after extraction with ethanol, evaporation, dissolution in water, extraction successively with chloroform, ether, and ethyl acetate, and chromatography on polyamide with elution by mixtures of ethanol (1-30%) and chloroform we obtained compounds (VI) and (VII) from the ethereal fraction and (VIII) and (IX) from the ethyl acetate fraction (see Table 1).

Compound (I), on acid hydrolysis, gave equimolar amounts of D-galactose and quercetin, $C_{15}H_{10}O_7$, with mp 309°C; mp of the pentaacetate 196-197°C, R_f 0.32 [TLC on Woelm silica gel in the toluene–ethyl formate–formic acid (5:4:1) system]. According to UV and NMR spectroscopy (Table 2) [2], the substance was identified as hyperin (quercetin 3-O-β-D-galactopyranoside).

Compound (II), according to the results of acid cleavage (L-arabinose and quercetin) and UV and NMR spectroscopy, was identified as guaiaverin (quercetin 3-O-α-L-arabopyranoside).

Compound (III), giving on hydrolysis D-galactose and kaempferol, $C_{15}H_{10}O_6$, with mp 274-280°C (tetraacetate with mp 186-188°C, R_f 0.38) was identical with trifolin (kaempferol 3-O-β-D-galactopyranoside).

Thus, from the leaves we have isolated glycosides of quercetin and kaempferol; however, acid hydrolysis of the combined flavonoids gave a very small amount of isorhamnetin, $C_{16}H_{12}O_7$, with mp 302-

TABLE 1. Physicochemical Constants of the Compounds Isolated

Substance	Yield, %	Composition	mp, °C	$[\alpha]_D^{20}$, deg	λ_{max}, nm	R_f*	
						1	2
I	0,23	$C_{21}H_{20}O_{12}\cdot H_2O$	224–226	−40,0 (*c* 1,2; formamide)	257, 362	0,60	0,40
II	0,28	$C_{20}H_{18}O_{11}\cdot\frac{3}{2}H_2O$	232–234	−59,7 (*c* 0,57; methanol)	257, 362	0,65	0,30
III	0,14	$C_{21}H_{20}O_{11}\cdot H_2O$	242–244	−7,0 (*c* 0,14; ethanol)	267, 353	0,70	0,42
IV	0,54	$C_{25}H_{24}O_{12}\cdot H_2O$	175–179	−336 (*c* 0,53; methanol)	217, 245, 301, 330	—	—
V	—	$C_{16}H_{15}O_9$	203–204	−33 (*c* 1; methanol)	218, 235, 245, 302, 329	—	—
VI	0,05	$C_{15}H_{10}O_5$	341–344	—	—	0,92	0,08
VII	0,09	$C_{15}H_{10}O_6$	320–324	—	—	0,84	0,06
VIII	0,29	$C_{21}H_{20}O_{10}$	221–224	−138,6 (*c* 0,66, formamide)	267, 334	0,63	0,23
IX	0,32	$C_{21}H_{20}O_{11}$	263–267	−54,6 (*c* 0,52, formamide)	256, 268, 350	0,40	0,15

*Chromatography was performed on type "M" ["slow"] Leningrad paper and the following solvent systems: 1) butan-1-ol–acetic acid–water (4:1:5) and 2) 15% acetic acid

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TABLE 2. NMR Spectra (100 MHz, TMS)*

Substance	Aromatic protons							Aliphatic protons	
	H-6'	H-2'	H-3'	H-5'	H-8	H-6	H-3	anomeric proton of the carbohydrate	other protons
I	doublet of doublets 7.71 J = 9 Hz J = 2.5 Hz	doublet 7.27 J = 2.5 Hz	–	doublet 6.77 J = 9 Hz	doublet 6.40 J = 2.5 Hz	doublet 6.10	–	Doublet 5.60, J = 7.5 Hz (1β-H of D-galactose in position 3)	Multiplet 3.3, 3.8 (6H of galactose)
II	J = 2.5 Hz	doublet 7.34 J = 2.5 Hz	–	doublet 6.87 J = 9 Hz	doublet 6.46 J = 2.5 Hz	doublet 6.15	–	Doublet 5.12, J = 2.5 Hz (1α-H of L-arabinose in position 3)	Signals of 5H of arabinose from 2.8 to 4.2
III	doublet (2H) 7.90 J = 9 Hz		doublet (2H) 6.80 J = 9 Hz		doublet 6.42 J = 2.5 Hz	doublet 6.10	–	Doublet 5.68, J = 7 Hz (1β-H of D-glucose in position 7)	Multiplet 3.38-3.88 (6H of galactose)
VI	doublet (2H) 8.10 J = 9 Hz		doublet (2H) 7.34 J = 9 Hz		doublet 7.60 J = 2.5 Hz	doublet 7.06	singlet 6.89		Singlets of 3 AcO groups 2.45, 2.36, 2.34
VII	multiplet (2H) 8.10-7.96		–	doublet 7.49 J = 9 Hz	doublet 7.62 J = 2.5 Hz	doublet 7.08	singlet 6.93		Singlets of 4 AcO groups 2.45, 2.34, 2.32
VIII	doublet (2H) 7.66 J = 9 Hz		doublet (2H) 6.78 J = 9 Hz		doublet 6.55 J = 2.5 Hz	doublet 6.20	singlet 6.26	Doublet 4.92, J = 6.5 Hz (1β-H of D-glucose in position 7)	Multiplet 3.5-4.15 (6H of galactose)
IX	doublet of doublets 7.33 J = 8 Hz J_1 = 2 Hz	doublet 7.23 J = 2 Hz	–	doublet 6.80 J = 8 Hz	doublet 6.57 J = 2 Hz	doublet 6.25	singlet 6.27	Doublet 4.87, J = 6.5 Hz (1β-H of D-glucose in position 7)	Multiplet 3.2-3.75 (6H of galactose)

*The spectra of compounds (VI) and (VII) were taken in the form of acetates in $CDCl_3$ (aliphatic protons) and in DMSO (aromatic protons), and those of compounds (I, II, III, VIII, and IX) after silylation [2] in CCl_4.

304°C (tetraacetate, mp 203-206°C, R_f 0.40), which could not be isolated in the form of a glycoside.

Compound (IV), according to NMR spectroscopy (solution in deuteropyridine, silylated derivative in CCl_4, and hexaacetate in $CDCl_3$), was identified as 3,4-dicaffeylquinic acid [3, 4] or, according to the tentative rules [5], 4,5-dicaffeylquinic acid. When (IV) was silylated, no inversion of the conformation of the quinic acid took place as has been reported for free quinic and chlorogenic acids [3].

Compound (V) was identical, according to IR and NMR spectroscopy and a direct comparison with an authentic sample [6], with chlorogenic acid.

Compounds (VI) and (VII) were identified, respectively, as apigenin (mp of the triacetate 182-183°C) and luteolin (mp of the tetraacetate 228-230°C).

Compound (VIII), on acid hydrolysis, gave D-glucose and apigenin with mp 343-348°C. The absence of changes in the UV spectrum on the addition of sodium acetate showed the attachment of the sugar residue to position 7 of the aglycone. A doublet with δ = 4.95 ppm and J = 6.5 Hz (see Table 2) in the NMR spectrum permitted the assumption of the β configuration of the glycosidic bond for (VIII), and calculation of the molecular rotation by Klyne's method showed the furanose form of the glucose. Consequently, compound (VIII) is apigenin 7-O-β-D-glucofuranoside [2, 7].

Compound (IX), giving on hydrolysis D-glucose and luteolin (mp 329-331°C) was identified by UV and NMR spectroscopy as luteolin 7-O-β-D-glucopyranoside.

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