The C-Glycosylflavone Pattern of *Passiflora incarnata* L.

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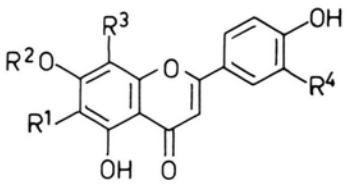
From the herbage of *Passiflora incarnata* have been isolated eight flavone-C-glycosides based on apigenin and luteolin, six of them had not been found before in that plant. The constitution of all compounds is prooven.

The herbage of *Passiflora incarnata*, which is widely used medically [1], has been reported to contain the C-glycosyl-flavones vitexin, isovitexin (**1**), orientin, isoorientin (**2**), and saponarin (**9**) [1–3]. When one of us tried to isolate some reference substances from that plant, it became evident, that the C-glycosyl flavone pattern was more complex than had been reported earlier.

Our findings are summarized in Table I. The starting material was a commercial dry extract, kindly provided by Messrs Dr. Willmar Schwabe, Karlsruhe, F.R.G., and manufactured from the herbage of *Passiflora incarnata* grown on the premises of that firm. The separation of the flavone glycosides was effected by chromatography on a column of polyamide-6 with a water-acetone gradient (sequence of elution with considerable overlapping: **7** ≈ **8** > **5** >

Table I. Structures, yields, M_r determined by FD-MS, and chromatographic behaviour of flavone C-glycosides from *Passiflora incarnata*.



	Substitution pattern				Yield [mg/ 100 g]	M_r	hR_f-values				Fluorescence	
	R^1	R^2	R^3	R^4			Cellulose 15% HAc	Cellulose TBA	Polyamide NM	Polyamide WEBP	untreated	NA
Isovitexin (**1**)	glc	H	H	H	216	432	38	73	16	35	d	gr
Isoorientin (**2**)	glc	H	H	OH	158	448	25	51	02	32	d	y
Isovitexin-2″-β-D-glucopyranoside (**3**)	soph	H	H	H	531	594	75	66	14	63	d	gr
Isoorientin-2″-β-D-glucopyranoside (**4**)	soph	H	H	OH	170	610	68	50	06	63	d	y
Schaftoside (**5**)	glc	H	ara	H	250	564	45	34	19	70	d	gr
Isoschaftoside (**6**)	ara	H	glc	H	152	564	34	28	17	67	d	gr
Vicenin-2 (**7**)	glc	H	glc	H	164	594	39	26	09	72	d	gr
Lucenin-2 (**8**)	glc	H	glc	OH	57	610	31	15	05	72	d	y
Saponarin (**9**)	glc	glc	H	H	not detected	594	60	52	17	74	d	gr

glc = β-D-glucopyranosyl; ara = α-L-arabinopyranosyl; soph = sophorose; Cellulose = precoated sheets Polygram CEL 400 (Macherey and Nagel, D-5160 Düren). Polyamide = F1700-Mikropolyamide sheets (Schleicher and Schüll, D-3345 Dassel). 15% HAc = 15% aqueous acetic acid; TBA = tert. butanol/acetic acid/water (3:1:1). NM = nitro methane/methanol (7:3); WEBP = water/ethanol/butanone/2,4-pentanedione (65:15:15:5). NA = sprayed with 0.5% methanolic diphenylboric acid – β-aminoethyl ester.

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6 > **3** ≈ **4** ⩾ **1** ≈ **2**). For the separation of the individual glycosides the following systems were used: Sephadex LH 20/20% aqueous methanol (**7** ≈ **8** ⩾ **5** ≈ **6** ⩾ **3** ≈ **4** ⩾ **1** > **2**); Polyclar AT/20% aqueous methanol (**7** ⩾ **8**; **3** ⩾ **4**; **5** > **6**); and Sephadex LH 20 with acetone/methanol/water (2:1:1) (for the elimination of polymers, which appear in the forerun). Finally the pure glycosides were crystallized from aqueous methanol.

The ^{13}C NMR spectra of **5**, **6**, **7** and **8** were identical with published spectra of these compounds [4, 5]. In combination with the FDMS and cochromatographic results this constitutes proof of identity for **7** and **8**; but does not distinguish the two isomers, **5** and **6**. However, the differences between the R_f-values of these two isomers are such, that on this basis the distinction can be made with confidence [5].

Compounds **3** and **4** are also known natural products [6, 7], but no published ^{13}C NMR data were available for comparison. These spectra (Table II) are readily interpreted in that the sugar region in both is almost superimpossible with that in the spectrum of vitexin-2″-O-β-D-glucopyranoside [8], while in the aromatic region the signals of **3** and **4** are as expected for a 6-C-glycosylated apigenin or luteolin [9]. Thus **3** and **4** are identified as isovitexin- and isoorientin-2″-O-β-D-glucopyranoside respectively. Compounds **1** and **2** were identified by direct comparison with authentic samples.

Saponarin (**9**), of which an authentic sample isolated from *Saponaria officinalis* L. [10] was at hand, could not be detected in *P. incarnata,* either by TLC of the extract, or by its colour reaction with I_2/KI [10, 11] in fresh leaves. Vitexin and orientin, which have also been reported to occur in *P. incarnata* could only be detected by TLC in amounts too small for isolation.

Table II. ^{13}C NMR spectra of isovitexin-2″-β-D-glucopyranoside (**3**) and isoorientin-2″-β-D-glucopyranoside (**4**)*.

Carbon No.	Signals **3**	**4**
2	163.4$^+$	163.5$^+$
3	102.7	102.9
4	181.9	182.0
5	161.1$^+$	161.2$^+$
6	107.9	108.1
7	160.9$^+$	163.5$^+$
8	93.4	93.4
9	156.4	156.6
10	102.7	103.4
1′	121.1	121.6
2′	128.4	113.4
3′	115.9	145.9
4′	161.1$^+$	149.8
5′	115.9	116.2
6′	128.4	119.1
1″	71.1	71.3
1‴	105.3	105.3
2″	81.5	81.7
2‴	74.6	74.8
3″	78.3	78.5
3‴	76.3	76.6
4″, 4‴	70.3, 69.3	70.6, 69.5
5″	80.8	81.1
5‴	76.3	76.6
6″, 6‴	61.3, 60.3	61.5, 60.5

* Solvent DMSO-d_6; assignments bearing the same superscript in any one spectrum may be reversed.

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