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A NEW ACYLATED C-GLYCOFLAVONE GLYCOSIDE FROM SILENE PRATENSIS LEAVES

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SUMMARY

In addition to isovitexin-7-glucoside, isoorientin-7-glucoside and isovitexin, a new apigenin derivative was isolated from leaves of *Silene pratensis* and identified as 7-0-(feruylglucosyl)-isovitexin.

1. INTRODUCTION

Silene pratensis (Rafn) Godron & Gren. (formerly called *Silene alba* (Miller) Krause, which name has been shown to be incorrect by McNeill & Prentice 1981), the white champion or white cockle, is a common weed, widely distributed over Europe. Both in petals and green parts a large variation has been found in the flavonoid glycosylation pattern (Van Nigtevecht & Van Brederode 1972, Van Brederode & Van Nigtevecht 1972, Van Brederode et al. 1979, Van Brederode & Kamps-Heibroek 1981). Except for some Armenian populations (Heinsbroek et al. 1980) isovitexin in most populations is the sole "aglycone" found in the petals. More variation was encountered in the green parts; in addition to isovitexin also isoorientin (Van Brederode et al. 1979, 1980) and isoscoparin (Van Brederode & Kamps-Heibroek 1981) and their glycosides were found. In the course of out investigations on the relation between the various flavonoid-patterns and the geographical distribution of *S. pratensis* (Mastenbroek et al., in preparation) a new apigenin derivative was found, which is described here.

2. MATERIALS AND METHODS

Fresh leaves of *Silene pratensis*, specimen no R 1907–40, originating from Galicia, Spain, were extracted with acetone. After filtration and addition of water lipophilic substances were removed with ligroin. The acetone-water extract was concentrated, acidified to pH 2 and extracted with butanol. The substances were purified by paper chromatography on Whatman no 1 with successively 15% acetic acid and butanol –27% acetic acid (1:1 v/v). They were identified by comparison of both the original product and its acid and/or alkaline hydrolysis products with the adequate referents for R_f values, colour reactions and UV spectra inclusive shifts (Jurd 1962). Sugars were also analysed on Whatman no 1

Table 1. R_f Values (× 100) and colour reaction of 7-0-(feruylglucosyl) isovitexin (FeGI) and its degradation products.

								colour	UV	reagent	
	TBA	BuAW	15HAc	H_2O	1%HCL	Phenol	BeAW	UV	+ NH_4OH	DNA/	soda
FeGI	42	54	57	21	19	78		ab	l.gn	Rs	Gb
7-0-glucosyl isovitexin	30	45	64	30	27	61		ab	l.gn	Y	OY
alk. hydr- FeGI 1		46	62		29	61		ab	l.gn	Y	OY
alk. hydr. FeGI 2		80	46		20(55)			b	b	Rs	l.B
ferulic acid		81	46(65)	27(76)	22(54)		76	b	b	Rs	l.B
acid hydr. FeGI 1	41	48	23	11	5	60		ab	d.bn	Y	Y
acid hydr. FeGI 2 (main c.)	55	67	48	21	14	78		ab	d.bn	Y	OY
acid hydr. FeGI 3 (A)	87	56(66)	32(56)					b	gnb	Rs	l.B
isovitexin	56	67	50	21	15	79		ab	d.bn	Y	OY
vitexin	42	50	27	11	6	60		ab	d.bn	Y	Y
alk. hydr. of A			44	24(76)			75	b	b	Rs	l.B

TBA: tert.butanol-acetic acid-water 3:1:1, BuAW: butanol-27% acetic acid 1:1, 15HAc: 15% acetic acid, Phenol: water saturated phenol, BeAW: benzene-acetic acid-water 125:72:3.
ab = absorbant, l.gn = light green, b = blue, d.bn = dark brown, Rs = rose-red, GB = grey-blue, Y = yellow, OY = orange-yellow, l.B = light blue. DNA = 0.05% *p*-nitrophenyldiazonium fluoroborate (oversprayed with a 10% soda solution).

and detected with a combination of flavone reagent and *p*-anisidine (NIEMANN 1979).

3. RESULTS

The major leaf flavone isolated in this investigation was isovitexin-7-glucoside. Additional flavonoids were isoorientin-7-glucoside, isovitexin and a new apigenin derivative with a comparatively high R_f value on paper in phenol (*table 1*). The UV spectrum of the latter compound showed an absorbance in the B-ring band at 327 nm which was higher than normal. The shifts observed with diagnostic reagents (JURD 1962) indicated the presence of 5 and 4'hydroxyl groups (*table 2*). Acid hydrolysis gave isovitexin and a blue fluorescent compound (B) as main products, some vitexin and only a trace of glucose. Compound B showed some similarity with ferulic acid in colour under UV and after spraying with diazotised *p*-nitroaniline (DNA), but no hypsochromic shift was obtained in its UV absorbance on the addition of NaAc, indicating the absence of a free carboxylic group (NIEMANN 1969). Alkaline hydrolysis of B gave a hypsochromic shift of 26 nm (in NaOH, corresponds with 6 nm under acid conditions), and ferulic acid and glucose as degradation products. Thus, B is the glucose ester of ferulic acid and the flavone is 7-0-(feruylglucosyl)-isovitexin.

The identity was confirmed by alkaline hydrolysis, yielding isovitexin-7-0-glucoside and free ferulic acid.

Quite recently ferulic acid derivatives of isovitexin have also been demonstrated in leaves of the closely related species *Silene dioica*, but they were not further identified (Kamps-Heinsbroek, personal communication). Other related cinnamates known are: feruyl-2''-isovitexin and its 4'glucoside from *Gentiana punctata* (LUONG & JACOT-GUILLARMOD 1977), vitexin-2''-0-*p*-coumarate from *Trigonella foenum-graecum* (SOOD et al. 1976), feruylvitexin from *Larix decidua* (NIEMANN & BAAS 1978), the 6''' *p*-coumaryl-, feruyl- and sinapoylderivatives of 2''-0-glucosylswertisin from *Zizyphus jujuba* (WOO et al. 1980) and sinapoyl-8-D-galactosyl-6-C-arabinosylapigenin and ferulic acid derivatives of the same di-C-glycoside or its isomer from *Triticum aestivum* (WAGNER et al. 1980).

Table 2. UV spectra of 7-0-(feruylglucosyl) isovitexin (FeGI) and its degradation products in methanol.

				+NaAC			+NaAC+ NaOH			$+AlCl_3$			
FeGI	269	327		266	330	392	262	273[s]	378	271	296	330	406
FeGI acid hydr. 2	270	325		276	310[s]	380	276		380				
FeGI acid hydr. 3 (A)	245[s]	281	320	246[s]	282	320		284[s]	366				
alk. hydr. of A		284	314					280[s]	340				
ferulic acid	228[s]	289[s]	313		283	305		282[s]	338				

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