Phytochemistry, 1975, Vol. 14, pp. 2267–2274. Pergamon Press. Printed in England.

STRUCTURAL DETERMINATION OF *C*-GLYCOSYLFLAVONES BY MASS SPECTROMETRY OF THEIR PERMETHYL ETHERS

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(*Received* 7 *February* 1975)

Key Word Index—MS; MS fragmentation; *C*-glycosylflavones; di-*C*-glycosylflavones; vicenin; lucenin; violanthin; schaftoside; permethylation.

Abstract—Permethylated *C*-glycosylflavones give well defined MS, including in all cases an important molecular peak. The observed fragmentations are characteristic for the nature and position of the sugar. The 6-*C* and 8-*C* glycosylated derivatives are clearly differentiated. In dissymmetrical 6,8-di-*C*-glycosylflavones, the natures of the sugar in both the 6- and 8- positions can be determined. The structures of several natural compounds are discussed.

INTRODUCTION

C-glycosylflavones [1,2] are being found more and more frequently in plant extracts, but generally in very small amounts. Therefore, analytical methods requiring less than 1 mg are very important.

About 10 years ago, the synthesis of a range of *C*-glycosyl-5,7-dihydroxyflavones was achieved [3]. The compounds obtained have permitted the identification or confirmation of structure of several natural *C*-glycosylflavonoids. In this work, chromatography, IR, NMR of acetyl or trimethylsilyl derivatives and MS of free compounds were routinely used with good results. None of these methods however is entirely satisfactory. For example, chromatography is not reliable for di-*C*-glycosylflavones, these products having very close R_f's. IR (KBr disc) requires identical crystallization conditions; NMR consumes too much product; MS of free compounds [4,5] gives good results with mono *C*-glycosylflavones, but does not differentiate 6 and 8-*C*-glycosylflavones. Only a few di-*C*-glycosylflavones give MS because the vaporisation temperature of these compounds is too high. The spectra obtained are pyrolysis spectra, i.e. the fragmentation proceeds by sequential loss of water, without providing a molecular peak.

However, previous reports dealing with the MS of acetylated derivatives of some *C*-glycosylflavones and xanthones [6], or with perdeuteriomethylated derivatives of *O*-glycosylflavonoids [7–10], have prompted a systematic study of permethylated *C*-glycosylflavonoid MS. Permethylated derivatives have been preferred to acetylated or trimethylsilylated compounds, because the mass increase is lower and they are more stable, which makes their purification easier. Permethyl (PM) *C*-glycosylflavones can be obtained, using the Brimacombe method [11], from very small amounts of the free compound (about 0·5 mg). Spectra are very easily performed. A molecular peak is always present and the fragmentation gives a great deal of information about the structure of the compounds studied.

RESULTS AND DISCUSSION

Formulae of the *C*-glycosylflavones that were permethylated are given in Table 1, the main characteristic peaks in Table 2 and the individual MS data in Table 3.

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Table 1. *C*-Glycosylflavones studied

Compound*
1 8-*C*-glucosylapigenin (vitexin)
2 8-*C*-glucosyl-luteolin (orientin)
3 8-*C*-xylosyl-luteolin
4 6-*C*-glucosylchrysin
5 6-*C*-glucosylapigenin (isovitexin)
6 6-*C*-glucosyl-luteolin (iso-orientin)
7 6-*C*-galactosylapigenin
8 6-*C*-rhamnosylapigenin
9 6-*C*-xylosyl-luteolin
10 6-*C*-arabinopyranosylapigenin
11 6-8-di-*C*-glucosylapigenin
12 6-8-di-*C*-glucosyl-luteolin
13 6-8-di-*C*-xylosylapigenin
14 6-8-di-*C*-rhamnosylapigenin
15 6-8-di-*C*-pentosylapigenin (*Melilotus alba*)
16 6-8-di-*C*-pentosylapigenin (*Hymenophytum leptopodum*)
17 violanthin
18 isoviolanthin
19 lucenin-1
20 lucenin-3
21 6-*C*-xylosylvitexin
22 schaftoside
23 isoschaftoside
24 neoschaftoside (*Catananche caerulea*)
25 6,8-di-*C*-glycosylacacetin (*Trigonella corniculata*)

* All sugars are in the pyranose form unless otherwise indicated. D-glucose, D-galactose and D-xylose are β-linked to the flavone nucleus, while L-rhamnose and L-arabinose are α-linked.

MS of PM mono-C-glycosylflavones

The MS of PM 8-*C*-glycosylflavones, as shown by the spectrum of PM vitexin (**1**) (Fig. 1a), is characterized by a very important molecular ion (60–80%) and a parent peak; **i** = Ar–CH=$\overset{+}{}$–Me (Ar = PM flavone radical); all intermediary peaks are very weak. This parent peak corresponds, for a *C*-hexosylflavone, to a loss of 175 mass units (m.u.) and appears in PM 8-*C*-xylosyl-luteolin (**3**), (Fig. 1b) [12] at M-131 (difference of 44 m.u.). The following peaks may be represented by the ions: **j** = Ar–CH=$\overset{+}{O}$H [M-189 (**1**); M-145 (**3**)], **k** = Ar-$\overset{+}{C}$H$_2$ [M-205 (**1**); M-161 (**3**)] and finally the PM flavone ion: **l** = Ar$^+$ [M-219 (**1**); M-175 (**3**)].

At lower masses, there are only peaks of very weak intensity. However, it is possible to recognize peaks coming from retro-Diels–Alder cleavage of the flavone [13] and derived from the A ring of some of the above ions. Ions coming from B ring can also be recognized in most cases. Finally the very intense ions: *m/e* 101 (Me–$\overset{+}{O}$=CH–CH=CH–OMe) and *m/e* 88 (MeO–CH=CH–OMe)$^+$ are characteristic fragments from permethylated carbohydrates [14].

Table 2. Main fragments in MS of permethyl *C*-glycosylflavones

Common fragments	Sugar-specific fragments: Hexose	Deoxyhexose	Pentose
a_1 (M-14)	**g** (M-103) **gh**	(M-73) **gd**	(M-59) **gp**
a_2 (M-15)	**h** (M-163) **hh**	(M-133) **hd**	(M-119) **hp**
a_3 (M-17)	**i** (M-175) **ih**	(M-145) **id**	(M-131) **ip**
b_1 (M-29)	**j** (M-189) **jh**	(M-159) **jd**	(M-145) **jp**
b_2 (M-30)	**k** (M-205) **kh**	(M-175) **kd**	(M-161) **kp**
b_3 (M-31)	**l** (M-219) **lh**	(M-189) **ld**	(M-175) **lp**
c_3 (M-47)			

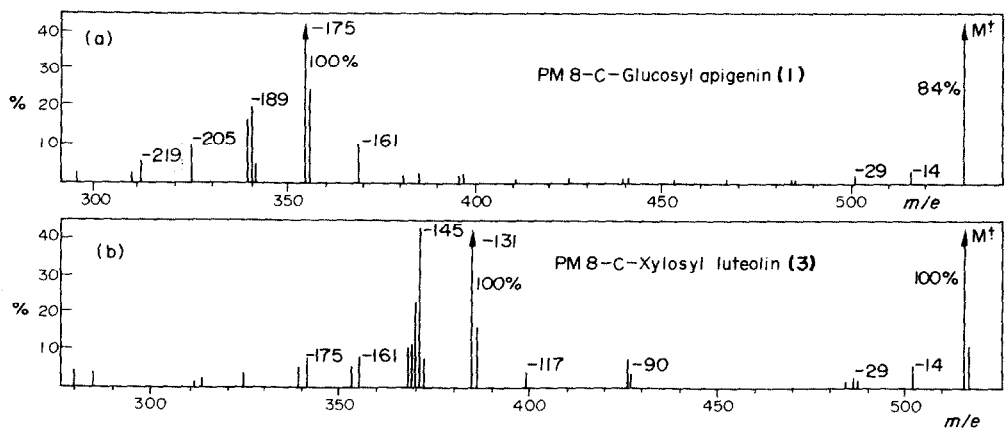

Fig. 1. (a–b).

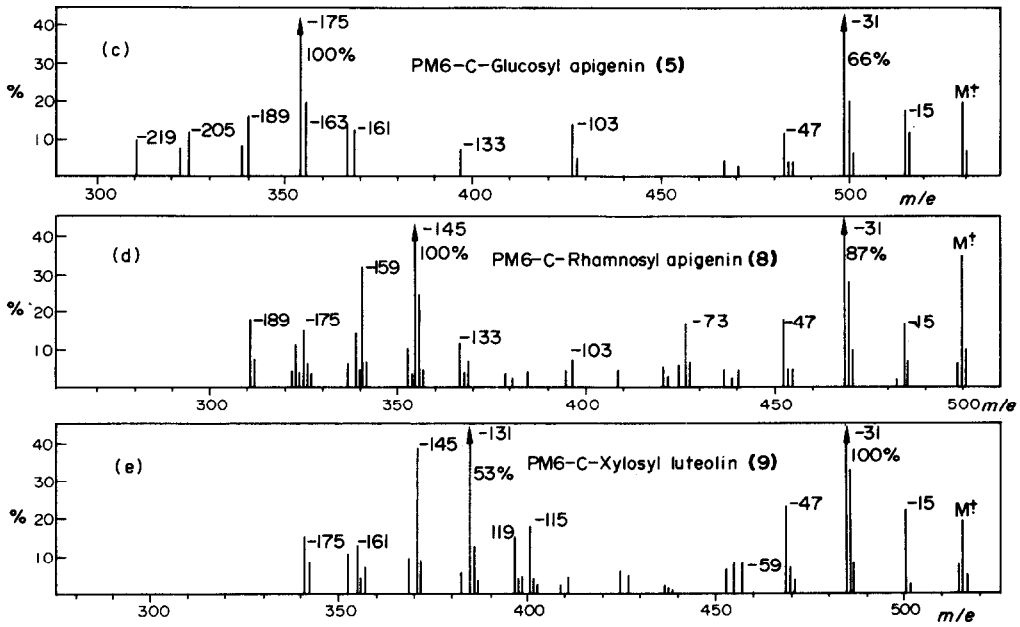

Fig. 1. (c–e).

Fig. 1. a–e: MS of PM mono-*C*-glycosyl flavones.

A comparison of the MS of compounds **1** and **2**, apigenin and luteolin derivatives, shows that the nature of the aglycone does not interfere with the fragmentation, but may modify the relative intensities of the peaks.

6-*C*-glycosylflavones (see PM isovitexin (**5**), (Fig. 1c), PM 6-*C*-rhamnosylapigenin (**8**), (Fig. 1d) [15] and PM 6-*C*-xylosylluteolin (**9**), (Fig. 1e) [12,16]), are clearly different from the isomeric 8-*C*-glycosyl-flavones. The parent peak remains

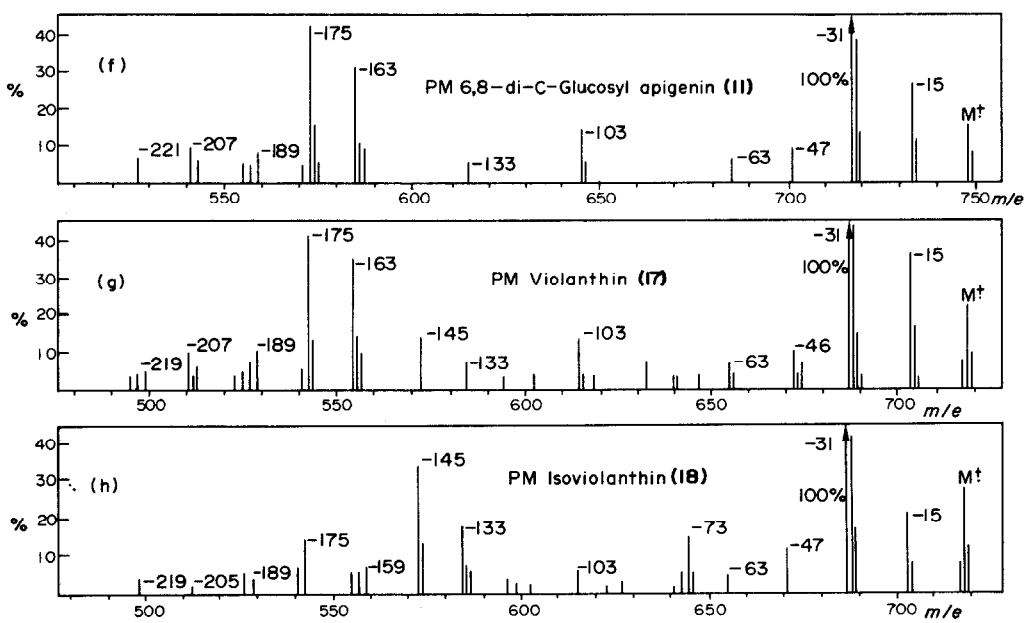

Fig. 1. (f–h).

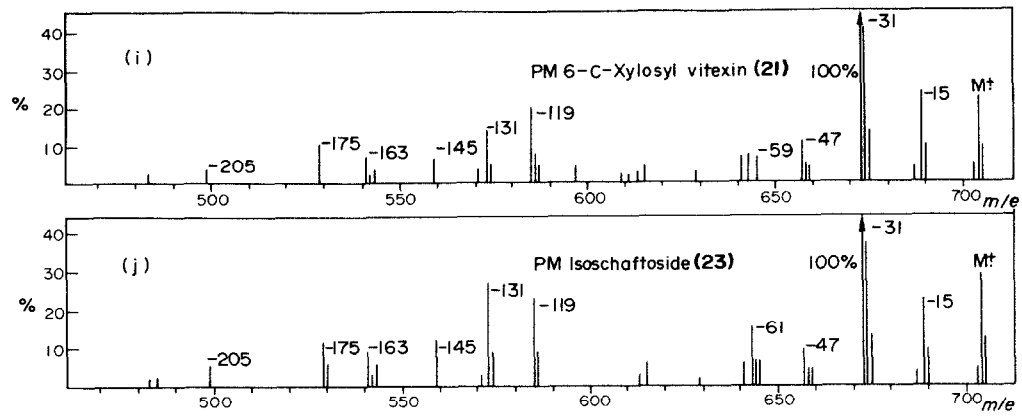

Fig. 1. (i–j).

Fig. 1. f–j: MS of PM di-*C*-glycosyl flavones.

the ion **i** [M-175 (**5**); M-145 (**8**); M-131 (**9**)], but the molecular ion is weaker (20–40%) and is followed by intense peaks absent from the 8-*C*-isomer spectra: $\mathbf{a_2}$ (M-15) (20–30%); $\mathbf{b_3}$ (M-31) (60–100%), which are much higher than the molecular peak and $\mathbf{c_3}$ (M-47). These peaks cannot be related to the carbohydrate substitution, whereas other peaks: **g** [M-103 (**5**); M-73 (**8**) and M-59 (**9**)] and **h** [M-163 (**5**); M-133 (**8**) and M-119 (**9**)] are characteristic of the sugar in the 6-position. As with 8-*C*-glycosylflavones, the parent peak (**i**) is followed by the ions **j**, **k** and **l** due to fragmentation of the sugar substituent. As expected these lower peaks are very weak. Again, the

Table 3. MS Data for PM *C*-glycosyl flavones: **1–12**

		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
M		(530)	(560)	(516)	(500)	(530)	(560)	(530)	(500)	(516)	(486)	(748)	(778)
Fragments		Relative intensity (%)											
	M^+	84	64	100	21	19	26	30	35	19	28	15	23
	$\mathbf{a_1}$	3	5	6	2	11	7	8	6	2	8	12	13
	$\mathbf{a_2}$	—	—	—	9	17	25	38	17	22	19	27	28
	$\mathbf{a_3}$	—	—	—	2,5	—	—	18	—	—	15	—	—
	$\mathbf{b_1}$	2	1,5	3	2	6	2	4	7	9	—	13	13
	$\mathbf{b_2}$	—	—	3	9	20	8	18	27	33	6	39	39
	$\mathbf{b_3}$	—	—	—	30	66	28	52	87	100	75	100	100
	$\mathbf{c_3}$	—	—	—	7	11	13	8	18	23	17	9	8
	gh	—	—	—	6	13	17	7	—	—	—	13	11
g	**gd**	—	—	—	—	—	—	—	17	—	—	—	—
	gp	—	—	—	—	—	—	—	—	9	9	—	—
	hh	—	—	—	7	13	19	18	—	—	—	32	25
h	**hd**	—	—	—	—	—	—	—	11	—	—	—	—
	hp	—	—	—	—	—	—	—	—	17	20	—	—
	ih	100	100	—	100	100	100	100	—	—	—	43	37
i	**id**	—	—	—	—	—	—	—	100	—	—	—	—
	ip	—	—	65	—	—	—	—	—	52	100	—	—
	jh	21	34	—	14	17	18	29	—	—	—	8	6
j	**jd**	—	—	—	—	—	—	—	32	—	—	—	—
	jp	—	—	44	—	—	—	—	—	40	58	—	—
	kh	10	13	—	10	13	20	14	—	—	—	6	5
k	**kd**	—	—	—	—	—	—	—	15	—	—	—	—
	kp	—	—	9	—	—	—	—	—	14	20	—	—
	lh	6	10	—	5	11	18	14	—	—	—	—	—
l	**ld**	—	—	—	—	—	—	—	18	—	—	—	—
	lp	—	—	8	—	—	—	—	—	16	25	—	—

Table 3. Continued MS Data for PM *C*-glycosyl flavones: **13–25**

		13	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
M		(660)	(688)	(660)	(660)	(718)	(718)	(734)	(734)	(704)	(704)	(704)	(704)	(704)
Fragments		Relative intensity (%)												
	M^+	18	33	23	23	23	27	20	15	22	17	29	20	22
	a_1	9	13	13	10	16	8	10	5	9	10	10	17	16
	a_2	21	24	28	29	36	21	21	28	23	26	22	32	16
	a_3	—	—	—	—	—	—	3	8	3	—	—	—	—
	b_1	11	15	15	15	15	17	13	13	13	11	12	14	18
	b_2	33	32	42	34	43	42	34	40	40	37	38	40	42
	b_3	100	100	100	100	100	100	100	100	100	100	100	100	100
	c_3	11	11	13	11	—	11	10	11	10	7	10	9	15
	gh	—	—	—	—	14	6	—	15	—	11	—	15	—
g	**gd**	—	21	—	—	—	15	—	—	—	—	—	—	—
	gp	6	—	10	10	—	—	6	—	6	—	9	—	24
	hh	—	—	—	10?	35	6	7	33	7	38	10	32	18
h	**hd**	—	21	—	—	7	18	—	—	—	—	—	—	—
	hp	20	15?	30	31	—	—	18	8	20	3	23	—	48
	ih	=**lp**	=**kd**	—	=**lp**	41	=**kd**	11	40	=**lp**	40	12	38	28
i	**id**	=**jp**	40	—	=**jp**	13	34	—	—	—	—	=**jp**	—	—
	ip	17	—	38	47	—	—	12	12	13	8	26	12	41
	jh	—	=**ld**	—	—	10	=**ld**	2	16	—	6	—	20	15
j	**jd**	—	17	—	—	—	6	—	—	—	—	—	—	—
	jp	11	=**id**	23	22	—	—	7	15	6	3	12	—	87
	kh	—	—	—	—	7	2	3	17	3	6	6	6	7
k	**kd**	—	10	—	=**lp**	=**ih**	15	—	—	=**lp**	—	=**ih**	—	—
	kp	11	7?	8	8	—	—	5	13	3	8	6	9	—
	lh	—	—	—	—	3	3	—	16	—	—	3	—	18
l	**ld**	—	10	—	—	=**jh**	4	—	—	—	—	—	—	—
	lp	3	=**kd**	5	3	—	—	11	=**ih**	10	=**ih**	=**ih**	=**ih**	=**ih**

nature of the aglycone does not influence the fragmentation pattern (compare (**4**) [17]; (**5**) and (**6**) MS, in Table 3).

The MS of PM 6-*C*-glucosylapigenin (**5**) and PM 6-*C*-galactosylapigenin (**7**) [18] are very similar. The same is true for the two *C*-pentosylflavones (**9**) [12] and (**10**) [19]. Only the ion **a_3** (M-17) observed respectively for the 6-*C*-galactosyl- and 6-*C*-arabinosylapigenins (**7**) and (**10**) and absent from the MS of **5** and **9**, and some differences in peak intensities, allows one to distinguish between these pairs of isomers.

However, an indirect proof may be obtained because of the difference in behaviour between the two *C*-pentosylflavones when subjected to permethylation. Indeed, when arabinose is present instead of xylose, the permethylation gives, as a by-product, a compound, the molecular peak of which ($M^{+\cdot}$ 340) appears at 28 m.u. above that of the PM flavone aglycone (6-formyl PM apigenin?).

MS of PM symmetrical 6,8-di-C-glycosylflavones

The PM 6,8-di-*C*-glucosylapigenin (**11**) MS (Fig. 1f) [20] is closely similar to that of PM 6-*C*-glucosylapigenin (**5**) (Fig. 1c) and shows that the sugar in the 6-position is more easily fragmented. This is also shown by the existence of the ion **b_3** (M-31), absent from the 8-*C*-glycosylflavone MS, which is here a parent peak. The MS of synthetic 6,8-di-*C*-xylosylapigenin (**13**) [12] and synthetic PM 6,8-di-*C*-rhamnosylapigenin (**14**) [15] show the same fragmentation patterns.

In all these spectra, the molecular ion is present with relatively high intensity (20–30%) and all 6-*C*-glycosylflavone peaks are found until **i** (Ar–CH $=\overset{+}{O}Me$) (Ar = PM 8-*C*-glycosylflavone radical) followed by corresponding peaks **j**, **k** and **l** with lower intensities. Some very weak peaks can be sometimes recognized of lower masses: RDA cleavage of previous ions; A-ring of ion **i** (*m/e* 415) and of ion **k** (*m/e* 385); B-ring (*m/e* 135). Ions *m/e* 101 and 88 are also present.

Again, comparison of the MS of PM 6,8-di-*C*-glucosyl-luteolin (**12**) (from permethylation of synthetic 6,8-di-*C*-glucosylchrysoeriol [21]) shows that the B-ring does not interfere with the fragmentation pattern. Compound **12** MS is quite identical (fragmentation and relative intensities) with that of a PM 6,8-di-*C*-glycosyl-luteolin isolated from *Spergularia rubra* and *Stellaria holostia* [22]. Therefore, this natural product is 6,8-di-*C*-β-D-glucopyranosyl-luteolin (lucenin-2) [23].

Permethylation of another natural compound, isolated from *Melilotus alba* [24] led to a PM 6,8-di-*C*-pentosylapigenin (**15**) MS. Comparison with PM 6,8-di-*C*-xylosylapigenin (**13**) MS showed the same fragmentation pattern, but important differences in the relative intensities of ions **hp**, **ip** and **jp**: in **13** MS, **hp** (M-119, 20%) > **ip** (M-131, 17%) > **jp** (M-145, 10%); in *Melilotus alba* compound (**15**): **ip** (38%) > **hp** (30%) > **jp** (23%).

The latter relative intensities were again observed with another natural 6,8-di-*C*-pentosylapigenin isolated from the moss *Hymenophytum leptopodum* [25]. Permethylation of this compound led to a byproduct, the MS of which corresponded to a PM 6-formyl 8-*C*-pentosylapigenin (M^+ 514). By analogy with the parallel behaviour of 6-*C*-arabinosylapigenin and 6-*C*-arabinosylvitexin (see later), this suggests the presence of a 6-*C*-arabinosyl residue in the 6,8-di-*C*-pentosylapigenin from *Hymenophytum leptopodum*.

MS of PM dissymmetrical 6,8-di-C-glycosyl-flavones

Natural compounds of this type are lucenin-1 and 3 [23] [PM derivatives (**19**) and (**20**)], identical respectively with synthetic 6-*C*-β-D-xylosyl-8-*C*-β-D-glucosyl and 6-*C*-β-D-glucosyl-8-*C*-β-D-xylosyl-luteolins [26], violanthin [PM derivative (**17**)]: 6-*C*-β-D-glucosyl-8-*C*-α-L-rhamnosyl apigenin [27] and schaftoside [PM derivative (**22**)] [28], the proposed structure of which is 6-*C*-β-D-glucosyl-8-*C*-α-L-arabinosylapigenin [29].

Here again, fragmentation of the sugar in the 6-position predominates.

Violanthin–isoviolanthin. Typical fragmentation of these compounds is observed in the spectra of PM violanthin (**17**), (Fig. 1g) and of its isomer (PM synthetic 6-*C*-α-L-rhamnosyl-8-*C*-β-D-glucosylapigenin) (**18**) (Fig. 1h) [30]. In the MS of **17** the more intense peaks **h** and **i** come from hexose fragmentation (M-163 and M-175 as in a PM 6-*C*-hexosylapigenin MS); on the contrary **18** is fragmented as a 6-*C*-rhamnosylapigenin (highest peaks are M-133 and M-145). The **g** peak is also characteristic; it occurs at M-73 in **18** MS, and at M-103 in **17** MS. However, in the MS of PM violanthin, the M-145 peak may show a 8-*C*-rhamnosyl moiety fragment very much smaller than that of the 6-*C*-glucosyl. These spectral studies confirm the structure proposed for violanthin [27].

Lucenin-1 and 3, vicenin-1. MS of PM derivatives of natural lucenin-1 and 3 (**19**) and (**20**) [23] are identical with MS of their synthetic equivalents [26]. These compounds show the same behaviour as violanthin and isoviolanthin, although the peaks are of weaker intensity: a fragmentation pattern of 6-*C*-pentosyl-luteolin type prevails in **19**, one of 6-*C*-hexosyl-luteolin type in **20**. Another example is the MS of PM 6-*C*-β-D-xylosyl-8-*C*-β-D-glucosylapigenin (**21**) (synthetic vicenin-1) [31] (Fig. 1i). As in the case of PM lucenin-1, there is the characteristic 6-*C*-xylosyl distribution: **hp** > **ip** > **jp**, observed with PM 6,8-di-*C*-xylosylapigenin (**13**) MS. These results confirm the proposed structures for lucenin-1 and 3 [26].

Schaftoside–isoschaftoside. The first information about the structure of schaftoside was obtained from the MS of the free compound. Although this MS lacked a molecular peak, the sequential losses of water in fragmentation showed that schaftoside was a 6,8-*C*-hexosyl-*C*-pentosylapigenin. The identification of the glycosyl residues as glucose and arabinose resulted from degradative studies. After acid treatment of schaftoside, several compounds with similar chromatographic behaviours are obtained. One of them, isoschaftoside, is identical (chromatography and IR spectrum) with the synthetic 6-*C*-α-L-arabinosyl 8-*C*-β-D-glucosylapigenin [32] and with a natural compound of *Flourentia cernua* [33]. MS of PM derivatives of these three compounds are quite identical (see **23** MS) (Fig. 1j). A 6-*C*-pentosyl fragmentation prevails with a distribution **ip** > **hp** > **jp** as in *Melilotus alba* 6,8-di-*C*-pentosylapigenin; and a 6-formyl 8-*C*-hexosylapigenin (M^+ 558) is obtained as a byproduct of permethylation. This pattern may

be characteristic of 6-*C*-arabinopyranosyl substitution and permits the differentiation of 6-*C*-pentosylflavone isomers.

It is interesting that the peak M-17, present in the MS of PM mono 6-*C*-arabinosylflavone (**10**) does not exist in the MS of 6,8-di-*C*-glycosylflavones **15** and **23**, although these compounds contain a *C*-arabinosyl moiety. By contrast, in the MS of PM schaftoside (**22**), the highest peaks are M-163, M-175 and M-103, all corresponding to a 6-*C*-hexosylapigenin. From all these results, it can be concluded that schaftoside is 6-*C*-β-D-glucosyl 8-*C*-α-L-arabinosylapigenin. The name isoschaftoside previously suggested for a product co-occurring with schaftoside in *Catananche cerulea* [34] is unsuitable. Indeed, the MS of this product PM derivative (**24**) shows that it is not a Wessely-Moser isomer of schaftoside, since peaks M-175 and M-163 corresponding to a 6-*C*-hexosylflavone are predominant. However, this product and schaftoside are interconvertible by acid treatment, possibly due to pyranose-furanose isomerization. We suggest it should be called neoschaftoside; the study of its structure is in progress.

6,8-*di*-C-*glycosylacacetin of* Trigonella corniculata. Finally, our technique shows that the structure of 6-8-di-*C*-glucosylacacetin given by Seshadri *et al.* [35] to a natural product of *Trigonella corniculata* is incorrect. The MS of the PM derivative (**25**) shows that it is in fact a 6-*C*-pentosyl 8-*C*-hexosylacacetin because the peaks corresponding to a 6-*C*-pentosylflavone are the highest and the relative intensities of **h**, **i** and **j** peaks can be related neither to a 6-*C*-xylosyl nor to a 6-*C*-arabinopyranosyl substitution. The free compound is chromatographically different from synthetic 6-*C*-β-D-xylopyranosyl 8-*C*-β-D-glucopyranosylacacetin [36].

EXPERIMENTAL

Permethylation was carried out on 0·5–1 mg of *C*-glycosylflavone using Me I and NaH in DMF [11] under anhydrous conditions and N_2. After 1 hr at room temp., work-up is accomplished by partition between $CHCl_3$ and H_2O. Pure products can be obtained by TLC (Si gel) using $CHCl_3$–Me_2CO (4:1) or $CHCl_3$–AcOEt–Me_2CO (5:4:1). The main product, with a blue fluorescence, is separated from by-products: DMF condensation by-products giving MS with M + 30, M + 60, M + 90 peaks are more abundant with 8-*C*-monoglycosyl compounds; degradation products such as 6-*C*-formylflavones are obtained with 6-*C*-arabinopyranosylflavones. The required derivative is always the major component and generally has the lower R_f. TLC (Si gel) of PM 6,8-di-*C*-glycosylflavones in $CHCl_3$–AcOEt–Me_2CO (5:4:1) (**11**) 0·46; (**12**) 0·37; (**19**) 0·40; (**20**) 0·27; (**21**) 0·49; (**22**) 0·32; (**23**) 0·26; (**24**) 0·37. Luteolin derivatives: pale-blue fluorescence; apigenin: violet–blue fluorescence. MS were recorded on an AEI MS 902 spectrograph, to 70 eV. Temperatures (sample and source in the same order) varied between 120 and 190°. Compound **12** MS also was registered on a Varian CH 5 spectrograph and the 2 graphs compared: fragmentation pattern and relative intensities were identical.

Acknowledgements—MS spectra were registered by courtesy of Prof. Badinand, Laboratoire de Chimie Analytique, UER des Sciences Pharmaceutiques, Université Lyon I, France. We are grateful to Drs Plouvier, Zoll, Proliac, Markham, Gorz and Sood and to Profs. Mabry and Wagner for samples of natural compounds.

REFERENCES

1. Chopin, J. (1966) *Actualités de Phytochimie Fondamentale* (Mentzer, C., ed.), 2e série, pp. 44–72. Masson, Paris.
2. Chopin, J. and Bouillant, M. L. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds.), Chapt. 12. Chapman Hall.
3. Chopin, J. (1971) *Pharmacognosy and Phytochemistry* (Wagner, H. and Horhammer, L. eds.), pp. 111–128. Springer, Berlin.
4. Prox, A. (1968) *Tetrahedron* **24,** 3697.
5. Biol, M. C. (1973) Thèse de Doctorat de 3è cycle no. 225, Université Claude Bernard, Lyon.
6. Aritomi, M., Komori, T. and Kawasaki, T. (1970) *Liebigs Ann. Chem.* **734,** 91.
7. Schmid, R. D. (1972) *Tetrahedron* **28,** 3259.
8. Schmid, R. D., Varenne, P. and Paris, R. (1972) *Tetrahedron* **28,** 5037.
9. Schmid, R. D. and Harborne, J. B. (1973) *Phytochemistry* **12,** 2269.
10. Schmid, R. D., Mues, R., McReynolds, J. H., Van der Velde, C., Nakatani, N., Rodriguez, E. and Mabry, T. J. (1973) *Phytochemistry* **12,** 2765.
11. Brimacombe, J. S., Jones, B. D., Stacey, M. and Willard, J. J. (1966) *Carbohyd. Res.* **2,** 167.
12. Chopin, J. and Bouillant, M. L. (1970) *C. R. Acad. Sci. Ser. C* **270,** 331.
13. Audier, A. (1966) *Bull. Soc. Chim.* **9,** 2892.
14. Kochetkov, N. K. and Chizhov, O. S. (1966) *Adv. Carbohyd. Chem.* **21,** 39.
15. Chopin, J. and Biol, M. C. (1972) *C. R. Acad. Sci. Ser. C* **275,** 1435.
16. Mabry, T. J., Yoshioka, H., Sutherland, S., Woodland, S., Rahman, W., Ilyas, M., Usmani, J. N., Hameed, N., Chopin, J. and Bouillant, M. L. (1971) *Phytochemistry* **10,** 677.
17. Chopin, J., Bouillant, M. L. and Durix, A. (1970) *C. R. Acad. Sci. Ser. C* **270,** 69.
18. Chopin, J., Bouillant, M. L. and Biol, M. C. (1971) *C. R. Acad. Sci. Ser. C* **273,** 1262.
19. Chopin, J., Biol, M. C. and Bouillant, M. L. (1972) *C. R. Acad. Sci. Ser. C* **274,** 1840.
20. Chopin, J., Roux, B., Bouillant, M. L., Durix, A., d'Arcy, A., Mabry, T. J. and Yoshioka, Y. N. (1969) *C. R. Acad. Sci. Ser. C* **268,** 980.
21. Chopin, J. and Planche, G. unpublished.
22. Compound isolated by Zoll, A. unpublished.

23. Seikel, M. K., Chow, J. H. S. and Feldman, L. (1966) *Phytochemistry* **5,** 439.
24. Compound isolated by Gorz, H. unpublished.
25. Compound isolated by Markham, K. R. unpublished.
26. Bouillant, M. L. and Chopin, J. (1972) *C. R. Acad. Sci. Ser. C* **274,** 193.
27. Wagner, H., Rosprim, L. and Düll, P. (1972) *Z. Naturforsch.* **27b,** 954.
28. Plouvier, V. (1967) *C. R. Acad. Sci. Ser. D* **265,** 516.
29. Chopin, J., Bouillant, M. L., Wagner, H. and Galle, K. (1974) *Phytochemistry* **13,** 2583.
30. Biol, M. C. and Chopin, J. (1972) *C. R. Acad. Sci. Ser. C* **275,** 1523.
31. Bouillant, M. L. and Chopin, J. (1971) *C. R. Acad. Sci. Ser. C* **273,** 1759.
32. Biol, M. C., Bouillant, M. L., Planche, G. and Chopin, J. (1974) *C. R. Acad. Sci. Ser. C* **279,** 409.
33. Compound isolated by Dillon, M. and Mabry, T. J. unpublished.
34. Proliac, A., Raynaud, J., Combier, H., Bouillant, M. L. and Chopin, J. (1973) *C. R. Acad. Sci. Ser. D* **277,** 2813.
35. Seshadri, T. R., Sood, A. R. and Varshney, I. P. (1972) *Indian J. Chem.* **10,** 26.
36. Chopin, J. and Bouillant, M. L. (1970) *C. R. Acad. Sci. Ser. C* **270,** 222.