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EFFECT OF CONFORMATION AND CONFIGURATION OF ARABINOSE RESIDUES ON THE CIRCULAR DICHROISM OF *C*-GLYCOSYLFLAVONES

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Key Word Index—*C*-Glycosylflavones; sugar conformations; *C*-arabinosylflavones; circular dichroism.

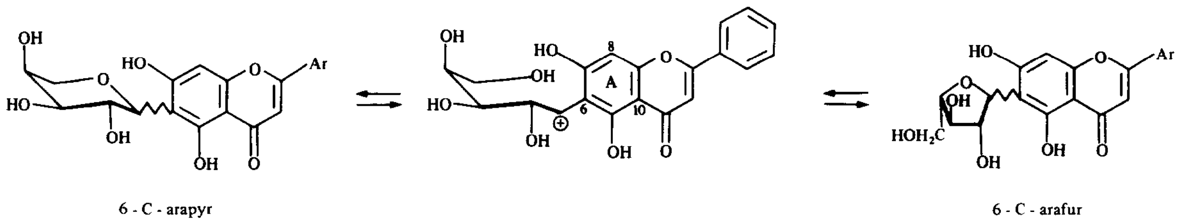
Abstract—Examination of a variety of arabinose containing *C*-glycosylflavones has shown that the sign and intensity of the CD band at 250–275 nm (charge-transfer band) reflect not only the point of attachment of the sugar to the flavone but also depend upon the absolute and anomeric configuration, ring-size and ring-conformation in addition to the preferred rotameric conformation of the sugar about the C-aryl, C-1″ bond. A change in stereochemistry of arabinose from the α to β anomer resulted in sign inversion of the 250–275 nm CD band for 6-*C*-L-arabinosylflavones. Furthermore, a 6-*C*-arabinosylflavone containing α-L-arabinose exhibited an oppositely signed charge-transfer CD band in comparison to one which contained α-D-arabinose. 6,8-Di-*C*-glycosylflavones containing arabinose and glucose exhibited CD bands resulting from contributions due to both sugars, if the arabinose was not present as the β-pyranose form ($^1C_4$ conformation).

INTRODUCTION

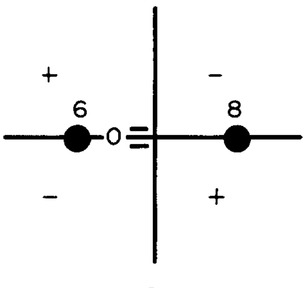
C-Glycosylflavones are widely distributed throughout the plant kingdom and have been isolated from sources as diverse as monocotyledons, dicotyledons, ferns, mosses and green algae [1]. While most of the *C*-glycosylflavones isolated in earlier reports contained only glucose, recent studies have described a variety of sugars attached to the flavone including arabinose. An interesting aspect of the chemistry of *C*-arabinosylflavones concerns their tendency to undergo an acid-catalysed isomerization of the carbohydrate leading to a mixture of anomeric *C*-arabinopyranosyl- and *C*-arabinofuranosylflavones which are readily separable on TLC after permethylation [2] (Scheme 1).

Although the structural determination of these compounds has primarily relied upon ^{1}H NMR and MS data, CD has proved the configuration of L-arabinose in schaftoside and its isomers based upon identical curves shown by natural isoschaftoside and synthetic 6-*C*-α-L-arabinopyranosylvitexin [3] (*vide infra*). An earlier CD investigation of a wide range of *C*-β-glycosylflavones showed that the sign of the 250–275 nm CD band is diagnostic of the point of attachment of the glycosyl residue to the phenolic moiety [4]. A positive CD band at 250–275 nm indicated a 6-*C*-linkage, as in isovitexin (6-*C*-β-D-glucopyranosylapigenin), whereas a negative CD band in this region signified an 8-*C*-linkage, as in vitexin (8-*C*-β-D-glucopyranosylapigenin). 6,8-Di-*C*-β-glycosylflavones generally showed two CD bands at 250–275 nm, a positive one at 263–275 nm and a negative one at 250–262 nm. The chiroptical properties of *C*-β-glycosylflavones were explained by postulating a quadrant rule based upon the substituted benzoyl chromophore present in these molecules. Viewing the flavone from the CO end of the C-10, CO bond resulted in the sector diagram shown, (I) [4]. The sign of the CD band related to the charge-transfer transition (250–275 nm) should be determined by whichever sector or sectors are predominantly occupied by the asymmetric substituent or perturbing group which is the carbohydrate group in a *C*-glycosylflavone.

This study reports CD data on permethylated derivatives of mono 6-*C*-L- and 8-*C*-L-arabinosylflavones, free and derivatized 6,8-di-*C*-glycosylflavones containing L-arabinose and D-glucose, several 6,8-di-*C*-glycosylflavones containing L-arabinose and a sugar other than glucose and a 6-*C*-D-arabinosylflavone. In particular, the effect upon the CD of different anomeric configurations and ring sizes of the arabinose residue may assist in



Scheme 1.



I

the assignment of preferred conformations about the C-aryl, C-1″ bond of the sugars in isomeric 6,8-di-*C*-glycosylflavones.

RESULTS

6-C-L-*Arabinosylflavones*

CD spectra of perdeuteromethyl (PDM) ethers of isomeric 6-*C*-L-arabinosylacacetins, **1**–**4**, (Table 1) showed significant differences from each other (Fig. 1). The CD band at 250–275 nm of the α-pyranosyl isomer, **1**, corresponded in shape and appearance to that reported for isovitexin and its magnitude was similar to that shown by the permethyl and peracetyl derivatives of isovitexin [4]. The CD band at 262 nm of the α-furanosyl isomer, **2**, also resembled that reported for isovitexin but was only one-third as intense as that exhibited by **1**.

The PDM ether of 6-*C*-β-L-arabinofuranosylacacetin, **3**, gave a CD similar to that reported for free or derivatized vitexin but less than one-half as intense [4]. Clearly, changing the stereochemistry of the sugar from α to β resulted in sign inversion of the charge-transfer band for 6-*C*-L-arabinofuranosylacacetins. Different sector contributions (see **I**) of the β-sugar in comparison to those of the α-sugar may reflect whether C-2″ is positioned above or below the plane of the flavone A-ring (*vide infra*). Examination of the CD of the β-pyranosyl isomer, **4**, yielded results less striking yet consistent with those shown by **3**. Although the 250–275 nm region of **4** was relatively featureless, a weak negative CD band was present at 265 nm in agreement with β-stereochemistry.

6-C-D-*Arabinosylflavones*

In order to ascertain the effect of different absolute configurations of arabinose upon the CD of a *C*-glycosylflavone, 6-*C*-α-D-arabinopyranosylapigenin (**5**) was prepared and its CD measured (Table 1). The presence of a CD band at 264 nm, in **5**, of opposite sign to that shown by the α-L-compound [4] demonstrated that knowledge of the anomeric configuration of the arabinose residue from ^{1}H NMR data will permit CD measurements to differentiate D-arabinose from L-arabinose in 6-*C*-arabinosylflavones.

8-C-L-*Arabinosylflavones*

The PDM derivative of 8-*C*-α-L-arabinopyranosylgenkwanin (PDM-**6**) showed a broad negative CD band at 250–275 nm (Fig. 2) approximately one-half as intense as that recorded by its underivatized parent molludistine, **6**, and by vitexin [4]. The high wavelength CD of the α-furanosyl isomer, **7**, resembles that shown by the α-pyranosyl compounds, **6** and PDM-**6**, but 250–275 nm CD band, although of the same sign in the isomeric α-anomers, is of much lower magnitude in **7** as noted in the previous section for related compounds of the 6-*C*-L-arabinosylflavone series. Acid isomerization of 8-*C*-arabinosylgenkwanin did not produce the β-pyranose and β-furanose isomers in quantities large enough to permit their isolation [2].

6,8-Di-C-*glycosylflavones containing* L-*arabinose and* D-*glucose*

Schaftoside, **8**, isolated from *Silene schafta* in 1967 [5], was shown to be 6-*C*-β-D-glucopyranosyl-8-*C*-α-L-arabinopyranosylapigenin on the basis of oxidative degradation and spectroscopic investigations [3] whereas its acid isomerization product, isoschaftoside (**9**), is identical with synthetic 6-*C*-α-L-arabinopyranosyl-8-*C*-β-D-glucopyranosylapigenin [3]. The arabinosyl residue of both **8** and **9** gave rise to larger CD bands at 250–275 nm than the glucosyl residue [4]. While the negative lower wavelength band dominated the CD of the 8-*C*-arabinosyl compound, **8**, the positive higher wavelength band was most prominent in the CD of the 6-*C*-arabinosyl isomer. Derivatized samples of **8** and **9** yielded less complex CD spectra, in the 250–275 region, than those of the parent compounds. The CD of PDM-**8** gave only a positive band at 261 nm attributed to the 6-*C*-glucosyl substitutent whereas the CD of PDM-**9** exhibited no discernible bands at 250–275 nm.

Acid isomerization of schaftoside produced two additional isomeric 6,8-di-*C*-glycosylapigenins containing arabinose and glucose, neoschaftoside (**10**) [6] and neoisoschaftoside (**11**) [7], which have been found to be identical with schaftoside and isoschaftoside, respectively, except that the arabinose of **10** and **11** is present as the β-L-pyranosyl configuration [8] [Besson, E. and Chopin, J., unpublished results]. The CD of PDM-**10**, which was clearly dominated by the presence of the 6-*C*-glucosyl group, resembled that reported for the permethyl and peracetyl derivatives of isovitexin [4] whereas the underivatized flavone glycoside, **10**, exhibited a weak positive CD band at 255 nm (Fig. 3).

The PM (permethyl) derivative of neoisoschaftoside (PM-**11**) afforded a featureless CD from 310 to 245 nm (Fig. 3). Synthetic PDM 6-*C*-β-L-arabinofuranosyl-8-*C*-β-D-glucopyranosylacacetin (PDM-**12**) gave a CD similar to that of PM-**11** at high and low wavelength but quite divergent at 250–275 nm reflecting the different contributions of a β-furanosyl and a β-pyranosyl sugar to the charge-transfer transition. The CD of underivatized neoisoschaftoside, **11**, which is dominated by a strong negative band at 271 nm attributed to the 8-*C*-glucosyl group, provides further evidence of the cancellation of CD contributions due to β-arabinopyranosyl residues (c.f. **4**, **10**, PDM-**10**, PM-**11**).

6,8-Di-C-*glycosylflavones containing* L-*arabinose and a sugar other than glucose*

The CD of corymboside (6-*C*-α-L-arabinopyranosyl-8-*C*-β-D-galactopyranosylapigenin), **13**, resembled that shown by isoschaftoside (**9**) whereas the CD of compound

Table 1. Circular dichroism* of C-arabinosylflavones, [θ] (λ)

Compound	$[\theta]_{>275}$	$[\theta]_{<250}$	$[\theta]_{250-275}$
6-C-L-Arabinosylacacetins			
PDM α-pyranosyl (**1**)	8080 (340)		
	−16,100 (310)	—	23,100 (262)
PDM α-furanosyl (**2**)	1870 (345)		
	−5140 (312)	−5420 (243)	7760 (262)
PDM β-furanosyl (**3**)	1790 (340)	860 (240)	−6970 (266)
PDM β-pyranosyl (**4**)	880 (350)		
	940 (335)	—	−1760 (265)
	−5430 (318)		
	420 (290)		
6-C-D-Arabinosylapigenin			
α-Pyranosyl (**5**)	5250 (395)	—	−19,700 (264)
	3060 (317)		
	−8970 (298)		
	21,700 (283)		
8-C-L-Arabinosylgenkwanins			
α-Pyranosyl (**6**)	4660 (350)		
	−8320 (282)	−7650 (238)	−12,000 (267)
PDM α-pyranosyl (PDM-**6**)	3510 (335)		−5800 (265)
	−3400 (285)	—	−5690 (253)
PDM α-furanosyl (**7**)	2590 (325)		
	−2220 (277)	—	−1930 (260)
6,8-Di-C-glycosylflavones containing L-arabinose and D-glucose			
Schaftoside (**8**)	12,500 (322)		2540 (275)
	17,100 (303)	—	−16,900 (250)
PDM-schaftoside (PDM-**8**)	10,300 (340)		
	−6670 (310)	−17,400 (235)	4040 (261)
Isoschaftoside (**9**)	3570 (345)		17,300 (272)
	−700 (322)	—	−5650sh (250)
	9030 (301)		
PDM Isoschaftoside (PDM-**9**)	20,200 (340)		
	−10,600 (307)	—	†
Neoschaftoside (**10**)	−3600 (318)	−6900 (216)	1160 (255)
PDM-neoschaftoside (PDM-**10**)	19,000 (345)		
	−11,700 (310)	−13,000 (230)	26,700 (262)
Neoisoschaftoside (**11**)	4340 (320)	−10,400 (233)	
	3470 (305)	15,600 (222)	−23,700 (271)
PM-neoisoschaftoside (PM-**11**)	4830 (337)	−7360 (234)	†
PDM-6-C-β-L-arabinofuranosyl-			−5120 (265)
8-C-β-D-glucopyranosylacacetin (PDM-**12**)	4270 (340)	−6220 (235)	−5610 (250)
6,8-Di-C-glycosylflavones containing L-arabinose and a sugar other than D-glucose			
Corymboside (**13**)	3450 (379)		10,300 (274)
	−1410 (324)	−9100 (233)	−5950 (250)
	4930 (301)		
Compound S (**14**)	2360 358)		5140 (271)
	−820 (327)	—	−4930sh (250)
6-C-β-D-Xylopyranosyl-8-C-α-L-	5140 (303)		
arabinopyranosylapigenin (**15**)	11,100 (302)	—	−9870 (250)

*CD values are expressed in terms of molecular ellipticity [θ] in units of $\mathrm{deg\cdot cm^2\cdot dmol^{-1}}$ with wavelength (λ) in nm. Measurements were obtained in methanol solutions at 27°.

†No maxima observed between 250 and 275 nm.

S (6-C-β-D-galactopyranosyl-8-C-α-L-arabinopyranosyl-apigenin), **14**, was similar to that of schaftoside, **8**, with the 6-C-galactosyl group providing a greater contribution to the CD than a 6-C-glucosyl group as noted earlier for related compounds [4]. 6-C-Xylosyl-8-C-arabinosyl-apigenin, **15**, gave a negative CD band at 250 nm presumably due to the 8-C-arabinose. Earlier studies have shown that the xylosyl group resulted in relatively weak CD contributions in C-glycosylflavones due to loss of the hydroxymethyl group at C-5″ [4].

DISCUSSION

Conformational preferences of C-*glycosylflavones*

Interpretation of the CD spectra of C-glycosylflavones

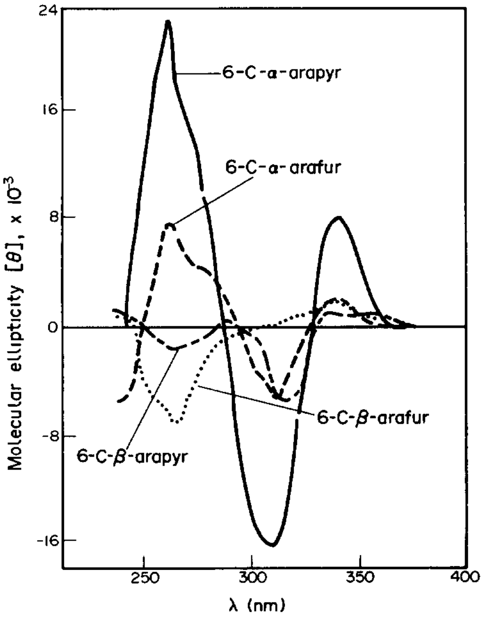


Fig. 1. Effect of different conformations and configurations upon the CD of derivatized 6-*C*-L-arabinosylflavones. CD spectra of PDM-6-*C*-α-L-arabinopyranosylacacetin (**1**) (——), PDM-6-*C*-α-L-arabinofuranosylacacetin (**2**) (– – – –), PDM-6-*C*-β-L-arabinofuranosylacacetin (**3**) (· · · ·), PDM-6-*C*-β-L-arabinopyranosylacacetin (**4**) (—·—·)

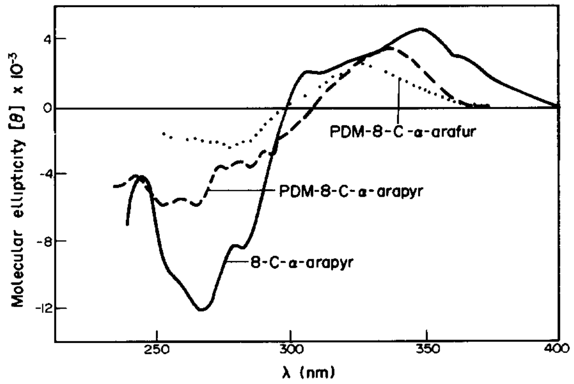


Fig 2. Effect of different conformations and derivatization upon the CD of 8-*C*-L-arabinosylflavones. CD spectra of 8-*C*-α-L-arabinopyranosylgenkwanin (**6**) (——), PDM-8-*C*-α-L-arabinopyranosylgenkwanin (PDM-**6**) (– – – –), PDM-8-*C*-α-L-arabinofuranosylgenkwanin (**7**) (·).

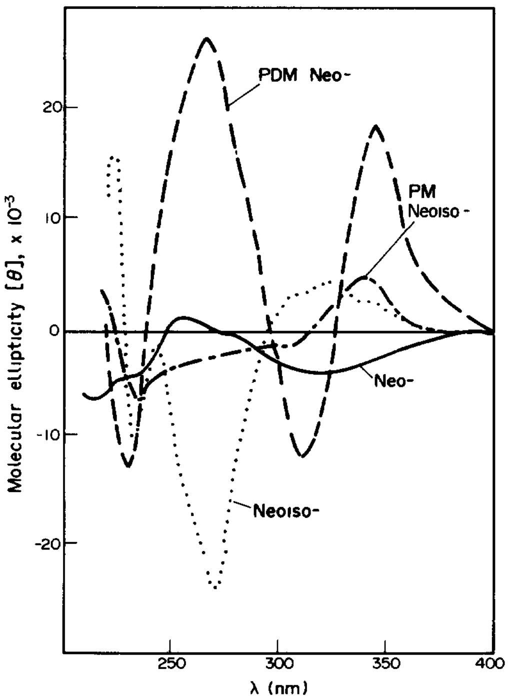


Fig. 3. Effect of positional isomerism and derivatization upon the CD of 6,8-di-*C*-glycosylflavones containing arabinose and glucose CD spectra of neoschaftoside (**10**) (——), PDM-**10** (– – – –), neoisoschaftoside (**11**) ( ), PM-**11** (—·—).

requires knowledge of both the preferred rotational conformation of the carbohydrate about the C-6 or C-8, C-1″ bond and the ring conformation of the sugar heterocycle. Evidence for the former suggests that *C*-glycosylflavones exist primarily in two principal rotational conformers with the plane of the sugar ring approximately perpendicular to the benzopyrone moiety, **II** and **III** (as illustrated for 8-*C*-glucosylflavones). Generally, the conformation having C-2″ above the benzopyrone group, **II**, has been favored. Thus, Eade *et al.* proposed **II** as the preferred conformation for bayin hexaacetate on the basis of ^{1}H NMR spectra [9] and Jurnak and Templeton established that a 6-bromohexaacetylated derivative of vitexin possessed a similar conformation in the solid state with the plane of the pyranosyl ring approximately perpendicular (86.5°) to the benzopyrone structure [10]. Conformer **II**, with the pyranose synclinal to the A-ring ($\theta \sim 45°$), also has been proposed by Gentili and Horowitz to account for shielding of the 2″-*O*-acetyl group by ring A and the 6″-*O*-acetyl group by ring B in acetylated 8-*C*-glucosylflavones [11]. More recently, ^{13}C NMR spectra of selected 6-*C*-glucosylflavones have suggested the presence of a slow conformational equilibrium where interconversion is rapid at 80° and slow at 30° [12].

Factors important in determining the $^4C_1 \leftarrow {}^1C_4$ equilibrium* of the β-pyranosyl ring conformation are the conformational free energy of the R group (flavone) at C-1″ and the gauche interaction between the C-2″ substituent and the flavone group. Due to the absence of the bulky hydroxymethyl group in aldopentopyranoses, such as arabinose, these sugars often exist in solution as equilibrium mixtures of $^4C_1$ and $^1C_4$ conformers [13]. The $^1C_4$ conformation appears energetically favored for *C*-β-L-arabinopyranosylflavones due to the equatorial disposition of the flavone and 4″-hydroxyl groups (cf. **4**).

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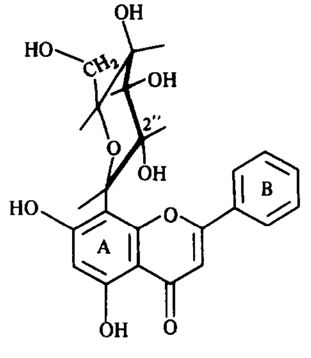
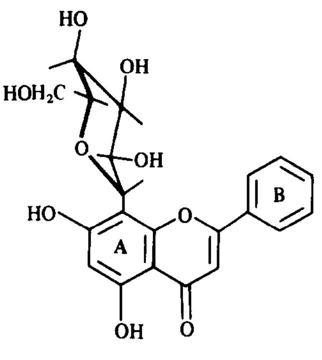
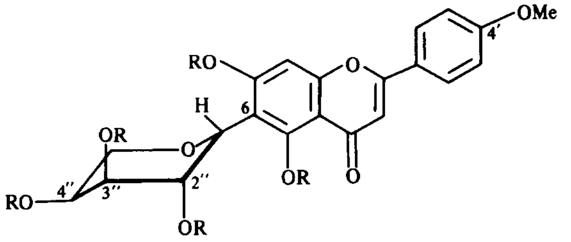
*When C-1″ is below the reference plane of the pyranoid ring (the plane containing O, C-2″, C-3″ and C-4″), the chair conformer is designated as $^4C_1$; when it is above the reference plane, as $^1C_4$ [13].



II



III



4 (R = CD_3)

Unfavorable interactions between either the 5- or 7-substituent on the A-ring and the hydrogens on C-3'' and C-5'' would further destabilize the $^4C_1$ conformation.

Mono-C-arabinosylflavones

CD spectra of α-pyranosyl, α- and β-furanosyl containing *C*-arabinosylflavones **1**–**3**, **6** and **7** and their derivatives may be interpreted with the aid of the benzoyl sector diagram, **I** [4]. *C*-Glycosylflavones **1**, **2**, **6** and **7** may be assumed to exist in a preferred conformation having the C-2'' atoms above the plane of the A-ring (cf. **II** in which the pyranose ring or C-2'' of the furanose is synclinal to the A-ring with θ ~ 45°), while **3** is predicted to have the C-2'' atom synclinal below the A-ring, as in **III**, at an angle of ~ −45°. Replacement of α-L-arabinopyranose with α-D-arabinopyranose at C-6 of a flavone, as in **5**, appeared to alter the preferred conformation of the sugar about the C-6, C-1'' bond to one in which the pyranose ring (or C-2'' atom) was at an angle of −45° (synclinal) to the A-ring. The sign of the charge-transfer band will reflect whichever sector is occupied by C-2'' and its substituent. Derivatization of *C*-glycosylflavones will alter both the conformation of the carbohydrate about the C-aryl, C-1'' bond and the contribution of perturbing atoms to the magnitude of the CD. The low magnitude of the 250–275 nm CD band shown by β-pyranosylflavone **4** may be due to the presence of nearly equal amounts of conformers **II** and **III** (or to conformations having the sugar perpendicular to the A-ring) resulting in cancelled contributions to the CD.

Schaftoside and its isomers

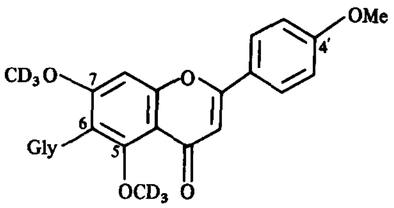
The conformational preference about each C-aryl, C-1'' bond in the highly congested permethylated di-*C*-glycosylflavones is complicated due to the presence of a second sugar in the molecule in addition to 5,7-dimethoxy substituents which may be forced out of the A-ring plane resulting in additional sector contributions. ^1H NMR spectra of **PDM-8** and **PDM-9** exhibited two doublets for the anomeric proton of each arabinose and glucose residue suggesting two conformers which interconvert very slowly or not at all [8]. The cancelled CD bands at 250–275 nm of **PDM-9** may reflect the presence of each sugar in nearly equal amounts of conformers **II** and **III** or in orientations perpendicular to the A-ring. On the other hand, a slight preponderance of the 6-*C*-glucosyl conformer having C-2'' synclinal above the plane of the A-ring (θ ~ 45°) could produce the weak positive band at 261 nm in the CD of **PDM-8**.

As a result of evidence from ^1H NMR spectra which showed the existence of **PDM-10** in two rotameric conformations about the C-aryl, C-1'' bonds in a ratio of 2:1 [8], the strong CD band at 262 nm could result from a preponderance of conformation **II** with the C-2'' substituent of the glucose group projecting (θ ~ 45°) into the upper left hand sector of diagram **I**. The lower magnitude of the same CD band in the underivatized **10** may be due to a more equal ratio of conformations **II** and **III**, a lessened contribution to the CD of the substituent (–OH vs. –OCD_3) or a different angle of twist of the glucosyl group about the C-6, C-1'' bond. The intense negative 271 nm band, which dominated the charge-transfer CD spectrum of **11**, suggested the presence of the 8-*C*-glucosyl residue in a preferred conformation having the C-2'' group synclinal above the plane of the A-ring projected into the upper right sector of **I**.

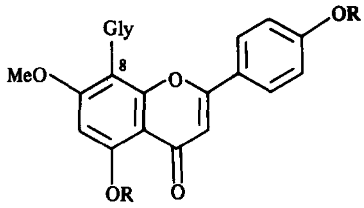
EXPERIMENTAL

The CD data recorded in Table 1 were measured in MeOH with the aid of a Cary 60 spectropolarimeter equipped with a 6003 circular dichroism accessory calibrated with (+)-10-camphorsulfonic acid as previously reported [14]. Operating procedures were performed as described earlier [4]

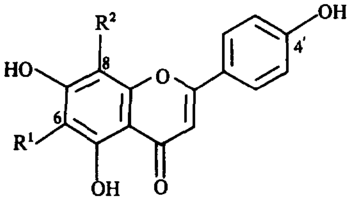
Neoschaftoside (**10**) was isolated from the liverwort *Radula complanata* by Dr. R Mues (Saarbrücken) and neoisoschaftoside (**11**) was isolated from *Gemmingia chinensis* by Dr K. Yagishita (Yamaguchi). **PDM-9**, **PM-11** and **PDM-12** were prepared [Besson, E. and Chopin, J., unpublished results] according to the procedure of Brimacombe, *et al.* [15]. Synthesis of **5** [Dubois,



1 Gly = PDM - α - L - arapyr,
2 Gly = PDM - α - L - arafur,
3 Gly = PDM - β - L - arafur,
4 Gly = PDM - β - L - arapyr,
5 Gly = α - D - arapyr, (5,7,4' - triOH)



6 Gly = α - L - arapyr, R = H
7 Gly = PDM - α - L - arafur, R = CD_3



8 R^1 = Glc, R^2 = α - L - arapyr
9 R^1 = α - L - arapyr, R^2 = Glc
10 R^1 = Glc, R^2 = β - L - arapyr
11 R^1 = β - L - arapyr, R^2 = Glc

12 R^1 = β - L - arafur, R^2 = Glc (4' - OMe)
13 R^1 = α - L - arapyr, R^2 = Gal
14 R^1 = Gal, R^2 = α - L - arapyr
15 R^1 = Xyl, R^2 = α - L - arapyr

M. A. and Chopin, J., unpublished results] was achieved by the procedure of Besson and Chopin [2].

The remaining compounds studied in this investigation were described in the following references. **1–4** and **7** [2]; **8** and **9** [3]; PDM-**8** and PDM-**10** [8], **6** and PDM-**6** [16]; **13** [17]; **14** [18] and **15** [19]

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