THE ROTATIONAL ISOMERS OF PERACETYLATED *C*-GLYCOSYL-FLAVONES •

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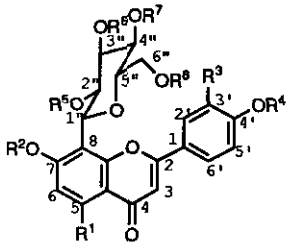
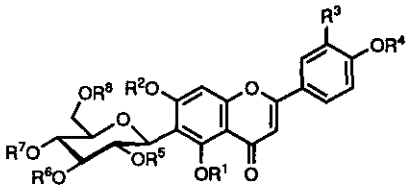
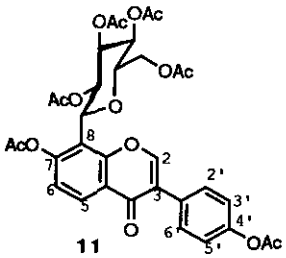
Abstract --- In ^{1}H- and ^{13}C-nmr of peracetylated 8-*C*- and 6-*C*-glycosyl-flavones, the signal doublings were observed due to the restricted rotation of the acetylated glucosyl moiety. The conformations of rotational isomers of hepta-*O*-acetylvitexin and octa-*O*-acetylorientin were decided as *+sp* (major) and *-sc* (minor) for both compounds by nmr ($CDCl_3$) spectral data. The characteristic chemical shift phenomena in nmr of glycosylflavonoid could be applicable to differentiate 8-*C*-glucoside from 6-*C*-glucoside.

In 1960's, the ^{1}H-nmr of *C*-glycosylflavone acetate in $CDCl_3$ at 60 MHz was widely investigated,[1-4] *e.g.*, the application of ^{1}H-nmr for the structure elucidation of glycosylflavones and the elimination of signal unsharpness at elevated temperature measurement caused by the existence of rotational isomer by Hillis and Horn,[1] the temperature dependent variation of rotational isomer ratio change and the conformer structures of 8-*C*-glucosylflavones by Eade *et al.*,[2] and the application of the long range proton-shielding for the structure determination of *C*-glycosylflavones by Gentili and Horowitz.[3,4] In 1987, Hori *et al.*[5] reported the ^{1}H-nmr spectrum of 8-*C*-glucosylflavone peracetate in which the rotational isomers were not mentioned, even measured at 400 MHz ($CDCl_3$). Also in 1987, Markham *et al.*[6] reported the rotational isomerisms of 6,8-di-*C*-glycosylflavones by ^{1}H-(80-400 MHz) and ^{13}C-nmr (20-100 MHz) with no isomer structure, but concluding that nmr measurement at ambient temperature and preferably at higher

• The paper is dedicated to Prof. Edward C. Taylor on the occasion of his 70th birthday.







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1; R^1=OH, R^2=R^4=R^6=R^7=R^8=H, R^3=OH, R^5=Ac
2; R^1=R^3=OH, R^2=R^4=R^6=R^7=H, R^5=R^8=Ac
5; R^1=OAc, R^2=R^4=R^5=R^6=R^7=R^8=Ac, R^3=H
6; R^1=R^3=OAc, R^2=R^4=R^5=R^6=R^7=R^8=Ac
7; R^1=R^3=H, R^2=R^4=R^5=R^6=R^7=R^8=Ac
8; R^1=OAc, R^2=R^3=H, R^4=R^5=R^6=R^7=R^8=Ac

3; R^1=R^2=R^4=R^6=R^7=R^8=H, R^3=OH, R^5=Ac
4; R^1=R^2=R^4=R^6=R^7=H, R^3=OH, R^5=R^8=Ac
9; R^1=R^2=R^4=R^5=R^6=R^7=R^8=Ac, R^3=H
10; R^1=R^2=R^4=R^5=R^6=R^7=R^8=Ac, R^3=OAc

Table I. Nmr Spectral Data for **1-4**.[a]

	[^{1}H-Nmr] (270 MHz)					[^{13}C-Nmr] [b]			
	1	**2**	**3**	**4**		**1**	**2**	**3**	**4**
H-3	6.66	6.70	6.68	6.70	C-5	160.7	160.9	160.6	160.0
H-6	6.24	6.27	-	-	C-6	97.7	97.8	106.8	106.5
H-8	-	-	6.45	6.47	C-7	162.2	162.4	163.1	162.4
H-2'	7.53	7.50	7.40	7.42	C-8	103.8	103.8	93.3	93.2
H-5'	6.89	6.95	6.89	6.91	C-8a	156.3	156.4	156.3	156.4
H-6'	7.59	7.55	7.41	7.43	C-1"	70.8	70.9	70.4	70.2
5-OH	13.19	13.22	13.60	13.65	C-2"	72.3	72.1	72.0	71.7
H-1"	4.84	4.92	4.77	4.81	C-3"	75.7	75.4	76.0	75.7
H-2"	5.28	5.37	5.51	5.56	C-4"	70.5	70.3	70.4	70.1
H-3"	3.2-3.9	3.2-3.9	3.2-3.8	3.2-3.6	C-5"	82.1	78.5	81.6	78.0
H-4"	3.2-3.9	3.2-3.9	3.2-3.8	3.2-3.6	C-6"	61.2	63.9	61.2	64.1
H-5"	3.2-3.9	3.2-3.9	3.2-3.8	3.2-3.6	Ac(2")	169.0	169.1	168.8	168.9
H-6"	3.2-3.9	4.77	3.2-3.8	4.43	Ac(2")	20.3	20.3	20.5	20.5
	-	4.12	-	3.97	Ac(6")	-	170.4	-	170.3
Ac(2")	1.69	1.72	1.75	1.77	Ac(6")	-	170.4	-	170.3
Ac(6")	-	1.93	-	2.02	Ac(6")	-	20.5	-	20.6

a)Measured in DMSO-d_6 contained a trace amounts of D_2O. b)The other signals in aglycone moiety not cited here were observed at same chemical shift positions in **1-4**,respectively.

field could provide evidence of value for determining the site of attachment of *C*-linked hexose in flavone *C*-glycosides. And also Markham *et al.* implied that the spectra at 90°C presented in a widely used compilation unfortunately failed to show signal doubling.[7a]

In the previous paper,[8] we reported on nmr data of acetyl *C*-glycosylflavones; 2"-*O*-acetylorientin(**1**), 2",6"-di-*O*-acetylorientin(**2**), 2"-*O*-acetylisoorientin(**3**), and 2",6"-di-*O*-acetylisoorientin(**4**). The differentiation of these 8-*C*-glucosides and 6-*C*-glucosides was difficult due to the similarity of their ^{1}H- and ^{13}C-nmr spectra as shown in Table I. In general, the identifications of these flavonoids are performed by the comparison of nmr and other spectral data of flavonoids (and acylated or alkylated derivatives) with those of the known compounds.[7] Markham *et al*.[6] claimed that the interaction of the primary hydroxyl group of 8-*C*-hexose moiety with B-ring might be the main cause for the signal doubling in 6,8-di-*C*-

Table II. ^{1}H-Nmr Spectral Data for **5**, **6** and **8**.[a)]

	5[b)]		**6**[c)]		**5**[d)]		**8**[e)]
	A	**B**	**A**	**B**	**A**	**B**	
H-3	6.69(s)	6.61(s)	6.66(s)	6.60(s)	7.06	6.99	6.64
H-6	6.79(s)	6.89(s)	6.80(s)	6.88(s)	7.15	7.15	6.55
H-2'	8.08(d,*J*=8.7)	7.88(d,*J*=8.6)	7.75(d,*J*=2.2)	7.92(d,*J*=1.8)	8.31	8.23	7.90
H-3'	7.40(d,*J*=8.7)	7.35(d,*J*=8.4)	-	-	7.44	7.41	7.34
H-5'	7.40(d,*J*=8.7)	7.35(d,*J*=8.4)	7.54(d,*J*=8.4)	7.37(d,*J*=8.4)	7.44	7.41	7.34
H-6'	8.08(d,*J*=8.7)	7.88(d,*J*=8.6)	8.02(dd,*J*=8.6,2)	7.68(dd,*J*=8.6,2)	8.31	8.23	7.90
H-1"	4.96(d,*J*=10.4)	5.33(d,*J*=10.2)	4.95(d,*J*=10.3)	5.36(d,*J*=9.7)	5.29	5.57	5.25-5.85
H-2"	5.84(t,*J*=9.7)	5.69(t,*J*=9.8)	5.79(t,*J*=9.6)	5.63(t,*J*=9.7)	5.73	5.51	5.25-5.85
H-3"	5.41(t,*J*=9.4)	5.41(t,*J*=9.4)	5.42(t,*J*=9.6)	5.44(t,*J*=9.7)	5.66	5.63	5.25-5.85
H-4"	5.48(t,*J*=9.7)	5.24(t,*J*=9.8)	5.36(t,*J*=9.6)	5.23(t,*J*=9.7)	5.37	5.11	5.25-5.85
H-5"	3.88-3.93(m)	3.88-3.93(m)	3.87-3.96(m)	3.87-3.96(m)	4.40	4.48	4.03
H-6"a	4.30(dd) (*J*=12.7,4.3)	4.44(dd) (*J*=12.6,4.5)	4.27(dd) (*J*=12.8,4.6)	4.46(dd) (*J*=12.5,4.4)	4.25	4.31	4.39
H-6"b	4.20(br d) (*J*=12.7)	4.01(br d) (*J*=12.6)	4.21(dd) (*J*=12.8,2.9)	4.00(br d) (*J*=12.1)	4.14	3.95	4.20
5-*O*-Ac	2.41(s)	2.41(s)	2.42(s)	2.42(s)	2.36	2.34	2.42
7-*O*-Ac	2.42(s)	2.44(s)	2.41(s)	2.43(s)	2.47	2.40	(7-OH,8.36)
3'-*O*-Ac	-	-	2.40(s)	2.37(s)	-	-	-
4'-*O*-Ac	2.35(s)	2.35(s)	2.36(s)	2.33(s)	2.34	2.34	2.36
2"-*O*-Ac	1.74(s)	1.69(s)	1.74(s)	1.69(s)	1.68	1.58	1.63
3"-*O*-Ac	1.99(s)	2.06(s)	2.00(s)	2.06(s)	1.94	2.01	2.10
4"-*O*-Ac	2.10(s)	2.08(s)	2.09(s)	2.07(s)	2.08	2.05	2.15
6"-*O*-Ac	1.90(s)	2.04(s)	1.93(s)	2.03(s)	1.83	1.98	2.03

a);δ(ppm),*J*(Hz). b);at 30°C, in $CDCl_3$ at 500 MHz, A:B=2:1. c);at 25°C, in $CDCl_3$ at 270 MHz, A:B=1:1. d);at 25°C, in DMSO-d_6 at 270MHz, A:B=4:1. e);at 25°C, in $CDCl_3$ at 270 MHz.

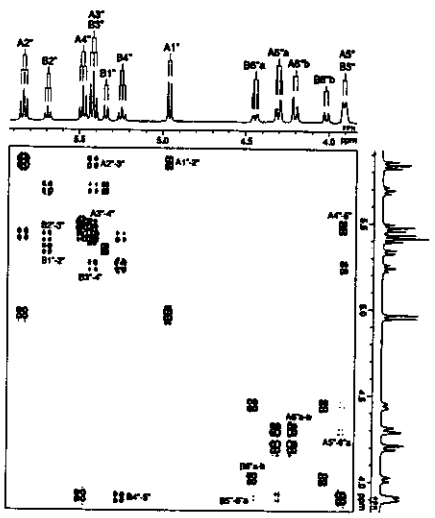

Figure 1 The sugar region of H-H COSY spectrum for 5. ($CDCl_3$, 30°C, 500 MHz)

glycosylflavones, because 6,8-dipentosyl, 6-hexosyl-8-pentosylflavones had not shown any signal doubling measured at ambient temperature. However, in ^{1}H- and ^{13}C-nmr of 8-*C*-hexosylflavones (**1** and **2**) shown in Table I, the rotational isomerisms were not observed. On the process of the structure elucidations for these compounds, the acetylated compounds showed the existence of two obvious rotational isomers as signal doublings on signals; such as acetyl groups, sugar moiety, and aromatics; in ^{1}H-nmr (270 MHz) and ^{13}C-nmr (67.8 MHz) in $CDCl_3$ at ambient temperature. This paper describes the closer conformations for these rotational isomers from the detailed analyses of nmr spectra, in particular, on sugar signals for the peracetylated 8- and 6-*C*-glucosylflavones. We took vitexin heptaacetate(**5**) and orientin octaacetate(**6**) as peracetylated 8-*C*-glucosyl-

Table III.
^{13}C-Nmr Spectral Data for **5** and **6**

	5		6	
	A	B	A	B
C-2	161.63	161.49	160.80	160.47
C-3	108.55	108.82	109.10	108.89
C-4	176.17	175.99	175.97	175.90
C-4a	115.80	115.04	115.79	115.52
C-5	150.50	150.41	150.47	150.53
C-6	114.63	116.58	114.76	116.65
C-7	152.51	153.71	152.56	153.73
C-8	114.89	114.89	114.83	114.83
C-8a	157.03	155.35	157.03	155.14
C-1'	128.81	128.74	129.89	129.57
C-2'	127.77	127.54	121.49	121.91
C-3'	122.74	122.91	142.97	142.97
C-4'	153.59	153.59	145.13	144.74
C-5'	122.74	122.91	124.67	124.54
C-6'	127.77	127.54	124.67	124.13
C-1"	72.93	72.62	72.93	72.58
C-2"	69.48	70.58	69.48	70.81
C-3"	73.99	74.59	74.43	74.04
C-4"	68.30	68.15	68.75	68.15
C-5"	76.76	76.87	77.00	77.00
C-6"	61.99	61.99	62.14	61.99
Acetyl groups				
	170.70	170.39	170.78	21.10
	170.32	170.32	170.40	21.01
	169.53	169.53	170.37	20.95
	169.37	168.90	170.08	20.79
	169.07	168.88	169.51	20.70
	168.82	168.82	169.42	20.65
	167.84	167.84	169.32	20.59
	21.16		169.05	20.54
	21.04		168.85	20.22
	20.93		168.18	20.16
	20.71		167.96	
	20.64		167.89	
	20.61		167.82	
	20.24		167.58	
	20.17			

Measured in $CDCl_3$ at 25°C.

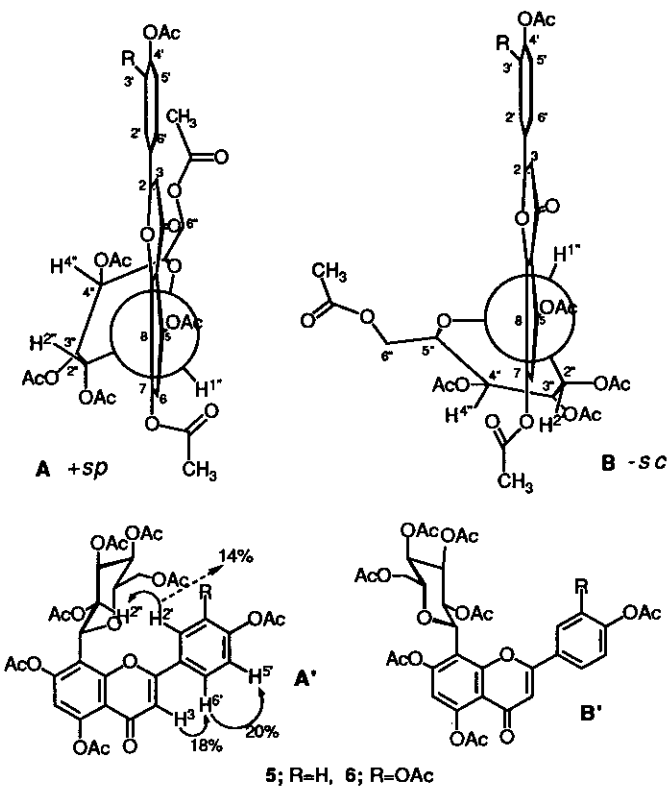

Figure 2 The conformations of rotational isomers (**A**) and (**B**).

flavones for the examination of conformations. Full ^{1}H- and ^{13}C-nmr spectral data of **5** and **6** were listed in Tables II and III. The assignments of signals were performed by ^{1}H-^{1}H and ^{13}C-^{1}H correlation spectroscopy (H-H & C-H COSY) and two dimensional nuclear Overhauser effect spectroscopy (NOESY) experiments. As shown in Figure 1 and Table II, ^{1}H-nmr spectra of **5** and **6** showed the two obvious components, A and B, the ratios of A to B were ca. 2:1 and ca. 1:1 in **5** and **6**, respectively, from the integrations of protons. In ^{13}C-nmr, the existence of two components, A and B, was also observed as shown in Table III. The acetyls at 2"- and 6"-*O* of **1** and **2** (Table I) were observed at around 1.7 and δ1.9 ppm, respectively, as Hillis and Horn[1] pointed out already at '60s : 2"-*O*-acetyl shifts to the highest affected by the anisotropy of the aromatic ring and 6"-*O*-acetyl comes to the next highest among pyranose acetate of 1'-phenyl glucupyranose tetraacetate.

When 7-*O* was acetylated in 8-*C*-glycosylflavone, the free rotation of acetylated pyranose ring was severely

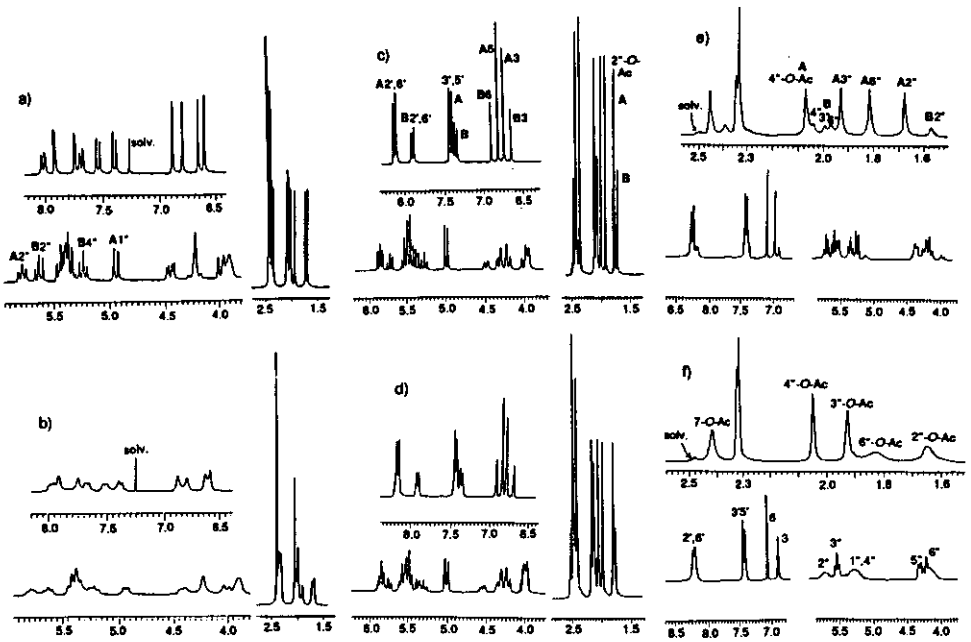

Figure 3 ^{1}H-nmr spectra for **5** and **6** at 270 MHz; a) **6** in $CDCl_3$ at 25°C, b) **6** in $CDCl_3$ at 50°C, c) **5** in $CDCl_3$ at 0°C, d) **5** in $CDCl_3$ at -40°C, e) **5** in DMSO-d_6 at 50°C, f) **5** in DMSO-d_6 at 90°C.

hindered and two rotamers became distinguishable in some nmr measurement energy levels. The chemical shifts of 2"-*O*-acetyl in **5A** (1.74) and **6A** (1.74) were slightly lower than those in **5B** (1.69) and **6B** (1.69), whereas the chemical shifts of 6"-*O*-acetyls in **5A** (1.90) and **6A** (1.93) were much higher than those in **5B** (2.04) and **6B** (δ2.03 ppm). The reversed effect of the flavone moiety on 2"-*O*- and 6"-*O*-acetyls in those isomers could be the first evident criteria from the acetyl group shifts for the isomer conformation. The conformations of isomers A and B were determined as *+sp* and *-sc*[9] taking O-1 and O-1" as the fiducial atoms on the C-8-C-1" axis (Figure 2), respectively, from the reasons as follows. The shielding effect to 2"-*O*-acetyl group by A-ring was expected more effective in *-sc* form(**5B**), and same effect to 6"-*O*-acetyl group by B-ring was expected the most effective in *+sp* form(**5A**), so that the chemical shift difference of 6"-*O*-acetyl (0.15) was larger than that of 2"-*O*-acetyl (0.05 ppm) between **A** and **B**. Concerning to the shift phenomena in sugar protons shown in Figure 1 and Table II, following characteristics were observed. H-1" in **5A** (*+sp*) could be shielded by the carbonyl of 7-*O*-acetyl group, whereas that in **5B** (*-sc*) would have no effect of the corresponding carbonyl. Apparently H-1" signal of **5A** was observed 0.37 ppm higher than that of **5B**. On the other hand, the diamagnetic effect of 7-*O*-acetyl group was observed by the signals of H-2" and H-4" in **5B** absorbing 0.15 and 0.24ppm higher,

Table IV. ^{1}H-Nmr Spectral Data for **9** and **10**. a)

	9			**10**		
	25°		50°	25°		50°
H-3	6.60(s)		6.57(s)	6.59(s)		6.57(s)
H-8	7.33(s)	[7.24]b)	7.32(br.s)	7.33(s)	[7.25]b)	7.33(br s)
H-2'	7.85(d,*J*=8.5)		7.83(d,*J*=8.5)	7.22(dd,*J*=8.5,2)		7.70(dd,*J*=8.5,2)
H-3'	7.25(d,*J*=8.5)		7.24(d,*J*=8.5)	7.36(d,*J*=8.5)		7.35(d,*J*=8.5)
H-5'	7.25(d,*J*=8.5)		7.24(d,*J*=8.5)	--		--
H-6'	7.85(d,*J*=8.5)		7.83(d,*J*=8.5)	7.68(d,*J*=2)		7.68(d,*J*=2)
H-1"	4.86(d,*J*=9.5)	[4.89]	4.86(d,*J*=9.5)	4.85(d,*J*=9.5)	[4.88]	4.85(d,*J*=9.5)
H-2"	5.73(t,*J*=9.5)	[5.65]	5.71(br.t-like)	5.73(t,*J*=9.5)	[5.64]	5.71(t,*J*=9.5)
H-3"	5.33(t,*J*=9.5)	[5.31]	5.30(t,*J*=9.5)	5.32(t,*J*=9.5)	[5.30]	5.30(t,*J*=9.5)
H-4"	5.17(t,*J*=9.5)	[5.20]	5.16(t,*J*=9.5)	5.17(t,*J*=9.5)	[5.20]	5.16(t,*J*=9.5)
H-5"	3.77-3.88(m)		3.77-3.87(m)	3.76-3.86(m)		3.74-3.84(m)
H-6"a	4.43(dd,*J*=13,5)	[4.45]	4.40(dd,*J*=12,5)	4.41(dd,*J*=12.5,5)	[4.44]	4.38(*dd*,*J*=12,4)
H-6"b	4.00(d,*J*=13)		4.02(d,*J*=12)	3.99(d,*J*=12.5)		4.01(*dd*,*J*=12,2)
Acetyls	2.49(s)x2	[2.53]	2.48(s)x2	2.50(s)	[2.52]	2.48(s)
	2.33(s)		2.31(s)	2.48(s)	[2.42]	2.45(br.s)
	2.07(s)	[2.09]	2.05(s)	2.35(s)		2.32(s)
	2.05(s)		2.04(s)	2.33(s)		2.30(s)
	2.03(s)		2.01(s)	2.07(s)	[2.09]	2.05(s)
	1.82(s)	[1.78]	1.81(s)	2.06(s)		2.03(s)
				2.03(s)		2.00(s)
				1.82(s)	[1.78]	1.80(br s)

a);Measured in $CDCl_3$ at 270 MHz,d(ppm),*J*(Hz). b);On the doubling signals at 25°C, chemical shifts of minor isomer were shown in brackets, approximate rotamer ratio; 5:1, and signals without bracket signal were integrated as 1H or 3H for proton and acetyl, respectively.

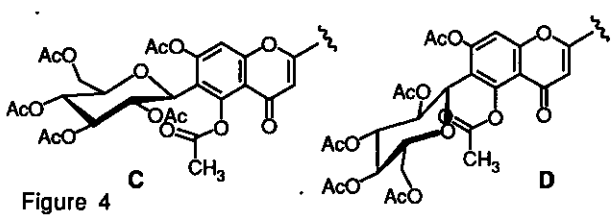

Figure 4
The conformations of rotational isomer for **9** and **10**.

respectively, than those of **5A**. While, the overall effect of the carbonyl groups of sugar moiety in **5A** could be to deshield the 2'-, 6'-,3'-,5'- and 3-protons, since in their closest approach to these aromatic protons when their effects would be the greatest, these protons would be roughly in the planes of the carbonyl bonds.[2] The signals of H-3" and H-5" were not doubled to indicate the same magnetic environment on the hindered rotation about the C-8-C-1" bond in both isomers, **5A** and **5B**.

The confirmation that H-2" was distant from H-2' comparing with those of H-3-H-6' or H-5'-H-6' by the NOE experiments as shown in Figure 2-A', prefers the *+sp* of the major isomer rather than *+sc* representation. While, in ^{1}H-nmr of 5,4',2",3",4",6"-hexa-*O*-acetylvitexin(**8**) shown in Table II, the signal doublings were not observed at 25°. The signals of H-1",-2",-3" and -4" in the sugar moiety were overlapped at the region of δ5.25-5.85ppm. High field absorption of H-1" like in **5A**, affected by the shielding effect of 7-*O*-acetyl group, was not observed. The chemical shifts of H-2',-6'; H-3',-5' and H-3 in **8** were similar to those undeshielded in **5B** than those deshielded in **5A**. And the acetyl signals were also

similar to those in **5B** than **5A**. (Table II) These findings indicated again *+sp* form for **5A** and *-sc* form for **5B**. On the rotational isomers (**6A**) and (**6B**), it is supposed that **6A** and **6B** form the very similar conformations to **5A** and **5B**, respectively, in $CDCl_3$ from the nmr spectral data in Table II and Figure 3.

Eade et al.[2] observed the changes of broadened signals to the sharp single signals at 60°C in the ^{1}H-nmr spectra (at 60 MHz, $CDCl_3$) of **5** and **7**. In Figure 3-a & b, ^{1}H-nmr spectra of **6** at 25°C and 50°C in $CDCl_3$ are shown. We examined the temperature dependent isomer variations of **5** in $CDCl_3$ and DMSO-d_6 at 270 MHz. The spectra at -40°C and 0°C in $CDCl_3$ (Figure 3-c, d) were similar to that shown in Figure 1. And in DMSO, the two obvious isomer signals were observed at 50°C, but the signals changed to the sharp singlets at 90°C except still broad signals of 2"-, 6"-*O*-acetyl and 1"-, 2"-, 4"-protons. (Figure 3-e, f) ^{1}H-Nmr of **5** and **6** exhibited the pair signals of isomer **A** and **B** at the range of -40°C to +50°C in $CDCl_3$, and seemed to keep the same conformations.

While, in the case of peracetylated 6-*C*-glucosylflavones, no signal doubling in the ^{1}H-nmr spectra of isovitexin heptaacetate(**9**) and isoorientin octaacetate(**10**) at 30-35°C ($CDCl_3$, 60 MHz)[4] and the sharp singlets at 0°C ($CDCl_3$, 60 MHz) for the signals of 2"-, 6"- and 7-*O*-acetyl groups [2] were reported.

However, as shown in Table IV, **9** and **10** exhibited a little signal doublings in H-8, sugar protons and acetyl signals at 25°C in $CDCl_3$ (270 MHz). These doubled signals were changed to the single signals at 50°C.

In the 6-*C*-glucosides (**9**) and (**10**), it is assumed that the carbonyl of 5-*O*-acetyl group located in the opposite side against the 4-carbonyl to avoid the heavy interaction. If this is the case, the possible conformations of two isomers are as shown in Figure 4. The interaction of the acetylated sugar ring with the 5-acetyl group could be expected to greater extent in conformer [**D**] than in [**C**]. It seems that these conformations contributed to the signal doublings especially of H-2", H-1", 2"-*O*-acetyl *etc.*

Interaction of B-ring and glucose moiety was examined by using puerarin peracetate (**11**). In ^{1}H-nmr of **11**, the signal doubling was not observed. But H-1", H-2" and H-6" in glucose moiety were observed as broadened signals, and H-2 and two acetyl signals at 7-*O* and 2"-*O* were also broadened. These observation show that the rotation of glucose was not inhibited by B-ring at 3 position though the acetyl group at 7-*O*-acetyl interact with glucose moiety. (see Experimental)

EXPERIMENTAL

Orientin, isoorientin, vitexin and isovitexin were obtained from *Rumex acetosa* L.,[8,10] and puerarin was purchased from Funakoshi Co., Ltd. Acetylation of vitexin (80 mg) was carried out by acetic anhydride (Ac_2O, 8 ml) with pyridine (8 ml) at ambient temperature, to give peracetate **5** (ca. 90%) and by-product **8** (ca. 5%). The other flavonoidal compounds (20-100 mg) were refluxed in Ac_2O (5-10 ml) under the presence of small amount of NaOAc, to give corresponding peracetates quantitatively. The melting points were taken on a Yanagimoto micromelting-point apparatus and are uncorrected. Fast atom bombardment mass spectra (FABms) were measured with a JEOL DX-300 spectrometer. The solution of DMSO-d_6 (Merck, 99.95 atom-% D) or $CDCl_3$ (Aldrich, 99.96 atom-% D) was used for nmr measurements with tetramethylsilane as internal reference. Nmr spectra of **5** at 25°C, were recorded on a JEOL JNM-GSX500: ^{1}H-nmr (500 MHz); pulse width (PW), 2.4 μs (45°); spectral width (SW), 5000 Hz; acquisition time (AT), 6.554 s; pulse delay time (PD), 4 s; data points, 64 K: proton decoupled ^{13}C-nmr (125.65 MHz); PW, 4.0 μs (45°); SW, 25000 Hz; AT, 0.655 s; PD, 2.5 s; data points, 32 K: H-H COSY: phase sensitive double quantum filter (PHDQF) mode; PW, 7.2 μs (90°); SW, 5 KHz; AT, 0.102 s; PD, 2.5 s; data points, 1024 (zero filling to 2048 points); column points, 256 (zero filling to 512 points). Other nmr spectra were measured with JEOL GX-270 : ^{1}H-nmr (270 MHz); PW, 8.0 μs (45°); SW, 6002.4 Hz; AT, 2.73 s; PD, 2.27 s; data points, 32 K: proton decoupled 13C-NMR (67.8 MHz); PW, 4.7 μs (45°); SW, 13020.8 Hz; AT, 1.258 s; PD, 0.5 s; data points, 32 K.

5: colorless needles, mp 258-259°C, FABms; *m/z* 727 $(M+H)^+$, ^{1}H- and ^{13}C-nmr (see Tables II and III), *Anal.* Calcd for $C_{35}H_{34}O_{17}$: C,57.85: H,4.72. Found: C,57.80: H,4.74.

6: colorless needles, mp 201-203°C, FABms; *m/z* 785 $(M+H)^+$, ^{1}H- and ^{13}C-nmr(see Tables II and III), *Anal.* Calcd for $C_{37}H_{36}O_{19}$: C,56.63: H,4.62. Found: C,56.35: H,4.53.

8: colorless needles, mp 145°C, FABms; *m/z* 685 $(M+H)^+$, ^{1}H-nmr (see Table II).

11: colorless needles, mp 134-135°C, FABms; *m/z* 669 $(M+H)^+$, ^{1}H-nmr ($CDCl_3$, 25°C, δ, ppm), 8.33 (1H, d, *J*=8.5 Hz, H-5), 8.10 (1H, br s, H-2), 7.60 (2H, d, *J*=8.5 Hz, H-2',6'), 7.19 (3H, d, *J*=8.5 Hz, H-6,3',5'), 5,7-5.9 (br, H-2), 5.38 (t, *J*=9 Hz, H-3"), 5.2-5.35 (br, H-4), 3.95-5.0 (br, H-1", 6"), 3.87 (ddd, *J*=9.5, 4.4, 2.2 Hz, H-5"), 2.45 (3H, br s, C-7-Ac), 2.33 (3H, s, C-4'-Ac), 2.08 (6H, s, Acx2), 2.04 (3H, s, Ac), 1.73 (3H, br s, C-2"-Ac).

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