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CIRCULAR DICHROISM OF HYDROLYSABLE TANNINS-II
DEHYDROELLAGITANNINS

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Summary The CD spectra of dehydroellagitannins and related compounds have empirically shown that the absolute configuration at C-1' of the dehydrohexahydroxydiphenoyl group can be determined by the Cotton effect around 200 nm.

Unexpectedly wide distribution of dehydroellagitannins has been found recently.[1] The absolute configurations R and S at C-1' of the hemiacetal-forming dehydrohexahydroxydiphenoyl (DHHDP) group in geraniin (**1**)[2] and isoterchebin (**2**)[3] were established by production and degradation of the phenazine derivatives, combined with the optical measurement The absolute configuration at C-1' of the other dehydroellagitannins was subsequently determined by the specific rotation of the phenazine derivative (**3**) produced from each tannin [1]

We have now attempted to correlate the CD spectra and the absolute configuration of the DHHDP group of dehydroellagitannins, in order to utilize this correlation for direct determination of the absolute configuration of the DHHDP group in new tannins

All of the dehydroellagitannins in this study for which the absolute configurations were independently determined via chemical degradation, exhibited a strong CD extremum at 200-210 nm and a weak one around 350 nm (Table). Three other Cotton effects were also exhibited at 230-290 nm, by the dehydroellagitannins possessing the galloyl group or both the galloyl and the hexahydroxydiphenoyl (HHDP) groups, in addition to the DHHDP group

1) Cotton Effects due to C-1' Configuration of DHHDP Group

The CD spectrum (Fig 1) of 4,6-O-[(1'S)-DHHDP]-D-glucose (**4**), which was prepared by complete degalloylation of **2** with tannase, showed the positive Cotton effects at 375 and 237 nm, and the negative one at 206 nm. These three CD bands would be ascribed respectively to the n-π^* and the first (K-band) and second π-π^* transitions of α,β-unsaturated ketones.[4] The positive n-π^* Cotton effect of **4** is consistent with that of paspalicine[5] and of (+)-7,12-dihydro-12-methyl-6,12-methanodibenzo[a,d]cycloocten-5(6H)-one,[6] whose conformations markedly resemble to that of the DHHDP group of **4** which is shown by I Moreover, the positive Cotton effect at 237 nm (K-band) is compatible with an expectation for the conformation I, the opposite sign would be found for the conformation II of the 1'R-DHHDP group.

The Cotton effect around 230 nm due to the DHHDP group in the dehydroellagitannins is overlapped by that of the HHDP group,[7] when this group is in the molecule. However, the prominent Cotton effect around 200 nm, of the sign opposite to that at 230 nm, is not overlapped, and is available for correlating the CD spectra with the absolute configuration at C-1'. This correlation of the two Cotton effects and the absolute configuration is supported by the comparison of the CD spectra of **1** and furosin (**5**).[8] The latter which lacks the HHDP group, shows a Cotton effect of the sign identical as that of the former at 202 nm, and another peak of opposite sign at 231 nm. Among the seven other dehydroellagitannins, those having the (1'*R*)-DHHDP group [**1**, mallotusinic acid (**6**),[9] terchebin (**7**),[10] dehydrogeraniin (**8**),[8] and furosinin (**9**)[8]] showed a positive Cotton effect, and those possessing (1'*S*)-DHHDP group [**2** and granatin B (**10**)[10]] showed negative Cotton effect around 200 nm (Fig. 1, Table).

This finding is in accord with the conclusion[4] that the 200-220 nm Cotton effect is primarily related to the absolute configuration of the 2-cyclohexenone ring (i.e. to the configuration at the allylic carbon C-1').

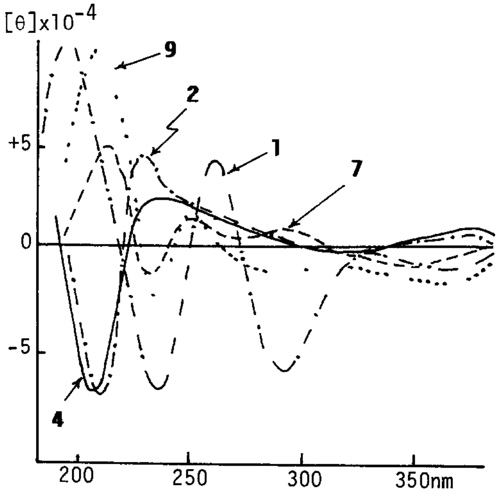


Fig. 1 CD Spectra of **1**, **2**, **4**, **7** and **9** in MeOH

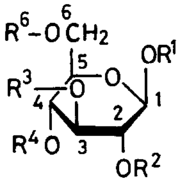
2) Interaction between DHHDP and Galloyl Groups

The CD extremum at 290 nm of **5** and **8** is attributable to the interaction between the aromatic ring of the DHHDP group and the adjacent galloyl group, since the extremum in this region is not shown by **9** which lacks the galloyl group at O-1. The extrema in this region of **1** and **10** are ascribed to the interaction between the galloyl group at O-1 and the HHDP group at O-3~O-6, based on the comparison of **1**, **10** and corilagin (**11**).[7] The extremum in this region is absent in the CD spectrum of **2**. This phenomenon is in accord with the spatially remote location of the benzene moiety of DHHDP group and the galloyl group at O-3 on the glucopyranose ring of the *C1* conformation, as the interaction among the galloyl groups at O-1, O-2 and O-3 are mutually cancelled.[7]

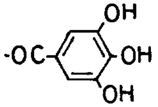
3) Phenazine Derivatives

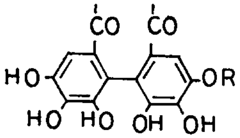
The absolute configuration at C-1' of the DHHDP group in dehydroellagitannins is confirmed by the CD curves of the phenazine derivatives prepared from these tannins by condensation with *o*-phenylenediamine. The stereochemical considerations indicate that the absolute configurations, *R* and *S*, of the phenazine derivatives are respectively induced by the (*R*)- and (*S*)-configurations at C-1' in the DHHDP group of the original tannins.[2] The (*S*)-phenazine derivative (**12**)[3] (λ_{max}^{MeOH} 217, 280 nm) from **2** showed significant Cotton effects which are positive at 275 nm and negative at 241 nm, while the (*R*)-phenazine derivative (phenazine B) (**13**)[2] (λ_{max}^{MeOH} 220, 280 nm) from **1** gave Cotton effects of reversed signs. This correlation was also observed without exception in the CD spectra of phenazine derivatives, (**14**)-(**16**) from **5**, **6** and **8** (Table).

The amplitudes of these Cotton effects of phenazine derivatives are large enough to indi-



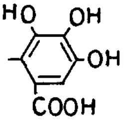
gall=





HHDP R=H

valoneoyl R=



1 R^1=gall, $R^2\sim R^4$=(1'R)-DHHDP (a), $R^3\sim R^6$=(R)-HHDP

2 R^1=R^2=R^3=gall, $R^4\sim R^6$=(1'S)-DHHDP (a)

4 R^1=R^2=R^3=H, $R^4\sim R^6$=(1'S)-DHHDP (a)

5 R^1=gall, R^3=R^6=H, $R^2\sim R^4$=(1'R)-DHHDP (a ⇄ b)

6 R^1=gall, $R^2\sim R^4$=(1'R)-DHHDP (a ⇄ b), $R^3\sim R^6$=(R)-valoneoyl

7 R^1=R^3=R^6=gall, $R^2\sim R^4$=(1'R)-DHHDP (a ⇄ b)

8 R^1=gall, $R^2\sim R^4$=$R^3\sim R^6$=(1'R)-DHHDP (a ⇄ b)

9 R^1=H, $R^2\sim R^4$=$R^3\sim R^6$=(1'R)-DHHDP (a ⇄ b)

10 R^1=gall, $R^2\sim R^4$=(1'S)-DHHDP (a), $R^3\sim R^6$=(R)-HHDP

11 R^1=gall, R^2=R^4=H, $R^3\sim R^6$=(R)-HHDP

12 R^1=R^2=R^3=gall, $R^4\sim R^6$=(S-phz)

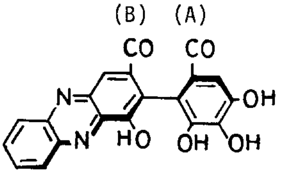
13 R^1=gall, $R^2\sim R^4$=(R-phz)

14 R^1=R^3=R^6=H, $R^2\sim R^4$=(R-phz)

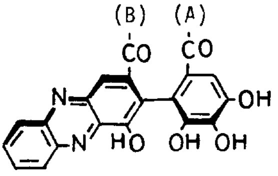
15 R^1=gall, $R^2\sim R^4$=(R-phz), $R^3\sim R^6$=(R)-valoneoyl

16 R^1=gall, $R^2\sim R^4$=$R^3\sim R^6$=(R-phz)

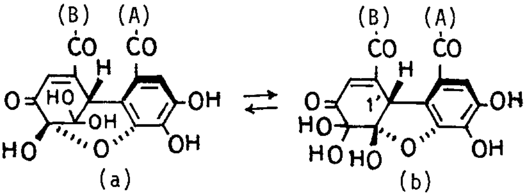
(S-phz)=



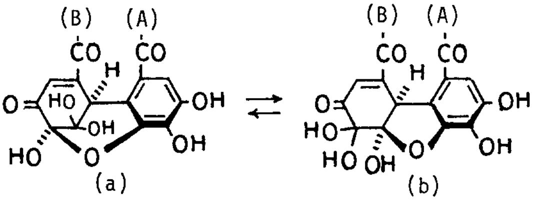
(R-phz)=

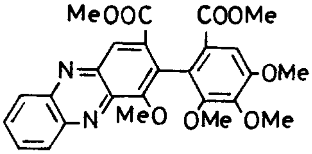


(1'S)-DHHDP=



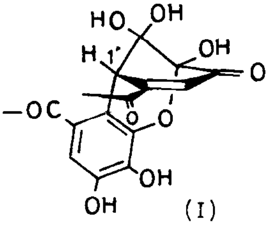
(1'R)-DHHDP=



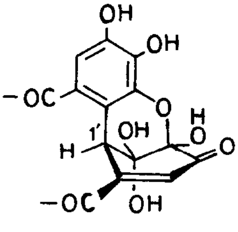


3

$R^2\sim R^4$	$R^3\sim R^6$	$R^4\sim R^6$
A=O-2	A=O-3	A=O-4
B=O-4	B=O-6	B=O-6



(I)



(II)

cate their absolute configurations in the presence of HHDP and galloyl groups, and the results are in accord with the absolute configurations at C-1' of original dehydroellagitannins directly estimated by the CD spectra. The amplitude of the Cotton effect around 280 nm in **16**,[8] which has two phenazine moieties in the molecule, was about twofold of that of **14**.

These correlations found for dehydroellagitannins, along with the empirical rule for ellagitannins and gallotannins,[7] are expected to allow facile determination of the absolute configurations of new hydrolysable tannins.

Table. CD Spectral Data of Dehydroellagitannins and Related Compounds

Compound	C-1'	Cotton effect, [θ] x 10^{-4}, (nm) (MeOH)				
geraniin (**1**)	R	-1.0 (361)	-6.2 (291)	+4.5 (261)	-7.1 (236)	+10.3 (196)
isoterchebin (**2**)	S	+0.8 (372)			+4.6 (228)	-7.4 (210)
4,6-O-DHHDP-D-glucose (**4**)	S	+0.9 (375)			+2.6 (237)	-7.1 (206)
furosin (**5**)	R	-1.0 (350)	-2.9 (290)	+1.7 (252)	-2.0 (231)	+5.1 (202)
mallotusinic acid (**6**)	R	-0.7 (360)	-4.8 (286)	+4.6 (251)	-6.3 (221)	+8.0 (198)
				+4.3 (238)		
terchebin (**7**)	R	-0.8 (350)	+1.1 (290)	+1.4 (251)	-1.3 (233)	+5.2 (213)
dehydrogeraniin (**8**)	R,R	-1.7 (358)	-3.9 (292)	+3.4 (250)	-0.5 (233)	+10.0 (202)
furosinin (**9**)	R	-1.9 (356)		+1.8 (250)	-2.6 (231)	+10.0 (210)
granatin B (**10**)	S	+1.1 (360)	-4.6 (285)	-0.8 (263)	-9.0 (243)	-7.1 (211)
isoterchebin-phenazine (**12**)				+6.2 (275)	-3.4 (241)	+5.1 (219)
geraniin-phenazine B (**13**)				-14.2 (280)	+8.8 (250)	-5.4 (219)
furosin-phenazine (**14**)				-14.0 (279)	+7 5 (245)	-2.1 (221)
mallotusinic acid-phenazine (**15**)				-18.0 (281)	+13.9 (247)	-13.4 (218)
					+15.4 (238)	
dehydrogeraniin-phenazine (**16**)				-22.1 (283)	+24.7 (246)	-13.4 (217)

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