CIRCULAR DICHROISM OF HYDROLYSABLE TANNINS-I
ELLAGITANNINS AND GALLOTANNINS

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Summary   The Cotton effects around 235, 265 and 285 nm in the CD spectra of twenty hydrolysable tannins and related compounds were empirically correlated with the stereostructures of ellagitannins and gallotannins.

   Although various ellagitannins and dehydroellagitannins of mutually correlated structures have been isolated recently,[1-10] there has been no chiroptical work directly applied to their structures.   The only way of determining the absolute configuration of chiral hexahydroxydiphenoyl (HHDP) group in these tannins has been the degradation of methylated tannins, followed by the measurement of specific rotation of dimethyl hexamethoxydiphenate (1), for which R-configuration of the dextrorotatory 1 was established.[4]   We have now measured the CD spectra of twenty hydrolysable tannins and related compounds, for which the absolute configurations had been determined via methanolysis, and found that the CD spectra afford a convenient empirical method of determining the absolute stereostructures of ellagitannins and gallotannins without chemical degradation.

1) Absolute Configuration and Number of HHDP Group

   a) In the Absence of Galloyl Group —— The CD spectra of (R)-1 and (S)-1, which were obtained by methanolysis of the polymethyl derivatives of corilagin (2)[6] and pedunculagin (3),[5] respectively, exhibited strong Cotton effects at 225 and 250 nm, of the signs opposite to each other (Fig. 1).   These Cotton effects are associated with the biphenyl conjugation bands in the UV spectra, and are indicative of the absolute configuration of HHDP group· the positive 250 nm Cotton effect corresponds to the (R)-configuration, and the negative one to the (S)-configuration.

   Then, 2,3-O-[(S)-HHDP]-D-glucose (4), 4,6-O-[(S)-HHDP]-D-glucose (5) and 3,6-O-[(R)-HHDP]-D-glucose (6) were prepared respectively by enzymatic hydrolysis of 2, 3 and tellimagrandin-I (7).[3,5,12]   These HHDP-
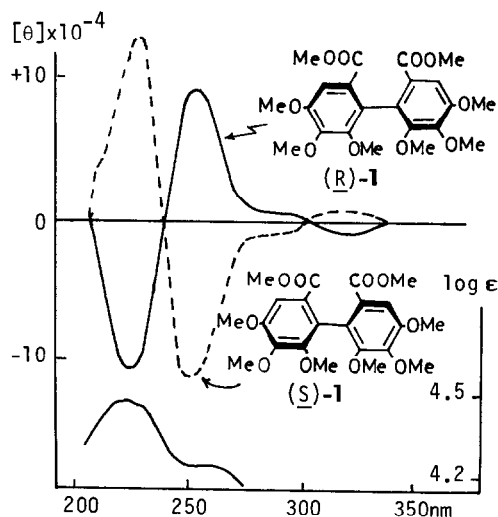

Fig. 1.   CD and UV Spectra of (R)-1 and (S)-1 in MeOH

glucoses showed the Cotton effects around 235 and 265 nm, with small red-shift from those of **1** due to decrease of the twist angle.[11]   The positive and negative Cotton effects around 265 nm are therefore attributable to the (R)- and (S)-configuration of the HHDP group in ellagitannins, respectively (Table).

The amplitudes of the Cotton effect around 235 nm in **3** and casuariin (**8**)[5] which have two HHDP groups in the molecule, were about twofold of that of **4** or **5**.

b) <u>In the Presence of Galloyl Group</u> ―― The CD spectra of **2, 7,** tellimagrandin-II (**9**)[3,5,12] and strictinin (**10**),[8] which have one to three galloyl groups along with a HHDP group, exhibited three Cotton effects around 235, 265 and 285 nm (Fig. 2, Table).   The Cotton effects at 235 and 265 nm are correlated, as those in **4, 5** and **6,** with the chemically determined absolute configuration of the HHDP group in these tannins.   The 235 nm peak was absent in the CD spectra of methyl 2,3-di-<u>O</u>-galloyl-α-D-glucoside (**11**), 1,2,6-tri-<u>O</u>-galloyl-β-D-glucose (**12**), 1,2,3-tri-<u>O</u>-galloyl-β-D-glucose (**13**) and penta-<u>O</u>-galloyl-β-D-glucose (**14**) (Table).   The Cotton effect at 235 nm is therefore diagnostic for the absolute configuration of the HHDP group in the tannins of this class [positive for the (S)-configuration and negative for the (R)-configuration]. This correlation apparently exists regardless of presence or absence of the galloyl group, and also of the conformation of the glucose residue.

Casuarictin (**15**),[5] casuarinin (**16**),[5] stachyurin (**17**)[7] and potentillin (**18**),[8] which have two HHDP groups and a galloyl group, also exhibited the three Cotton effects around 235, 265 and 285 nm (Fig. 2, Table).   The amplitude of 235 nm peak of **15** and **16**, analogously to that of **3** and **8**, is about twofold of those of **7, 9** and **2**, and also of **4** and **5**, in accord with the number of HHDP groups.

2) <u>Interaction between Galloyl Groups</u>

Polygalloylglucoses (**11**) and (**12**) showed the split Cotton effect centered near 273 nm, which corresponds to the intramolecular charge-transfer transition (277 nm) of the galloyl group in the UV spectra.   This Cotton effect is analogous to that of dibenzoate congener (**19**), with red-shift of ca. 40 nm, due to the polyphenolic structures (Table).   The sign of the first Cotton effect around 285 nm is in agreement with the chirality between the galloyl groups, when the exciton chirality rule[13] is applied.   This Cotton effect of **15** is small, and is accounted for by the chiralities at C-1~C-2 and at C-2~C-3, which are opposite to each other.

3) <u>Interaction between Galloyl and HHDP Groups</u>

Analogously, the Cotton effect around 285 nm of **2, 3, 7** and **18** may be regarded as a part of a split-type Cotton effect induced by the interaction between a galloyl and a HHDP group or between two HHDP groups.   The sign of this Cotton effect is correlated in an empirical manner, to the chirality between two axes illustrated by **2** and **3a**.   Between the two conformations of glucose ring in **2**, <u>1C</u> and <u>1B</u>, which are indicated by the coupling constants in the ^{1}H NMR spectra,[14] only the former may give this Cotton effect due to the interaction of the two aromatic groups. However, the sign and the amplitude of this Cotton effect are indistinguishable between **7** and **11**, and also between **9** and **13**.   The galloyl group at O-3 and the HHDP group at O-4~O-6 in these molecules, are therefore considered to have no significant interaction.   The CD spectrum of **10**, which is almost superimposable on that of **5**, also indicates that the interaction between the

galloyl group at β-O-1 and the HHDP group at O-4~O-6 on the glucose residue of the <u>C1</u> conformation is negligible.

The correlations described above were successfully applied to agrimoniin (**20**),[8] a dimeric ellagitannin (Table), for which the absolute configurations were determined also <u>via</u> the chemical degradation.
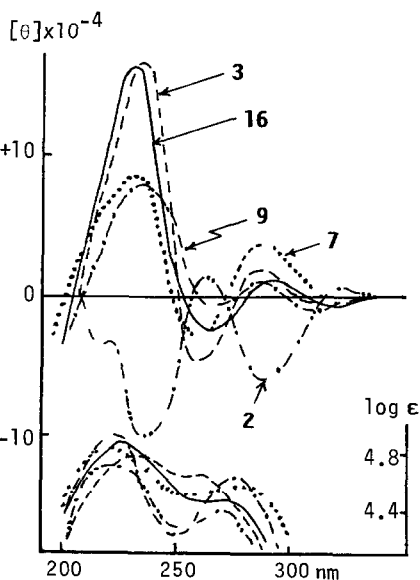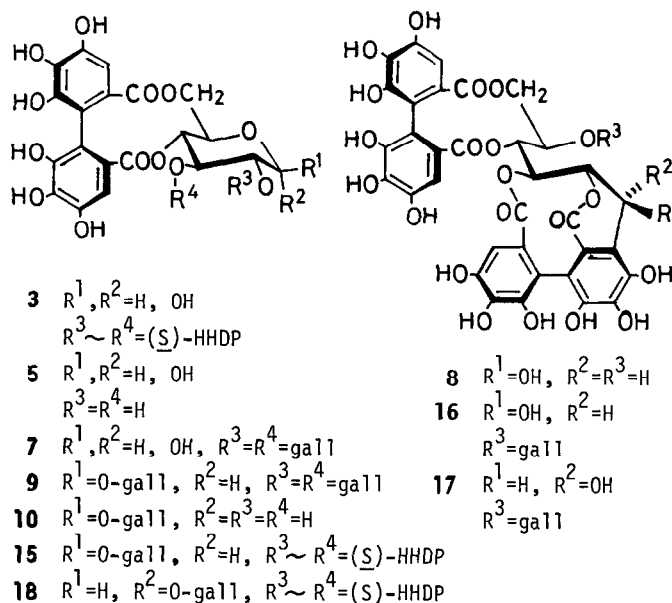

3 R[1],R[2]=H, OH
R[3]~ R[4]=(<u>S</u>)-HHDP

5 R[1],R[2]=H, OH
R[3]=R[4]=H

7 R[1],R[2]=H, OH, R[3]=R[4]=gall

9 R[1]=O-gall, R[2]=H, R[3]=R[4]=gall

10 R[1]=O-gall, R[2]=R[3]=R[4]=H

15 R[1]=O-gall, R[2]=H, R[3]~ R[4]=(<u>S</u>)-HHDP

18 R[1]=H, R[2]=O-gall, R[3]~ R[4]=(<u>S</u>)-HHDP

8 R[1]=OH, R[2]=R[3]=H

16 R[1]=OH, R[2]=H
R[3]=gall

17 R[1]=H, R[2]=OH
R[3]=gall

gall=-CO〈〉OH OH OH

(<u>S</u>)-HHDP=

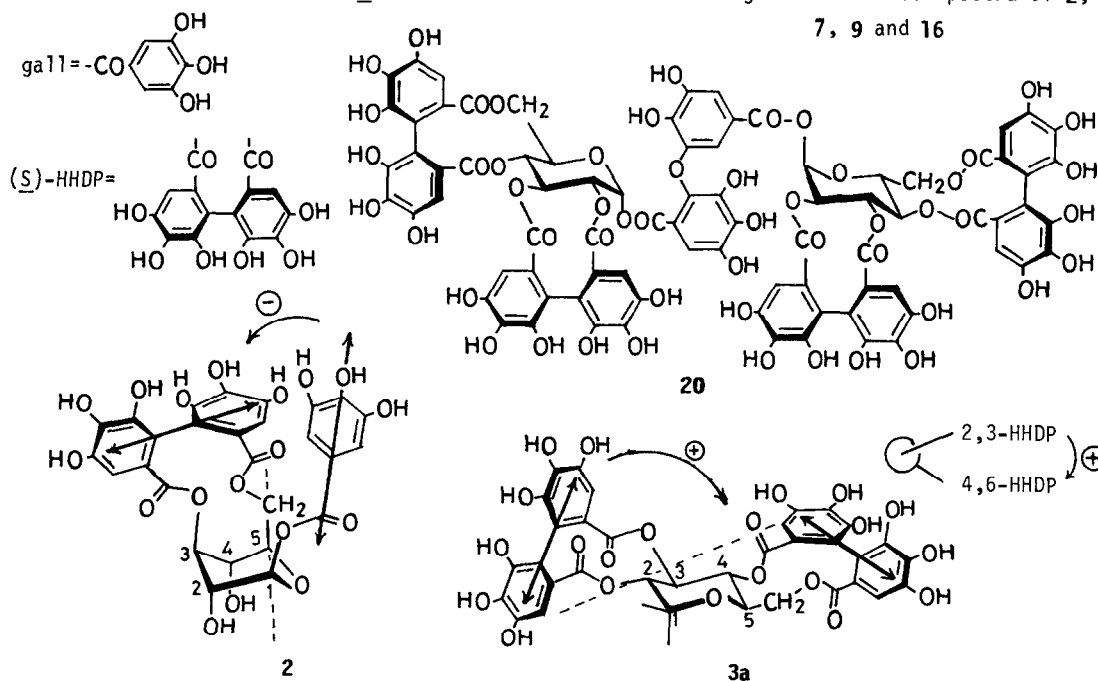Fig. 2. CD and UV spectra of **2**, **3**, **7**, **9** and **16**

20

2

3a

Table. CD Spectral Data of Hydrolysable Tannins and Related Compounds[15]

Compound	Cotton effect, $[\theta] \times 10^{-4}$, (nm)(MeOH)		
(R)-dimethyl hexamethoxydiphenate (1)		+4.8 (250)	-5.5 (225)
(S)-dimethyl hexamethoxydiphenate (1)		-5.6 (250)	+6.7 (225)
corilagin (2)	-6.6 (284)	+1.7 (262)	-10.3 (237)
pedunculagin (3)	+2.1 (282)	-5.4 (259)	+16.8 (233)
2,3-O-[(S)-HHDP]-D-glucose (4)	-0.1 (287)	-2.7 (262)	+10.2 (235)
4,6-O-[(S)-HHDP]-D-glucose (5)	+0.2 (286)	-2.2 (264)	+8.9 (237)
3,6-O-[(R)-HHDP]-D-glucose (6)	-0.4 (290)	+2.4 (265)	-8.5 (236)
tellimagrandin-I (7)	+4.0 (284)	-3 7 (259)	+8.8 (232)
casuariin (8)	+1.9 (281)	-3.1 (261)	+17.8 (231)
tellimagrandin-II (9)	+0.8 (285)	-1.0 (264)	+8.1 (235)
strictinin (10)	-0.2 (288)	-3 2 (265)	+12.2 (235)
methyl 2,3-di-O-galloyl-α-D-glucoside (11)	+3.0 (284)	-1.7 (260)	+3 1 (215)
1,2,6-tri-O-galloyl-β-D-glucose (12)	-3 5 (284)	+2.2 (261)	-3.3 (215)
1,2,3-tri-O-galloyl-β-D-glucose (13)	+1.1 (280)	-0.1 (257)	
penta-O-galloyl-β-D-glucose (14)	+1.5 (270)	+0 2 (240)	+1.2 (225)
casuarictin (15)	+0.7 (281)	-5.3 (261)	+20 2 (234)
casuarinin (16)	+1.2 (283)	-3.3 (262)	+16.7 (231)
stachyurin (17)	+2.4 (282)	-4.4 (259)	+16.0 (230)
potentillin (18)	+3.3 (282)	-4.1 (260)	+14.8 (236)
methyl 2,3-di-O-benzoyl-α-D-glucoside (19)		+5 1 (233)	-1.6 (217)
agrimoniin (20)	+9.7 (282)	-10.6 (260)	+36.5 (235)

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15. Preparations of 11~14 and 19 will be presented later.