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Spectral and Chromatographic Analyses of Tannins. I. ^{13}C Nuclear Magnetic Resonance Spectra of Hydrolyzable Tannins

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The ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectra of hydrolyzable tannins, in which D-glucopyranose takes the $^4C_1$ conformation, have been analyzed and the ^{13}C resonances of the glucose carbons fully assigned. The peak sequences of carbons in glucose are different among several types of hydrolyzable tannins, reflecting differences of the acyl (galloyl, hexahydroxydiphenoyl and dehydrohexahydroxydiphenoyl) groups, as found upon comparison of penta-*O*-galloyl-β-D-glucose (**1**), casuarictin (**7**), tellimagrandin II (**13**) and isoterchebin (**15**). The additive character of galloylation and hexahydroxydiphenoylation shifts can be used for locating the positions of the acyl groups. The substituents and substitution mode at C-1 and C-2 of glucose in these tannins can be deduced from the diagnostic ^{13}C chemical shift of the anomeric carbon. The ^{13}C resonances of the dimeric hydrolyzable tannins were assigned on the basis of the data for their monomeric units.

Keywords——hydrolyzable tannin; galloylglucose; ellagitannin; ^{13}C-NMR; assignment of glucose carbon signal; galloylation shift; hexahydroxydiphenoylation shift; dimeric hydrolyzable tannin

Considerable amounts of hydrolyzable tannins have been isolated from various plants to date. Most of them contain a monosaccharide, mainly D-glucose, or a cyclic polyalcohol core which is esterified with polyphenolic acids. Dimeric and trimeric hydrolyzable tannins have also been found to occur in nature.[1] The ^1H nuclear magnetic resonance (NMR) spectra and the partial hydrolysis of tannins with tannase and hot water have been important tools for structural elucidation of these tannins, and the recently proposed empirical rules in the circular dichroism (CD) spectra[2] facilitate stereochemical assignments. The ^{13}C-NMR spectra also provide useful structural information including the nature and number of the polyphenol groups, *e.g.* galloyl, hexahydroxydiphenoyl (HHDP), dehydrohexahydroxydiphenoyl (DHHDP) groups and others. However, only a small number of ^{13}C-NMR studies have dealt with the carbohydrate moieties, while determination of the locations of acyl groups on the carbohydrate moieties is most important for the structure elucidation of the tannins of this class. Published assignments of the ^{13}C resonances have appeared for corilagin,[3] penta-*O*-galloyl-β-D-glucopyranose (**1**),[1f] its depsidically linked galloyl derivatives (gallotannins),[1f,4] and some C-glucosidic hydrolyzable tannins.[5] If the assignments are established, the ^{13}C-NMR spectroscopy should be more informative than other spectroscopic techniques in locating the positions of the acyl groups on the glucose core.

In order to facilitate the structural assignments of new oligomeric hydrolyzable tannins as well as monomers, we have now tried to establish a systematic assignment of the glucose moieties of known hydrolyzable tannins. Particular attention has been paid to the changes of

the chemical shifts of the glucose carbon signals caused by differences in the nature and position of polyphenol ester groups on the glucopyranose ring.

In a number of studies on the ^{13}C-NMR spectra of carbohydrates, several useful rules have been exploited, and they include use of the acylation shifts,[6] glucosidation shifts[7] and methylation shifts,[8] which have been successfully applied to the structural and stereochemical assignments of naturally occurring glycosides such as flavonoid glycosides,[9] saponins,[10] acyl glycosides,[11] *etc.* Among them, acylation shifts induced by a variety of acyl groups were rationalized in terms of a linear relationship between the ^{13}C chemical shift of the carbinyl carbon (C_α) of the ester and the pK_a value of the parent acid.[12] More recently, the parameters of acylation shifts applicable to a wide range of acyl groups, including the cinnamoyl group, were proposed.[6d] However, application of these acylation shift rules was limited mainly to mono- and diacylsugars.[6d] Therefore, ^{13}C-NMR analyses of a series of hydrolyzable tannins and related polyphenols (**1**—**16**) should be valuable not only for examining the general applicability of this rule to glucosides esterified with more than three acyl groups, including those of bulky polyphenolic acids, but also for exploring the galloylation and hexahydroxydiphenoylation shifts, which have not yet been investigated systematically.

Experimental

Materials——2,3-(*S*)-Hexahydroxydiphenoyl-D-glucose (**18**) and 4,6-(*S*)-valoneoyl-D-glucose (**23**) were prepared by partial hydrolysis of pedunculagin (**19**) and rugosin A (**14**) with tannase, respectively. Other tannins as follows were of natural origin: (i) galloylglucoses; 1,2,3,6-tetra-*O*-galloyl-*β*-D-glucose (**2**),[13a] 1,2,3-tri-*O*-galloyl-*β*-D-glucose (**4**),[13b] 1,2,6-tri-*O*-galloyl-*β*-D-glucose (**5**),[13b] 1,3,6-tri-*O*-galloyl-*β*-D-glucose (**6**),[13c] (ii) monomeric ellagitannins; casuarictin (**7**),[13d] rugosin C (**8**),[13b] praecoxin C (**9**),[13e] potentillin (**10**),[1a] agrimonic acid A (**11**),[13f] sanguiin H-4 (**12**),[1d] tellimagrandin II (**13**),[13g] rugosin A (**14**),[13b] isoterchebin (**15**),[13g] strictinin (**16**),[13d] pedunculagin (**19**),[13d] gemin F (**20**),[13h] tellimagrandin I (**21**),[13d] gemin D (**22**),[1d] (iii) dimeric ellagitannins; agrimoniin (**24**),[1a] rugosin D (**25**),[1c] coriariin A (**26**),[1h] gemin A (**27**),[1b] gemin B (**28**),[1d] gemin C (**29**),[1d] rugosin F (**30**).[1c]

Measurements of ^{13}C-NMR Spectra——Pulse Fourier-transform (FT) NMR spectra were recorded on a JEOL FX-200 spectrometer operating at 50.1 MHz. The chemical shifts are given in δ values (ppm) downfield from tetramethylsilane (TMS) as an internal standard. Unless otherwise stated, the spectra were measured in acetone-d_6, a solvent sufficiently polar for dissolving a wide range of hydrolyzable tannins and related polyphenols. FT-NMR spectra were recorded under the following conditions: spectral width, 12004 Hz; pulse flipping angle, 80 °; acquisition time, 1 s; pulse repetition, 1.5 s; number of data points, 16 K.

Results and Discussion

The C-1 and C-6 signals of glucose in tannins have been easily assigned on the basis of the chemical shifts and multiplicities in the single frequency off-resonance decoupling spectrum except for the C-1 peak of C-glucosidic hydrolyzable tannins.[5b] Definite assignments of the C-2—C-5 resonances have been accomplished by the {^{1}H}-^{13}C single frequency selective decoupling (PSD) technique on a high resolution FT-NMR instrument which provide a fairly well-resolved signal of each proton of the glucose moiety in ^{1}H-NMR measurement (200 MHz).

Galloylglucoses

The ^{13}C chemical shifts of glucose carbons in the positional isomers, (**2**—**6**), of tetra- and trigalloylglucoses are listed in Table I. Based on these data, galloylation shifts at each position on the glucopyranose ring were calculated, and the results are summarized in Table II. The trends of these shifts are analogous to those of other acylsugars. Thus, galloylation produces a downfield shifts of the signal of the α-carbon and an upfield shift for the β-carbon(s), whereas the γ- and δ-carbons exhibit only small shifts. These results indicate the applicability of the general acylation shift rule to the series of polygalloylated glucoses, although the shift values are variable depending on the position of the galloyl group. The unusual upfield shift of C_α

TABLE I. ^{13}C Resonances of the Glucose Moiety in Hydrolyzable Tannins (50.1 MHz, δ from TMS in Acetone-d_6)

Compound	Carbon number					
	C-1	C-2	C-3	C-4	C-5	C-6
Galloylglucoses						
1,2,3,4,6-Penta-*O*-galloyl-glu[a] (**1**)	93.4	71.9	73.5	69.5	74.1	62.9
1,2,3,6-Tetra-*O*-galloyl-glu (**2**)[b]	93.5	71.9	76.0	69.5	76.1	63.7
1,2,4,6-Tetra-*O*-galloyl-glu (**3**)[c]	93.4	73.8	73.3	71.7	74.0	63.1
1,2,3-Tri-*O*-galloyl-glu (**4**)	94.2	72.5	76.7	69.8	79.2	62.4
1,2,6-Tri-*O*-galloyl-glu (**5**)[b]	93.6	73.9	75.5	71.2	76.0	64.0
1,3,6-Tri-*O*-galloyl-glu (**6**)[b]	95.6	72.3	78.8	69.4	75.8	64.0
Monomeric ellagitannins						
Casuarictin (**7**)[b]	92.4	76.0	77.3	69.3	73.5	63.1
Rugosin C (**8**)	92.8	76.4	77.6	69.8	74.0	63.5
Praecoxin C (**9**)	92.9	76.4	77.5	69.9	73.9	64.5
Potentillin (**10**)[b]	90.7	74.1	76.0	69.1	71.0	63.2
Agrimonic acid A (**11**)	91.7	75.0	76.9	69.9	73.8	64.1
Sanguiin H-4 (**12**)[c,d]	91.4	74.5	79.1	68.0	76.6	61.8
Tellimagrandin II (**13**)[b]	93.8	71.8	73.3	70.8	73.1	63.1
Rugosin A (**14**)	94.2	72.2	73.6	71.2	73.6	63.6
Isoterchebin (**15**)[b]	92.9	71.1	72.9	73.4	69.2	65.9
Strictinin (**16**)[b]	95.9	74.7	75.6	72.8	73.2	63.7

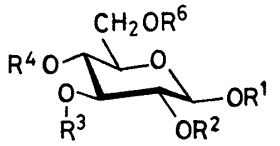
a) glu; β-D-glucopyranose.
b) Assignments were confirmed by selective decoupling experiments.
c) Data taken from ref. 1*f*, presented without assigning each carbon signal. Assignments were made in the present study.
d) Measured in MeOH-d_4.

TABLE II. Galloylation Shifts[a] for D-Glucopyranose ($^4C_1$) Gallates

Entry	Compound	Galloylation position	Carbon number					
			C-1	C-2	C-3	C-4	C-5	C-6
1	**6** → **2**	2	−2.1	−0.4	−2.8			
2	**5** → **2**	3		−2.0	+0.5	−1.7		
3	**5** → **4**	3		−1.4	+1.2	−1.4		
4	**3** → **1**	3		−1.9	+0.2	−2.2		
5	**2** → **1**	4			−2.5	0	−2.0	
6	**5** → **3**	4			−2.2	+0.5	−2.0	
7	**4** → **2**	6					−3.1	+1.3

a) Calculated as $\delta_{(gallate)} - \delta_{(alcohol)}$; downfield shift is indicated by a positive value.

observed upon going from **6** to **2** is analogous to that reported for methyl 2-*O*-myristoyl-β-D-glucoside[6d] and polyacetylated glucoses.[14] Since the preferred $^4C_1$ conformation of the glucopyranose ring is retained in both compounds, as revealed by their ^1H-NMR spectra, this anomaly induced by the acylation at C-2 of glucose may be interpreted, as discussed for methyl 2-*O*-myristoyl-β-D-glucose,[6d] in terms of conformational difference of ester groups which are on C-2 and the other positions. Differences in the shift values of C_α on galloylation at the same position [entries 2—4 (at C-3) and entries 5 and 6 (at C-4) in Table II] can be attributed to different degrees of upfield shift caused by changes in the interactions with adjacent substituents.



	R^1	R^2	R^3	R^4	R^6
1	G	G	G	G	G
2	G	G	G	H	G
3	G	G	H	G	G
4	G	G	G	H	H
5	G	G	H	H	G
6	G	H	G	H	G

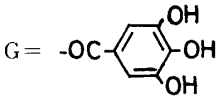


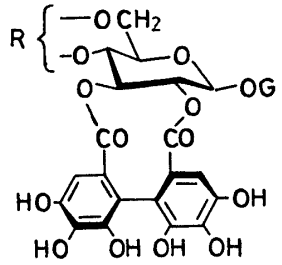
Chart 1

The ^{13}C chemical shifts calculated for 4-*O*- and 6-*O*-galloylation of 1,2,3-tri-*O*-galloyl-*β*-D-glucose (**4**) using mean values of the data in Table II are in agreement with those observed for penta-*O*-galloyl-*β*-D-glucose (**1**). This result indicates that these galloylation shift values are useful as additive parameters for assigning the position of the galloyl group(s) in hydrolyzable tannins in which glucose adopts the $^4C_1$ conformation.

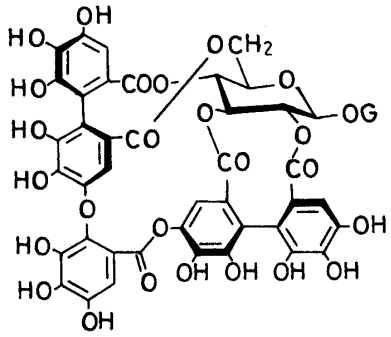
Ellagitannins

The ^{13}C-NMR analyses were then extended to ellagitannins which possess the D-glucopyranose residue adopting the $^4C_1$ conformation, as in the case of galloylglucoses. Amongst the hydrolyzable tannins, ellagitannins of this class are most widely distributed in the plant kingdom. However, unequivocal full assignments of the ^{13}C resonances due to glucose carbons of these tannins have not appeared in the literature, although tentative assignments for some ellagitannins in which D-glucose is fully acylated were reported.[1e-g] The reported assignments are based on the sequence of the ^{13}C signals for penta-*O*-galloyl-*β*-D-glucose (**1**). For example, Haslam *et al.*[1g] made the following assignments for casuarictin (**7**) in acetone-d_6: C-1 (92.1), C-2 (73.4), C-3 (77.2), C-4 (69.2), C-5 (77.2) and C-6 (63.1). In order to examine the validity of this assigning method, firstly PSD experiments for **7**, **13** and **15** were attempted. The results, as shown in Tables I and III, revealed that the sequences of the individual signals of glucose residue differed from each other, reflecting the differences of the polyphenol (galloyl, HHDP and DHHDP) groups, and none of them was in accord with that of penta-*O*-galloyl-*β*-D-glucose (**1**).

On the other hand, in the ^{13}C-NMR spectra of **8** and **9**, which are structurally related to **7**, the signals due to glucose carbons coincided (with variance of within 0.6 ppm) with those of **7**, thus leading to the straightforward assignments of **8** and **9** as in Table I. The data for **10** and **13** similarly permitted the assignments of the spectra of the related tannins, **11** and **14**, respectively. These data suggest that replacement of the HHDP group by a valoneoyl group at C-4 and C-6 of D-glucopyranose does not disturb the relative position of each resonance of glucose carbons, and that an analogous correlation is present with the galloyl group and the dehydrodigalloyl (DHDG) group at C-1. The differences of chemical shifts between **7** and its α-anomer (**10**) are in accord with the well-documented shifts for α- and *β*-anomers of D-glucose and methyl glucoside.[15] Thus, no significant difference of shift is observed between the two



7 : R=(S)-HHDP
8 : R=(S)-valoneoyl



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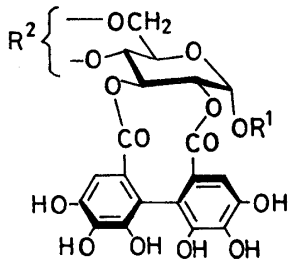
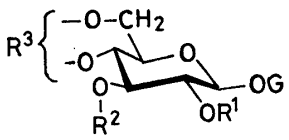
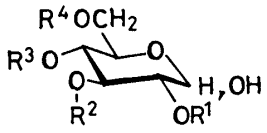
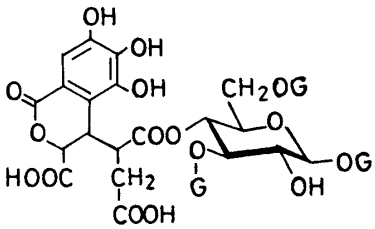


10 : R^1=G, R^2=(S)-HHDP
11 : R^1=DHDG, R^2=(S)-HHDP
12 : R^1=G, R^2=H, H



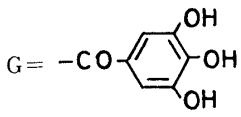
	R^1	R^2	R^3
13	G	G	(S)-HHDP
14	G	G	(S)-valoneoyl
15	G	G	(S)-DHHDP
16	H	H	(S)-HHDP



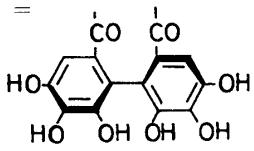


17

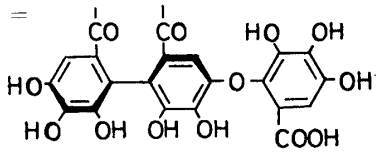
18 : R^1–R^2=(S)-HHDP, R^3=R^4=H
19 : R^1–R^2=(S)-HHDP, R^3–R^4=(S)-HHDP
20 : R^1–R^2=(S)-HHDP, R^3=H, R^4=caffeoyl
21 : R^1=R^2=G, R^3–R^4=(S)-HHDP
22 : R^1=H, R^2=G, R^3–R^4=(S)-HHDP
23 : R^1=R^2=H, R^3–R^4=(S)-valoneoyl



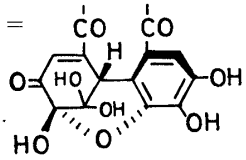
(S)-HHDP



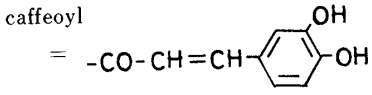
(S)-valoneoyl



(S)-DHHDP



caffeoyl



DHDG

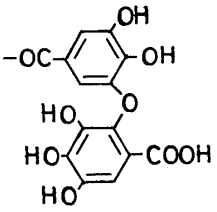


Chart 2

TABLE III. Relative Positions of the ^{13}C Resonances of the ($^4C_1$) Glucose Residue in Hydrolyzable Tannins Having Different Acyl Groups

Compound	Sequence of carbon signals
	Lower field ←
1	C-1 ← C-5 ← C-3 ← C-2 ← C-4 ← C-6
7	C-1 ← C-3 ← C-2 ← C-5 ← C-4 ← C-6
13	C-1 ← C-3 ← C-5 ← C-2 ← C-4 ← C-6
15	C-1 ← C-4 ← C-3 ← C-2 ← C-5 ← C-6

TABLE IV. Hexahydroxydiphenoylation Shifts for Ellagitannins

Compound	HHDP[a] position	Carbon number					
		C-1	C-2	C-3	C-4	C-5	C-6
16 → **7**	2, 3	−3.5	+1.3	+1.7	−3.5		
4 → **13**	4, 6			−3.4	+1.0	−6.1	+0.7
12 → **10**	4, 6			−3.1	+1.1	−5.6	+1.4

a) HHDP: hexahydroxydiphenoyl.

anomers for the peaks of C-4 and C-6, which are remote from the anomeric center, and the remaining peaks (C-1—3 and C-5) of **10** exhibit upfield shifts from those of **7**, due to the increase in steric crowding caused by the change of orientation of the anomeric acyl group from equatorial to axial. The changes of the chemical shifts upon esterification of the hydroxyl group with HHDP were estimated by comparisons of the data for **16** and **12** with those for **7** and **10**, respectively. The hexahydroxydiphenoylation shifts thus obtained are listed in Table IV.

Additivity was also observed for the dual β-effects on the chemical shift of C-5 upon hexahydroxydiphenoylation at C-4 and C-6 of the glucopyranose ring (Table IV). Comparisons of roughly estimated shifts due to galloylation and hexahydroxydiphenoylation show that the shifts of both C_α and C_β in the latter are slightly larger, and show smaller deviations for acylation at different positions, than those in the former. These differences may be attributable to the steric (rigid) and electronic characteristics of the HHDP ester bridge. It was expected that significant differences between the effect on the β-carbon (C-1, −2.0 ppm) induced by galloylation at C-2 and that (−3.5 ppm) induced by hexahydroxydiphenoylation at C-2 and C-3 would lead to a diagnostic C-1 chemical shift which should be useful in distinguishing the substituent at C-2. In fact, as shown in Table V, the position of the anomeric carbon signal was sensitive to differences of substituents and substitution mode at C-1 and C-2, although an exception was found for **15**. In the case of hydrolyzable tannins which have a free anomeric hydroxyl group and form a mixture of α- and β-anomers, the difference ($\Delta\delta^{\beta\alpha}$) between the chemical shifts of the α- and β-anomeric carbon signals can be used for evaluating the substituent at C-2. It is noteworthy that these diagnostic values are independent of the substituents at C-3—C-6. These findings seem to provide a basis for facile assignment of the structures of newly isolated tannins of this class, since the ^{13}C resonance of the anomeric carbon is assigned most easily without the need for any complex technique.

Comparison of **4** with **15** provides dehydrohexahydroxydiphenoylation shift values (C-3, −3.8 ppm; C-4, +3.6 ppm; C-5, −10 ppm; C-6, +3.5 ppm). However, since **15** is the sole example so far of a tannin which has a DHHDP group attached to glucose with $^4C_1$ conformation, the generality of these values will need to be confirmed by studies of further examples.

Dimeric Hydrolyzable Tannins

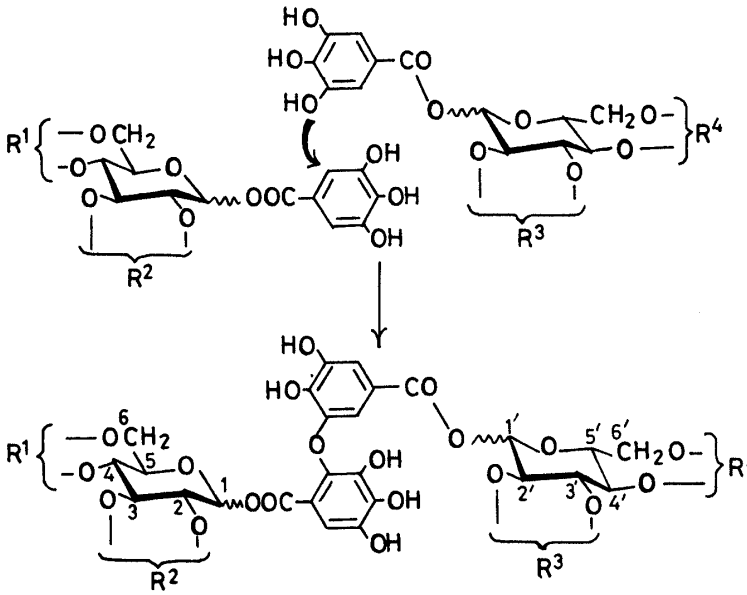
Since most of the known dimeric hydrolyzable tannins isolated to date have the glucose core in the $^4C_1$ conformation, the ^{13}C-NMR analyses described above were further extended to the dimers. Although great difficulties are usually encountered in direct assignment of the glucose moieties of dimers by the PSD technique, because of the complexity of the ^1H-NMR spectra, the individual glucose carbon signals have been found to be assignable on the basis of the ^{13}C-NMR data for monomeric units. The ^{13}C-NMR of **24** which is biogenetically

TABLE V. The Anomeric Carbon Resonances for Various Substitution Modes at C-1 and C-2 of Glucopyranose ($^4C_1$)

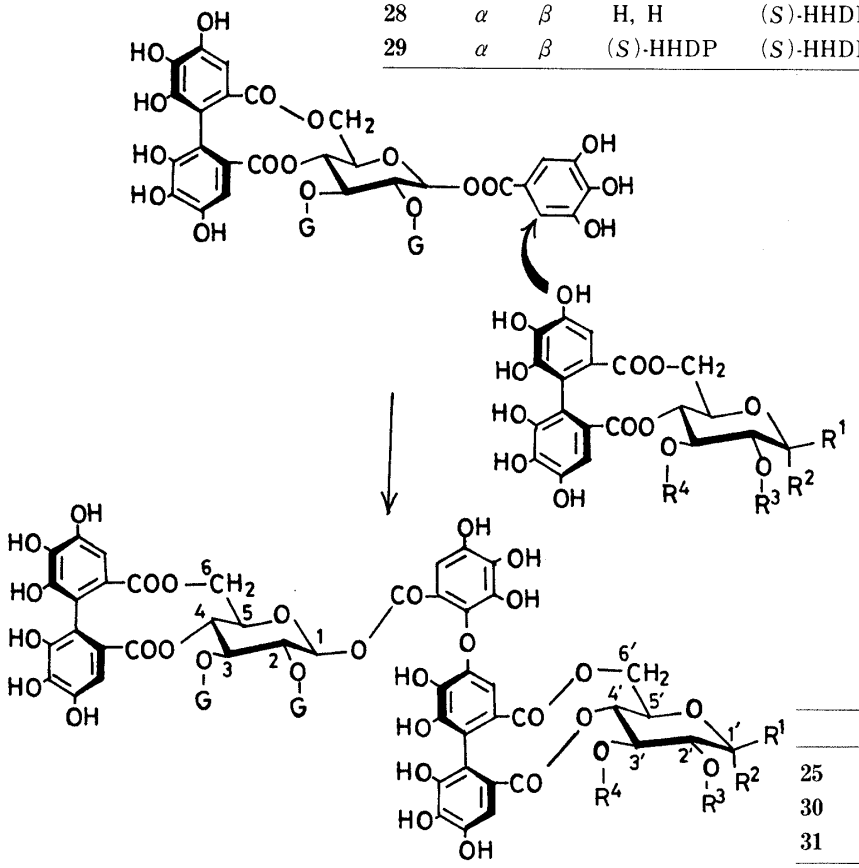
Compound	Substituent					δ_{C-1}	Diagnostic value of δ_{C-1}
	O-1	O-2	O-3	O-4	O-6		
6	G[a](β)	H	G	H	G	95.6	
16	G(β)	H	H	(*S*)-HHDP[b]		95.9	95.0—96.0
17	G(β)	H	G	Cheb[c]	G	95.1[d]	
1	G(β)	G	G	G	G	93.4	
2	G(β)	G	G	H	G	93.5	
3	G(β)	G	H	G	G	93.4	
4	G(β)	G	G	H	H	94.2	93.4—94.3
5	G(β)	G	H	H	G	93.6	
13	G(β)	G	G	(*S*)-HHDP		93.8	
14	G(β)	G	G	(*S*)-Valoneoyl		94.2	
15	G(β)	G	G	(*S*)-DHHDP[e]		92.9	
7	G(β)	(*S*)-HHDP		(*S*)-HHDP		92.4	
8	G(β)	(*S*)-HHDP		(*S*)-Valoneoyl		92.8	92.4—92.9
9	G(β)	(*S*)-HHDP		(*S*)-Valoneoyl		92.9	
10	G(α)	(*S*)-HHDP		(*S*)-HHDP		90.7	
11	DHDG[f](α)	(*S*)-HHDP		(*S*)-HHDP		91.7	90.7—91.7
12	G(α)	(*S*)-HHDP		H	H	91.4	
2,3-HHDP-glu[g] (**18**)	H	(*S*)-HHDP		H	H	95.3(β) 91.9(α)	
Pedunculagin (**19**)	H	(*S*)-HHDP		(*S*)-HHDP		95.6(β) 92.2(α)	$\Delta\delta^{\beta\alpha}$ 3.4—3.7[h]
Gemin F (**20**)	H	(*S*)-HHDP		H	Caffeoyl	95.4(β) 92.0(α)	
Tellimagrandin I (**21**)	H	G	G	(*S*)-HHDP		97.2(β) 91.9(α)	$\Delta\delta^{\beta\alpha}$ *ca.* 5.3
Gemin D (**22**)	H	H	G	(*S*)-HHDP		99.2(β) 94.5(α)	$\Delta\delta^{\beta\alpha}$
4,6-Valoneoyl-glu (**23**)	H	H	H	(*S*)-Valoneoyl		99.1(β) 94.1(α)	4.7—5.0

a) G: galloyl. *b*) HHDP: hexahydroxydiphenoyl. *c*) Cheb: chebuloyl.
d) Data taken from ref. 1*f*. *e*) DHHDP: dehydrohexahydroxydiphenoyl.
f) DHDG: dehydrodigalloyl. *g*) Glu: D-glucopyranose.
h) Calculated as $\delta_{C-1}^{\beta\text{-anomer}} - \delta_{C-1}^{\alpha\text{-anomer}}$.

producible by intermolecular C–O oxidative coupling[1g,16] between galloyl groups at C-1 of **10**, exhibited glucose carbon signals corresponding to those of **10** (Chart 3, Table VI). Upon comparisons of **25** and **26** with their monomeric unit **13**, an analogous correlation of the ^{13}C chemical shifts was also observed. The dimers, **27**—**30**, in contrast to **24** and **25**, are regarded as the products of different monomeric precursors (**27** from **10** and **13**; **28** from **12** and **13**; **29** from **10** and **4**; **30** from **7** and **13**), and the shifts of glucose carbon signals of these dimers were also found to correspond to those of the respective monomeric precursors. Assignment of the glucose carbons of **27** was confirmed by means of PSD experiments, and therefore it was substantiated that the glucose carbons in dimers of this type can be completely assigned based on the corresponding carbon peaks in the monomers.



	configuration C-1	C-1′	R^1	R^2	R^3	R^4
24	α	α	(S)-HHDP	(S)-HHDP	(S)-HHDP	(S)-HHDP
26	β	β	(S)-HHDP	G, G	G, G	(S)-HHDP
27	α	β	(S)-HHDP	(S)-HHDP	G, G	(S)-HHDP
28	α	β	H, H	(S)-HHDP	G, G	(S)-HHDP
29	α	β	(S)-HHDP	(S)-HHDP	G, G	H, H



	R^1	R^2	R^3	R^4
25	O-G	H	G	G
30	O-G	H	(S)-HHDP	
31	H, OH		G	G

Chart 3

Initially it was suspected that application of this method to dimers which have free anomeric hydroxyl group(s) in the molecule might be difficult, as such dimers give complicated paired signals arising from the α- and β-anomers of glucopyranose. However, the diagnostic

TABLE VI. ^{13}C Resonances of the Glucose Moiety in Dimeric Hydrolyzable Tannins (50.1 MHz, δ from TMS in Acetone-d_6)

Compound	Carbon number											
	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
Agrimoniin (**24**)[a]	91.5[b]	75.1	76.5[c]	69.7[d]	71.5	63.8	91.9[b]	75.1	76.7[c]	69.3[d]	71.5	63.8
Rugosin D (**25**)	94.2[b]	72.4	73.9[c]	71.2	73.6[d]	63.7	93.9[b]	72.4	73.8[c]	71.2	73.5[d]	63.7
Coriariin A (**26**)	93.1[b]	71.7	73.5	70.8	72.8	63.3	93.6[b]	71.7	73.5	70.8	72.8	63.3
Gemin A (**27**)[e]	90.6	74.1	75.9	68.9	71.2	63.1	93.9	71.5	73.1	70.6	73.1	63.0
Gemin B (**28**)[a]	91.3	74.5	79.1	67.6	76.3	61.5	94.4	72.2	74.0	71.3	73.6	63.7
Gemin C (**29**)	90.8	74.3	76.0[b]	69.1	71.4	63.2	93.6	71.8	76.1[b]	69.1	78.5	61.7
Rugosin F (**30**)	93.4	71.9	73.5	70.7	73.1	63.2	92.3	75.9	77.2	69.3	73.5	63.2

a) Measured in MeOH-d_4.
b—*d*) Values with the same superscript in each row are interchangeable.
e) Assignments were confirmed by selective decoupling experiments.

^{13}C chemical shifts for anomeric carbons and $\Delta\delta^{\beta\alpha}$ values in Table V are useful for this type of dimers, assisting a partial structural assignment. For example, the dimer **31**[1c] which contains an HHDP, a valoneoyl and four galloyl groups attached to the two $^4C_1$ glucose cores, exhibited three anomeric carbon signals at δ 96.6, 93.3 and 91.2, among which the peak at δ 93.3 (of highest intensity) is characteristic of tannins possessing the β-*O*-galloyl group or its equivalent at C-1, and also a galloyl group at C-2 as in **13** and **25**. The $\Delta\delta^{\beta\alpha}$ value (5.4 ppm) between the α- and β-anomeric carbon signals (δ 96.6 and 91.2) suggests the presence of a galloyl, but not an HHDP group at C-2′ (see Table V), leading immediately to a tentative structure **31**.

As there can be variation in the composition and coupling mode of the monomers, further new oligomeric hydrolyzable tannins may be found in nature. The data presented in this study, combined with the application of general empirical rules relating to the CD spectrum, are expected to be valuable aids in the assignments of new hydrolyzable tannins.

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References and Notes

1) *a*) T. Okuda, T. Yoshida, M. Kuwahara, M. U. Memon, and T. Shingu, *J. Chem. Soc., Chem. Commun.*, **1982**, 163; *b*) T. Yoshida, T. Okuda, M. U. Memon, and T. Shingu, *J. Chem. Soc., Chem. Commun.*, **1982**, 351; *c*) T. Okuda, T. Hatano, and N. Ogawa, *Chem. Pharm. Bull.*, **30**, 4234 (1982); *d*) T. Yoshida, Y. Maruyama, T. Okuda, M. U. Memon, and T. Shingu, *Chem. Pharm. Bull.*, **30**, 4245 (1982); *e*) G. Nonaka, T. Tanaka, and I. Nishioka, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 1067; *f*) R. K. Gupta, S. M. K. Al-Shafi, K. Layden, and E. Haslam, *J. Chem. Soc., Perkin Trans.1*, **1982**, 2525; *g*) E. Haslam, *Fortschr. Chem. Org. Naturst.*, **41**, 1 (1982); *h*) T. Okuda, T. Hatano, and S. Hattori, the 103rd Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, April 1983.
2) T. Okuda, T. Yoshida, T. Hatano, T. Koga, N. Toh, and K. Kuriyama, *Tetrahedron Lett.*, **23**, 3937, 3941 (1982).
3) T. Yoshida and T. Okuda, *Heterocycles*, **14**, 1743 (1980).
4) *a*) M. Nishizawa, T. Yamagishi, G. Nonaka, and I. Nishioka, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 2963; *b*) *Idem, ibid.*, **1983**, 961.
5) *a*) T. Yoshida, K. Seno, Y. Takama, and T. Okuda, *Phytochemistry*, **21**, 1180 (1982); *b*) T. Okuda, T. Yoshida, M. Ashida, and K. Yazaki, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1765.
6) For example, *a*) D. E. Dorman, D. Bauer, and J. D. Roberts, *J. Org. Chem.*, **40**, 3729 (1975); *b*) Y. Terui, K. Tori, and N. Tsuji, *Tetrahedron Lett.*, **1976**, 621; *c*) K. Yoshimoto, Y. Itatani, K. Shibata, and Y. Tsuda, *Chem. Pharm. Bull.*, **28**, 208 (1980); *d*) *Idem, ibid.*, **28**, 2065 (1980).

7) For example, *a*) R. Kasai, M. Suzuo, J. Asakawa, and O. Tanaka, *Tetrahedron Lett.*, **1977**, 175; *b*) S. Seo, Y. Tomita, K. Tori, and Y. Yoshimura, *J. Am. Chem. Soc.*, **100**, 3331 (1978).
8) D. E. Dorman, S. J. Angyal, and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 1351 (1970).
9) M. Kuroyanagi, M. Fukuoka, K. Yoshihara, S. Natori, and K. Yamazaki, *Chem. Pharm. Bull.*, **26**, 3594 (1978), and references cited therein.
10) For example, K. Yamazaki, R. Kasai, Y. Masaki, M. Okihara, and O. Tanaka, *Tetrahedron Lett.*, **1977**, 1231.
11) R. K. Chaudhuri, F. U. Afifi-Yazar, and O. Sticher, *Tetrahedron*, **36**, 2317 (1980), and references cited therein.
12) S. W. Pelletier, Z. Djarmati, and C. Page, *Tetrahedron*, **32**, 995 (1976).
13) *a*) T. Okuda, T. Hatano, N. Ogawa, and R. Kira, Unpublished data; *b*) T. Okuda, T. Hatano, K. Yazaki, and N. Ogawa, *Chem. Pharm.* Bull., **30**, 4230 (1982); *c*) T. Okuda, T. Hatano, H. Nitta, and R. Fujii, *Tetrahedron Lett.*, **21**, 4361 (1980); *d*) T. Okuda, T. Yoshida, and M. Ashida, *Heterocycles*, **16**, 1681 (1981); *e*) T. Okuda, T. Hatano, and K. Yazaki, *Chem. Pharm. Bull.*, **31**, 333 (1983); *f*) T. Yoshida, M. Kuwahara, and T. Okuda, the 102nd Annual Meeting of the Pharmaceutical Society of Japan, Osaka, April 1982; *g*) T. Okuda, T. Hatano, and T. Yasui, *Heterocycles*, **16**, 1321 (1981); *h*) T. Yoshida, T. Okuda, M. U. Memon, and T. Shingu, the 103rd Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, April 1983.
14) H. Komura, A. Matsuno, and Y. Ishido, *Carbohydr. Res.*, **65**, 271 (1978).
15) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, 1972, p. 461.
16) O. T. Schmidt and W. Mayer, *Angew. Chem.*, **68**, 103 (1956).