Tannins and Related Compounds. Part 37.[1] Isolation and Structure Elucidation of Elaeocarpusin, a Novel Ellagitannin from *Elaeocarpus sylvestris* var. *Ellipticus*

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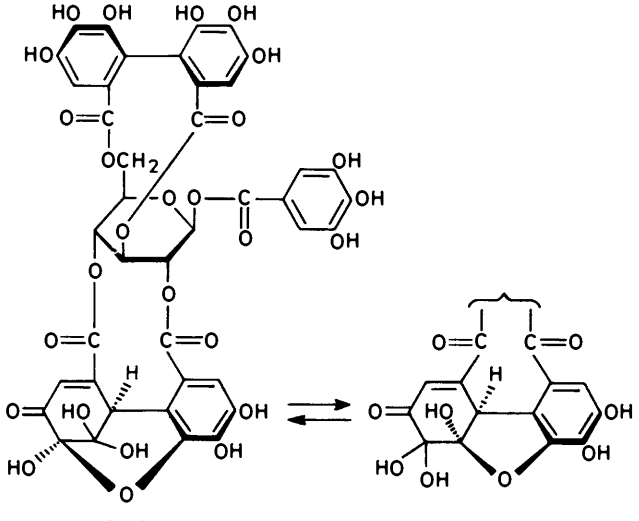
A new hydrolysable tannin, elaeocarpusin, isolated from the leaves of *Elaeocarpus sylvestris* var. *Ellipticus*, has been characterized on the basis of chemical, spectroscopic, and *X*-ray analyses to be a novel ellagitannin in which a unique acid ester group probably derived by a condensation of a hexahydroxydiphenoyl group and dehydroascorbic acid is attached to the 2,4-positions of 1-*O*-galloyl-3,6-(*R*)-hexahydroxydiphenoyl-D-glucopyranose (corilagin). This structural feature suggests the possibility of the participation of dehydroascorbic acid as a co-enzyme in oxidative metabolism of the hexahydroxydiphenoyl group to the corresponding dehydro group.

Structural work on hydrolysable tannins has shown that ellagitannins are derived biosynthetically from gallotannins by oxidative carbon-to-carbon coupling of two appropriately positioned galloyl ester groups attached to the polyalcohol (mostly D-glucopyranose) moiety, and that the 4,4',5,5',6,6'-hexahydroxydiphenoyl ester group(s) in ellagitannins is frequently transformed by oxidation of one of the aromatic rings to a dehydrohexahydroxydiphenoyl ester group(s).[2] A relatively smaller group of the metabolites possessing this dehydrohexahydroxydiphenoyl ester group(s) is distributed rather widely in the plant kingdom. In particular, geraniin (**1**),[3] one of the



(**1a**) (**1b**)

ellagitannins of this class, occurs in various members of the Geraniaceae,[4,5] Euphorbiaceae,[4] Aceraceae,[5] Cercidiphyllaceae,[5] and Simaroubaceae families,[5] *etc.*[5] This characteristic ellagitannin is supposed to be produced enzymatically *via* dehydrogenation of the hexahydroxydiphenoyl group† of 1-*O*-galloyl-2,4;3,6-bis[(*R*)-hexahydroxydiphenoyl]-β-D-glucose (**2**),[2] although details of the dehydrogenation process are still obscure. In the course of a search for medicinally important tannins in plants, we have encountered large accumulations of geraniin (**1**) and a structurally unknown ellagitannin (**3**) in the leaves of *Elaeocarpus sylvestris* var. *Ellipticus* (Elaeocarpaceae) which is regarded as a rich source of tannins, and is utilized as a dyeing agent in southern Japan. The ellagitannin (**3**), for which we propose the trivial name elaeocarpusin, appears to be a key intermediate in the biosynthesis of geraniin (**1**) from the ellagitannin (**2**), and we now report its isolation and structural elucidation in detail.

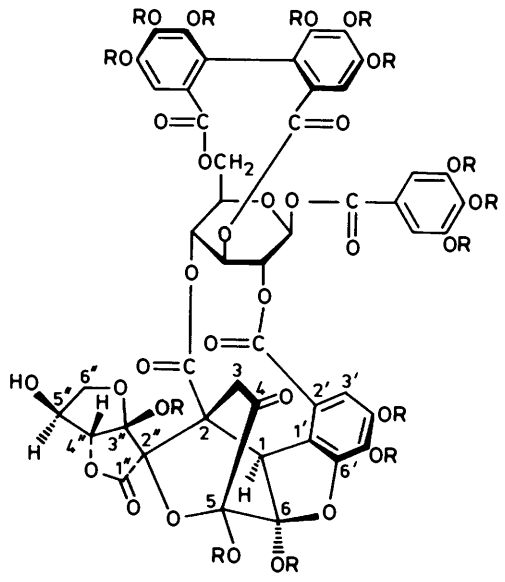
† Throughout this refers to hexahydroxy biphenyl-2,2'-dicarbonyl group.

Results and Discussion

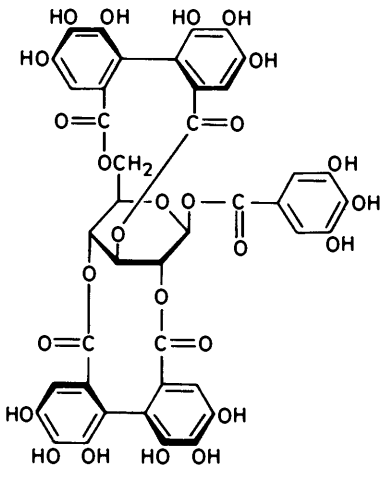
Chromatography of the aqueous acetone extract on Sephadex LH-20 and highly porous polystyrene gel (MCI-gel CHP-20P) with various solvent systems as outlined in previous papers[6] afforded geraniin (**1**) and the new tannin, elaeocarpusin (**3**) in remarkably high yields (*ca.* 2% each from the fresh leaves). In addition, these tannins were accompanied by simple gallic acid esters in lower concentrations: these were identified as 1-*O*-galloyl-β-D-glucose (β-glucogallin) (**4**)[7] and methyl 6-*O*-galloyl-β-D-glucopyranoside (**5**)[8] by comparisons of their physical and spectral data with those of authentic samples.

Elaeocarpusin (**3**) was characterized as an ellagitannin by the brown colouration it gave with nitrous acid,[9] and by examination of its ^{1}H and ^{13}C n.m.r. spectra which clearly revealed the presence of 4,4',5,5',6,6'-hexahydroxydiphenoyl and galloyl ester groups and a carbohydrate moiety (see Table 1). In the ^{1}H n.m.r. spectrum, the sugar 1-H was unusually deshielded by esterification, the chemical shift (δ 6.51) being in close agreement with that of geraniin (**1**) (δ 6.56). The pattern of the equally smaller coupling constants (≈4 Hz) for the sugar protons was also similar to that observed in geraniin (**1**).

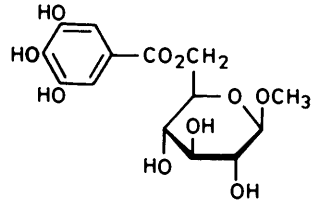
In solution, elaeocarpusin (**3**) was extremely unstable, and gradually formed a yellow substance. Since elaeocarpusin itself is almost colourless, this colouring suggested the formation of a new conjugation system in the molecule. The yellow compound, obtained in a high yield when an aqueous solution of elaeocarpusin was heated (90 °C, 1 h), was found to be identical with geraniin (**1**). Although geraniin (**1**) has been shown to exist in solution as an equilibrium mixture of hydrated six- and five-membered hemiacetal forms (**1a**) and (**1b**),[3] ^{1}H and ^{13}C n.m.r. analyses indicated that such an equilibrium was absent in elaeocarpusin (**3**). These observations, in conjunction with the absence of ^{1}H and ^{13}C n.m.r. resonances for an olefinic group conjugated with a carbonyl function, suggested that elaeocarpusin (**3**) possesses a rigid phenylcyclohexanone moiety easily convertible into the dehydrohexahydroxydiphenoyl group.



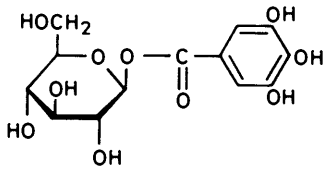
(3) R = H
(6) R = Me



(2)



(5)



(4)

Table 1. ^{13}C N.m.r. characteristics of elaeocarpusin (3): δ values in p.p.m. from $SiMe_4$ in CD_3COCD_3

Glucose	C-1	92.4	Hexahydroxydiphenoyl	C-1,1′	116.5		
	C-2	68.8			116.7		
	C-3	74.4		C-2,2′	123.1		
	C-4	63.5			125.0		
	C-5	74.4		C-3,3′	109.3		
	C-6	64.4			110.1		
				C-4,4′	144.7		
Galloyl	C-1	120.3			144.9		
	C-2	110.5		C-5,5′	137.4		
	C-3	146.1			137.5		
	C-4	139.7		C-6,6′	145.1		
	C-5	146.1			145.4		
	C-6	110.5					
2,4-Acyl group	C-1	51.8	C-1′	116.1	C-1″	170.7	
	C-2	49.8	C-2′	118.5	C-2″	80.7	
	C-3	38.0	C-3′	114.1	C-3″	109.1	
	C-4	197.7	C-4′	147.6	C-4″	89.4	
	C-5	96.3	C-5′	136.2	C-5″	73.7	
	C-6	108.1	C-6′	148.6	C-6″	76.5	

A molecular weight determination (3) by means of mass spectrometry (field-desorption and fast atom bombardment) for elaeocarpusin proved impossible because of facile decomposition, but the methyl ether (6) prepared by ordinary phenol methylation, showed an intense molecular ion peak at *m/z* 1 306 in the field-desorption mass spectrum. Taking the molecular weight (1 148) of a geraniin methyl ether into account, the molecular mass of 1 306 indicated that a relatively bulky group is attached to the phenylcyclohexanone moiety.

Hydrolysis of the methyl ether (6) in alkaline solution, followed by methylation with diazomethane, afforded a colourless crystalline hydrolysate (7), together with methyl 3,4,5-trimethoxybenzoate (8) and dimethyl (*R*)-4,4′,5,5′,6,6′-hexamethoxydiphenoate (9). The molecular formula of $C_{27}H_{30}O_{16}$ for compound (7), obtained by a combination of elemental analysis and electron impact mass spectrometry (M^+, *m/z* 610), was in agreement with the carbon and hydrogen atom numbers as deduced from the respective ^{13}C and ^1H n.m.r. spectra. A precise examination of the ^{13}C n.m.r. spectrum of the compound (7) showed, together with a penta-substituted aromatic ring and seven methoxy groups including two methoxycarbonyls, the presence of three acetal carbons (δ 99.5, 112.1, and 118.4), two of which were assumed to be correlated with those existing in geraniin (1). A carbonyl and benzylic methine signal appeared at δ 197.6 and 49.0, respectively, the chemical shifts being similar to those observed in geraniin: (1a), δ 191.8, 46.2; (1b), 194.8, 51.9. Other distinctive features were the observations of four oxygen-carrying carbon signals, which were characterized as a methylene (δ 76.3), methine (δ 72.9 and 83.3), and a quaternary carbon (δ 80.3) on the basis of a proton off-resonance measurement.

The presence of one hydroxy group in compound (7) was confirmed by acetylation which afforded the monoacetate (10). Comparison of the ^{13}C n.m.r. spectra of the acetate (10) and compound (7) showed that on acetylation the methine signal at δ 72.9 was shifted downfield by 1.7 p.p.m., while the methylene signal at δ 76.3 and the methine at δ 88.3 were shifted upfield

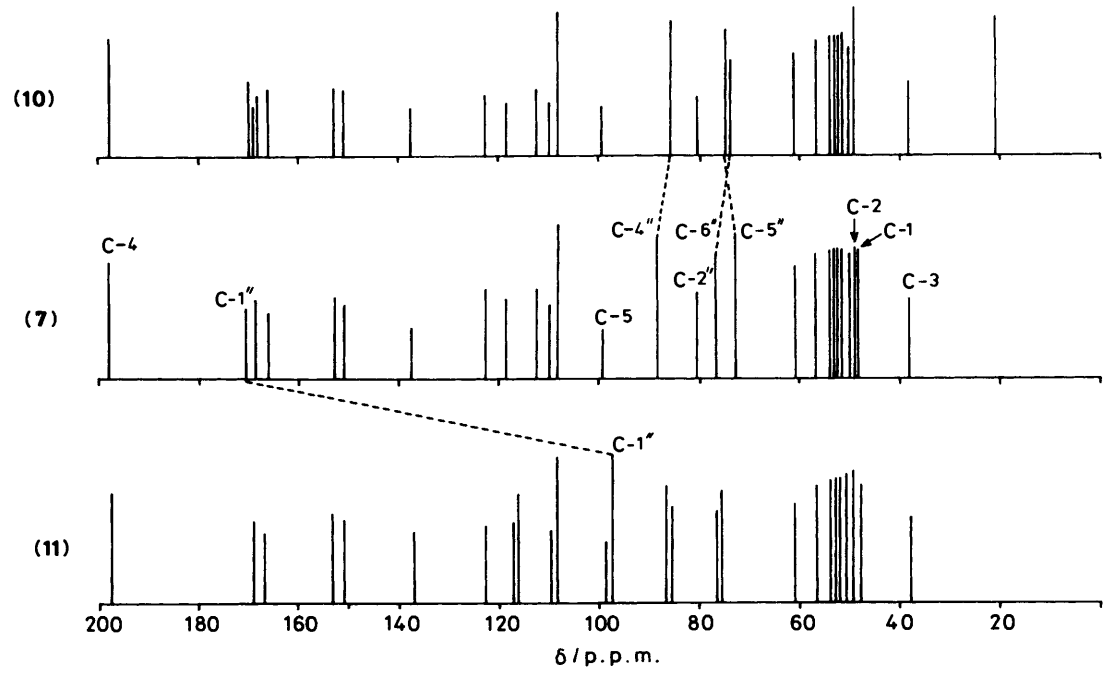
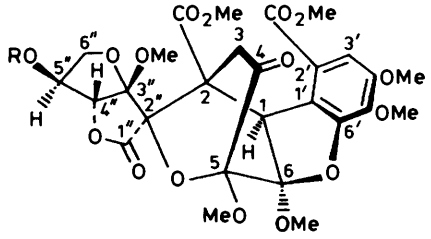
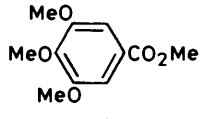


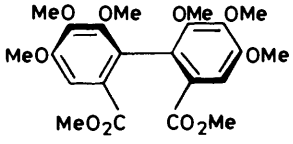
Figure 1. ^{13}C N.m.r. spectra of compounds (**7**), (**10**), and (**11**) (solvent $CDCl_3$; $SiMe_4$ as internal standard)



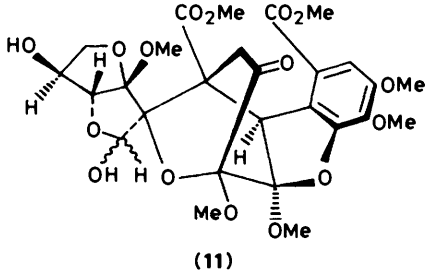
(**7**) R = H
(**10**) R = Ac



(**8**)



(**9**)



(**11**)

by 2.2 and 2.9 p.p.m. respectively (Figure 1). The observation of these characteristic acylation shifts was consistent with the ^1H n.m.r. data (with spin-decoupling) of the acetate (**10**), which showed the presence of an independent ABMX system (δ 4.06, dd, *J* 2, 10 Hz; δ 4.21, dd, *J* 4, 10 Hz; δ 4.76, s; 5.34, dd, *J* 2, 4 Hz) corresponding to the partial structure $-OCH_2-CH(OH)-CH(O-)-$.

A carbonyl stretching absorption at 1 798 cm^{-1} in the i.r. and a carboxyl resonance at δ 170.1 in the ^{13}C n.m.r. spectra of compound (**7**) suggested the presence of a γ-lactone ring. On treatment with sodium borohydride in methanol, this lactone was easily reduced to form a hemiacetal ring (Figure 1), while contrary to our expectation a second carbonyl group mentioned above was intact. In the ^1H n.m.r. spectrum ($CDCl_3$ + D_2O) of the reduction product (**11**), the newly observed sharp singlet resonance (δ 6.52) arising from the hemiacetal methine proton suggested that the carbon adjacent to the carboxyl group is quaternary. Furthermore, a considerable upfield shift (−0.92 p.p.m.) of the benzylic methine signal caused by reduction was observed. This observation implied the existence of a through-space interaction between the lactone carbonyl group and the benzylic methine proton; therefore they were shown to be located stereochemically in close vicinity to each other.

As mentioned above, elaeocarpusin (**3**) was easily decomposed to give geraniin (**1**) in a good yield when refluxed in aqueous solution. Re-examination of this reaction resulted in the isolation and characterization of a further degradation product. The reaction mixture, after removal of geraniin (**1**) by Sephadex LH-20 chromatography, showed strong acidity and was treated with *p*-bromophenacyl bromide to yield a crystalline compound (**12**). The ^{13}C n.m.r. spectrum of compound (**12**) exhibited, together with signals arising from a *p*-bromophenacyl group, six signals due to a carboxyl (δ 169.9), an α,β-unsaturated double bond (δ 119.6 and 149.8), two methines bearing an oxygen atom (δ 74.5 and 68.7), and a methylene (δ 61.5), consistent with 3-O-*p*-bromophenacylascorbic acid. Comparison of the physical and spectral data with those of a sample prepared from L-ascorbic acid established structure (**12**) including absolute stereochemistry.

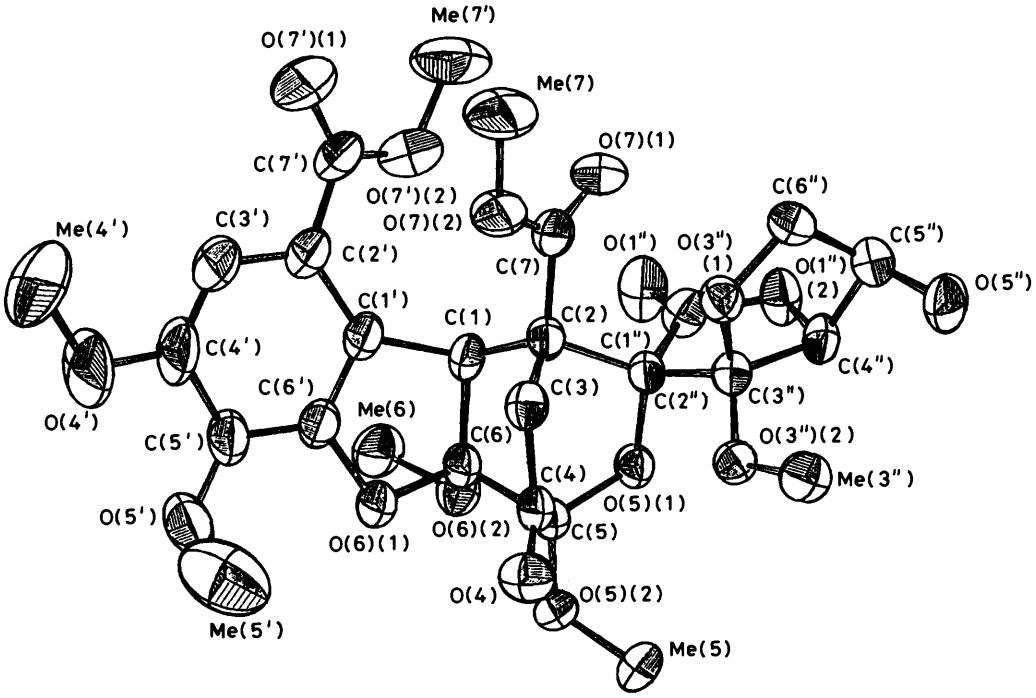
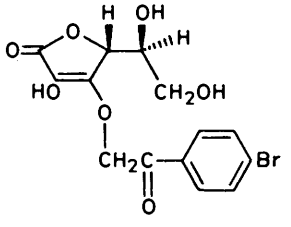


Figure 2. An ORTEP drawing of compound (7)



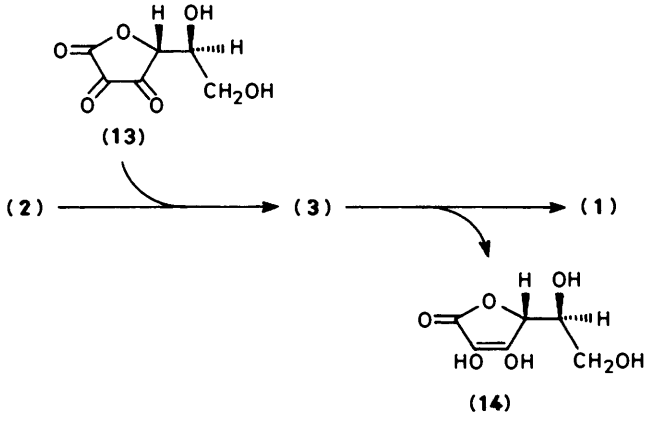
(12)

To elucidate completely the structure of the acyl group connected to the 2,4-positions of the glucose moiety, a single crystal of compound (7) obtained by recrystallization from methanol was subjected to *X*-ray analysis. The crystal data were as follows: $C_{27}H_{30}O_{16}$, M = 610.53, size 0.3 × 0.45 × 0.50 mm, orthorhombic; space group $P2_12_12_1$, Z = 4; cell dimensions a = 18.324(3), b = 18.296(3), c = 8.746(2) Å, V = 2 931(1) Å^3. The 2 409 unique intensities were collected by 2θ—ω scan method within 2θ < 120° on a Rigaku AFC-5 FOS four-circle diffractometer using graphite monochromated Cu-K_α (λ = 1.5418 Å) radiation. Twenty-eight plausible atomic positions were revealed by the direct method (MULTAN)[10] and several cycles of isotropic least-squares and subsequent Fourier synthesis gave those of the remaining non-hydrogen atoms. The hydrogen atoms except for that of the hydroxy group were generated on the basis of stereochemical and geometrical considerations. The structure was refined by the block diagonal least-squares method (UNICS III)[11] to a *R*-value of 0.057 for the total reflections.* Anisotropic thermal parameters for the determination are available as a supplementary publication [SUP No. 56409 (2 pp.)].† The structure factors for the study are available from the Editorial office.

An ORTEP[12] drawing of (2) (less hydrogen atoms) is shown in Figure 2. Taking into account the presence of L-ascorbic acid in the decomposition products of elaeocarpusin (3), the absolute stereo-structure is regarded to be the antipode of the Figure.

On the basis of this evidence, the structure of elaeocarpusin was finally established as that shown in (3).

Elaeocarpusin (3) represents a new class of ellagitannin which may be formed biosynthetically from condensation between the hexahydroxydiphenoyl ester group in the ellagitannin (2) and dehydroascorbic acid (13). Since it is well known that ascorbic acid (14) and dehydroascorbic acid (13) play an important role in enzymatic oxidation–reduction reactions, the structure of elaeocarpusin (3) suggests that dehydroascorbic acid is involved in the oxidative metabolism of a hexahydroxydiphenoyl group to a dehydrohexahydroxydiphenoyl group.



Experimental

M.p.s were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were

* All the calculations were performed on a computer TOSBAC DS-600.

† For details of the Supplementary publications scheme, see Instructions for Authors (1986), *J. Chem. Soc., Perkin Trans. 1*, 1986, Issue 1.

measured with a JASCO DIP-4 digital polarimeter. I.r. spectra were recorded on a JASCO DS-301 spectrophotometer. Electron impact mass spectra were measured with a JEOL JMS D-300 spectrometer equipped with a direct inlet system, while field desorption and fast atom bombardment mass spectra were taken with a JEOL JMS DX-300 instrument. ^1H (100 MHz) and ^{13}C (25.05 MHz) N.m.r. spectra were recorded on JEOL PS-100 and JEOL FX-100 spectrometers, respectively. ^1H (400 MHz) and ^{13}C (100 MHz) N.m.r. spectra were recorded on a JEOL FX-400 spectrometer. Circular dichroism curves were determined on a JASCO J-20 apparatus. Column chromatography was performed using Sephadex LH-20 (25—100 μm; Pharmacia Fine Chemicals), MCI-gel CHP-20P (75—150 μm; Mitsubishi Chemical Industries Ltd.), Avicel micro-crystalline cellulose (Funakoshi), Bondapak C_{18}/Porasil B (Waters Associates), and Kieselgel 60 (70—230 mesh; Merck). T.l.c. was conducted on precoated Kieselgel 60 F_{254} plates (0.20 mm; Merck) in the solvent systems benzene–ethyl formate–formic acid (1:7:1, v/v), benzene–acetone (3:1 and 4:1, v/v), and benzene–ethanol (20:3, v/v), or precoated cellulose F_{254} plates (0.10 mm; Merck) using the solvent system 2% acetic acid. Spots on t.l.c. were detected by their blue fluorescence under u.v. light and with 2% ethanolic iron(III) chloride spray.

Isolation of Tannins.—The fresh leaves (13 kg) of *Elaeocarpus sylvestris* var. *Ellipticus* were extracted at room temperature with acetone–water [9:1 (v/v); 50 l). Concentration of the extract under reduced pressure (*ca.* 40 °C), afforded dark green precipitates consisting mainly of chlorophylls. After removal of the precipitates by filtration, the filtrate was further concentrated to 2 l. The solution was left at room temperature overnight to give a brown precipitate, which was purified by crystallization from water–methanol to afford music acid (1.5 g). The mother liquor, after concentration, was applied to a column (10.5 cm i.d. × 50 cm) of Sephadex LH-20. Elution with water containing increasing amounts of methanol gave three fractions: I (*ca.* 500 g), II (203 g), and III (639 g). Fraction I was chromatographed over MCI-gel CHP-20P (9.0 cm i.d. × 50 cm) using water–methanol [4:1 (v/v)], followed by separation on a Sephadex LH-20 column (6.5 cm i.d. × 60 cm) using propan-1-ol, to give β-glucogallin (**4**) (7.6 g) and methyl 6-*O*-galloyl-β-D-glucopyranoside (**5**) (1.6 g). A part (50 g) of fraction III consisting mainly of geraniin and elaeocarpusin, was successively chromatographed over Sephadex LH-20 with ethanol and with water–methanol (3:2, v/v), Bondapak C_{18}/Porasil B with water–methanol [9:1 (v/v)], and finally MCI-gel CHP-20P with water containing increasing amounts of methanol to afford geraniin (**1**) (23 g) and elaeocarpusin (18.8 g).

Elaeocarpusin (**3**).—This compound was obtained as an off-white amorphous powder, $[\alpha]_D^{26}$ + 55.4° (*c* 1.1 in methanol) (Found: C, 47.7; H, 3.4. $C_{47}H_{34}O_{22}\cdot 4H_2O$ requires C, 47.7; H, 3.6%); R_F [benzene–ethyl formate–formic acid, 1:7:1 (v/v)] 0.16; $\nu_{max.}$ 1 794 (γ-lactone) and 1 725 cm^{-1} (CO_2); $\delta_H(CD_3COCD_3)$ 2.21 (1 H, d, *J* 19 Hz, 3-H), 3.01 (1 H, br d, *J* 19 Hz, 3-H), 4.00—4.30 (3 H, m, 6″-H and glucose 6-H), 4.57—4.83 (4 H, m, 4″-H, 5″-H, and glucose 6-H and 5-H), 4.91 (1 H, d, *J* 4 Hz, glucose 3-H), 5.44 (1 H, br d, *J* 4 Hz, glucose 2-H), 5.75 (1 H, br s, 1-H), 6.51 (1 H, d, *J* 4 Hz, glucose 1-H), 6.93 and 7.03 (each 1 H, s, H of HHDP*), 7.21 (2 H, s, galloyl-H), and 7.28 (1 H, s, 3′-H).

Decomposition of Elaeocarpusin (**3**) *into Geraniin* (**1**).—A solution of elaeocarpusin (**3**) (500 mg) in water (50 ml) was heated on a water-bath for 1 h. The solution was concentrated under reduced pressure to yield a yellow precipitate, which was filtered off and recrystallized from water to afford geraniin (**1**) (160 mg).

Methylation of Elaeocarpusin (**3**).—A mixture of elaeocarpusin (**3**) (600 mg), dimethyl sulphate (2.5 ml), and anhydrous potassium carbonate (2.5 g) in dry acetone (25 ml) was heated under reflux for 4.5 h. The inorganic salts were filtered off and the filtrate concentrated to a syrup, which was chromatographed over silica gel. Elution with benzene–acetone (4:1 v/v) afforded the *tetradecamethyl ether* (**6**) (310 mg) as a pale yellow, crystalline powder (from methanol), m.p. > 300 °C; $[\alpha]_D^{25}$ +30.7° (*c* 1.2 in chloroform) (Found: C, 55.8; H, 4.8. $C_{61}H_{62}O_{32}$ requires C, 56.05; H, 4.8%); R_F [benzene–acetone, 3:1 (v/v)] 0.30; $\nu_{max.}$ 1 802 (γ-lactone), 1 750, 1 720, and 1 712 cm^{-1} (CO); *m/z* 1 306 [M^+, 100%, field-desorption (FD)], 653 (M^{2+}, 42); $\delta_H(CDCl_3)$ 2.26 (1 H, d, *J* 19 Hz, 3-H), 2.88 (1 H, dd, *J* 2 and 19 Hz, 3-H), 4.93 (1 H, s, 4″-H), 5.17 (1 H, d, *J* 4 Hz, glucose 3-H), 5.49 (1 H, br s, glucose 2-H), 5.72 (1 H, d, *J* 2 Hz, 1-H), 6.05 (1 H, br s, glucose 4-H), 6.66 (1 H, d, *J* 3 Hz, glucose 1-H), 6.77, 6.81 (each 1 H, s, H of HMDP†), 7.18 (2 H, s, galloyl-H), 7.34 (1 H, s, 3′-H); $\delta_C(CDCl_3)$ 38.1 (C-3), 49.0 (C-1), 49.6 (C-2), 61.7 (glucose C-4), 63.8 (glucose C-6), 67.8, 70.5, 72.6 (glucose C-2, C-3, and C-5), 72.8 (C-5″), 77.9 (C-6″), 80.6 (C-2″), 89.2 (C-4″), 92.0 (glucose C-1), 99.2 (C-5), 105.9 (HMDP C-3), 107.1 (galloyl C-2 and C-6), 107.4 (HMDP C-3′), 109.1 (C-1′), 110.3 (C-3′), 112.0 (C-3″), 116.7 (C-6), 120.0 (galloyl C-1), 122.6 (HMDP C-1), 123.1 (C-2′), 124.1 (HMDP C-1′), 126.0, 127.2 (HMDP C-2 and C-2′), 138.2 (C-5′), 143.3 (galloyl C-4), 144.7, 145.3 (HMDP C-5 and C-5′), 151.3 (C-6′), 164.3, 164.4, 165.0, 166.8, 167.0 (CO_2), 169.8 (C-1″), and 196.7 p.p.m. (C-4).

The *monoacetate* prepared with acetic anhydride and pyridine) was obtained as a white amorphous powder, $[\alpha]_D^{25}$ +31.6° (*c* 0.3 in chloroform) (Found: C, 55.8; H, 4.8. $C_{63}H_{64}O_{33}$ requires C, 56.11; H, 4.8%); R_F [benzene–acetone, 4:1 (v/v)] 0.38; *m/z* 1 348 (M^+, 100%, FD); $\nu_{max.}$ 1 808 (γ-lactone), 1 750, 1 720, and 1 714 cm^{-1} (CO); $\delta_H(CDCl_3)$ 2.13 (3 H, s, OAc) 2.26 (1 H, d, *J* 19 Hz, 3-H), 2.80 (1 H, dd, *J* 2 and 19 Hz, 3-H), 4.06 (1 H, dd, *J* 2 and 10 Hz, 6″-H), 4.21 (1 H, dd, *J* 4 and 10 Hz, 6″-H), 4.76 (1 H, s, 4″-H), 5.34 (1 H, dd, *J* 2 and 4 Hz, 5″-H), 5.83 (1 H, d, *J* 2 Hz, 1-H), and 7.20 (1 H, s, 3′-H).

Hydrolysis of the Tetradecamethyl Ether (**6**).—A solution of the methyl ether (**6**) (100 mg) in 5% aqueous sodium hydroxide (3 ml) and acetone (2 ml) was heated (80 °C) for 30 min. The mixture was acidified with hydrochloric acid and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. The residue was treated with ethereal diazomethane for 1 h, and the solution was concentrated to a syrup, which was chromatographed over silica gel. Elution with benzene–acetone (97:3, v/v) yielded methyl 3,4,5-trimethoxybenzoate (**8**) as colourless prisms (from methanol) (5 mg), m.p. 81—83 °C, and dimethyl (*R*)-4,4′,5,5′,6,6′-hexamethoxydiphenoate (**9**) as a colourless syrup (34.3 mg), $[\alpha]_D^{27}$ +26.4° (*c* 0.9 in chloroform), identified by t.l.c. and i.r. comparisons with authentic samples. Subsequent elution with benzene–acetone [22:3 (v/v)] gave *compound* (**7**) as colourless prisms (from methanol) (40.5 mg), m.p. 203—205 °C, $[\alpha]_D^{25}$ +51.4° (*c* 0.9 in chloroform) (Found: C, 52.8; H, 4.95. $C_{27}H_{30}O_{16}$ requires C, 53.1; H, 4.95%); R_F [benzene–acetone, 4:1 (v/v)] 0.26; *m/z* 610 [M^+, 27%, electron impact (EI)]; $\nu_{max.}$ 3 521 (OH), 1 798 (γ-lactone), 1 762, 1 745, and 1 728 cm^{-1} (CO); $\lambda_{max.}$ (methanol) 217 (ε 27 000 $dm^3\ mol^{-1}\ cm^{-1}$), 264 (7 900), and 297 nm (3 900); c.d. (*c* 4.1 × 10^{-5} in methanol) $[\theta]_{229}$ +5.73 × 10^4, $[\theta]_{265}$ −2.93 × 10^4, and $[\theta]_{305}$ +0.78 × 10^4; $\delta_C(CDCl_3)$ 38.0 (t, C-3), 49.0 (d, C-1), 49.1 (s, C-2), 72.9 (d, C-5″), 76.3 (t, C-6″), 80.3 (s, C-2″), 88.3 (d, C-4″), 99.5 (s, C-5), 108.1 (d,

* HHDP = Hexahydroxydiphenoyl.

† HHDP = Hexahydroxydiphenoyl.

Table 2. ^{1}H N.m.r. characteristics of compounds (**7**), (**10**), and (**11**) in $CDCl_3$: chemical shifts (δ values, $SiMe_4$): coupling constants *J* (Hz)

	(7)	(10)	(11)
1-H	5.83 (d, *J* 2)	6.83 (d, *J* 2)	4.91 (d, *J* 3)
3-H	2.22 (d, *J* 19) 2.87 (dd, *J* 19, 2)	2.26 (d, *J* 19) 2.80 (dd, *J* 19, 2)	2.10 (d, *J* 19) 2.99 (dd, *J* 19, 2)
3′-H	7.18 (s)	7.20 (s)	7.01 (s)
1″-H	—	—	6.53 (d, *J* 13)
4″-H	4.72 (s)	4.76 (s)	4.39 (s)
5″-H	4.59 (br d, *J* 3)	5.34 (dd, *J* 2, 4)	4.32 (br d, *J* 3)
6″-H	4.05 (br d, *J* 3)	4.06 (dd, *J* 10, 2) 4.21 (dd, *J* 10, 4)	3.92 (d, *J* 3)
OMe	3.36, 3.45, 3.49, 3.71 3.75, 3.89, 3.95 (each s)	3.31, 3.46, 3.49, 3.70, 3.75, 3.90, 3.96 (each s)	3.32, 3.37, 3.51, 3.72, 3.83, 3.88, 3.92 (each s)
Acetyl	—	2.13 (s)	—
OH		—	4.69 (1″-OH, d, *J* 13)

C-3′), 109.8 (s, C-1′), 112.1 (s, C-3″), 118.4 (s, C-6), 122.4 (C-2′), 137.2 (s, C-5′), 150.7 (s, C-6′), 152.6 (s, C-4′), 165.9 (s, C-7′), 168.4 (s, C-7), 170.1 (s, C-1″), and 197.6 p.p.m. (C-4).

The *monoacetate* (**10**) (prepared with acetic anhydride and pyridine) was obtained as a white amorphous powder, $[\alpha]_D^{25}$ +70.2° (*c* 0.5 in chloroform); R_F [benzene–acetone, 4:1 (v/v)] 0.47; $\delta_C(CDCl_3)$ 20.8 ($COCH_3$), 38.0 (C-3), 74.1 (C-6″), 74.6 (C-5″), 80.1 (C-2″), 85.4 (C-4″), 99.6 (C-5), 108.2 (C-3′), 109.8 (C-1′), 112.0 (C-3″), 118.4 (C-6), 122.2 (C-2′), 137.3 (C-5′), 150.6 (C-6′), 152.6 (C-4′), 165.9 (C-7′), 168.5, 168.9 (C-7 and $COCH_3$), 169.2 (C-1″), and 197.4 p.p.m. (C-4).

Reduction of Compound (**7**).—To a solution of compound (**7**) (100 mg) in methanol (3 ml) was added sodium borohydride (150 mg) at 0 °C, and the mixture was stirred for 30 min. The reaction mixture was poured into 0.5M-hydrochloric acid solution (15 ml), and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. The residue was crystallized from methanol to afford *compound* (**11**) as colourless needles (90 mg), m.p. 209—210 °C, $[\alpha]_D^{25}$ +21.8° (*c* 0.7 in chloroform) (Found: C, 51.4; H, 5.5. $C_{27}H_{32}O_{16}\cdot H_2O$ requires C, 51.4; H, 5.4%); R_F [benzene–acetone, 3:1 (v/v)] 0.23; *m/z* 612 (M^+, 17%, EI); $\nu_{max.}$ 3 460 (OH), 1 758, 1 734, 1 720, and 1 714 cm^{-1} (CO); $\delta_C(CDCl_3)$ 37.9 (t, C-3), 47.4 (s, C-2), 49.6 (d, C-1), 75.4 (d, C-5″), 76.1 (t, C-6″), 85.7 (s, C-2″), 86.4 (d, C-4″), 97.4 (d, C-1″), 98.8 (s, C-5), 108.1 (d, C-3′), 109.8 (s, C-1′), 116.1 (s, C-3″), 116.9 (s, C-6), 122.4 (s, C-2′), 136.6 (s, C-5′), 150.8 (s, C-6′), 152.7 (s, C-4′), 166.6 (s, C-7′), 168.8 (s, C-7), and 198.1 p.p.m. (C-4).

Characterization of L-*Ascorbic Acid* (**14**) *formed by Decomposition of Elaeocarpusin* (**3**).—Elaeocarpusin (**3**) (20 g), slightly contaminated with geraniin, was heated in water (350 ml) at 90 °C on a water-bath for 2 h. The solvent was evaporated off under reduced pressure to leave a brown gum, which was chromatographed on a column of Sephadex LH-20 (4.4 cm i.d. × 38 cm). Elution with water (500 ml) and evaporation yielded a residue, half of which in ethanol (10 ml) was neutralized with 5% aqueous sodium hydro-oxide and treated with *p*-bromophenacyl bromide (500 mg) in ethanol (3 ml). The mixture was refluxed for 2.5 h, and after removal of the ethanol by evaporation, the aqueous solution was extracted with ethyl acetate. The organic layer was dried (Na_2SO_4) and evaporated

Table 3. Fractional atomic co-ordinates*

Atom	*x*	*y*	*z*
C(1)	2 407(3)	2 785(3)	5 680(6)
C(2)	2 876(3)	2 915(3)	4 222(7)
C(3)	2 498(3)	2 543(3)	2 839(7)
C(4)	1 765(3)	2 880(3)	2 549(7)
C(5)	1 562(3)	3 444(3)	3 810(7)
C(6)	1 604(3)	3 020(3)	5 357(7)
C(7)	3 660(3)	2 689(3)	4 469(7)
C(1′)	2 313(3)	1 977(3)	6 079(8)
C(2′)	2 755(4)	1 455(4)	6 779(10)
C(3′)	2 487(4)	738(4)	6 827(15)
C(4′)	1 821(4)	555(4)	6 320(13)
C(5′)	1 342(4)	1 068(3)	5 669(9)
C(6′)	1 615(3)	1 776(3)	5 645(8)
C(7′)	3 470(4)	1 586(5)	7 439(11)
C(1″)	3 236(3)	4 246(3)	5 027(7)
C(2″)	2 850(3)	3 756(3)	3 855(6)
C(3″)	3 207(3)	3 976(3)	2 304(6)
C(4″)	3 583(3)	4 722(3)	2 662(7)
C(5″)	4 350(3)	4 685(4)	2 026(8)
C(6″)	4 498(3)	3 858(4)	1 994(9)
Me(5)	797(4)	4 212(3)	2 291(8)
Me(6)	1 232(4)	3 115(4)	7 989(7)
Me(7)	4 510(4)	1 715(5)	4 123(13)
Me(4′)	2 016(7)	−733(5)	6 659(20)
Me(5′)	517(5)	872(6)	3 622(15)
Me(7′)	4 287(4)	2 502(6)	8 429(11)
Me(3″)	2 882(4)	4 099(4)	−337(7)
O(4)	1 359(2)	2 723(2)	1 537(5)
O(5)(1)	2 111(2)	3 999(2)	3 903(5)
O(5)(2)	893(2)	3 763(2)	3 670(5)
O(6)(1)	1 187(2)	2 348(2)	5 081(5)
O(6)(2)	1 270(2)	3 437(2)	6 464(4)
O(7)(1)	4 122(2)	3 053(2)	5 039(6)
O(7)(2)	3 767(2)	2 001(2)	3 960(6)
O(4′)	1 523(3)	−146(3)	6 286(12)
O(5′)	653(3)	896(3)	5 232(7)
O(7′)(1)	3 920(3)	1 131(3)	7 741(11)
O(7′)(2)	3 580(3)	2 294(3)	7 811(7)
O(1″)(1)	3 170(3)	4 245(2)	6 383(5)
O(1″)(2)	3 630(2)	4 765(2)	4 317(5)
O(3″)(1)	3 793(2)	3 505(2)	1 917(5)
O(3″)(2)	2 667(2)	3 964(2)	1 220(4)
O(5″)	4 378(2)	4 941(3)	481(5)

* Standard deviation for the last digit is given in parentheses.

to afford a residue, which was chromatographed over silica gel. Elution with benzene–ethanol [20:3 (v/v)] gave 3-O-*p*-bromophenacyl-L-ascorbic acid (**12**) as colourless needles (from benzene–methanol) (46 mg), m.p. 177—178 °C, $[\alpha]_D^{19}$ −15.5° (*c* 0.7 in acetone) (Found: C, 44.55; H, 3.65. $C_{14}H_{13}O_7Br\cdot 0.25H_2O$ requires C, 44.5; H, 3.6%); R_F [benzene–ethanol, 20:3 (v/v)] 0.26; $\nu_{max.}$ 3 410 (OH), 1 740, and 1 685 cm^{-1} (CO); *m/z* 374 [(M + 2)$^+$, 100%, FD], 372 (M^+, 94); $\delta_H(CD_3COCD_3 + D_2O)$ 3.72 (2 H, d, *J* 6 Hz, 6-H), 4.05 (1 H, m, 5-H), 4.98 (1 H, d, *J* 2 Hz, 4-H), 5.77, 5.96 (each 1 H, d, *J* 17 Hz, CH_2), 7.75 (2 H, d, *J* 8 Hz, 3′-H and 5′-H), and 7.96 (2 H, d, *J* 8 Hz, 2′-H and 6′-H); $\delta_C(CD_3SOCD_3)$ 61.5 (t, C-6), 68.7 (d, C-5), 72.3 (t, CH_2), 74.5 (d, C-4), 119.6 (s, C-2), 127.9 (s, C-4′), 129.6 (d, C-2′ and C-6′), 131.9 (d, C-3′ and C-5′), 132.7 (s, C-1′), 149.8 (s, C-3), 169.9 (s, C-1), and 192.5 p.p.m. (s, CO). This compound was identified by ^{1}H n.m.r. and i.r. comparisons and mixed m.p. with an authentic sample prepared from L-ascorbic acid in the same way.

Geraniin.—This compound was obtained as a yellow powder, $[\alpha]_D^{22}$ −141.2° (*c* 1.10 in methanol); $\delta_H(CD_3COCD_3)$ 5.20 (1

Table 4. Bond lengths and their standard deviations (Å)

C(1)–C(2)	1.555(8)	C(1)–C(6)	1.559(7)	C(1)–C(1′)	1.529(8)
C(2)–C(3)	1.551(8)	C(2)–C(7)	1.510(8)	C(2)–C(2″)	1.572(7)
C(3)–C(4)	1.498(8)	C(4)–C(5)	1.555(8)	C(4)–O(4)	1.191(7)
C(5)–C(6)	1.561(8)	C(5)–O(5)(1)	1.431(6)	C(5)–O(5)(2)	1.363(6)
C(6)–O(6)(1)	1.468(6)	C(6)–O(6)(2)	1.376(6)	C(7)–O(7)(1)	1.186(7)
C(7)–O(7)(2)	1.349(7)	C(1′)–C(2′)	1.393(9)	C(1′)–C(6′)	1.384(8)
C(2′)–C(3′)	1.400(10)	C(2′)–C(7′)	1.451(10)	C(3′)–C(4′)	1.341(12)
C(4′)–C(5′)	1.405(10)	C(4′)–O(4′)	1.393(9)	C(5′)–C(6′)	1.388(8)
C(5′)–O(5′)	1.356(8)	C(6′)–O(6)(1)	1.397(7)	C(7′)–O(7′)(1)	1.200(10)
C(7′)–O(7′)(2)	1.351(9)	C(1″)–C(2″)	1.535(8)	C(1″)–O(1″)(1)	1.192(7)
C(1″)–O(1″)(2)	1.344(7)	C(2″)–C(3″)	1.559(7)	C(2″)–O(5)(1)	1.426(6)
C(3″)–C(4″)	1.560(7)	C(3″)–O(3″)(1)	1.417(6)	C(3″)–O(3″)(2)	1.371(6)
C(4″)–C(5″)	1.512(8)	C(4″)–O(1″)(2)	1.452(7)	C(5″)–C(6″)	1.537(9)
C(5″)–O(5″)	1.431(8)	C(6″)–O(3″)(1)	1.445(7)	Me(5)–O(5)(2)	1.469(7)
Me(6)–O(6)(2)	1.459(7)	Me(7)–O(7)(2)	1.466(8)	Me(4′)–O(4′)	1.441(12)
Me(5′)–O(5′)	1.430(14)	Me(7′)–O(7′)(2)	1.454(9)	Me(3″)–O(3″)(2)	1.439(7)

Standard deviation for the last digit is given in parentheses.

Table 5. Bond angles and their standard deviations (°)

C(2)–C(1)–C(6)	109.3(4)	C(1″)–C(2″)–O(5)(1)	103.5(4)	O(7)(1)–C(7)–O(7)(2)	124.0(5)
C(6)–C(1)–C(1′)	101.6(4)	C(2″)–C(3″)–C(4″)	103.6(4)	C(1)–C(1′)–C(6′)	107.4(5)
C(1)–C(2)–C(7)	111.5(4)	C(2″)–C(3″)–O(3″)(2)	107.0(4)	C(1′)–C(2′)–C(3′)	116.8(6)
C(3)–C(2)–C(7)	114.6(4)	C(4″)–C(3″)–O(3″)(2)	118.0(4)	C(3′)–C(2′)–C(7′)	117.2(7)
C(7)–C(2)–C(2″)	109.0(4)	C(3″)–C(4″)–C(5″)	107.3(4)	C(3′)–C(4′)–C(5′)	122.4(6)
C(3)–C(4)–C(5)	111.5(4)	C(5″)–C(4″)–O(1″)(2)	108.2(4)	C(5′)–C(4′)–O(4′)	111.1(7)
C(5)–C(4)–O(4)	122.4(5)	C(4″)–C(5″)–O(5″)	111.4(5)	C(4′)–C(5′)–O(5′)	122.7(5)
C(4)–C(5)–O(5)(1)	110.2(4)	C(5″)–C(6″)–O(3″)(1)	106.5(4)	C(1′)–C(6′)–C(5′)	125.2(5)
C(6)–C(5)–O(5)(1)	105.3(4)	C(5)–O(5)(2)–Me(5)	114.8(4)	C(5′)–C(6′)–O(6)(1)	120.1(5)
O(5)(1)–C(5)–O(5)(2)	109.4(4)	C(6)–O(6)(2)–Me(6)	116.1(4)	C(2′)–C(7′)–O(7′)(2)	112.8(6)
C(1)–C(6)–O(6)(1)	106.8(4)	C(4′)–O(4′)–Me(4′)	115.8(7)	C(2″)–C(1′)–O(1″)	127.9(5)
C(5)–C(6)–O(6)(1)	104.3(4)	C(7′)–O(7′)(2)–Me(7′)	118.2(6)	O(1″)(1)–C(1″)–O(1″)(2)	121.0(5)
O(6)(1)–C(6)–O(6)(2)	110.3(4)	C(3″)–O(3″)(1)–C(6″)	113.1(4)	C(2)–C(2″)–C(3″)	114.6(4)
C(2)–C(7)–O(7)(2)	110.1(4)			C(1″)–C(2″)–C(3″)	103.6(4)
C(1)–C(1′)–C(2′)	134.2(5)	C(2)–C(1)–C(1′)	113.3(4)	C(3″)–C(2″)–O(5)(1)	110.3(4)
C(2′)–C(1′)–C(6′)	118.3(5)	C(1)–C(2)–C(3)	108.9(4)	C(2″)–C(3″)–O(3″)(1)	111.6(4)
C(1′)–C(2′)–C(7′)	125.8(6)	C(1)–C(2)–C(2″)	107.4(4)	C(4″)–C(3″)–O(3″)(1)	104.2(4)
C(2′)–C(3′)–C(4′)	122.8(7)	C(3)–C(2)–C(2″)	104.8(4)	O(3″)(1)–C(3″)–O(3″)(2)	111.8(4)
C(3′)–C(4′)–O(4′)	126.3(7)	C(2)–C(3)–C(4)	110.6(4)	C(3″)–C(4″)–O(1″)(2)	105.9(4)
C(4′)–C(5′)–C(6′)	113.8(6)	C(3)–C(4)–O(4)	125.9(5)	C(4″)–C(5″)–C(6″)	102.3(4)
C(6′)–C(5′)–O(5′)	123.2(5)	C(4)–C(5)–C(6)	105.8(4)	C(6″)–C(5″)–O(5″)	107.3(5)
C(1′)–C(6′)–O(6)(1)	114.5(5)	C(4)–C(5)–O(5)(2)	115.8(4)	C(5)–O(5)(1)–C(2″)	116.2(3)
C(2′)–C(7′)–O(7′)(1)	126.3(7)	C(6)–C(5)–O(5)(2)	109.5(4)	C(6)–O(6)(1)–C(6′)	106.1(4)
O(7′)(1)–C(7′)–O(7′)(2)	120.5(7)	C(1)–C(6)–C(5)	109.9(4)	C(7)–O(7)(2)–Me(7)	115.7(5)
C(2″)–C(1″)–O(1″)(2)	110.6(4)	C(1)–C(6)–O(6)(1)	116.4(4)	C(5′)–O(5′)–Me(5′)	116.4(6)
C(2)–C(2″)–C(1″)	114.9(4)	C(5)–C(6)–O(6)(2)	108.2(4)	C(1″)–O(1″)(2)–C(4″)	112.9(4)
C(2)–C(2″)–O(5)(1)	109.1(4)	C(2)–C(7)–O(7)(1)	125.8(5)	C(3″)–O(3″)(2)–Me(3″)	116.9(4)

Standard deviation for the last digit is given in parentheses.

H, s, DHHDP* 1-H), 5.40—5.72 (3 H, m, 2-H, 3-H, and 4-H), 6.54 (1 H, s, DHHDP 3-H), 6.56 (1 H, br s, 1-H), 6.67 (1 H, s, H of HHDP), 7.13 (1 H, s, DHHDP H-3′), and 7.19 (3 H, s, H of HHDP and galloyl H); $\delta_C(CD_3COCD_3)$ (**1a**) 46.2 (DHHDP C-1), 90.6 (glucose C-1), 128.4 (DHHDP C-3), 154.0 (DHHDP C-2), 191.4 (DHHDP C-4); (**1b**) 51.9 (DHHDP C-1), 91.6 (glucose C-1), and 194.1 p.p.m. (DHHDP C-4). Spectral characteristics coincided with those described in the literature.[3]

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* DHHDP = Dehydrohexahydroxydiphenoyl.

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