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Carbohydrate Research 335 (2001) 245–250

CARBOHYDRATE RESEARCH

Synthesis of gallotannins

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Received 29 May 2001; accepted 18 August 2001

Abstract

As a contribution to the synthesis of gallotannins, four *O*-galloyl-D-glucoses (3-*O*-, 6-*O*-, 3,6-di-*O*-, 3,4,6-tri-*O*-galloyl-D-glucose) have been prepared by the reaction of tri-*O*-benzylgalloyl chloride and partially protected glucose derivatives (1,2-*O*-, and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose), followed successively by catalytic debenzylation (Pd–C) and controlled acid hydrolysis. Their structures were established from their behavior on TLC and from their ^{1}H and ^{13}C NMR spectra. © 2001 Published by Elsevier Science Ltd.

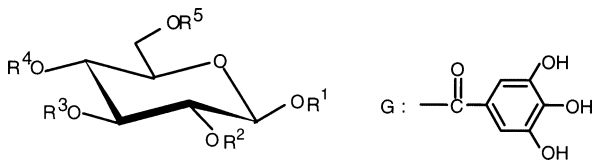
Keywords: Gallotannin; 3-*O*-Galloyl-D-glucose; 6-*O*-Galloyl-D-glucose; 3,6-Di-*O*- galloyl-D-glucose; 3,4,6-Tri-*O*-galloyl-D-glucose

1. Introduction

O-Galloyl-D-glucoses (see Scheme 1) occur naturally in some plants. Such 'gallotannins' exhibit various useful properties.[1] For example, these compounds serve as radical scavengers and antioxidants and figure importantly in protein precipitation and enzyme inhibition. There are several reports that these properties are dependent largely on the number of galloyl groups and their positions on the glucose core. Thus, it has been shown that an increase in the number of galloyl groups enhances the association of proteins and galloylglucoses,[2] and also increases the ability of gallotannins to scavenge 1,1-diphenyl-2-picrylhydrazyl (DPPH) radicals.[3] The same seems to pertain to interaction with biological entities and enzymes, and the inhibitory effect of gallotannins on glucosyltransferase from *Streptococcus mutans* follows the sequence,

$$PGG > TeGG > TriGG > DiGG^{4}$$

The activity is dependent on other factors such as the position of the galloyl groups.[5] The importance of the placement of the galloyl groups on the glucose core was indicated by a study of the inhibitory effects of 1,2,6-, 1,3,6- and 3,4,6-TriGG on lipid peroxidation in mitochondria and microsomes of liver where the greatest antioxidative effect was exhibited by 1,3,6-TriGG and the least effect by 3,4,6-TriGG.[6] More recently, it was shown that 1,2,3,6-TeGG had a strong effect on the affinity of gallotannins to galloyltransferase, whereas 1,3,4,6-TeGG was inactive.[7]



Scheme 1. The model structure of gallotannins [MoGG, one of R^1–R^5 is a galloyl group (G); DiGG, two of R^1–R^5 are G; TriGG, three of R^1–R^5 are G; TeGG, four of R^1–R^5 are G; PGG, R^1–R^5 are G].

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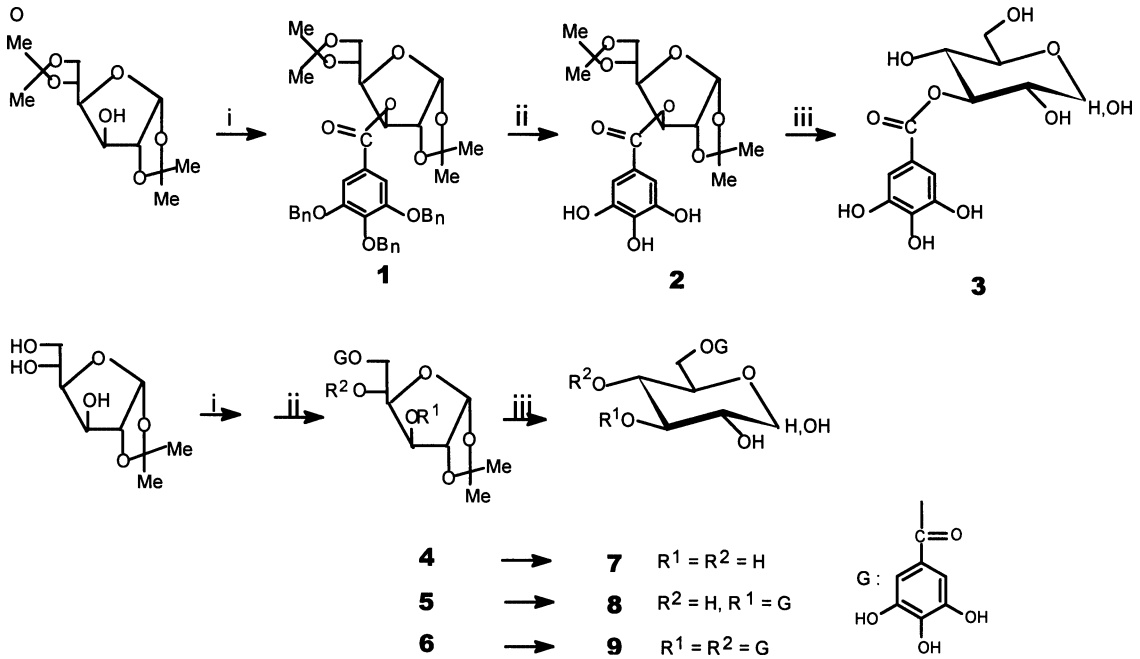
0008-6215/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.

PII: S0008-6215(01)00236-1



Scheme 2. Synthetic route for the compounds **3**, **7**, **8** and **9**. Reagents and conditions: (i) tri-*O*-benzylgalloyl chloride, pyridine, $CHCl_3$, 60 °C, 11 h (**7**, **8** and **9**), 8 h (**3**); (ii) Pd–C, H_2, THF, 7 h (**7**, **8** and **9**), 3 h (**3**); (iii) HCl, H_2O, 90 °C, 50 min.

More recently, *O*-galloyl-D-glucoses are mainly isolated from hydrolysates of extracts from sources like Chinese gall nuts and Turkish gall,[8] but only few natural galloylated furanoses have been isolated.[9] Dependence on natural materials in short supply, and difficulties in the isolation and purification have limited the research work and the practical utilization of gallotannins. Thus chemical synthesis is desirable, and some methods have been developed for the synthesis of gallotannins.[10–12] A programme to develop such synthesis with the galloyl groups located at specified sites in D-glucose is being undertaken, and as part of this work the preparation of four *O*-galloyl-D-glucoses is reported herein.

2. Results and discussion

Synthetic route.—The phenolic hydroxyl groups of gallic acid were protected by benzylation. Reaction of tri-*O*-benzylgalloyl chloride[13] with D-glucose in pyridine–chloroform and debenzylation of the product gave a mixture (TLC) showing no selectivity for the galloylation. Therefore, *O*-isopropylidenation of glucose was employed to protect a number of the hydroxyl groups (Scheme 2).

The first exploration was designed to introduce one galloyl group into a specific site of glucose. For this purpose, 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose[14] was condensed in equimolar amount with tri-*O*-benzylgalloyl chloride in pyridine–chloroform to afford compound **1**. Without purification, **1** was hydrogenated over 10% Pd–C in tetrahydrofuran to cleave the benzyl groups to give compound **2**, which was purified by chromatography on a column of Sephadex LH-20. The compound gave a positive test for a polyphenol with potassium ferricyanide–ferric chloride solution. On partial acid hydrolysis (1 M HCl, 90 °C, 50 min) the *O*-isopropylidene groups were cleaved to afford 3-*O*-galloyl-D-glucose (**3**) as a 2:1 mixture of α and β anomers as shown by ^1H NMR spectroscopy.

1,2-*O*-Isopropylidene-α-D-glucofuranose,[15] having three hydroxyl groups (3,5,6-) reactive for esterifying, was used to explore the method of introducing additional galloyl groups to predicted sites of glucose based on the same procedures described for **3**. Reaction of tri-*O*-benzylgalloyl chloride and 1,2-*O*-isopropylidene-α-D-glucofuranose in a molar ratio of 3:1 and debenzylation of the product afforded compounds **4**, **5** and **6** in yields of 40.8, 30.2 and 11.8%, respectively, after purifi-

cation on Sephadex LH-20. The yields indicated that the C-6 hydroxyl group of 1,2-*O*-isopropylidene-α-D-glucofuranose has the highest esterification activity, while the C-5 hydroxyl group has the lowest. On partial hydrolysis, the furanose ring of **4**, **5** and **6** was reverted to the pyranose form and correspondingly afforded the *O*-galloyl-D-glucoses **7**, **8** and **9**. For compound **6**, the reversion (**6**→**9**) occurred with the migration of one galloyl group from the 5-*O* to 4-*O*-position of glucose. Like **3**, compounds **7**, **8** and **9** all occurred as a mixture of α and β anomers in a ratio of 3:2 as determined by ^{1}H NMR spectroscopy.

Characterization of compounds **2**–**9** — *Compound* **2**. The ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **2** indicated the presence of one galloyl group [δ 7.16 (s, 2 H)] and two *O*-isopropylidene groups [δ 1.1–1.4 (4 s, 12 H, 4 × CH_3), 3.5 (t, 1 H, $J_{2,3}$ 3.3 Hz, H-3), 4.1–4.5 (5 H, H-2,4,5,6,6′), 5.88 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1)] in the molecule. Furthermore, as H-3 was shown to be downfield compared to that of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofucanose [^{1}H NMR spectrum (300 MHz, $CDCl_3$) δ 1.31–1.40 (4 s, 12 H, CH_3-iso), 2.91 (dd, 1 H, H-3), 3.93–4.52 (5 H, H-2,4,5,6,6′), 5.88–5.93 (d, 1 H, H-1)] due to the influence of the galloyl group, one could conclude that the glucofuranose moiety is acylated at C-3. The structure of 3-*O*-galloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2**) was further supported by its ^{13}C NMR spectrum [(75 MHz, $CDCl_3$) δ 25.2, 26.3, 26.5, 26.6 (4 × CH_3), 64.3 (C-6), 68.9 (C-5), 78.8 (C-4), 81.1, 82.5 (C-2, C-3), 104.3 (C-1), 110 (2 C, galloyl C-2, C-6), 111.9, 112.8 (2 C-iso), 121.1 (galloyl C-1), 138.5 (galloyl C-4), 145.9 (2 C, galloyl C-3,C-5), 166.9 (–COO–)].

Compound **3**. That the glucose ring in compound **3** had reverted to the α, β pyranose form was shown by TLC and the ^{1}H NMR spectrum [(300 MHz, CD_3COCD_3) δ 3.55–4.52 (m, 5 H, H-2,4,5,6,6′), 4.74 (d, 0.33 H, $J_{1,2}$ 8 Hz, β anomer, H-1), 5.21 (t, 0.67 H, $J_{2,3}$ 9 Hz, α anomer, H-3), 5.30 (d, 0.67 H, $J_{1,2}$ 3 Hz, α anomer, H-1), 5.50 (t, 0.33 H, β anomer, H-3), 7.25 (s, 2 H, galloyl). The presence of both a smaller coupling constant ($J_{1,2}$ 3 Hz) and a larger one ($J_{1,2}$ 8 Hz) of H-1 is a well-known proof for α and β anomers in a glucopyranose spectrum. The ratio of the α and β anomers as determined by the peak areas was 2:1, which is in agreement with the TLC analysis. In the ^{13}C NMR spectrum of compound **3** [(75 MHz, CD_3COCD_3) δ 63.7 (d, α-C-6), 64.3 (d, β-C-6), 70.8, 71.9, 73.2, 73.8, 74, 74.7, 76 (C-2, C-3, C-4, C-5), 93.4 (d, α-C-1), 96.6 (d, β-C-1), 110.2 (d, galloyl C-2, C-6), 121.3 (s, galloyl C-1), 138.6 (s, galloyl C-4), 145.8 (s, galloyl C-3, C-5), 166.9 (s, –COO–)], CH_3 isopropylidene peaks disappeared whilst C-1 shifted from 104.3 to 93.4–96.6 compared to that in compound **2**, which is further evidence of the reversion of **2** to **3**. The physicochemical and spectral data of **3** were identical with those of the naturally occurring sample.[16]

Compound **4**. The ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4** indicated the presence of one galloyl group [δ 7.10 (s, 2 H)] and one isopropylidene group [δ 1.31–1.48 (2 s, 6 H, 2 × CH_3), 3.2 (t, 1 H, $J_{2,3}$ 3 Hz, H-3), 4–4.32 (m, 2 H, H-4,5), 4.38 (t, 1 H, $J_{1,2}$ 3.7 Hz, H-2), 4.41–4.56 (2 H, H-6,6′), 5.90 (d, 1 H, H-1)] in the molecule. Furthermore, as H-6 and H-6′ are shifted downfield compared to those resonances of 1,2-*O*-isopropylidene-α-D-glucofuranose [^{1}H NMR spectrum (300 MHz, $CDCl_3$) δ 1.29–1.40 (2 s, 6 H, 2 × CH_3), 3.0 (t, 1 H, H-3), 3.4–3.6 (dd, 2 H, H-6,6′), 4.04 (t, 1 H, H-4), 4.31 (t, 1 H, H-5), 4.43 (t, 1 H, H-2), 5.90 (d, 1 H, H-1)] due to the influence of the galloyl group, one could conclude that the glucofuranose moiety is acylated at C-6. The structure of 6-*O*-galloyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**4**) was further confirmed by its ^{13}C NMR spectrum [(75 MHz, $CDCl_3$) δ 26.1, 26.6 (2 C, CH_3-iso), 66 (C-6), 69.5 (C-5), 79.5, 82.7, 83.5 (C-2, C-3, C-4), 105 (C-1), 109.8 (2 C, galloyl C-2, C-6), 112.1 (C-iso), 121 (galloyl C-1), 138.5 (galloyl C-4), 144.9 (2 C, galloyl C-3,C-5), 167.2 (–COO–)].

Compound **7**. The 6-*O*-galloyl-D-glucose structure with α and β anomers of compound **7** was confirmed by the ^{1}H NMR spectrum [(300 MHz, CD_3COCD_3) δ 3.12–4.41 (m, 4 H, H-2,3,4,5), 4.50–4.63 (m, 2 H, H-6, 6′), 4.86 (d, 0.4 H, $J_{1,2}$ 8 Hz, β anomer, H-1), 5.20 (d, 0.6 H, $J_{1,2}$ 3 Hz, α anomer, H-1), 7.13 (s, 2 H, galloyl)] and the ^{13}C NMR spectrum [(75

MHz, CD_3COCD_3) δ 64.5 (C-6), 70.2, 70.9, 71.1, 73.0, 74.1, 74.5, 75.5, 77.0 (C-2, C-3, C-4, C-5), 93.2 (d, α-C-1), 96.9 (d, β-C-1), 109.7 (galloyl C-2, C-6), 121 (s, galloyl C-1), 138.7 (s, galloyl C-4), 145.6 (galloyl C-3, C-5), 167.1 (s, –COO–)] based on elucidations similar to those used for compound **3**. The ratio of the α and β anomers as determined by peak areas was 3:2, which is in agreement with the TLC analysis. The behavior of **7** was identical to 6-*O*-galloyl-D-glucose by direct comparison with the report by Nonaka and Nishioka.[17]

Compound **5**. The ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **5** indicated the presence of two galloyl groups [δ 7.10 (s, 2 H), 7.23 (s, 2 H)] and one *O*-isopropylidene group [δ 1.33–1.45 (2 s, 6 H, $2 \times CH_3$), 4.20–4.34 (m, 2 H, H-4,5), 4.42 (t, 1 H, $J_{2,3}$ 2.9 Hz, H-2), 4.45–4.61 (2 H, H-6,6′), 5.27 (t, 1 H, $J_{3,4}$ 3.8 Hz, H-3), 5.88 (d, 1 H, $J_{1,2}$ 4 Hz, H-1)] in the molecule. Furthermore, as H-6, H-6′ and H-3 are shifted downfield compared to those resonances of 1,2-*O*-isopropylidene-α-D-glucofuranose as above due to the influence of the galloyl group, one can conclude that the glucofuranose moiety is acylated at C-6 and C-3. The structure of 3,6-di-*O*-galloyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**5**) was further confirmed by its ^{13}C NMR spectrum [(75 MHz, $CDCl_3$) δ 26.1, 26.3 (CH_3-iso), 67.1 (C-6), 69.3 (C-5), 79.1 (C-4), 83.3, 84.4 (C-2, C-3), 105.5 (C-1), 110, 110.2 (galloyl C-2, C-6), 111.9 (C-iso), 121.2, 121.5 (galloyl C-1), 138.4, 138.6 (galloyl C-4), 145.6, 145.7 (galloyl C-3, C-5), 166.7–166.8 (–COO–)].

Compound **8**. The 3,6-di-*O*-galloyl-D-glucose structure with α and β anomers of compound **8** was confirmed by its ^{1}H NMR spectrum [(300 MHz, 9:1 CD_3COCD_3–D_2O) δ 3.45 (dd, 0.4 H, $J_{1,2}$ 8, $J_{2,3}$ 9 Hz, β anomer, H-2), 3.61 (dd, 0.6 H, $J_{1,2}$ 4 Hz, α anomer, H-2), 3.63–4.28 (m, 2 H, H-4,5), 4.4–4.73 (m, 2 H, H-6,6′), 4.77 (d, 0.4 H, β anomer, H-1), 5.22 (d, 0.6 H, α anomer, H-1), 5.25–5.34 (m, 1 H, H-3), 7.15–7.16 (m, 4 H, galloyl)] and the ^{13}C NMR spectrum [(75 MHz, 9:1 CD_3COCD_3–D_2O) δ 63.9 (C-6), 70.7, 71.0, 72.9, 73.3, 74.0, 75.8 (C-2, C-3, C-4, C-5), 93 (d, α-C-1), 96.3 (d, β-C-1), 110.0, 110.2 (galloyl C-2, C-6), 121.3, 121.5 (galloyl C-1), 138.2, 138.5 (galloyl C-4), 145.8 (d, galloyl C-3, C-5), 166.6, 166.9 (–COO–) based on elucidations similar to those used for compound **3**. The ratio of the α and β anomers, as determined by peak areas was 3:2, which is in agreement with the TLC analysis. The behavior of **8** is identical to 3,6-di-*O*-galloyl-D-glucose obtained as a hydrolysate of extracts from Chinese gall nuts.[18]

Compound **6**. The ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **6** indicated the presence of three galloyl groups [δ 7.08 (s, 2 H), 7.14 (s, 2 H), 7.17 (s, 2 H)] and one isopropylidene group [δ 1.30–1.47 (2 s, 6 H, CH_3-iso), 4.21 (t, 1 H, $J_{4,5}$ 8 Hz, H-4), 4.43 (t, 1 H, $J_{1,2}$ 4 Hz, H-2), 4.56–4.85 (m, 3 H, H-5,6,6′), 5.32 (t, 1 H, $J_{2,3}$ 3.7 Hz, H-3), 5.80 (d, 1 H, H-1)] in the molecule. Furthermore, as H-6, H-6′, H-5 and H-3 are shifted downfield compared to the corresponding resonances of 1,2-*O*-isopropylidene-α-D-glucofuranose as above due to the influence of the galloyl group, one can conclude that the glucofuranose moiety is acylated at C-6, C-5 and C-3. The 3,5,6-tri-*O*-galloyl-1,2-*O*-isopropylidene-α-D-glucofuranose structure of compound **6** was further confirmed by its ^{13}C NMR spectrum [(75 MHz, $CDCl_3$) δ 26.1, 26.2 (CH_3-iso), 67.2 (C-6), 70 (C-5), 79.8 (C-4), 83.5 (C-2), 85.1 (C-3), 105.7 (C-1), 110.1, 110.2 (galloyl C-2, C-6), 112.7 (C-iso), 121.4, 121.5 (galloyl C-1), 138.3, 138.5, 138.7 (galloyl C-4), 145.5 (galloyl C-3, C-5), 165.6, 166.5 (–COO–)].

Compound **9**. The 3,4,6-tri-*O*-galloyl-D-glucose structure with α and β anomers of compound **9** was confirmed by the ^{1}H NMR spectrum [(300 MHz, 9:1 CD_3COCD_3–D_2O) δ 3.57 (dd, 0.4 H, $J_{1,2}$ 8, $J_{2,3}$ 9 Hz, β anomer, H-2), 3.69 (dd, 0.6 H, $J_{1,2}$ 3 Hz, α anomer, H-2), 4.39–4.76 (m, 3 H, H-5,6,6′), 4.84 (d, 0.4 H, β anomer, H-1), 5.43 (d, 0.6 H, α anomer, H-1), 5.48–5.60 (m, 1 H, H-1), 5.62 (t, 0.4 H, β anomer, H-3), 5.75 (dd, 0.6 H, $J_{3,4}$ 8 Hz, α anomer, H-3), 7.05–7.21 (6 H, galloyl)] and the ^{13}C NMR spectrum [(75 MHz, 9:1 CD_3COCD_3–D_2O) δ 63.1 (C-6), 71.5, 72.4, 72.6, 73.3, 73.6, 75.0, 75.4, 76.0 (C-2, C-3, C-4, C-5), 93.1 (d, α-C-1), 95.5 (d, β-C-1), 110.1, 110.3 (galloyl C-2, C-6), 120.7, 121.2, 121.9 (galloyl C-1), 138.2, 138.8 (galloyl C-4), 145.9 (t, galloyl C-3, C-5), 165.5, 166.1, 166.6

(–COO–)] based on the analogous elucidations as for compound **3**. This means that one galloyl group had migrated from the 5-*O* to 4-*O*-position of glucose when the furanose ring of compound **6** reverted to the pyranose form of compound **9**. The ratio of the α and β anomers, as determined by peak areas, was 3:2, which is in agreement with the TLC analysis.

3. Experimental

General methods.—Solutions were concentrated on a rotary evaporator under reduced pressure at 30–35 °C. For quantitative analysis, samples were dried at 60 °C (5 mmHg) to constant weight. The TLC analyses were carried out on DC: Alufolien Cellulose F plates that were developed at 12 ± 2 °C. Samples were separated into two dimensions with solvent systems: (A) 6:94 AcOH–water; and (B) 14:1:5 *n*-butanol–AcOH–water. Detection was first by UV light (260–300 nm) as fluorescent spots, and then a color was developed by spraying with a solution of 1:1 0.1% ferric chloride–0.1% potassium ferricyanide. ^{1}H and ^{13}C NMR spectra were recorded using Bruker AC 300 and AM 300 spectrometers. Spin-decoupling experiments were used when necessary for assigning the position of hydrogen atoms. The purified samples were obtained by chromatography on a column (120 × 2 cm i.d.) of Sephadex LH-20 using 9:1 EtOH–water as eluant. Elemental analyses were performed on a Carlo–Erba EA 1108 instrument.

3-O-*Galloyl-1,2:5,6-di*-O-*isopropylidene*-α-D-*glucofuranose* (**2**).—A mixture of tri-*O*-benzylgalloyl chloride (2.0 g, 4.4 mmol), 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (1.15 g, 4.4 mmol), pyridine (5 mL) and $CHCl_3$ (50 mL) was stirred, and the pale-yellow solution was heated to 60 °C and allowed to react for 8 h during which time pyridine hydrochloride was precipitated and the solution darkened. The cooled mixture was filtered, and the filtrate was concentrated, washed with water, and dried to a white powder. This product was reduced by H_2 in THF (50 mL) at rt using 10% Pd–C (0.3 g) as the catalyst. Hydrogen absorption ceased after 3 h, and the mixture was then filtered, and the catalyst was washed with a small amount of THF. The filtrate was concentrated, and the crude product was purified on a Sephadex LH-20 column (120 × 2 cm i.d.). Based on TLC analysis, purified compound **2** (1.15 g, 2.8 mmol, 63.3%) was obtained as a white solid: R_f 0.70 (A), R_f 0.24 (B). Anal. Calcd for $C_{19}H_{24}O_{10}$: C, 55.32; H, 5.87. Found: C, 55.37; H, 5.85.

O-*Galloyl-1,2*-O-*isopropylidene*-α-D-*glucofuranoses* (**4**, **5**, *and* **6**).—Based on the route to synthesize compound **2**, a mixture of tri-*O*-benzylgalloyl chloride (6.8 g, 15 mmol), 1,2-*O*-isopropylidene-α-D-glucofuranose (1.1 g, 5 mmol), pyridine (6 mL) and $CHCl_3$ (60 mL) was stirred at 60 °C for 11 h. The product was debenzylated (7 h) as in the previous example, and the filtrate was concentrated. Separation of 2.6 g of the residue by column chromatography at a flow rate of 1 mL/min afforded the following fractions: (1) 400 mL, discarded; (2) Tubes 12–25, compound **4**, 760 mg (white solid, 40.8%): R_f 0.72 (A), R_f 0.30 (B). Anal. Calcd for $C_{16}H_{20}O_{10}$: C, 51.60; H, 5.42. Found: C, 51.39; H, 5.43; (3) Tubes 38–43, compound **5**, 791 mg (pale-yellow solid, 30.2%): R_f 0.25 (A), R_f 0.36 (B). Anal. Calcd for $C_{23}H_{24}O_{14}$: C, 52.66; H, 4.61. Found: C, 52.55; H, 4.60; (4) Tubes 46–52, compound **6**, 402 mg (pale-yellow solid, 11.8%): R_f 0.11 (A), R_f 0.42 (B). Anal. Calcd for $C_{30}H_{28}O_{18}$: C, 53.24; H, 4.17. Found: C, 53.40; H, 4.18; (5) Column residue, 566 mg, unknown composition.

O-*Galloyl*-D-*glucoses* (**3**, **7**, **8**, *and* **9**).—*O*-Galloyl-α-D-glucofuranoses (**2**, **4**, **5**, and **6**) were each separately stirred in 1 M HCl at 90 °C for 50 min. After evaporation of the solvent, each residue was purified by Sephadex LH-20 column chromatography (120 × 2 cm i.d.). The purified *O*-galloyl-D-glucose derivatives were collected based on TLC analyses. Traces of gallic acid and glucose could be detected by TLC on further hydrolysis.

3-*O*-Galloyl-D-glucose (**3**) was isolated as a light brown solid, yield 81%: R_f 0.76 (A), R_f 0.20 (B). Anal. Calcd for $C_{13}H_{16}O_{10}\cdot H_2O$: C, 44.56; H, 5.18. Found: C, 44.66; H, 5.15; 6-*O*-galloyl-D-glucose (**7**) was isolated as a light brown solid, yield 71.7%: R_f 0.75 (A), R_f

0.26 (B). Anal. Calcd for $C_{13}H_{16}O_{10}\cdot H_2O$: C, 44.56; H, 5.18. Found: C, 44.48; H, 5.14; 3,6-Di-*O*-galloyl-D-glucose (**8**) was isolated as a buff amorphous solid, yield 66.3%: R_f 0.28 (A), R_f 0.35 (B), lit.[18] R_f 0.28 (A), R_f 0.34 (B). Anal. Calcd for $C_{20}H_{20}O_{14}\cdot H_2O$: C, 47.80; H, 4.42. Found: C, 47.86; H, 4.43; 3,4,6-Tri-*O*-galloyl-D-glucose (**9**) was isolated as a buff solid, yield 49.5%: R_f 0.13 (A), R_f 0.40 (B). Anal. Calcd for $C_{27}H_{24}O_{18}\cdot 0.5\ H_2O$: C, 50.22; H, 3.91. Found: C, 50.27; H, 3.89; All the R_f data are the average values of two very close-running zones (α and β anomers).

Acknowledgements

We thank the Natural Science Foundation of China for the financial support of this work (29872025).

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