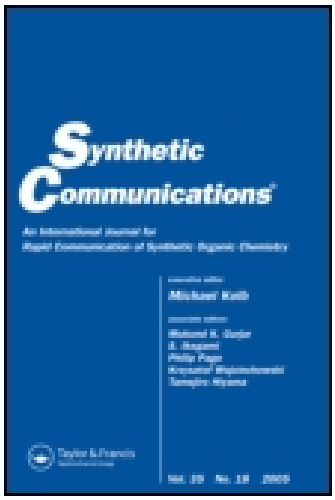

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A Novel, Convenient Synthesis of the 3-*O*-β-D- and 4′-*O*-β-D-Glucopyranosides of *trans*-Resveratrol

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ABSTRACT

trans-Resveratrol-3-*O*-β-D-glucupyranoside (*trans*-piceid, **2**) and *trans*-resveratrol-4′-*O*-β-D-glucupyranoside (*trans*-resveratroloside **3**) are the naturally occurring *O*-glucoside conjugates of the polyphenolic stilbenoid *trans*-resveratrol **1**. Recently, attention has been drawn towards the interesting biological properties of the glucoside conjugates **2** and **3** as well as those of the aglycone **1**. The fact that only limited quantities can be obtained by extraction from natural sources has prompted the development of novel syntheses of **2** and **3**, based on a convergent Heck-coupling strategy, which now conveniently allows for the preparation of multi-milligram to gram quantities of each.

Key Words: *trans*-Resveratrol; Glucupyranoside; Glucosidation; Heck reaction.

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INTRODUCTION

trans-Resveratrol [(*E*)-3,4′,5-trihydroxystilbene, **1**] (Fig. 1) is a polyphenolic stilbenoid derivative produced by certain plants as a natural antibiotic to protect against fungal attack.[1] **1** has been detected in pharmacologically significant quantities in foodstuffs such as peanuts[2] and in red wines.[3] A number of independent studies attest to the ability of **1** to exert an impressively wide array of biological activities. For example, **1** has been observed to display anti-platelet aggregation activity,[4] anti-leukemic[5] and anti-fungal activity,[6] and vasorelaxant action.[7] Indeed, **1** has probably been most famously implicated in the so-called "French Paradox."[8] Regular ingestion of **1** by the red wine-drinking population is believed to contribute to lower rates of coronary heart disease in some regions of France than would be expected due to the typical diet rich in fat and alcohol.[9]

Although pharmacological attention has centered mainly on the aglycone **1**, red wine also contains *trans*-resveratrol-3-*O*-*β*-D-glucopyranoside **2**[10] (also known as *trans*-piceid or polydatin, Fig. 1) which is endowed with anti-platelet aggregation[11] and anti-cancer activity.[12] Appreciable quantities of **2** have been found in the roots of *Polygonum cuspidatum*,[13] an Asian plant that has been used in traditional Chinese herbal medicines for the treatment of hypertension and cancer. The regioisomeric *trans*-resveratrol-4′-*O*-*β*-D-glucopyranoside **3** (also known as *trans*-resveratroloside, Fig. 1) has also been identified in extracts from certain varieties of *Polygonum cuspidatum*[14] and in *Vitis vinifera* cell cultures.[15,16] Kinase[17] and endopeptidase[18] inhibitory properties have been ascribed to **3**.

Although increasing interest in the biological properties of such polyphenolic stilbenoids has recently led to a number of elegant new syntheses[19–23] of the aglycone **1**, it is rather surprising to find that comparatively few methods

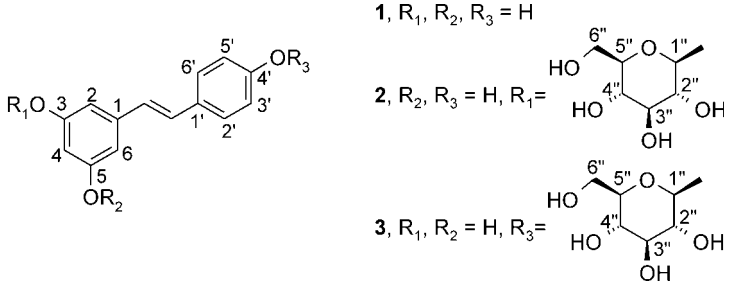

Figure 1. Chemical structures of trans-resveratrol **1**, *trans*-resveratrol-3-*O*-*β*-D-glucupyranoside **2**, and *trans*-resveratrol-4′-*O*-*β*-D-glucupyranoside **3**.

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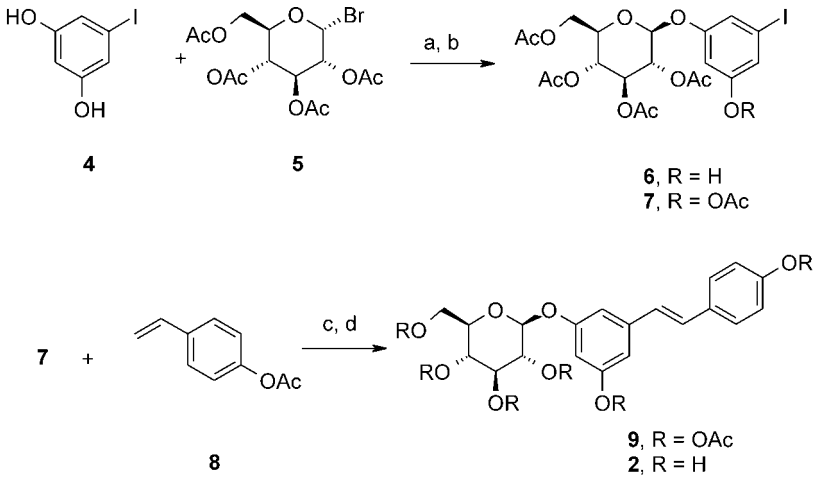
exist for the chemical synthesis of **2**, and to the best of the author's knowledge, no synthesis of **3** has been yet disclosed. Orsini et al. reported[11,24] a synthesis of **2** based on a Wittig olefination strategy to form the core stilbenic skeleton, which requires chromatographic separation of the *cis*- and *trans*-olefinic isomers. Brandolini et al. described a direct glucosidation of **1**, although the conversion of **1** to **2** is quite low.[25] From this laboratory there was recently reported a novel method for the preparation of the corresponding 3-*O*-β-D- and 4′-*O*-β-D-glucuronide conjugates of **1** based on a novel Heck coupling of iodoaryl-*O*-β-D-glucuronate esters with appropriately substituted styrenes.[26] In the present study, it is shown that a similar convergent strategy can now be conveniently applied to the synthesis of the corresponding glucosides **2** and **3**.

The present synthesis of *trans*-resveratrol-3-*O*-β-D-glucopyranoside **2** is outlined in Sch. 1.

The aryl iodide was preferred due to the generally greater reactivity over the corresponding aryl bromides in the palladium-catalyzed Heck coupling reaction, which was employed as the key step in forming the fully functionalized stilbenoid. Accordingly, 3,5-dihydroxyiodobenzene **4** was prepared from commercially available 3,5-dimethoxyaniline via Sandmeyer reaction (59% yield) and demethylation (57% HI, 90% yield) as previously described by Deboves et al.[27] Reaction of **4** with commercially available acetobromo-α-D-glucose **5** in acetonitrile in the presence of silver carbonate afforded the



Scheme 1. Synthesis of *trans*-resveratrol-3-*O*-β-D-glucupyranoside **2**. Reagents: (a) Ag_2CO_3, CH_3CN, rt; (b) Ac_2O, py, DMAP, CH_2Cl_2, rt; (c) $Pd(OAc)_2$, $BnEt_3N^+Cl^-$, Bu_3N, CH_3CN, 85°C; and (d) 0.2 M $NaOCH_3/CH_3OH$, rt.

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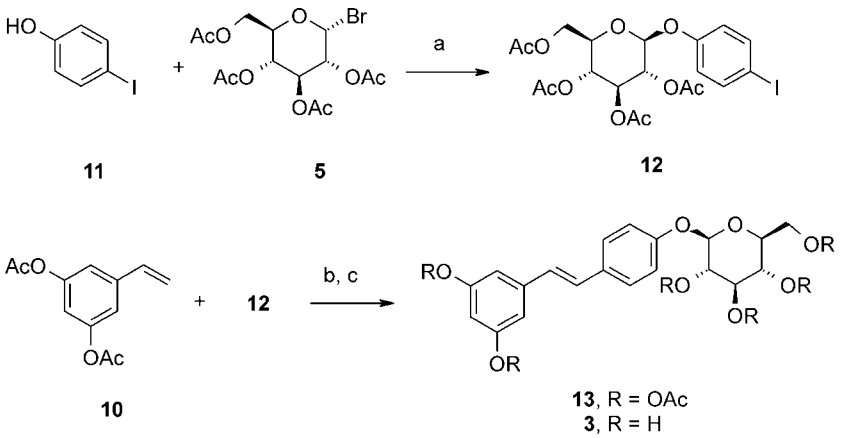
3-*O*-*β*-D-glycosylated iodophenol **6** in moderate yield (38%) exclusively as the *β*-anomer. Unreacted **4** could be recovered (20%) by chromatographic separation and recycled. Protection of the phenol as the *O*-acetate proceeded uneventfully to provide **7**, which was then successfully coupled with commercially available 4-acetoxystyrene **8** ($Pd(OAc)_2$, $BnEt_3N^+Cl^-$, Bu_3N) in warm acetonitrile to give the fully protected glucoside **9** in moderate yield (40%). Deprotection of the acetyl protecting groups of **9** proceeded smoothly with dilute methanolic sodium methoxide solution at room temperature to provide *trans*-resveratrol-3-*O*-*β*-D-glucopyranoside **2** in 94% yield. HPLC analysis showed that this product was ≥98% homogenous.

Accordingly, preparation of *trans*-resveratrol-4′-*O*-*β*-D-glucopyranoside **3** followed along similar lines (Sch. 2).

3,5-Diacetoxystyrene **10** was prepared as previously reported by Guiso et al. from commercially available 3,5-dihydroxybenzaldehyde.[19] The iodo-4-*O*-*β*-D-glucosidated phenol **12** was obtained exclusively as the *β*-anomer by reaction of commercially available 4-iodophenol **11** with acetobromo-*α*-D-glucose **5** and silver carbonate in acetonitrile (30% yield). **12** subsequently underwent smooth palladium-catalyzed coupling with styrene **10** under very slightly different conditions previously used to give the fully *O*-acetyl protected 4′-*O*-*β*-D-glycoside **13** in quite respectable (61% yield). Basic hydrolysis of the protecting groups afforded *trans*-resveratrol-4′-*O*-*β*-D-glucopyranoside **3** (97% yield) and HPLC analysis again revealed homogeneity ≥98%.



Scheme 2. Synthesis of *trans*-resveratrol-4′-*O*-*β*-D-glucopyranoside **2**. Reagents: (a) Ag_2CO_3, CH_3CN, rt; (b) Ac_2O, py, DMAP, CH_2Cl_2, rt; (c) $Pd(OAc)_2$, $BnEt_3N^+Cl^-$, Bu_3N, CH_3CN, 100°C; and (d) 0.2 M $NaOCH_3/CH_3OH$, rt.

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CONCLUSIONS

Novel, convenient syntheses are described for *trans*-resveratrol-3-*O*-*β*-D-glucupyranoside (*trans*-piceid, **2**) and *trans*-resveratrol-4′-*O*-*β*-D-glucupyranoside (*trans*-resveratroloside **3**), which allow for convenient preparation of pure, multi-milligram to gram quantities of either glucoside.

EXPERIMENTAL SECTION

Melting points were measured in open capillary tubes on an Electrothermal Model 9100 hot stage apparatus and are uncorrected. NMR spectra were recorded on a Bruker Avance DPX (400 MHz) spectrometer with solvent used as internal standard, and data are reported in the order: chemical shift (ppm), number of protons, approximate coupling constant in Hertz, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet; dd, double doublet; br, broad), and assignment of the signal. IR spectra were measured with a Bomem Hartmann & Braun MB Series FTIR spectrometer using KBr discs. Analytical HPLC was performed on an automated Agilent 1100 Series HPLC, using LiChrospher 100 RP-18 (5 μm) LiChroCart 250-4 Cartridges (Merck) in combination with acetonitrile/water (1% formic acid) mixtures. Analytical TLC was performed on pre-coated silica gel plates (either Merck 60 Kieselgel F_{254} or Merck RP-18 F_{254s}) and visualized with UV light. Preparative chromatography was done on Merck 60 Kieselgel (0.063–0.2 mm). Optical rotation determinations were performed on a Jasco DIP-1000 digital polarimeter at the sodium *d* line (589 nm), at 25°C using a 50 mm path length cell. Elemental analyses were performed on a Fisons EA 1110 CHNS instrument and all analyses are consistent with theoretical values to within ±0.4% unless otherwise indicated. 4-Acetoxystyrene **8** was purchased from Aldrich and acetobromo-*α*-D-glucose **5** from Lancaster and these were used as received.

3-Hydroxy-5-iodophenyl-2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranoside 6. To a stirred solution of **4** (2.0 g, 8.47 mmol) and acetobromo-*α*-D-glucose **5** (3.48 g, 8.47 mmol) in acetonitrile (20 cm^3) at room temperature was added silver carbonate (2.34 g, 8.47 mmol) in portions. The resulting suspension was stirred for 8 hr and then filtered through a short Celite pad. The filtrate was evaporated (40°C, water-aspirator pressure) to leave a dark brown gum. Chromatography over silica gel (petroleum ether/ethyl acetate, 2/1) afforded the major product as a slightly hygroscopic white foam (1.82 g, 38%). $[\alpha]_D^{25} = -39.6^\circ$ (*c* 0.32, MeOH); (Found: C, 42.49; H, 4.09. $C_{20}H_{23}IO_{11}$ requires C, 42.42; H, 4.09%); ν_{max} (KBr disc)/cm^{-1} 3359 (OH) and 1755 (CO); δ_H (400 MHz, DMSO-*d*6) 7.0 (1H, s, H-2), 6.9 (1H, s, H-6), 6.5 (1H, s, H-4), 5.9 (1H, s, phenolic OH), 5.32–5.21 (2H, m,

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H-2″, H-3″), 5.13 (1H, m, H-4″), 5.03 (1H, d, *J* 7.6, anomeric H-1″), 4.25–4.13 (2H, m, H-6″A, H-6″B), 3.91–3.87 (1H, m, H-5″), and 2.14–2.03 (12H, 4 × s, 4 × CH_3); δ_C (100 MHz, DMSO-*d*6) 171.5 (CO), 170.9 (CO), 170.1 (CO), 170.0 (CO), 158.6 (C-5), 157.9 (C-3), 120.5 (C-2), 118.8 (C-6), 105.3 (C-4), 99.3 (anomeric C-1″), 94.3 (C-1), 73.2 (C-2″), 72.7 (C-5″), 71.6 (C-3″), 68.9 (C-4″), 62.6 (C-6″), 21.4 (CH_3), and 21.2 (3 × CH_3).

3-Acetoxy-5-iodophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside 7. To a stirred solution of phenol **6** (1.60 g, 2.83 mmol) in dichloromethane (10 cm^3) at room temperature was added pyridine (0.28 g, 3.53 mmol), 4-dimethylaminopyridine (0.02 g) followed by acetic anhydride (0.36 g, 3.53 mmol) dropwise. The resulting mixture was stirred for 30 min, whereupon ice/water (10 cm^3) was added. The organic phase was separated and washed with dilute hydrochloric acid (10 cm^3), water (10 cm^3), and brine (10 cm^3), then dried over anhydrous magnesium sulfate, filtered, and evaporated (40°C, water-aspirator pressure). Toluene (10 cm^3) was added to the residue and re-evaporated to leave a colorless gum (1.68 g, 98%) which was used without further purification. $[\alpha]_D^{25} = -43.6°$ (*c* 0.3, MeOH); (Found: C, 43.61; H, 4.00. $C_{22}H_{25}O_{12}$ requires C, 43.43; H, 4.14%); ν_{max} (KBr disc)/cm^{-1} 1750 (CO); δ_H (400 MHz, DMSO-*d*6) 7.22 (1H, s, H-2), 7.19 (1H, s, H-6), 6.74 (1H, s, H-4), 5.32–5.23 (2H, m, H-2″, H-3″), 5.16–5.11 (1H, m, H-4″), 5.07 (1H, d, *J* 7, anomeric H-1″), 4.25–4.18 (2H, m, H-6″A, H-6″B), 3.93–3.88 (1H, m, H-5″), 2.24 (3H, s, CH_3), 2.13 (3H, s, CH_3), 2.08 (3H, s, CH_3), 2.07 (3H, s, CH_3), and 2.02 (3H, s, CH_3); δ_C (100 MHz, DMSO-*d*6) 171.2 (CO), 170.7 (CO), 170.0 (CO), 169.8 (CO), 169.3 (CO), 158.0 (C-5), 152.0 (C-3), 125.8 (C-2), 123.4 (C-6), 111.4 (C-4), 99.2 (anomeric C-1″), 93.6 (C-1), 73.1 (C-2″), 72.8 (C-5″), 71.5 (C-3″), 68.7 (C-4″), 62.7 (C-6″), 22.02 (CH_3), 21.5 (CH_3), 21.4 (CH_3), 21.2 (CH_3), and 21.1 (CH_3).

(*E*)-1-(3-Acetoxy-5-*O*-2,3,4,6-tetraacetyl-β-D-glucopyranosidophenyl)-2-(4′-acetoxyphenyl)ethene 9. A mixture of **7** (1.63 g, 2.69 mmol), 4-acetoxystyrene **8** (0.44 g, 2.69 mmol), palladium(II) acetate (0.03 g, 0.13 mmol), benzyltriethylammonium chloride (0.61 g, 2.69 mmol), and tributylamine (1.31 g, 7.06 mmol) in acetonitrile (20 cm^3) was stirred at 85°C for one and a half hours under argon, and then allowed to cool to room temperature. The mixture was filtered through a short Celite path and evaporated to dryness (40°C, water-aspirator pressure). The residue was dissolved in dichloromethane (20 cm^3) and washed with dilute hydrochloric acid (10 cm^3), water (10 cm^3), and brine (10 cm^3), then dried over anhydrous magnesium sulfate, filtered, and evaporated (40°C, water-aspirator pressure). The residue was chromatographed over silica gel (petroleum ether/ethyl acetate, 3/2) to give a pale yellow foam that was recrystallized from diethyl ether to give a white powder (0.69 g, 40%) of m.p. 109–110°C; $[\alpha]_D^{25} = -68.7°$

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(*c* 0.25, MeOH); (Found: C, 59.63; H, 4.99. $C_{32}H_{34}O_{14}$ requires C, 59.81; H, 5.33%); ν_{max} (KBr disc)/cm^{-1} 1756 (CO); δ_H (400 MHz, DMSO-*d*6) 7.51 (2H, d, *J* 8.4, H-2′, H-6′), 7.11 (2H, d, *J* 8.4, H-3′, H-5′), 7.05–6.94 (4H, m, H-2, H-4, 2 × vinylic CH), 6.7 (1H, s, H-6), 5.34–5.27 (2H, m, H-2″, H-3″), 5.2–5.13 (2H, m, anomeric H-1″, H-4″), 4.32–4.27 (1H, m, H-6″A), 4.21–4.18 (1H, m, H-6″B), 3.94–3.92 (1H, m, H-5″), 2.32 (6H, s, 2 × CH_3), 2.09 (3H, s, CH_3), 2.07 (6H, s, 2 × CH_3), and 2.05 (3H, s, CH_3); δ_C (100 MHz, DMSO-*d*6) 171.1 (CO), 170.8 (CO), 170.0 (CO), 169.9 (CO), 169.8 (CO), 158.1 (C-3), 150.9 (C-4′), 150.2 (C-6), 150.0 (C-1), 140.2 (C-2), 135.0 (C-1′), 130.1 (vinylic C), 128.2 (vinylic C), 127.9 (C-6′), 122.5 (C-5′), 99.3 (anomeric C-1″), 73.2 (C-3″), 72.6 (C-2″), 71.6 (C-4″), 68.9 (C-5″), 62.6 (C-6″), 21.7 (CH_3), 21.2 (CH_3), and 21.1 (CH_3).

***trans*-Resveratrol-3-*O*-β-D-glucopyranoside 2.** To a suspension of **9** (0.55 g, 0.86 mmol) in methanol (30 cm^3) at room temperature was added a 0.2 M methanolic solution of sodium methoxide (30 cm^3). The resulting mixture was stirred for 1 hr, whereupon sufficient Dowex 50WX8-100 ion exchange resin was added in portions to maintain pH ∼2. The resin was filtered off and washed with methanol (5 cm^3). The combined filtrate was evaporated (40°C, water-aspirator pressure), and the residue was dried at 45°C over phosphorus pentoxide to give the product as a beige solid (0.31 g, 94%) of m.p. 226–229°C (lit.,[28] 228–230°C); $[\alpha]_D^{25} = -64^\circ$ (*c* 0.32, MeOH) (lit.,[25] $[\alpha]_D^{25} = -62^\circ$); (Found: C, 58.16; H, 6.32. $C_{20}H_{22}O_8 1{\cdot}3H_2O$ requires C, 57.97; H, 6.00%); ν_{max} (KBr disc)/cm^{-1} 3367 (OH, very broad) and 1592; δ_H (400 MHz, DMSO-*d*6) 9.59 (1H, s, phenolic OH), 9.46 (1H, s, phenolic OH), 7.40 (2H, d, *J* 8.2, H-2′, H-6′), 7.03 (1H, d, *J* 16.3, vinylic CH), 6.86 (1H, d, *J* 16.3, vinylic CH), 6.76 (2H, d, *J* 8.2, H-3′, H-5′), 6.7 (1H, s, H-6), 6.6 (1H, s, H-2), 6.3 (1H, s, H-4), 4.80 (1H, d, *J* 7.3, anomeric H-1″), 3.73–3.71 (1H, m, H-6″A), and 3.69–3.14 (5H, m, H-2″, H-3″, H-4″, H-5″, H-6″B); δ_C (100 MHz, DMSO-*d*6) 159.9 (C-5), 159.3 (C-3), 158.3 (C-4′), 140.3 (C-1), 129.5 (vinylic C), 128.9 (C-6′), 126.2 (vinylic C), 116.5 (C-5′), 108.2 (C-2), 105.7 (C-6), 103.7 (C-4), 101.6 (anomeric C-1″), 78.13 (C-5″), 77.69 (C-3″), 74.29 (C-2″), 70.6 (C-4″), and 61.7 (C-6″).

4-Iodophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside 12. To a stirred solution of 4-iodophenol (1.0 g, 4.54 mmol) and acetobromo-α-D-glucose **5** (2.80 g, 6.82 mmol) in acetonitrile at room temperature was added silver carbonate (1.88 g, 6.82 mmol) in portions. The resulting mixture was stirred in the dark for 48 hr, and then filtered through a short Celite pad. The filtrate was evaporated to dryness (40°C, water-aspirator pressure) to leave an oil that solidified on standing. Recrystallization from a dichloromethane/isopropanol mixture afforded the product as a white solid (0.75 g, 30%) of m.p. 142–143°C; $[\alpha]_D^{25} = -51.6^\circ$ (*c* 0.29, MeOH); (Found: C, 43.84; H, 4.33. $C_{20}H_{23}IO_{10}$ requires C, 43.65; H, 4.21%); ν_{max} (KBr disc)/cm^{-1} 1747 (CO); δ_H

(400 MHz, DMSO-*d*6) 7.57 (2H, d, *J* 8, H-3, H-5), 6.75 (2H, d, *J* 8, H-2, H-6), 5.30–5.22 (2H, m, H-2″, H-3″), 5.15 (1H, m, H-4″), 5.03 (1H, d, *J* 8, anomeric H-1″), 4.27 (1H, dd, *J* 4 and 12, H-6″A), 4.15 (1H, dd, *J* 4 and 12, H-6″B), 3.86–3.82 (1H, m, H-5″), and 2.08–2.03 (12H, 4 × s, 4 × CH_3); δ_C (100 MHz, DMSO-*d*6) 170.4 (CO), 170.1 (CO), 169.2 (CO), 169.1 (CO), 156.5 (C-1), 138.4 (C-3), 119.2 (C-2), 99.0 (anomeric C-1″), 86.3 (C-4), 78.2 (C-5″), 72.7 (C-2″), 71.2 (C-3″), 68.3 (C-4″), 62.0 (C-6″), 21.0 (CH_3), 20.9 (CH_3), and 20.8 (CH_3).

(*E*)-1-(3,5-Diacetoxy)-2-(4′-*O*-2,3,4,6-tetraacetyl-β-D-glucopyranosidophenyl)ethene 13. A mixture of 3,5-diacetoxystyrene **10** (0.20 g, 0.89 mmol), **12** (0.49 g, 0.89 mmol), palladium(II) acetate (0.01 g, 0.044 mmol), benzyltriethylammonium chloride (0.20 g, 0.89 mmol) and tributylamine (0.43 g, 2.34 mmol) in acetonitrile was stirred at 100°C for 2 hr under argon, and then allowed to cool to room temperature. The mixture was filtered through a short Celite pad and then evaporated to dryness (40°C, water-aspirator pressure). The residue was taken up in dichloromethane (20 cm^3) and washed with dilute hydrochloric acid (10 cm^3), water (10 cm^3), and brine (10 cm^3), then dried over anhydrous magnesium sulfate, filtered, and evaporated (40°C, water-aspirator pressure) to leave an oil that solidified on standing. Recrystallization from dichloromethane/isopropanol gave the product as white crystals (0.35 g, 61%) of m.p. 169–170°C; $[\alpha]_D^{25} = -46.4^\circ$ (*c* 0.35, MeOH); (Found: C, 59.75; H, 5.42. $C_{32}H_{34}O_{14}$ requires C, 59.81; H, 5.33%); ν_{max} (KBr disc)/cm^{-1} 1747 (CO); δ_H (400 MHz, DMSO-*d*6) 7.40 (2H, d, *J* 8, H-2′, H-6′), 7.10 (2H, m, H-2, H-6), 7.02 (1H, d, *J* 16, vinylic H), 6.97 (2H, d, *J* 8, H3′, H5′), 6.90 (1H, d, *J* 16, vinylic H), 6.79 (1H, m, H-4), 5.30–5.28 (2H, m, H-2″, H-3″), 5.17 (1H, m, H-4″), 5.09 (1H, d, *J* 8, anomeric H-1″), 4.30 (1H, dd, *J* 4 and 12, H-6″A), 4.17 (1H, dd, *J* 4 and 12, H-6″B), 3.89–3.86 (1H, m, H-5″), 2.31 (6H, s, 2 × CH_3), and 2.09–2.04 (12H, 4 × s, 4 × CH_3); δ_C (100 MHz, DMSO-*d*6) 170.1 (CO), 169.3 (CO), 168.9 (CO), 156.5 (C-4′), 139.6 (C-1), 132.0 (C-1′), 129.6 (vinylic C), 127.9 (C-2′), 126.1 (vinylic C), 117.2 (C-2, C-6) 116.8 (C-3′), 114.2 (C-4), 99.0 (anomeric C-1″), 72.8 (C-2″), 72.2 (C-5″), 71.2 (C-3″), 68.4 (C-4″), 62.1 (C-6″), 21.5 (CH_3), 21.0 (CH_3), and 20.9 (CH_3).

***trans*-Resveratrol-4′-*O*-β-D-glucopyranoside 3.** To a suspension of **13** (0.29 g, 0.45 mmol) in methanol (20 cm^3) at room temperature was added a 0.2 M methanolic solution of sodium methoxide (20 cm^3). The resulting mixture was stirred for 1 hr, whereupon sufficient Dowex 50WX8-100 ion exchange resin was added in portions to maintain pH ~2. The resin was filtered off and washed with methanol (5 cm^3). The combined filtrate was evaporated (40°C, water-aspirator pressure), and the residue was dried at 45°C over phosphorus pentoxide to give the product as a beige solid (0.17 g, 97%)

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of m.p. 210–215°C; $[\alpha]_D^{25} = -73.9^\circ$ (*c* 0.39, MeOH); (Found: C, 60.96; H, 6.22. $C_{20}H_{22}O_8 \cdot H_2O$ requires C, 61.22; H, 6.16%); ν_{max} (KBr disc)/cm^{-1} 3429 (OH, very broad) and 1600; δ_H (400 MHz, $(CH_3)_2CO$-*d*6) 9.23 (2H, s, phenolic OH), 7.48 (2H, d, *J* 8, H-2′, H-6′), 7.06–7.02 (3H, vinylic H, H-3′, H-5′), 6.94 (1H, d, *J* 16, vinylic H), 6.54 (2H, s, H-2, H-6), 6.27 (1H, s, H-4), 4.97 (1H, d, *J* 7.7, anomeric H-1″) 3.89 (1H, dd, *J* 2.6 and 11.8, H-6″A), 3.70 (1H, dd, *J* 2.6 and 11.8, H-6″B), and 3.55–3.44 (4H, m, H-2″, H-3″, H-4″, H-5″); δ_C (100 MHz, $(CH_3)_2CO$-*d*6) 159.4 (C-3, C-5), 158.3 (C-4′), 140.5 (C-1), 132.3 (C-1′), 128.5 (vinylic C), 128.4 (C-2′), 128.1 (vinylic C), 117.5 (C-3′), 105.7 (C-2), 102.8 (C-4), 101.8 (anomeric C-1″), 77.9 (C-2″), 74.7 (C-5″), 71.3 (C-4″), and 62.7 (C-6″).

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