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Reactivity of Glucosyl Radical in the Presence of Phenols

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Abstract: Glucosyl radicals from the photoreaction of α-bromo-2,3,4,6-tetra-*O*-acetylglucose (**ABG**) with hexabutylditin react with phenols. 4-$H_3COC_6H_4O\bullet$ was identified by means of EPR spectroscopy in the case of 4-methoxyphenol, and the corresponding α-*O*-glucoside was isolated along with 1- and 2-deoxysugars and the dimers of glucosyl radical. The present results are consistent with the formation of α-*O*-glucosides observed in the electrochemical reaction of **ABG** and phenols, although in this case the dimers represent the main reaction products.

The electrochemical reduction of α-bromo-2,3,4,6-tetra-*O*-acetylglucose (**ABG**) in the presence of acrylonitrile[1] and of phenols[2] affords low amounts of α-*C*-glucosides and α-*O*-glucosides, respectively, whose formation can be accounted for by admitting the presence of an intermediate glucosyl radical. While the addition of glucosyl radicals to electron-deficient olefins is well established,[3] the formation of α-*O*-glucosides in the presence of phenols seems less straightforward, and prompted us to undertake an EPR and product study of this reaction with the aim of getting a deeper insight of its mechanism.

In analogy with the reduction of alkyl halides,[4] the first step of the electrochemical process is no doubt the reduction of the glucosyl halide to the corresponding radical-anion; this undergoes rapid loss of the bromide anion to give the glucosyl radical which, at least in the case of acrylonitrile, is the species responsible of the observed reactivity. The isolation of α-*O*-glucosides in the presence of phenols cannot be accounted for through an ionic mechanism, but most likely involves coupling of glucosyl and phenoxyl radicals. Because the formation of the latter species cannot take place under the experimental conditions *via* anodic oxidation, it must occur through an intermediate glucosyl radical. In order to further prove the role played by the glucosyl radical, this species was generated and reacted with phenols under conditions such that no ionic process could take place. The reaction products were identified and quantified in the case of 4-methoxyphenol, and the transient radical intermediates were characterised by means of EPR spectroscopy. On the basis of the nature of the characterised products, the product distribution of the previous electrochemical studies has been reconsidered.

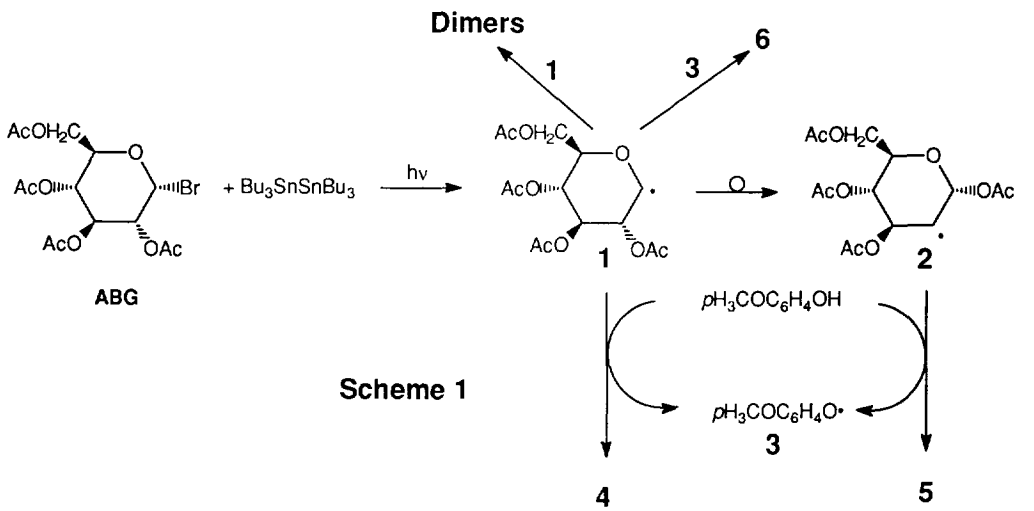
RESULTS AND DISCUSSION

Argon purged benzene solutions of **ABG** and hexabutylditin were photolysed at 250 nm at room temperature for 8 hrs either in the absence or in the presence of 4-methoxyphenol. In both cases, **ABG** was totally converted; 2,3,4,6-tetra-*O*-acetyl-1,5-anhydroglucitol **4**,[5] 1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose **5**[6] and a mixture of the isomeric dimers[*] were isolated in both the experiments. In the presence of the phenol, 1-*O*-(2',3',4',6'-tetra-*O*-acetyl-α-D-glucopyranosyl)-4-methoxybenzene **6** and a complicated mixture of C-glucosilated phenolic oligomers were additionally obtained. The product distribution for the two cases is shown in Table 1.

Table 1 - Yield % of isolated products

4-MeO-Phenol	4	5	Dimers	6	Oligomers
Absent[a, b]	4.5	12	42	------	------
Present[c]	33	15	25	4	8
Present[d]	37	23	< 3	0	16

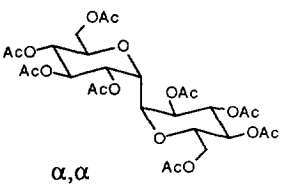
[a]A significative amount (12%) of isomeric 1-butyl-2,3,4,6-tetra-*O*-acetyl-1,5-anhydroglucitols (**7**) (ratio α:β ≅ 1:1) was isolated. [b]Ratio **ABG**: hexabutylditin = 1:1; [**ABG**] = 0.18 M. [c]Ratio **ABG**: hexabutylditin: 4-methoxyphenol = 1:1:2; [**ABG**] = 0.18 M. [d]Ratio **ABG**: hexabutylditin: 4-methoxyphenol = 1:1:29; [**ABG**] = 0.1 M.



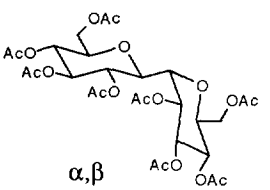
Scheme 1

[*]1,3,4,5,8,9,10,12-Octa-*O*-acetyl-D-gluco-L-altro-L-erythro-2,6:7,11-dianhydrododecitol (α,β-biglucosyl derivative); 1,3,4,5,8,9,10,12-octa-*O*-acetyl-D-gluco-D-galacto-L-erythro-2,6:7,11-dianhydrododecitol(β,β-biglucosylderivative);1,3,4,5,8,9,10,12-octa-*O*-acetyl-D-gluco-L-ido-L-erythro-2,6:7,11-dianhydrododecitol (α,α-biglucosylderivative). These compounds are treated for convenience as biglucosyl derivatives. The anomeric carbon atoms are referred to as C-1 (α configuration) and C-1' (β configuration).

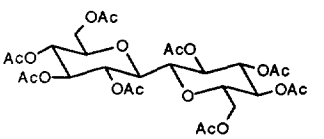
The reaction obviously proceeds through the initial formation of glucosyl radical **1** whose reactivity dictates the products distribution. Thus, in the absence of the phenol radical **1** mainly undergoes dimerisation, and, to a minor extent, reduction through hydrogen abstraction from another sugar molecule, giving rise to traces of unidentified different products.[7] In the presence of 4-methoxyphenol, on the other hand, the two deoxyderivatives **4** and **5** predominate, while the amount of dimers is reduced. This provides evidence that the glucosyl radical readily abstracts the phenolic hydrogen; the isolation of α-*O*-glucoside **6**, which may result from a coupling between radical **1** and a phenoxyl radical, gives further support to the hydrogen abstraction from the phenol. The different ratios between products **4** and **5** may be seen in two alternative ways. In the absence of the phenolic compound, the rearrangement of radical **1** to radical **2** competes successfully with hydrogen abstraction from another sugar molecule thus affording a larger amount of **5** with respect to **4**. If the presence of 4-methoxyphenol does not affect the rearrangement process, the ratio between dimers and reduction products will decrease in favour of **4**, the amount of **5** being roughly unchanged; if, on the other hand, hydrogen abstraction competes with the rearrangement, the formation of **4** should prevail over that of **5**. In order to find out if control over the acetoxy migration could be achieved to some extent, the photolysis of **ABG** was repeated in the presence of a large excess of 4-methoxyphenol. As shown in Table 1, this resulted in the disappearence of the dimers and α-*O*-glucoside **6** in favour of the 1- and 2-deoxy sugars and of the oligomers. Contrary to expectations, however, while the amount of 1,5-anhydroglucitol **4** was only slightly altered, that of the rearranged 2-deoxyglucose **5** was significantly increased. An explanation of this finding might be found in the greater hydrogen-abstracting ability of radical **2** with respect to **1**, which, on the other hand, can be more readily scavenged by phenolic dimers, formed owing to the presence of greater concentrations of phenoxy radical, to give larger amounts of oligomers.



α,α



α,β



β,β

The most likely overall reaction sequence can be described as outlined in Scheme 1. The unexpected isolation of a significative amount of 1-butyl-2,3,4,6-tetra-*O*-acetyl-1,5-anhydroglucitol **7** could be justified with a photoalkylation of **ABG** by hexabutylditin, by envisaging a photoinduced electron transfer from the ditin compound to the sugar in analogy with previously observed photoalkylation of pyridine derivatives,[8] tetracyanobenzene and benzil.[9]

EPR experiments were carried out to try and intercept the transient radical species involved in the reactions outlined in Scheme 1. When an argon purged benzene solution of 4-methoxyphenol was photolysed at room temperature inside the cavity of an EPR spectrometer no spectrum of the phenoxyl radical was observed, while the expected signal[10] was detected by addition of some di-*tert*-butyl peroxide to the solution being photolysed. A similarly deoxygenated benzene solution of **ABG** was EPR silent under photolysis; on the other hand, when some hexabutylditin was added a signal was observed which, on the basis of its hyperfine

spectral parameters $a(H_1)$=18.12 G, $a(H_2)$= 12.69 G, $a(H_5)$= 3.47 G, $a(H_3)$= 1.41G, g = 2.0029_5, could be attributed to the anomeric radical[11] resulting from bromine abstraction by the *in situ* generated Bu_3Sn•.

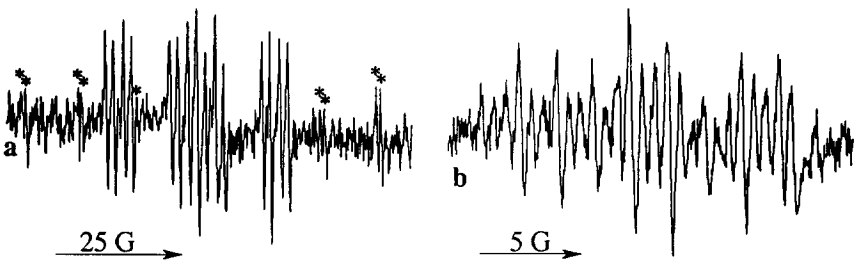


Figure 1

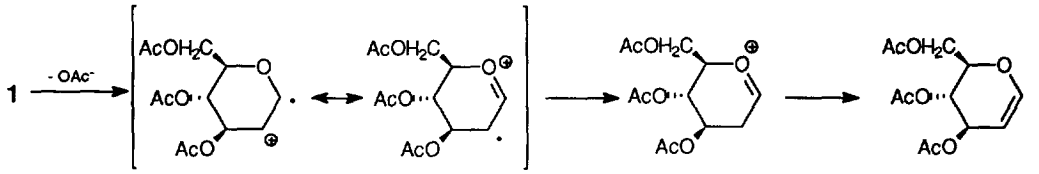
a) EPR spectrum observed when irradiating deoxygenated benzene solutions of **ABG** and Bu_6Sn_2 at ca. 40°C. The main spectrum is due to radical **1** while the starred lines are due to the rearranged radical **2**. **b)** EPR spectrum of radical **3** observed when irradiating a deoxygenated benzene solution of **ABG**, Bu_6Sn_2, and 4-methoxyphenol at room temperature.

When the temperature of the solution was let to rise to about 40°C, some new weak lines appeared at the wings of the main spectrum (see Figure 1a) owing to the formation of a second radical **2** [$a(H_1)$= 11.07 G, $a(H_5)$= 0.86, $a(H_2)$= 21.92, $a(H_3)$= 37.13 G, g = 2.0026_6] resulting from migration of an acetoxy group of **1** from carbon 2 to the anomeric carbon, such rearrangement being in line with previous reports.[11]

On the other hand, when a solution of **ABG** containing a large amount of 4-methoxyphenol and Bu_6Sn_2 was similarly photolysed at room temperature, a totally different spectrum (Figure 1b) was observed which could be attributed to 4-methoxyphenoxyl radical [$a(H_{3,5})$= 0.61 G, $a(H_{2,6})$= 5.45 G, $a(H_{OCH_3})$= 1.86 G, g = 2.0046_5].[10] As in separate experiments no signals were observed by photolysis of benzene solutions of either the phenol and the ditin compound or the phenol and **ABG**, the appearance of the phenoxyl signal can only be attributed to abstraction of the hydroxylic hydrogen by the anomeric radical **1** and/or by the rearranged radical **2**. Similar experiments carried out by irradiating solutions of **ABG**, Bu_6Sn_2, and different benzene soluble phenolic compounds, such as 2,6-dimethoxyphenol and 2,6-dimethylphenol, did not afford any EPR signal belonging either to the phenoxyl radical or to the sugar radical. The failure to observe the latter species is most likely an indication that the sugar radicals, which must be formed under the experimental conditions, react with the phenol, and that the resulting phenoxyl radicals undergo rapid dimerisation, possibly at the unsubstituted *para*-position characterised by a high spin density.

The ability of sugar radicals to abstract hydrogens from such solvents as toluene and THF[11] or from ACN or other sugar molecules[7] is documented, and, because the photolysis of solutions of **ABG** and Bu_6Sn_2 resulted in the EPR observation of solvent derived radicals along with **1** but not with **2**,[11] the latter species was held responsible for hydrogen abstraction. On the other hand, a similar ability of sugar radicals to abstract phenolic hydrogens was not foreseen on the basis of the known behaviour of carbon centred radicals, and indeed no spectra were obtained when reacting 4-methoxyphenol with such radicals as $\bullet C(CN)(CH_3)_2$ or $\bullet CH_2OC_6H_5$, photolytically generated *in situ* from AIBN or phenoxyacetic acid and IBDA,[12] respectively. In the present

investigation, the observation of only the spectrum of 4-methoxyphenoxyl radical at room temperature suggests that the phenolic hydrogen abstraction should be imputed also to the anomeric radical **1**.



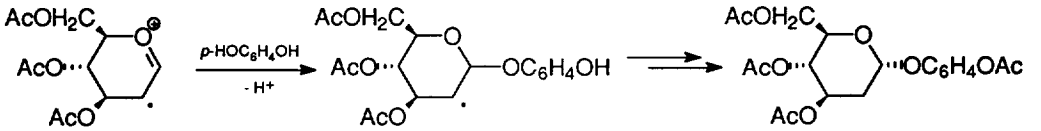
Scheme 2

The isolation of substantial amounts of dimers in the photoreaction of **ABG** with Bu_6Sn_2 both in the absence and in the presence of 4-methoxyphenol has prompted us to reconsider the product distribution observed in previous electrochemical experiments[2] which had been mainly aimed to the characterisation of α-*O*-glycosides. By repeating the electrolysis under the same experimental conditions it was found that indeed the three isomeric dimers accounted for ca. 70% of the reaction products, the isomer ratio being roughly 2 : 1 : 1 (α,β : α,α: β,β). Interestingly, the yield of dimers proved independent of the presence, the nature and the amount of added phenolic compound. We believe that the different product distribution observed in the electrochemical reactions does not imply a different reaction mechanism. Indeed the preferential formation of dimers can be attributed to a high local concentration of radical **1** at the electrode surface, which would favour dimerisation and prevent diffusion of the radical into the reaction medium.

Another remarkable difference between the photochemical and electrochemical experiments is the isolation in the latter case of a significant amount (10-15%) of 3,4,6-tri-*O*-acetyl-D-glucal **10**. As outlined in Scheme 2, formation of the radical cation **8** by loss of an acetate anion could initially occur as previously suggested by other authors for the radical from methoxyalkyl acetate[13] or for α-alkoxy-β-acetoxyalkyl radicals[14] in water. The radical cation **8** would then evolve to the cation **9** via hydrogen abstraction from the solvent and to glucal **10** by subsequent loss of a proton, or, in the electrochemical experiments, undergo reduction to **10**. The fact that in the photochemical experiments only a very small amount (ca 2 %) of the glucal **10** was recovered can be attributed to the different nature of the medium that, being essentially apolar, disfavours the elimination of the acetate anion. The formation of the glucal might be alternatively explained with a previously hypothesised ionic mechanism involving a two-electron C-Br bond cleavage,[15] coupled to a very fast elimination of the acetate anion; in our experiences the nature of the main reaction products and the complete disappearance of **ABG** after passage of approximately one equivalent of charge *per* mole of **ABG** are instead in agreement with a single electron-transfer process.

Traces of 1-*O*-(2'deoxy-3',4',6'-tetra-*O*-acetyl-α-D-glucopyranosyl)-4-*O*-acetyl-hydroquinone **12** (Scheme 3) were also isolated when **ABG** was electrolysed in the presence of hydroquinone and the products acetylated. The same intermediate radical-cation **8** could justify the isolation of **12**. In analogy with the finding that MeO-CH(OH)-CH_2• is detected among the radicals originating from hydrogen abstraction from 2-

methoxyethyl acetate in water,[13] an E1 mechanism could be envisaged involving **8** and **11** as intermediates and phenol as nucleophile, the reaction being terminated by a hydrogen abstraction. Alternatively, the formation of **12** could be explained with a nucleophilic attack of the hydroquinone on the cation **9**.



8 **11** **12**

Scheme 3

Concluding remarks

In the present investigation we have provided evidence towards the ability of sugar radicals to abstract phenolic hydrogens and, what is of greater synthetic relevance, that sugar dimers can be conveniently obtained in rather high yields through electrochemical reactions carried out under mild conditions.

EXPERIMENTAL

General methods

^1H and ^{13}C NMR were recorded on Bruker AC 300P and AMX 500 spectrometers at 303K. Chemical shifts are expressed in ppm downfield from TMS; attributions were made through COSY, TOXY, HMQC and HMBC experiments. Rayonet RPR 208 (Southern New England Ultraviolet Company) and RLU-2537 A lamps (Hg low Pressure, 120 watts, λ= 254 nm) were used for photochemical reactions. Flash-chromatography was performed using silica gel 60 (230-400 Mesh, Merck).

EPR spectra were recorded at room temperature with a Bruker ER200D spectrometer, equipped with an NMR gaussmeter for field calibration and a frequency counter for the determination of *g*-factors that were corrected with respect to that of perylene radical cation in conc. sulphuric acid. Typical samples, consisting of argon-purged benzene solutions of **ABG** (ca.10^{-3} M), the appropriate phenol (ca. 10^{-3} M), and some hexabutylditin, were photolysed at room temperature with the unfiltred light from a Hanovia high-presssure 1 kW mercury lamp.

General procedures

Details of the electrochemical procedure have already been described.[2] The photolytic experiments were carried out as described in the preceding section with the reagent ratios reported in Table 1, and do not need further explanations. The resulting benzene solutions were evaporated under reduced pressure and the crude residues were flash-chromatographed on silica gel; **4**, **5**, **6** and **7** were eluted with hexane - ethyl acetate (5:3), while more polar mixtures were used for the oligomers (hexane - ethyl acetate, 4:6) and the dimers (hexane - ethyl acetate, 2:8). The three dimers were separated by fractional crystallisation from isopropanol: the first and more abundant isomer to crystallise is the α,β followed by the α,α. The residue obtained by evaporation of the mother liquor was recrystallized to give the β,β isomer.

Characterisation of the products

Compounds **4**, **5** and **10** were identified by comparison with authentic samples, while compounds **6** and **7**, the dimers and compound **12** were identified on the basis of their Mass and ^1H and ^{13}C-NMR parameters.

2,3,4,6-tetra-*O*-acetyl-1,5-anhydroglucitol (4)

^1H ($CDCl_3$) δ : 2.05 (9H, 3xs, $OCOCH_3$); 2.10 (3H, s, $OCOCH_3$); 3.31 (1H, t, H-1A, $J_{1A\text{-}1B}$= $J_{1A\text{-}2}$= 11.0 Hz); 3.61 (1H, ddd, H-5, $J_{4\text{-}5}$= 10.0 Hz, $J_{5\text{-}6A}$= 2.5 Hz, $J_{5\text{-}6B}$= 5.0 Hz); 4.13 (1H, dd, H-6, $J_{6A\text{-}6B}$= 12.0 Hz); 4.16

(1H, dd, H-1B, J_{1B-2}= 5.5 Hz); 4.22 (1H, dd, 1H, H-6B); 5.00 (1H, dt, H-2); 5.02 (1H, t, H-4, J_{3-4}= 10.0 Hz); 5.20 (1H, t, H-3, J_{2-3}= 10.0 Hz). MS (EI) m/z: 331(7), 212(34), 170(68), 157(68), 115(100), 98(77).

1-*O*-(2',3',4',6'-tetra-*O*-acetyl-α-D-glucopyranosyl)-4-methoxybenzene (6)

^{13}C (C_6D_6) δ : 20.8 ($OCO\underline{C}H_3$); 55.8 ($O\underline{C}H_3$); 62.4 (C-6'); 69.2 (C-5'); 69.6 (C-4'); 71.4 (C-3'); 71.8 (C-2'); 96.1 (C-1'); 115.6, 118.8 (C-2/6, C-3/5, phenol); 151.3 (C-1, phenol), 158.68 (C-4, phenol); 170.0, 170.4 ($O\underline{C}OCH_3$).

1-butyl-2,3,4,6-tetra-*O*-acetyl-1,5-anhydroglucitol (7)

^{13}C (C_6D_6) δ : 14.1, 14.2 ($\underline{C}H_3CH_2CH_2CH_2$); 20.2, 20.3, 20.4 ($OCO\underline{C}H_3$); 22.5, 22.8, 25.1, 27.4, 31.3 ($CH_3\underline{C}H_2\underline{C}H_2\underline{C}H_2$); 62.2 (C-6$_\beta$); 62.5 (C-6$_\alpha$); 69.0 (C-4$_\beta$, C-5$_\alpha$); 69.5 (C-4$_\alpha$); 71.1 (C-2$_\alpha$, C-3$_\alpha$); 72.4 (C-2$_\beta$); 72.7 (C-1$_\alpha$); 75.0 (C-3$_\beta$); 76.0 (C-5$_\beta$); 77.9 (C-1$_\beta$). ^{1}H ($C_6D_6$) δ : 0.77-0.85 (6H, complex, $\underline{C}H_3CH_2CH_2CH_2$); 1.1-1.35 (8H, complex, $CH_3\underline{C}H_2\underline{C}H_2CH_2$); 1.35-1.6 (4H, complex, $CH_3CH_2CH_2\underline{C}H_2$); 1.58, 1.66, 1.68, 1.69, 1.69, 1.70, 1.70, 1.72 (24H, 8xs, $OCOCH_3$); 3.13 (1H, ddd, H-1$_\beta$, $J_{1-2'}$= 9.8 Hz, J=3.0 Hz; J= 8.0 Hz); 3.22 (1H, ddd, H-5$_\beta$, J_{4-5}= 9.8 Hz, J_{5-6A}= 2.3 Hz, J_{5-6B}= 4.7 Hz); 3.68 (1H, ddd, H-5$_\alpha$, J_{4-5}= 9.3 Hz, J_{5-6A}= 2.5 Hz, J_{5-6B}= 5.2 Hz); 4.03 (1H, dd, H-6A$_\beta$, J_{6A-6B}= 10.1 Hz); 4.03-4.11 (1H, m, H-1$_\alpha$); 4.11 (1H, dd, H-6A$_\alpha$, J_{6A-6B}= 12.0 Hz); 4.23 (1H, dd, H-6B$_\alpha$); 4.26 (1H, dd, H-6B$_\beta$); 5.07 (1H, dd, H-2$_\beta$, J_{2-3}= 9.4 Hz); 5.20 (1H, t, H-4$_\alpha$, J_{3-4}= 9.2 Hz); 5.26 (1H, dd, H-4$_\beta$, J_{3-4}= 9.25 Hz); 5.27 (1H, dd, H-2$_\alpha$, J_{1-2}= 3.0 Hz, J_{2-3}= 9.5 Hz); 5.36 (1H, dd, H-3$_\beta$); 5.58 (1H, dd, H-3$_\alpha$). MS (EI) m/z: 389 (M^+ + 1; 2), 329 (14), 211 (84), 195 (70), 169 (88), 166 (60), 153 (88), 43 (100).

1,3,4,5,8,9,10,12-octa-*O*-acetyl-D-gluco-L-altro-L-erythro-2,6:7,11-dianhydrododecitol (α,β-biglucosyl derivative)

^{13}C ($CDCl_3$) δ: 21 (q), 21.3 (q), 62.9 (t), 63.3 (t), 69.0 (d), 69.1 (d), 69.2 (d), 70.1 (d), 70.4 (d), 71.1 (d), 72.7 (d), 74.8 (d), 76.6 (d), 81.0 (d), 170.1 (s), 170.4 (s), 170.7 (s), 171.2 (s). ^{1}H ($CDCl_3$) δ : 1.9 - 2.1 (24 H, 8xs, $OCOCH_3$); 3.65 (1H, ddd, H-5', $J_{4'-5'}$ = 9.0 Hz, $J_{5'-6'A}$= 2.0 Hz, $J_{5'-6'B}$= 5.0 Hz); 3.80 (1H, dd, H-1', $J_{1'-2'}$= 9.0 Hz, $J_{1'-1}$= 2.0 Hz); 4.0 (1H, dd, H-1, J_{1-2}= 5.0 Hz); 4.1 (1H, dd, H-6'A, $J_{6'A-6'B}$=12 Hz); 4.03-4.2 (3H, m, H-6A, H-6B, H-5); 4.15 (1H, dd, H-6'B); 4.90 (1H, t, H-4, J_{4-5} = J_{3-4}=8.0 Hz); 4.95 (1H, t, H-4', $J_{3'-4'}$=9.0 Hz); 5.1 (1H, t, H-3', $J_{2'-3'}$=9.0 Hz); 5.15 (1H, t, H-2'); 5.2 (1H, dd, H-2, J_{2-3}=8.0 Hz); 5.6 (1H, t, H-3). MS (EI) m/z: 663(M^+ + 1, 0.9), 603(3.3), 589(1.6), 542(0.5), 500(10), 427(30), 367(5), 331(25), 211(72), 169(100). M.p. = 183-185. $[\alpha]^{25}_d$ = +32.6 (c = 0.1 g/ml, $CHCl_3$)

1,3,4,5,8,9,10,12-octa-*O*-acetyl-D-gluco-D-altro-L-erythro-2,6:7,11-dianhydrododecitol (α,α-biglucosyl derivative)

^{13}C ($CDCl_3$) δ: 21.0 (q), 62.2 (t), 68.1 (d), 69.7 (d), 69.9 (d), 70.7 (d), 73.1 (d), 170-171 (s). ^{1}H ($CDCl_3$) δ: 2.0 - 2.1 (12 H, 3xs, $OCOCH_3$); 4.15 - 4.30 (4H, m, H-1, H-5, H-6A, H-6B); 4.95 (1H, t, H-4, J_{3-4} = J_{4-5}=7.0 Hz); 5.05 (1H, dd, H-2, J_{2-3} = 7.0 Hz, J_{1-2}= 3.0 Hz); 5.3 (1H, t, H-3). MS (EI) m/z: 663(M^+ + 1, 0.5), 603(3, 589(1.5), 542(0.5), 500(10), 427(20), 367(3), 331(30), 211(70), 169(100).

1,3,4,5,8,9,10,12-octa-*O*-acetyl-L-gluco-L-altro-L-erythro-2,6:7,11-dianhydrododecitol (β,β-biglucosyl derivative)

^{13}C ($CDCl_3$) δ: 21.0 (q), 63.1 (t), 68.5 (d), 69.5 (d), 75.0 (d), 75.5 (d), 77.3 (d), 169-171 (s). ^{1}H ($CDCl_3$) δ: 1.9 - 2.1 (12 H, 4xs, $OCOCH_3$); 3.3 (1H, d, H-1, J_{1-2} = 7.5 Hz); 3.45 (1H, ddd, H-5, J_{4-5}=7.5 Hz, J_{5-6A}=4.8 Hz, J_{5-6B}=2.5 Hz); 4.05 (1H, dd, H-6B, J_{6A-6B}=12.0 Hz); 4.15 (1H, dd, H-6A); 4.95 (1H, t, H-4, J_{3-4}=7.5 Hz); 5.15 (1H, t, H-3, J_{2-3}=7.5 Hz); 5.25 (1H, t, H-2). MS (EI) m/z:663(M^+ + 1, 0.3), 603(1.3), 589(0.5), 542(0.1), 500(6), 427(17), 367(3), 331(35), 211(75), 169(100).

1-*O*-(2'deoxy-3',4',6'-tri-*O*-acetyl-α-D-glucopyranosyl)-4-*O*-acetyl-hydroquinone (12)

^{1}H ($CDCl_3$) δ: 1.5 (1H, ddd, H-2'A, $J_{2'A-2'B}$= 18.0 Hz, $J_{2'A-3'}$= 1.8 Hz, $J_{1'-2'A}$= 2.0 Hz); 1.7 - 1.8 (12H, 4xs, $OCOCH_3$); 2.2 (1H, ddd, H-2'B, $J_{2'B-3'}$= 8.1 Hz, $J_{1'-2'B}$= 1.8 Hz); 3.85 (1H, ddd, H-5', $J_{4'-5'}$= 9.9 Hz, $J_{5'-6'B}$= 4.5 Hz, $J_{5'-6'A}$= 2.0 Hz); 3.87 (1H, dd, H-6'A, $J_{6'A-6'B}$= 12.0 Hz); 4.2 (1H, dd, H-6'B); 5.05 (1H, dd, H-1'); 5.25 (1H, t, H-4', $J_{3'-4'}$= 9.9 Hz); 5.7 (1H, ddd, H-3'); 6.85 (2H quinone, d, J_{ortho}= 10.5 Hz); 6.92 (2H quinone, d).

A very complicated mixture of C-glucosilated phenolic oligomers was partially characterised. It consisted of at least four components (**A**-**D**), two of which being more abundant (**A** and **B**). In the mass spectrum a peak at m/z 576 (5) indicated the presence of compounds made of an unit of sugar and two units of 4-methoxyphenol. The several ^{1}H and ^{13}C-NMR experiments carried out to assign the chemical shifts of the sugar moieties of **A**, **B**, **C**, and **D** suggest that all the forms are tetra-*O*-acetylated and 1-C-glucosilated.

Oligomer A
^{13}C (C_6D_6) δ: 61.3 (C-6); 68.2 (C-4); 71.0 (C-2); 74.1 (C-3); 76.2 (C-5); 78.8 (C-1). ^{1}H (C_6D_6) δ: 3.33 (H-5); 3.88 (H-6A); 4.19 (H-6B); 4.40 (H-1); 5.37 (H-4); 5.47 (H-3); 5.62 (H-2).
Oligomer B
^{13}C (C_6D_6) δ: 61.8 (C-6); 68.0 (C-4); 69.6 (C-3); 70.0 (C-2); 71.7 (C-5); 71.9 (C-1). ^{1}H (C_6D_6) δ: 3.92 (H-5); 4.07 (H-6A); 4.18 (H-6B); 5.15 (H-4); 5.45 (H-1); 5.50 (H-2); 5.82 (H-3).
Oligomer C
^{13}C (C_6D_6) δ: 62.2 (C-6); 68.8 (C-4); 68.8 (C-2); 74.6 (C-3); 76.2 (C-5); 80.0 (C-1). ^{1}H (C_6D_6) δ: 3.47 (H-5); 4.05 (H-1); 4.07 (H-6A); 4.32 (H-6B); 5.34 (H-4); 5.41 (H-2); 5.49 (H-3).
Oligomer D
^{13}C (C_6D_6) δ: 61.9 (C-6); 70.0 (C-3); 70.3 (C-5); 71.2 (C-2); 72.8 (C-4); 72.9 (C-1). ^{1}H (C_6D_6) δ: 3.84 (H-5); 4.06 (H-6A); 4.28 (H-6B); 5.33 (H-1); 5.34 (H-4); 5.51 (H-2); 5.92 (H-3).

The spectrum of the mixture showed the presence of complicated phenolic structures that could reasonably be linked to the anomeric carbon. For each of the four components **A-D** the presence of a sugar-phenol C-glucosidic bond was indicated by the long-range correlation between the phenolic hydrogens and the anomeric carbon, between the H-2 of the glucosidic ring and the quaternary phenolic carbon, and between the anomeric hydrogen and the tertiary aromatic carbons.

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