Pergamon

Tetrahedron 56 (2000) 6291–6297

TETRAHEDRON

Acetobromomaltose, a New Source of Carbohydrate Radicals. EPR Characterisation of Maltosyl and 2-Deoxymaltos-2-yl Radicals and Syntheses of Tetrasaccharide-like Mimics, Maltal, 3-α-Maltosyl Propiononitrile, 1,5-Anhydromaltitol and 2-Deoxymaltopyranoside

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Received 10 February 2000; revised 30 May 2000; accepted 15 June 2000

Abstract—The acetoxy-protected maltosyl radical **1**, obtained through bromine abstraction from acetobromomaltose (ABM), was studied by means of EPR spectroscopy. At room temperature, only the spectrum of **1** was observed, but at higher temperatures a second radical, the acetoxy-protected 2-deoxymaltos-2-yl radical **2**, was detected, resulting from migration of an acetoxy group from position 2 to position 1. Some acetoxy-protected maltose derivatives were prepared from ABM, via different radical pathways involving **1** and **2** as intermediates. Electroreduction on silver provides tetrasaccharide-like mimics **7** and maltal **8**. Photochemical generation of **1**, followed by trapping with tributyltinhydride or with acrylonitrile, leads respectively to 1,5-anhydromaltitol **9** and to 3-α-maltosyl propiononitrile **10**. Generation of **2** at 80°C by **1**→**2** isomerisation, followed by trapping with tributyltinhydride, leads to 2-deoxymaltopyranoside **11**. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Radical reactions have been largely exploited in the synthesis and derivatisation of saccharides.[1] In particular, several studies have been carried out on anomeric glycosyl radicals,[2,3] which have often been used as intermediates to synthesise 2-deoxy sugars and C-glycosides;[3] as a matter of fact, C–C bond radical formation appears to be a suitable approach to the latter compounds.[4] C-glycosides, which in most cases are not 'true' sugars, are stable carbohydrate analogues that have received much attention as molecules of potential biological activity and that are also useful for enzymatic and metabolic studies. More recently, carbohydrates with C-interglycosidic bonds were synthesised with the aim of checking their biological activity.[5] Many radicals derived from carbohydrates have also been studied by means of ESR spectroscopy, the technique of choice for the study of paramagnetic species.[6,7]

As far as we know, there have been no reports on disaccharide radical based synthetic procedures, nor on the characterisation of these species through an ESR spectroscopic approach. This prompted us to undertake an ESR investigation of the acetoxy-protected maltosyl radical **1**, originated via bromine abstraction from acetobromomaltose (ABM), and of its 2-deoxy isomer **2**, deriving from a 2,1 shift of an acetoxy group. We also endeavoured to investigate the synthetic potential of these radicals in polysaccharide chemistry, and in particular in extending the chemistry of anomeric radicals such as **1** from monosaccharides to more complex carbohydrates.

Results and Discussion

ESR studies

The acetoxy-protected maltosyl radical **1** was generated inside the cavity of an ESR spectrometer following the well-established procedure outlined in Scheme 1, i.e. through bromine abstraction from ABM by tributyltin centred radicals photogenerated in situ. At room temperature, only the spectrum of **1** was observed, but as the

Keywords: radicals and radical reactions; carbohydrates; electron spin resonance; electrochemical reactions.
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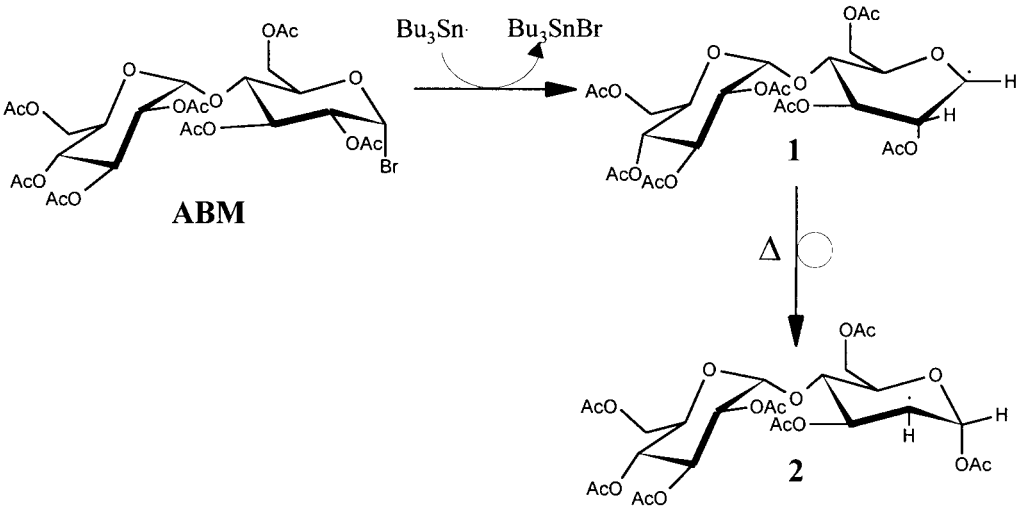
PII: S0040-4020(00)00567-6



Scheme 1.

temperature was raised, a second radical was detected. This could be identified as radical **2** resulting from migration of the acetoxy group from position 2 to position 1, a process already evidenced[8] in the case of radicals from monosaccharides.

In principle one might expect that substitution of the protecting group in position 4 of the sugar with a glucosyl unit should not affect too much the properties of a radical where the unpaired electron is located in position 1, and it may thus be interesting drawing a comparison between the properties of heptaacetoxymaltosyl and heptaacetoxymaltos-2-yl radicals with those of the two tetraacetoxygalactosyl and two tetraacetoxyglucos-2-yl radicals **3a/4a** and **3b/4b** shown in Scheme 2.[8,9]

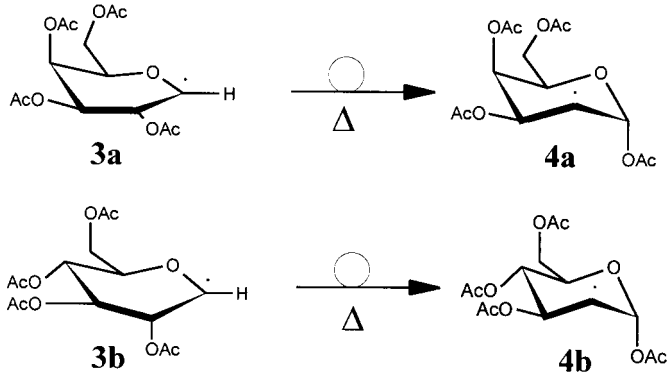
From the data collected in Table 1 it emerges that the spectral parameters exhibited by radicals **1** and **2** correlate well with those exhibited by radicals **3** and **4**, respectively. The hyperfine splitting constant of a hydrogen atom β to a π radical centre depends on the dihedral angle between the singly occupied orbital and the C–H_β bond, according to the Heller–McConnel equation:[10]

$$a(H_\beta) = A + B \times \cos^2 \vartheta \qquad (1)$$

where ϑ is the dihedral angle, and A (ca. 0.3 mT) and B (ca. 4.8 mT) are constants accounting for spin polarisation and hyperconjugation, respectively. On the other hand, it has been recently shown that when the carbon bearing the β-hydrogen is also linked to an electronegative substistuent such as fluorine or, as in the present case, oxygen, Eq. (1) should be replaced by the Guerra equation (2):[11]

$$a(H_\beta) = A + B \times \cos^2 \vartheta + C \times \cos \vartheta \sin \vartheta \qquad (2)$$

In this equation, besides spin polarisation (A=0.386 mT) and hyperconjugation (B=3.91 mT), the electronegativity of the substituent is taken into account through the introduction of a third element (C=1.264 mT in the case of oxygen). The lower value of the H_β splitting in **1** as compared to that measured in **3b** suggests that in the maltosyl radical this hydrogen is closer to the plane of the sp^2 carbon than it is in the glucosyl radical. Through the use of Eq. (2) the angle ϑ between the SOMO and the C_2-hydrogen bond in **1** is actually computed as 78.3°. In the rearranged radical **2** there are two different hydrogen atoms β to the radical carbon, that is those in positions 1 and 3. Applying again the Guerra equation, the dihedral angle ϑ between the SOMO and the C_3-hydrogen bond is calculated as 37.9° and that between the SOMO and the C_1-hydrogen bond as 69.1°. The hydrogen in position 3 would therefore have a marked 'axial' character whereas that in position 1 would be much closer to an 'equatorial' situation. It should, however,



Scheme 2.

Table 1. Hyperfine spectral parameters for radicals **1**–**4** (coupling constants in mT)

Radical	$a(H_\alpha)$	$a(H_{\beta1})$, $a(H_{\beta2})$	$a(H_{\gamma1})$, $a(H_{\gamma2})$
1	1.869	0.789	0.344, 0.196
2	2.174	1.306, 3.433	0.086
3a	1.648	2.873	0.268
3b	1.817	1.245	0.355
4a	2.160	4.142, 0.707	0.059
4b	2.182	1.065, 3.753	0.092

be borne in mind that the value of the angle ϑ for C_1–H is likely to be underestimated to some extent, because Eq. (2) only accounts for one electronegative substituent whereas C_1 is in fact bound to two oxygen atoms.

Although, as already mentioned, the spectral parameters of radicals **1** and **2** are consistent with those of radicals **3** and **4**, the situation is less clear as far as the rearrangement **1→2** is concerned. Actually, in a previous careful study of the dependence on temperature of the isomerisation of the radicals obtained via bromine abstraction from acetobromogalactose and acetobromoglucose,[8] the activation energy for this process was determined as 12.8 kcal mol^{-1} for **3a→4a** and 8.7 kcal mol^{-1} for **3b→4b**.

When we tried to undertake a similar study of the **1→2** process, we found that the quality of the EPR spectra of the maltosyl radical **1** was '*reasonably good*' at room temperature, but became much poorer as the temperature was raised in order to induce the radical translocation. Indeed we only succeeded in obtaining a '*decent*' (see Fig. 1) spectrum showing the presence of radicals **1** and **2** in nearly equal amount at ca. 50°C, and careful study of the process proved impossible.

On the other hand, in a recent report Walton suggested the possibility of determining the activation energy for a rearrangement, E_r, through Eq. (3) given the so-called mid-point temperature (T_{mid}), defined as the temperature at which the rearranged and unrearranged species have equal concentration.[12]

$$E_r/\text{kcal mol}^{-1} = 0.044 \times T_{mid} + 0.22 \quad (3)$$

Substituting in the above equation 323 for T_{mid} leads to an activation energy value E_r=14.43 kcal mol^{-1}, a value some 2–4 kcal mol^{-1} larger than those reported for the isomerisation of the glycosyl radicals.[8] The observed discrepancy is likely to reflect inaccuracy in determining the relative amount of radicals **1** and **2**. Actually, owing to the poor signal to noise ratio of the experimental spectra $a\pm15\%$ error in the resulting E_a value is possible. On the other hand, the possibility that Eq. (3) overestimates the activation energy value should not be ruled out a priori despite the fact that this equation has been tested on a large number of radical rearrangements. Actually, although we do not know the appropriate T_{mid} values for the rearrangement of the glycosyl radicals, by introducing into Eq. (3) the measured activation energies,[8] i.e. 12.8 and 8.7 kcal mol^{-1}, T_{mid} values are obtained (285 and 192 K) at which experimentally only the unrearranged radicals **3a** and **3b** are observed. On the other hand, it has been claimed that these rearrangements proceed through a five-membered cyclic transition state,[13] and the higher value of the activation energy for **1→2** than for **3→4** might reflect a greater rigidity of **1** with respect to **3** and conformational situations making it more difficult for the former than for the latter to attain the transition state. As will be discussed in the next section, higher activation energies for the rearrangement result in lower yields of the 2-deoxyderivative **11**.

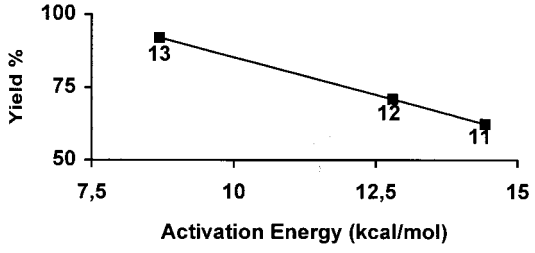


Diagram 1. Dependence of yields of rearranged sugars **11**, **12**, **13** on activation energy.

Maltose derivatisation

Electrosynthesis. Electroreduction of acetoxy-protected glycosyl bromides on silver was found to be a useful approach to the synthesis of C-disaccharide-like mimics.[14] For example acetobromoglucose (ABG) provided a mixture of α,α-, α,β-, and β,β-biglucosyl derivatives,[9,14] along with significant amounts of 3,4,6-tri-*O*-acetyl-glucal.[14] Based on several pieces of evidence we justified the formation of the former products through dimerisation of radical **3b**, as outlined in Eqs. (4) and (5):

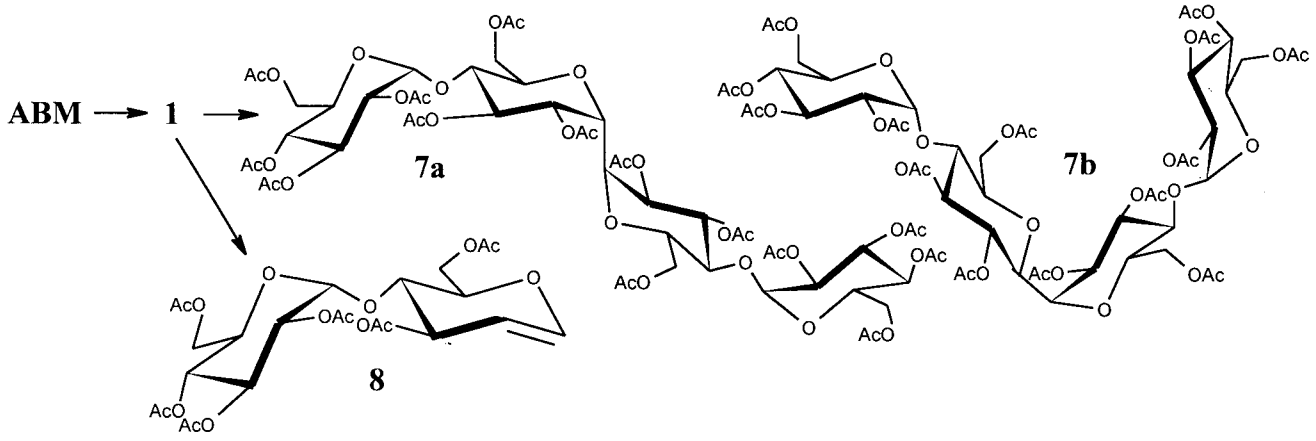
$$\text{ABG} + e^- \rightarrow \mathbf{3b} + Br^- \quad (4)$$

$$2\ \mathbf{3b} \rightarrow \text{biglucosyl derivatives} \quad (5)$$

While a single electron-transfer followed by loss of a bromide anion accounts well for the formation of the dimers, a two electrons cleavage of the C–Br bond and a subsequent very fast elimination of an acetate anion, justify the formation of the unsaturated sugar.

Electroreduction of ABM leads to results quite similar to those obtained with ABG. Thus, controlled potential (−1.28 V vs SCE) electrolysis of ABM in acetonitrile at a silver electrode afforded the bimaltosyl derivatives **7a** and **7b** with an overall 40% yield, together with maltal **8** (25%). The process is outlined in Scheme 3: once **1** is formed in a fashion similar to that indicated in Eq. (4) for ABG, its subsequent dimerisation leads to the α,α (**7a**) and α,β (**7b**) diastereomeric bimaltosyl derivatives (**7b/7a**=1.5). This is in contrast with the reduction of ABG, from which the three diastereoisomeric biglucosyl derivatives were obtained in a statistical ratio.[9]

Incidentally, we also note that ABG displays at a silver cathode one irreversible peak at E_p=−1.28 V vs SCE. Actually, electroreduction of the ABG and ABM C–Br bonds on silver does not seem to be influenced by the



Scheme 3.

substitution of the OAc group in position 4 of the glucose with an *O*-glucosyl unit: nevertheless, the difference in the diastereoselectivity allows us envisage the possibility of some stereochemical control of this electrochemical dimerisation.

Despite the low yields, ABM electroreduction shows some interesting aspects as it is a one-pot chemoselective derivatisation of a commercially available product and provides, under clean and mild conditions, new structures such as the bimaltosyl derivatives **7** along with more common compounds like maltal **8**, a member of the family of glycals which are important chiral building blocks.[15]

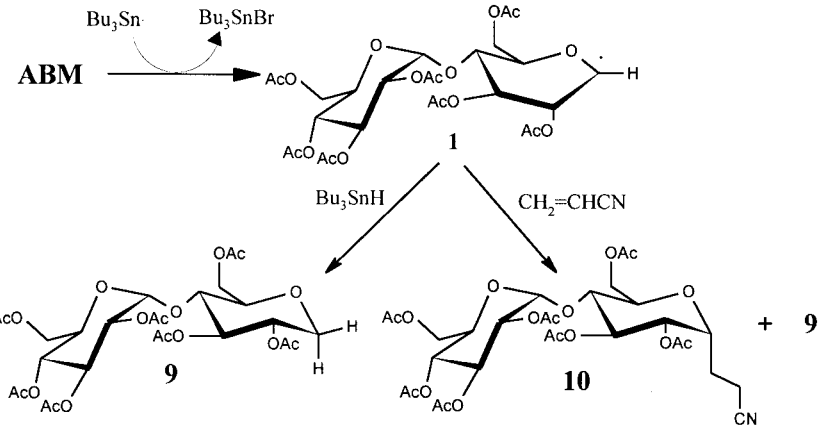
Photochemical syntheses. Photolysis of a THF solution of tributyltin hydride and ABM led to the formation of **1** via bromine abstraction by tributyltin radical. **1** was quantitatively converted to maltitol **9** by the tributyltinhydride (Scheme 4). Addition of excess acrylonitrile led to the isolation of 3-α-maltosyl propiononitrile **10** (69%) together with **9** (20%). Owing to the anomeric effect,[1b] this reaction is totally diastereoselective.

Synthesis of 2-deoxymaltopyranoside 11. Heating a toluene solution of ABM containing tributyltin hydride and a catalytic amount of AIBN [azobis(isobutyronitrile)] at 353 K resulted in the formation of maltitol **9** (34%) and of compound **11** (56%). As outlined in Scheme 5, the isolated products reflect the reactivity of radical **1**, generated from ABM by bromine abstraction brought about by tributyltin radical. In agreement with the ESR results reported in the preceding section, the product distribution can be interpreted on the basis of the partial isomerisation (*cis*-selective migration of an acetoxy group at high temperature) of **1** to **2**, which in turn is trapped by tinhydride affording **11**. This approach had already been used to synthesise 2-deoxygalactopyranoside **12** and 2-deoxyglucopyranoside **13** via **3a→4a** and **3b→4b** isomerisations, respectively.[13]

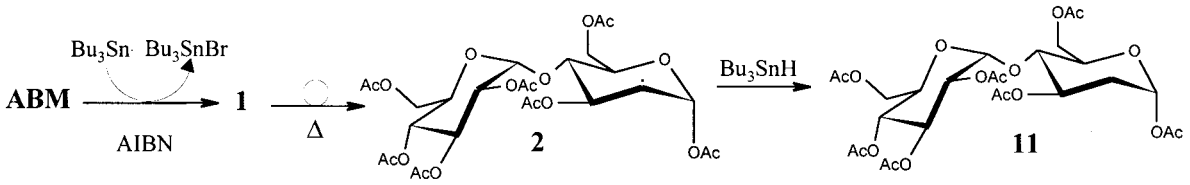
It seems worthwhile to note the existence of an inverse relationship between the activation energies characterising the rearrangements of **3a** (12.87 kcal mol^{-1}),[8] **3b** (8.7 kcal mol^{-1})[8] and **1** (14.43 kcal mol^{-1}) with the yields (**12**, 71%;[13] **13**, 92%;[13] **11**, 56%). The qualitative correlation shown in Diagram 1 is probably too good to be true, but it nevertheless gives us confidence in the estimated activation energy for the **1→2** rearrangement, which does not seems to exceed the expected value.

Conclusion

The radical **1** is generated from ABM both via electrochemical and chemical pathways and used to prepare



Scheme 4.



Scheme 5.

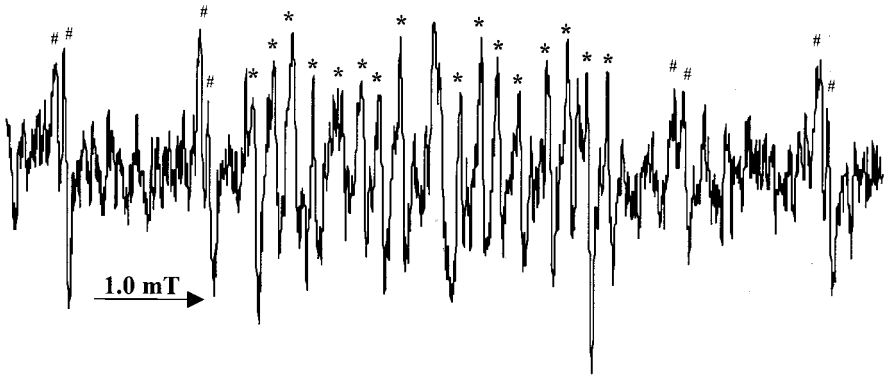


Figure 1. EPR spectrum observed at 50°C upon photolysis of a deoxygenated benzene solution of ABM containing some hexabutylditin. The spectrum of radical **1** consists of the starred lines (*), whereas the low-field and high-field doublets (#) are part of the spectrum of radical **2**.

different compounds like **7**–**11**. The presence of the *O*-glucosyl substituent in position 4 does not influence significantly the chemistry of this radical centred on the anomeric position of a glucose unit, except for its rearrangement to **2**. In agreement with the glycosyl radicals **3a** and **3b**, **1** undergoes the acetoxy group migration from position 2 to position 1, but EPR study and synthetic results indicate that it is characterised by a higher activation energy.

Experimental

General methods

^{1}H and ^{13}C NMR were recorded on Bruker AC 300P and AMX 500 spectrometers at 303 K. Chemical shifts are expressed in ppm downfield from TMS; assignments were made through COSY and HMQC experiments. To identify and confirm the multiplicities of the proton signals the coupling constants have been refined using the WINDAISY Bruker program.

Observed rotations at the Na_D line were obtained at 20°C using a Propol Dr Kernchen polarimeter. Matrix Assisted Laser/Desorption Ionization—Time of Flight mass spectra (MALDI-TOF MS) were acquired on a Shimadzu–Kratos Kompact Maldi II instrument operating in the linear mode with an accelerating potential of 20 kV and equipped with a UV pulsed laser (N_2, λ=337 nm, 100 mJ per shot, 3 ns pulse width of a single laser shot) and time delayed extraction. All the spectra were acquired by scanning the sample spot along the *x* axis and averaging 100 laser shots. Mass calibration was achieved using the matrix and γ-cyclodextrin as internal references. A 65 mM solution of the matrixes were prepared by dissolving 2,5-dihydroxybenzoic acid (DHB) or α-cyano-4-hydroxycinnamic acid (CHCA) (Sigma) in 2:3 (v/v) mixture of acetonitrile and aqueous 0.1% (v/v) trifluoroacetic acid (TFA). The concentration of the carbohydrate solutions was kept close to 100 pmol/μl, corresponding to 0.1 mM. The samples were prepared by mixing 0.5 μL of matrix solution with 0.5 μl of analyte solution directly on the sample slide and allowing evaporation of the solvent under a gentle N_2 stream.

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 ABM (ca. 10^{-3} M) and some hexabutylditin, were photolysed with the unfiltred light from a Hanovia high-pressure 1 kW mercury lamp.

An Amel 553 potentiostat was used to drive electrolysis under potentiostatic control. A 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).

General procedures

Preparative electrolysis. Controlled potential electrolysis was carried out in acetonitrile in a two-compartment cell at E_p=−1.4 V. The cathode consisted of a silver plate, cathodic solution 0.04 M ABM, 0.1 M tetraethylammonium perchlorate (TeaP) as supporting electrolyte. A silver plate in ACN-saturated tetraethylammonium bromide was used as anode to provide a harmless counter-reaction (namely, $Ag+Br \rightarrow AgBr+e^{-}$). A glass diaphragm was used to separate anodic and cathodic compartments. ABM was

exhaustively electrolysed. **7a**, **7b** and **8** were isolated from the catholyte by flash chromatography on silica gel, after salt removal. **8** was eluted with hexane–ethyl acetate (1:1), while a more polar mixture (hexane–ethyl acetate, 3:7) was used for **7a** and **7b**. **7**–**8** were identified on the basis of their mass and ^{1}H and ^{13}C NMR parameters.

1-α-(α′-Maltosyl)-1,5-anhydro-maltitol (7a). The compound was isolated as a white solid, mp 82–84°C; $[\alpha]_D^{20}$=+66 (*c* 0.2, $CHCl_3$); MALDI-MS: *m/z*=1260.8 $[M+Na]^+$, 1276.7 $[M+K]^+$; ^{1}H NMR (500 MHz, C_6D_6, *J* values in Hz) δ: 1.64, 1.65, 1.69, 1.73, 1.85, 1.90, 1.96, 2.06 (42H, 8s, $COCH_3$), 3.78 (1H, dd, J_{3-4}=4.7 Hz, J_{4-5}=7.1 Hz, H-4), 4.26 (1H, m, H-5), 4.27 (1H, dd, H-6b), 4.33 (1H, ddd, $J_{4'-5'}$=10.0 Hz, $J_{5'-6'a}$=4.0 Hz, $J_{5'-6'b}$=2.6 Hz, H-5′), 4.36 (1H, dd, $J_{6'a-6'b}$=12.4 Hz, H-6′b), 4.41 (1H, dd, H-6′a), 4.44 (1H, d, J_{1-2}=4.2 Hz, H-1), 4.49 (1H, dd, H-6a), 5,11 (1H, dd, $J_{1'-2'}$=3.8 Hz, $J_{2'-3'}$=10.4 Hz, H-2′), 5.23 (1H, dd, J_{2-3}=6.0 Hz, H-2), 5.37 (1H, dd, $J_{3'-4'}$=9.5 Hz, H-4′), 5.47 (1H, dd, H-3), 5.51 (1H, d, H-1′), 5.73 (1H, dd, H-3′); ^{13}C NMR (125 MHz, C_6D_6) δ: 61.8 (C-6′), 62.6 (C-6), 68.8 (C-4′), 69.0 (C-1, C-5′), 69.3 (C-2), 70.1 (C-3′), 70.7 (C-2′), 71.4 (C-3), 72.8 (C-5), 74.7 (C-4), 97.4 (C-1′).

1-α-(β′-Maltosyl)-1,5-anhydro-maltitol (7b). The compound was isolated as a white solid, mp 100–101°C; $[\alpha]_D^{20}$=+81 (*c* 0.35, $CHCl_3$); MALDI-MS: *m/z*=1261.2 $[M+Na]^+$, 1277.0 $[M+K]^+$; the four rings are named for convenience A–B–C–D: ^{1}H NMR (500 MHz, C_6D_6, *J* values in Hz) δ: 1.60–1.90 (30H, 8s, $COCH_3$), 1.99, 2.02, 2.15 (12H, 4s, $COCH_3$), 2.97 (1H, ddd, J_{5C-6Cb}=2.5 Hz, J_{5C-6Ca}=7.4 Hz, H-5C), 3.63 (1H, ddd, J_{4C-5C}=9.6 Hz, H-4C), 3.67 (1H, dd, J_{1B-1C}=5.2 Hz, J_{1C-2C}=9.6 Hz, H-1C), 3.74 (1H, m, H-4B), 4.08 (1H, m, H-6Ca), 4.13 (1H, ddd, J_{1B-2B}=4.9 Hz, H-1B), 4.21 (1H, dd, $J_{6Ca-6Cb}$= 11.9 Hz, H-6Cb), 4.23 (1H, m, H-5D), 4.28 (1H, m, H-5B), 4.29 (3H, m, H-6Aa, H-6Da, H-6Ba), 4.37 (1H, m, H-5A), 4.42 (3H, m, H-6Bb, H-6Ab, H-6Db), 5.07 (2H, dd H-2A, H-2D, J_{2A-3A}=10.4 Hz, J_{2D-3D}=10.6 Hz), 5.15 (1H, dd, J_{2C-3C}=9.0 Hz, H-2C), 5.29 (1H, m, H-4D), 5.33 (1H, dd, J_{3C-4C}=8.1 Hz, H-3C), 5.36 (2H, m, J_{2B-3B}=6.0 Hz, H-4A, H-2B), 5.39 (1H, d, J_{1D-2D}=4.1 Hz, H-1D), 5.52 (1H, d, J_{1A-2A}=4.1 Hz, H-1A), 5.70 (1H, dd, H-3B), 5.74 (1H, dd, J_{3A-4A}=9.5 Hz, H-3A), 5.82 (1H, dd, J_{3D-4D}= 9.5 Hz, H-3D); ^{13}C NMR (125 MHz, C_6D_6) δ: 61.9 (C-6B, C-6A, C-6D), 63.9 (C-6C), 68.7 (C-4D), 68.9 (C-4A, C-5A, C-2B), 69.4 (C-5D), 69.9 (C-3D), 70.1 (C-3A), 70.5 (C-1B), 70.7 (C-2A), 70.7 (C-2D), 70.9 (C-3B), 71.1 (C-2C), 73.1 (C-5B), 73.9 (C-4C), 74.4 (C-4B), 76.3 (C-5C), 76.6 (C-3C), 77.3 (C-1C), 96.3 (C-1D), 97.2 (C-1A).

Maltal (8). This was isolated as a white foam; $[\alpha]_D^{20}$=+72.2 (*c* 0.2, $CHCl_3$); MALDI-MS: *m/z*=583.1 $[M+Na]^+$, 599.0 $[M+K]^+$; ^{1}H NMR (500 MHz, C_6D_6, *J* values in Hz) δ: 1.74, 1.76, 1.85, 1.88 (18H, 4s, $COCH_3$), 3.75 (1H, q, H-5), 4.02 (1H, t, J_{4-5} and J_{4-3}=8.2 Hz, H-4), 4.20 (1H, m, H-11), 4.20 (2H, dd, H-6a, H-6b), 4.31 (1H, dd, J_{12a-11}=4.1 Hz, $J_{12a-12b}$=12.4 Hz, H-12a), 4.36 (1H, dd, J_{12b-11}=2.7 Hz, $J_{12b-12a}$=12.4 Hz, H-12b), 4.60 (1H, dd, J_{2-1}=6.02 Hz, J_{2-3}=3.09 Hz, H-2), 4.99 (1H, dd, J_{8-9}=10.4 Hz, J_{8-7}=3.9 Hz, H-8), 5.34 (1H, m, H-3), 5.35 (1H, t, H-10), 5.652 (1H, d, H-7), 5.834 (1H, dd, J_{9-10}=9.6 Hz, H-9), 6.01 (1H, dd, J_{1-3}=1.1 Hz, H-1). Anal. calcd for $C_{24}H_{32}O_{15}$: C, 51.43; H, 5.71. Found: C, 49.28; H, 5.63.

Synthesis of maltitol (9)

A solution of ABM (0.3 M) and tributyltinhydride (0.37 M) in anhydrous THF under argon atmosphere was photolysed for 6 h. THF was evaporated at reduced pressure. The residue was dissolved in acetonitrile. The acetonitrile phase was washed with pentane, to remove tin derivatives. Acetonitrile was then evaporated and the residue flash-chromatographed on silica-gel with hexane–ethyl acetate (3:7) to give **9**, which was identified on the basis of its mass and ^{1}H and ^{13}C NMR parameters.

1,5-Anhydromaltitol (9). This compound was isolated as a white solid, mp 120–123°C; $[\alpha]_D^{20}$=+16.8 (*c* 0.6, $CHCl_3$); MALDI-MS: *m/z*=643.4 $[M+Na]^+$, 659.4 $[M+K]^+$; ^{1}H NMR (500 MHz, C_6D_6, *J* values in Hz) δ: 1.60, 1.66, 1.68, 1.74, 1.79, 1.81, 1.94 (21H, 7s, $COCH_3$), 2.83 (1H, ddd, J_{5-6b}=2.8 Hz, J_{5-6a}=2.8 Hz, J_{4-5}=9.9 Hz, H-5), 2.89 (1H, t, J_{1a-1b} and J_{1a-2}=10.8 Hz, H-1a), 3.69 (1H, dd, J_{1b-2}=5.7 Hz, H-1b), 3.82 (1H, t, J_{4-3}=9.2 Hz, H-4), 4.07 (1H, dd, J_{6a-5}=4.4 Hz, J_{6a-6b}=12.3 Hz, H-6a), 4.21 (1H, dt, $J_{5'-4'}$=9.7 Hz, H-5′), 4.33–4.36 (2H, m, H-6′a, H-6′b), 4.44 (1H, dd, J_{6b-5}=3.9 Hz, H-6b), 4.90 (1H, ddd, J_{2-3}=9.8 Hz, H-2), 5.09 (1H, dd, $J_{2'-1'}$=4.0 Hz, $J_{2'-3'}$=10.5 Hz, H-2′), 5.29 (1H, t, $J_{4'-3'}$=9.0 Hz, H-4′), 5.39 (1H, t, H-3′), 5.55 (1H, d, H-1′), 5.84 (1H, t, H-3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 61.5 (C-6′). 63.0 (C-6), 66.0 (C-1), 68.0 (C-4′,C-5′), 69.5 (C-3′), 70.0 (C-2,C-2′), 72.5 (C-4), 76.0 (C-3), 76.5 (C-5), 95.0 (C-1′). Anal. calcd for $C_{26}H_{36}O_{17}$: C, 50.32; H, 5.81. Found: C, 48.90; H, 5.63.

Synthesis of 3-α-maltosyl propiononitrile (10)

A solution of ABM (0.07 M), tributyltinhydride (0.1 M) and acrilonitrile (0.7 M) in anhydrous THF under argon atmosphere was photolysed for 6 h. Same work-up as described for **9**. The residue was flash-chromatographed with hexane–ethyl acetate (1:1) to give **9** and **10**; **10** was identified on the basis of its mass and ^{1}H and ^{13}C NMR parameters.

3-α-Maltosyl propiononitrile (10). This compound was isolated as a colourless oil; $[\alpha]_D^{20}$=+74.4 (*c* 0.4, $CHCl_3$); MALDI-MS: *m/z*=696.6 $[M+Na]^+$; ^{1}H NMR (500 MHz, C_6D_6, *J* values in Hz) δ: 1.65, 1.67, 1.68, 1.78, 1.82, 1.95 (21H, 6s, $COCH_3$), 1.11 (1H, m, H-3′), 1.50 (1H, m, J_{3-4}=4.8 Hz, H-3), 1.65 (2H, m, H-2, H-2′), 3.52 (1H, ddd, J_{7-8}=6.8 Hz, $J_{8-9'}$=3.3 Hz, J_{8-9}=6.2 Hz, H-8), 3.61 (1H, dd, J_{6-7}=6.52 Hz, H-7), 3.73 (1H, m, H-4), 4.14 (1H, m, H-9′), 4.19 (1H, m, H-9), 4.28 (1H, m, H-14, J_{13-14}= 10.3 Hz), 4.34 (2H, m, H-15, H-15′), 4.82 (1H, dd, J_{4-5}= 4.6 Hz, J_{5-6}=6.9 Hz, H-5), 5.05 (1H, dd, J_{10-11}=3.9 Hz, J_{11-12}=10.5 Hz, H-11), 5.25 (1H, dd, J_{6-7}=6.5 Hz, H-6), 5.31 (1H, dd, J_{12-13}=9.4 Hz, J_{13-14}=10.3 Hz, H-13), 5.43 (1H, d, J_{10-11}=3.9 Hz, H-10), 5.80 (1H, dd, J_{12-13}=9.4 Hz, J_{11-12}=10.5 Hz, H-12); ^{13}C NMR (125 MHz, C_6D_6) δ: 19.5–21.2 (–OCH_3), 13.2 (C-2), 23.5 (C-3), 61.8 (C-15), 62.3 (C-9), 68.7 (C-13), 69.0 (C-14), 69.6 (C-4), 69.7 (C-5), 69.8 (C-12), 70.6 (C-11), 71.02 (C-8), 71.4 (C-6), 73.8 (C-7), 97.0 (C-10), 119 (C-1, CN). Anal. calcd for

$C_{29}H_{39}NO_{17}$: C, 51.71; H, 5.79; N, 2.08. Found: C, 53.20; H, 5.97; N, 2.01.

Synthesis of 2-deoxymaltopyanoside (11)

3.5 ml of a solution of tributyltinhydride (0.3 M) and AIBN (0.06 M) in anhydrous toluene was slowly dropped (10 ml/h) in 13 ml of a stirred solution of ABM (0.078 M) in anhydrous toluene at 354 K. At the end of the dropping, the reaction was further stirred for 30 min at 354 K. After evaporation of toluene, same work-up as described for **9**. The residue was flash-cromatographed with hexane–ethyl acetate (1:1) to give **9** and **11**; **11** was identified on the basis of its mass and ^1H and ^{13}C NMR parameters.

2-Deoxymaltopyranoside (11). This compound was isolated as a white foam; $[\alpha]_D^{20}=+145$ (*c* 0.5, $CHCl_3$); MALDI-MS: *m/z*=643.1 $[M+Na]^+$, 659.4 $[M+K]^+$; ^1H NMR (500 MHz, $CDCl_3$, *J* values in Hz) δ: 1.70 (1H, ddd, H-2a), 1.9–2.1 (21H, m, $COCH_3$), 2.20 (1H, ddd, J_{2b-1}=1.7 Hz, J_{2b-3}=5.3 Hz, J_{2b-2a}=13.5 Hz, H-2b), 3.90 (2H, m, H-4, H-5′), 4.0 (2H, m, H-5, H-6′a), 4.15–4.2 (2H, m, H-6a, H-6′b), 4.40 (1H, dd, J_{6b-5}=2.6 Hz, J_{6a-6b}=12.2 Hz, H-6b), 4.70 (1H, dd, $J_{2'-1'}$=4.0 Hz, $J_{2'-3'}$=9.9 Hz, H-2′), 5.0 (1H, t, $J_{4'-3'}$ and $J_{4'-5'}$=9.9 Hz, H-4′), 5.15 (1H, dd, H-3), 5.3–5.40 (1H, t, H-3′), 5.50 (1H, d, H-1′), 6.10 (1H, dd, H-1, J_{1-2a}=3.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 33.0 (C-2), 61.0 (C-6′), 62.5 (C-6),68.0 (C-4′, C-5′), 69.0 (C-3′), 70.0 (C-2′, C-5), 71.5 (C-3), 72.5 (C-4), 90.0 (C-1), 95.5 (C-1′). Anal. calcd for $C_{26}H_{36}O_{17}$: C, 50.32; H, 5.81. Found: C, 50.27; H, 5.83.

Acknowledgements

The authors are grateful to Marc Robert (Laboratoire d'Electrochimie Moléculaire de l'Université Denis Diderot, Paris, France) for the voltammetries and E_p determinations. They are also indebted to MURST-CNR (Rome) for financial support.

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