Abstract: A series of di- and trisaccharides containing 6-O-linked galactofuranose were synthesized as an anomeric mixture of methyl glycosides using silica-supported perchloric acid.

Key words: carbohydrates, galactofuranose, glycosylations, ring transformation, HClO4-SiO2.

The synthesis of oligosaccharides containing furanose units is a topic of increasing interest in the field of glyco-biology. D-Galactofuranosido moieties are constituents of many cell-wall polysaccharides of pathogenic bacteria such as Mycobacteria, Corynebacteria, Nocardia, and Rhodococcus and fungi such as Aspergillus and Penicil- lium, as well as pathogenic protozoa such as Trypanosoma cruzi and certain Leishmania species, and they are claimed to be immunodominant in many bacterial antigens. Carbohydrate haptens containing furanose moieties could therefore be useful in the design of bacterial cell-wall biosynthesis inhibitors as well as for the preparation of artificial carbohydrate antigens for vaccine preparations. Previously, (1→6)-linked glycosyl galacto-furanosides were evaluated as inhibitors of Mycobacteria cell-wall biosynthesis. Synthesis of oligosaccharides containing galactofuranose has been reported using galactofuranose pentabenzoxa- te, galactofuranosyl trichloroacetimidate, acyl glycosyl donors and O-pentenyl galactofuranoside derivatives. We envisioned that silica-supported perchloric acid (HClO4-SiO2) catalyzed rearrangement of the galactopyranose ring in the oligosaccharides into galactofuranose under acidic conditions at elevated temperature, could result in the formation of oligosaccharides containing the galactofuranose moiety. Recently, we have reported a number of organic transformations using this environmentally benign catalyst and several carbohydrate transformation and glycosylation reactions have been carried out by us and others.

In order to synthesize a series of di- and trisaccharides containing the D-galactopyranosyl moiety, 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose was coupled with a series of mono- and disaccharide thioethylglycoside derivatives using a modified procedure involving N-isoduccinnimide (NIS) and HClO4-SiO2 as the glycosylation activator. The yields were comparable with earlier reports and the stereochemical outcome of the glycosylation reactions was confirmed by comparing their NMR spectral data with those of previously reported products (Scheme 1, Table 1). Having achieved a number of (1→6)-linked di- and trisaccharides, we turned our attention to the conversion of pyranose structures to the corresponding furanose. As a model, 2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1→6)-1,2,3,4-di-O-isopropylidene-α-D-galactopyranose was treated with HClO4-SiO2 and methanol in acetonitrile at 70 °C. Full consumption of the starting material and formation of a more polar product was observed by TLC, and the crude product was then acetylated using Ac2O and HClO4-SiO2 to furnish per-O-acetylated methyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1→6)-β-D-galactofuranose. Optimization trials showed that the use of HClO4-SiO2 (100 mg/mmol of substrate) and methanol (3.0 equiv) in acetonitrile at 70 °C furnished the best results with respect to the formation of the required galactofuranose derivatives. Under similar reaction conditions, a series of di- and trisaccharides containing di-O-isopropylidene-α-D-galactopyranose at the reducing end were converted into galactofuranose containing di- and trisaccharides as their methyl glycosides in excellent yield (Table 2). The formation of the galactofuranose moiety in the products was unambiguously confirmed by the NMR spectral data which matched previously reported assignments for the galactofuranose moiety. Use of other commonly used, less polar solvents (e.g. CH2Cl2, CHCl3, THF) resulted in no reaction or very low product yields. Interglycoside linkages remained unaffected under the reaction conditions. In most cases, a mixture of anomers was obtained, the ratio of which was determined from the NMR spectra.

Scheme 1 Reagents and conditions: (a) NIS, HClO4-SiO2, CH2Cl2, 0 °C (b) R′OH, HClO4-SiO2, MeCN, 70 °C (c) Ac2O, HClO4-SiO2, r.t.
Table 1  Synthesis of Di- and Trisaccharides Containing 1,2;3,4-Di-O-isopropylidene-\(\alpha\)-d-galactopyranose Using \(N\)-Iodosuccinimide and HClO\(_4\)-SiO\(_2\)

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<th>Ref.</th>
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Table 1  Synthesis of Di- and Trisaccharides Containing 1,2:3,4-Di-O-isopropylidene-α-D-galactopyranose Using N-Iodosuccinimide and HClO$_4$-SiO$_2$ (continued)

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Table 2  Synthesis of Methyl Glycosides of Di- and Trisaccharides Containing Galactofuranose Using HClO$_4$·SiO$_2$

<table>
<thead>
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<th>Entry</th>
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In a comparative study, pyranose-furanose isomerization was attempted with 70% HClO₄ instead of using HClO₄-SiO₂, however, no formation of furanosidic glycoside was observed. This may be due to the presence of water in the 70% HClO₄ leading to the formation of the hemiacetal only. Use of HClO₄-SiO₂ maintained the anhydrous reaction conditions and furanosidic glycosides were obtained in excellent yields. Furthermore, since HClO₄ was supported over silica gel, the amount of catalyst required could be significantly reduced due to the increased surface area.

### Table 2  Synthesis of Methyl Glycosides of Di- and Trisaccharides Containing Galactofuranose Using HClO₄-SiO₂ (continued)

<table>
<thead>
<tr>
<th>Entry</th>
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</table>

A plausible pathway for the rearrangement is shown in Scheme 2. Initially, the isopropylidene groups may be removed in the presence of acid and then recyclization takes place to the thermodynamically favored five-membered ring via an open-chain form of the galactose.

In summary, we have synthesized a series of di- and trisaccharides containing a galactofuranosyl moiety at the reducing end, in a concise manner, by using HClO₄-SiO₂ to catalyze both the glycosylation reactions as well as the ring transformation. This reaction protocol can be scaled up for large-scale preparation of (1→6)-linked glycosyl galactofuranosides for biological evaluation.

All reactions were monitored by TLC using silica gel coated plates. Commercially available grades of organic solvents of adequate purity were used without further purification. 1H NMR and 13C NMR spectra were recorded on Bruker Avance DPX 200 MHz and 300 MHz using CDCl₃ as solvent and TMS as internal reference. Chemical shift values are expressed in ppm. ESI-MS were recorded on a MICROMASS QUTTRO II triple quadrupole mass spectrometer. Optical rotations were measured at 25 °C on a Rudolf Autopol III polarimeter. Commercially available grades of organic solvents of adequate purity were used without further purification.

Preparation of Glycosyl-(1→6)-1,2,3,4-di-O-isopropylidene-a-D-galactopyranose (10–18); Typical Procedure

To a solution of 1,2:3,4-di-O-isopropylidene-a-D-galactopyranose (260 mg, 1.0 mmol) and ethyl 2,3,4,6-tetra-O-acetyl-1-thio-b-D-glucopyranoside (470 mg, 1.2 mmol) in anhydrous CH₂Cl₂ (10 mL) were added 4 Å molecular sieves (1.0 g) and N-iodosuccinimide (315 mg, 1.4 mmol) and the reaction mixture was stirred under argon at r.t. for 30 min. After cooling the reaction mixture was stirred at 0 °C for 45 min. After the reaction was complete (indicated by TLC), the reaction mixture was filtered and the solid was washed with CH₂Cl₂ (30 mL). The organic layer was then washed withaq Na₂S₂O₄ (10%, 5 mL), sat. aq NaHCO₃ (2 × 30 mL) and H₂O (50 mL). The organic layer was then dried (Na₂SO₄) and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane–EtOAc, 5:1) to afford pure 2,3,4,6-tetra-O-acetyl-b-D-glucopyranosyl-(1→6)-1,2,3,4-di-O-isopropylidene-a-D-galactopyranose (10).

2,3,4,6-Tetra-O-acetyl-b-D-glucopyranosyl-(1→6)-1,2,3,4-di-O-isopropylidene-a-D-galactopyranose (10)

Yield: 500 mg (81%); colorless oil; [α]D⁰ = 36.9 (c 1.5, CHCl₃).

IR (neat): 1753, 1596, 1379, 1226, 1138, 1071, 1008 cm⁻¹.

1H NMR (200 MHz, CDCl₃): δ = 5.45 (d, J = 4.9 Hz, 1 H), 5.11 (t, J = 9.4 Hz, 1 H), 5.00 (t, J = 8.4 Hz, 1 H), 4.96 (t, J = 7.8 Hz, 1 H), 4.57 (d, J = 7.7 Hz, 1 H), 4.53 (dd, J = 7.4, 2.3 Hz, 1 H), 4.31–4.23 (m, 2 H), 4.16–4.14 (m, 2 H), 4.08–3.95 (m, 1 H), 3.92–3.82 (m, 1 H), 3.68–3.57 (m, 2 H), 2.08, 2.06, 2.01, 1.99 (4 × 12 H, 4 × COCH₃).

13C NMR (75 MHz, CDCl₃): δ = 170.2, 170.1, 170.0, 169.5, 110.7, 110.8, 109.6, 103.3, 73.1, 72.1, 71.6, 71.4, 71.0, 70.8, 69.8, 68.8, 68.2, 62.0, 26.4, 26.3, 25.5, 24.7, 20.9 (2 × C), 20.8 (2 × C).

ESI-MS: m/z = 613.2 [M + Na]⁺.

Anal. Calcd for C₂₆H₃₈O₁₅: C, 52.88; H, 6.49. Found: C, 52.70; H, 6.72.

2,3,4,6-Tetra-O-acetyl-b-D-glucopyranosyl-(1→6)-1,2,3,4-di-O-isopropylidene-a-D-galactopyranose (11)

Colorless oil; [α]D⁰ = 36.9 (toluene–EtOAc, 2:1); [α]D⁰ = 36.9 (c 1.5, CHCl₃).

IR (neat): 1753, 1597, 1437, 1380, 1225, 1069, 1040, 1005, 900 cm⁻¹.

1H NMR (200 MHz, CDCl₃): δ = 5.45 (d, J = 4.9 Hz, 1 H), 5.11 (t, J = 9.4 Hz, 1 H), 5.00 (t, J = 8.4 Hz, 1 H), 4.96 (t, J = 7.8 Hz, 1 H), 4.57 (d, J = 7.7 Hz, 1 H), 4.53 (dd, J = 7.4, 2.3 Hz, 1 H), 4.31–4.23 (m, 2 H), 4.16–4.14 (m, 2 H), 4.08–3.95 (m, 1 H), 3.92–3.82 (m, 1 H), 3.68–3.57 (m, 2 H), 2.08, 2.06, 2.01, 1.99 (4 × 12 H, 4 × COCH₃).

13C NMR (75 MHz, CDCl₃): δ = 170.5, 170.1, 169.3 (2 × C), 111.7, 110.7, 108.9, 96.5, 73.9, 72.1, 71.6, 71.4, 71.0, 70.8, 69.8, 68.8, 68.2, 62.0, 26.4, 26.3, 25.5, 24.7, 20.9 (2 × C), 20.8 (2 × C).

ESI-MS: m/z = 613.2 [M + Na]⁺.

Anal. Calcd for C₂₆H₃₈O₁₅: C, 52.88; H, 6.49. Found: C, 52.70; H, 6.72.

2,3,4,6-Tetra-O-acetyl-a-D-galactopyranosyl-(1→6)-1,2,3,4-di-O-isopropylidene-a-D-galactopyranose (12)

Colorless solid; mp 58–60 °C; [α]D⁰ = 0.34 (toluene–EtOAc, 2:1); [α]D⁰ = 0.34 (c 1.5, CHCl₃).

IR (KBr): 1753, 1596, 1379, 1226, 1138, 1071, 1008 cm⁻¹.

1H NMR (200 MHz, CDCl₃): δ = 5.46 (d, J = 5.0 Hz, 1 H), 5.32–5.10 (m, 3 H), 4.82 (brs, 1 H), 4.58 (dd, J = 7.8, 2.3 Hz, 1 H), 4.33–4.19 (m, 3 H), 4.13–4.04 (m, 2 H), 3.94 (ddd, J = 6.3, 4.8, 1.4 Hz, 1 H), 3.81–3.64 (m, 2 H), 2.16, 2.09, 2.04, 1.98 (4 × 12 H, 4 × COCH₃).

13C NMR (75 MHz, CDCl₃): δ = 170.2, 170.1, 169.7, 109.6, 108.9, 100.9, 95.0, 70.2, 69.6, 69.5 (2 × C), 69.3, 68.5, 67.4, 66.8, 65.8, 59.8, 24.9 (2 × C), 24.0, 23.2, 19.6 (2 × C), 19.4 (2 × C).

ESI-MS: m/z = 613.3 [M + Na]⁺.
Alkaloids of {	extit{Aeginetia indica}} L. and their Antioxidant Activities: A Molecular Model for their Biological Functions  

C. Mukherjee, A. K. Misra

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Abstract: The isolated alkaloids were found to possess good antioxidant activities.

Keywords: Aeginetia indica L., alkaloids, antioxidant activity, DPPH, ABTS+.

1. Introduction

The genus {	extit{Aeginetia}} is a member of the family Acanthaceae and is commonly known as "Bhusham" in Odia. The plant is widely distributed in the Indian subcontinent and is commonly used in traditional medicine for treating various ailments. In this study, we investigated the alkaloid content and antioxidant activities of the plant.

2. Materials and Methods

The plant material was collected from the wild and identified by a local botanist. The alkaloids were isolated using a combination of silica gel column chromatography and reversed-phase HPLC. The antioxidant activities were evaluated using the DPPH and ABTS+ assays.

3. Results and Discussion

The isolated alkaloids were characterized by various spectroscopic techniques including UV, IR, and NMR. The antioxidant activities were found to be in the range of 70 to 80%, as compared to the standard antioxidant, trolox.

4. Conclusion

The results of this study indicate that the alkaloids of {	extit{Aeginetia indica}} L. possess good antioxidant activities, which could be due to their ability to scavenge free radicals.

Acknowledgments: This work was supported by the Indian Council of Medical Research (ICMR).

References


5. Supporting Information

The Supporting Information includes spectra of the isolated alkaloids and the antioxidant activity assay methods.


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This paper is devoted to the study of the alkaloids of {	extit{Aeginetia indica}} L., a plant commonly known as "Bhusham" in Odia. The plant is widely distributed in the Indian subcontinent and is used in traditional medicine for various ailments. The isolated alkaloids were characterized by various spectroscopic techniques, and their antioxidant activities were evaluated using the DPPH and ABTS+ assays. The results indicate that the isolated alkaloids possess good antioxidant activities, which could be due to their ability to scavenge free radicals. This study provides valuable information on the alkaloid content and antioxidant activities of {	extit{Aeginetia indica}} L., which could be useful for the development of new pharmaceutical products.

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2.02, 2.00 (7 × s, 21 H, 7 × COCH₃). 1.48, 1.42 [2 × s, 6 H, C(CH₃)₃]. 1.30 [s, 6 H, C(CH₃)₂].

13C NMR (75 MHz, CDCl₃): δ = 170.5, 170.3 (2 × C), 170.1, 169.8 (2 × C), 169.3, 169.6, 108.8, 101.3, 96.4, 95.7, 76.0, 75.7, 73.0, 72.3, 71.6, 71.0, 70.7, 70.3, 69.7 (2 × C), 68.7, 68.4, 68.1, 63.2, 61.7, 26.4, 26.3, 25.4, 24.7, 21.2 (2 × C), 21.1, 20.9, 20.8 (3 × C).

ESI-MS: m/z = 901.4 [M + Na]⁺.


**Conversion of Galactopyranose to Galactofuranose Derivatives (19–30): Typical Procedure**

To a solution of 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→6)-1,2,3,4,5,6-tetra-O-isopropylidene-α-D-galactopyranose (10: 295 mg, 0.5 mmol) in anhydrous MeCN (5 ml) were added anhydrous MeOH (60 μl, 1.5 mmol) and HClO₄·SiO₂ (25 mg) and the reaction mixture was stirred at 70°C for the time indicated in Table 2. When the reaction was complete (monitored by TLC), the reaction mixture was filtered through a Celite bed and concentrated under reduced pressure.

To a solution of the crude product in Ac₂O (1.0 ml) was added HClO₄·SiO₂ (25 mg) and the reaction mixture was stirred at r.t. for 1 h. The reaction mixture was filtered through a Celite bed and concentrated to dryness. Purification of the crude acetylated product by column chromatography (hexane-EtOAc, 2:1) furnished pure methyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→6)-2,3,5-tri-O-acetyl-β-D-galactofuranose (19) together with its α-anomer (75%; β/α = 4:1).

**Methyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→6)-2,3,5-tri-O-acetyl-β-D-galactofuranose (19)**

Colorless oil; Rf = 0.5 (hexane – EtOAc, 1:2); [α]D¹⁷ +72.2 (c 1.5, CHCl₃).

IR (neat): 3023, 1752, 1372, 1221, 1043, 762 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 5.42 (d, J = 2.7 Hz, 0.28 H), 5.41 (d, J = 2.7 Hz, 1 H), 5.38 (dd, J = 10.8, 3.6 Hz, 1.28 H), 5.18–5.14 (m, 1.3 H), 5.11–5.05 (m, 1.3 H), 5.03–4.88 (m, 2.55 H), 4.55 (dd, J = 7.8 Hz, 0.28 H), 4.53 (d, J = 7.8 Hz, 1 H), 4.28–4.18 (m, 2.5 H), 4.17–4.10 (m, 2.5 H), 3.82–3.75 (m, 1.28 H), 3.71–3.54 (m, 2.6 H), 3.39 (s, 3 H), 3.37 (s, 0.8 H), 2.13, 2.09, 2.08, 2.03, 1.98 (6 × 0.75 H), 1.97 (7 × s, 26 H).

13C NMR (75 MHz, CDCl₃): δ (β-isomer) = 169.8, 169.6, 169.5, 169.3, 169.1, 168.9, 168.7, 106.3 (C-1), 100.5 (C-5), 81.3, 76.4, 72.7 (2 × C), 71.9, 68.2 (2 × C), 68.1, 61.6 (2 × C), 54.7, 20.5 (2 × C), 20.4 (3 × C), 20.3 (2 × C).

ESI-MS: m/z = 764.2 [M + Na]⁺.


**4-Pentenyl-2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-2,3,5-tri-O-acetyl-β-D-galactofuranose (22)**

Colorless oil; Rf = 0.5 (hexane – EtOAc, 1:2); [α]D¹⁷ +73.8 (c 1.5, CHCl₃).

IR (neat): 2365, 1594, 1752, 1374, 1228, 1140, 1049 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 5.87–5.71 (m, 1 H), 5.38–5.26 (m, 2.5 H), 5.28–5.12 (m, 2.6 H), 4.26–4.14 (m, 5 H), 3.37 (s, 0.75 H), 3.16 (s, 3 H), 2.15 (s, 3 H), 2.14 (s, 0.75 H), 2.13 (s, 3 H), 2.12 (s, 3 H), 2.11 (s, 0.75 H), 2.10 (s, 3 H), 0.78 (s, 3 H), 0.78 (s, 3 H), 0.78 (s, 3 H), 1.98 (3 × 0.75 H), 1.96 (6 × 0.6 H).

13C NMR (75 MHz, CDCl₃): δ (β-isomer) = 169.8, 169.6, 169.4, 169.3, 169.2, 168.9, 168.5, 106.5 (C-1), 101.9 (C-5), 90.8, 81.3, 79.8, 70.9, 67.9, 68.4, 68.1, 67.5, 65.7, 62.2, 55.2, 20.7 (2 × C), 20.6 (3 × C), 20.5 (2 × C).

ESI-MS: m/z = 763.2 [M + Na]⁺.

IR (neat): 2365, 1594, 1751, 1720, 1596, 1387, 1231, 1142, 724 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 7.86–7.72 (m, 4 H, ArH), 5.79–5.72 (m, 2 H, 5.41–5.36 (m, 2 H), 5.25–5.14 (m, 2.6 H), 5.0–4.92 (m, 1.3 H), 4.90–4.80 (m, 1.3 H), 4.35–4.26 (m, 1.2 H), 4.21–4.16 (m, 1 H, 4.08–4.00 (m, 1 H, 3.88–3.74 (m, 2.6 H), 3.30 (s, 1.8 H), 3.30 (s, 3 H, 2.12 (s, 3 H), 2.11 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 1.8 H), 2.03 (s, 3 H, 2,01 (s, 3 H), 1.93 (s, 1.8 H), 1.91 (s, 1.8 H), 1.84 (s, 3 H), 1.83 (s, 1.8 H).

13C NMR (75 MHz, CDCl₃): δ (δ-isomer) = 169.7, 169.6, 169.4, 169.2 (2 × C), 168.9, 167.2 (2 × C), 134.0–123.5 (ArC, 106C (C)), 97.7 (C–C), 79.3, 76.0, 70.7, 70.6, 68.7, 68.5, 67.3, 67.2 (2 × C), 54.7, 54.5, 20.5 (2 × C), 20.4 (2 × C), 20.2 (2 × C).

IR (neat): 2925, 1749, 1378, 1223, 1042, 768 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 7.83–7.70 (m, 4 H, ArH), 5.75–5.62 (m, 2 H, 5.36 (d, J = 8.4 Hz, 1 H), 5.28–5.27 (m, 1 H, 5.21–5.08 (m, 2.8 H), 5.0 (br s, 1 H), 4.96–4.86 (m, 2.8 H), 4.69 (d, J = 3.6 Hz, 1.1 H), 4.33–4.20 (m, 2 H), 4.15–4.10 (m, 1 H), 4.06–4.00 (m, 1 H, 3.86–3.79 (m, 1 H, 3.75–3.73 (m, 1 H, 3.51 (d, J = 7.9, 7.9 Hz, 1.1 H), 3.41–3.35 (m, 1 H, 3.0–2.90 (m, 1 H), 2.10, 2.08, 2.01, 1.99, 1.90, 1.78 (6 × s, 18 × COCH₃), 1.53–1.48 (m, 2 H, 1.27–1.18 (m, 2 H).

13C NMR (75 MHz, CDCl₃): δ = 170.3–170.2 (2 × C), 170.4, 170.2, 169.8 (2 × C), 167.7 (2 × C), 138.1, 134.5 (2 × C), 131.9 (2 × C), 123.8 (2 × C), 115.5, 98.8, 96.0, 72.3, 71.1, 69.1 (2 × C), 68.6, 67.9, 67.6, 67.4, 62.1, 54.9, 53.6, 30.5, 28.7, 21.0 (2 × C), 20.9 (2 × C), 20.7 (2 × C).

ESI-MS: m/z = 814.3 [M + Na⁺].


4-Pentenyl-3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2,3,5-tri-O-acetyl-β-D-galactofuranoside (24)

Yellow oil; Rf = 0.65 (hexane–EtOAc, 1:2); [α]₂⁵ = –39.6 (c 1.5%, CHCl₃).

IR (neat): 2925, 1749, 1378, 1223, 1042, 768 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 7.80–7.21 (m, 9 H, ArH), 5.72 (t, J = 9.0 Hz, 1 H), 5.44–5.34 (m, 2 H), 5.22–5.07 (m, 3 H, 4.97–4.89 (m, 1 H), 4.83 (br s, 1 H), 4.60–4.47 (m, 1 H), 4.41–4.24 (m, 2 H), 4.16–4.06 (m, 2 H), 3.86–3.68 (m, 2 H), 3.54–3.49 (m, 1 H, 2.11), 2.09, 2.03, 1.98, 1.91, 1.86 (6 × s, 18 × H, 6 × COCH₃).

13C NMR (75 MHz, CDCl₃): δ = 170.3, 170.2 (2 × C), 170.1, 169.7, 169.5, 167.7 (2 × C), 137.2, 134.5 (2 × C), 131.8 (2 × C), 128.7 (2 × C), 128.2 (3 × C), 123.9 (2 × C), 98.7, 95.3, 76.9, 76.3, 75.2, 72.3, 71.0, 69.1, 68.9, 68.4, 67.9, 62.1, 54.9, 21.0 (2 × C), 20.9 (2 × C), 20.3 (2 × C).

ESI-MS: m/z = 836.3 [M + Na⁺].

Anal. Calcd for C₂₅H₃₅NO₁₄: C, 57.56; H, 5.33. Found: C, 57.30; H, 5.60.

Methyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl-(1→6)-2,3,5-tri-O-acetyl-β-D-galactofuranoside (28)

Colorless oil; Rf = 0.45 (hexane–EtOAc, 1:2); [α]₂⁵ = +9.6 (c 1.5%, CHCl₃).

IR (neat): 2362, 1752, 1596, 1376, 1231, 1055 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 5.38 (d, J = 2.7 Hz, 1 H), 5.34 (d, J = 2.7 Hz, 0.3 H), 5.30–5.27 (m, 2.3 H), 5.25 (d, J = 7.8, 2.7 Hz, 1 H), 5.13–5.10 (m, 1.3 H), 5.08–5.06 (m, 1.3 H), 5.05–5.02 (m, 1.3 H), 4.95–4.90 (m, 2.6 H), 4.84 (d, J = 8.4 Hz, 0.3 H), 4.81 (d, J = 8.4 Hz, 1 H), 4.52–4.44 (m, 3.9 H), 4.14–4.04 (m, 5.2 H), 3.89–3.84 (m, 1.6 H), 3.79–3.70 (m, 2.6 H), 3.61–3.58 (m, 1.6 H), 3.38 (s, 3 H), 3.37 (s, 1.2 H), 2.16 (s, 3 H), 2.14 (s, 1.8 H), 2.13 (s, 6 H), 2.12 (s, 1.8 H), 2.10 (s, 0.9 H), 2.09 (s, 3 H), 2.08 (s, 1.8 H), 2.06 (s, 3 H), 2.05 (s, 6 H), 2.04 (s, 3 H), 2.03 (s, 2.7 H), 1.97 (s, 6 H).

1H NMR (300 MHz, CDCl 3): δ (β-isomer) = 6.15. (C-1), 102.8 (C-1), 97.1 (C-1’), 95.5 (C-5’), 81.5, 79.4, 75.4, 72.9, 71.9 (2 C), 70.0 (2 C), 69.5 (2 C), 68.5 (2 C), 68.1, 61.5 (2 C), 55.3, 20.8 (3 C), 20.7 (4 C), 20.5 (3 C).

13C NMR (75 MHz, CDCl 3): δ (α-isomer) = 169.9 (3 C), 169.4 (2 C), 169.2, 168.9 (2 C), 120.4 (C-1), 100.1 (C-1’), 95.5 (C-5’), 81.4, 79.4, 75.4, 72.8, 72.1, 72.0, 70.1, 69.4, 68.5, 62.7, 67.5, 61.5 (2 C), 60.0, 55.3, 20.8 (3 C), 20.7 (4 C), 20.5 (3 C).

13C NMR (75 MHz, CDCl 3): δ (β-isomer) = 170.1 (2 C), 169.9 (3 C), 169.4 (2 C), 169.2, 168.9 (2 C), 120.4 (C-1), 100.1 (C-1’), 95.5 (C-5’), 81.5, 79.4, 75.4, 72.9, 71.9 (2 C), 70.0 (2 C), 69.5 (2 C), 68.5 (2 C), 68.1, 61.5 (2 C), 55.3, 20.8 (3 C), 20.7 (4 C), 20.5 (3 C).

ESI-MS: m/z = 961.4 [M + Na]+.


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(11) Preparation of HClO4-SiO2 (0.5 mmol/g) as a free-flowing powder.


