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Easy Access to Sauropunols A−D: Synthesis and Spectroscopy Correlation of Their Natural Methyl and Ethyl Glycosides

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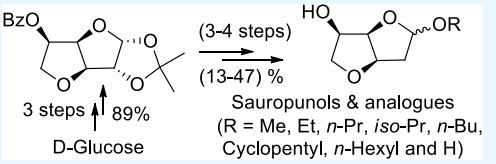
ABSTRACT: 3,6-Anhydro-2-deoxy-hexofuranoside, the natural product core, is present in natural sauropunols (A−D) and in their natural methyl and ethyl glycosides, now, namely, sauropunol H and sauropunol F. The easily synthesized D-glucose-derived 3,6-anhydro-1,2-*O*-isopropylidene-5-*O*-benzoyl-α-D-glucofuranose was elaborated to final targets employing the $TsOH{\cdot}H_2O$-catalyzed glycosylation reaction with seven different alcohols, subsequent radical deoxygenation, and appropriate deprotection reactions involving mild conditions with excellent functional group tolerance. A short total synthesis of sauropunols (A−D), sauropunol H, and the first total synthesis of sauropunol F are reported herein. The correlation of spectroscopy data of sauropunol H and sauropunol F has been derived through these syntheses.



INTRODUCTION

The plants, *Sauropus rostratus* and *Sauropus spatulifolius*, belonging to the genus *Sauropus* of the *Euphorbiaceae* family,[1] are used in traditional Chinese medicine. The water decoction of leaves of *S. rostratus* is used to treat cough, constipation, and bronchitis,[2] while the water extract of the plant possessed anti-inflammatory and analgesic effects.[3] The *n*-butanol liquor from the water extract of *S. rostratus* showed potent antibacterial activities against *Staphylococcus aureus*, *Salmonella typhi*, and *Escherichia coli*,[4] and the methanol extract of the plant exhibited extraordinary free-radical-scavenging activities.[5] *S. rostratus* also possessed antianaphylaxis effect,[6] whereas the leaves of *S. spatulifolius* are used to treat asthma, cough, bronchitis, and pneumonia.[7] Thus, the plants of sauropus genus are very important in terms of bioactivity.

Toward the search for bioactive compounds from the genus, the isolation of *n*-butyl 3,6-anhydro-2-deoxy-α-D-glucofuranoside (**1**) (sauropunol A), *n*-butyl 3,6-anhydro-2-deoxy-β-D-glucofuranoside (**2**) (sauropunol B), 3,6-anhydro-2-deoxy-D-glucofuranose (**3/4**)[8] (sauropunol C/D), and methyl 3,6-anhydro-2-deoxy-β-D-galactofuranoside (**5**) from the leaves of the *S. rostratus* (Figure 1) was carried out by Wang et al.[6] Subsequently, Zhang et al.[7] in 2022 isolated ethyl 3,6-anhydro-2-deoxy-α-L-allofuranoside (**6**) and ethyl 3,6-anhydro-2-deoxy-β-D-glucofuranoside (**7**) (now, namely, sauropunol F), along with sauropunol C/D (**3/4**) from the leaves of *S. spatulifolius* (Figure 1). Cytotoxicity studies of the compounds (**1−4**) exhibited nontoxic properties and a high level of safety profile against the human promyelocytic leukemia cell line (HL60) and normal HELF cell line.[9] The *in vivo* activity study of the β-glycoside anomer (sauropunol B) (**2**) showed anti-inflammatory activities, which was comparable to indomethacin, an anti-inflammatory drug.[9] In another study, compounds **3/4**, **6**, and **7** exhibited low toxicity against the RLE-6TN cell with a top

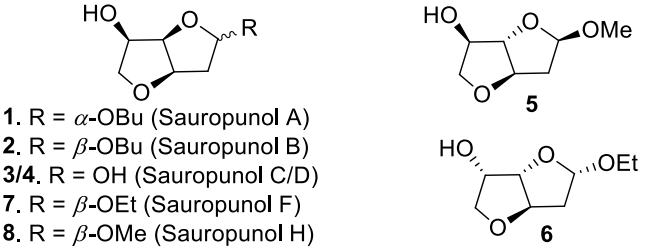


Figure 1. Naturally occurring 3,6-anhydro-2-deoxy hexofuranose (**3/4**) and hexofuranosides (**1**, **2**, **5−8**).

level of safety profile,[7] while **3/4** displayed strong inhibition activities on the TGF-β1-induced lung fibroblast differentiation.[7] Methyl 3,6-anhydro-2-deoxy-β-D-glucofuranoside (**8**), now, namely, sauropunol H, was isolated by Van Kiem et al.[10] from the plant *Tetrastigma erubescens*, but no biochemical data was reported so far. Again, the unnatural nitrate derivatives **9** and **10** (Figure 2) of sauropunol B displayed stronger vasorelaxation activities than the drug isosorbide dinitrate (ISDN).[11]

With an aim to search for other medical properties of **1−4** and **7−8**, adequate quantities of the compounds, which could be done by synthesis, are essentially required. So far, four different syntheses of sauropunols (A−D) (**1−4**) were reported involving either the use of costly 2-deoxy-D-

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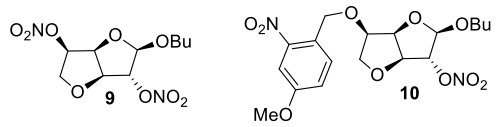


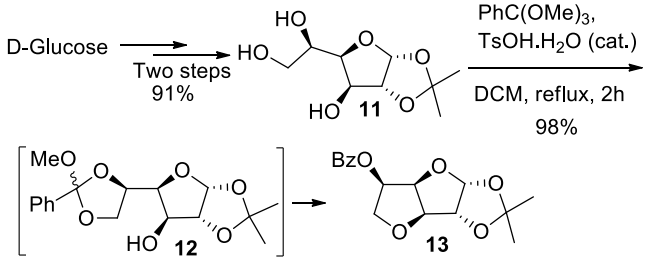
Figure 2. Bioactive nitrate derivatives (**9**–**10**) of sauropunol B.

glucose[12,13] or D-glucose with judicious manipulation of multiple protecting groups and their deprotections[9] or by chiral synthesis.[14] One synthesis of **8** was reported using isoglucal[15] before its discovery, but the synthesis of **7** is yet to be reported. The development of expedient and flexible synthetic routes to sauropunols A–D (**1**–**4**) and sauropunol H (**8**) thus remains unabated. We report herein a cost-effective and viable synthesis of sauropunols (A–D) and sauropunol H, along with other *O*-glycosides of sauropunols with *β*-anomer as major products using seven aliphatic alcohols. During the process, we have also completed the first total synthesis of natural sauropunol F (**7**).

RESULTS AND DISCUSSION

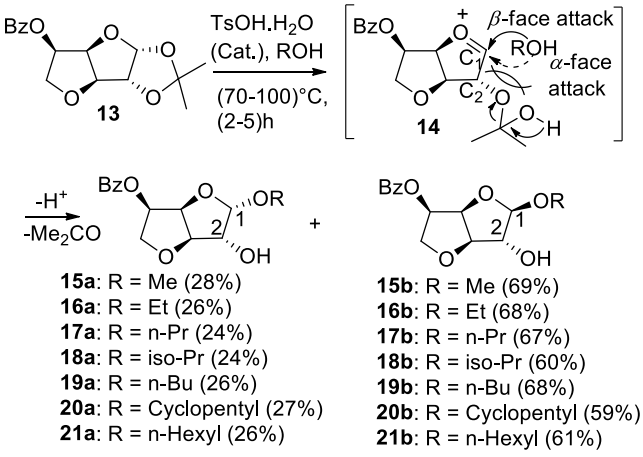
To realize our aspiration, we plan as follows. Cheap and commercially available D-glucose was first converted to 1,2-*O*-isopropylidene-*α*-D-glucofuranose (**11**) with a 91% yield in two steps according to the literature procedure.[16] Treatment of **11** with the literature[17] protocol using $PhC(OMe)_3$ and catalytic $TsOH.H_2O$ but under reflux condition in 2 h resulted in the desired 3,6-anhydro-5-*O*-benzoyl-1,2-*O*-isopropylidene-*α*-D-glucofuranose (**13**) (98% yield) through the nonisolable orthoester intermediate **12** (Scheme 1), and this was the highest yielding (89% from D-glucose in three steps) method for the construction of 3,6-anhydro-1,2-*O*-isopropylidene-*α*-D-glucofuranose core structure reported[9,12−15,18,19] so far. The success of this reaction was evident from the occurrence of five aromatic proton signals in the ^1H NMR spectra of **13**, and the benzoate ester group was confirmed by the appearance of a peak at ν_{max}1722 cm^{-1} in its IR spectra. Finally, the structural confirmation of **13** was obtained from a single-crystal X-ray crystallographic study [Supporting Information, Figure S3].

Scheme 1. Synthesis of 3,6-Anhydro-1,2-*O*-isopropylidene-5-*O*-benzoyl-*α*-D-glucofuranose (13)

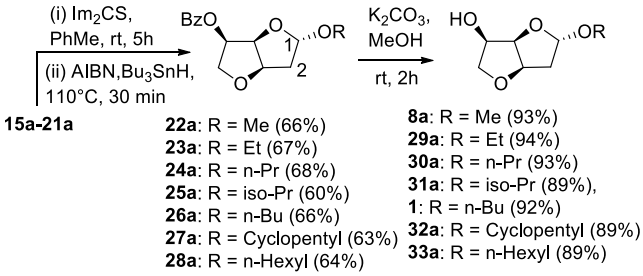


Acetonide deprotection of **13** and subsequent *O*-glycosylation reaction under the modified methanolysis procedure[20] were carried out in the presence of the catalytic amount of $PTSA.H_2O$ using different alcohols (ROH) including methanol, ethanol, *n*-propanol, *iso*-propanol, *n*-butanol, cyclopentanol, and *n*-hexanol to obtain a pair of anomeric glycosides with *β*-anomer as major products for each alcohol (Scheme 2). As the *α*-face of intermediate **14**, obtained from **13**, was blocked by C-2 hemiacetal,[21] the approach of the incoming alcohols (ROH) toward the C-1 center of intermediate **14** took place preferentially from *β*-face to obtain *α*-anomers (**15a**–**21a**) as minor products (24–28% yield) and *β*-anomers (**15b**–**21b**) as major products (59–69% yield). Glycosylation reaction conditions varied with the nature of alcohol. For bulky alcohols, it required a high temperature and longer time. Regarding the structure of the glycosides (**15a/b-21a/b**), the absence of the methyl proton signals of the isopropylidene group and the appearance of different *O*-alkyl proton signals in the ^1H and ^{13}C NMR spectra clearly suggested the formation of the products, whereas the anomeric stereochemistry was established based on the splitting pattern and the coupling constant of the C-1 proton. The relationship of the C-1 and C-2 protons was cis in *α*-anomers (**15a**–**21a**) and trans in *β*-anomers (**15b**–**21b**), and as expected in the furanose system,[9] a sharp doublet was found for the C-1 proton between *δ* (5.10–5.22) with coupling constant (*J*) between (4.0–4.5)Hz for all *α*-anomers (**15a**–**21a**) and a singlet peak was found between *δ* (5.02–5.13) for all of the *β*-anomers (**15b**–**21b**). Similarly, in the ^{13}C NMR, the C-1 signals appeared between *δ* (102.4–103.9) for the *α*-anomers and *δ* (108.2–110.2) for the *β*-anomers and the values are quite consistent with literature values.[9] Finally, the relative stereochemistry at C-1 of both the *α*-and *β*-anomers was established from the X-ray structure analysis of the representative molecules **15a**, **15b**, and **16a** (see the Supporting Information, Figures S4–S6, respectively).

Scheme 2. Glycosylation Reaction of 13 under the Modified Methanolysis Procedure Using Seven Different Alcohols



Scheme 3. Synthesis of Sauropunol A (1), Sauropunol G (8a), Sauropunol E (29a), and Its Other *O*-Glycoside Analogues (30a–33a)



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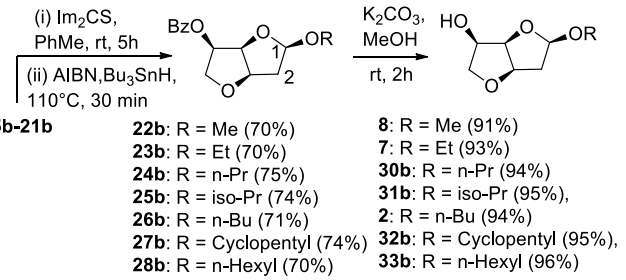
Scheme 4. Synthesis of Sauropunol B (2), Sauropunol H (8), Sauropunol F (7), and Its Other *O*-Glycoside Analogues (30b−33b)

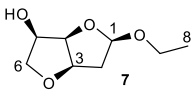
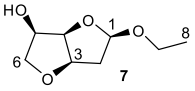
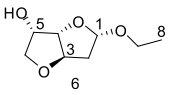


zothiocarbonyl esters on subsequent reduction under the Barton−McCombie condition[22,23] produced (**22a−28a**) and (**22b−28b**), respectively, in good yields. The deoxygenation reaction produced a methylene unit, which could be deduced from the usual NMR spectral evidence. In the ^{1}H NMR spectrum, signals for the two protons at C-2 were observed between δ (2.08−2.25) (m) for **22a−28a** and between δ (2.12−2.20) (m) for **22b−28b**, while the ^{13}C NMR spectra contained signals for the C-2 carbons between δ (40.6−40.9) for **22a−28a** and between δ (41.5−41.9) for **22b−28b**. Finally, the formation of the $-CH_2-$ unit at C-2 of all of the compounds was established from the X-ray structure analysis of a representative molecule **27b** (see the Supporting Information, Figure S7). Debenzoylation of (**22a−28a**) by the treatment of K_2CO_3 in MeOH smoothly furnished **8a**[15] (now, namely, sauropunol G), **29a** (now, namely, sauropunol E), **30a, 31a, 1** (sauropunol A), **32a**, and **33a** (Scheme 3), while similar debenzoylation of (**22b−28b**) furnished **8**[15] (sauropunol H), **7** (sauropunol F), **30b**, **31b, 2** (sauropunol B), **32b**, and **33b** (Scheme 4) in excellent yields. In all of the final products, the absence of aromatic proton signals as well as carbon signals in the NMR spectra clearly indicated the success of the final debenzoylation reaction. Finally, the structure of all of the final compounds was established from the X-ray structure analysis of the representative molecules **8**, **30b, 31b**, and **32a** (see the Supporting Information, Figures S8−S11, respectively). The ^{1}H and ^{13}C NMR spectra of sauropunol A (**1**) and sauropunol B (**2**) were consistent with the literature values,[9,12−14] while those of sauropunol G (**8a**)[15] and sauropunol H (**8**)[10,15] were also correlated with the literature value and they were congruent.

Spectroscopy (NMR Data) Correlation of Sauropunol F (7). NMR spectra were generated from the compound isolated from natural sources[7] as well as from the synthesized compound. The structure of **7** (obtained synthetically) was confirmed not only by NMR spectra but also through the preceding X-ray crystallography analysis of **16a**. One important observation was that the reported ^{1}H NMR and ^{13}C NMR data of **7**,[7] isolated from natural sources, in column A (Table 1) did not match with the NMR data of **7**, obtained synthetically, in column B. More interestingly, the NMR data of **7** in column B matched with that reported for natural product **6**[7] in column C within experimental error for $\delta_H \sim 0.02$ and $\delta_C \sim 0.5$. This NMR data correlation clearly indicated that in the literature[7] the NMR spectra of compounds **6** and **7** were interchanged with respect to their structure and wrongly tagged.

For the preparation of sauropunol C/D (**3**/**4**), one of the high-yielding final β-anomeric glycosides (e.g., **8**) was subjected to hydrolysis by using 50% aqueous CF_3CO_2H to produce sauropunol C/D (**3**/**4**) (70% yield) as a mixture of

Table 1. Correlation of NMR Data of Sauropunol F (7)[a]

Position	Column A (NMR-data of **7** isolated from natural sources[7]) 		Column B (NMR-data of **7** obtained through synthesis) 		Column C (NMR-data of natural product **6**[7]) 	
	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C
1	5.31 (d, J = 4.0 Hz, 1H)	106.3	5.25 (t, J = 3.3 Hz, 1H),	105.8	5.23 (t, J = 3.2 Hz, 1H),	106.3
2a	2.21 (m, 1H)	40.5	2.19-2.18 (m, 2H),	40.0	2.16 (m, 2H)	40.5
2b	2.11 (m, 1H)					
3	4.73 (m, 1H)	81.9	4.59-4.57 (m, 1H),	81.4	4.56 (m, 1H),	81.9
4	4.52 (t, J = 5.0 Hz, 1H)	84.6	4.69 (t, J = 5.8 Hz, 1H),	84.2	4.67 (t, J = 5.8 Hz, 1H),	84.6
5	4.18 (dd, J = 11.8, 5.9 Hz, 1H)	71.4	4.19-4.15 (m, 1H),	70.9	4.15 (m, 1H),	71.4
6a	3.81 (dd, J = 9.4, 5.9 Hz, 1H)	73.6	3.87 (dd, J = 9.3, 4.9 Hz, 1H),	73.2	3.85 (dd, J = 9.3, 5.3 Hz, 1H),	73.6
6b	3.53 (t, J = 8.0 Hz, 1H),		3.74 (dd, J = 9.3, 5.2 Hz, 1H),		3.72 (dd, J = 9.3, 5.3 Hz, 1H),	
7a	3.72 (dd, J = 8.9, 6.4 Hz, 1H),	64.7	3.82 (dq, J = 9.6, 7.2 Hz, 1H),	64.3	3.80 (m, 1H),	64.7
7b	3.44 (t, J = 8.1 Hz, 1H),		3.56 (dq, J = 9.6, 7.2 Hz, 1H),		3.54 (m, 1H),	
8	1.16 (t, J = 7.1 Hz, 3H)	15.0	1.24 (t, J = 7.1 Hz, 3H),	14.6	1.22 (t, J = 7.1 Hz, 3H)	15.0
OH	Not reported	-	3.06 (brs, 1H),	-	Not reported	-

[a]Spectra were recorded as ^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$). Data in column B did not match with column A; rather, it matched with column C within experimental error for $\delta_H \sim 0.02$ and $\delta_C \sim 0.5$.

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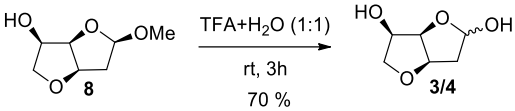
ACS Omega 2023, 8, 39739−39748

anomers (Scheme 5). The NMR spectra of **3/4** were consistent with the reported values.[9,12−14]

Scheme 5. Synthesis of Sauropunol C/D (3/4)



CONCLUSIONS

In conclusion, we identified the compound (**13**) as the key intermediate to prepare 14 3,6-anhydro-2-deoxy-D-glucofuranoside in good yields starting from D-glucose. In this synthetic approach, compound 13 under the modified Fisher glycosylation reaction with seven different alcohols exposed its 2-hydroxyl group without affecting their 5-*O*-benzoyl group. Subsequent radical deoxygenation and appropriate deprotection yielded the desired glycosides along with natural sauropunol A (**1**) (14%), sauropunol B (**2**) (40%), sauropunol F (**7**) (39%), and sauropunol H (**8**) (39%) in six steps and sauropunol C/D (**4**/**5**) (27%) in seven steps from D-glucose. The present strategy reported the first synthesis of sauropunol F, and its spectroscopy correlation was done. The final compounds are expected to be important for the evaluation of medicinal properties of the plants *S. rostratus* and *S. spatulifolius*. Sauropunol B, having anti-inflammatory properties, inspired us to study this activity of all of the new *ß*-anomeric glycosides. Considering the advantage of the strategy and related approaches, attempts could be initiated for the synthesis of natural furanodictines A−B[24] and other analogues of the natural sauropunol B to search for new potent synthetic analogues.[11,19,25−27] Furthermore, as sauropunol F (**7**) and sauropunol H (**8**), both the ß-anomers, are present in nature, it is expected that the presence of their *α*-anomers **29a** (sauropunol E) and **8a** (sauropunol G) could be present in nature like sauropunol A (**1**) that exist in both anomers.

EXPERIMENTAL SECTION

General Methods. Oven-dried glassware were used for the moisture-sensitive reactions, and the reactions were carried out under N_2 (g). Precoated plates (0.25 mm, Silica Gel 60 F254) were used for TLC analysis and visualized by UV light (254 nm) and chemical dyeing with the Liebermann−Burchard reagent. Column chromatography was performed using silica gel (100−200 mesh) or neutral alumina (70−230 mesh) as applicable by applying pressure through an air pump. Melting points were determined in open capillaries and are uncorrected. Specific rotations were measured with an Anton Paar Modular Circular Polarimeter (MCP) 200 using a sodium lamp source (589 nm) and are reported as $[\alpha]_D^{T^oC}$ (c = g/100 mL, solvent). ^{1}H and ^{13}C NMR spectra were recorded using 300, 400, 500, or 600 MHz spectrometers. For reference, residual solvent signals or internal standards were used. NMR spectra are reported as chemical shifts (δ) in parts per million (ppm), and to show multiplicities, the following abbreviations were used: s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublet, t = triplet, q = quartet, dt = doublet of triplet, dq = doublet of quartet, hept = heptet, and m = multiplet. Coupling constants (J) are reported in Hz. ESI mass spectral analysis was recorded using an LCQ-ORBI-TRAP-XL instrument. X-ray diffraction data of compounds **13, 15a, 15b, 16a, 27b, 8, 30b, 31b**, and **32a** were collected on a Bruker SMART APEX2 area detector. Details of the preparation of single crystals were given in the characterization data section of each compound. CCDC (2233181−2233189) contains the crystallographic data (CIF files) of the compounds and can be obtained at https://summary.ccdc.cam.ac.uk/structure-summary form.

*3,6-Anhydro-1,2-isopropylidene-5-O-benzoyl-α-D-glucofuranose (**13**).* To a solution of **11** (15 g, 68.11 mmol) in DCM (200 mL) were added trimethylorthobenzoate (31.6 mL, 170 mmol) and PTSA.H_2O (1.3 g, 6.81 mmol) and heated at reflux for 2 h. It was neutralized with Et_3N (1 mL) at 0°C. The solution was washed with water (2 × 100 mL), dried (Na_2SO_4), and concentrated to afford a gummy mass, which was then purified by column chromatography on silica gel (100−200 mesh). Elution with ethyl acetate−petroleum ether (1:9) afforded **13** (21.9 g, 98%) as a white solid. mp 60 °C; $[\alpha]_D^{25}$ = +17.1 (c 0.69, MeOH); IR (KBr): ν_{max} 2983, 2972, 2938, 1722 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 5.96 (d, J = 3.3 Hz, 1H), 5.34−5.29 (m, 1H), 5.07 (t-like, J = 3.6, 3.9 Hz, 1H), 4.63 (d, J = 3.3 Hz, 1H), 4.58 (d, J = 3.4 Hz, 1H), 4.16 (t-like, J = 7.0, 8.4 Hz, 1H), 3.87 (t-like, J = 8.0, 8.4 Hz, 1H), 1.49 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 133.4, 129.9, 129.9, 129.4, 128.4, 128.4, 112.9, 107.3, 85.4, 84.9, 81.2, 73.8, 69.2, 27.5, 26.9; HRMS (ESI, m/z) calcd for $C_{16}H_{18}O_6$ [M + Na]$^+$ 329.1001, found 329.0964.

General Procedure for the TsOH·H_2O-Catalyzed Glycosylation Reaction of 13. To a solution of **13** (3.0 g, 9.11 mmol) in selected alcohol (ROH) (30 mL) was added TsOH·H_2O (15 mol %) and stirred at room temperature for 15 min; then, it was heated at (70−100)°C for (2−5) h. After heating, the reaction mixture was cooled to 0°C and neutralized by adding Et_3N. The solvent was evaporated under vacuum, and the crude mass was extracted with DCM (3 × 30 mL). The organic layer was washed with water (3 × 30 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford a gummy mass. The crude product was purified by silica gel (100−200 mesh) column chromatography to obtain the desired *α*- and *β*-anomeric glycosides **15a−21a** and **15b−21b**.

*Methyl 3,6-Anhydro-5-O-benzoyl-α-D-glucofuranoside (**15a**) and Methyl 3,6-Anhydro-5-O-benzoyl-β-D-glucofuranoside (**15b**).* Compounds **15a** and **15b** were prepared from **13** and MeOH with the general procedure as described before at 70 °C in 2 h of duration. Elution with $CHCl_3$−PE (4:1) furnished **15a** (28%) and with $CHCl_3$-EA (9:1) furnished **15b** (69%) as white solids.

Compound **15a**: mp 95−96 °C; $[\alpha]_D^{25}$ = +104.3 (c 0.45, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.06 (m, 2H), 7.60−7.56 (m, 1H), 7.48−7.44 (m, 2H), 5.27 (dd, J = 11.6, 6.0 Hz, 1H), 5.01 (d, J = 4.4 Hz, 1H), 4.93 (t-like, J = 5.6, 5.2 Hz, 1H), 4.52 (dd, J = 5.6, 2.8 Hz, 1H), 4.20 (dd, J = 4.4, 2.8 Hz, 1H), 4.15−4.11 (m, 1H), 3.94 (dd, J = 9.6, 6.4 Hz, 1H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 133.4, 129.8, 129.8, 129.6, 128.6, 128.6, 104.9, 87.9, 78.5, 77.6, 73.2, 69.3, 56.0; HRMS (ESI, m/z) calcd for $C_{14}H_{16}O_6$ [M + Na]$^+$ 303.0845, found 303.0844.

Compound **15b**: mp 99−100 °C; $[\alpha]_D^{25}$ = +32.3 (c 0.48, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.04 (m, 2H), 7.59−7.56 (m, 1H), 7.47−7.43 (m, 2H), 5.24−5.16 (m, 2H), 4.95 (s, 1H), 4.54 (d, J = 9.6 Hz, 1H), 4.26 (s, 1H), 4.19 (dd, J

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ACS Omega 2023, 8, 39739−39748

= 8.4, 7.2 Hz, 1H), 4.05 (t-like, J = 8.0, 8.8 Hz, 1H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 133.5, 129.9, 129.9, 129.5, 128.7, 128.6, 111.1, 87.8, 81.8, 80.8, 73.8, 68.9, 55.5; HRMS (ESI, m/z) calcd for $C_{14}H_{16}O_6$ $[M + H]^+$ 281.1025, found 281.1013.

*Ethyl 3,6-Anhydro-5-O-benzoyl-α-D-glucofuranoside (**16a**) and Ethyl 3,6-Anhydro-5-O-benzoyl-β-D-glucofuranoside (**16b**).* Compounds **16a** and **16b** were prepared from **13** and EtOH with the general procedure as described before at 80 °C in 3 h of duration. Elution with EA-PE (1:4) and EA-PE (1:3) furnished **16a** (26%) and **16b** (68%), respectively, as a white solid and colorless oil, respectively.

Compound **16a**: mp 85−86 °C; $[\alpha]_D^{25}$ = +94.5 (c 0.40, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.5 Hz, 2H), 7.58 (t-like, J = 7.0, 7.5 Hz, 1H), 7.45 (t-like, J = 8.0, 7.5 Hz, 2H), 5.27 (dd, J = 11.5, 6.0 Hz, 1H), 5.13 (d, J = 4.0 Hz, 1H), 4.94 (t-like, J = 5.5, 5.0 Hz, 1H), 4.51 (dd, J = 5.0, 2.5 Hz, 1H), 4.18 (s, 1H), 4.12 (dd, J = 9.5,6.0 Hz, 1H), 3.93 (dd, J = 9.5, 5.6, Hz, 1H), 3.79 (dq, J = 9.6, 7.1 Hz, 1H), 3.50 (dq, J = 9.6, 7.1 Hz, 1H), 2.71 (d, J = 2.5 Hz, 1H), 1.18 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 133.3, 129.8, 129.8, 129.6, 128.4, 128.4, 103.7, 87.9, 78.4, 77.3, 73.3, 69.3, 64.5, 15.0; ESI-MS (m/z) = 317.10 $(M + Na)^+$. HRMS (ESI, m/z) calcd for $C_{15}H_{18}O_6$ $[M + Na]^+$ 317.1001, found 317.0995.

Compound **16b**: $[\alpha]_D^{25}$ = +39.8 (c 0.51, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.45 (t-like, J = 8.0, 7.5 Hz, 2H), 5.23−5.18 (m, 1H), 5.16 (t, J = 5.0 Hz, 1H), 5.04 (s, 1H), 4.56 (d, J = 5.0 Hz, 1H), 4.27 (s, 1H), 4.19 (t-like, J = 8.0, 7.5 Hz, 1H), 4.12 (t, J = 8.5 Hz, 1H), 3.79 (dq, J = 9.4, 7.1 Hz, 1H), 3.44 (dq, J = 9.4, 7.1 Hz, 1H), 2.13 (brs, 1H), 1.19 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 133.3, 129.7, 129.7 129.6, 128.4, 128.4, 109.8, 87.8, 81.5, 81.1, 73.8, 68.8, 63.5, 14.8; HRMS (ESI, m/z) calcd for $C_{15}H_{18}O_6$ $[M + Na]^+$ 317.1001, found 317.1004.

*n-Propyl 3,6-Anhydro-5-O-benzoyl-α-D-glucofuranoside (**17a**) and n-Propyl 3,6-Anhydro-5-O-benzoyl-β-D-glucofuranoside (**17b**).* Compounds **17a** and **17b** were prepared from **13** and n-propanol with the general procedure as described before at 85 °C in 3 h of duration. Elution with EA-PE (3:5) and EA-PE (1:4) furnished **17a** (24%) and **17b** (67%), respectively, as colorless liquids.

Compound **17a**: $[\alpha]_D^{25}$ = +83.4 (c 0.48, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.3 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 5.27 (dd, J = 12.0, 6.0 Hz, 2H), 5.11 (d, J = 4.5 Hz, 1H), 4.93 (t-like, J = 5.5, 5.0 Hz, 1H), 4.51 (dd, J = 5.5, 2.5 Hz, 1H), 4.19−4.17 (m, 1H), 4.11 (dd, J = 9.5, 6.0 Hz, 1H), 3.94 (dd, J = 9.5, 6.5 Hz, 1H), 3.68 (dt, J = 9.6, 6.7 Hz, 1H), 3.39 (dt, J = 9.6, 6.7 Hz, 1H), 2.70 (d, J = 7.0 Hz, 1H), 1.64−1.54 (m, 2H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 133.3, 129.8, 129.8 129.6, 128.4, 128.4 103.8, 87.9, 78.4, 77.4, 73.3, 70.6, 69.3, 22.7, 10.4; HRMS (ESI, m/z) calcd for $C_{16}H_{20}O_6$ $[M + Na]^+$ 331.1158, found 331.1157.

Compound **17b**: $[\alpha]_D^{25}$ = +41.3 (c 0.47, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.0 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 5.22−5.15 (m, 2H), 5.03 (s, 1H), 4.56 (d, J = 5.0 Hz, 1H), 4.27 (s, 1H), 4.19 (t-like, J = 8.0, 7.5 Hz, 1H), 4.12 (t, J = 8.5 Hz, 1H), 3.70 (dt, J = 9.3, 6.9 Hz, 1H), 3.30 (dt, J = 9.4, 7.0 Hz, 1H), 2.13 (brs, 1H), 1.62−1.57 (m, 2H), 0.86 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 133.3, 129.8, 129.8, 129.6, 128.4, 128.4, 110.2, 87.8, 81.4,81.1, 73.8, 70.0, 68.7, 22.5, 10.5; HRMS (ESI, m/z) calcd for $C_{16}H_{20}O_6[M + H]^+$ 331.1158, found 331.1167.

*Isopropyl 3,6-Anhydro-5-O-benzoyl-α-D-glucofuranoside (**18a**) and Isopropyl 3,6-Anhydro-5-O-benzoyl-β-D-glucofuranoside (**18b**).* Compounds **18a** and **18b** were prepared from **13** and isopropanol with the general procedure as described before at 85 °C in 5 h of duration. Elution with EA-PE (3:5) and EA-PE (1:4) furnished **18a** (24%) and **18b** (60%), respectively, as colorless oils.

Compound **18a**: $[\alpha]_D^{25}$ = +67.1 (c 0.68, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.45 (t-like, J = 8.0, 7.5 Hz, 2H), 5.27 (dd, J = 11.5, 5.0 Hz, 1H), 5.22 (d, J = 4.5 Hz, 1H), 4.94 (t-like, J = 5.0, 5.5 Hz, 1H), 4.49 (dd, J = 5.0, 2.0 Hz, 1H), 4.14 (brs, 1H), 4.10 (dd, J = 9.5, 6.0 Hz, 1H), 3.94 (dd, J = 9.5, 6.0 Hz, 1H), 3.88 (dd, J = 12.0,6.0, Hz, 1H), 2.70 (d, J = 7.0 Hz, 1H), 1.17 (d, J = 6.0 Hz, 3H), 1.10 (d, J = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 133.2, 129.8, 129.8, 129.7, 128.4, 128.4, 102.4, 87.8, 78.3, 73.3, 71.4, 69.4, 23.3, 21.8; HRMS (ESI, m/z) calcd for $C_{16}H_{20}O_6$ $[M + Na]^+$ 331.1158, found 331.1165.

Compound **18b**: $[\alpha]_D^{25}$ = +27.7 (c 0.53, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 5.23−5.18 (m, 1H), 5.17 (s, 1H), 5.13 (t, J = 5.0 Hz, 1H), 4.56 (d, J = 4.8 Hz, 1H), 4.23 (s, 1H), 4.22−4.15 (m, 2H), 3.94 (dt, J = 12.3, 6.2 Hz, 1H), 1.20 (d, J = 6.3 Hz, 3H), 1.13 (d, J = 6.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 133.3, 129.8, 129.8, 129.6, 128.4, 128.4, 108.2, 87.7, 81.3, 81.2, 73.9, 69.8, 68.5, 23.2, 21.0; HRMS (ESI, m/z) calcd for $C_{16}H_{20}O_6$ $[M + Na]^+$ 331.1158, found 331.1157.

*Butyl 3,6-Anhydro-5-O-benzoyl-α-D-glucofuranoside (**19a**) and Butyl 3,6-Anhydro-5-O-benzoyl-β-D-glucofuranoside (**19b**).* Compounds **19a** and **19b** were prepared from **13** and n-butanol with the general procedure as described before at 85 °C in 3 h of duration. Elution with EA-PE (3:5) and EA-PE (1:4) furnished **19a** (26%) and **19b** (68%), respectively, as colorless oils.

Compound **19a**: $[\alpha]_D^{25}$ = +82.7 (c 0.295, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 5.26 (dd, J = 11.6, 5.7 Hz, 1H), 5.10 (d, J = 4.2 Hz, 1H); 4.92 (t, J = 5.2 Hz, 1H), 4.50 (dd, J = 5.1, 2.5 Hz, 1H); 4.17 (s, 1H); 4.10 (dd, J = 9.4, 5.9 Hz, 1H); 3.92 (dd, J = 9.4, 4.8 Hz, 1H); 3.72 (dt, J = 9.6, 6.6 Hz, 1H); 3.41 (dt, J = 9.6, 6.6 Hz, 1H), 2.67 (brs, 1H), 1.59−1.49 (m, 2H), 1.38−1.24 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 133.4, 129.9, 129.9, 129.6, 128.5, 128.5, 103.9, 87.9, 78.5,73.3, 69.4, 68.8, 31.5, 19.2, 13.9; HRMS (ESI, m/z) calcd for $C_{17}H_{22}O_6$ $[M + Na]^+$ 345.1314, found 345.1322.

Compound **19b**: $[\alpha]_D^{25}$ = +46.9 (c 0.33, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 5.22−5.13 (m, 2H); 5.02 (s, 1H); 4.55 (d, J = 4.6 Hz, 1H), 4.26 (s, 1H); 4.19 (t, J = 7.7 Hz, 1H); 4.09 (t, J = 8.4 Hz, 1H), 3.73 (dd, J = 16.0, 7.1 Hz, 1H), 3.34 (dd, J = 16.0, 7.1 Hz, 1H), 1.64 (brs, 1H), 1.58−1.51 (m, 2H), 1.32−1.21 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H), OH proton exchanged with solvent: ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 133.4, 129.8, 129.8, 129.6, 128.5, 128.5, 110.2, 87.8, 81.5, 81.1, 73.9, 68.8, 68.3, 31.5, 19.4, 13.9; HRMS (ESI, m/z) calcd for $C_{17}H_{22}O_6$ $[M + Na]^+$ 345.1314, found 345.1315.

*Cyclopentyl 3,6-Anhydro-5-O-benzoyl-α-D-glucofuranoside (**20a**) and Cyclopentyl 3,6-Anhydro-5-O-benzoyl-β-D-glucofuranoside (**20b**).* Compounds **20a** and **20b** were

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prepared from **13** and cyclopentanol with the general procedure as described before at 110 °C in 5 h of duration. Elution with EA-PE (3:5) and EA-PE (1:4) furnished **20a** (24%) and **20b** (59%), respectively, as colorless oils.

Compound **20a**: $[\alpha]_D^{25}$ = +75.8 (*c* 0.38, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.0 Hz, 2H), 7.58 (app t, *J* = 7.4 Hz, 1H), 7.45 (app t, *J* = 7.7 Hz, 2H), 5.27 (dd, *J* = 11.5, 5.5 Hz, 1H), 5.18 (d, *J* = 4.5 Hz, 1H), 4.93 (app t, *J* = 5.3 Hz, 1H), 4.48 (dd, *J* = 5.3, 2.3 Hz, 1H), 4.19−4.16 (m, 1H), 4.15−4.12 (m, 1H), 4.09 (dd, *J* = 9.5, 5.9 Hz, 1H), 3.94 (dd, *J* = 9.5, 6.2 Hz, 1H), 2.66 (d, *J* = 7.0 Hz, 1H), 1.7−1.48 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 133.2, 129.8, 129.8, 129.6, 128.4, 128.4, 102.8, 87.8, 80.7, 78.4, 77.2, 73.3, 69.4, 33.2, 32.0, 23.3, 23.1; HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{22}O_6$ $[M + H]^+$ 335.1495, found 335.1497.

Compound **20b**: $[\alpha]_D^{25}$ = +32.8 (*c* 0.36, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.45 (app t, *J* = 7.3 Hz, 2H), 5.19 (m, *J* = 8.8, 1H), 5.14 (app t, *J* = 5.3 Hz, 1H), 5.10 (s, 1H), 4.56 (d, *J* = 4.5 Hz, 1H), 4.27−4.18 (m, 3H), 4.14 (t, *J* = 7.8 Hz, 1H), 1.74−1.57 (m, 6H), 1.52−1.42 (m, 2H), OH proton exchanged with solvent; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 133.3, 129.8, 129.8, 129.5, 128.4, 128.4, 108.8, 87.8, 81.3, 81.2, 79.2, 73.9, 68.6, 32.9, 31.2, 23.3, 23.2; HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{22}O_6$ $[M + H]^+$ 335.1495, found 335.1496.

*n-Hexyl 3,6-Anhydro-5-O-benzoyl-α-D-glucofuranoside (**21a**) and n-Hexyl 3,6-Anhydro-5-O-benzoyl-β-D-glucofuranoside (**21b**).* Compounds **21a** and **21b** were prepared from **13** and *n*-hexanol with the general procedure as described before at 110 °C in 3 h of duration. Elution with EA-PE (3:5) and EA-PE (1:4) furnished **21a** (26%) and **21b** (61%), respectively, as colorless oils.

Compound **21a**: $[\alpha]_D^{25}$ = +63.5 (*c* 0.65, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.06 (m, 2H), 7.60−7.56 (m, 1H), 7.48−7.43 (m, 2H), 5.27 (dd, *J* = 11.6, 6.0 Hz 1H), 5.11−5.10 (m,1H), 4.93 (app t, *J* = 5.3 Hz, 1H), 4.51 (dd, *J* = 5.2, 2.4 Hz, 1H), 4.18 (dd, *J* = 4.4, 2.8 Hz, 1H), 4.11 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.71 (dt,*J* = 9.6, 6.8 Hz, 1H), 3.40 (dt, *J* = 9.6, 6.8 Hz, 1H), 3.43−3.39 (m, 1H), 1.56−1.52 (m, 2H), 1.29−1.24 (m, 6H), 0.88−0.85 (m, 3H), OH proton exchanged with solvent; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 133.4, 129.9, 129.9, 129.6, 128.5, 128.5, 103.9, 87.9, 78.4, 77.4, 73.3, 69.3, 69.2, 31.6, 29.5, 25.7, 22.6, 14.1. HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{26}O_6$ $[M + H]^+$ 351.1808, found 351.1813.

Compound **21b**: $[\alpha]_D^{25}$ = +47.2 (*c* 0.69, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.06 (m, 2H), 7.60−7.56 (m, 1H), 7.47−7.43 (m, 2H), 5.22−5.15 (m, 2H), 5.03 (s, 1H), 4.57 (d, *J* = 4.8 Hz, 1H), 4.27 (s, 1H), 4.21−4.18 (m, 1H), 4.11 (t, *J* = 8.4 Hz, 1H), 3.73 (dt, *J* = 9.6, 6.8 Hz, 1H), 3.33 (dt, *J* = 9.2, 7.2 Hz, 1H), 1.58−1.55 (m, 2H), 1.25−1.22 (m, 6H), 0.87−0.83 (t, *J* = 6.8 Hz, 3H), OH proton exchanged with the solvent; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 133.4, 129.9, 129.9, 129.6, 128.5, 128.5, 110.2 87.9, 81.5, 81.1, 73.9, 68.8, 68.5, 31.7, 29.8, 25.8, 22.7, 14.1; HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{26}O_6$ $[M + H]^+$ 351.1808, found 351.1806.

General Procedure for the C-2 Deoxygenation of (15a−21a) and (15b−21b) through the Barton−McCombie Reaction. To a solution of the selected substrate in a minimum volume of dry toluene was added Im_2CS (1.3 equiv) and stirred at room temperature for 5 h. A mixture of AIBN (0.5 equiv) and Bu_3SnH (2.2 equiv) in a minimum volume of dry toluene was added dropwise to the reaction mixture at reflux condition under a N_2 atmosphere and stirred at the same temperature for 30 min. It was cooled to room temperature and concentrated under reduced pressure. The crude mass was purified by silica gel (100−200 mesh) column chromatography using EA-PE (1:9) to furnish the desired products.

*Methyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-α-D-glucofuranoside (**22a**).* **15a** was converted to **22a** (66%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +95.9 (*c* 0.29, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.02 (m, 2H), 7.57 (dd, *J* = 4.9, 3.7 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 5.29 (dd, *J* = 11.2, 6.5 Hz, 1H), 5.19 (dd, *J* = 4.8, 2.7 Hz, 1H), 4.86−4.83 (m, 2H), 4.09 (dd, *J* = 9.3, 6.0 Hz, 1H), 3.94 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.28 (s, 3H), 2.26−2.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 133.3, 129.9, 129.9, 129.8, 128.5, 128.5, 107.2, 82.1, 79.7, 73.8, 68.7, 55.3, 40.7; HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{16}O_5$ $[M + Na]^+$ 287.0895, found 287.0889.

*Methyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-β-D-glucofuranoside (**22b**).* **15b** was converted to **22b** (70%) as a white solid with the general procedure as described before. mp 59−61 °C; $[\alpha]_D^{25}$ = +43.1 (*c* 0.35, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.24−5.17 (m, 1H), 5.08 (t, *J* = 3.2 Hz, 1H), 4.96 (t, *J* = 5.2 Hz, 1H), 4.81 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.20−4.12 (m, 2H), 3.32 (s, 3H), 2.22−2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 133.3, 129.9,129.9, 129.7, 128.5, 128.5, 106.5, 82.4, 82.0, 74.2, 68.2, 55.4, 41.5; HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{16}O_5$ $[M + Na]^+$ 287.0895, found 287.0905.

*Ethyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-α-D-glucofuranoside (**23a**).* **16a** was converted to **23a** (67%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +80.0 (*c* 0.32, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.31−5.27 (m, 2H), 4.86−4.81 (m, 2H), 4.07 (dd, *J* = 9.3, 6.0 Hz, 1H), 3.94 (dd, *J* = 9.3, 6.7 Hz, 1H), 3.66 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.36 (dq, *J* = 9.7, 7.1 Hz, 1H), 2.26−2.16 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 133.3, 129.9, 129.9, 129.8, 128.5, 128.5, 105.9, 82.1, 79.6, 73.9, 68.8, 63.6, 40.8, 15.1; HRMS (ESI, *m*/*z*)calcd for $C_{15}H_{18}O_5$ $[M + Na]^+$ 301.1052, found 301.1050.

*Ethyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-β-D-glucofuranoside (**23b**).* **16b** was converted to **23b** (70%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +50.2 (*c* 0.59, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.57 (app t, *J* = 7.4 Hz, 1H), 7.45 (app t, *J* = 7.7 Hz, 2H), 5.20−5.12 (m, 2H), 4.95 (t, *J* = 5.3 Hz, 1H), 4.82 (dd, *J* = 7.3, 4.9 Hz, 1H), 4.24 (app t, *J* = 8.6 Hz, 1H), 4.15 (app t, *J* = 7.9 Hz, 1H), 3.76 (dq, *J* = 9.4, 7.1 Hz, 1H), 3.38 (dq, *J* = 9.4, 7.1 Hz, 1H), 2.22−2.19 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 133.3, 129.8, 129.8, 129.7, 128.4, 128.4, 105.1, 82.4, 81.7, 74.3, 67.9, 63.3, 41.6, 14.9; HRMS (ESI, *m*/*z*)calcd for $C_{15}H_{18}O_5$ $[M + Na]^+$ 301.1052, found 301.1057.

*n-Propyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-α-D-glucofuranoside (**24a**).* **17a** was converted to **24a** (68%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +53.5 (*c* 0.325, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.30−5.25 (m, 2H), 4.84−4.80 (m, 2H), 4.06 (dd, *J* = 9.3, 6 Hz, 1H), 3.93 (dd, *J* = 9.5, 6.8 Hz, 1H), 3.53 (dt, *J* = 9.5, 6.8 Hz, 1H), 3.23 (dt, *J* = 9.5, 6.8 Hz, 1H), 2.21−2.12 (m, 2H), 1.56−1.45 (m, 2H, merged with solvent H_2O), 0.83 (t, *J*

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= 7.4 Hz, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 133.2, 129.8, 129.8, 129.7, 128.4, 128.4, 106.1, 82.1, 79.5, 73.8, 69.8, 68.8, 40.6, 22.8, 10.5; HRMS (ESI, m/z) calcd for $C_{16}H_{20}O_5$ $[M + Na]^+$ 315.1208, found 315.1188.

*n-Propyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-β-D-glucofuranoside (**24b**).* **17b** was converted to **24b** (75%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +53.3 (c 0.345, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.4 Hz, 2H), 7.57 (app t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 5.18−5.13 (m, 2H), 4.94 (t, J = 5.3 Hz, 1H), 4.82 (dd, J = 7.4, 4.6 Hz, 1H), 4.23 (app t, J = 8.4 Hz, 1H), 4.14 (app t, J = 7.8 Hz, 1H), 3.66 (dd, J = 16.2, 6.9 Hz, 1H), 3.24 (dd, J = 16.3, 7.1 Hz, 1H), 2.21−2.17 (m, 2H), 1.62−1.53 (m, 2H, merged with solvent H_2O), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 133.2, 129.8, 129.8, 129.7, 128.4, 128.4, 105.4, 82.3, 81.6, 74.3, 69.8, 67.8, 41.6, 22.6, 10.6; HRMS (ESI, m/z)calcd for $C_{16}H_{20}O_5$ $[M + Na]^+$ 315.1208, found 315.1197.

*iso-Propyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-α-D-glucofuranoside (**25a**).* **18a** was converted to **25a** (60%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +70.7 (c 0.30, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 8.4, 1.2 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 5.38 (t, J = 4.1 Hz, 1H), 5.29 (dd, J = 11.5, 5.9 Hz, 1H), 4.86 (t, J = 5.2 Hz, 1H), 4.80 (dd, J = 9.5, 5.3 Hz, 1H), 4.05 (dd, J = 9.4, 5.9 Hz, 1H), 3.95 (dd, J = 9.4, 6.3 Hz, 1H), 3.80−3.71 (m, 1H), 2.17−2.15 (m, 2H), 1.10 (d, J = 6.2 Hz, 3H), 1.04 (d, J = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 133.2, 129.9, 129.9,129.9, 128.5, 128.5, 104.4, 82.1, 79.5, 73.9, 69.9, 69.0, 40.9, 23.5, 21.7; HRMS (ESI, m/z) calcd for $C_{16}H_{20}O_5$ $[M + Na]^+$ 315.1208, found 315.1212.

*iso-Propyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-β-D-glucofuranoside (**25b**).* **18b** was converted to **25b** (74%) as a white solid with the general procedure as described before. mp 78−80 °C; $[\alpha]_D^{25}$ = +40.6 (c 0.33, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.1, 1.0 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 5.32 (d, J = 5.3 Hz, 1H), 5.23−5.13 (m, 1H), 4.91 (app t, J = 5.1 Hz, 1H), 4.81 (app t, J = 5.3 Hz, 1H), 4.35−4.23 (m, 1H), 4.15 (app t, J = 7.8 Hz, 1H), 3.91−3.89 (m, 1H), 2.24−2.13 (m, 2H), 1.20 (d, J = 6.3 Hz, 3H), 1.10 (d, J = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 133.3, 129.8, 129.8, 129.8, 128.4, 128.4, 103.2, 82.4, 81.6, 74.5, 69.2, 67.6, 41.9, 23.4, 21.1; HRMS (ESI, m/z) calcd for $C_{16}H_{20}O_5$ $[M + Na]^+$ 315.1208, found 315.1210.

*n-Butyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-α-D-glucofuranoside (**26a**).* **19a** was converted to **26a** (66%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +67.2 (c 0.48, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 6.8 Hz, 1H), 7.45 (app t, J = 7.2 Hz, 2H), 5.32−5.26 (m, 2H), 4.83 (dd, J = 9.2, 5.2 Hz, 2H), 4.07 (dd, J = 9.6, 6.4 Hz, 1H), 3.96−3.92 (m, 1H), 3.62−3.56 (m, 1H), 3.32−3.26 (m, 1H), 2.20−2.17 (m, 2H), 1.51−1.44 (m, 2H), 1.34−1.26 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 133.3, 129.9, 129.9, 129.8, 128.5, 128.5, 106.2, 82.2, 79.6, 73.9, 68.8, 68.0, 40.7, 31.7, 19.3, 13.9; HRMS (ESI, m/z) calcd for $C_{17}H_{22}O_5$ $[M + Na]^+$ 329.1365, found 329.1353.

*n-Butyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-β-D-glucofuranoside (**26b**).* **19b** was converted to **26b** (71%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +70.3 (c 0.44, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 2H), 7.57 (app t, J = 7.6 Hz, 2H), 5.20−5.14 (m, 2H), 4.94 (t, J = 5.2 Hz, 1H), 4.83 (t, J = 3.6 Hz, 1H), 4.23 (t, J = 8.8 Hz, 1H), 4.15 (app t, J = 8.8 Hz, 1H), 3.71 (dd, J = 16, 6.8 Hz, 1H), 3.30 (dd, J = 16, 7.2 Hz, 1H), 2.20−2.19 (m, 2H), 1.59−1.51 (m, 2H), 1.32−1.26 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 133.3, 129.8, 129.8, 129.7, 128.4, 128.4, 105.5, 82.4, 81.7, 74.3, 68.0, 67.8, 41.6, 31.6, 19.4, 13.9; HRMS (ESI, m/z) calcd for $C_{17}H_{22}O_5$ $[M + Na]^+$ 329.1365, found 329.1354.

*cyclo-Pentyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-α-D-glucofuranoside (**27a**).* **20a** was converted to **27a** (63%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +59.3 (c 0.29, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 7.2, 1.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 5.33−5.27 (m, 2H), 4.84 (t, J = 5.2 Hz, 1H), 4.79−4.76 (m, 2H), 4.05−4.01 (m, 2H), 3.96−3.93 (m, 1H), 2.15−2.12 (m, 2H), 1.65−1.40 (m, 8H, merged with the solvent peak); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 133.2, 129.8, 129.8,129.8, 128.4, 128.4, 104.9, 82.0, 79.5, 79.4, 73.9, 68.9, 40.8, 33.2, 31.8, 23.5, 23.2; HRMS (ESI, m/z)calcd for $C_{18}H_{22}O_5$ $[M + Na]^+$ 341.1365, found 341.1358.

*cyclo-Pentyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-β-D-glucofuranoside (**27b**).* **20b** was converted to **27b** (74%) as a white solid with the general procedure as described before. mp 112−114 °C;$[\alpha]_D^{25}$ = +51.2 (c 0.38, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.9 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 5.29−5.25 (m, 1H), 5.19−5.13 (m, 1H), 4.92 (t, J = 5.1 Hz, 1H), 4.82 (t, J = 5.6 Hz, 1H), 4.26−4.19 (m, 2H), 4.15 (t, J = 7.7 Hz, 1H), 2.23−2.12 (m, 2H), 1.80−1.44 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 133.2, 129.8, 129.8, 129.7, 128.3, 128.3, 103.9, 82.4, 81.5, 78.8, 74.4, 67.6, 41.9, 32.9, 31.3, 23.3, 23.2; HRMS (ESI, m/z) calcd for $C_{18}H_{22}O_5$ $[M + Na]^+$ 341.1365, found 341.1355.

*n-Hexyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-α-D-glucofuranoside (**28a**).* **21a** was converted to **28a** (64%) as a colorless oil with the general procedure as described before.

$[\alpha]_D^{25}$ = +60.9 (c 0.305, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 5.31−5.25 (m, 2H), 4.85−4.79 (m, 2H), 4.06 (dd, J = 9.3, 6.0 Hz, 1H), 3.93 (dd, J = 9.2, 6.6 Hz, 1H), 3.57 (dt, J = 9.6, 6.8 Hz, 1H), 3.26 (dt, J = 9.6, 6.8 Hz, 1H), 2.19−2.14 (m, 2H), 1.50−1.43 (m, 2H), 1.30−1.23 (m, 6H), 0.85 (t, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 133.2, 129.8, 129.8, 129.8, 128.4, 128.4, 106.1, 82.1, 79.5, 73.8, 68.8, 68.3, 40.6, 31.6, 29.5, 25.7, 22.6, 14.0; HRMS (ESI, m/z) calcd for $C_{19}H_{26}O_5$ $[M + Na]^+$ 357.1678, found 357.1667.

*n-Hexyl 3,6-Anhydro-2-deoxy-5-O-benzoyl-β-D-glucofuranoside (**28b**).* **21a** was converted to **28b** (70%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +65.8 (c 0.29, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 5.18−5.13 (m, 2H), 4.93 (t, J = 5.2 Hz, 1H), 4.81 (dd, J = 7.4, 4.6 Hz,1H), 4.22 (t, J = 8.5 Hz, 1H), 4.14 (t, J = 7.8 Hz, 1H), 3.72−3.66 (m, 1H), 3.28 (dd, J = 16.4, 7.2 Hz, 1H), 2.24−2.16 (m, 2H), 1.58−1.51 (m, 2H), 1.34−1.22 (m, 6H), 0.84 (t, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 133.2, 129.8, 129.8, 129.7, 128.4, 128.4, 105.4, 82.3, 81.6, 74.3, 68.3, 67.7, 41.6, 31.6, 29.4, 25.9, 22.6, 14.0; HRMS (ESI, m/z) calcd for $C_{19}H_{26}O_5$ $[M + Na]^+$ 357.1678, found 357.1637.

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General Procedure for the Debenzoylation Reaction of (22a−28a) and (22b−28b). To a solution of starting material in a minimum volume of dry MeOH was added K_2CO_3 (1.5 equiv), and the reaction mixture was stirred at room temp for 2 h. The solvent was evaporated under reduced pressure. The crude mass was dissolved in ethyl acetate, and it was washed with water (2 × 30 mL), dried (Na_2SO_4), and evaporated. The crude product was purified by column chromatography on neutral alumina (70−230 mesh) using EA-PE (1:3) as an eluent to obtain the desired compound.

*Methyl 3,6-Anhydro-2-deoxy-β-D-glucofuranoside (**8a**) (Sauropunol G).* **22a** was converted to **8a** (93%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +147.0(*c* 0.44, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.15 (dd, *J* = 5.3, 2.3 Hz, 1H), 4.84 (d, *J* = 6.7 Hz, 1H), 4.67−4.64 (m, 1H), 4.29 (t, *J* = 4.8 Hz, 1H), 4.05−4.02 (m, 1H), 3.67 (dd, *J* = 8.1, 6.5 Hz, 1H), 3.28−3.32 (m, 1H, merged with the solvent peak), 3.23 (s, 3H), 2.06 (ddd, *J* = 14.0, 7.2, 2.4 Hz, 1H), 1.97 (ddd, *J* = 14.0, 5.2, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 106.7, 81.5, 81.1, 71.9, 69.7, 54.9, 41.3; HRMS (ESI, *m*/*z*) calcd for $C_7H_{12}O_4Na$ [M + Na]$^+$ 183.0634, found 183.0624.

*Methyl 3,6-Anhydro-2-deoxy-α-D-glucofuranoside (**8**) (Sauropunol H).* **22b** was converted to **8** (91%) as a white semisolid (at ∼30 °C) with the general procedure as described before; $[\alpha]_D^{25}$ = −56.6 (*c* 0.38, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.02 (d, *J* = 6.0 Hz, 1H), 4.62 (d, *J* = 6.3 Hz, 1H), 4.60−4.54 (m, 1H), 4.39 (app t, *J* = 4.9 Hz, 1H), 4.05−3.98 (m, 1H), 3.63 (t, *J* = 7.2 Hz, 1H), 3.54 (dd, *J* = 9.3, 7.5 Hz, 1H), 3.23 (s, 3H), 2.09 (dt, *J* = 14.4, 6.0 Hz, 1H), 1.88 (dd, *J* = 14.4, 0.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 106.2, 84.1, 81.5, 72.0, 69.8, 55.0, 41.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18−5.09 (m, 1H), 4.69 (t, *J* = 5.7 Hz, 1H), 4.62−4.54 (m, 1H), 4.19 (t, *J* = 6.6 Hz, 1H), 3.85 (dd, *J* = 9.3, 5.1 Hz, 1H), 3.75 (dd, *J* = 9.3, 5.4 Hz, 1H), 2.90 (d, *J* = 7.4 Hz, 1H), 2.25−2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.8, 84.8, 81.9, 73.7, 71.5, 56.4, 40.4; HRMS (ESI, *m*/*z*) calcd for $C_7H_{12}O_4$ [M + Na]$^+$ 183.0634, found 183.0637.

*Ethyl 3,6-Anhydro-2-deoxy-α-D-glucofuranoside (**29a**) (Sauropunol E).* **23a** was converted to **29a** (94%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +127.6 (*c* 0.27, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.26 (dd, *J* = 5.2, 2.5 Hz, 1H), 4.81 (d, *J* = 6.8 Hz, 1H), 4.67−4.63 (m, 1H), 4.31 (t, *J* = 4.8 Hz, 1H), 4.06−3.99 (m, 1H), 3.69−3.58 (m, 2H), 3.44−3.35 (m, 2H, merged with the solvent peak), 2.08−1.94 (m, 2H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 105.4, 81.6, 81.1, 71.9, 69.8, 62.8, 41.5, 15.6; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.34 (dd, *J* = 5.4, 2.3 Hz, 1H), 4.77−4.74 (m, 1H), 4.56 (t, *J* = 5.3 Hz, 1H), 4.22 (t, *J* = 5.8 Hz, 1H), 3.85 (dd, *J* = 9.3, 5.7 Hz, 1H), 3.75 (dq, *J* = 9.9, 7.1 Hz, 1H), 3.57 (dd, *J* = 9.4, 6.4 Hz, 1H), 3.47 (dq, *J* = 9.8, 7.1 Hz, 1H), 2.59 (d, *J* = 1.2 Hz, 1H), 2.26−2.22 (m, 1H), 2.16−2.12 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 105.7, 81.5, 80.1, 71.6, 71.3, 63.1, 40.4, 14.67; HRMS (ESI, *m*/*z*)calcd for $C_8H_{14}O_4$ [M + Na]$^+$ 197.0790, found 197.0791.

*Ethyl 3,6-Anhydro-2-deoxy-β-D-glucofuranoside (**7**) (Sauropunol F).* **23b** was converted to **7** (93%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = −41.0 (*c* 0.49, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.13 (d, *J* = 5.6 Hz, 1H), 4.58−4.54 (m, 2H), 4.39 (t, *J* = 4.8 Hz, 1H), 4.05−3.98 (m, 1H), 3.83−3.76 (m, 1H), 3.65−3.58 (m, 2H), 3.39−3.34 (m, 1H, merged with the solvent peak), 2.12−2.06 (m, 1H), 1.90−1.86 (m, 1H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 104.9, 84.1, 81.6, 72.0, 69.9, 62.8, 41.4, 15.4; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.25 (t, *J* = 3.4 Hz, 1H), 4.69 (t, *J* = 5.8 Hz, 1H), 4.58 (dt, *J* = 5.5, 3.7 Hz, 1H), 4.19−4.17 (m, 1H), 3.88 (dd, *J* = 9.0, 4.8 Hz, 1H), 3.83 (dq, *J* = 9.6, 7.2 Hz, 1H),3.75 (dd, *J* = 9.4, 5.2 Hz, 1H), 3.57 (dq, *J* = 9.6, 7.2 Hz, 1H), 3.06 (brs, 1H), 2.19−2.18 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 105.8, 84.2, 81.4, 73.2, 70.9, 64.3, 39.9, 14.6; HRMS (ESI, *m*/*z*)calcd for $C_8H_{14}O_4$ [M + Na]$^+$ 197.0790, found 197.0791.

*n-Propyl 3,6-Anhydro-2-deoxy-α-D-glucofuranoside (**30a**).* **24a** was converted to **30a** (93%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +122.6 (*c* 0.49, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.25 (dd, *J* = 5.3, 2.4 Hz, 1H), 4.81 (d, *J* = 6.7 Hz, 1H), 4.67−4.65 (m, 1H), 4.30 (t, *J* = 4.8 Hz, 1H), 4.06−3.99 (m, 1H), 3.67 (dd, *J* = 8.1, 6.5 Hz, 1H),3.52 (dt, *J* = 9.6, 6.7 Hz, 1H), 3.36−3.28 (m, 2H), 2.09−2.03 (m, 1H), 1.99−1.94 (m, 1H), 1.54−1.45 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d^6) δ 105.6, 81.6, 81.1, 71.9, 69.7, 69.1, 41.4, 22.9, 11.1; HRMS (ESI, *m*/*z*) calcd for $C_9H_{16}O_4$ [M + Na]$^+$ 211.0946, found 211.0945.

*n-Propyl 3,6-Anhydro-2-deoxy-β-D-glucofuranoside (**30b**).* **24b** was converted to **30b** (94%) as a colorless semisolid (at ∼30 °C) with the general procedure as described before. $[\alpha]_D^{25}$ = −40.8 (*c* 0.49, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.13 (d, *J* = 5.8 Hz, 1H), 4.57−4.54 (m, 2H), 4.39 (t, *J* = 4.9 Hz, 1H), 4.05−3.98 (m, 1H), 3.71 (dt, *J* = 9.3, 6.7 Hz, 1H), 3.65−3.58 (m, 2H), 3.25 (dt, *J* = 9.3, 6.7 Hz, 1H), 2.10 (dt, *J* = 14.4, 6.1 Hz, 1H),1.89 (dd, *J* = 14.4, 0.5 Hz, 1H), 1.55−1.46 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d^6) δ 105.3, 84.1, 81.6, 72.0, 69.9, 69.3, 41.4, 22.8, 11.2; HRMS (ESI, *m*/*z*) calcd for $C_9H_{16}O_4$ [M + Na]$^+$ 211.0946, found 211.0954.

*iso-Propyl 3,6-Anhydro-2-deoxy-α-D-glucofuranoside (**31a**).* **25a** was converted to **31a** (89%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +128.5 (*c* 0.54, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.37 (dd, *J* = 5.1, 2.7 Hz, 1H), 4.78 (d, *J* = 6.7 Hz, 1H),4.66−4.62 (m, 1H), 4.31 (t, *J* = 4.8 Hz, 1H), 4.06−3.99 (m, 1H), 3.81 (hept, *J* = 6.0 Hz, 1H), 3.66 (dd, *J* = 8.1, 6.4 Hz, 1H), 2.04−1.92 (m, 2H), 1.11 (d, *J* = 6.2 Hz, 3H), 1.06 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d^6) δ 103.7, 81.6, 80.8, 71.9, 69.8, 68.9, 41.7, 24.0, 22.2; HRMS (ESI, *m*/*z*) calcd for $C_9H_{16}O_4$ [M + Na]$^+$211.0946, found 211.0938.

*iso-Propyl 3,6-Anhydro-2-deoxy-β-D-glucofuranoside (**31b**).* **25b** was converted to **31b** (95%) as a colorless semisolid (at ∼30 °C) with the general procedure as described before. $[\alpha]_D^{25}$ = −55.0 (*c* 0.60, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.28 (d, *J* = 5.9 Hz, 1H), 4.58−4.50 (m, 2H), 4.38 (t, *J* = 5.0 Hz, 1H), 4.02−3.98 (m, 1H), 3.93 (hept, *J* = 6.2 Hz, 1H), 3.69−3.59 (m, 2H), 2.11 (dt, *J* = 14.3, 6.2 Hz, 1H), 1.83 (dd, *J* = 14.4, 0.5 Hz, 1H), 1.14 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 103.1, 84.0, 81.7, 72.1, 70.1, 68.7, 41.6, 23.7, 21.7; HRMS (ESI, *m*/*z*) calcd for $C_9H_{16}O_4$ [M + Na]$^+$211.0946, found 211.0945.

*n-Butyl 3,6-Anhydro-2-deoxy-α-D-glucofuranoside (**1**).* **26a** was converted to **1** (92%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +111.7 (*c* 0.54, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.24 (dd, *J* = 5.3, 2.4 Hz, 1H), 4.81 (d, *J* = 6.7 Hz, 1H), 4.67−4.63 (m, 1H), 4.29 (t, *J* = 4.8 Hz, 1H), 4.06−3.99 (m, 1H), 3.67 (dd, *J* = 8.1,

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ACS Omega 2023, 8, 39739−39748

6.5 Hz, 1H), 3.57 (dt, J = 9.7, 6.6 Hz, 1H), 3.37−3.31 (m, 2H merged with the solvent peak), 2.08−2.02 (m, 1H), 1.99−1.94 (m, 1H), 1.49−1.43 (m, 2H),1.42−1.27 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 105.6, 81.6, 81.1, 71.9, 69.7, 67.1, 41.4, 31.7, 19.4, 14.2; HRMS (ESI, m/z) calcd for $C_{10}H_{18}O_4$ [M + Na]$^+$ 225.1103, found 225.1105.

*n-Butyl 3,6-Anhydro-2-deoxy-ß-D-glucofuranoside (**2**).* **26b** was converted to **2** (94%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = −38.7 (c 0.53, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.12 (d, J = 6.0 Hz, 1H), 4.57−4.54 (m, 2H), 4.39 (t, J = 4.9 Hz, 1H), 4.03−3.98 (m, 1H), 3.75 (dt, J = 9.4, 6.6 Hz, 1H), 3.64−3.57 (m, 2H), 3.28 (dt, J = 9.4, 6.6 Hz, 1H), 2.09 (dt, J = 14.4, 6.1 Hz, 1H), 1.89 (dd, J = 14.4, 0.5 Hz, 1H), 1.51−1.44 (m, 2H), 1.36−1.28 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 105.3, 84.1, 81.6, 72.0, 69.9, 67.1, 41.4, 31.7, 19.5, 14.29; HRMS (ESI, m/z) calcd for $C_{10}H_{18}O_4$ [M + Na]$^+$ 225.1103, found 225.1105.

*cyclo-Pentyl 3,6-Anhydro-2-deoxy-ß-D-glucofuranoside (**32a**).* **27a** was converted to **32a** (88%) as a white semisolid (at ∼30 °C) with the general procedure as described before. $[\alpha]_D^{25}$ = +117.0 (c 0.50, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.32 (dd, J = 5.0, 2.8 Hz, 1H), 4.80 (d, J = 6.4 Hz, 1H), 4.63 (ddd, J = 6.7, 4.6, 3.5 Hz, 1H), 4.29 (t, J = 4.8 Hz, 1H), 4.14−4.09 (m, 1H), 4.06−3.99 (m, 1H), 3.66 (dd, J = 8.1, 6.5 Hz, 1H), 3.35−3.30 (m, 1H, merged with the solvent), 2.07−1.91 (m, 2H), 1.72−1.41 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 104.4, 81.6, 80.9, 78.6, 71.9, 69.8, 41.7, 33.5, 32.0, 23.6, 23.4; ESI-HRMS (ESI, m/z) calcd for $C_{11}H_{18}O_4$ [M + Na]$^+$ 237.1103, found 237.1102.

*cyclo-Pentyl 3,6-Anhydro-2-deoxy-ß-D-glucofuranoside (**32b**).* **27b** was converted to **32b** (95%) as a white semisolid with the general procedure as described before; $[\alpha]_D^{25}$ = −59.2 (c 0.49, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.22 (d, J = 5.8 Hz, 1H), 4.55−4.52 (m, 2H), 4.38 (t, J = 4.9 Hz, 1H), 4.26−4.23 (m, 1H), 4.05−3.98 (m, 1H), 3.65−3.59 (m, 2H), 2.10 (dt, J = 14.3, 6.1 Hz, 1H), 1.84 (dd, J = 14.4, 0.6 Hz, 1H), 1.72−1.41 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 103.9, 84.1, 81.7, 78.6, 72.1, 70.1, 41.6, 32.9, 31.5, 23.4, 23.4; HRMS (ESI, m/z) calcd for $C_{11}H_{18}O_4$ [M + Na]$^+$ 237.1103, found 237.1111.

*n-Hexyl 3,6-Anhydro-2-deoxy-α-D-glucofuranoside (**33a**).* **28a** was converted to **33a** (89%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = +105.8 (c 0.48, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.24 (dd, J = 5.2, 2.4 Hz, 1H), 4.80 (d, J = 6.7 Hz, 1H), 4.67−4.63 (m, 1H), 4.29 (t, J = 4.8 Hz, 1H), 4.06−3.99 (m, 1H), 3.66 (dd, J = 8.1, 6.5 Hz, 1H), 3.56 (dt, J = 9.6, 6.7 Hz, 1H), 3.36−3.00 (m, 2H), 2.05 (ddd, J = 14.1, 7.1, 2.4 Hz, 1H), 1.96 (ddd, J = 14.1, 5.3, 3.1 Hz, 1H), 1.48−1.1.44 (m, 2H), 1.31−1.22 (m, 6H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 105.6, 81.6, 81.1, 71.9, 69.7, 67.4, 41.4, 31.6, 29.6, 25.9, 22.6, 14.4; HRMS (ESI, m/z) calcd for $C_{12}H_{22}O_4$ [M + Na]$^+$ 253.1416, found 253.1415.

*n-Hexyl 3,6-Anhydro-2-deoxy-ß-D-glucofuranoside (**33b**).* **28b** was converted to **33b** (96%) as a colorless oil with the general procedure as described before. $[\alpha]_D^{25}$ = −34.5 (c 0.54, MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.12 (d, J = 5.8 Hz, 1H), 4.57−4.54 (m, 2H), 4.38 (t, J = 4.9 Hz, 1H), 4.04−3.98 (m, 1H), 3.75 (dt, J = 9.4, 6.7 Hz, 1H), 3.64−3.57 (m, 2H), 3.27 (dt, J = 9.4, 6.7 Hz, 1H), 2.09 (dt, J = 14.4, 6.1 Hz, 1H),1.88 (dd, J = 14.4, 0.4 Hz, 2H), 1.51−1.45 (m, 2H), 1.32−1.24 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 105.3, 84.1, 81.2, 72.0, 69.9, 67.7, 41.4, 31.6, 29.5, 25.9, 22.6, 14.4; HRMS (ESI, m/z) calcd for $C_{12}H_{22}O_4$ [M + Na]$^+$ 253.1416, found 253.1415.

*3,6-Anhydro-2-deoxy-D-glucofuranoside (Sauropunol C/D) (**3/4**).* Compound **8** (50 mg, 0.27 mmol) was dissolved in 1:1 TFA: H_2O (3 mL) and stirred at room temperature for 3 h. The solvent was evaporated under vacuum. The oily residue was dissolved in EtOAc (30 mL) and washed with saturated $NaHCO_3$ (3 × 10 mL) and brine (2 × 10 mL). The organic layer was dried (Na_2SO_4), evaporated, and purified by silica gel (100−200 mesh) column chromatography using EtOAc as an eluent to obtain an anomeric mixture of sauropunol C/D (**3/4**) (28 mg, 70%, ratio 72:28) as a colorless liquid.
Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (t, J = 4.2 Hz, 1H), 4.79−4.74 (m, 1H), 4.72−4.68 (m, 1H, merged with another proton signal of major isomer), 4.26−4.20 (m, 1H), 3.85 (dd, J = 9.4, 5.8 Hz, 1H),3.56 (dd, J = 9.4, 6.2 Hz, 1H), 2.23−2.17 (m, 2H), signal for two H not discernible; ^{13}C NMR (75 MHz, $CDCl_3$) δ 100.9, 81.9, 81.1, 72.2, 71.8, 41.7.
Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57 (d, J = 5.1 Hz, 1H), 4.72−4.68 (m, 1H, merged with another proton signal of minor isomer), 4.48 (t, J = 5.1 Hz, 1H), 4.32−3.27 (m, 1H), 4.02 (dd, J = 10.4, 2.1 Hz, 1H), 3.65 (dd, J = 10.3, 4.3 Hz, 1H), 2.29 (d, J = 14.5 Hz, 1H), 2.14 (merged dt, J = 14.6, 5.2 Hz, 1H), signal for two H not discernible; ^{13}C NMR (75 MHz, $CDCl_3$) δ 100.8, 84.4, 83.3, 76.2, 71.0, 40.2; HRMS (ESI, m/z) calcd for $C_6H_{10}O_4$ [M + Na]$^+$ 169.0477, found 169.0478.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c05742.

Additional experimental details of single-crystal X-ray structure of **13**, **15a**, **15b**, **16a**, **27b**, **8**, **30b**, **31b**, and **32a** spectroscopy and analytical data for all compounds (PDF)

Accession Codes

CCDC 2233181−2233189 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes

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