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Facile conversion of glycosyloxymethyl-furfural into γ-keto-carboxylic acid building blocks towards a sustainable chemical industry†

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Carbohydrates, as cheap mass-products, promise to be outstanding candidates as sustainable raw materials (F. W. Lichtenthaler and S. Peters, *C. R. Chim.*, 2004, **7**, 65–90). To achieve the goal of carbohydrate utilisation as industry raw materials, environmental low impact conversions from sugars to high value reactive intermediates are needed. Here we present the facile access to γ-keto-carboxylic acid building blocks from the sucrose-based glycosyloxymethyl-furfural (GMF). Employing an oxidative ring opening strategy under careful selection of reaction conditions, allows for high yield conversions of the furan aglycon into γ-keto-carboxylic acid moieties without alteration of the sugar moiety attached. The resulting glycosylated building blocks were converted into selected heterocyclic products of the pyridazinone and benzodiazepinone type to exemplify the synthetic potential of these building blocks. All synthetic manipulations employed low environmental impact solvents, reagents, oxidants and protecting group free conversions.

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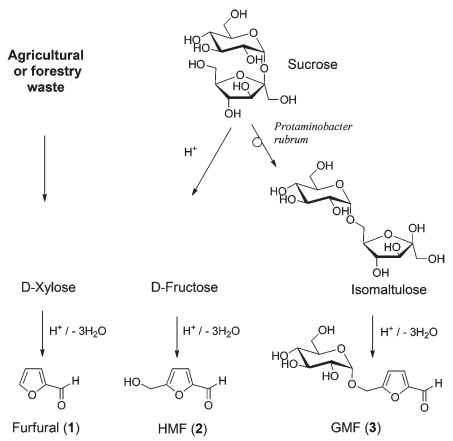
Introduction

Mankind is facing the end of cheap oil, with the peak of production already passed.[2] The chemical industry is heavily reliant on oil or coal based hydrocarbons, which form the foundation of our modern lifestyle. This discrepancy creates the inevitable necessity for a progressive changeover towards renewable and, hence, sustainable feedstock to fulfil the industry's raw material needs.[3] Carbohydrates are by far the most abundant organic compounds and represent the major portion of the renewable biomass. Carbohydrate utilization for the production of low cost and eco-friendly chemicals of versatile industrial applicability is of central importance for relieving the industry's reliance on petrochemical raw materials.[1,3–7]

The conversion of carbohydrates into chemical raw materials requires dehydration to utilize the sugar-inherent carbon backbone. These kinds of initial down-functionalizing conversions include fermentation to ethanol or lactic acid, oxidation to carboxylic acids, introduction of keto-moieties or poly-dehydration to furan compounds (Scheme 1).[8]

Furans represent prototypes of industrially useful building blocks and the conversion to furfural (**1**) has already been performed on an industrial scale from biomass-derived D-xylose, building the foundation of industrial furan chemistry.[9] Due to economic reasons, the hexose-derived 5-hydroxymethylfurfural (HMF, **2**) is not yet commercially viable. But progress has been made to realize its industrial use, as HMF (**2**) has been recognized as a potential building block for a range of industrial applications.[10–13] An analogous dehydration of the fructose part of disaccharides is possible.[14] In particular, isomaltulose, produced enzymatically from sucrose in industrial scales,[1,5] is readily converted into a glycosyl-substituted hydroxymethylfurfural derivative. In this process, an acid



Scheme 1 Synthesis of furfurals (**1**, **2**, **3**) from bulk carbohydrates.

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† Part 46 of the series Sugar-Derived Building Blocks. (Part 45)[25]

catalyzed dehydration of the fructose moiety of isomaltulose is performed under conditions retaining the intersaccharidic linkage.[1,5,14] This conversion has been validated on an industrial pilot scale in a continuous flow reactor with an acidic ion exchange resin in DMSO at 120 °C.[1,5] Thus, 5-α-D-glucosyloxymethyl-furfural (α-GMF, **3**)[14,15] is of particular interest as it is potentially accessible on the industrial scale and as it combines a carbohydrate moiety with a furfural aglycon promising for the production of chemical raw materials with novel characteristics.

In contrast to this already well-established access to furfurals, further processing towards reactive intermediates is still under-investigated, in particular, with regard to sustainable low environmental impact pathways.

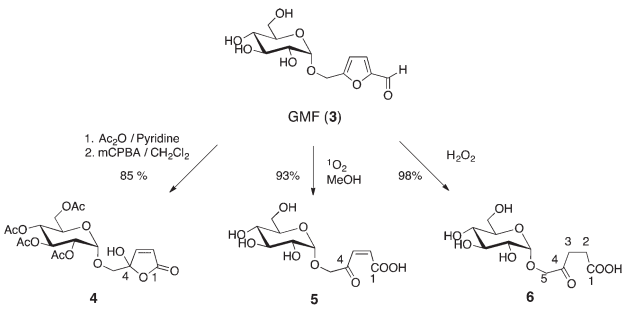
We have reported in the past on the conversions of carbohydrates and carbohydrate derived furfurals into nitrogen heterocycles.[16–18] This work focuses on the conversion of GMF (**3**) into glycosylated analogues of γ-keto-carboxylic acids, which are not only suitable building blocks for the synthesis of heterocycles but also have potential to be used for the synthesis of *e.g.* γ-amino acids, or biopolymer building blocks.[19–21]

Results

In a previous work we could show how oxidative ring opening of furans can lead to synthetically interesting 1,4-diketo building blocks as intermediates towards heterocycles of the pyrrole, thiophene, pyridazine and benzodiazepine type.[18] In this report we focus on the direct conversion of GMF (**3**) without the use of protecting groups and how the selection of oxidation conditions and the reaction environment can be used to obtain a variety of useful γ-keto-carboxylic acid building blocks in high yields and industrial conversion feasibility. Per-acetylated-GMF[15,18] can be oxidized in organic aprotic media (dichloromethane) employing *m*-CPBA resulting in oxidative ring opening under decarboxylation and intramolecular ring closure to the hydroxyl-furanone product **4**[18] (Scheme 2). While this reaction is straightforward and high yielding (overall yield 85%) we were interested in making improvements towards more environmentally friendly alternatives, employing benign solvents, reagents and oxidants.

A range of oxidation agents/solvent pairs was investigated to perform the furfural oxidations. Unprotected GMF (**3**) was treated with photochemically created singlet oxygen in methanol. Methylene blue was used as a photocatalytic reagent and irradiation was performed with a conventional 50 W halogen light source at −40 °C.[18] Complete conversion was monitored after 5 h to deliver the unsaturated open chain γ-keto-carboxylic acid **5** in 93% yield.

The product obtained was chromatographically homogeneous and further purification was not necessary. When performing the oxidation of GMF (**3**) in an aqueous solution of 30% hydrogen peroxide a 5-glycosyloxy-analogue of levulinic acid (**6**) was formed in 98% yield. Also this reaction was



Entry	^{13}C-NMR chemical shift [ppm]					
	C-1	C-2	C-3	C-4	C-5	$^3J_{H2\text{-}H3}$
4	171.0	152.2	125.1	105.7	71.0	5.7 Hz
5	172.7	155.2	124.8	211.5	70.6	5.7Hz
6	175.5	32.1	32.5	180.0	87.6	-

Scheme 2 Conversion of GMF (**3**) into ketocarboxylic acids of type **4**, **5** and **6**. Oxidation conditions and reaction media determine the chemical entity formed. The table shows the NMR assignment of selected signals indicative of the structure.

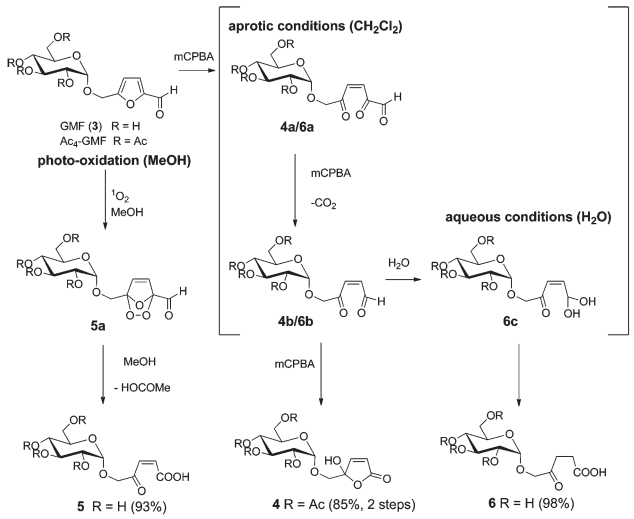
quantitative and resulted in a homogeneous product so that a further purification step was not necessary. These protecting group free, high yielding entry reactions represent straightforward conversions to novel building blocks with a high potential as raw materials for industrial applications.

All structures of products **4**, **5** and **6** were investigated by ^{1}H and ^{13}C NMR. The table in Scheme 2 summarizes a selection of NMR signals obtained for the aglycon portion of the synthesized γ-keto-carboxylic acids. The obtained chemical shifts and coupling constants confirm clearly the proposed structures of building blocks **4**, **5** and **6**.

Particularly indicative is the comparison of the ^{13}C chemical shift of carbon-4 in compound **4** relating to a hydroxy-furanone-actal chemical environment (105.7 ppm) while compounds **5** and **6** show a strong deep field shift (211.5 ppm with respect to 180 ppm) indicative of a open chain ketone-chemical environment. Both compounds **5** and **6** show a proton coupling constant between H-2 and H-3 of 5.7 Hz, which relates to a *Z*-configuration fixated structure. The levulinic acid analogue **6** is clearly determined by the *C*-2 and *C*-3 methylene signals (32.1, 32.5 ppm) and the *C*-4 chemical shift indicative of a keto-function (180 ppm). Thus, a ring–chain tautomerisation is not observed for **6**.

The formation of different γ-keto-carboxylic acids can be sufficiently explained by the proposed mechanism (Scheme 3) of oxidative ring opening and the solvent properties employed.

Oxidative conversion of per-acetylated-GMF (Ac_4-GMF)[15] is performed under aprotic conditions with *m*-CPBA.[18] The oxidative ring opening[22] results in a keto-aldehyde **4a** intermediate which is further oxidized to an unstable keto-carboxylic acid, which immediately decarboxylates to a α,β unsaturated aldehyde **4b**. Further oxidation yields the final unsaturated keto-carboxylic acid **4** with the cyclic 5-hydroxy-2(5*H*)-furanone form as the most stable end product under the applied aprotic conditions.

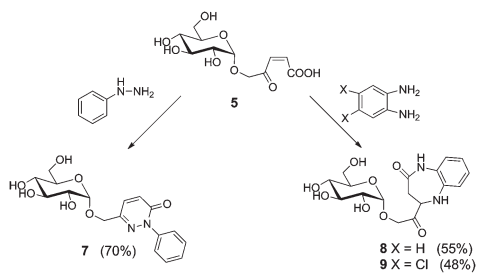


Scheme 3 Selection of reaction conditions (oxidant and media) determines the product formation due to different mechanistic pathways.

When performing the same reaction in water with hydrogen peroxide, instead of oxidation of the α,β unsaturated aldehyde intermediate, an aldehyde hydrate is formed (**6c**), preventing further oxidation. Further tautomerization finally yields the levulinic acid analogue **6**. During the singlet oxidation[23,24] of GMF (**3**) in methanol a bicyclic *endo*-peroxide **5a** is formed. Induced by the formation of a methanol hemiacetal followed by elimination of formic acid–methylester, the final α,β-unsaturated keto-carboxylic acid **5** is formed.

In initial experiments we have used the α,β-unsaturated-4-keto-carboxylic acid building block **5** as a synthetic precursor for the synthesis of some selected heterocycles to exemplify their potential use (Scheme 4).

Treatment of **5** dissolved in water (pH 4 adjusted with acetic acid) with phenyl hydrazine affords the phenyl hydrazone, which readily cyclized under slightly acidic conditions to the phenyl-pyridazinone **7**. While in a previous work[18] we have used the building block **4** as a reactive intermediate for the synthesis of benzodiazepinones, we now use the α,β-unsaturated keto-carbonic acid **5** in a protecting group free approach. Thus, reaction with 1,2-diaminobenzene or 1,2-diamino-4,5-dichloro-benzene in methanol (0 °C) delivered in good yield (55% and 48%) the benzodiazepinones **8** and **9**.[18]



Scheme 4 Conversion of the γ-keto-carboxylic acid building block into select heterocycles of the pyridazinone (**7**) and benzodiazepinone (**8**, **9**) type.

Conclusion

Access to reactive synthesis intermediates is necessary to incorporate renewable carbohydrates into chemical production processes for the chemical industry. The formation of furfurals from pentoses, hexoses and disaccharides is an ideal entry reaction as it down functionalizes the carbohydrate moiety, making them amenable for further chemical modifications. While the formation of furfurals **1**, **2** and **3** is well investigated, their further transformation into industrially viable products, from **2** and particularly **3** is considerably less developed mainly due to the simultaneous presence of an aromatic furan skeleton and multiple hydroxyl groups. Thus with the oxidative ring opening strategy presented here we are able to arm the furan system, generating highly reactive γ-keto-carboxylic acid synthesis intermediates (**4**, **5**, **6**), with outstanding potential as building blocks for the chemical industry. The developed reaction pathways from renewable sugars have potential for direct industrial applicability, employing low cost, low environmental impact reagents, solvents and oxidants. The generated building blocks have been validated for their synthetic potential by producing pyridazinone (**7**) as well as benzodiazepinone heterocycles (**8** and **9**) in only 2 steps from GMF (**3**). We are herewith clearing the path towards the generation of fully green and sustainable products from carbohydrate sources.

Experimental

Analytical instrumentation used: melting points (uncorrected values) recorded on a Bock monoskop instrument. Spectral measurements were performed on: Perkin Elmer 241 (rotations), Varian MAT 311 A (MS), Bruker WM 300 instruments (^{1}H at 300, ^{13}C NMR at 75.5 MHz, respectively). A Perkin-Elmer 240 elemental analyzer was used for compound microanalysis and purity confirmation. TLC on Kieselgel 60 F254 plastic sheets (Merck) was used to monitor the reactions and to ascertain the purity of the products (a single point on a TLC plate); eluents employed and R_f values observed are given in the appropriate experiment; detection of TLC plates was performed with UV-light or by charring with sulfuric acid. Column chromatography: Kieselgel 60 (63-200 mesh, Macherey-Nagel).

5-(α-D-Glucopyranosyloxy)-4-oxo-pent-2-enoic acid (5)

A stirred and cooled (−40 °C) solution of GMF (**3**, 4.0 g, 13.9 mmol) in tri-MeOH (50 mL) was irradiated in the presence of a few crystals of methylene-blue with a halogen lamp (Tungsram, 500 W). Oxygen gas was transferred into the solution under vigorous magnetic stirring and TLC indicates complete transformation into product **5** after 5 hours (**5**: R_f 0.45, 1 : 1 $CHCl_3$–MeOH). Deoxygenating with nitrogen gas (30 min) was followed by the addition of Me_2S (0.86 g, 14 mmol), a temperature increase to ambient, and decolourization with activated charcoal. Evaporation of the resulting clear filtrate yields 3.77 g (93%) chromatographic homogeneous (TLC) **5** in

the form of a colourless hard foam. (Found: C, 45.20; H, 5.50; O, 49.30% $C_{11}H_{16}O_9$ requires C, 45.21; H, 5.52; O, 49.27%); δ ^{1}H NMR (300 MHz, CD_3OD): 3.25–3.42 (m, 4 H, 2′-H, 3′-H, 4′-H, 5′-H), 3.55–3.70 (m, 2 H, 5-H_a, 6′-H_a), 3.75–3.85 (m, 2 H, 5-H_b, 6′-H_b), 4.76 (d, 1 H, 1′-H), 6.20 (d, 1 H, 2-H), 7.48 (d, 1 H, 3-H). $J_{2,3}$ = 5.7 Hz; δ ^{13}C NMR (75 MHz, CD_3OD): 62.6 (C-6′), 70.6 (C-5), 71.6 (C-4′), 73.5 (C-5′), 74.1 (C-3′), 74.8 (C-2′), 100.5 (C-1′), 124.8 (C-2), 155.2 (C-3), 172.7 (*C*OOH), 211.5 (C-4). MS (FD): m/z = 292 (M^+).

5-(α-D-Glucopyranosyloxy)-4-oxo-pentanoic acid (6)

A solution of GMF (**3**, 1.0 g, 3.5 mmol) in 40 mL of 30% hydrogen peroxide solution was stirred at room temperature for 18 hours. Removal of the solvent was performed under reduced pressure at 50 °C. Residual water was removed by azeotropic co-evaporation with toluene. The crude syrup was finally dried under high vacuum to deliver the product **6** in the form of a colourless hard foam (1 g, 98%). The obtained product did not require further purification due to its chromatographic homogeneity. The product was highly hygroscopic and required storage in a desiccator over P_2O_5. – R_f 0.22 ($CHCl_3$–MeOH 1 : 1). – $[\alpha]_D^{20}$ + 94.5 (*c* 0.85, MeOH). (Found: C, 44.80; H, 6.20; O, 49.00% $C_{11}H_{18}O_9$ requires C, 44.90; H, 6.17; O, 48.93%); δ ^{1}H NMR (300 MHz, CD_3OD): 2.52–2.54 (m, 2 H, 3-H_2), 2.61–2.64 (m, 2 H, 2-H_2), 3.34 (dd, 1 H, 4′-H), 3.47 (dd, 1 H, 2′-H), 3.62 (m, 1 H, 5′-H), 3.63 (dd, 1 H, 3′-H), 3.78 (dd, 1 H, 6′-H_a), 3.81 (dd, 1 H, 6′-H_b), 5.11 (d, 1 H, 1′-H), 5.37, 5.39 (2 d je 1 H, 5-CH_2). $J_{gem,\ 5\text{-}H2}$ = 6.4, $J_{1',2'}$ = 3.6, $J_{2',3'}$ = 9,8, $J_{3',4'}$ = 9.2, $J_{4',5'}$ = 9.2, $J_{5',6'a}$ = 2.3, $J_{gem,\ 6'\text{-}H2}$ = 12.0 Hz. δ ^{13}C NMR (75.5 MHz, CD_3OD): 32.1, 32.5 (C-2, C-3), 63.6 (C-6′), 72.6 (C-4′), 72.9 (C-2′), 74.8 (C-3′, C-5′), 87.9 (C-5), 100.8 (C-1′), 175.5 (COOH), 179.9 (C-4). MS (FD): m/z = 294 (M^+).

3-(α-D-Glucopyranosyloxymethyl)-1-phenyl-6(1*H*)-pyridazinone (7)

A solution of keto-pentenoic acid **5** (0.42 g, 1.44 mmol) in 10 mL of water/acetic acid (pH 4) was treated with phenylhydrazine (0.15 mL, 1.44 mmol) at room temperature. TLC indicated complete transformation into the product. Removal of water under reduced pressure resulted in an orange syrup which was purified on silica gel (3 × 20 cm) with $CHCl_3$–MeOH 5 : 1 as the eluent. Combined fractions with R_f 0.22 yielded after the evaporation of the solvent 0.35 g (70%) an orange hard foam of the pyridazinone **7**. (Found: C, 56.10; H, 5.50; N, 7.70; O, 30.7% $C_{17}H_{20}N_2O_7$ requires C, 56.04; H, 5.53; N, 7.69, O, 30.74%); δ ^{1}H NMR (300 MHz, DMSO): 3.05–3.15 (m, 1 H, 5′-H), 3.20–3.30 (m, 1 H, 2′-H), 3.40–3.50 (m, 3 H, 3′-H, 4′-H, 6′-H_{2a}), 3.65–3.68 (m, 1 H, 6′-H_{2b}), 4.45 (d, 1 H, 3–CH_{2a}), 4.48 (t, 1 H, 6′-OH), 4.56 (d, 1 H, 3-CH_{2b}), 4.77–4.81 (m, 3 H, 3 OH), 7.11 (d, 1 H, 4-H), 7.39–7.56 (m, 5 H, C_6H_5), 7.64 (d, 1 H, 5-H). $J_{4,5}$ = 9.5, $J_{gem,\ 3\text{-}CH_2}$ = 12.5, $J_{1',2'}$ = 5.7 Hz. δ ^{13}C NMR (75.5 MHz, DMSO): 61.2 (C-6′), 67.5 (3-*C*H_2), 70.6 (C-5′), 72.2 (C-2′), 73.6 (C-4′, C-3′), 99.1 (C-1′), 126.5, 128.3, 129.0, 141.7 (C_6H_5), 131.2, 133.0 (C-4, C-5), 145.6 (C-3), 159.3 (C-6). MS (FD): m/z = 364 (M^+), 202 ($M^+ - C_6H_{11}O_5$).

4*R*- and 4*S*-[(α-D-Glucopyranosyloxy)-acetyl]-1,3,4,5-tetrahydro-2*H*-1,5-benzodiazepin-2-one (8a and 8b)[18]

A cooled (0 °C) solution of the α,β-unsaturated keto-carbonic acid **5** (0.24 g, 0.8 mmol) in abs. MeOH (10 mL, molecular sieve 3 Å) was treated in portions with *o*-phenylenediamine (80 mg, 0.8 mmol). TLC monitoring indicated disappearance of starting material after 2 hours of reaction. After filtration the solvent was removed *in vacuo* resulting in a crude product which was purified on silica gel (3 × 20 cm) with $CHCl_3$–MeOH (5 : 1) as the eluent. Evaporation of fractions with R_f 0.5 [$CHCl_3$–MeOH (1 : 1)] yielded **8** (167 mg, 55%) in the form of a colourless foam as a 1 : 1 mixture of its diastereomers **8a** and **8b**. (Found: C, 53.40; H, 5.80; N, 7.30, O, 33.50% $C_{17}H_{22}N_2O_8$ requires C, 53.40; H, 5.80; N, 7.33 O, 33.47%).

δ ^{1}H NMR (300 MHz, CD_3OD): 2.85 (m, 1 H, 3-H_a), 3.05 (m, 1 H, 3-H_b), 3.12–3.50 (m, 6 H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H_2), 4.20–4.52 (m, 3 H, 4-H, OCH_2CO), 4.85 (d, 1 H, 1′-H), 6.68–7.36 (m, 4 H, C_6H_4). – $J_{1',2'}$ = 3.8 Hz; δ ^{13}C NMR (75.5 MHz, CD_3OD): δ 40.3 (C-3), 50.7, 50.8 (C-4 of diastereomers **8a** and **8b**), 60.9 (C-6′), 70.0 (C-2′, C-5′), 71.7 (O*C*H_2CO), 73.0 (C-4′), 73.1 (C-3′), 98.7 (C-1′), 117.6, 124.1, 127.7, 128.0 (C-6, C-7, C-8, C-9), 133.5, 136.2 (C-5a, C-9a), 168.3 (C-2), 205.8, 205.9 (4-*C*O of diastereomers **8a** and **8b**). MS (FD): m/z = 382 (M^+).

4*R*- and 4*S*-7,8-Dichloro-4-[(-α-D-glucopyranosyloxy)-acetyl]-1,3,4,5-tetrahydro-2*H*-1,5-benzodiazepin-2-one (9a and 9b)[18]

Benzodiazepine **9** was synthesized under identical conditions as **8**. The reaction of **5** (0.24 g, 0.8 mmol) with 3,4-dichlorophenylenediamine (140 mg, 0.8 mmol) and column purification on silica gel (3 × 20 cm) with $CHCl_3$–MeOH (10 : 1) as the eluent yielded product **9**. Evaporation of fractions with R_f 0.85 [$CHCl_3$–MeOH (2 : 1)] yielded **9** (172 mg, 48%) as a colourless mixture of both diastereomers **9a** and **9b**.

(Found: C, 45.30; H, 4.50; N, 6.20% $C_{17}H_{20}Cl_2N_2O_8$ requires C, 45.25; H, 4.47; N, 6.21; O, 28.36; Cl, 15.71%).

δ ^{1}H NMR (300 MHz, CD_3OD): 2.85 (m, 1 H, 3-H_a), 3.05–3.19 (m, 2 H, 3-H_b, 5′-H), 3.25 (m, 3 H, 3′-H, 4′-H, 6′-H_b), 4.10 (d, 1 H, OCH_{2a}CO), 4.20 (d, 1 H, OCH_{2b}CO), 4.23 (m, 1 H, 4-H), 4.74 (d, 1 H, 1′-H), 6.87 (s, 2 H, 6-H, 9-H). – $J_{1'2'}$ = 3.8, $J_{2',3'}$ = 9.6 $J_{gem,\ OCH_2CO}$ = 17.1 Hz, δ ^{13}C NMR (75.5 MHz, CD_3OD): δ 40.3 (C-3), 50.7, 50.8 (C-4 of diastereomers **9a** and **9b**), 60.8 (C-6′), 70.0 (C-2′, C-5′), 71.7 (O*C*H_2CO), 73.0 (C-4′), 73.1 (C-3′), 98.7 (C-1′), 113.8, 115.4 (C-6, C-9), 118.2 (C-7), 123.9 (C-8), 125.9, 134.1 (C-5a, C-9a), 166.3 (C-2), 205.8 (4-*C*O). MS (FD): m/z = 450 (M^+).

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