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Practical aqueous reactions leading to skeletally diverse carbohydrate-derived ketones†

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Four types of skeletally diverse compounds have been synthesized from protected aldosyl hemiacetals and methyl ketones using cheap catalysts in water in one pot. Among the four skeletons, two of them are not accessible by current methods. The reactions are operationally simple, high yielding and scalable, which opens a practical channel for utilizing carbohydrates to produce chemical and pharmaceutical intermediates and products.

Introduction

Carbohydrates are annually renewable and the quantities produced exceed those for other renewable organic compounds. Therefore utilizing carbohydrates for chemical, energy and material supplies to replace fossil fuels is an important area for sustainable development.[1] Partially modified carbohydrates are important drugs, such as iminosugars which are used to treat diabetes.[1f,2] When carbohydrates are dehydrated and cyclized, they form hydroxymethyl furfural, which is a potential green fuel, and can then be transformed into a series of chemicals.[3] In the synthesis of natural products and other chemicals, carbohydrates are often transformed into basic building blocks.[1c,d,4] In these processes, expensive reagents, harsh reaction conditions, prolonged reaction times or organic solvents are often required, which make the manufacture of these carbohydrate-derived products impractical due to high costs and adverse environmental effects.[2–4] Therefore, it is beneficial to develop operationally simple and economical procedures to produce carbohydrate-derived chemicals using green media and cheap catalysts. Herein, the synthesis of dienediketones, enetriketones, furanyl-substituted α,β-unsaturated ketones and furanyl-substituted diketones from protected carbohydrates and methyl ketones using inexpensive catalysts in water is reported.

Results and discussion

Previously, we synthesized (*S*,*Z*)-3-(1,3-bis(benzyloxy)-4-hydroxy-1-butenyl)-1,5-diphenyl-1,5-pentanedione (Scheme 2, **Ia**) from a reaction between *O*-benzyl-protected D-xylosyl hemiacetal and acetophenone catalyzed by 2.0 equiv. of LiOH mediated by water.[5] In that work, the 1,5-pentanedione product was isolated and purified after TLC indicated that the aldol reaction was complete. In this work, after the completion of the aldol reaction, the reaction mixture was treated with 2.5 equiv. of 10% HCl, in which 2.0 equiv. of HCl was used to neutralize the 2.0 equiv. of LiOH and the remaining 0.5 equiv. of HCl was used to catalyze the hydrolysis of the enolether. The reaction was then continued at 60 °C for 8 h, to give furanyl-substituted diketone **Ia** (Scheme 1) in 83% yield after in-flask extraction and filtration through a silica gel pad.

To test the scope of the reaction, a series of substituted acetophenones were used for the condensation reactions with *O*-benzyl-protected D-glucosyl and D-xylosyl hemiacetals, followed by one-pot hydrolysis. Using different substituents on the phenyl rings had little impact on the reaction yields and rates (Scheme 1, **1a–1g**) showing that the scope of usable substrates is wide. The reaction yields varied from 73–87% and the reaction times from 8–32 h.

Subjecting aliphatic ketones and carbohydrates to a similar reaction led to another type of product, α,β-unsaturated ketones (Scheme 1, **2a–e**). The reaction yields ranged from 76–95% and the reaction times were 2–20 h. In the synthesis of both **1** and **2**, the reaction times for *O*-benzyl-protected D-glucosyl hemiacetals were much longer than those of *O*-benzyl-protected D-xylosyl hemiacetals (**1g**, 32 h and **2b**, 20 h; **1a**, 8 h and **2a**, 2 h). When more catalyst was used (3.0 equiv. of HCl), the reaction times for **1g** and **2b** were shortened from 32 h and 20 h to 3 h and 2 h respectively. The reactions are easily scalable since similar yields of both **1a** and **2b** were produced when the amounts of aldosyl hemiacetal starting materials were raised from 0.1 g to 10 g.

These furanyl-substituted products are also accessible staring from furfurals and methyl ketones *via* aldol reactions.[6] The method reported here provides an alternative to known methods with advantages of using carbohydrates instead of furfurals and using water as the solvent. The better performance

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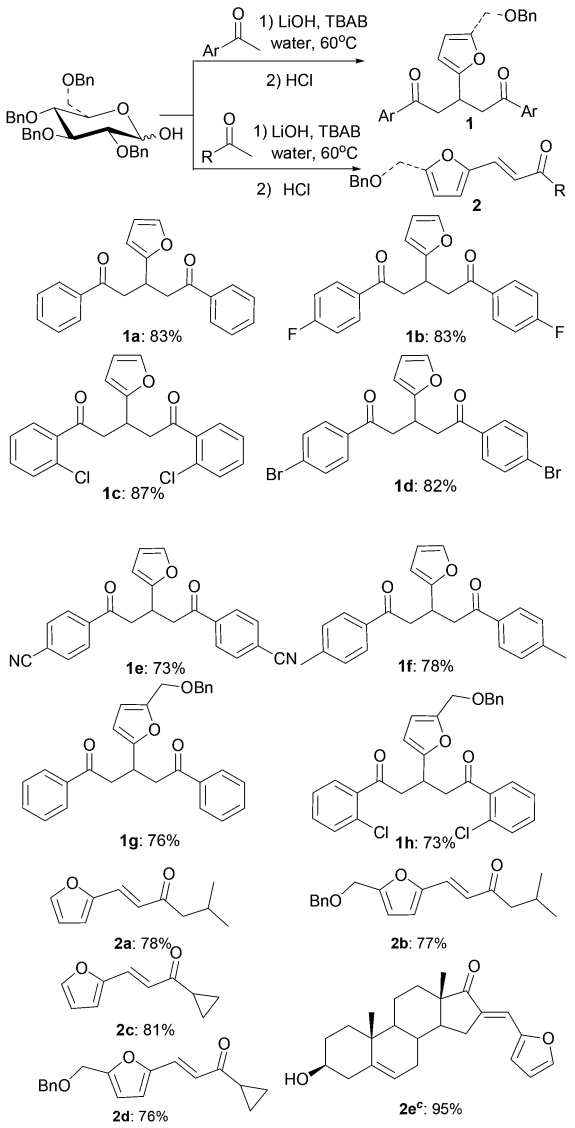
† Electronic supplementary information (ESI) available: General experimental information, general procedure for all products, spectral data for all products, references for known compounds, NMR spectra of the products, See DOI: 10.1039/c4ra14457k



Scheme 1 One-pot synthesis of furanyl-substituted diketones **1** and furanyl-substituted α,β-unsaturated ketones **2** from aldosyl hemiacetals and methyl ketones[a,b]. [a]Reaction conditions: (1) aldosyl hemiacetal (0.25 mmol), methyl ketone (6.0 equiv. for **1a–1h**, 3.0 equiv. for **2a–2d**), LiOH (2.0 equiv.), TBAB (1.0 equiv.), water (0.5 mL), 60 °C, 15 min for **1** and **2**. (2) 10% HCl aq (2.5 equiv.) 8 h for **1a–1f**, 32 h for **1g** and **1h**, 2 h for **2a**, **2c** and **2e**, 20 h for **2b** and **2d**. [b]Isolated yields. [c]3β-hydroxyandrost-5-en-17-one (0.25 mmol), aldosyl hemiacetal (2.2 equiv.).

of the water-mediated aldol reaction than the organic solvent-mediated one is attributed to the heteroatom effects.[5] The furan-forming step could be achieved in organic solvents and in water.[7]

A possible pathway for the one-pot reaction is shown in Scheme 2. First, the acidic hydrolysis of the enolether group of the aldol product **Ia** condensed from two methyl ketones and a carbohydrate to give **IIa**, which eliminated benzyl alcohol, yielding the *trans*-unsaturated ketone **IIIa**.[8] The *cis*-unsaturated ketone **IVa** is in equilibrium with the *trans* isomer **IIIa** under the acidic conditions. Only the former is capable of cyclizing to form furan **Va**. A bulkier substituent on the γ position of **IIIa** results in a lesser amount of *cis*-unsaturated ketone **IVa** in the equilibrium.[7] Therefore the reactions starting from xylose (Scheme 1, **1a**, **2a**) were much faster than those starting from glucose (Scheme 1, **1g**, **2b**). The aldol reaction product **Ib** was transformed into **Vb** *via* a pathway that is similar to that for **Ia**.

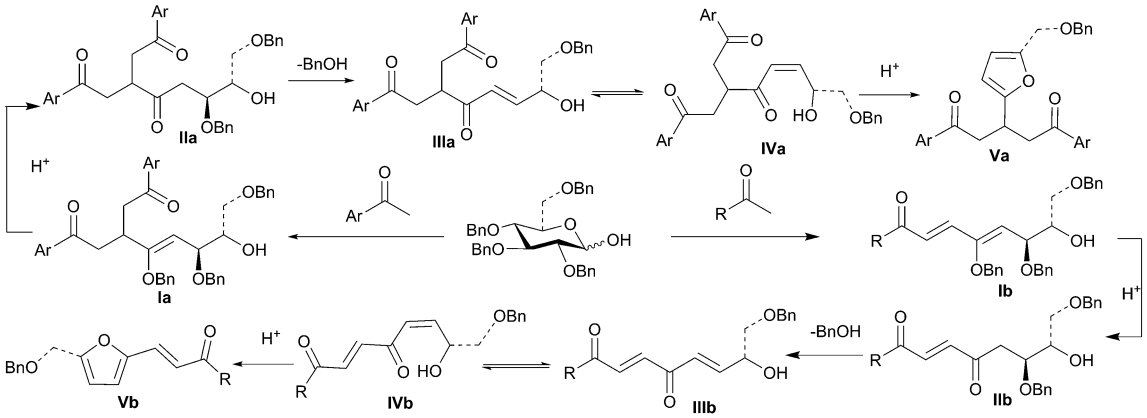
To obtain useful chemical intermediates as well as to prove the reaction mechanism, the reaction conditions used in Scheme 1 were modified by treating the aldol condensation reaction mixture from the acetophenone and *O*-benzyl-protected D-xylosyl hemiacetal with less HCl (2.1 equiv. instead of 2.5 equiv. of Scheme 1). The reaction took 10 min at 60 °C to produce triketone **3a** (Scheme 3) in 86% yield. Further transformation of **3a** into furan **1a** was successfully avoided by a timely workup.

A series of substituted aryl methyl ketones were then reacted with *O*-benzyl-protected D-glucosyl and D-xylosyl hemiacetals under these conditions to produce triketones **3a–3o** (Scheme 3). The substituents on the aromatic ring of the methyl ketones included electron-withdrawing (F_3C– on **3e**, **3m** and F– on **3b**, **3g**), electron-neutral (H– on **3a**, **3i**) and electron-donating (BnO– on **3f**, **3o**) groups. All the reactions proceeded expeditiously and gave good to excellent yields. Enetriketone **3a** was prepared starting with 10 g of *O*-benzyl-protected D-xylosyl hemiacetal with a similar reaction rate and yield as those obtained with 0.1 g of the hemiacetal.

Several methods to prepare triketones have been reported in the literature. A four-component radical coupling reaction of iodide, CO, α,β-unsaturated ketones and tin enolates leading to triketones was reported by Hosomi and Ryu *et al.*[9] Stetter and Simons reported that a thiazolium salt-catalyzed addition of aldehydes to 2-methylene-l,4-ketoketals produces triketones.[10] However, the enetriketone skeleton reported here has not been described in any references. Extending the known methods to build this type of skeleton would be expected to be quite difficult in regards to achieving the desired chemoselectivities and with respect to the availability of starting materials. Furthermore, the known methods use volatile organic solvents, expensive reagents or high pressures. Our one-pot procedure employs water as the reaction media and the phase transfer catalyst (TBAB) and catalyst (HCl) are cheap and water-soluble. The hydroxyl and benzyloxy functional groups on the enetriketone skeleton are additional advantages of our approach.

Encouraged by the successful synthesis of **3a–3o** (Scheme 3), we attempted to prepare dienediketone **4a** (Scheme 4) *via* a similar reaction. However, reacting crude aldol product (*S*,5*E*,7*Z*)-7,9-bis(benzyloxy)-10-hydroxy-2-methyl-5,7-decadien-4-one (Scheme 2, **Ib**)[5] from the reaction between 4-methyl-2-pentanone and *O*-benzyl-protected D-xylosyl hemiacetal with less HCl (≤2.5 equiv.) at temperatures ranging from 0 to 60 °C led to the formation of furan **2a** (Scheme 1), and in all cases **4a** was not formed.

So the crude aldol product was subjected to in-flask extraction and concentration, which was then treated with different acids (AcOH, $ZnCl_2$, H_2SO_4, TsOH, $AlCl_3$, BF_3 or



Scheme 2 A possible pathway for the one-pot synthesis of furanyl-substituted diketones and furanyl-substituted α,β-unsaturated ketones.

$FeCl_3 \cdot 6H_2O$) in different solvents (DMSO, toluene, $CHCl_3$, CH_2Cl_2, methanol, 1,4-dioxane or EtOAc). The reactions catalyzed by all the acids except $FeCl_3 \cdot 6H_2O$ led to furan **2a** as the major product. The reaction catalyzed by $FeCl_3 \cdot 6H_2O$ did not occur in DMSO and was sluggish (>10 h) in methanol and 1,4-dioxane. The reaction went to completion in toluene, $CHCl_3$ and CH_2Cl_2 but the products were contaminated with substantial amounts of furan **2a**. The reaction product was pure only when mediated by ethyl acetate. The amount of $FeCl_3 \cdot 6H_2O$ was optimized by screening catalyst loads from 0.1 to 2.0 equiv. and 1.5 equiv. was found to be optimal. If less than 1.5 equiv. of $FeCl_3 \cdot 6H_2O$ were used, the reaction was slow and the side product **2a** formed. The better performance of the ethyl acetate-mediated reaction is probably due to the chelation of the lone paris of ethyl acetate oxygen atoms with $FeCl_3$, which does not occur for toluene, $CHCl_3$ and CH_2Cl_2. The ethyl acetate chelates with $FeCl_3$ which prevents it from further catalyzing reactions that lead to the side product furan.

Altogether nine dienediketones (Scheme 4, **4a–i**) were obtained in good to excellent yields using these conditions ($FeCl_3 \cdot 6H_2O$ catalyst in ethyl acetate). There was a slight difference in the method used to synthesize the glucose-derived dienediketones and that for the xylose-derived dienediketones. For the glucose-derived dienediketones (**4b**, **4d**, **4f**, **4i**), 1.0 equiv. of $FeCl_3 \cdot 6H_2O$ was used, and the yields were good to excellent (81–91%). For the xylose-derived dienediketones (**4a**, **4c**, **4e**, **4g**, **4h**), the amount of catalyst was increased to 1.5 equiv. in order to increase the reaction rate. This decreased the production of the side product furans. These reaction conditions are tolerant to ketone (**4a–i**), ketal (**4c**, **4d**), olefin (**4g**), small rings (**4e**, **4f**), hydroxyl (**4h**, **4i**) and ether (**4g**) groups. In addition the reaction was scalable and the amount of *O*-benzyl-protected D-glucosyl hemiacetal starting material could be increased from 0.1 g to 10 g for the preparation of **4b** with the same yield and reaction rate.

Followings are two relevant research reports in the literature. On the nonenzymatic generation of oxidized lipids, it was reported that a six-step procedure starting from 1-hexyne and substituted furans leads to 2,4-diene-1,4-diketones in less than 30% yield.[11] In the mechanism research for the transformation of hexose to hydroxymethyl furfural, 3,4-deoxyglucosene was proposed to be an intermediate.[12] The dienediketones synthesized here are an advanced skeleton, which are not accessible *via* extending the known methods.

Experimental

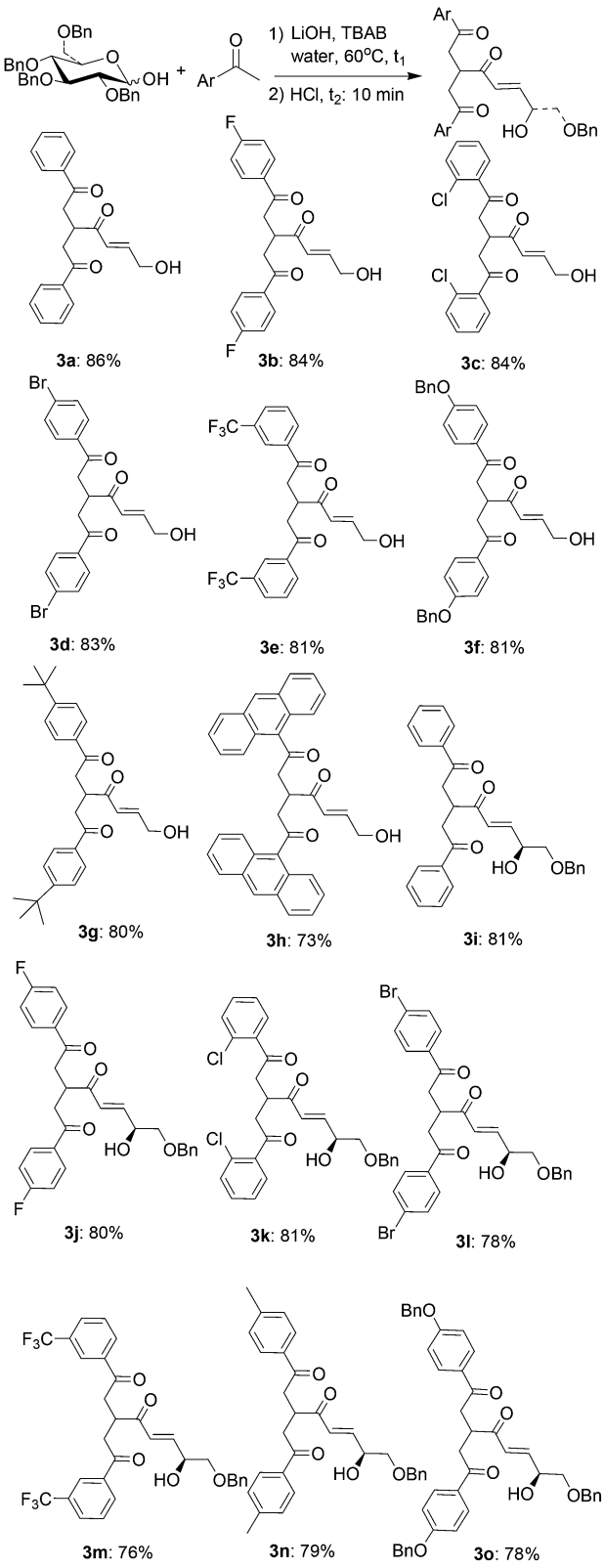
General experimental information

All of the chemicals were obtained from commercial sources or prepared according to standard methods. NMR spectra were recorded with a 600 MHz spectrometer for ^{1}H NMR, 151 MHz for ^{13}C NMR using TMS as an internal standard. Chemical shifts (δ) are reported relative to TMS (^{1}H) or $CDCl_3$ (^{13}C). Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), dd (doublet of doublets) and dt (doublet of triplets). Coupling constants were reported in Hertz (Hz). Melting points were recorded with a micro melting point apparatus. Infrared analyses (KBr pellet) were performed by FT-IR. High resolution spectra (HRMS) were recorded on a QTOF mass analyzer with electrospray ionization (ESI†).

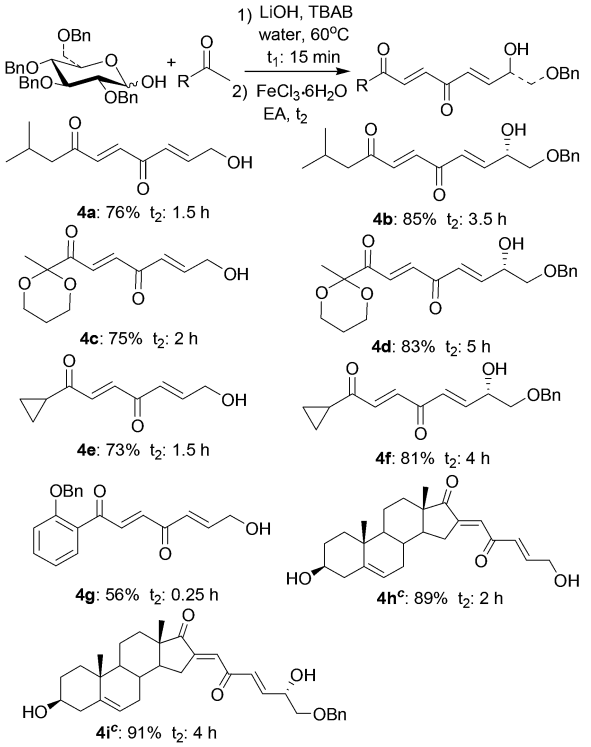
General procedure for the synthesis of furanyl-substituted diketone 1

To a 10 mL test tube were added aldosyl hemiacetal (0.25 mmol), methyl ketone (6 equiv.), LiOH (2 equiv.), TBAB (1 equiv.) and water (0.5 mL). The mixture was stirred and heated at 60 °C for 15 min and TLC indicated completion of the first step. Then 10% HCl aq. (2.5 equiv.) was added to the test tube, which was kept at 60 °C until TLC indicated completion of the reaction (**1a–f** 8 h, **1g**, **1h** 32 h). The reaction was stopped and in-tube extracted with ethyl acetate (3 × 2 mL), dried over Na_2SO_4 and purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give products **1a–1h**.

The synthesis of **1a** starting from 10 g of *O*-benzyl-protected D-xylosyl hemiacetal was performed in a 100 mL round-bottom flask in the same conditions yielding **1a** (6.5 g, 86%, t_1: 0.33 h, t_2: 9 h).



Scheme 3 One-pot synthesis of enetriketones from aldosyl hemiacetals and methyl ketones. [a]Reaction conditions: (1) aldosyl hemiacetal (0.25 mmol), methyl ketone (6.0 equiv.), LiOH (2.0 equiv.), TBAB (1.0 equiv.), water (0.5 mL), 60 °C, 15 min except for **3f** (3 h), **3j** (1 h), **3n** (0.5 h), **3o** (13 h). (2) 10% HCl aq (2.1 equiv.), 10 min. [b]Isolated yields.



Scheme 4 Synthesis of dienediketones from aldosyl hemiacetals and methyl ketones. [a]Reaction conditions: (1) aldosyl hemiacetal (0.5 mmol), methyl ketone (3.0 equiv.) except for (**4h**, **4i**), LiOH (2.0 equiv.), TBAB (1.0 equiv.), water (1 mL), 60 °C, 15 min. (2) $FeCl_3 \cdot 6H_2O$ (1.5 equiv.) for **4a**, **4c**, **4e**, **4g**, **4h**, (1.0 equiv.) for **4b**, **4d**, **4f**, **4i**, ethyl acetate (2 mL), rt. [b]Isolated yields. [c]For **4h** and **4i** 3β-hydroxyandrost-5-en-17-one (0.25 mmol), aldosyl hemiacetal (2.2 equiv.).

General procedure for the synthesis of furanyl-substituted α,β-unsaturated ketones 2

To a 10 mL test tube were added aldosyl hemiacetal (0.25 mmol), methyl ketone (3 equiv.), LiOH (2 equiv.), TBAB (1 equiv.) and water (0.5 mL). The mixture was stirred and heated at 60 °C for 15 min and TLC indicated completion of the first step. Then 10% HCl aq. (2.5 equiv.) was added to the test tube, which was kept at 60 °C until TLC indicated completion of the reaction (**2a**, **2c** 2 h, **2b**, **2d** 20 h). The reaction was stopped and in-tube extracted with ethyl acetate (3 × 2 mL), dried over Na_2SO_4 and purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give products **2a–2d**.

The synthesis of **2b** starting from 10 g of *O*-benzyl-protected D-glucosyl hemiacetal was performed in a 100 mL round-bottom flask in the same conditions yielding **2b** (4.63 g, 84%, t_1: 0.33 h, t_2: 22 h).

To a 10 mL test tube were added 3β-hydroxyandrost-5-en-17-one (0.25 mmol), aldosyl hemiacetal (1.2 equiv.), LiOH (2 equiv.), TBAB (1 equiv.) and water (0.5 mL). The mixture was stirred and heated at 60 °C for 1.5 h. Then more aldosyl hemiacetal (1 equiv.) was added. After 0.5 h, TLC indicated completion of the first step. Then 10% HCl aq. (2.5 equiv.) was added and the reaction was stirred at 60 °C until TLC indicated completion of the reaction (2 h). The reaction was stopped and

in-tube extracted with ethyl acetate (3 × 2 mL), dried over Na_2SO_4 and purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give product **2e**.

General procedure for the synthesis of enetriketone 3

To a 10 mL test tube were added aldosyl hemiacetal (0.25 mmol), methyl ketone (6 equiv.), LiOH (2 equiv.), TBAB (1 equiv.) and water (0.5 mL). The mixture was stirred and heated at 60 °C for 15 min and TLC indicated completion of the first step. Then 10% HCl aq. (2.1 equiv.) was added to the test tube, which was kept at 60 °C for 10 min. The reaction was stopped and in-tube extracted with ethyl acetate (3 × 2 mL), dried over Na_2SO_4 and purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give products **3a–3o.**

The synthesis of **3a** starting from 10 g of *O*-benzyl-protected D-xylosyl hemiacetal was performed in a 100 mL round-bottom flask in the same conditions yielding **3a** (7.04 g, 88%, t_1: 0.33 h, t_2: 0.25 h).

General procedure for the synthesis of dienediketone 4

To a 10 mL test tube were added aldosyl hemiacetal (0.25 mmol), methyl ketone (3 equiv.), LiOH (2 equiv.), TBAB (1 equiv.) and water (0.5 mL). The mixture was heated and stirred at 60 °C for 15 min and TLC indicated completion of the reaction. The reaction was in-tube extracted with ethyl acetate (3 × 2 mL), dried over Na_2SO_4. After concentration to about 2 mL, $FeCl_3 \cdot 6H_2O$ (1.5 equiv. for **4a**, **4c**, **4e**, **4g**, 1.0 equiv. for **4b**, **4d**, **4f**) was added to the ethyl acetate solution, which was stirred at rt for a certain period (**4a** 1.5 h, **4b** 3.5 h, **4c** 2 h, **4d** 5 h, **4e** 1.5 h, **4f** 4 h, **4g** 0.25 h). The reaction was stopped by addition of Na_2CO_3 (5 equiv.) under stirring. Then the solution was filtered and the filtrate was purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give products **4a–4g**.

The synthesis of **4b** starting from 10 g of *O*-benzyl-protected D-glucosyl hemiacetal was performed in a 100 mL round-bottom flask in the same conditions yielding **4b** (5.09 g, 87%, t_1: 0.33 h, t_2: 4 h).

To a 10 mL test tube were added 3β-hydroxyandrost-5-en-17-one (0.25 mmol), aldosyl hemiacetal (1.2 equiv.), LiOH (2 equiv.), TBAB (1 equiv.) and water (0.5 mL). The mixture was heated and stirred at 60 °C for a certain period (**4h** 1.5 h, **4i** 2 h), then more aldosyl hemiacetal (1 equiv.) was added. After 0.5 h, TLC indicated completion of the reaction, which was in-tube extracted with ethyl acetate (3 × 2 mL), dried over Na_2SO_4. After concentration to about 2 mL, $FeCl_3 \cdot 6H_2O$ (1.5 equiv. for **4h**, 1.0 equiv. for **4i**) was added to the ethyl acetate solution, which was stirred at rt for a certain period (**4h** 2 h, **4i** 4 h). The reaction was stopped by addition of Na_2CO_3 (5 equiv.) under stirring. Then the solution was filtered and the filtrate was purified on a silica gel pad (eluted with petroleum ether/ethyl acetate) to give products **4h** and **4i**.

Conclusions

In conclusion, one-pot methods to synthesize four types of skeletally diverse compounds starting from carbohydrates and methyl ketones have been developed. Two of these skeletons are not accessible *via* current methods. Inexpensive catalysts were used in all cases and in most cases, aqueous media were used. The reaction yields were good to excellent and the operations simple. The four types of ketones have all been scaled up to using 10 g of carbohydrate starting material. The products should be useful intermediates for chemical and pharmaceutical industries. In his paper on the principles of utilizing carbohydrates to produce chemicals, Lichtenthaler *et al.* stated that: "Unlike fossil resources, which essentially are devoid of oxygen, carbohydrates are overfunctionalized with hydroxyl groups, thus requiring efficient methodologies for the simultaneous reduction of their oxygen content and the introduction of C=C and C=O unsaturations".[4a,1] This work meets these requirements. Research on transforming these C=O and C=C containing compounds into other chemicals is currently underway in our laboratory.

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