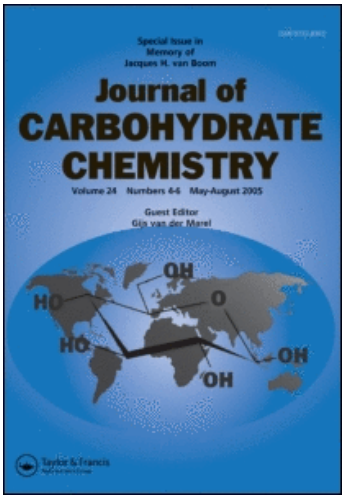

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SYNTHESIS OF NEW 2,3-UNSATURATED *O*-GLYCOSIDES THROUGH FERRIER REARRANGEMENT[1]

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SYNTHESIS OF NEW 2,3-UNSATURATED *O*-GLYCOSIDES THROUGH FERRIER REARRANGEMENT[1]

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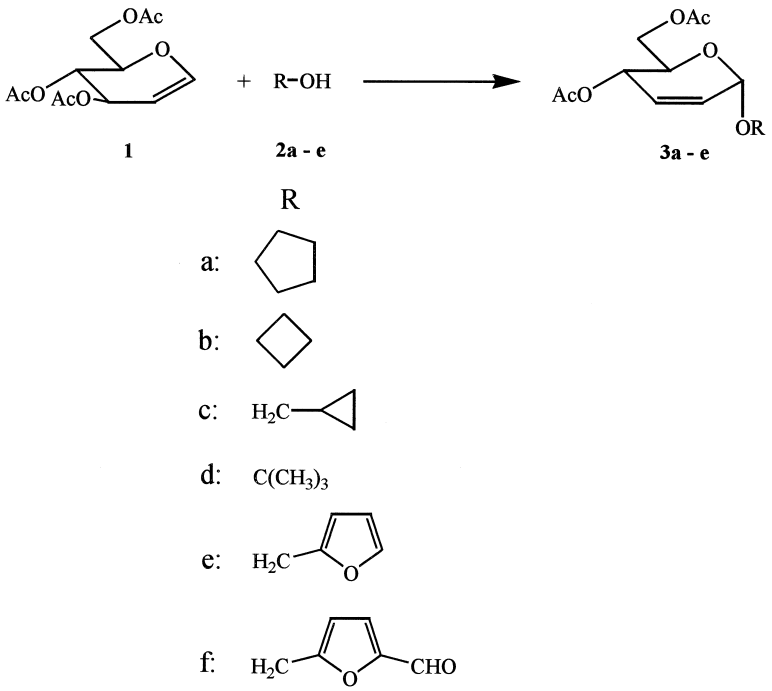
ABSTRACT

The synthesis of five new 2,3-unsaturated *O*-glycosides (**3a—e**) employing Ferrier's rearrangement with different catalysts, is reported.

INTRODUCTION

Glycals are key compounds in the synthesis of several groups of natural products[2–4] and 2,3-unsaturated sugars[4,5] and have also been used in electrophilic addition reactions.[6] Similarly 2,3-unsaturated glycosides are very versatile chiral synthetic intermediates,[3] and precursors of 2,3-dideoxy sugars, important structural units in many bioactive natural products such as antibiotics.[7]

The Lewis acid-catalysed rearrangement of glycals in the presence of alcohol, known as the Ferrier reaction,[8] is an important method employed to obtain 2,3-unsaturated glycosides.[9,10] In the present work, the glycosidation reaction of 3,4,6-tri-*O*-acetyl-D-glucal with six alcohols has been examined. The purpose of making these glycosides was twofold: first, these unsaturated glycosides are starting materials for other interesting carbohydrates including aminosugars; second, hydrogenation of the double bond can lead to alkyl 4,6-di-*O*-acetyl-α-D-*erythro*-



Scheme 1.

hexopyranosides, compounds of interest for anomeric effect studies. This paper describes the synthesis of unsaturated glycosides **3a–f** from **2a–f** and **1** (Scheme 1). To our knowledge, none of these glycosides have been reported in the literature.

RESULTS AND DISCUSSIONS

The reaction of alcohols **2a–d** with tri-*O*-acetyl-D-glucal was carried out in the presence of montmorillonite K-10[11] (Method A) or boron trifluoride[8] (Method B). However with K-10 as the catalyst, the work-up is much simpler and the yields of products **3a–d** are also better (Table 1).

Table 1. *O*-glycosidation of **1** with Alcohols **2a–d**

Glycal	Alcohol	Product	Method A (%)	Method B (%)
1	**2a**	**3a**	82	71
1	**2b**	**3b**	86	76
1	**2c**	**3c**	87	72
1	**2d**	**3d**	75	68

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Table 2. *O*-glycosidation of **1** with Furanic Alcohols **2e, f*** (Method C)

Enter	Catalyst (eq/**1**) (solvent, t °C, time/h)	**3e** % (α/β)	**3f** % (α/β)
1	Monmorillonite K-10 (30%w/w) (CH_2Cl_2, 40, 1)	degradation	degradation
2	$FeCl_3$(2 mmol/gr; 0.15 eq) (CH_2Cl_2 or C_6H_5Cl, 25, 8)	38 (80/20)	45 (80/20)
3	$FeCl_3$ (1 eq) (C_6H_5Cl, 25, 24)	54 (75/25)	82 (88/12)
4	BF_3Et_2O (0.1eq) (C_6H_5Cl, 25, 8)		51 (75/25)
5	BF_3Et_2O (0.1 eq) (CH_2Cl_2, 25, 24)	27 (81/19)	86 (87/13)
6	$SnCl_2$ (0.2 eq) (CH_3CN, 25, 8)	40 (80/20)	
7	$LiBF_4$ (1eq) (CH_3CN, 25, 8)	14 (82/18)	20 (80/20)
8	$LiBF_4$ (1eq), $SnCl_2$(0.1eq) (CH_3CN, 25, 8)	20 (85/15)	93 (85/15)

* Four equivalents of **2** with a molar concentration of 0.4 M were used for one equivalent of **1**.

Compounds **2e, f** and tri-*O*-acetyl-D-glucal were allowed to react with different catalysts in different solvents (Method C, Table 2). With montmorillonite K-10, heating led to polymeric compounds whereas the reaction was too slow at room temperature. With ferric chloride adsorbed on the montmorillonite K-10, unsaturated glycosides **3e, f** were obtained in moderate yield (entry 2), but with pure ferric chloride (entry 3) the yields were higher when one molecular equivalent of ferric chloride relative to **1** was used. Boron trifluoride as the catalyst led to 80% of **3f** with dichloromethane as solvent (entry 5). Babu *et al.*[12] reported the synthesis of 2,3-unsaturated thioglycosides mediated by lithium tetrafluoroborate in acetonitrile, but in our hands using this catalyst, the furanic alcohols **2e,f** gave poor yields (entry 7). The best yield was obtained with **2f** using a mixture of lithium tetrafluoroborate and tin(II) chloride. It should be noted that the reaction with 5-methylfurfuryl alcohol led generally to degradation products whatever the catalytic system.

As far as the mechanism of formation of 2,3-unsaturated glycosides is concerned, Ferrier[8, 13] had proposed two possibilities. First, the Lewis acid may complex on the oxygen atom of the C-3 *O*-acetyl group, and loss of this group would then lead to the formation of an allyl carbocation followed by the attack of alcohol to give the product. Since the alcohol did not attack at C-3, this hypothesis was not considered. The other possibility is the S_N2' attack of the alcohol oxygen at C-1 with subsequent elimination of the complexed *O*-acetyl group. This leads to β-anomer, which can anomerize to give the α-anomer because of the anomeric effect. This point was discussed by Toshima *et al.*[11] as well.

In the case of compounds **3a–d**, no β-anomer has been observed after purification by chromatography. The reason for this is that we used an excess of alcohol and the reaction time was a little longer. With furanic compounds **3f,e** it is not possible to separate the mixture of isomers. The amount of α-anomer ranged from 70 to 88 %, according to the catalyst employed, and was calculated from ^{13}C NMR spectra.

The products **3a–d** were characterized by ^{1}H NMR spectroscopy (300MHz), elemental analysis and optical rotations and their structures assigned on the basis of their NMR spectra. The anomeric proton of **3a** appeared at δ 5.02 ppm as a broad singlet. One olefinic proton appeared at δ 5.72 as a doublet of two doublets (ddd, J= 10.5, 2.4 and 1.5Hz) and the other at δ 5.78ppm (J=10.5 and 1.2Hz). Irradiation of the anomeric proton simplified the signal at δ 5.72 into a doublet of doublets (dd, J=10.5 and 2.1Hz), thus confirming the identity of this signal as H-2. The other signal at δ 5.78 is therefore due to H-3. It was also possible to observe that H-1 couples with H-2, H-3 and H-4 respectively. The chemical shifts of all other protons are given in the experimental section. Compounds **3b, 3c** and **3d** had ^{1}H NMR spectra which agreed with their structures. The furanic compounds **3e,f** were characterized by ^{1}H (250MHz) and ^{13}C (50MHz) spectroscopy. According to Card[14] it was only possible to obtain α and β **3e** pure after hydrolysis, separation of unsaturated alcohol and reacetylation. The chemical shifts of protons and carbons relative to **3f** αand β were determined with 2D ^{1}H-^{3}C NMR spectroscopy of the anomeric mixture.

CONCLUSION

In this paper, we have shown here the preparation of **3a–d** from **2a–d** and 3,4,6-tri-*O*-acetyl-D-glucal **1** catalysed by $BF_3.Et_2O$, montmorillonite K-10. With **2e**, the best yield is obtained with ferric chloride. Use of $BF_3.Et_2O$ catalyst in dichloromethane led to **3f** with a yield of 86%, which was increased up to 93% using a mixture of lithium tetrafluoroborate and tin(II) chloride in acetonitrile. These different syntheses showed the influence of the catalytic system and of the solvent relative to the structure of the alcohol.

EXPERIMENTAL

IR spectra were recorded as films on KBr using a Bruker IFFS66 series Fourier transform spectrophotometer. The 300 MHz ^{1}H NMR spectra were recorded with a Varian Unity Plus spectrophotometer or a Bruker DRX 300 in $CDCl_3$ with TMS as an internal standard, whereas the 200 MHz ^{1}H NMR and 50MHz ^{13}C NMR were recorded with a Bruker AC spectrometer. Elemental analysis were performed in the Department of Fundamental Chemistry, Federal University of Pernambuco, Recife (Brazil) or in CNRS Analysis Department of Solaize (France). Optical rotations were measured with a Perkin-Elmer 141 polarimeter in Villeurbanne (France). Thin-layer chromatography (TLC) was carried out on plates coated with silica gel 60 followed by the exposure of the plates in a

chamber to iodine vapors or spraying the plates with dilute sulfuric acid in the case of furanic compounds.

General Methods for the Preparation of Unsaturated Sugars 3a–e.

Method A: To a mixture of 3,4,6-tri-*O*-acetyl-D-glucal **1** (4.00g, 14.7mmol) and an appropriate alcohol (2.84 g, 33.05 mmol) in CH_2Cl_2 (50 mL) was added montmorillonite K-10 (1.2g) at 0 °C. After stirring for 1.5 h at 45 °C, the reaction mixture was filtered and the filtrate was concentrated in vacuum. The crude product was purified by chromatography on silica gel using hexane/ethyl acetate (8:2 v/v) as eluent. The fractions with the same R_f values were combined and solvent evaporated to give pure, colorless and viscous material. Their details are given below.

Method B: 3,4,6-Tri-*O*-acetyl-D-glucal **1** (0.5 g, 1.83 mmol), alcohols **2a–d** (0.186 g, 2.0 mmol) and dry CH_2Cl_2 (30 mL) were stirred in a 100 mL round-bottom flask under nitrogen atmosphere. Boron trifluoride etherate (0.1 mL) was added to it and the stirring continued for 45 min. Thin-layer chromatography (CH_2Cl_2/AcOEt 9:1 v/v) showed the disappearance of the starting material. The mixture was neutralized by addition of $NaHCO_3$. After the solution was stirred for 30 min, the solids were filtered off and the filtrate was concentrated in vacuum. The residue was chromatographed (hexane/ethyl acetate 8:2 v/v) to give **3a–d.** The fractions containing **3a–d** were combined and solvent was evaporated to give pure product (yield, Table 1).

Method C: To a mixture of 3,4,6-tri-*O*-acetyl-D-glucal **1** (mmol) and appropriate furanic alcohol (4 mmol) in solvent (1mL) was added the catalyst at 0°C. The mixture was stirred at room temperature and the reaction followed by thin-layer chromatography (CH_2Cl_2/AcOEt 5.0/0.5 v/v). After filtration on celite and neutralisation with aqueous $NaHCO_3$, the aqueous phase was extracted with CH_2Cl_2. The organic phases were washed with water, then brine, dried (Mg SO_4) and concentrated. The raw product was purified by silica gel column (CH_2Cl_2/AcOEt 5.0/0.5 v/v) to give a mixture ofα, βanomers **3e or f**. The yields are reported in the Table 2.

Cyclopentyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside 3a. Compound **3a** with $R_f = 0.74$($CHCl_3$/EtOAc 8:2 v/v) was obtained as an oil in an 87% yield after chromatography. The specific rotation of pure material is $[\alpha]_D^{25}$ +99° (*c* 0.98, $CHCl_3$);

^{1}H NMR ($CDCl_3$) δ 1.45–1.75 (m, 8H, $4CH_2$), 2.00 (s, 3H, OAc), 2.02 (s, 3H, OAc), 4.02 (m, 1H, C_4H_8-C*H*-O), 4.07 (ddd, 1H, $J_{4,5} = 10.4$Hz, $J_{5,6} = 5.7$Hz, $J_{5,6'} = 2,7$Hz H-5), 4,13 (dd, 2H, $J_{6,6'} = 10.4$Hz and $J_{5,6} = 6.3$Hz, H-6), 4.17 (dd, 1H, $J_{6,6'} = 9.9$Hz and $J_{5,6'} = 3.0$Hz), 5.02 (bs, 1H, H-1), 5.24 (dddd, 1H, $J_{4,5} = 9.9$Hz, $J_{3,4-} = -1.2$Hz, $J_{4,2} = 1.8$Hz and $J_{4,1-} = 1.5$, H-4), 5.72 (ddd, 1H, $J_{2,3} = 10.5$Hz, $J_{2,4} = 2.4$Hz, $J_{2,1} = 1.5$Hz, H-3), 5.78 (dd, 1H, $J_{3,2} = 10.5$Hz, $J_{3,4} = 1.2$Hz, H-3); IR υ_{max} (Liq film): 1746, 1664, 1234, 1038 cm^{-1}.

Anal. Calcd for $C_{15}H_{22}O_6$ (298.33): C, 60.39; H, 7.43. Found: C, 60.25; H, 7.30.

Cyclobutyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside 3b. The reaction product showed the R_f value of 0.68 ($CHCl_3$/EtOAc 8:2 v/v);

$[\alpha]_D^{25}$ 97° (*c* 1.11, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.76−1.44 (m, 4H, $2CH_2$), 2.20–2.32 (m, 2H, CH_2), 2.04 (s, 3H, OAc), 2.06 (s, 3H, OAc), 4.09 (ddd, 1H, $J_{4,5}$ = 9.6Hz, $J_{5,6}$ = 5.4Hz and $J_{5,6'}$ = 2.4Hz, H-5), 4.20 (dd, 1H, J = 12.2Hz and J = 2.4Hz, H-6) 2.22 (dd, 1H, J = 12.3Hz and J = 1.5Hz, H-6′), 4.24 (m, 1H,-C*H*-O), 5.04 (d,1H, J = 0.6Hz, H-1), 5.30 (dddd, 1H, J = 9.6Hz, J = 1.8Hz, J = 1.5Hz and J = 1.0Hz, H-4), 5.80 (ddd, 1H, $J_{2,3}$ = 10.08Hz, $J_{2,4}$ = 2.4 Hz, $J_{2,1}$ = 1.8Hz, H-2), 5.88 (dd, 1H, $J_{2,3}$ = 1.1Hz, $J_{3,4}$ = 1.2Hz, H-3); IR υ_{max} (Liq film): 1745, 1371, 1239, 1028 cm^{-1}.

Anal. Calcd for $C_{14}H_{20}O_6$ (284.30): C, 59.15; H, 7.09. Found: C, 58.97; H, 6,96.

Cyclopropylmethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside 3c. The work-up was the same as in **3a.** Yield 86% (0.90 g). R_f = 0.69 ($CHCl_3$/EtOAc 8:2 v/v); $[\alpha]_D^{25}$ +116° (*c* 1.11, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 0.20–0.60 (m, 4H, CH_2), 1.10 (m, 1H, CH), 2.08 (s, 3H, OAc), 2.09 (s, 3H, OAc), 3.45 (m, 1H,-C*H*-O), 4.14 (ddd, 1H, $J_{4,5}$ = 9.9Hz, $J_{5,6}$ = 6.0Hz, $J_{5,6'}$ = 2.4Hz, H-5), 4.20 (dd, 1H, J = 10.2Hz, J = 0.9Hz, H-6) 4.24 (dd, 1H, J = 10.5Hz, J=1.2Hz, H-6′), 5.08 (d, 1H, J = 1.8Hz, H-1), 5.32 (dd, 1H, $J_{4,5}$ = 9.6Hz, $J_{3,4}$ = 1.8Hz, H-4), 5.86 (dd, 1H, $J_{2,3}$ = 10.8Hz, J = 1.5 Hz, H-2), 5.92 (d, 1H, $J_{3,2}$ = 10.8Hz, H-3); IR υ_{max} (Liq film): 1744, 1372, 1233, 1040 cm^{-1}.

Anal. Calcd for $C_{14}H_{20}O_6$ (284.30): C, 59.15; H, 7.09. Found: C, 59.07; H, 7.12.

***tert*-Butyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside 3d.** The reaction was carried out as described for **3a.** Yield 75% (1.55 g). R_f = 0.69 ($CHCl_3$/EtOAc 8:2 v/v); $[\alpha]_D^{25}$ +100° (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.20 (s, 9H, $3CH_3$), 1.99 (s, 3H, OAc), 2.00 (s, 3H, OAc), 4.12 (dd, 1H, $J_{4,}5$ = 10.2Hz, $J_{5,6}$ = 5.7Hz, $J_{5,6'}$=1,5, H-5), 4.20 (m, 2H, H-6,6′), 5.24 (d, 1H, $J_{1,2}$ = 2.4Hz), 5.18 (dddd, 1H, $J_{4,5}$ = 9.6Hz, $J_{2,4}$ = 1.8Hz, $J_{1,4}$ = 1.5Hz, $J_{3,4}$ = 3.3Hz, H-4), 5.66 (ddd, 1H, $J_{2,3}$ = 10,2Hz, $J_{2,4}$ = 2,7, $J_{1,2}$ = 1,8Hz, H-2), 5,76 (dd, 1H, $J_{3,2}$ = 10,2, $J_{3,4}$=1,8Hz, H-3); IR υ_{max} (Liq film): 1746, 1632, 1227, 1034 cm^{-1}.

Anal. Calcd for $C_{14}H_{22}O_6$ (286.22): C, 58.73; H, 7.74. Found: C, 58.56; H, 6.47.

Furfuryl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside 3e. Compound **3e** αwas obtained as a light yellow oil. The specific rotation of pure material is $[\alpha]_D^{25}$ −40° (*c* 1, $CHCl_3$); ^1H NMR (200MHz; $CDCl_3$): δ 2.09 (s, 3H, OAc), 2.15 (s, 3H, OAc), 4.14 (m, 1H, H-5), 4.18 (dd, 1H, $J_{6,6'}$ = 11Hz, $J_{5,6}$ = 2Hz, H-6), 4.28 (dd, 1H, $J_{6'5}$ = 5.3Hz, $J_{6',6}$ = 11Hz, H-6′), 4.59 (d, 1H, $J_{7,7'}$ = 12.7Hz, H-7), 4.71 (d, 1H, H-7′), 5.16 (dd, 1H, $J_{1,2}$ = 0.7Hz, $J_{1,3}$ = 0.7Hz, H-1), 5.35 (ddd, 1H, $J_{4,2}$ = 1,8Hz, $J_{4,3}$ = 1.8Hz, $J_{4,5}$ = 9.7Hz, H-4), 5.85 (ddd, 1H, $J_{3,1}$ 0.7Hz, $J_{3,2}$ = 10.6Hz, $J_{3,4}$ = 1.8Hz, H-3), 5.88 (ddd, 1H, $J_{2,1}$ = 7Hz, $J_{2,3}$ = 10,6Hz, $J_{2,4}$ = 1.8Hz, H-2), 6.36 (d, 2H, $J_{9,10}$ = 1.3Hz, H-9, H-10), 7.44 (t, 1H, $J_{11,10}$ = $J_{11,9}$ = 1.3Hz, H-11); ^{13}C NMR ($CDCl_3$): δ 20.96–20.99 (CH_3), 61.79 (C-7), 62.92 (C-6), 65.29 (C-4), 67,10 (C-5), 93.31 (C-1), 110.41 (C-9), 125.97 (C-10), 127.60 (C-3), 129.48 (C-2), 143.07 (C-11), 151.14 (C-8), 170.29 (*C*OCH_3).

Anal. Calcd for $C_{15}H_{18}O_7$ (310.29): C, 58.06; H, 5.85. Found: C, 58.06; H, 5.67.

Furfuryl 4,6-di-*O*-acetyl-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside 3e. Compound **3e** βwas obtained as a light yellow oil. The specific rotation of pure material is $[\alpha]_D^{25}$ +81° (*c* 0.45, $CHCl_3$); ^{1}H NMR (200MHz; $CDCl_3$): δ 2.06 (s, 3H, OAc), 2.14 (s, 3H, OAc), 4.12 (m, 1H, H-5), 4.23 (dd, 1H, $J_{6,6'}$ = 9.4Hz, $J_{5,6}$ = 2.4Hz, H-6), 4.27 (dd, 1H, $J_{6'5}$ = 4.7Hz, $J_{6',6}$ = 9.4Hz, H-6′), 4.60 (d, 1H, $J_{7,7'}$ = 12.7Hz, H-7), 4.72 (d, 1H, H-7′), 5.13 (s, 1H, H-1), 5.44 (ddd, $J_{4,2}$ = 1,4Hz, $J_{4,3}$ = 1.7Hz, $J_{4,5}$ = 9.6Hz, H-4), 5.85 (ddd, 1H, $J_{3,1}$ = 0.8Hz, $J_{3,2}$ = 10.3Hz, $J_{3,4}$ = 1.7Hz, H-3), 5.91 (ddd, 1H, $J_{2,1}$ = 1.1Hz, $J_{2,3}$ = 10,3Hz, $J_{2,4}$ = 1.4Hz, H-2), 6.36 (d, 2H, $J_{9,10}$ = 1.3Hz, H-9, H-10), 7.43 (t, 1H, $J_{11,10}$ = $J_{11,9}$ = 1.3Hz, H-11); ^{13}C NMR ($CDCl_3$): δ 20.82–20.85 (CH_3), 61.23 (C-7), 63.49 (C-6), 64.19 (C-4), 72.86 (C-5), 93.33 (C-1), 109.47 (C-9), 125.90 (C-10), 127.59 (C-3), 130.26 (C-2), 143.09 (C-11), 150.89 (C-8), 170.67 and 170.79 (*C*OCH_3).

Anal. Calcd for $C_{15}H_{18}O_7$ (310.29): C, 58.06; H, 5.85. Found: C, 58.02; H, 5.78%.

Furfuraldehyde-5-methyl 4,6-di-*O*-acetyl-2,3-dideoxy-α and β-D-*erythro*-hex-2-enopyranoside 3f. After chromatography, we were not able to separate the mixtureα,β which was obtained as a yellow oil.

3f α: ^{1}H NMR (300MHz; $CDCl_3$): δ 2.05 (s, 3H, OAc), 2.08 (s, 3H, OAc), 4.10 (m, 1H, H-5), 4.18 (dd, 1H, $J_{6,6'}$ = 9.9Hz, $J_{5,6}$ = 2.5Hz, H-6), 4.23 (dd, 1H, $J_{6'5}$ = 4.9Hz, $J_{6',6}$ = 9.9Hz, H-6′), 4.64 (d, 1H, $J_{7,7'}$ = 13.3Hz, H-7), 4.77 (d, 1H, H-7′), 5.14 (dd, 1H, $J_{1,2}$ = 1Hz, $J_{1,3}$ = 1.5Hz H-1), 5.32 (ddd, $J_{4,2}$ = 1Hz, $J_{4,3}$ = 1.6Hz, $J_{4,5}$ = 4.9Hz, H-4), 5.84 (ddd, 1H, $J_{3,1}$ = 1.5Hz, $J_{3,2}$ = 11Hz, $J_{3,4}$ = 1.6Hz, H-3), 5.96 (ddd, 1H, $J_{2,1}$ = 1Hz, $J_{2,3}$ = 11Hz, $J_{2,4}$ = 1Hz, H-2), 6.54 (d, 1H, $J_{9,10}$ = 3.53Hz, H-9), 7.2 (d, 1H, $J_{9,10}$ = 3.53Hz, H-10), 9.61 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ 21.34 (CH_3), 62.38 (C-7), 63.12 (C-6), 65.47 (C-4), 67.59(C-5), 94.38 (C-1), 112.12 (C-9), 122.35 (C-10), 127.37 (C-3), 130.29 (C-2), 153.17 (C-11), 157.81 (C-8), 170.65 and 171.06 (*C*OCH_3), 178.18 (CHO).

3f β: ^{1}H NMR (300MHz; $CDCl_3$): δ 2.05 (s, 3H, OAc), 2.08 (s, 3H, OAc), 4.09 (m, 1H, H-5), 4.13 (dd, 1H, $J_{6,6'}$ = 9.9Hz, $J_{5,6}$ = 4.9Hz, H-6), 4.25 (dd, 1H, $J_{6'5}$ = 2.5Hz, $J_{6',6}$ = 9.9Hz, H-6′), 4.66 (d, 1H, $J_{7,7'}$ = 13.3Hz, H-7), 4.86 (d, 1H, H-7′), 5.23 (dd, 1H, $J_{1,2}$ = 1.5Hz, $J_{1,3}$ = 1.5Hz H-1), 5.34 (m, 1H, H-4), 5.84 (ddd, 1H, $J_{3,1}$ = 1.5Hz, $J_{3,2}$ = 11,7Hz, $J_{3,4}$ = 2Hz, H-3), 6.01 (ddd, 1H, $J_{2,1}$ = 1.5Hz, $J_{2,3}$ = 10.7Hz, $J_{2,4}$ = 1.5Hz, H-2), 6.54 (d, 1H, $J_{9,10}$ = 3.53Hz, H-9), 7.2 (d, 1H, $J_{9,10}$ = 3.53Hz, H-10), 9.60 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$): δ 21.19 (CH_3), 61.79 (C-7), 63.70 (C-6), 64.33 (C-4), 73.26 (C-5), 94.54 (C-1), 112.04 (C-9), 122.35 (C-10), 127.00 (C-3), 129.97 (C-2), 153.12 (C-11), 157.89 C-8), 170.65 and 171.14 (*C*OCH_3), 178.12 (CHO).

Anal. Calcd for $C_{16}H_{18}O_8$ (338.3): C, 56.80; H, 5.36. Found: C, 56.25; H, 5.52.

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