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BF_3 etherate-induced formation of $C_{3–11}$-alkenyl 2,3-unsaturated glucosides

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BF_3 etherate-induced formation of C_{3-11}-alkenyl 2,3-unsaturated glucosides was used as the key step in their synthesis from glucose and C_3-C_{11}-alkenols.

Keywords: synthesis of C_{3-11}-alkenyl 2,3-unsaturated glucosides, Ferrier reaction.

INTRODUCTION

Carbohydrates are involved in a large number of biological processes, *e.g.,* cell-recognition and regulatory processes.[1] In order to gain a better knowledge of the biological role of carbohydrates and their interactions with other biomolecules, *e.g.,* proteins, they have been extensively studied during the past decades. For many of these bilogical studies it was necessary to attach the carbohydrate to a carrier such as a protein or a lipid, *i.e.,* have a bifunctional spacer arm as a link between the carbohydrate moiety and the carrier in order to avoid shielding parts of the oligosaccharide structure from the carrier. Since the first synthetic glucoprotein was reported in 1929,[3,4] many different spacer arms and methods for coupling oligosaccharides to different carrier have been developed.[2,5,6] Micelles (liposomes) offer an alternative method for biological studies of carbohydrates. Furthermore, amphiphilic molecules such as long chain alkyl glucosides, can form a variety of different liquid crystalline phases some of which are believed to play a vital role in biological processes such as membrane fusion and andocytosis.[7,8]

Since their implementation in 1988,[9] *n*-pentenyl glucosides have proved valuable for the synthesis of oligosaccharides[10,11] and enantiopure compounds[12] for mechanistic studies of glucosides hydrolysis[9,13] and electrophilic additions,[14] and for determining the relative reactivities of differently protected saccharides.[15] The olefinic moi-

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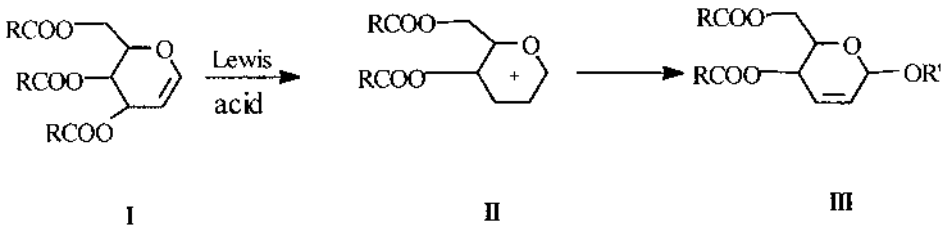


Scheme 1.

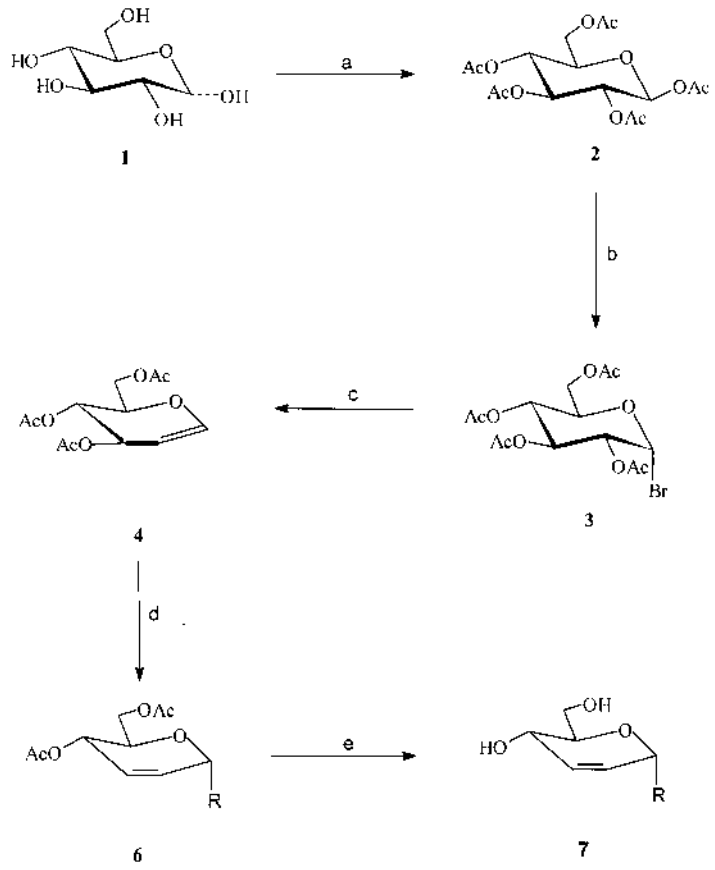
ety should allow for ready transformation into spacer functionalities, as has been exemplified by Vliegenthart and co-workers.[16] Versatility would, therefore, be enhanced, because after having served as a donor or acceptor in the synthesis of a saccharide, a given *n*-pentenyl glucoside could further serve for the elaboration of the spacer arm. With this in mind, we intended to synthesize some C_3–C_{11}-alkenyl 2,3-unsaturated glucosides starting from renewable material (glucose). The Lewis acid-catalyzed rearrangement of glycals in the presence of alcohols, known as the Ferrier reaction,[17] is the method of choice for this synthesis. The reaction, as originally stated by Ferrier, involves an intermediate cyclic allylic oxocarbenium ion **II** (Scheme 1) to which the nucleophile adds preferentially in the quasi-axial orientation. The most commonly employed Lewis acid to effect this transformation is boron trifluoride etherate ($BF_3 \cdot Et_2O$).

RESULTS AND DISCUSSION

In our previous work,[18] it was demonstrated that some alkenols, under the influence of Lewis acids, such as $BF_3{\cdot}Et_2O$, $SnCl_4$ and $AlCl_3$, cyclize to tetrahydrofuran and/or tetrahydropyran type ethers. For this reason it was considered interesting to investigate the competitivity of the Ferrier reaction and cyclization in the case of alkenols. The present work has been shown that under the employed reaction conditions (short reaction times, low temperature), the Ferrier reaction prevails over the cyclization of the alkenols. As consequence of this, C_3–C_{11}-alkenyl 2,3-unsaturated glusocides have been successfully synthesized from glucose and C_3–C_{11}-alkenols using the Ferrier reaction. As depicted in the synthetic Scheme 2, treatment of glucose **1** with Ac_2O and molten anhydrous NaOAc at 120 ºC gives exclusively the -D-glucose pentaacetate (**2**) which on treatment with HBr/AcOH leads to glucosyl bromide **3**. Reductive elimination with Zn-Cu affords tri-*O*-acetyl glucal (**4**). Glycosylation with alkenol **5** and boron trifluoride etherate proceeds by nucleophilic attack at the anomeric center of the glucal **4**. By an allylic rearrangement, the activated ester function at C-3 leaves the molecule to give the alkenyl 2,3-unsaturated glucoside **6** / with the -anomer largely prevailing (**6** : **6** = 7 : 1).

Following chromatographic purification the peracetylated products are deesterified with the mixture methanol : triethylamine : water (2 : 1 : 1) to give alkenyl -glucoside (**7**).

For structural assignments extensively NMR studies were employed (^{1}H -^{1}H homonuclear and ^{1}H -^{13}C heteronuclear chemical correlation spectroscopy (COSY) experiments were performed).



5/6/7	R	5/6/7	R
a	CH_2=$CHCH_2$	f	(*E*)-$CH_3(CH_2)_2CH$=$CHCH_2$
b	CH_2=$CH(CH_2)_2$	g	CH_2=$CH(CH_2)_5$
c	CH_2=$CH(CH_2)_3$	h	CH_2=$CH(CH_2)_6$
d	CH_2=$CH(CH_2)_4$	i	CH_2=$CH(CH_2)_7$
e	(*Z*)-CH_3CH=$CH(CH_2)_3$	j	CH_2=$CH(CH_2)_9$

a) Ac_2O, NaOAc b) HBr, AcOH c) Cu-Zn d) ROH (**3**) e) MeOH-Et_3N-H_2O 2:1:1

Scheme 2

As starting alcohols some primary alkenols were used. For this reason, 3-buten-1-ol (**5b**), 4-penten-1-ol (**5c**), 5-hexen-1-ol (**5d**), 6-hepten-1-ol (**5g**), 7-octen-1-ol (**5h**) and 8-nonen-1-ol (**5i**) were sunthesized according to known procedures.

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EXPERIMENTAL

General

Column chromatography: Merck silica gel 60, particle size 0.04–0.06 mm. *IR-spectra*: Perkin Elmer Model 137B spectrophotometer. *NMR spectra*: Varian Gemini 200 (200 MHz) in $CDCl_3$ or Bruker 250 (62.9 MHz) in DMSO-d_6. *Mass spectra*: finnigan Mat 8320 spectrometer.

Reactants and products

The substrate alcohol 4-penten-1-ol (**5c**), b.p. 135–136 ºC, was prepared from tetrahydrofurfuryl alcohol, *via* tetrahydrofurfuryl chloride.[19] 5-Hexen-1-ol (**5d**) (b.p. 63 ºC at 17 mbar) was prepared in several steps in 15 % overall yield: the Grignard reaction of allyl chloride with magnesium and paraformaldehyde gave 3-buten-1-ol (**5b**, 46 %),[20,21] which was converted by means of phosphorous tribromide to 1-bromo-3-butene (73 %).[20] Alkylation of diethyl malonate with this 1-bromo-3-butene (70 %) and decarboxylation of the formed diester by the DMSO-NaCl general procedure (76 %),[22] followed by reduction of the resulting ethyl ester of 5-hexenoic acid with $LiAlH_4$ in diethyl ether (93 %), 5-hexen-1-ol (**5d**) was obtained. 6-Hepten-1-ol (**5g**), 7-octen-1-ol (**5h**) and 8-nonen-1-ol (**5i**) were prepared from the corresponding dicarboxylic acids (suberic, azelaic and sebacic acid, respectively): decarboxylation of their mono-methyl esters[23] by means of lead tetraacetate.[24] Lead tetraacetate (LTA) gave the methyl esters of the terminally unsaturated monocarboxylic acids, which were reduced with $LiAlH_4$ in diethyl ether. The tri-*O*-acetyl glucal (**4**) was prepared according to the literature procedure,[25,26] *via* acetylated sugar **2** and glucosyl bromide **3** (Scheme 2).

*Prop-2-enyl 4,6-di-O-acetyl-2,3-dideoxy-*α*-D-*erythro-*hex-2-enopyranoside (**6a**)*

General procedure. To a stirred solution of glucal (**4**, 1.36 g, 5.00 mmol) in dry toluene (25 ml) were added 2-propen-1-ol (**5a**, 0.33 ml, 4.95 mmol) and a catalytic amount of $BF_3 \cdot Et_2O$ (0.4 ml, 3.25 mmol). The mixture was allowed to react for 1 h and then neutralized by addition of Na_2CO_3 (2 g). After the solution had been stirred for 30 min, the solids were filtered off and the filtrate was successively washed with a saturated aqueous solution of $NaHCO_3$ and distilled water. After drying with anhydrous Na_2SO_4, the solvent was evaporated on a rotary evaporator under vacuum affording a syrup (1.30 g). The residue was purified by dry flash chromatography (toluene–ethyl acetate) to afford **6a** in 96 % yield as a 7:1 mixture of - and -prop-2-en-1-yl glucosides. MS: m/z = 271 $(M+H)^+$, 213, 153.

*But-3-enyl 4,6-di-O-acetyl-2,3-dideoxy-*α*-D-*erythro-*hex-2-enopyranoside (**6b**).*

Tri-*O*-acetyl glucal (**4**, 1.36 g, 5.00 mmol) in dry toluene (25 ml) was treated with 3-buten-1-ol (**5a**, 0.42 ml, 4.88 mmol) and a catalytic amount of $BF_3 \cdot Et_2O$ (0.4 ml, 3.25 mmol) as described for **6a**. The described work-up and removal of the solvent gave 1.15 g of a syrupy residue. The residue was purified by dry flash chromatography (toluene–etyl acetate) to afford **6b** in 83 % yield as a 7:1 mixture of - and -but-3-en-1-yl glucosides. MS: m/z = 285 $(M+H)^+$, 213, 153.

*Pent-4-enyl 4,6-di-O-acetyl-2,3-dideoxy-*α*-D-*erythro-*hex-2-enopyranoside (**6c**).*

Tri-*O*-acetyl glucal (**4**, 1.36 g, 5.00 mmol) in dry toluene (25 ml) was treated with 4-penten-1-ol (**5c**, 0.5 ml, 4.84 mmol) and a catalytic amount of $BF_3 \cdot Et_2O$ (0.4 ml, 3.25 mmol) as described for **6a**. The described work-up and removal of solvent gave 1.25 g of a syrupy residue. The residue was purified by dry flash chromatography (toluene–ethyl acetate) to afford **6c** in 87 % yield as a 6:1 mixture of - and -pent-4-en-1-yl glucosides. MS : m/z = 299 $(M+H)^+$, 239 $(M-60)^+$, 213, 153.

*Hex-5-enyl 4,6-di-O-acetyl-2,3-dideoxy-*α*-D-*erythro-*hex-2-enopyranoside (**6d**).*

Tri-*O*-acetyl glucal (**4**, 1.36 g, 5.0 mmol) in dry toluene (25 ml) was treated with 5-hexen-1-ol (**5d**, 0.6 ml, 5.08 mmol) and a catalytic amount of $BF_3 \cdot Et_2O$ (0.40 ml, 3.25 mmol) as described for **6a**. The described work-up and removal of the solvent gave 1.34 g of a syrupy residue. The residue was purified by dry flash chromatography (toluene–ethyl acetate) to afford **6d** in 86 % yield as a 7:1 mixture of - and -hex-4-en-1-yl glucosides. MS : m/z = 313 $(M+H)^+$, 253 $(M+H-60)^+$, 213, 153.

*Hex-(E)-2-enyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-*erythro-*hex-2-enopyranoside (**6e**).*

Tri-*O*-acetyl glucal (**4**, 1.36 g, 5.0 mmol) in dry toluene (25 ml) was treated with (*E*)-2-hexen-1-ol (**5e**, 0.6 ml, 5.0 mmol) and a catalytic amount of $BF_3 \cdot Et_2O$ (0.40 ml, 3.25 mmol) as described for **6a**. The described work-up and removal of the solvent gave 1.27 g of a syrupy residue. The residue was purified by dry flash chromatography (toluene–ethyl acetate) to afford **6e** in 81 % yield as a 7:1 mixture of - and -hex-(*E*)-2-en-1-yl glucosides. MS: *m*/*z* = 313 $(M+H)^+$, 253 $(M+H-60)^+$, 213, 153.

*Hex-(Z)-4-enyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-*erythro-*hex-2-enopyranoside (**6f**).*

Tri-*O*-acetyl glucal (**4**, 1.36 g, 5.0 mmol) in dry toluene (25 ml) was treated with (*Z*)-4-hexen-1-ol (**5f**, 0.6 ml, 5.0 mmol) and a catalytic amount of $BF_3 \cdot Et_2O$ (0.40 ml, 3.25 mmol) as described for **6a**. The described work-up and removal of the solvent gave 1.29 g of a syrupy residue. The residue was purified by dry flash chromatography (toluene–ethyl acetate) to afford **6f** in 83 % yield as a 7:1 mixture of - and -hex-(*Z*)-4-en-1-yl glucosides. MS: *m*/*z* = 313 $(M+H)^+$, 253 $(M+H-60)^+$, 213, 153.

*Hept-6-enyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-*erythro-*hex-2-enopyranoside (**6g**).*

Tri-*O*-acetyl glucal (**4**, 0.680 g, 2.5 mmol) in dry toluene (25 ml) was treated with 6-hepten-1-ol (**5g**, 0.285 ml, 2.5 mmol) and a catalytic amount of $BF_3 \cdot Et_2O$ (0.20 ml, 1.60 mmol) as described for **6a**. The described work-up and removal of the solvent gave 0.81 g of a syrupy residue. The residue was purified by dry flash chromatography (toluene–ethyl acetate) to afford **6g** in 99 % yield as a 9:1 mixture of - and -hept-6-en-1-yl glucosides. MS: *m*/*z* = 327 $(M+H)^+$, 267 $(M+H-60)^+$, 213, 153.

*Oct-7-enyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-*erythro-*hex-2-enopyranoside (**6h**).*

Tri-*O*-acetyl glucal (**4**, 1.36 g, 5.0 mmol) in dry toluene (25 ml) was treated with 7-octen-1-ol (**5h**, 0.640 ml, 4.99 mmol) and a catalytic amount of $BF_3 \cdot Et_2O$ (0.4 ml, 3.25 mmol) as described for **6a**. The described work-up and removal of the solvent gave 1.41 g of a syrupy residue. The residue was purified by dry flash chromatography (toluene–ethyl acetate) to afford **6h** in 83 % yield as a 7:1 mixture of - and -oct-7-en-1-yl glucosides. MS: *m*/*z* = 314 $(M+H)^+$, 281 $(M+H-60)^+$, 213, 153.

*Non-8-enyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-*erythro-*hex-2-enopyranoside (**6i**).*

Tri-*O*-acetyl glucal (**4**, 0.680 g, 2.5 mmol) in dry toluene (12.5 ml) was treated with 8-nonen-1-ol (**5i**, 0.360 ml, 2.59 mmol) and a catalytic amount of $BF_3 \cdot Et_2O$ (0.20 ml, 1.62 mmol) as described for **6a**. The described work-up and removal of the solvent gave 0.850 g of a syrupy residue. The residue was purified by dry flash chromatography (toluene–ethyl acetate) to afford **6i** in 96 % yield as a 6:1 mixture of - and -non-8-en-1-yl glucosides. MS: *m*/*z* = 355 $(M+H)^+$, 295 $(M+H-60)^+$, 213, 153.

*Undec-10-enyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-*erythro-*hex-2-enopyranoside (**6j**).*

Tri-*O*-acetyl glucal (**4**, 1.35 g, 5.0 mmol) in dry toluene (12.5 ml) was treated with 10-undecen-1-ol (**5j**, 1.0 ml, 5.0 mmol) and a catalytic amount of $BF_3 \cdot Et_2O$ (0.40 ml, 3.25 mmol) as described for **6a**. The described work-up and removal of the solvent gave 1.43 g of a syrupy residue. The residue was purified by dry flash chromatography (toluene–ethyl acetate) to afford **6j** in 85 % yield as a 6:1 mixture of - and -undec-8-en-1-yl glucosides. MS: *m*/*z* = 383 $(M+H)^+$, 323 $(M+H-60)^+$, 213, 153.

The resulting material was deacetylated by treatment of the purified sample (100–200 mg) with 2 ml of MeOH–Et_3N–H_2O 2:1:1 at room temperature for 24 hours to give alkenyl 2,3-dideoxi- -D-*erythro*-hex-2-enopyranosides (**7**).

TABLE II. ^{13}C-NMR data of compounds **6a-j** (50.0 MHz, $CDCl_3$) and **7a, b, e** (62.9 MHz, DMSO-d_6).

Carbon	**6a**	**6b-d**, **6g-j**	**6e**	**6f**	**7a**	**7b**	**7e**
C-1	93.4	94.1–94.4	92.9	94.3	93.4	93.5	92.8
C-2	129.0	128.7–129.0	128.8	128.8	135.6	135.8	134.7
C-3	127.6	127.7–127.8	127.7	127.8	134.8	134.4	133.5
C-4	65.1	65.1–65.2	65.0	65.1	73.1	72.8	72.9
C-5	66.7	66.6–66.8	66.6	66.7	62.4	62.4	62.6
C-6	62.7	62.8–63.0	62.7	62.9	61.4	61.0	61.1
C-1’	69.0	68.0–68.8	68.7	68.2	68.2	66.8	67.9
$(CH_2)_n$		25.4–34.0	21.8, 34.1	23.2, 29.4		33.8	22.1, 34.0
$CH=CH_2$	117.2	113.9–116.5			117.2	116.4	
$CH=CH$			125.4, 135.1	124.4, 129.5			125.6, 126.9
$CH=CH_2$	133.9	134.9–138.9			126.0	125.5	
$CHCH_3$			13.4	12.6			13.7

ИЗВОД

BF_3-ЕТЕРАТОМ ИНДУКОВАНО ФОРМИРАЊЕ C_3–C_{11}-АЛКЕНИЛ-2,3-НЕЗАСИЋЕНИХ ГЛУКОЗИДА

СТАНИМИР КОНСТАНТИНОВИЋ[а], ЈАСМИНА ПРЕДОЈЕВИЋ[а], СВЕТИСЛАВ ГОЈКОВИЋ[б] и ВЛАДИМИР ПАВЛОВИЋ[ц]

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BF_3-Етератом индуковано формирање C_3-C_{11}-алкенил-2,3-незасићених глукозида је примењено у њиховој вишестепеној синтези која полази од глукозе и C_3-C_{11}-алкенола.

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TABLE I. ^{1}H-NMR data of the compounds **6a-j** (200 MHz, $CDCl_3$)[a)]

	6a	**6b**	**6c**	**6d**	**6e**	**6f**	**6g**	**6h**	**6i**	**6j**
H-1. C*H*=CH_2	5.06–5.38	4.98–5.33	4.93–5.10	4.92–5.12		5.28–5.53	4.90–5.07	4.83–5.08	4.88–5.12	4.90–5.10
H-2.3; CH=CH_2	5.7–6.0	5.70–5.94	5.72–5.96	5.71–5.97	5.51–5.97	5.80–6.0	5.70–5.96	5.64–5.92	5.70–5.97	5.70–5.94
H-4	5.06–5.38	5.33	5.32	5.31	5.31		5.31	5.27	5.32	5.31
H-5.6	4.0–4.32	4.03–4.26	4.0–4.3	4.0–4.3	3.96–4.32	4.0–4.31	4.0–4.3	3.97–4.25	4.01–4.31	4.0–4.3
C*H*=C*H*					5.51–5.97	5.28–5.53				
H-1a’	4.0–4.32	3.56	3.53	3.52		3.51	3.50	3.46	3.51	3.54
H-1b’	4.0–4.32	3.81	3.80	3.78		3.79	3.78	3.72	3.77	3.78
H-2’		2.32	1.72	1.62		1.69	1.61	1.57	1.58	1.58
CH_2CH=C			2.12	2.08		2.0–2.2	2.06	2.05	2.07	2.02
CH_3CO	2.08, 2.08	2.06, 2.07	2.09, 2.10	2.09, 2.10	2.08, 2.10	2.09, 2.10	2.08, 2.10	2.04, 2.05	2.09, 2.10	2.07, 2.09
(CH_2)*n*				1.50	1.41		1.40	1.30	1.33	1.30
CH_3CH					0.91	1.61				

[a)] In all compounds the coupling constants in the 2,3-unsaturated glucosyl ring are approximately the same as follows: $^{3}J_{3,4}$ = 0.8 Hz, $^{3}J_{4,5}$ = 9.6 Hz, $^{3}J_{5,6a}$ = 2.4 Hz, $^{3}J_{5,6b}$ = 5.1 Hz, $^{2}J_{6a.6b}$ = –11.7 Hz, $^{3}J_{1a',2'} = {}^{3}J_{1b',2'}$ = 6.3 Hz, $^{2}J_{1a',1b'}$ = 9.6 Hz.