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Direct vinylation of glucose derivatives with acetylene

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Abstract—Vinyl ethers, promising chiral carbohydrate synthons, have been synthesized by the addition of glucose acetals (1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, 1,2-*O*-cyclohexylidene-α-D-glucofuranose, methyl α-D-glucopyranoside) to acetylene under atmospheric and elevated pressures in an autoclave in the presence of superbase catalytic systems (KOH–DMSO, *t*-BuOK–DMSO). The complete vinylation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose and methyl α-D-glucopyranoside has been realized under elevated pressure of acetylene in the system KOH–THF as well.

1. Introduction

The availability, optical purity, and the presence of several easily transformable functional groups make carbohydrates unique chiral synthons. Additional functionalization of carbohydrates by the selective modification of one or more hydroxyl groups enhances significantly their synthetic potential and opens up new possibilities for modern asymmetric synthesis.[1,2] Sugar-based ethenyl ethers are particularly interesting chiral tools because of the versatile reactivity on the enol ether function and the importance of the derived products[2–14] including oligosaccharides[10–14] and hybrid carbohydrate-synthetic polymers.[9,15]

Currently for the syntheses of vinyl ethers of sugars and, in particular vinyl glycosides, indirect procedures are used such as the transvinylation of carbohydrates with vinyl ethers[4,15–18]or esters[14] (butyl- or isobutylvinyl ethers, vinyl acetate) in the presence of mercury acetate[4,15–17]or transition metal complexes,[14,18] prototropic isomerization of allylglycosides,[5,6,11,12,19] elimination reactions (i.e., decomposition of mixed acetals,[8] Hofmann's degradation[16] or pyrolysis of selenoxides[20]). Application of the Tebbe[21] reagent allows the oxygen carbonyl atom in the sugar ester to be replaced with the methylene group to afford vinyl[9] or isopropenyl[10,12,13,22] ethers of sugars. Photolysis of oxopentylglycosides[23] as well as the reaction of glycosylhalogenides with bis(acylmethyl) derivatives of mercury[6,10,22,24] result in vinyl glycosides. Vinyl sulfones[7,25] as acetylene synthones are also employed for the vinylation of carbohydrates.

As compared to the methods aforementioned, the direct vinylation of sugars with acetylene in the presence of bases seems to be more simple and effective process, because it involves the sugars and not their derivatives. In addition, the catalysis with alkali hydroxides or alkoxides is considerably cheaper and safer than that with mercury salts or noble and rare metal complexes.

A number of works reporting on the direct vinylation of sugars with acetylene are known.[26–29] These works relate to cyclic acetone derivatives of glucose[26] and galactose,[27] mono- and dicyclohexylideneglucose,[28] as well as methyl α-D-glucopyranoside.[29] However, the structures of the compounds synthesized was not thoroughly proved. In the recent years, the direct reaction with acetylene to give vinyl ethers of sugars has been undeservedly neglected.

Current applications of superbase catalytic media for the intensification of nucleophilic addition to acetylene[30,31] have proved their high efficiency for the vinylation of various protogenic functions including hydroxyl moieties. For example, superbase catalytic systems like KOH–polar non-hydroxyl solvent (DMSO, HMPA) make it possible to improve fundamentally the vinylation of alcohols and

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polyols (with significant decreases of temperature and an atmospheric pressure of acetylene[31]). At the same time the problem of adaptation of superbase catalytic systems to the processes of carbohydrates vinylation remains unsolved.

The present work is aimed at the development of efficient routes for the direct vinylation of carbohydrates with acetylene in the presence of superbase catalysts. One can suppose that it will allow the reaction to proceed under milder conditions that ensure increased selectivity and a safe protocol.

2. Results and discussion

The vinylation of derivatives of glucose containing one (1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **1**), two (methyl 4,6-*O*-benzylidene-α-D-glucopyranoside **2**), three (1,2-*O*-cyclohexylidene-α-D-glucofuranose **3**) or four (methyl α-D-glucopyranoside **4**) hydroxyl groups has been studied (Fig. 1).

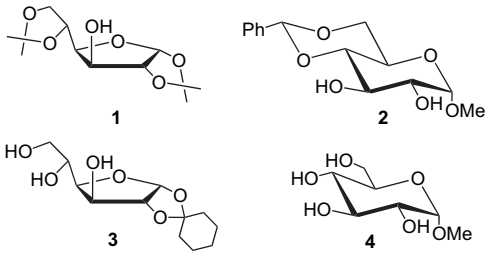
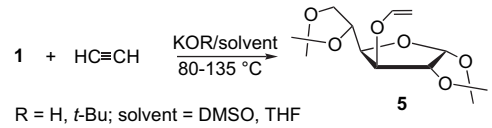


Figure 1.

Glucofuranose **1** in the systems KOH–DMSO or *t*-BuOK–DMSO reacts with acetylene under atmospheric (107–118 °C) and elevated pressure (autoclave, initial pressure of acetylene at room temperature 14–16 atm, reaction temperature 80–89 °C) to furnish the corresponding vinyl ether **5** in 68–70 and 80% yields, respectively (Scheme 1, Table 1, entries 1–3).

In the lower basicity system KOH–THF[31] vinyl ether **5** is not formed even at higher temperatures (100–110 °C) under



Scheme 1.

pressure (Table 1, entry 4). Further increase of the temperature in the same system (125–135 °C) results in a small yield of the target ether (Table 1, entry 5).

Previously glucofuranose **1** was vinylated under more severe conditions[26b] (150 °C, 7 h, acetylene pressure 90 atm at 150 °C, KOH–dioxane), but the yield of the reaction product **5** was only 55%.

Thus, new modifications for glucofuranose **1** vinylation using the system KOH–DMSO appear to be more technologically feasible and safe such that this valuable chiral carbohydrate synthone[2,32] might be commercially accessible.

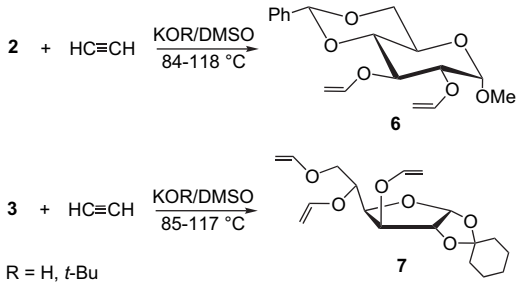
The vinylation of glucose derivatives bearing several free hydroxyl groups is usually a more complicated process characterized by low selectivity. It was reported that the treatment of methyl α-D-glucoside **4** with acetylene under pressure (25–30 atm, 150 °C, 12 h) in the presence of KOH (THF,[29b] aqueous THF,[29b] aqueous dioxane[29c]) affords a mixture of products of incomplete vinylation (0.3–1.5 vinyloxy groups per molecule). Exhaustive vinylation of 1,2-isopropylidene-,[26c] 1,2-chloroethylidene-[27b] and 1,2-cyclohexylidene-D-glucoses,[28] as well as methyl α-D-glucoside[29a] has been carried out in the system KOH–dioxane (125–150 °C, 6–11 h) using a large excess of acetylene under pressure (15 atm at rt).

These sugars were not vinylated with acetylene under atmospheric pressure.

We have managed to vinylate exhaustively glucose derivatives having two or three free hydroxyl groups (**2** and **3**) under atmospheric pressure at 113–118 °C in superbase system *t*-BuOK–DMSO (Scheme 2). Divinyl **6** and trivinyl **7** ethers

Table 1. Vinylation of glucose derivatives with acetylene

Entry	Sugar (mmol)	Base (mmol)	Solvent (mL)	Acetylene pressure at 20 °C (atm)	Temp (°C)	Time (h)	Product	Yield (%)
1	**1** (10)	KOH (3.5)	DMSO (40)	1	113–118	4	**5**	70
2	**1** (10)	*t*-BuOK (3.5)	DMSO (40)	1	107–112	9	**5**	68
3	**1** (20)	KOH (7.0)	DMSO (50)	14–16	80–89	3	**5**	80
4	**1** (20)	KOH (7.0)	THF (50)	12–14	100–110	5	**5**	Trace
5	**1** (20)	KOH (7.0)	THF (50)	12–14	125–135	4	**5**	42
6	**2** (10)	*t*-BuOK (7.5)	DMSO (40)	1	117–118	10	**6**	90
7	**2** (5.7)	KOH (6.0)	DMSO (30)	11–12	84–85	2	**6**	60
8	**3** (10)	*t*-BuOK (7.5)	DMSO (50)	1	113–117	15	**7**	79
9	**3** (15)	KOH (11.8)	DMSO (50)	12–14	85–90	2	**7**	83
10	**4** (35)	KOH (60)	DMSO (100)	14–16	100–105	2	**8**	25
11	**4** (55)	KOH (75)	DMSO (100)	18–20	90–95	3	**8**	38
12	**4** (30)	KOH (40)	DMSO (100)+MeOH (3)	16–18	85–87	0.75	**8**	75
13	**4** (30)	KOH (30)	THF (100)	14–16	130–140	6	**8**	60
14	**4** (20)	KOH (20)	THF (90)+MeOH (10)	18–20	125–135	5	**8**	69
15	**4** (30)	NaOH (40)	THF (95)+MeOH (5)	15–17	130–140	5	**8**	15
16	**4** (10)	KOH (10)	DMSO (40)	1	112–117	8	**8**	28
17	**4** (10)	KOH (10)	DMSO (40)+MeOH (3)	1	112–115	8	**8**	43
18	**4** (10)	*t*-BuOK (10)	DMSO (40)	1	110–114	8	**8**	51
19	**4** (10)	*t*-BuOK (10)	DMSO (40)+MeOH (3)	1	114–116	8	**8**	47



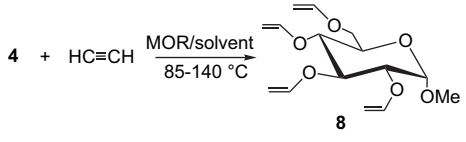
Scheme 2.

are formed in 90 and 79% yields, respectively (Table 1, entries 6 and 8).

Under pressure, in the KOH–DMSO system (autoclave, initial pressure at room temperature 11–14 atm, 80–90 °C, 2 h) the derivatives of glucose **2** and **3** are effectively vinylated (yield up to 80%) (Scheme 2, Table 1, entries 7 and 9). The system KOH–THF in the analogous conditions is ineffective in this process.

Vinylation of methyl α-D-glucopyranoside **4** is complicated by its low solubility in most organic solvents including dioxane, which was used formerly in the reaction.[29a] Unlike dioxane, DMSO not only increases the basicity of the reaction medium and dissolution of acetylene,[30,31] but also dissolves readily α-D-glucoside **4**. The exhaustive vinylation of the latter is a complex multistep process, which may result in the formation of 14 different vinyl ethers (not to mention their possible isomerization in cyclic acetals[30]).

We have fully vinylated glucoside **4** in good selectivity in the KOH–DMSO or *t*-BuOK–DMSO systems to synthesize tetravinyl ether **8** in yield up to 75% (Scheme 3). As expected the best results are obtained under pressure (Table 1, entries 10–12). Under atmospheric pressure this vinyl ether could be prepared in 51% yield (Table 1, entry 18). The systems KOH–THF and KOH–THF–MeOH (autoclave, initial pressure of acetylene at room temperature 14–20 atm, 125–140 °C, 5–6 h) turns out to be effective for the exhaustive vinylation of methyl glucoside **4**, the yield of the ether **8** reaching 69% (Table 1, entries 13 and 14).



M = K, R = H, *t*-Bu; solvent = DMSO, THF, DMSO + MeOH (3-7%), THF + MeOH (5-10%). M = Na, R = H; solvent = THF + MeOH (5%)

Scheme 3.

Vinylation of glucoside **4** with acetylene under atmospheric pressure (flow system) in *N*-methyl-2-pyrrolidinone (*t*-BuOK, 120–130 °C, 5–6 h) or di(ethylene glycol) dimethyl ether (KOH, *t*-BuOK, 120–145 °C, 19–25 h) does not proceed.

The spectra (IR, NMR) of purified tetravinyl ether **8** do not contain the indicators of hydroxyl and acetal groups, though the ^{1}H and ^{13}C NMR spectra of crude products show weak signals of the CH_3CH groups of acetals—cyclization products of partial vinyl ethers.

3. Conclusion

We have developed a simple, efficient and scalable synthetic pathway to carbohydrate-derived vinyl ethers. Superbase systems (alkali metal hydroxides or alkoxides—polar non-hydroxylic solvent) have been successfully used to vinylate directly diverse glucose derivatives with acetylene, both under elevated and atmospheric pressure and at lower temperature than in the known procedures. An advantage of the vinylations developed as compared to the previously reported methods is application of lesser amount of the base per the hydroxyl group.[33] It is expected that this simple approach to vinyl ethers will find considerable use, particularly in asymmetric synthesis.

4. Experimental

4.1. General

Chemicals from Aldrich Chemical Co. were used without further purification. 1,2-*O*-Cyclohexylidene-α-D-glucofuranose was obtained according to the known procedure.[34] IR spectra were recorded on Bruker JFS-25 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX-400 spectrometer with HMDS as an internal standard and $CDCl_3$ as solvent. Optical rotations were measured on a Polamat A polarimeter at 22 °C.

4.2. General procedure for vinylation of acetal derivatives of glucose (1–3) and methyl α-D-glucopyranoside (4) with acetylene under increased pressure (Table 1)

Into a 0.5 L steel rotating autoclave were placed glucose derivatives **1**, **2** or **3** (5.7–20 mmol), KOH or *t*-BuOK (3.5–11.8 mmol) and solvent (DMSO or THF, 30–50 mL), then acetylene was fed under an initial pressure of 11–16 atm and the mixture was heated with stirring. The reaction was monitored by acetylene consumption. The quantity of reagents and solvent, temperature (80–135 °C) and duration (2–5 h) of every run are given in Table 1 (entries 3–5, 7, 9).

Methyl α-D-glucopyranoside **4** was vinylated by the same procedure in a 1 L autoclave using acetylene under pressure of 14–20 atm (20–55 mmol of **4**, 20–75 mmol of base, 100–103 mL of solvent, 85–140 °C, 0.75–6 h) (Table 1, entries 10–15).

Approximately a half of the solvent was distilled under atmospheric (THF) or reduced (DMSO) pressure from the reaction mixture obtained from the autoclave. The remaining reaction mixture was diluted with a 2-fold amount of water and extracted with diethyl or petroleum ether (6×30 mL), the extract was washed with water (3×20–30 mL) and dried over K_2CO_3. After removal of the solvent, monovinyl **5** or trivinyl **7** ethers of glucofuranose were isolated by distillation of the residue in vacuum, methyl glucoside tetravinyl ether **8**—by distillation in vacuum or recrystallization from hexane, divinyl ether **6**—by recrystallization from hexane. Yields of the compounds **5**–**8** thus obtained are given in Table 1.

4.3. General procedure of vinylation of acetal derivatives of glucose 1–3 and methyl α-D-glucopyranoside (4) with acetylene under atmospheric pressure (Table 1)

Derivatives of glucose **1**, **2**, **3** or **4** (typically 10 mmol) were dissolved in DMSO or in a mixture of DMSO and methanol (typically 40–50 mL), KOH or *t*-BuOK was added (3.5–10 mmol, that is, 0.25–0.35 mol per OH group of sugar), then acetylene was passed in a rate of ~2 L/h and the mixture was heated under stirring (107–118 °C, 4–15 h). The reaction was monitored by the appearance and growth of absorption bands of vinyloxy groups, mainly the band at 1620–1640 cm^{-1} in the IR spectra of the compounds.

The vinylation products **5**–**8** were isolated by extraction of the reaction mixtures with ether using the procedure described above. Yields of the products are given in Table 1 (entries 1, 2, 6, 8, 16–19).

4.3.1. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-vinyl-α-D-glucofuranose (5). Colorless viscous liquid, bp 127–130 °C (3 mmHg), n_D^{20} 1.4628, $[\alpha]_D^{22}$ −26.7 (*c* 2, CCl_4) [lit.[15] bp 68 °C (0.008 mmHg), n_D^{20} 1.4593, $[\alpha]_D^{20}$ −30.5 (*c* 1, $CHCl_3$); lit.[25] $[\alpha]_D^{20}$ −32.0 (*c* 2.1, $CHCl_3$); lit.[26b] bp 115–116 °C (1.5 mmHg), n_D^{20} 1.468]. ^{1}H NMR δ (ppm) 6.37 (dd, ^3J=14.2 Hz, ^3J=6.8 Hz, 1H, =C*H*O), 5.85 (d, ^3J=3.7 Hz, 1H, H-1), 4.55 (d, ^3J=3.7 Hz, 1H, H-2), 4.37 (dd, ^3J=14.2 Hz, ^2J=2.2 Hz, 1H, =CH_{trans}), 4.32 (d, ^3J=2.8 Hz, 1H, H-3,), 4.27 (dd, ^3J=7.8 Hz, ^3J=5.9 Hz, 1H, H-5), 4.16 (dd, ^3J=7.6 Hz, ^3J=2.8 Hz, 1H, H-4), 4.13 (dd, ^3J=6.8 Hz, ^2J=2.2 Hz, 1H, =CH_{cis}), 4.06 (dd, ^3J=6.1 Hz, ^2J=8.6 Hz, 1H, H-6), 3.99 (dd, ^3J=5.5 Hz, ^2J=8.6 Hz, 1H, H-6), 1.49 (s, 3H, Me), 1.40 (s, 3H, Me), 1.31 (s, 3H, Me), 1.29 (s, 3H, Me). ^{13}C NMR δ (ppm) 149.9 (=*C*HO), 111.9 (O*C*O), 109.1 (O*C*O), 105.0 (C-1), 89.5 (=*C*H_2), 81.9 (C-2), 80.4 (C-3, C-4), 72.1 (C-5), 67.1 (C-6), 26.7 (Me), 26.6 (Me), 26.1 (Me), 25.3 (Me). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[9,25] IR (film, cm^{-1}): 3110, 3060 (ν, CH=, CH_2=), 1631, 1610 (ν, C=C), 1373, 1327, 963, 847 (δ, CH=, CH_2=). Anal. Calcd for $C_{14}H_{22}O_6$ (%): C, 58.73; H, 7.74. Found: C, 58.70; H, 7.76.

4.3.2. Methyl 4,6-*O*-benzylidene-2,3-*O*-divinyl-α-D-glucopyranoside (6). Colorless needles, mp 87–88 °C (hexane), $[\alpha]_D^{22}$ +68.3 (*c* 1.5, CCl_4). ^{1}H NMR δ (ppm) 7.35–7.41 (m, 5H, Ph), 6.44 (dd, ^3J=14.0 Hz, ^3J=6.4 Hz, 1H, OC*H*=), 6.39 (dd, ^3J=13.8 Hz, ^3J=6.4 Hz, 1H, =C*H*O), 5.64 (s, 1H, OC*H*O), 4.93 (d, *J*=3.5 Hz, 1H, H-1), 4.32 (dd, ^3J=14.0 Hz, ^2J=1.6 Hz, 1H, =CH_{trans}), 4.23 (dd, *J*=9.6, *J*=4.3 Hz, 1H, H-6), 4.21 (dd, ^3J=13.8 Hz, ^2J=1.2 Hz, 1H, =CH_{trans}), 4.10 (t, *J*=9.1 Hz, 1H, H-3), 4.02 (dd, ^3J=9.1 Hz, ^3J=3.5 Hz, 1H, H-2), 3.99 (dd, ^3J=6.4 Hz, ^2J=1.6 Hz, 1H, =CH_{cis}), 3.86 (dd, ^3J=6.4 Hz, ^2J=1.2 Hz, 1H, =CH_{cis}), 3.78–3.63 (m, 3H, H-4, H-5, H-6), 3.34 (s, 3H, OMe). ^{13}C NMR δ (ppm) 154.4 (=*C*HO), 152.5 (=*C*HO), 137.8 (C–Ph), 128.9 (C–Ph), 128.4 (2C–Ph), 126.7 (2C–Ph), 100.6 (O*C*O), 97.6 (C-1), 89.5 (=*C*H_2), 88.6 (=*C*H_2), 79.9 (C-3), 79.2 (C-2, C-4), 68.2 (C-6), 62.1 (C-5), 55.1 (OMe). IR (KBr, cm^{-1}): 3114, 3066, 3041 (ν, CH=, CH_2=), 1637, 1669 (ν, C=C), 1371, 1354, 970, 846 (δ, CH=, CH_2=). Anal. Calcd for $C_{18}H_{22}O_6$ (%): C, 64.66; H, 6.63. Found: C, 64.88; H, 6.71.

4.3.3. 1,2-*O*-Cyclohexylidene-3,5,6-*O*-trivinyl-α-D-glucofuranose (7). Colorless viscous liquid, bp 142–148 °C (3 mmHg), n_D^{20} 1.5041, $[\alpha]_D^{22}$ −10.7 (*c* 2.3, $CHCl_3$). [lit.[28] bp 120–123 °C (0.1 mmHg), n_D^{20} 1.5020]. ^{1}H NMR δ (ppm) 6.37 (dd, ^3J=14.2 Hz, ^3J=6.7 Hz, 1H, =C*H*O), 6.30 (dd, ^3J=14.2 Hz, ^3J=6.6 Hz, 1H, =C*H*O), 6.26 (dd, ^3J=13.8 Hz, ^3J=6.3 Hz, 1H, =C*H*O), 5.88 (d, ^3J=3.7 Hz, 1H, H-1), 4.56 (d, ^3J=3.7 Hz, 1H, H-2), 4.39 (dd, ^3J=14.2 Hz, ^2J=2.3 Hz, 1H, =CH_{trans}), 4.36 (d, ^3J=3.0 Hz, 1H, H-3), 4.35 (dd, ^3J=13.8 Hz, ^2J=1.8 Hz, 1H, =CH_{trans}), 4.31 (dd, ^3J=9.3 Hz, ^3J=3.0 Hz, 1H, H-4), 4.25 (dd, ^3J=5.8 Hz, ^3J=1.9 Hz, 1H, H-5), 4.22 (dd, ^3J=14.2 Hz, ^2J=2.0 Hz, 1H, =CH_{trans}), 4.14 (dd, ^3J=6.7 Hz, ^2J=2.3 Hz, 1H, =CH_{cis}), 4.07 (dd, ^2J=11.2 Hz, ^3J=1.9 Hz, 1H, H-6), 4.00 (dd, ^3J=6.6 Hz, ^2J=2.0 Hz, 1H, =CH_{cis}), 3.99 (dd, ^3J=6.3, ^2J=1.8 Hz, 1H, =CH_{cis}), 3.85 (dd, ^2J=11.2 Hz, ^3J=5.8 Hz, 1H, H-6), 1.73–1.60 (m, 4H, 2CH_2 of cyclohexyl), 1.56–1.48 (m, 4H, 2CH_2 of cyclohexyl), 1.39–1.36 (m, 2H, CH_2 of cyclohexyl). ^{13}C NMR δ (ppm) 151.9 (=*C*HO), 151.5 (=*C*HO), 149.8 (=*C*HO), 113.0 (OCO), 104.8 (C-1), 90.0 (=*C*H_2), 89.7 (=*C*H_2), 87.2 (=*C*H_2), 81.5 (C-2), 80.3 (C-3), 77.5 (C-4), 75.5 (C-5), 68.4 (C-6), 36.5, 35.9, 24.9, 24.0, 23.7 (cyclohexyl). IR (film, cm^{-1}): 3118, 3000 (ν, CH=, CH_2=), 1636, 1622 (ν, C=C), 1369, 1321, 953, 846 (δ, CH=, CH_2=). Anal. Calcd for $C_{18}H_{26}O_6$ (%): C, 63.89; H, 7.74. Found: C, 62.84; H, 7.73.

4.3.4. Methyl 2,3,4,6-*O*-tetravinyl-α-D-glucopyranoside (8). Colorless needles, mp 52 °C (hexane), bp 120–122 °C (2 mmHg), $[\alpha]_D^{22}$ +142.4 (*c* 2.4, CCl_4) [lit.[29a] bp 138–138.5 °C (3 mmHg), n_D^{20} 1.4820, $[\alpha]_D^{20}$ +146.3 (CCl_4)]. ^{1}H NMR δ (ppm) 6.47 (dd, ^3J=14.1 Hz, ^3J=6.8 Hz, 1H, =C*H*O), 6.32 (dd, ^3J=13.9 Hz, ^3J=6.6 Hz, 1H, =C*H*O), 6.28 (dd, ^3J=13.8, ^3J=6.3 Hz, 1H, =C*H*O), 6.26 (dd, ^3J=13.8 Hz, ^3J=6.4 Hz, 1H, =C*H*O), 4.88 (d, *J*=3.5 Hz, 1H, H-1), 4.41 (dd, ^3J=13.9 Hz, ^2J=2.3 Hz, 1H, =CH_{trans}), 4.38 (dd, ^3J=13.8 Hz, ^2J=1.8 Hz, 1H, =CH_{trans}), 4.35 (dd, ^3J=13.8 Hz, ^2J=1.7 Hz, 1H, =CH_{trans}), 4.23 (dd, ^3J=14.1, ^2J=2.3 Hz, 1H, =CH_{trans}), 4.11 (dd, *J*=9.6 Hz, *J*=8.1 Hz, 1H, H-3), 4.06 (dd, ^3J=6.6 Hz, ^2J=2.3 Hz, 1H, =CH_{cis}), 4.04 (dd, ^3J=6.8 Hz, ^2J=2.3 Hz, 1H, =CH_{cis}), 4.01 (dd, ^3J=6.4 Hz, ^2J=1.8 Hz, 1H, =CH_{cis}), 3.96 (dd, ^3J=6.3 Hz, ^2J=1.7 Hz, 1H, =CH_{cis}), 3.88 (m, 2H, H-6), 3.86 (m, 1H, H-5), 3.84 (m, 2H, H-2, H-4), 3.43 (s, 3H, MeO). ^{13}C NMR δ (ppm) 152.4 (=*C*HO), 151.9 (=*C*HO), 151.5 (=*C*HO), 151.0 (=*C*HO), 97.4 (C-1), 89.9 (=*C*H_2), 89.8 (=*C*H_2), 89.5 (=*C*H_2), 87.5 (=*C*H_2), 81.0 (C-3), 78.1 (C-2), 77.5 (C-4), 68.4 (C-5), 66.0 (C-6), 55.5 (OMe). IR (KBr, cm^{-1}): 3116, 3070, 3033, 3007 (ν, CH=, CH_2=), 1623, 1637 (ν, C=C), 1324, 963, 827 (δ, CH=, CH_2=). Anal. Calcd for $C_{15}H_{22}O_6$ (%): C, 60.39; H, 7.43. Found: C, 60.20; C, 7.13.

More detail information on spectral and X-ray diffraction characteristics of tetravinyl ether of methyl α-D-glucopyranoside has been published previously.[35]

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References and notes

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