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Note

Regioselective methylation of methyl α-L-fucopyranoside with diazomethane in the presence of tin(II) chloride*

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Our earlier studies[1–4] on the role of tin(II) chloride in the regioselective activation of certain hydroxyl groups of a sugar moiety for subsequent alkylation reaction enabled us to establish both a tentative mechanism for complexation and a possible model of a tin(II) chloride–methyl glycoside intermediate complex. The results presented have been based largely on indirect experimental methods, because the complex tin(II) chloride–methyl glycoside cannot be isolated and subjected to further investigations as, for example, were the di- and tri-butylstannylene glycosides[5]. Selection of suitable solvents for complexation has been mainly of empirical nature as, to the best of our knowledge, insufficient data exist[6,7] concerning the nature and stability of both the adducts of tin(II) chloride with various solvents and the tin(II) chloride–methyl glycoside intermediate complexes.

In our previous investigations[1–4], we used methyl α-L-rhamnopyranoside and methyl α-D-mannopyranoside as model compounds, and observed with both a favored complexation of their *cis*-2,3-diol groupings with tin(II) chloride. It was of interest to ascertain whether the *cis*-3,4-diol system in methyl α-L-fucopyranoside (**1**) is also preferentially activated by complexation with the catalyst.

Compound **1** was treated with an excess of diazomethane in the presence of tin(II) chloride in the selected solvents (see Table I), and the reaction products were analyzed and identified. It had already been shown[3] that they may provide valuable information on the formation of a tin(II) chloride–methyl glycoside intermediate complex and on its coordination sites. Initial complexation at HO-2 and HO-3 should afford methyl 2- and 3-*O*-methyl-α-L-fucopyranosides (**2** and **3**). The former compound coordinates quite readily at HO-3,4, in contrast to the latter, giving rise to methyl 2,3- and 2,4-di-*O*-methyl-α-L-fucopyranoside (**4** and **5**). Theoretically, in a similar way, complexation starting at HO-3,4 follows, giving rise

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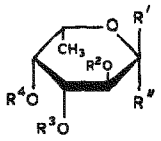

	R'	R''	R^2	R^3	R^4
1	OMe	H	H	H	H
2	OMe	H	Me	H	H
3	OMe	H	H	Me	H
4	OMe	H	Me	Me	H
5	OMe	H	Me	H	Me
6	OMe	H	H	Me	Me
7	H	OMe	H	Me	H
8	H	OMe	Me	Me	H
9	H	OMe	Me	H	Me
10	H	OMe	H	H	H

to the respective methyl ethers. Thus, the presence of an appreciable proportion of **4** (see Table I), and the absence of any detectable amount (by g.l.c.) of methyl 3,4-di-*O*-methyl-α-L-fucopyranoside (**6**) in the reaction mixtures clearly indicate favored complexation at HO-2,3. In addition, methylation in pyridine proceeded much more slowly than in other solvents, and the intermediate compound **2** could also be detected, supporting the suggested mode of complexation.

The X-ray structure[8] of α-L-fucose shows the O-2–O-3 and O-3–O-4 distances to be 293.5 and 284.3 pm, respectively. The hydroxyl groups are *gauche*-disposed, with O-2–C-2–C-3–O-3 and O-3–C-3–C-4–O-4 dihedral angles of 61.8 and 59.2°, respectively. Thus, the distances of both diols, HO-2,3 and HO-3,4, fulfil the requirement[3] for complexation, and, from this standpoint, the diols should be equally suitable for coordination with a tin(II) atom. However, it is known[9] from the literature that HO-3 and HO-2 in **1** have a higher relative reactivity than the axial HO-4, and this could be one of the main factors influencing the selectivity of initial complexation for HO-2,3. Nevertheless, it has also been reported[9] that some substitutions at HO-2 may enhance reactivity of HO-4, and this might be a plausible explanation for our observation that compound **2** coordinates readily with tin(II) at HO-3,4 in all solvents examined, except pyridine (see later).

Variations in the yields of methylated products, depending on the solvent used, clearly demonstrate its effect on the regioselectivity of alkylation. This is not surprising, as the bond strength of the coordinated solvent molecules to a tin(II) atom, and the stereochemistry of the adducts created, seem to play an important role in both the formation and the stability of the $SnCl_2$–methyl glycoside intermediate complexes. Thus far, little is known[3] in this field, and the influence of solvent on regioselectivity is not yet predictable, but solvent selection is clearly a useful, experimental variable.

TABLE I

DISTRIBUTION OF THE METHYLATION PRODUCTS FROM **1** AND ITS DEPENDENCE ON THE SOLVENTS AND REACTION TIME USED

Solvent	*Time (min)*	*Composition (mol %)*								
		1	**2**	**3**	**4**	**5**	**7**	**8**	**9**	**10**
Acetone	5	—	—	42.3	37.8	19.9	—	—	—	—
	10	—	—	41.5	38.5	20.0	—	—	—	—
	30	—	—	40.0	39.8	20.0	traces	0.1	0.1	—
	60	—	—	38.6	41.0	19.3	0.2	0.4	0.5	—
	120	—	—	36.5	42.3	18.7	0.5	0.8	1.2	—
	1440	—	—	20.1	56.5	16.9	1.6	2.1	2.8	—
2-Propanol	5	—	—	59.0	22.4	18.6	—	—	—	—
	10	—	—	59.0	22.4	18.6	traces	traces	traces	—
	30	—	—	58.6	22.5	18.3	0.1	0.2	0.3	—
	60	—	—	58.4	22.3	17.5	0.4	0.6	0.8	—
	120	—	—	57.5	21.8	16.9	0.9	1.3	1.6	—
	1440	—	—	55.4	21.9	14.3	1.8	2.8	3.8	—
Pyridine	5	88.0	2.3	9.2	0.5	—	—	—	—	—
	10	77.4	2.4	19.2	1.0	—	—	—	—	—
	30	46.0	2.2	48.0	3.4	0.4	—	—	—	traces
	60	19.8	2.1	69.8	6.2	1.4	0.3	—	—	0.4
	120	7.5	1.7	75.7	11.0	3.1	0.8	traces	traces	0.2
	1440	—	—	78.6	13.4	4.4	1.8	1.2	0.6	—
Tetrahydrofuran	5	—	—	47.6	31.0	21.4	—	—	—	—
	10	—	—	46.9	31.8	21.3	—	—	—	—
	30	—	—	45.2	33.5	21.3	—	—	—	—
	60	—	—	42.9	35.7	21.4	—	—	—	—
	120	—	—	38.5	40.1	21.4	—	—	—	—
	1440	—	—	26.0	51.2	20.3	0.7	0.8	1.0	—
Ethyl acetate	5	traces	—	36.2	42.1	21.7	—	—	—	—
	10	—	—	35.9	42.5	21.6	—	—	—	—
	30	—	—	34.2	44.1	21.7	—	—	—	—
	60	—	—	32.9	45.5	21.6	—	—	—	—
	120	—	—	31.0	47.4	21.6	—	—	—	—
	1440	—	—	19.0	58.3	21.2	0.5	0.4	0.6	—
1,4-Dioxane	5	—	—	58.4	22.0	19.6	—	—	—	—
	10	—	—	55.7	24.5	19.8	—	—	—	—
	30	—	—	53.1	27.1	19.8	—	—	—	—
	60	—	—	51.4	28.9	19.7	—	—	—	—
	120	—	—	50.2	30.1	19.7	—	—	—	—
	1440	—	—	42.0	37.8	19.5	0.2	0.2	0.3	—

Except for the reaction in pyridine, the initial methylation of the $SnCl_2$–methyl glycoside complex with the carbocation was found to be very rapid. After 5 min, no starting material could be detected (in ethyl acetate, traces only). In 2-propanol, the content of the main reaction-products, analyzed at given time intervals, remained almost constant. The small changes in composition resulted mainly from a progressive anomerization. In other solvents examined (except for pyridine), a marked decrease of the initial content of **3** could be observed after 24 h. This finding supports our previous observation[3] that those solvents that coordinate apparently weakly to tin(II) may be displaced by a diol system in which one of the hydroxyl groups has been substituted by a Me group. It appears, however, that both steps, namely, displacement and subsequent coordination to tin(II), do not proceed so readily, and to such an extent, as in the case of a free diol grouping, judging from a moderate decrease of **3** in the respective reaction-mixtures at the given time-intervals, and from the degree of its conversion after 24 h. In our previous work[3], dependence of the reaction-product distribution on time was not monitored, and so, a slow conversion of **3** could not be noticed in most selected solvents. An evident increase of the content of **4** (after 24 h) in the reaction mixtures again supports favored complexation at O-2 and O-3 in **3**.

In pyridine, the presumed initial complexation at HO-2 and HO-3 in **1** is indicated by the almost exclusive presence of **2** and **3** among the methyl ethers after 5 min of reaction. In the course of the reaction, continuous conversion of **1** affords mainly compound **3**, which points to preferential methylation of HO-3. The initial, low yields of the corresponding dimethyl ethers are connected mainly with meagre formation of intermediate **2** and also with the fact that the HO-3,4 grouping of this moiety does not coordinate to tin(II) as readily as in other solvents. In addition, conversion of **3** into **4** through complexation with the catalyst was not observed. There have been reports[6] that tin(II) chloride forms, with pyridine, stable addition-compounds in which nitrogen acts as the donor atom. Therefore, it seems reasonable to assume coordination of pyridine to the tin(II) atom, in preference to OH groups of a sugar unit. In consequence, displacement of the donor solvent might be retarded, and the activation of hydroxyl groups for the methylation reaction is apparently moderate only.

In contrast with methyl α-L-rhamnopyranoside[3] and methyl α-D-mannopyranoside[4], a slight anomerization was observed during $SnCl_2$–CH_2N_2 methylation of **1** in all solvents used, and methyl 3-*O*-methyl- and 2,3- and 2,4-di-*O*-methyl-β-L-fucopyranoside (**7**, **8**, and **9**) were detected by g.l.c., in comparison with authentic standards. In pyridine, anomerization of starting **1** afforded a detectable amount of the β-L anomer (**10**). We assume that the metal ion, intramolecular hydrogen-bonding, and the anomeric effect may all exert influences on the formation of the corresponding β-L anomers.

Variations in the structure of the carbohydrate derivative, including the configuration of the parent sugar and the nature of the substituent groups, also have an effect on the regioselectivity of alkylations catalyzed by tin(II) chloride. We

have found[10] that the use of different blocking-groups, such as benzyl or triphenylmethyl, instead of methyl, can cause noticeable changes in the regioselection and yields of alkylated products. There does not appear to be any clear correlation thus far recognizable between types of blocking groups and regioselectivity.

A large-scale, $SnCl_2$–CH_2N_2 methylation of **1** was accomplished in 2-propanol, and the products were isolated by column chromatography on silica gel. A small amount of **6** could also be isolated (see Experimental section), indicating some initial complexation at HO-3,4.

The findings presented provide further information on the complicated problem of the regioselective activation of sugar hydroxyl groups by tin(II) chloride for subsequent alkylations. It is obvious that much more, detailed work will be necessary before the foregoing conclusions can be accepted as final. Nevertheless, $SnCl_2$–CH_2N_2 methylation of **1** can serve as an alternative method to the preparation of corresponding methyl ethers in a single methylation step, whereby their yields and distribution can be influenced by the selection of suitable solvents and the proper reaction-time.

EXPERIMENTAL

General methods. — All solvents used were purified and dried. Anhydrous tin(II) chloride was prepared as described[1]. Melting points were determined on a Kofler hot-stage and are uncorrected. Unless otherwise stated, optical rotations were measured for solutions in methanol with a Perkin–Elmer Model 141 polarimeter at 22°. T.l.c. was performed with *A* 19:1 chloroform–methanol, *B* 10:1 benzene–acetone, *C* 9:1 chloroform–methanol, or *D* 5:3 light petroleum (b.p. 35–50°)–acetone, and detection by charring after spraying with 20% aqueous ammonium sulfate. Dry-column chromatography was carried out on Silikagel L (40–100 μm, Lachema n.p. Brno) in the same solvent systems. Solutions were concentrated below 50° under diminished pressure. $SnCl_2$–CH_2N_2 methylations were conducted in a nitrogen atmosphere.

G.l.c. of methylated products from the $SnCl_2$–CH_2N_2 methylations was performed with a Hewlett–Packard Model 5711 A chromatograph using a column (200 × 0.32 cm) of 3% of OV-225 on 80–100 mesh Chromosorb W AW-DMCS, over a programmed temperature-range of 130 (8 min) to 210° at 2°/min.

N.m.r. spectra were recorded at 100 MHz with a Jeol FX-100, or at 300 MHz with a Bruker AM-300, instrument for solutions in methanol-d_4 or chloroform-*d*, with tetramethylsilane as the internal reference standard.

Methyl α- and β-L-fucopyranoside (**1** and **10**) were prepared as described elsewhere[11]. The former had m.p. 155–157°, $[\alpha]_D$ −185° (*c* 0.5, water); lit.[11] m.p. 158–159°, $[\alpha]_D^{18}$ − 191° (*c* 2.0, water), and the latter had m.p. 124–126°, $[\alpha]_D$ +12.3° (*c* 0.6, water); lit.[11] m.p. 126–127°, $[\alpha]_D^{18}$ +10.5° (*c* 1.0, water).

Anal. Calc. for $C_7H_{14}O_5$: C, 47.18; H, 7.92; OMe, 17.42. Found: C, 47.12; H, 7.96; OMe, 17.48.

Methyl 2-O-methyl-α-L-fucopyranoside (**2**). — A mixture of **1** (2.5 g, 14 mmol) and tin(II) chloride–pyridine complex, $SnCl_2 \cdot C_5H_5N$ (30 mg, 0.11 mmol) in dry acetone (90 mL) was stirred[12] occasionally, and then heated in a sealed tube for 24 h at 110°. The solution was cooled, concentrated to a low volume, and then methyl 3,4-*O*-isopropylidene-α-L-fucopyranoside (2.7 g, 89%) was isolated by chromatography on a column (4 × 50 cm) of silica gel with *A*. The syrupy product had $[\alpha]_D$ −169° (*c* 0.7, water); lit.[13] $[\alpha]_D^{15}$ −160° (*c* 1.0, water).

To a cooled solution of methyl 3,4-*O*-isopropylidene-α-L-fucopyranoside (1.7 g, 7.79 mmol) in dry 1,2-dimethoxyethane (15 mL) was added sodium hydride (0.37 g, 15.4 mmol) in small portions, and the mixture was stirred for 2 h at room temperature. Methyl iodide (4 mL, 64.2 mmol) was then added, and the reaction was monitored by t.l.c. in solvent *B*. After complete methylation and the usual work-up, the product (1.7 g, 94%) was hydrolyzed with Dowex 50W X-8 (H^+) resin in aqueous methanol (70 mL) for 3 h at 50°. The subsequent purification on a column (3 × 40 cm) of silica gel, using *C* as the eluant, afforded syrupy **2** (1.3 g, 92%); $[\alpha]_D$ −138.6° (*c* 2.2); lit.[14] $[\alpha]_D^{25}$ −196° (*c* 1.20, water).

$SnCl_2$–CH_2N_2 methylations. — To a solution of methyl α-L-fucopyranoside (**1**; 12 mg) in a selected solvent (2 mL) containing tin(II) chloride (5 mmol.dm^{-3}) was added diazomethane (from *N*-nitrosomethylurea[15]) in hexane portionwise, at room temperature, awaiting disappearance of the yellow color before addition of the next portion. Sample aliquots were withdrawn at given time-intervals (see Table I) and evaporated to dryness; methanol (100 μL) was added to each sample, and the resulting solutions were then directly injected into the g.l.c. column.

A large-scale methylation was performed as follows. To a mixture of **1** (6 g, 33.7 mmol), 2-propanol (200 mL), and tin(II) chloride (190 mg, ~1 mmol) was slowly added an excess of diazomethane in hexane until the yellow color persisted. After 24 h, the solution was evaporated to dryness, the residue dissolved in a small volume of chloroform (20 mL), and the solution applied batchwise onto a column (5 × 90 cm) of silica gel. The following compounds were eluted successively from the column with solvent *D*.

Methyl 2,4-di-O-methyl-β-L-fucopyranoside (**9**; 250 mg, 3.6%); m.p. 114–115°, $[\alpha]_D$ −22.3° (*c* 0.65).

Anal. Calc. for $C_9H_{18}O_5$: C, 52.41; H, 8.80; OMe, 45.14. Found: C, 52.37; H, 8.77; OMe, 45.21.

Methyl 3,4-di-O-methyl-α-L-fucopyranoside (**6**; 22 mg, 0.3%); m.p. 94–96°, $[\alpha]_D$ −153.9° (*c* 1.08, chloroform); lit.[13] m.p. 100°, $[\alpha]_D^{20}$ −213° (*c* 1.3, water).

Found: C, 52.44; H, 8.84; OMe, 45.19.

Methyl 2,3-di-O-methyl-α-L-fucopyranoside (**4**; 1.4 g, 20.2%); syrup; $[\alpha]_D$ −140.7° (*c* 0.72); lit.[16] $[\alpha]_D^{29}$ −189.5° (1.38, acetone).

Methyl 2,4-di-O-methyl-α-L-fucopyranoside (**5**; 0.9 g, 13%); m.p. 79–80°, $[\alpha]_D$ −99.6° (*c* 1.71).

Found: C, 52.43; H, 8.82; OMe, 45.17.

TABLE II

^{1}H-N.M.R. DATA FOR METHYLATED DERIVATIVES OF **1** AND **10**

Compound[a]	*Chemical shifts*[b] *(δ)*									*Coupling constants (Hz)*				
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*Me*	*OMe*	*OAc*	*OH*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	J_{5,CH_3}
2	4.92d	3.53q	3.94q	3.82q	3.92o	1.32d	3.43; 3.48	—	2.85bs	3.6	9.8	3.4	0.9	6.7
2*	4.92d	3.65q	5.25q	5.28q	4.10o	1.15d	3.44; 3.47	2.17; 2.20	—	3.6	9.8	3.5	0.9	6.7
3	4.79d	3.90q	3.43q	[c]	3.89o	1.39d	3.46; 3.55	—	2.66bs	3.5	9.5	3.5	1.0	6.5
3*	4.89d	5.03q	3.70q	5.36q	4.03o	1.19d	3.39; 3.40	2.15; 2.19	—	3.5	10.0	3.5	1.2	6.5
4	4.83d	3.38—3.56m		3.88bq	4.87o	1.20d	3.30; 3.37; 3.38	—	2.90bs	3.0	10.0	3.5	1.1	6.5
4*	4.72d	3.53q	3.45q	5.33q	4.00o	1.19d	3.44; 3.54	2.19	—	3.0	9.5	3.5	1.2	6.5
5	4.75d	3.38q	3.84q	3.30q	3.81o	1.28d	3.28; 3.37; 3.53	—	2.91	3.6	10.0	3.5	1.1	6.5
5*	4.85d	3.73q	5.16q	[c]	3.88o	1.30d	3.45; 3.53; 3.56	2.18	—	3.5	10.0	3.2	1.2	6.5
6	4.78d	3.97q	3.42q	3.47q	3.86	1.28d	3.41; 3.52; 3.59	—	vb	3.9	9.6	3.4	1.0	6.5
6*	4.89d	5.15q	3.64q	3.50q	3.88q	1.28d	3.36; 3.49; 3.59	2.11	—	3.5	10.5	3.13	1.0	6.5
7	4.16d	3.63q	3.21q	3.85q	3.64o	1.38d	3.51; 3.55	—	2.30	7.8	9.6	3.3	1.0	6.5
7*	4.35d	5.08q	3.39q	5.37q	3.75o	1.28d	3.39; 3.54	2.14; 2.22	—	8.9	10.1	3.4	0.9	6.7
9	4.13d	3.16q	3.53q	[c]	[c]	1.38d	3.54; 3.65	—	2.58bs	7.5	9.5	3.5	[c]	6.5
9*	4.17d	3.28q	4.75q	[c]	4.15o	1.38d	3.41; 3.51	2.25	—	7.5	10.0	3.5	1.1	6.5

[a]An asterisk (*) denotes the acetylated derivative. [b]Key: b, broad; d, doublet; m, multiplet; o, octet; q, quartet; s, singlet; vb, very broad. [c]The first-order splitting was not observed.

TABLE III

^{13}C-N.M.R. DATA FOR METHYLATED DERIVATIVES OF **1** AND **10**

Compound	*Chemical shifts (δ)*									
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*Me*	*MeO-1*	*MeO-2*	*MeO-3*	*MeO-4*
2	96.9	78.0	69.5	71.5	65.3	16.1	55.3	57.9		
3	99.5	68.1	80.6	68.3	65.5	16.3	55.5		57.4	
4	97.7	77.0	79.2	69.0	65.0	16.6	55.3	57.6	58.8	
5	98.5	79.5	71.0	83.5	66.7	16.7	55.0	57.9		62.0
6	101.0	69.5	80.2	82.3	67.5	16.6	55.6		58.2	61.0
7	103.5	70.5	82.9	70.5	67.8	16.3	56.8		57.3	
9	104.2	81.4	74.1	81.4	70.5	16.6	56.5	60.7		62.2

Methyl 2,3-di-O-methyl-β-L-fucopyranoside (**8**; 180 mg, 2.6%); m.p. 74–76°, $[\alpha]_D$ −3.9° (*c* 0.52); lit.[16] m.p. 78°, $[\alpha]_D^{30}$ −1.23° (*c* 0.98, acetone).

Found: C, 52.44; H, 8.82; OMe, 45.19.

Methyl 3-O-methyl-α-L-fucopyranoside (**3**; 3.5 g, 54.1%); m.p. 96–97°, $[\alpha]_D$ −135.8° (*c* 0.62); lit.[14] m.p. 76–78°, $[\alpha]_D^{26}$ −200° (*c* 1.10, water).

Anal. Calc. for $C_8H_{16}O_5$: C, 49.99; H, 8.39; OMe, 32.29. Found: C, 49.94; H, 8.39; OMe, 32.35.

Methyl 3-O-methyl-β-L-fucopyranoside (**7**; 110 mg, 1.7%); m.p. 104–105°, $[\alpha]_D$ −12.4° (*c* 0.61).

Found: C, 49.95; H, 8.34; OMe, 32.26.

^{1}H- and ^{13}C-N.m.r. data (see Tables II and III) are given for those compounds that are either novel or whose m.p. and $[\alpha]_D$ obtained here differed substantially from those reported earlier.

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