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Anomeric Distribution of Sugar Acetates Synthesized *via* Peracetylation of Monosaccharides under Acidic and Basic Conditions

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Peracetylation of D-glucose (**1a**), D-galactose (**1b**), D-mannose (**1c**), D-fructose (**1d**) and L-arabinose (**1e**) with stoichiometric amount of acetic anhydride was performed in the presence of either 1.7 mol% $HClO_4$ or 30 mol% NaOAc as catalyst to yield corresponding sugar acetates (**2a-e**). Upon direct column chromatography of the crude reaction mixtures, the products were obtained in good to excellent yield (up to 96.1%). Composition of α-pyranose, β-pyranose, α-furanose, β-furanose and open-chain anomers present in the sugar acetates (**2a-e**) was determined by ^{1}H NMR. Pyranose was the major anomer produced in all the cases except, the NaOAc-catalyzed peracetylation of a ketohexose (**1d**) exclusively produced furanose.

Keywords: Carbohydrate, Catalysis, Glycoside, Perchloric acid, Sodium acetate, Synthesis.

INTRODUCTION

The cyclic and open-chain structures of D-glucose are commonly explored to explain the phenomenon of mutarotation observed in carbohydrates [1]. The six membered pyranose ring adopts chair conformation, which is comparably more stable than the five membered furanose ring. In addition, anomeric carbon-skeletal arrangement further differentiates them into α- and β-configurations. Ha *et al.* [2] reported that the free energy difference between the α- and β-anomers of D-glucopyranose in aqueous solution is $\Delta G(\alpha \rightarrow \beta)$ = -0.33 kcal /mol at 20 ºC and the solvation stabilizes the β-anomer. However, there is a significant intramolecular electrostatic that favours the α-anomer. Consequently, the anomeric distribution is 36% α-D-glucopyranose:64% β-D-glucopyranose. They have also highlighted that the anomeric effect is more evident in a substituted sugar. Furthermore, the $HClO_4$ catalyzed peracetylation of D-glucose with acetic anhydride exclusively produces α-D-glucose pentaacetate, while the use of NaOAc gives β-D-glucose pentaacetate [3].

Peracetylation is an important tool for the protection of hydroxyl groups in carbohydrates. Structure elucidation of natural compounds containing carbohydrates is often facilitated through the peracetylation approach; however, complexity may arise when different isomers are co-existing. Peracetylated sugars also dispense useful intermediates in the synthesis of naturally occurring glycosides and glyco-conjugates [4-8]. Pyridine [9], DMAP [10], NaOAc [11,12], DABCO [13], H_2SO_4 [14] and $HClO_4$ [15] are used as catalysts for the peracetylation of sugars with acetic anhydride. Some Lewis acids such as $ZnCl_2$ [16], $FeCl_3$ [17], $Sc(OTf)_3$ [18], $Cu(OTf)_3$ [19], $In(OTf)_3$ [20], $Bi(OTf)_3$ [21], $Ce(OTf)_3$ [22], $V(OTf)_2$ [23], *etc*. have also been explored.

Herein, the peracetylation of sugars (**1a-e**) with acetic anhydride in the presence of either $HClO_4$ or NaOAc was performed to obtain sugar acetates (**2a-e**). This study was aimed to know the anomeric distribution in the sugar acetates produced through the peracetylation. This study will not only beneficial for the cost-effective synthesis of the target drug molecules but also highly desirable due to its relevance to the biological systems [24]. Interestingly, the compositions of

pyranose and furanose anomers in the products using two different catalytic conditions were varied, which led us to assign the ^{1}H NMR signals of each sugar acetate anomer formed.

EXPERIMENTAL

D-Glucose (**1a**) (Qualigens), D-galactose (**1b**) (Loba), D-mannose (**1c**) (Himedia), D-fructose (**1d**) (Rankem), L-arabinose (**1e**) (Loba), magnesium powder (Himedia) and other chemicals were purchased. Acetic anhydride was freshly prepared in the laboratory [25,26]. Silica gel 60 F_{254} plate (Merck) was used for thin layer chromatography. The chromatogram was visualized with *p*-anisaldehyde stain. Column chromatography was performed using silica gel of 100-200 Mesh (Fischer Scientific). NMR spectra were recorded on Ascend Neo 400 NMR spectrophotometer (Bruker).

Typical procedure: Peracetylation of D-glucose

(1) $HClO_4$ as acid catalyst: A mixture of D-glucose (**1a**, 1 mmol, 0.182 g) and 1.2 equiv. of acetic anhydride (1.2 × 5 OH = 6 mmol, 0.57 mL) was cooled at 0 ºC. To this was added 1.7 mol% of $HClO_4$ (0.017 × 5 OH = 0.085 mmol, 5 µL) *via* a micro syringe and then warmed to room temperature. The reaction was monitored by TLC (hexane/ethyl acetate, 1:1). After 3 h, the reaction was stopped. The reaction mixture was directly purified by column chromatography eluting with a hexane/ethyl acetate mixture (1:1) to obtain D-glucose pentaacetate (**2a**) (0.345 g, 88.2%) as an anomeric mixture of 86.91% 1,2,3,4,6-penta-O-acetyl-α-D-glucopyranose (**2aαP**) and 13.09% 1,2,3,4,6-penta-O-acetyl-β-D-glucopyranose (**2aβP**).

(2) NaOAc as base catalyst: A mixture of **1a** (1 mmol, 0.182 g), 1.2 equiv. of acetic anhydride (1.2 × 5 OH = 6 mmol, 0.57 mL) and 30 mol% of fused NaOAc (0.3 × 5 OH = 1.5 mmol, 0.123 g) was stirred at 90 ºC. The reaction was monitored, stopped after 3 h, cooled and then directly purified as described above to obtain **2a** (0.352 g, 90.1%) as an anomeric mixture of 28.77% **2aαP** and 71.23% **2aβP**.

Analytical data of sugar acetates (2a-e)

D-Glucose pentaacetate (2a): R_f = 0.46 (hexane/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, CD_3OD) δ ppm: 1,2,3,4,6-penta-O-acetyl-α-D-glucopyranose (**2aαP**) = 6.29 (d, *J* = 2.8 Hz, H-1), 5.45 (t, *J* = 9.8 Hz, H-3), 5.13 (t, *J* = 10.1 Hz, H-4), 5.05 (dd, *J* = 3.0, 9.7 Hz, H-2), 4.28 (dd, *J* = 2.4, 12.2 Hz, H-5), 4.20-4.17 (m, H_a-6), 4.09-4.06 (m, H_b-6), 2.18 (s, CH_3), 2.05 (s, CH_3), 2.03 (s, CH_3), 2.00 (s, CH_3), 1.99 (s, CH_3) [27,28]; 1,2,3,4,6-penta-O-acetyl-β-D-glucopyranose (**2aβP**) = 5.82 (d, *J* = 8.4 Hz, H-1), 5.35 (t, *J* = 9.2 Hz, H-3), 5.05-5.02 (m, H-4 and H-2), 4.28 (dd, *J* = 2.4, 12.2 Hz, H_a-6), 4.11 (dd, *J* = 1.6, 10.8 Hz, H_b-6), 4.03-4.01 (m, H-5), 2.08-1.98 (5 CH_3) [27,28].

D-Galactose pentaacetate (2b): R_f = 0.44 (hexane/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, CD_3OD) δ ppm: 1,2,3,4,6-penta-O-acetyl-α-D-galactopyranose (**2bαP**) = 6.33 (s, H-1), 5.51 (s, H-4), 5.37-5.34 (m, overlap, H-2), 5.26-5.23 (m, H-3), 4.45 (t, *J* = 4.4 Hz, H-5), 4.16-4.05 (m, overlap, H_a-6 and H_b-6), 2.16 (CH_3), 2.15 (s, CH_3), 2.01 (s, CH_3), 2.00 (s, CH_3), 1.97 (s, CH_3) [28,29]; 1,2,3,4,6-penta-O-acetyl-β-D-galactopyranose (**2bβP**) = 5.80 (d, *J* = 2.4 Hz, H-1), 5.42 (s, H-4), 5.18 (d, *J* = 0.8 Hz, H-2), 5.15 (d, *J* = 2.0 Hz, H-3), 4.25-4.23 (m, overlap, H-5), 4.16-4.05 (m, overlap, H_a-6 and H_b-6), 2.10-1.96 (5 CH_3) [28,29]; 1,2,3,5,6-penta-O-acetyl-β-D-galactofuranose (**2bβF**) = 6.15 (s, H-1), 5.37-5.34 (m, overlap, H-5), 5.10 (d, *J* = 1.2 Hz, H-2), 5.00 (d, *J* = 8.5 Hz, H-3), 4.41-4.40 (m, H-4), 4.16-4.05 (m, overlap, H_a-6 and H_b-6), 2.07 (s, CH_3), 2.05 (s, CH_3), 2.04 (s, CH_3), 2.02 (s, CH_3), 2.01 (s, CH_3) [30].

D-Mannose pentaacetate (2c): R_f = 0.41 (hexane/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, CD_3OD) δ ppm: 1,2,3,4,6-penta-O-acetyl-α-D-mannopyranose (**2cαP**) = 6.03 (s, H-1), 5.33-5.27 (m, H-2, H-4 and H-3), 4.28 (dd, *J* = 2.4, 12.3 Hz, H_a-6), 4.14-4.12 (m, H_b-6), 4.07 (d, *J* = 12.4 Hz, H-5), 2.17 (2 CH_3), 2.05 (2 CH_3), 1.97 (CH_3) [29]; 1,2,3,4,6-penta-O-acetyl-β-D-mannopyranose (**2cβP**) = 5.97 (s, H-1), 5.48 (s, H-2), 5.35 (s, H-4), 5.09 (s, H-3), 4.56 (d, *J* = 11.4 Hz, H_a-6), 4.21 (d, *J* = 7.9 Hz, H_b-6), 3.96-3.93 (m, H-5), 2.16-2.03 (5 CH_3) [29].

D-Fructose pentaacetate (2d): R_f = 0.63 (hexane/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, CD_3OD) δ ppm: 1,2,3,4,5-penta-O-acetyl-α-D-fructopyranose (**2dαP**) = 5.38 (s, H-3), 5.36-5.29 (m, H-5 and H-4), 4.40-4.29 (m, H_a-1 and H_b-1), 4.21-4.15 (m, H_a-6 and H_b-6), 2.15 (s, CH_3), 2.09 (s, CH_3), 2.07 (s, CH_3), 2.05 (s, CH_3), 1.97 (s, CH_3); 1,2,3,4,5-penta-O-acetyl-β-D-fructopyranose (**2dβP**) = 5.67 (d, *J* = 8.6 Hz, H-3), 5.56 (m, H-5), 5.20 (d, *J* = 3.4 Hz, H-4), 4.98 (d, *J* = 17.6 Hz, H_a-1), 4.79 (d, *J* = 17.6 Hz, H_b-1), 4.31 (d, *J* = 12.3 Hz, H_a-6), 4.12 (dd, *J* = 4.3, 12.4 Hz, H_b-6), 2.17 (s, CH_3), 2.12 (s, CH_3), 2.07 (s, CH_3), 2.05 (s, CH_3), 2.03 (s, CH_3); 1,2,3,4,6-penta-O-acetyl-α-D-fructofuranose (**2dαF**) = 5.51 (d, *J* = 10.4 Hz, H-3), 4.99-4.97 (m, H-4), 4.65 (d, *J* = 11.8 Hz, H_a-1), 4.55 (d, *J* = 11.8 Hz, H_b-1), 4.12 (d, *J* = 11.6 Hz, H-5), 4.04 (d, *J* = 13.4 Hz, H_a-6), 3.90 (d, *J* = 13.8 Hz, H_b-6), 2.09-2.05 (5×CH_3); 1,2,3,4,6-penta-O-acetyl-β-D-fructofuranose (**2dβF**) = 5.78 (d, *J* = 2.4 Hz, H-3), 5.15–5.14 (m, H-4), 4.64 (d, *J* = 12.0 Hz, H_a-1), 4.54 (d, *J* = 12.0 Hz, H_b-1), 4.43-4.29 (m, H-5 and H_a-6), 4.19 (dd, *J* = 3.6, 12.7 Hz, H_b-6), 2.25 (s, CH_3), 2.15 (s, CH_3), 2.09 (s, CH_3), 2.07 (2 CH_3).

L-Arabinose tetraacetate (2e): R_f = 0.54 (hexane/ethyl acetate, 1:1); ^{1}H NMR (400 MHz, CD_3OD) δ ppm: 1,2,3,4-tetra-O-acetyl-α-L-arabinopyranose (**2eαP**) = 5.70 (d, *J* = 5.5 Hz, H-1), 5.40 (s, H-2), 5.33 (s, H-3), 5.24 (s, H-4), 3.99 (d, *J* = 13.8 Hz, H_a-5), 3.87 (d, *J* = 13.4 Hz, H_b-5), 2.12 (s, CH_3), 2.08 (s, CH_3), 2.05 (s, CH_3), 2.03 (s, CH_3); 1,2,3,4-tetra-O-acetyl-β-L-arabinopyranose (**2eβP**) = 6.29 (s, H-1), 5.40 (s, H-2), 5.36 (s, H-3), 5.27 (s, H-4), 4.13 (d, *J* = 13.1 Hz, H_a-5), 3.81 (d, *J* = 13.3 Hz, H_b-5), 2.15 (s, CH_3), 2.14 (s, CH_3), 2.00 (s, CH_3), 1.99 (s, CH_3); 1,2,3,5-tetra-O-acetyl-α-L-arabinofuranose (**2eαF**) = 6.15 (s, H-1), 5.29 (s, H-2), 5.20 (s, H-3), 5.08 (s, H-4), 4.38-4.35 (m, H_a-5), 4.28-4.25 (m, H_b-5), 2.12-2.00 (4 CH_3); 1,2,3,5-tetra-O-acetyl-β-L-arabinofuranose (**2eβF**) = 6.34 (s, H-1), 5.25-5.23 (m, overlap, H-2), 4.41-4.40 (m, H-3), 4.32-4.31 (m, H-4), 4.23-4.22 (m, H_a-5), 4.20-4.19 (m, H_b-5), 2.05-1.99 (4 CH_3).

RESULTS AND DISCUSSION

This work was begun with recording of ^{1}H NMR spectra of the commercially available monosaccharides (**1a-e**) in

D_2O. The composition of α-pyranose (αP), β-pyranose (βP), α-furanose (αF) and β-furanose (βF) anomers present in the monosaccharides was determined and the data are presented in Table-1.

Now, monosaccharides **1a-e** were peracetylated in the presence of a catalytic amount of $HClO_4$ (acidic condition) or NaOAc (basic condition) under air and neat conditions. A slight excess of acetic anhydride (1.2 equiv. per OH group) was used as an acetylating reagent. After completion of the reaction, the reaction mixture was directly loaded into a silica gel column without work-up and the column was eluted with hexane/ethyl acetate mixtures to afford the corresponding sugar acetates **2a-e**. Molecular structures of all the sugar acetate anomers along with selected ^{1}H NMR chemical shifts (ppm) are presented in **Scheme-I**. The results of the peracetylation reactions and the composition of αP, βP, αF, βF and/or open-chain isomers present in the sugar acetates as determined by ^{1}H NMR are summarized in Table-2.

In consistent with the literature, the $HClO_4$-catalyzed peracetylation of D-glucose (**1a**) exclusively produced α-D-glucose pentaacetate and the use of NaOAc provided β-D-glucose pentaacetate (Table-2, entries 1 and 2). ^{1}H NMR of the purified product obtained through the $HClO_4$-catalyzed peracetylation is shown in Fig. 1a. More or less, a similar result outcome was also observed in the peracetylation of D-galactose (**1b**) (Table-2, entries 3 and 4). In addition, ~ 8% of open-chain form of D-galactose pentaacetate (**2b**) was also observed when the peracetylation of **1b** was performed under the acidic reaction conditions (Table-2, entry 3). In ^{1}H NMR, the aldehydic peak was appeared as a singlet at δ 9.84 ppm. Two doublets at 7.87 (J = 8.2 Hz, 2 H) and 7.09 (J = 8.3 Hz, 2 H) were assigned for the protons H-2, H-3, H-4 and H-5 (Fig. 1b). The chemical shift at δ 3.90 ppm was due to the methylene protons. 1,2,3,5,6-Penta-O-acetyl-β-D-galactofuranose (**2bβF**) was also obtained in the peracetylation of D-galactose (**1b**) under both the reaction conditions employed (Table-2, entries 3 and 4).

In contrast, the peracetylation of D-mannose (**1c**) in both the reaction conditions exclusively produced α-D-mannose pentaacetate (Table-2, entries 5 and 6). Furthermore, in the $HClO_4$-catalyzed peracetylation of **1c**, formation of 1,2,3,5,6-penta-O-acetyl-β-D-mannofuranose (**2cβF**) and open-chain form of D-mannose pentaacetate (**2c**) was also confirmed by NMR spectroscopy (Table-2, entry 5) (Fig. 1c). Anomer **2cβF** was formed in a trace amount (~ 2%) which gave 7 weak signals at δ 6.18, 5.62, 5.56, 5.42, 4.61, 3.86 and 3.80 ppm for the protons in the ring. Formation of ~ 3% of the open-chain form was ascertained by detection of an aldehydic proton as a singlet at δ 9.84 ppm. Two doublets at 7.87 (J = 8.4 Hz, 2 H) and 7.09 (J = 8.1 Hz, 2 H) were assigned for the protons H-2, H-3, H-4 and H-5. For the methylene protons, a singlet at δ 3.90 ppm was also detected.

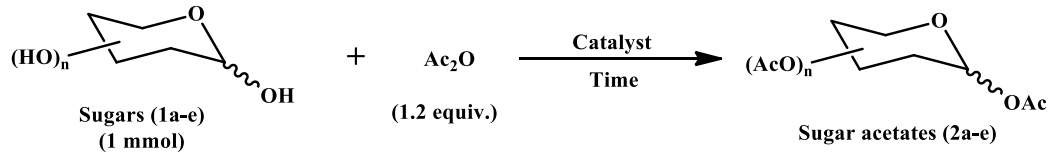
D-Fructose (**1d**) is a ketohexose. In the substrate, β-D-fructopyranose (65.99%) was found to be predominant followed by β-D-fructofuranose (34.01%) at equilibrium in D_2O. In the $HClO_4$-catalyzed peracetylation of **1d**, 1,2,3,4,5-penta-O-acetyl-β-D-fructopyranose (**2dβP**) was the preponderant anomer (62.55%), followed by 1,2,3,4,6-penta-O-acetyl-α-D-fructofuranose (**2dαF**), 1,2,3,4,5-penta-O-acetyl-α-D-fructopyranose (**2dαP**) and then 1,2,3,4,6-penta-O-acetyl-β-D-fructofuranose (**2dβF**) (Table-2, entry 7) (Fig. 1d). On the other hand, using NaOAc as catalyst predominantly produced **2dβF** (Table-2, entry 8). Fortunately, two fractions were compiled in the chromatographic purification of the reaction mixture obtained in later experiment. And, the initially eluted fraction constituted of **2dβF** and **2dβP**; while the subsequent fraction contained **2dαP** and **2dαF**. This separation led us to identify the NMR signals of all the anomers. To the best of our knowledge, synthesis and the NMR spectral assignment of all the pyranose and furanose anomers of D-fructose pentaacetate (**2d**) have never been reported.

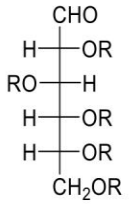
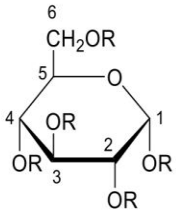
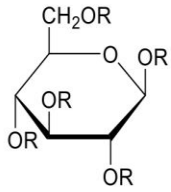
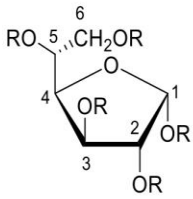
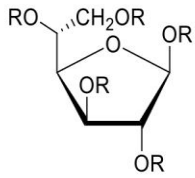
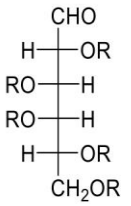
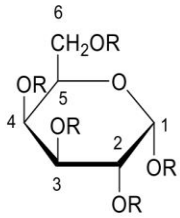
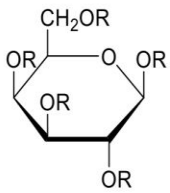
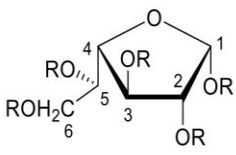
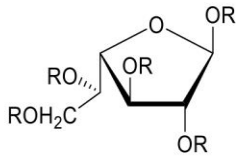
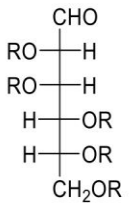
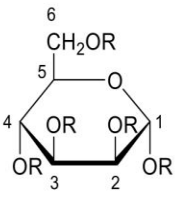
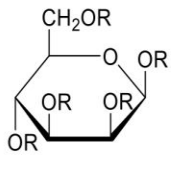
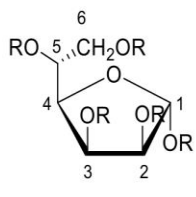
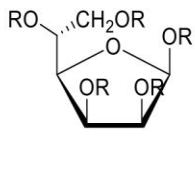
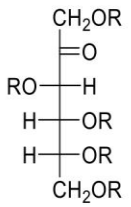
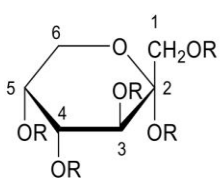
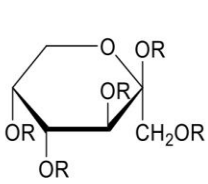
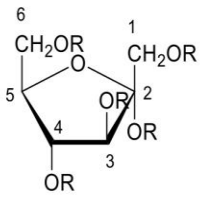
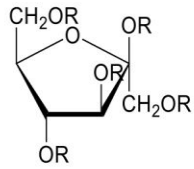
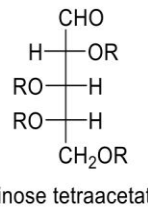
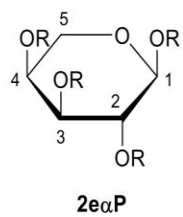
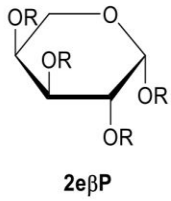
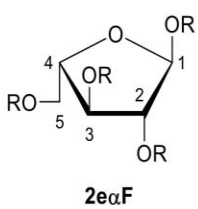
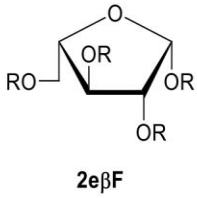
Peracetylation of L-arabninose (**1e**) afforded 1,2,3,4-tetra-O-acetyl-α-L-arabinopyranose (**2eαP**), 1,2,3,4-tetra-O-acetyl-β-L-arabinopyranose (**2eβP**), 1,2,3,5-tetra-O-acetyl-α-L-arabinofuranose (**2eαF**) and 1,2,3,5-tetra-O-acetyl-β-L-arabinofuranose (**2eβF**) (Table-2, entries 9 and 10) (Fig. 1e). For NMR study, Summerfelt *et al.* [34] peracetylated **1e** in the presence of pyridine and reported the chemical shift values of the protons in the anomeric carbons of **2eαP**, **2eβP**, **2eαF** and **2eβF** in $CDCl_3$ but the chemical shifts of all other NMR signals of these compounds have never been reported and are presented above. In many cases, signals of the protons in the

TABLE-1
COMPOSITION OF MONOSACCHARIDE ANOMERS IN D_2O AT ~ 20 ºC

Entry	Monosaccharide	Composition (%)[a]				Ref.
		αP	βP	αF	βF	
1	D-Glucose (**1a**)	36.63 {5.24 (s, H-1)}	63.37 {4.65 (d, H-1)}	0	0	
		[37.63]	[61.96]	[0.11]	[0.28]	[31]
2	D-Galactose (**1b**)	33.67 {5.28 (d, H-1)}	61.62 {4.60 (d, H-1)}	trace	4.71 {5.23 (d, H-1)}	
		[31.20]	[62.70]	[2.30]	[3.68]	[31]
3	D-Mannose (**1c**)	60.24 {5.20 (s, H-1)}	39.76 {4.91 (s, H-1}	0	0	
		[66.23]	[32.85]	[0.64]	[0.24]	[31]
4	D-Fructose (**1d**)	0	65.99 {3.80 (d, H-3)}	0	34.01 {4.12 (d, H-3)}	
		[2.67]	[68.23]	[6.24]	[22.35]	[32]
5	L-Arabinose (**1e**)	60.78 {4.52 (d, H-1)}	35.33 {5.25 (s, H-1)}	trace	3.89 {5.31 (s, H-1)}	
		[60.0]	[35.5]	[2.5]	[2.0]	[33]

[a]Chemical shifts (δ ppm) of the protons in the anomeric carbon are given inside braces. α-Pyranose (αP), β-pyranose (βP), α-furanose (αF) and β-furanose (βF) compositions reported in the literature are shown in square brackets.



Chain	α-Pyranose	β-Pyranose	α-Furanose	β-Furanose
				
D-Glucose pentaacetate (**2a**)	**2aαP**	**2aβP**	**2aαF**	**2aβF**
	6.29 (d, H-1)	5.82 (d, H-1)		
				
D-Galactose pentaacetate (**2b**)	**2bαP**	**2bβP**	**2bαF**	**2bβF**
	6.33 (s, H-1)	5.80 (d, H-1)		6.15 (s, H-1)
				
D-Mannose pentaacetate (**2c**)	**2cαP**	**2cβP**	**2cαF**	**2cβF**
	6.03 (s, H-1)	5.97 (s, H-1)		6.18 (s, H-1)
				
D-Fructose pentaacetate (**2d**)	**2dαP**	**2dβP**	**2dαF**	**2dβF**
	5.38 (s, H-3)	5.67 (d, H-3)	5.51 (d, H-3)	5.78 (d, H-3)
				
L-Arabinose tetraacetate (**2e**)	**2eαP**	**2eβP**	**2eαF**	**2eβF**
	5.70 (d, H-1)	6.29 (s, H-1)	6.15 (s, H-1)	6.34 (s, H-1)

Scheme-I: Peracetylation of monosaccharides (**1a-e**) to afford sugar acetates (**2a-e**) under acidic and basic conditions. R = –$COCH_3$. ^1H NMR chemical shifts for the proton equilibrated in CD_3OD are given

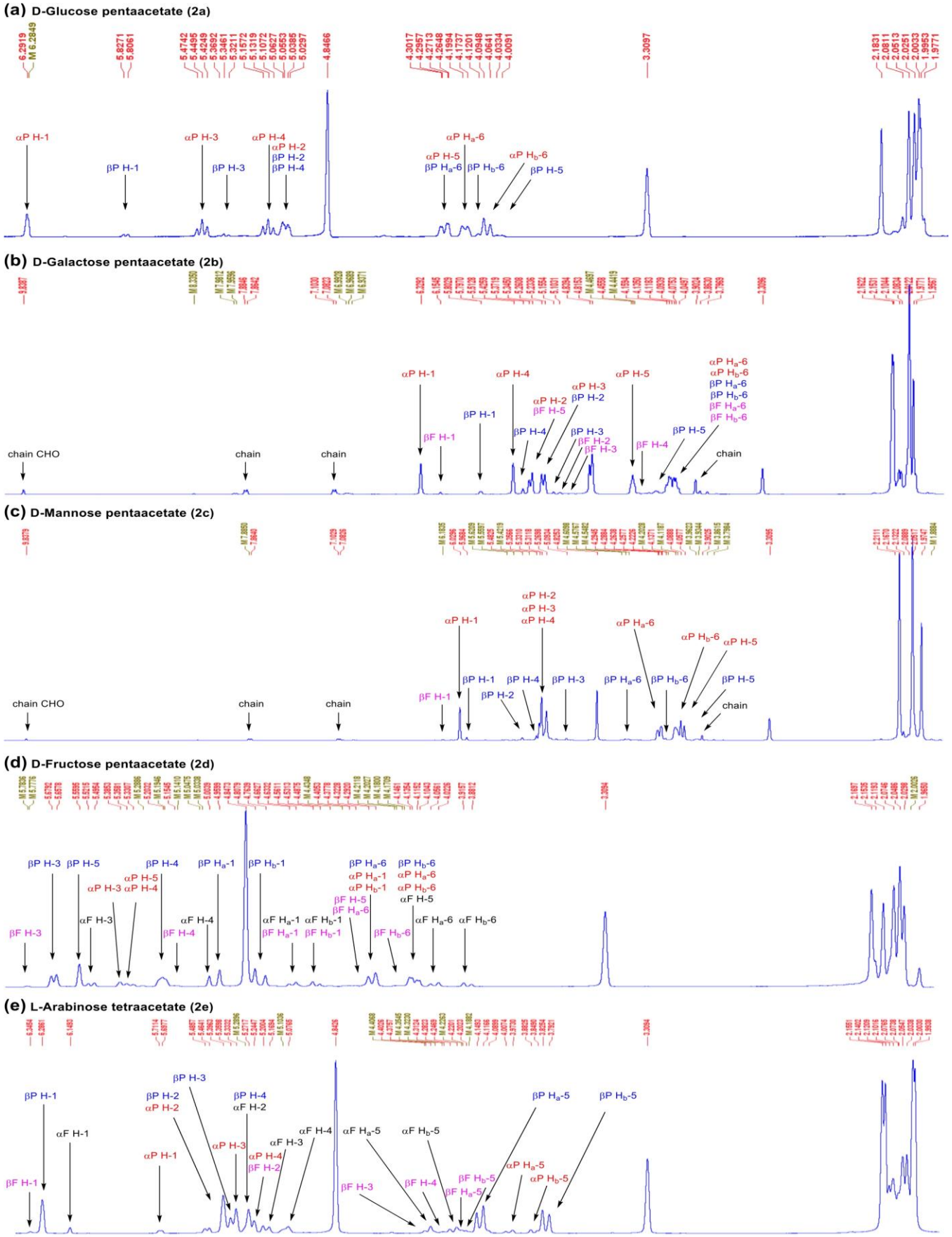


Fig. 1. ^{1}H NMR spectra (in CD_3OD) of sugar acetates (**2a-e**) obtained through the $HClO_4$-catalyzed peracetylation

TABLE-2
SUMMARY OF PERACETYLATION OF MONOSACCHARIDES AT DIFFERENT REACTION CONDITIONS[a]

Entry	Peracetylated product	Catalyst used	Reaction time (h)	Isolated yield (%)	Composition[b]				
					αP	βP	αF	bF	Chain
1	**2a**	$HClO_4$	3	88.2	86.91	13.09	0	0	0
2		NaOAc	3	90.1	28.77	71.23	0	0	0
3	**2b**	$HClO_4$	2	96.0	74.41	11.69	1.19	4.41	8.30
4		NaOAc	2	88.1	25.79	63.51	0	10.70	0
5	**2c**	$HClO_4$	2	90.0	86.31	8.02	0	2.29	3.38
6		NaOAc	3	84.8	93.46	6.54	0	0	0
7	**2d**	$HClO_4$	3	86.7	12.75	62.55	21.77	2.93	0
8		NaOAc	3	74.0	11.95	29.19	7.18	51.68	0
9	**2e**	$HClO_4$	2	75.6	10.44	74.31	10.10	5.15	0
10		NaOAc	3	96.1	62.21	11.78	17.57	8.44	0

[a]Monosaccharides (**1a-e**, 1 mmol) and acetic anhydride (1.2 equiv./OH) were added in the reaction tubes. In acidic condition, $HClO_4$ (1.7 mol%/OH) was added at 0 ºC and then stirred at 23 ºC. In basic condition, NaOAc (30 mol%/OH) was added at 23 ºC and then stirred at 90 ºC. [b]Estimated by ^{1}H NMR analysis of the isolated product in CD_3OD. αP = α-pyranose, βP = β-pyranose, αF = α-furanose and βF = β-furanose.

NMR analysis of the peracetylated sugars were appeared as singlets either due to the rejection of first order coupling, as Horton & Durette [35] have already indicated this probability or magnetic field strength of the NMR spectrophotometer used.

Conclusion

Equilibrium composition of monosaccharides in aqueous solution has been studied by several authors to understand the carbohydrate chemistry. Several catalysts have been explored for the peracetylation of carbohydrates. In this work, we have synthesized peracetylated derivatives of five commercially available monosaccharides by using $HClO_4$ or NaOAc as catalyst. Although NMR spectroscopy becomes an indispensable tool for the conformational analysis, the peak assignment of carbohydrates is always a tedious and challenging task because of obtaining complex ^{1}H NMR spectrum due to the presence of multiple isomers. Since two different reaction conditions were employed for the peracetylation, resulting different anomeric compositions of the acetates, which facilitated in assigning the NMR signals. It can be concluded that the choice of a catalyst has a significant impact on the anomeric distribution of the product, regardless of a substituent effect of the acetyl group.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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