Pergamon

Tetrahedron Vol. 51, No. 23, pp. 6529-6540, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00291-X

A New Method of Acetonation with the Zeolite HY as Catalyst. Synthesis of *O*-Isopropylidene Sugar Derivatives.

Amélia P. Rauter,[a,]* Fernando Ramôa-Ribeiro,[b] Ana C. Fernandes[a] and José A. Figueiredo[c]

[a] Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Rua Ernesto de Vasconcelos, ed. C1, 5º, Campo Grande, 1700 Lisboa, Portugal.

[b] Grupo de Estudos de Catálise Heterogénea, Instituto Superior Técnico,1096 Lisboa.

[c] Departamento de Química, Universidade da Beira Interior, 6200 Covilhã.

Abstract: Zeolite HY proved to be a suitable catalyst for the acetonation of sugars. The method consists of a very simple and economic experimental procedure, in which the catalyst is recovered and can be regenerated. Reaction with D-galactose, L-arabinose, D-glucose, D-xylose, L-sorbose, D-glucofuranurono-6,3-lactone, D-ribose and its methyl glycoside led to the formation of di-*O*- and/or mono-*O*-isopropylidene derivatives in yields from 37-75%. Reaction with D-galactose and L-arabinose afforded the synthesis of the corresponding furanose derivatives as major products, together with minor quantities of the thermodynamically more stable pyranose derivatives.

INTRODUCTION

The condensation of acetone with aldoses, aldosides and ketoses leading to the formation of *O*-isopropylidene derivatives has been widely used in synthesis, structural and conformational studies[1] and its importance to the carbohydrate chemist has become inestimable. Also pharmacological properties were found in *O*-isopropylidene derivatives, namely anti-inflammatory and antipyretic activities of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose derivatives, compounds which also showed a very low toxicity.[2]

Several methods to synthesize *O*-isopropylidene derivatives have been reported in the literature. The conventional method consists of the condensation of a diol with acetone in the presence of a catalyst under anhydrous conditions. As catalyst several agents have been used such as mineral acid,[3] anhydrous zinc chloride together with phosphoric acid,[4] ion exchange resins,[5] anhydrous copper (II) sulfate,[6] iodine,[7] anhydrous ferric chloride,[8] boron trifluoride etherate[9] and anhydrous aluminum chloride.[10] The major products formed in these reactions are reported to be the thermodynamically more stable, except when anhydrous copper(II) sulfate is used. In this case it appears that some kinetic control is introduced.[6]

Other reagents than acetone used for condensation are known, namely 2-methoxypropene, in dimethylformamide and in the presence of *p*-toluenesulfonic acid. This reaction occurs exclusively under kinetic control.[11]

Zeolites have a great number of uses as ion exchangers, molecule filters and catalysts. Synthetic zeolites extended their use to the fine chemical industry and biotechnology. Nowadays they are applied in medicine and in agriculture, having still a great future as catalysts for chemical reactions. The acidity of thermally decomposed ammonium exchanged Y-type zeolites (Y Type is a Faujasite zeolite with a cavity of 7.4 $\overset{o}{A}$)[12] allows their use as catalysts for cumene cracking, isobutane alkylation, hydrocarbon pyrolysis, among others.

In this work we report a new method to synthesize *O*-isopropylidene derivatives by condensation of acetone in the presence of the zeolite HY, a simple procedure leading to moderate to good yields, with possible regeneration of the catalyst.

The method developed consists of the reaction of the monosaccharide with acetone for 48 h at 50° C in the presence of the zeolite HY, obtained by calcination of the ammonium exchanged Y zeolite at 500° C under oxygen. The substrates used were D-galactose, D-glucose, D-xylose, D-ribose, methyl β-D-ribofuranoside, D-glucofuranurono-6,3-lactone, L-arabinose and L-sorbose (see Table 1, Fig.1 and Fig. 2).

The major component of acetonation of D-galactose with an acid catalyst is reported in the literature as having the structure of 1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose (**2**), which is the thermodynamically favored compound. It may be presumed that the furanose derivative **1** is destabilized by the *endo*-5,6-acetal ring and it was only obtained in 3% yield under these experimental conditions.[13] In the absence of acid using anhydrous cupric sulfate as catalyst, in dimethylformamide under reflux, conditions which are known to confer some kinetic control to the acetonation, **1** could be isolated in 22% yield, together with the pyranose form **2** in proportion 6:5, respectively.[6] We found that using the zeolite HY as catalyst, the furanose diacetal **1** was formed in 40% yield, together with the pyranose diacetal **2**, obtained only in 20% yield. This result makes it easier to synthesize the galactofuranose diacetal, which has found only limited use because it was obtained from D-glucose derivatives in three- and six step syntheses[14] or from D-galactose in maximum 22% yield.[6] The structures of the two isomers were established on the basis of their ^{1}H NMR, ^{13}C NMR and mass spectrometric data (see Tables 2, 3 and 4). **2** had the highest mobility in TLC (see Table 1) and its ^{1}H NMR presented a doublet at δ5.57 corresponding to H-1 at higher field than H-1 for **1**, which appeared at δ5.80 as expected for this furanose ring. H-3 of **1** was found at higher field than H-3 of **2**, because the former is in the neighbourhood of a hydroxyl group and the second of an acetal group. The inverse occurred with H-5, which appeared at higher field for **2** than for **1**. The absence of the coupling between H-2 and H-3 in **1** confirmed the proposed furanose structure. The pyranose form **2** presented a coupling constant of $J_{2,3}$ = 2.3 Hz. This three

ring system **2** was described in the literature in terms of a mixed conformation $^{0}T_{2} + B_{2,5}$ for the pyranose ring and ^{3}E and $^{2}T_{1} \rightarrow {}^{2}E$ respectively for the 1,2- and 3,4-dioxolane rings.[14]

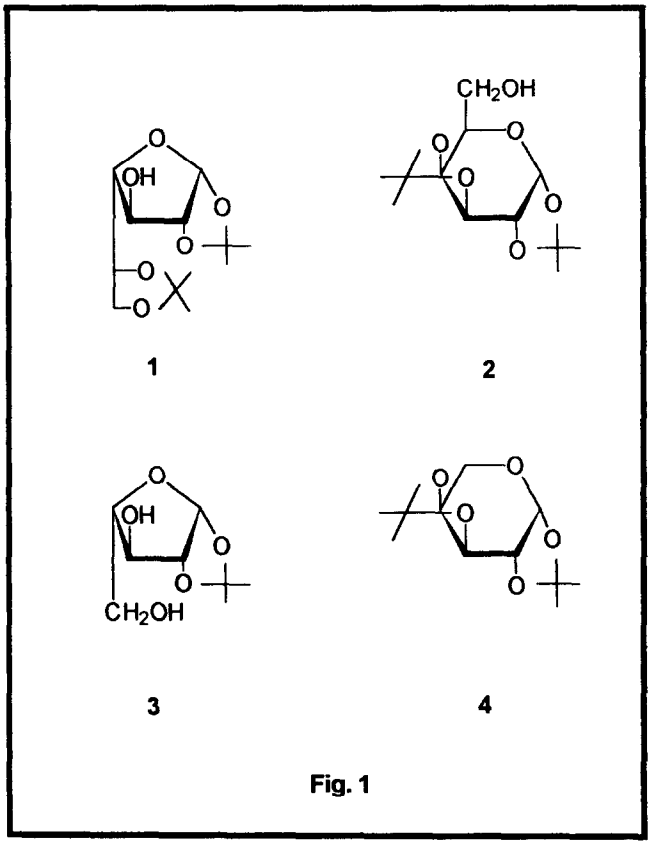

Fig. 1

The electron impact mass spectrometry is an alternative method which allows one to distinguish the di-*O*-isopropylidene furanose- and pyranose forms. The most characteristic process for the furanose form is the scission of C-4/C-5 bond[14] resulting in two typical fragments at m/z 101 with a 100% relative intensity for **1** and m/z 159 with an intensity of 11.8% (see Table 4). In the fragmentation pattern of **2** the base peak was at m/z 245 (M^{+} -Me). The peaks at m/z 187 (M^{+} -Me-acetone), m/z 185 (M^{+} -Me-AcOH) and m/z 127 (M^{+} -acetone-AcOH) appeared with the relative intensities of 68%, 27% and 58%, respectively. The corresponding fragments of the furanose series are expected to be lessened in intensity, what was in fact the case for **1**. The

fragments at m/z 245, 187 and 127 showed relative intensities of 49%, 25% and 23% respectively and the fragment at m/z 185 was absent.

Table 1. Isopropylidenation of Sugars Using Zeolite HY as Catalyst

Substrate	Product	R_f	Yield(%)
D-Galactose	1,2;5,6-di-*O*-isopropylidene-α-D-galactofuranose (**1**)	0.56[a]	40
D-Galactose	1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose (**2**)	0.60[a]	20
L-Arabinose	1,2-*O*-isopropylidene-β-L-arabinofuranose (**3**)	0.12[b]	37
L-Arabinose	1,2;3,4-di-*O*-isopropylidene-β-L-arabinopyranose (**4**)	0.83[b]	24
L-Sorbose	2,3;4,6-di-*O*-isopropylidene-α-L-sorbofuranose (**5**)	0.54[b]	37
L-Sorbose	1,2-*O*-isopropylidene-α-L-sorbopyranose (**6**)	0.64[c]	44
D-Glucose	1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose (**8**)	0.60[b]	50
D-Xylose	1,2;3,5-di-*O*-isopropylidene-α-D-xylofuranose (**9**)	0.74[b]	55
D-Ribose	2,3-*O*-isopropylidene-D-ribofuranose (**10**)	0.41[b]	47
Methyl β-D-ribofuranoside	methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (**11**)	0.59[b]	75
D-glucurono-6,3-lactone	1,2-*O*-isopropylidene-α-D-glucofuranurono-6,3-lactone (**12**)	0.44[a]	57

[a] In ethyl acetate/toluene (1/2). [b] In ethyl acetate/toluene (2/1). [c] In acetone.

When L-arabinose was submitted to the same experimental conditions, the 1,2-*O*-Isopropylidene-β-L-arabinofuranose (**3**) was isolated in 37% yield, together with 24% of the expected di-O-isopropylidenepyranose derivative **4**. Structure elucidation of **3** was easily accomplished by the examination of its ^{1}H NMR spectrum, which showed H-1 at δ5.94 as a doublet, followed by H-2 at δ 4.58, which appeared as a doublet, coupling only with H-1. H-3 was found as a singlet at δ4.26 and both H-5 and H-5' were present as a multiplet between δ3.84 and 3.71. Only two methyl signals corresponding to one isopropylidene were shown. This spectrum was quite different from the one of the di-*O*-isopropylidene-β-L-arabinopyranose (**4**). In this case H-1 appeared at δ 5.51 as expected for a pyranose ring, and H-2 was coupled with H-1 and also with H-3 presenting $J_{2,3}$ = 3.3 Hz, which did not occur with the furanose form. H-5 and H-5' formed an AB system at δ3.86, 3.82, 3.69 and

3.65, each signal appearing as a br s, due to a small coupling with H-4. Four singlets at δ1.54, 1.49, 1.36 and 1.34 corresponded to the methyl groups of the two isopropylidene systems present. The mass spectrum of **4** showed the fragments characteristic for this molecule (see Table 4).

Table 2.[1] H NMR Spectroscopic Data (δ in ppm, J in Hz) in $CDCl_3$

Comp. Nr.	H-1	H-2	H-3	H-4	H-5	H-5'	H-6	H-6'	CH_3	J
1	5.80 d	4.49 d	4.05-3.98 m	3.81-3.75 m	4.30 m	-	4.05-3.98 m	3.81-3.75 m	1.48 1.39 1.31 1.28	$J_{1,2}$=4.2
2	5.57 d	4.33 dd	4.62 dd	4.27 d	3.88-3.73 m	-	3.88-3.73 m	3.88-3.73 m	1.53 1.42 1.34 1.34	$J_{1,2}$=5.0 $J_{2,3}$=2.3 $J_{3,4}$=7.9
3	5.94 d	4.58 d	4.26 brs	4.10 m	3.84-3.71 m	3.84-3.71 m	-	-	1.53 1.33	$J_{1,2}$=4.1
4	5.51 d	4.31 dd	4.56 dd	4.23 br d	3.86[a] 3.82[a] AB syst.	3.69[b] 3.65[b] AB syst.	-	-	1.54 1.49 1.36 1.34	$J_{1,2}$=4.7 $J_{2,3}$=3.3 $J_{3,4}$=6.1 $J_{5,5'}$=12
5	3.92-3.88[c] m	-	4.10 br s	4.09-4.07 m	3.92-3.88 m	-	4.09-4.07 m	4.09-4.07 m	1.47 1.38 1.32 1.28	
6	4.16[d] 4.12[d] 3.95[e] 3.91[e]		3.40 br s	3.74-3.63 m	3.74-3.63 m	-	3.74-3.63 m	3.74-3.63 m	1.49 1.44	$J_{1,1'}$=8.8
7	3.98-3.72[c] m	-	5.04 d	5.44 t	4.99 ddd	-	3.98-3.72 m	3.98-3.72 m	1.48 1.42 2.08[f] 2.03[f] 2.02[f]	$J_{3,4}$=10.3 $J_{4,5}$= 9.7 $J_{5,6}$= 6.0 $J_{5,6'}$=10.3
10[g]	5.43 s	4.59 d	4.85 d	br s	3.81-3.66 m	3.81-3.66 m	-	-	1.58 1.41	$J_{2,3}$=5.9
11	4.97 s	4.58 d	4.83 d	4.43 t	3.72-3.59 m	3.72-3.59 m	-	-	1.49 1.32 3.43	$J_{2,3}$=5.9 $J_{4,5}$=2.4

[a] Part A of AB system, each peak a br s. [b] Part B of AB system, each peak a br s. [c] H-1' is also contained in this multiplet.
[d] Part A of AB system. [e] H-1', part B of AB system. [f] CH_3 of the acetyl groups. [g] Data corresponding to the β-anomer.

Table 3. ^{13}C NMR Spectroscopic Data (δ in ppm) in $CDCl_3$.

Comp. Nr.	C-1	C-2	C-3	C-4	C-5	C-6	CH_3	Cisop.
1	104.91	87.57	76.14	85.88	75.31	65.64	25.23 26.51 26.77 27.39	109.88 113.60
2	96.27	70.55	70.74	71.59	68.05	62.33	24.27 24.91 25.91 26.01	108.66 109.45
3	105.49	87.24	75.93	87.83	62.40	-	26.14 26.88	112.73
5	60.50	97.50	74.35[a]	72.56[a]	79.50	72.95	19.19 25.39 26.42 28.60	110.64 111.29
6	71.90	105.30	71.22[a]	69.98[a]	75.67	63.22	26.28 26.66	112.28
7[b]	71.50	103.54	69.01	71.18	69.19	59.97	26.36 25.90 20.64[c] 20.56[c]	112.50
10	103.07	86.89[a]	81.68[a]	87.82[a]	63.65	-	24.74 26.28	112.06
11	109.87	85.77	81.41	88.29	63.95	-	24.59 26.30 55.41[d]	112.05

[a] These signals may be interchanged because the 2D C-H correlation did not allow us to make an unequivocal assignment. [b] The C=O of the acetyl groups appears at δ170.31, 170.01 and 169.88. [c] CH_3 of the acetyl groups. [d] This signal corresponds to the methoxyl group.

Synthesis of di-*O*-isopropylidene derivatives **5**, **8** and **9** was accomplished by this method, using as substrates L-sorbose , D-glucose and D-xylose, respectively. **5** and **8** are compounds of commercial interest, **5** being used for the synthesis of vitamin C and **8** as starting material for a great diversity of bioactive molecules such as antibiotics, cytotoxic agents, anti-inflammatory and antipyretic agents. The yields obtained were 37%, 50% and 55% respectively for **5**, **8** and **9**. The identification of **8** and **9** was achieved by comparison with authentic samples, synthesized by us using the conventional methods.[4]

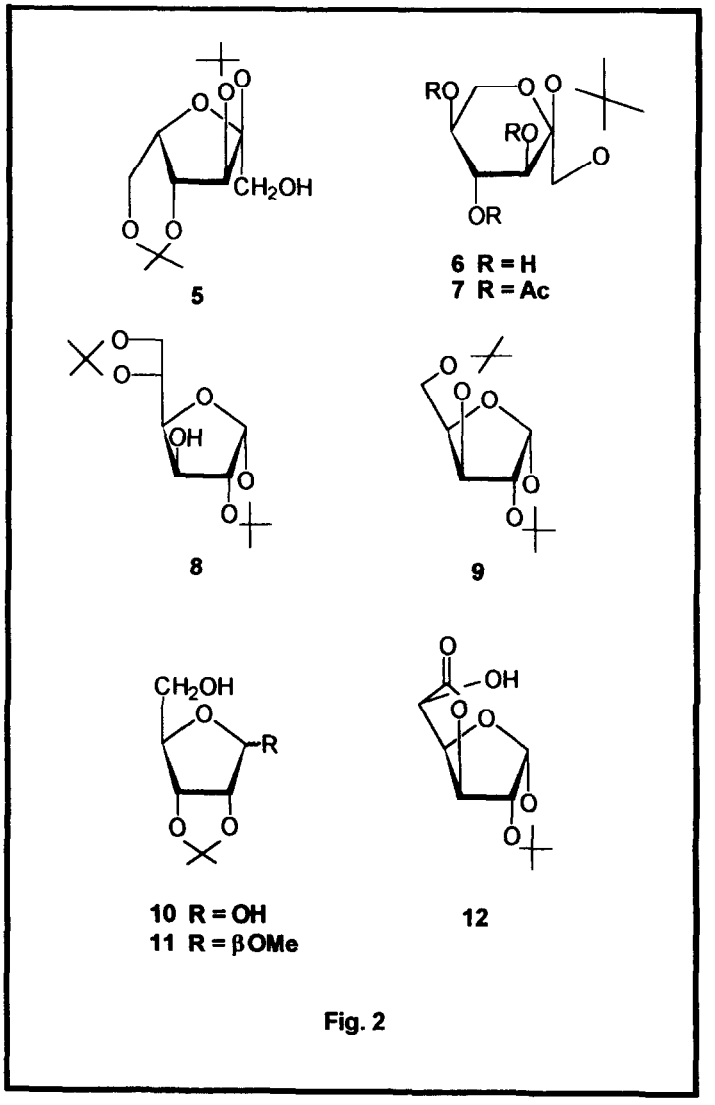

Fig. 2

^{1} NMR spectrum of **5** showed four singlets at δ1.47, 1.38, 1.32 and 1.28, corresponding each to 3 protons, which confirmed the presence of two *O*-isopropylidene groups in this molecule. A broad singlet at δ 4.10 and two multiplets at δ4.09-4.07 and δ3.92-3.88, containing each 3H were assigned by 2D ^{1} NMR, C-H correlation and DEPT as corresponding to H-3 (the broad singlet), to H-6, H-6' and H-4 the multiplet at lower field, and to H-1, H-1' and H-5 the other multiplet present. ^{13}C NMR data confirmed the proposed structure (see Table 3). The mass spectrum of **5** (see Table 4) presented the peak at m/z 159 with relative intensity of 22%, which is characteristic of this sorbose derivative, and was in full agreement with the one reported for it in the literature.[14] The derivative **6** isolated in 44% yield, possessed only one isopropylidene group as it could be inferred from its ^{1} H NMR and ^{13}C NMR (see Tables 2 and 3). Its location was easily deduced by the presence of an AB system at δ4.16, 4.12, 3.95 and 3.91, corresponding to H-1 and H-1', with a $J_{1,1'}$=8.8 Hz. Also C-2 showed a chemical shift of 105.30 ppm, differing from that of **5**, which was 97.50 ppm. The presence of a multiplet at δ3.74-3.63 containing the signals of H-4, H-5, H-6 and H-6' did not allow us to conclude if **6** is in the pyranosidic or in the furanosidic form. Acetylation with acetic anhydride/pyridine overnight at room temperature led to the synthesis of **7**. In its ^{1} H NMR spectrum, the protons assigned to H-3, H-4 and H-5 appeared at lower field than those of **6**, what indicated that the hydroxyl groups at these positions were acetylated, confirming the presence of a pyranosidic form. Also the existance of the 1,2-O-isopropylidene unit was inferred from these results. The trans-diaxial coupling constant $J_{3,4}$ = 10.3 was also in accordance to the proposed structure. Its ^{1} H NMR data were in full agreement with those reported in the literature for this compound.[15] The examination of the spectroscopic data of **6** and **7** allowed assigning the structure of **6** as that of 1,2-*O*-isopropylidene-α-L-sorbopyranose. Its mass spectrum confirmed it exhibiting the peaks at m/z 220 and 205, corresponding to M^+ and M^+ -Me, as well as the characteristic fragments at m/z 145, 117 and 72, which were due to the presence of the 1,2-*O*-isopropylidene group. This was again an interesting result of the acetonation catalysed by the zeolite HY, which allowed a regioselective protection of positions 1 and 2, directly from L-sorbose in 44% yield. This compound **6** is known to be an intermediate for the formation of **5**.[16] When D-ribose, methyl β-D-ribofuranoside and D-glucofuranurono-6,3-lactone were used as starting materials, the corresponding mono-*O*-isopropylidene derivatives **10**, **11** and **12** were obtained and isolated respectively in 47%, 75% and 57% yields. ^{1} H NMR of **10** showed the presence of an anomeric mixture in the proportion α/β (1/6). For the β-anomer, H-1 appeared as a singlet at δ5.43, H-2 and H-3 signals occurred each as a doublet with coupling constants of $J_{2,3}$= 5.9 Hz, and the hydroxymethyl group produced a multiplet at δ3.81-3.66. This is in full agreement with the spectrum of the furanose form, which is the thermodynamically more stable compound. The proposed structure of **10** as 2,3-*O*-isopropylidene-D-ribofuranose, was confirmed by its ^{13}C NMR (see Table 3) and by its mass spectrum (see Table 4).

When methyl β-D-ribofuranoside was submitted to this reaction, the 2,3- monoacetal **11** was isolated in 75% yield. Its ^{1}H NMR (see Table 2) was in perfect agreement with the data known from the literature.[17] Its ^{13}C NMR and electron impact mass spectrometry data (see Tables 3 and 4) confirmed the expected structure. Finally the 1,2-*O*-isopropylidene derivative **12** was prepared when glucofuranurono-6,3-lactone was used as starting material, and isolated in 57% yield. Its structure was confirmed by comparison with an authentic sample.

Table 4. Characteristic Fragments of Mass Spectra
m/z (Relative Intensity in %).

Comp. Nr.	
1	M^+ -Me 245 (49); M^+ -Me-acetone 187 (25); M^+ -$C_5H_9O_2$ 159 (11.8); M^+ - Me-acetone-AcOH 127 (23); $C_5H_9O_2$ 101 (100); $C_4H_5O_2$ 85 (7).
2	M^+ -Me 245 (100), M^+ -Me-acetone 187 (68), M^+ - Me- AcOH 185 (27), M^+ -Me-acetone-AcOH 127 (58), $C_5H_9O_2$ 101 (21); $C_5H_8O_2$ 100 (69), $C_4H_5O_2$ 85 (60); C_2H_3O 43 (91).
4	M^+ -Me 215 (7), M^+ -Me-acetone 157 (15), M^+ -Me-AcOH 155 (3.8), $C_5H_9O_2$ 101 (15), $C_5H_8O_2$ 100 (2.5), M^+ -Me-acetone-AcOH 97 (25), $C_4H_5O_2$ 85 (31.5), C_2H_4O 44 (100), C_2H_3O 43 (79).
5	M^+ 260 (0.5), M^+ -Me 245 (63.6), M^+ -acetone 202 (2.3), M^+ - Me-acetone 187 (5.3), M^+ -$C_5H_9O_2$ 159 (22), $C_6H_9O_2$ 113 (7.6), M^+ -$C_7H_{11}O_4$ 101 (50), $C_4H_5O_2$ 85 (18.2), C_3H_7O 59 (100), C_2H_3O 43 (99).
6	M^+ 220 (1), M^+ -Me 205 (3), $C_6H_9O_4$ 145 (7), $C_5H_9O_3$ 117 (19), C_4H_8O 72 (7), C_3H_7O 59 (31), C_2H_3O 43 (100).
10	M^+ -Me 175 (12.4), M^+ -CH_2OH 159 (7.6), $C_5H_9O_2$ 101 (8.6), $C_4H_5O_2$ 85 (13.8), C_3H_7O 59 (100), C_2H_3O 43 (99).
11	M^+ - Me 189 (18.6), M^+ -CH_2OH 173 (16.8), M^+ - CH_2 - AcOH 113 (28), $C_5H_9O_2$ 101 (5.6), $C_4H_5O_2$ 85 (23.3), C_3H_7O 59 (100), C_2H_3O 43 (99).

In conclusion, a spectroscopic differentiation of isomeric aldo- and keto-hexose-, and aldopentose *O*-isopropylidene derivatives was presented in this work. A new method for their preparation was developed, which consists of a simple experimental procedure, in which the acid catalyst is easily separated by filtration and can be regenerated and used again. The synthesis of furanose derivatives seemed to be favored in comparison to that of the pyranose forms. To the best of our knowledge these are the first results of acetonation reactions with acetone under acid catalysis, which produced a major formation of compounds thermodynamically less stable.

EXPERIMENTAL

^{1}H NMR spectra were measured at 300 MHz with a Brucker CXP 300. Chemical shifts are expressed in parts per million downfield from TMS. ^{13}C NMR spectra were recorded with a Brucker AC-250 P spectrometer at 62.90 MHz. Mass spectra were obtained with a JEOL JMS-DX 300 Spectrometer at 70 eV. The progress of all reactions was monitored by TLC using aluminum sheets precoated with silica gel $60F_{254}$ to a thickness of 0.2 mm (Merck). Preparative TLC was performed with aluminum plates coated with the same type of silica gel to a thickness of 0.5 mm (Merck). Compounds were detected by spraying the sheets with a 3% vanillin-sulfuric acid solution. Column chromatography was conducted under medium pressure by elution of columns of silica gel (0.040-0.063 mm, Merck). Melting points were determined with a melting point apparatus (Tottoli) and were uncorrected.

General procedure for the sugar acetonation. 1 mM of sugar was added to 50 ml of anhydrous acetone, which contained 160 mg of zeolite HY. The reaction mixture was stirred and heated under reflux for 48 hours. The zeolite is separated by filtration and the solution concentrated under vacuum. Column chromatography or preparative TLC was used to purify the sugar derivatives **1-6** and **8-12** obtained, which physical properties were in agreement with those reported for them in the literature.

Zeolite preparation and regeneration. Ammonium exchanged NaY zeolite, obtained by its treatment with a 2M aqueous solution of ammonium nitrate, repeated for three times, was calcinated at 500^{0} C under oxygen ($1.6x10^{-4}$ l/h.g.) with a tubular oven, for 6 hours. The zeolite HY obtained was cooled in an excicator under vacuum and stored to be used several times. Its regeneration is possible by treatment with ammonium chloride, heating at 100-250^{0} C followed by calcination at 500^{0} C under oxygen.[18]

ACKNOWLEDGEMENT

The authors thank Junta Nacional de Investigação Científica e Tecnológica for a research grant, Prof. Manuela Brotas and Prof. João Silva for the zeolite calcination.

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(*Received in UK* 3 *February* 1995; *revised* 10 *April* 1995; *accepted* 12 *April* 1995)