Enzymatic Regioselective Alkoxycarbonylation of Hexoses and Pentoses with Carbonate Oxime Esters

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Hexoses and pentoses have been alkoxycarbonylated with different preparations of *Candida antarctica* lipase, using acetone *O*-(alkoxycarbonyl)oximes. A wide variety of alkoxycarbonyl groups are introduced in an easy manner at the primary hydroxy group of several pentoses and hexoses. Of especial importance are the introduction of allyloxy- and benzyloxy-carbonyl groups.

Selective synthetic transformations of polyhydroxylated compounds such carbohydrates and nucleosides by means of enzymes are increasingly popular. Monoesters of some monosaccharides and disaccharides have been obtained using lipases or proteases in polar organic solvents.[1,2] Different kinds of reagents have been used in enzymatic acylation of sugars, such acids,[3] activated esters,[1,2] enol esters[4] or oxime esters.[5]

A further relevant transformation in the carbohydrate field is regioselective alkoxycarbonylation. Carbonates of primary and secondary hydroxy groups are useful intermediates in carbohydrate chemistry since their selective cleavage in the presence of other functional groups can be easily achieved. Of especial note is the cleavage of benzyl- and allyl-oxycarbonyl groups under neutral conditions.[6,7]

To the best of our knowledge, enzymatic alkoxycarbonylation has been little investigated, the reaction not having been extended to carbohydrate field, despite the importance of these sugar derivatives. Recently the synthesis of fatty carbonate esters[8] and the transesterification of carbonates with a wide variety of alcohols have been described.[9] In our laboratory, the alkoxycarbonylation has been applied to the resolution of several alcohols,[10] and in the synthesis of carbonates of nucleosides.[11]

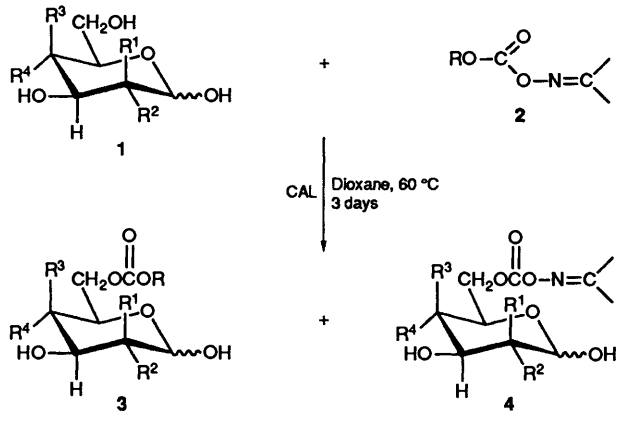
Results and Discussion

Oxime esters have been used in the acylation of carbohydrates[5] and nucleosides,[12] the best results being achieved when lipases from *Pseudomonas cepacia* and *Candida antarctica* were employed; these allowed selective acylation of the primary hydroxy group of the compounds tested. The satisfactory results obtained with the oxime esters in these processes, due to the behaviour of the oxime as a good leaving group, have encouraged us to develop a set of alkoxycarbonylating reagents based on this property.[11] We describe here the synthesis of monocarbonates of hexoses (D-galactose, D-glucose, D-mannose, and L-sorbose) and pentoses (D-ribose and D-, and L-arabinose) using acetone *O*-(alkoxycarbonyl)oximes **2**, previously applied for the preparation of 3′-carbonates of 2′-deoxynucleosides and 5′-carbonates of nucleosides.[11]

The standard organic solvents used in the acylation of sugars with enzymatic catalysis (pyridine,[1] dimethylformamide,[2] 2-pyrrolidone[13]) showed no properties suitable for the enzymatic alkoxycarbonylation of the carbohydrates tested, the starting sugar being recovered without modification. In the alkoxycarbonylation of nucleosides, good results were obtained when less polar solvents, such as tetrahydrofuran or dioxane were used. Preliminary experiments led us to select dioxane as the most suitable for the alkoxycarbonylation of sugars.

Alkoxycarbonylation of Hexoses.—*D-Galactopyranose, D-glucopyranose, D-mannopyranose and L-sorbopyranose.* Chemically selective formation of cyclic and acyclic carbonates of methyl D-glycosides and sugar derivatives using carbamates and thiocarbamates of 2-mercapto-5-methyl-1,3,4-thiadiazole and 3-alkoxycarbonylthiazolidine-2-thiones or 1,1′-carbonyldiimidazole has been previously reported.[14,15]

D-Galactopyranose, D-glucopyranose and D-mannopyranose reacted with acetone oxime carbonate esters in dioxane at 60 °C in presence of lipase from *Candida antarctica* (Novo SP435) to afford compounds **3a–j**, products from selective carbonylation of the primary hydroxy group; product identification was confirmed by a *ca.* 7 ppm shift downfield of the sugar C-6 in the ^{13}C NMR spectra (Scheme 1).[16] Even when a ratio of 1:2 of



Scheme 1 Reaction of D-galactose ($R^1 = R^4 = H$, $R^2 = R^3 = OH$), D-glucose ($R^2 = R^4 = OH$, $R^1 = R^3 = H$) and D-mannose ($R^1 = R^4 = OH$, $R^2 = R^3 = H$) with acetone *O*-(alkoxycarbonyl)oximes **2**

sugar–alkoxycarbonylating reagent was used, only the monocarbonate product was detected. The results are summarized in Table 1. In the reaction of D-glucopyranose and D-mannopyranose with acetone *O*-(allyloxycarbonyl)oxime **2c** and acetone *O*-(benzyloxycarbonyl)oxime **2b** some by-products were obtained (compounds **4a**, **b**). In these cases the allyl and benzyl moieties of the reagents acted as leaving groups to yield the corresponding acetone *O*-(alkoxycarbonyl)oxime derivatives **4a**, **b** in a ratio of *ca.* 1:3 with respect to the acylated compounds **3**. In the case of L-sorbopyranose and D-galactopyranose such products could not be detected. Despite the low polarity of the solvent employed a wide variety of oxycarbonyl groups could be introduced in moderate yields (see Table 2). In absence of the enzyme no reaction was observed.

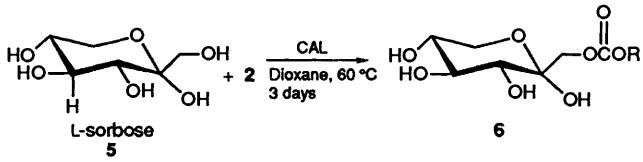
The primary hydroxy group of the ketohexose L-sorbopyranose was alkoxycarbonylated to give the 1-*O*-alkoxycarbonyl

Table 1 Reaction of D-galactose ($R^1 = R^4 = H, R^2 = R^3 = OH$), D-glucose ($R^2 = R^4 = OH, R^1 = R^3 = H$) and D-mannose ($R^1 = R^4 = OH, R^2 = R^4 = H$) with *O*-(alkoxycarbonyl)oximes **2** catalysed by *Candida antarctica* lipase

Entry	R	R^1	R^2	R^3	R^4	Yield (%)[a,b]	$[\alpha]_D^{25}$ (*c*, solvent)	Enzyme	R_F(solvent)[c]
3a	Me	H	OH	OH	H	55	45.4 (0.7, MeOH)	SP435	0.26 (A)
3b	$PhCH_2$	H	OH	OH	H	68	23.5 (2.0, MeOH)	SP435	0.44 (A)
3c	$CH_2{=}CHCH_2$	H	OH	OH	H	43	50.7 (0.8, MeOH)	SP435A	0.43 (A)
3d	Me	H	OH	H	OH	67	50.6 (0.9, MeOH)	SP435	0.24 (A)
3e	$PhCH_2$	H	OH	H	OH	72	48.1 (1.0, H_2O)	SP435	0.37 (A)
3f	$CH_2{=}CHCH_2$	H	OH	H	OH	44	57.6 (0.5, H_2O)	SP435	0.36 (A)
3g	$CH_2{=}CH$	H	OH	H	OH	15	49.4 (0.3, MeOH)	SP435	0.44 (A)
3h	Me	OH	H	H	OH	47	21.2 (0.5, MeOH)	SP435	0.33 (A)
3i	$PhCH_2$	OH	H	H	OH	53	15.0 (2.0, MeOH)	SP435	0.41 (A)
3j	$CH_2{=}CHCH_2$	OH	H	H	OH	44	25.7 (0.5, MeOH)	SP435	0.41 (A)
4a	—	H	OH	H	OH	24[d]	55.8 (0.2, MeOH)	SP435	0.20 (A)
4b	—	OH	H	H	OH	22[e]	12.8 (1.2, MeOH)	SP435	0.20 (A)

[a] Calculated respect to **1**. [b] All compounds were obtained as syrups. [c] Solvent A: AcOEt–MeOH–H_2O (20:2:1). [d] Yield for the reaction of D-glucose with acetone *O*-(benzyloxycarbonyl)oxime. [e] Yield for the reaction of D-mannose with acetone *O*-(benzyloxycarbonyl)oxime.

Scheme 2 Reaction of α-L-sorbopyranose with acetone *O*-(alkoxycarbonyl)oximes **2**



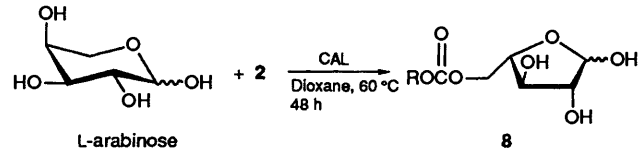
L-sorbose **5** — **6**

Table 2

Entry[a]	R	Yield (%)[b]	$[\alpha]_D^{25}$ (*c*, solvent)	Enzyme	R_F(solvent)[c]
6a	Me	52	−14.6 (2.0, MeOH)	SP382	0.40 (A)
6b	$PhCH_2$	62	−13.3 (2.0, MeOH)	SP382	0.20 (B)
6c	$CH_2{=}CHCH_2$	36	−15.3 (2.0, MeOH)	SP382	0.46 (A)

[a] All compounds were obtained as syrups. [b] Calculated respect to **5**. [c] Solvent system B: CH_2Cl_2–MeOH (98:2).

Scheme 3 Reaction of L-arabinose with acetone *O*-(alkoxycarbonyl)oximes **2**



L-arabinose **7** — **8**

Table 3

Entry[a]	R	Yield (%)[b]	$[\alpha]_D^{25}$ (*c*, solvent)	Enzyme	R_F(solvent)[c]
8a	Me	45	−11.6 (0.6, MeOH)	SP382	0.36 (C)
8b	$PhCH_2$	49	−4.5 (1.5, MeOH)	SP382	0.36 (C)
8c	$CH_2{=}CHCH_2$	38	4.1 (1.5, MeOH)	SP382	0.37 (B)

[a] All compounds were obtained as syrups. [b] Calculated respect to **7**. [c] Solvent C: AcOEt–MeOH (98:2).

derivatives **6a–c** when a different preparation of *Candida antarctica* lipase (Novo SP382) was used.*

With D-fructopyranose the reaction gave a complex mixture of several uncharacterized products.

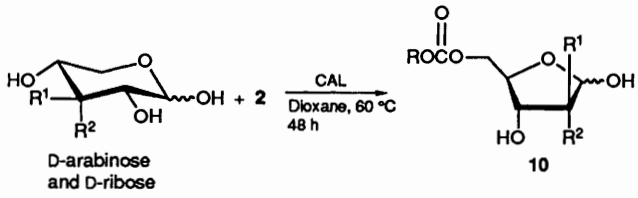
Lipase from *Pseudomonas cepacia* gave unsatisfactory results in the alkoxycarbonylation of sugars, a fact which contrasts with the results achieved for the acylation of the same sugars;[5] this is probably due to structural differences in the reagents used.

* Lipase Novo SP382 is a crude mixture of two lipases (lipase A and lipase B) isolated from *Candida antarctica*. Lipase Novo SP435 is a cloned version of the lipase B of *Candida antarctica* immobilized in a polyacrylic resin, lipase Novo SP435A is the same lipase B immobilized in acurrell.

Alkoxycarbonylation of Pentoses.—*D-Ribose and* D- *and* L-*arabinose.* Different immobilized lipases from *Candida antarctica* were assayed in the alkoxycarbonylation of pentoses: with D-ribofuranose three samples (Novo SP382, Novo SP435 and Novo SP435A) gave good results, whilst with D- and L-arabinose only the Novo SP382 and the Novo SP435 showed good selectivity. The best results were obtained using the conditions previously described (dioxane, 60 °C). The ^{13}C NMR spectra with a downfield shift of *ca.* 4–7 ppm for C-5 led us to deduce that the alkoxycarbonylation occurs at the primary hydroxy group of the furanose ring.[16]

An excess of the alkoxycarbonylating reagent was not used in the case of the pentoses although a wide variety of carbonate moieties could be introduced (see Tables 3 and 4).

Scheme 4 *Reaction of* D-arabinose (R^1 = OH, R^2 = H) and D-ribose (R^1 = H, R^2 = OH) with compounds **2**



D-arabinose and D-ribose **9**

10

Table 4

Entry[a]	R	R^1	R^2	Yield (%)[b]	$[\alpha]_D^{25}$ (*c*, solvent)	R_F(solvent)[c]
10a	Me	H	OH	41[b]	−32.3 (2.1, MeOH)	0.37 (C)
10b	$PhCH_2$	H	OH	52[b]	28.8 (0.9, MeOH)	0.35 (B)
10c	CH_2=$CHCH_2$	H	OH	37[b]	26.7 (0.3, MeOH)	0.40 (B)
10d	Me	OH	H	44[c]	−17.3 (1.1, MeOH)	0.29 (C))

[a] Calculated respect to **9**. [b] Employing enzyme preparation Novo SP435A. [c] Employing enzyme preparation Novo SP382.

Analogously to the acylation process,[5] with D-xylose and D-lyxose, complex mixtures of uncharacterized products were obtained.

Conclusions.—We have shown that the reaction of hexoses with oxime carbonate esters is a general method for the regioselective alkoxycarbonylation of carbohydrates. This methodology, complementary to the chemical selective alkoxycarbonylation, makes feasible the introduction of a wide variety of carbonate groups in an easy manner, employing solvents of low polarity. In addition, we have introduced groups, such as benzyl- and allyl-oxycarbonyl that can be easily removed.[6,7] The reaction has also been extended to the pentoses D-ribose and D- and L-arabinose.

Experimental

Pseudomonas cepacia lipase, Amano PS, was purchased from the Amano Pharmaceutical Co. The enzyme was kept under reduced pressure (10^{-6} mmHg) for two days prior to use. *Candida antarctica* lipase, Novo SP435, was kindly donated by Novo Nordisk A/S. All reagents were of commercial grade and were purchased from the Aldrich Chemie Co.

Acetone *O*-(alkoxycarbonyl)oximes **2** were obtained in almost quantitative yield by direct reaction of the alkyl chloroformates with acetone oxime in pyridine after extraction and distillation under reduced pressure.[11] Dioxane was dried by distillation over $LiAlH_4$ and stored under nitrogen. TLC was performed on pre-coated silica gel 60 sheets Merck F254 (for R_F see Tables). For column chromatography Merck silica gel 60 230–400 mesh was used. As eluents, mixtures of AcOEt–MeOH–H_2O (20:2:1 for hexoses), AcOEt–MeOH (98:2 for pentoses) or CH_2Cl_2–MeOH (90:10, also for pentoses) were used. ^{13}C NMR spectra were obtained using a Bruker 300 AC spectrometer fitted with an Aspect 3000 computer, operating at 300.13 and 75.5 MHz respectively in D_2O or [$^2H_4$]methanol with Me_4Si as internal reference.

Optical rotations were measured using a Perkin-Elmer 241 polarimeter and are recorded in units of 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded on a Perkin-Elmer 1720-X FT spectrometer as KBr pellets.

General Procedure for the Synthesis of Hexose Carbonate Esters.—To the aldohexose (0.45 g, 2.5 mmol) in dry dioxane (20 cm^3) were added the acetone *O*-(alkoxycarbonyl)oxime (5 mmol) and Novo SP435 or Novo SP382 (only for the ketohexose α-L-sorbopyranose) lipase (0.3 g). The reaction mixture was incubated in an orbital shaker at 60 °C and 150 rpm. Monitoring of the reaction by TLC (using the solvent systems detailed in the Tables) showed that after 2–3 days it was complete. The reaction was then stopped by filtering off the enzyme. The crude enzyme was washed twice with methanol (2 × 15 cm^3). The combining filtrate and washings were evaporated under reduced pressure and the resulting syrup was purified by column chromatography to yield the corresponding monocarbonate.

General Procedure for the Synthesis of Pentose Carbonate Esters.—To the pentose (0.38 g, 2.5 mmol) in dry dioxane (20 cm^3) were added the acetone *O*-(alkoxycarbonyl)oxime (2.5 mmol) and Novo SP435 or Novo SP382 lipase (0.2 g); Novo SP435A is also efficient in the alkoxycarbonylation of D-ribose. The mixture was incubated in an orbital shaker at 60 °C and 150 rpm. The reaction was then monitored by TLC in order to control the reaction time. After 2 days the enzyme was filtered off and washed twice with methanol (2 × 15 cm^3). The combined filtrate and washings were evaporated under reduced pressure until dryness and the resulting syrup purified by column chromatography.

Characterization of Products.—Tables 1–4 show the optical rotations and the R_F values. All compounds gave satisfactory microanalyses C ± 0.31, H ± 0.15 the results of which are available as a supplementary publication [Supp. No. 56933 (2 pp.)].*

3a ν/cm^{-1}: 3371 (OH), 1748 (CO); δ_C(D_2O; anomeric ratio α/β = 38/62) 156.85 (C=O), 156.82 (C=O), 97.08 (CH), 92.99 (CH), 73.19 (CH), 73.04 (CH), 72.32 (CH), 69.83 (CH), 69.54 (CH), 69.29 (CH), 68.81 (CH), 68.63 (CH), 68.04 (CH_2), 67.77 (CH_2) and 56.02 (CH_3).

3b ν/cm^{-1} 3380 (OH) and 1747 (CO); δ_C(D_2O; anomeric ratio α/β = 45/55) 155.93 (C=O), 135.61 (C), 129.46 (CH), 128.97 (CH), 97.06 (CH), 92.97 (CH), 73.17 (CH), 72.99 (CH), 72.31 (CH), 70.86 (CH_2), 69.78 (CH), 69.51 (CH), 69.24 (CH), 68.80 (CH), 68.58 (CH), 68.09 (CH_2) and 67.79 (CH_2).

3c ν/cm^{-1} 3399 (OH) and 1748 (CO); δ_C(CD_3OD; anomeric ratio α/β = 42/58) 156.75 (C=O), 156.69 (C=O), 133.51 (CH), 119.06 (CH_2), 98.96 (CH), 94.50 (CH), 75.00 (CH), 74.10 (CH), 73.80 (CH), 71.29 (CH), 71.19 (CH), 70.60 (CH), 70.51 (CH), 69.73 (CH_2), 69.42 (CH), 68.86 (CH_2) and 68.61 (CH_2).

3d ν/cm^{-1} 3393 (OH) and 1745 (CO); δ_C(D_2O; anomeric ratio α/β = 58/42) 156.84 (C=O), 156.80 (C=O), 96.56 (CH), 92.73 (CH), 76.07 (CH), 74.53 (CH), 73.91 (CH), 73.14 (CH),

* For details see Instructions for Authors (1993), *J. Chem. Soc., Perkin Trans. 1*, 1993, Issue 1.

71.91 (CH), 66.99 (CH), 69.89 (CH), 69.70 (CH), 67.23 (CH_2) and 55.94 (CH_3).

3e ν/cm^{-1} 3404 (OH) and 1745 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 53/47) 155.93 (C=O), 135.52 (C), 129.17 (CH), 128.84 (CH), 128.79 (CH), 96.59 (CH), 92.70 (CH), 76.18 (CH), 74.61 (CH), 73.97 (CH), 73.26 (CH), 71.98 (CH), 70.60 (CH_2), 70.52 (CH_2), 70.19 (CH), 70.11 (CH), 69.74 (CH) and 67.50 (CH_2).

3f ν/cm^{-1} 3397 (OH) and 1747 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 55/45) 155.97 (C=O), 131.92 (CH), 119.58 (CH_2), 96.58 (CH), 92.74 (CH), 76.11 (CH), 74.56 (CH), 73.93 (CH), 73.17 (CH), 71.94 (CH), 70.04 (CH), 69.93 (CH), 69.74 (CH + CH_2) and 67.25 (CH_2).

3g ν/cm^{-1} 3427 (OH) and 1751 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 36/64) 153.45 (C=O), 142.67 (CH), 99.28 (CH_2), 96.28 (CH), 92.46 (CH), 75.76 (CH), 74.23 (CH), 73.53 (CH), 72.82 (CH), 71.61 (CH), 70.84 (CH), 69.54 (CH), 69.35 (CH) and 67.24 (CH_2).

3h ν/cm^{-1} 3392 (OH) and 1748 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 69/31) 156.95 (C=O), 94.82 (CH), 94.44 (CH), 74.19 (CH), 73.51 (CH), 71.75 (CH), 71.21 (CH), 70.74 (CH), 70.69 (CH), 67.61 (CH_2), 67.23 (CH), 66.99 (CH) and 56.04 (CH_3).

3i ν/cm^{-1} 3384 (OH) and 1745 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 68/32) 155.95 (C=O), 135.53 (C), 129.22 (CH), 128.86 (CH), 94.74 (CH), 94.35 (CH), 74.27 (CH), 73.54 (CH), 71.71 (CH), 71.25 (CH), 70.82 (CH), 70.74 (CH), 70.60 (CH_2), 67.89 (CH_2), 67.39 (CH) and 67.12 (CH).

3j ν/cm^{-1} 3386 (OH) and 1745 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 68/32) 156.06 (C=O), 131.96 (CH), 119.56 (CH_2), 94.78 (CH), 94.40 (CH), 74.15 (CH), 73.48 (CH), 71.72 (CH), 71.18 (CH), 70.67 (CH), 69.76 (CH_2), 67.58 (CH_2), 67.19 (CH) and 66.95 (CH).

4a ν/cm^{-1} 3391 (OH) and 1767 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 55/45) 168.74 (C=N), 155.44 (C=O), 96.63 (CH), 92.79 (CH), 76.14 (CH), 74.59 (CH), 73.94 (CH), 73.21 (CH), 71.97 (CH), 70.08 (CH), 69.97 (CH), 69.74 (CH), 67.74 (CH_2), 21.32 (CH_3) and 17.01 (CH_3).

4b ν/cm^{-1} 3385 (OH) and 1792 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 72/28) 168.78 (C=N), 155.50 (C=O), 94.84 (CH), 94.45 (CH), 74.13 (CH), 73.49 (CH), 71.75 (CH), 71.20 (CH), 70.73 (CH), 70.62 (CH), 67.97 (CH_2), 67.16 (CH), 66.89 (CH), 21.31 (CH_3) and 16.99 (CH_3).

6a ν/cm^{-1} 3404 (OH) and 1747 (CO); $\delta_C(D_2O)$ 156.64 (C=O), 97.14 (CH), 74.20 (CH), 71.45 (CH), 69.95 (CH), 68.97 (CH_2), 62.57 (CH_2) and 56.21 (CH_3).

6b ν/cm^{-1} 3392 (OH) and 1748 (CO); $\delta_C(D_2O)$ 156.66 (C=O), 137.22 (C), 129.85 (CH), 129.77 (CH), 129.52 (CH), 97.83 (CH), 75.89 (CH), 72.80 (CH), 71.61 (CH), 70.97 (CH_2), 69.74 (CH_2) and 63.80 (CH_2).

6c ν/cm^{-1} 3414 (OH) and 1748 (CO); $\delta_C(D_2O)$ 155.81 (C=O), 131.98 (CH), 119.64 (CH_2), 97.15 (CH), 74.17 (CH), 71.41 (CH), 69.94 (CH), 69.78 (CH + CH_2), 68.86 (CH_2) and 62.57 (CH_2).

8a ν/cm^{-1} 3384 (OH) and 1748 (CO); $\delta_C(CD_3OD$; anomeric ratio α/β = 55/45) 157.21 (C=O), 103.62 (CH), 97.64 (CH), 83.68 (CH), 81.95 (CH), 80.86 (CH), 78.41 (CH), 78.36 (CH), 76.98 (CH), 70.37 (CH_2), 68.71 (CH_2) and 55.37 (CH_3).

8b ν/cm^{-1} 3404 (OH) and 1745 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 61/39) 155.96 (C=O), 135.56 (C), 129.44 (CH), 128.92 (CH), 101.78 (CH), 95.88 (CH), 81.73 (CH), 80.95 (CH), 79.01 (CH), 76.45 (CH), 76.24 (CH), 74.58 (CH), 70.88 (CH_2), 68.86 (CH_2) and 67.80 (CH_2).

8c ν/cm^{-1} 3407 (OH) and 1745 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 57/43) 155.92 (C=O), 131.84 (CH), 119.50 (CH_2), 101.71 (CH), 95.79 (CH), 81.64 (CH), 80.92 (CH), 78.97 (CH), 76.36 (CH), 76.17 (CH), 74.43 (CH), 69.82 (CH_2), 69.71 (CH_2), 68.62 (CH_2) and 67.65 (CH_2).

10a ν/cm^{-1} 3404 (OH) and 1748 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 36/64) 156.92 (C=O), 156.84 (C=O), 101.78 (CH), 97.11 (CH), 80.56 (CH), 80.14 (CH), 75.60 (CH), 71.21 (CH), 71.00 (CH), 70.68 (CH), 68.67 (CH_2), 68.08 (CH_2) and 56.09 (CH_3).

10b ν/cm^{-1} 3377 (OH) and 1748 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 35/65) 155.88 (C=O), 135.55 (C), 129.22 (CH), 128.85 (CH), 101.78 (CH), 96.96 (CH), 80.63 (CH), 80.08 (CH), 75.54 (CH), 71.21 (CH), 71.10 (CH), 70.93 (CH), 70.59 (CH_2), 68.97 (CH_2) and 68.03 (CH_2).

10c ν_{max}/cm^{-1} 3396 (OH) and 1748 (CO); $\delta_C(D_2O$; anomeric ratio α/β = 37/63) 156.05 (C=O), 131.95 (CH), 119.58 (CH_2), 101.73 (CH), 97.07 (CH), 80.55 (CH), 80.09 (CH), 75.55 (CH), 71.19 (CH), 70.92 (2CH), 70.63 (CH), 69.76 (CH_2), 68.56 (CH_2) and 67.99 (CH_2).

10d ν_{max}/cm^{-1} 3393 (OH) and 1745 (CO); $\delta_C(CD_3OD$; anomeric ratio α/β = 38/62) 157.52 (C=O), 103.95 (CH), 97.97 (CH), 83.99 (CH), 82.31 (CH), 81.19 (CH), 78.72 (CH), 77.35 (CH), 70.66 (CH_2), 69.06 (CH_2) and 55.67 (CH_3).

Acknowledgements

The work was funded by DGICYT (Project PB88-0499). R. P. gratefully acknowledges the support of Spanish Ministry of Education and Science for a postgraduate scholarship. We also thank Dr. F. Björkling for the information about the different preparations from *Candida antarctica* lipase of Novo Nordisk A/S and to this company for the generous donation of enzymes.

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Paper 2/05172I
Received 25th *September* 1992
Accepted 5th *November* 1992