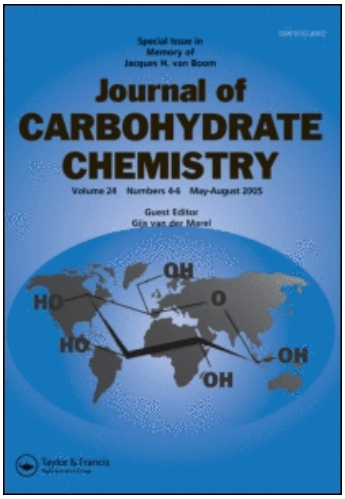

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AUTOCLEAVAGE OF *O*-ISOPROPYLIDENE PROTECTED *O*-PHOSPHONO- AND *O*- THIONOPHOSPHONO ESTERS OF SUGARS

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ABSTRACT

Phosphorylation of D-glucose, D-galactose, D-fructose, glycerol and xylitol acetals with diethoxy- or diphenoxy(thiono)phosphoryl chloride gave the corresponding esters. A novel method of partially and fully deprotecting these compounds, which we have called "autocatalytic cleavage", was effected by simply refluxing in water. Antifungal and insecticidal properties of these compounds are presented.

INTRODUCTION

Numerous *O*-phosphonoesters and *O*- or *S*-thionophosphonoesters, possessing a variety of aliphatic and aromatic groups, are known to possess herbicide and insecticide activities.[1-3] Our interest has been directed towards related esters with partially and fully protected sugars and alditols which enable a choice of HLB (hydrophilic-lipophilic balance) in accordance with the number of unprotected hydroxyl groups.[4,5] The HLB is known to influence phloem mobility and systemic effect.[6] As part of this work we now report a more convenient and regiospecific synthesis of diethoxy- and diphenoxy (thiono) phosphoryl esters of D-glucose, D-galactose, D-fructose, glycerol and xylitol protected by isopropylidene groups. Also, we describe a novel method of deprotection, which we have

termed "autocatalytic cleavage", and which involves simply refluxing in water. The extent of deprotection can be controlled in accordance with reaction time, to give either partially or fully protected derivatives.

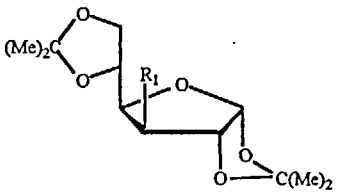
RESULTS AND DISCUSSION

Synthesis of the protected *O*-phosphono ester derivatives.

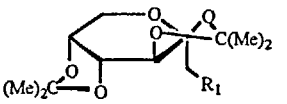
Routes commonly used to synthesize *O*-phosphono esters are (i) phosphite introduction followed by oxidation,[7-11] (ii) substitution of an acidic phosphate hydroxyl group[12,13] and (iii) base catalysed substitution of a phosphoryl halide. Route (iii) has been used by previous workers[14,15] to synthesize the diethoxy- and diphenoxyphosphono esters of diacetone glucose **1a** (84%) and **1c** (63%), required for this study employing thallium ethoxide[14] which is highly toxic. The ester **4c**, also required for the study, was synthesised using phase transfer catalysis (98%) but only on a small scale (10 mg).[15] Route (iii) has the advantage of being direct but suffers from the inconvenience of using the hazardous thallium oxide as a base. In this work we have investigated a variety of reaction conditions (base, solvent) with a view to improving yields but avoiding the use of toxic thallium derivatives. *O*-Isopropylidene derivatives[16] of D-glucose (**1**), D-fructose (**2** and **3**), D-galactose (**4**), xylitol (**5**), glycerol (**6**) were converted to the corresponding diethyl phosphate (**1a-6a**) and diethyl thionophosphate (**1b**, **4b-6b**) derivatives by an improved methodology which involved reaction of diethoxyphosphoryl or diethoxythionophosphoryl chloride (1.2 eq) with a protected monosaccharide and *t*-BuOK (1.5 eq) in CH_2Cl_2. In each case the reaction was complete after 1 h and the pure ester derivative was isolated in good yield (68-94%) except for 3-*O*-diethoxyphosphoryl-1,2:5,6-di-*O*-isopropylidene-β-D-fructopyranose (**3a** ; 36%). Also, a similar methodology using $(PhO)_2PSCl$ was employed to obtain the diphenyl thionophosphates **1d**, **4d-6d** (60-75%). In contrast, modest yields of diphenyl phosphates were obtained using $(PhO)_2POCl$. For example, 3-*O*-diphenoxyphosphoryl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1c**) was obtained in 40% yield along with 2% of the byproduct 6-*O*-diphenoxyphosphoryl-1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose (**1'c**) resulting from phosphoryl group migration. A significant improvement in the yield of **1c** (90%)

was obtained when *t*-BuOK was replaced by 4-dimethylaminopyridine-pyridine (4 eq-4 eq). Similar conditions gave **4c-6c** in 69-98%. In contrast, the related dithiophenyl analogous **1e**, **4e** and **6e** were obtained in poor yields (15%, 16% and 9%) using $(PhS)_2POCl$ perhaps due to the instability of this reagent. The reaction giving **6e** also furnished low yields of unexpected byproducts, namely, 1-*O*-thiophenoxyphosphoryl-2,3-*O*-isopropylidene-D,L-glycerol (**6'e**) (10%) and 1-*O*-phosphoryl-2,3-*O*-isopropylidene-D,L-glycerol (**6''e**) (6%).

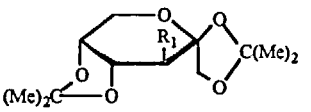
Diethyl dithiophosphates **4f-6f** were prepared from iodinated monosaccharide derivatives and sodium, ammonium and lithium diethyl dithiophosphates (1 eq) in refluxing acetonitrile. However, the best yields were obtained using lithium salts. Thus **5f** and **6f**



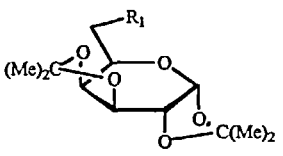
1a : R_1=OP(O)(OEt)2 ; (1h;70%)
1b : R_1=OP(S)(OEt)2 ; (1h;85%)
1c : R_1=OP(O)(OPh)2 ; (1h;90%)
1d : R_1=OP(S)(OPh)2 ; (1h;60%)
1e : R_1=OP(O)(SPh)2 ; (2h;15%)
1f : R_1=SP(S)(OEt)2 ; (4h;0%)



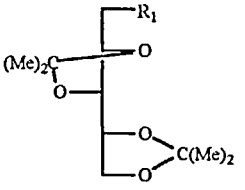
2a : R_2=OP(O)(OEt)2 ; (1h;68%)



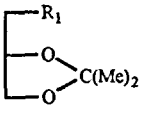
3a : R_1=OP(O)(OEt)2 ; (1h;36%)



4a : R_1=OP(O)(OEt)2 ; (1h;89%)
4b : R_1=OP(S)(OEt)2 ; (1h;80%)
4c : R_1=OP(O)(OPh)2 ; (1h;98%)
4d : R_1=OP(S)(OPh)2 ; (1h;75%)
4e : R_1=OP(O)(SPh)2 ; (2h;16%)
4f : R_1=SP(S)(OEt)2 ; (4h;12%)



5a : R_1=OP(O)(OEt)2 ; (1h;70%)
5b : R_1=OP(S)(OEt)2 ; (1h;94%)
5c : R_1=OP(O)(OPh)2 ; (1h;69%)
5d : R_1=OP(S)(OPh)2 ; (1h;60%)
5f : R_1=SP(S)(OEt)2 ; (4h;60%)



6a : R_1=OP(O)(OEt)2 ; (1h;89%)
6b : R_1=OP(S)(OEt)2 ; (1h;94%)
6c : R_1=OP(O)(OPh)2 ; (1h;75%)
6d : R_1=OP(S)(OPh)2 ; (1h;75%)
6e : R_1=OP(O)(SPh)2 ; (2h;9%)
6f : R_1=SP(S)(OEt)2 ; (4h;51%)

Figure 1 : Protected *O*-phosphono esters

were isolated in 60% and 51% yields respectively, but the yield remained low for the galactose derivative **4f** (12%) and no reaction was observed in the D-glucose case.

Deprotection of phosphono esters.

Partial and total deprotection of phosphono ester derivatives possessing *O*-isopropylidene groups is generally achieved using mineral or organic acidic catalysts [17-19] or wet acidic resins.[20] However, our attempts to prepare 1-*O*-(diethoxyphosphoryl)-D,L-glycerol (**7a**) using these methods were either unsuccessful or gave modest yields (Table 1). In contrast, an excellent yield (94%) of **7a** was obtained by simply refluxing its isopropylidene derivative **6a** in water. We observed an acidic pH (3-4) for aqueous solutions of phosphonoesters in spite of there being no hydroxyl group present on the phosphorous atom. The advantage of this property was realised in the ability of these compounds to undergo deprotection in water, without an additional acidic reagent. Aqueous solutions of the phosphono esters **6a**, **6b** and **6f** (0.4 M in each case) were refluxed to give **7a**, **7b** and **7f**, respectively, in good yield (70-94 %) following removal of water and purification by silica gel column chromatography (Table 1).

Tables 2 and 3 summarise results obtained from the autocatalytic deprotection of **1-5**. Partial and total deprotection were achieved for compounds **1-3** subject to reaction time.

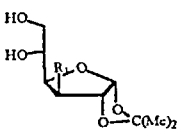
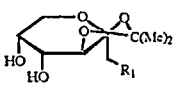
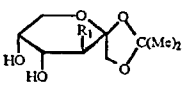
Table 1 : Deacetalation of glycerol diethoxyphosphono esters.

Compound	R_1		solvent	acid catalyst	T (°C)	time (h)	yield (%)
	$OP(O)(OEt)_2$	(7a)	Dioxane-H_2O	HCl (0.6 M)	60	0.25	35
			Dioxane	AcOH (0.6 M)	60	4	0
R_1			Dioxane	AcOH (1.5 M)	60	12	0
OH			Dioxane	Amberlyst wet 15 H^+ (10 $g.L^{-1}$)	60	1	54
OH			H_2O	none	reflux	1	94
	$OP(S)(OEt)_2$	(7b)	H_2O	none	reflux	2	81
	$SP(S)(OEt)_2$	(7f)	H_2O	none	reflux	2.5	70

Partial deprotection.

Partial deprotection of the di-*O*-isopropylidene groups of **1-3** was accomplished due to their differential lability to acid catalysed hydrolysis. Thus, partial deprotection of the diethoxyphosphono esters of D-glucose (**8a**) and D-fructose (**9a** and **10a**) was achieved in 72, 61 and 60% yields, respectively, by refluxing in water for 0.2 - 3 h (Table 2). However, these conditions resulted in poor selectivity for the partial deprotection of the diisopropylidene protected derivative **1b**. Both partially and totally deprotected derivatives **8b** and **11b** were obtained in the ratio 2:1 (isolated in 45 and 25% yield respectively after chromatography) when 95% of the starting material had been consumed (0.8 h). Attempts to improve selective deprotection by lowering the reaction temperature were unsuccessful. In contrast improved selectivity was achieved with 1,4-dioxane-H_2O-HCl at 40°C for 30 min to give **8b** and **11b** in the ratio 5:1 (isolated in 72% and 15% yield respectively after column chromatography).

Table 2 : Partial deprotection of diethoxy-*O*-phosphono esters 1-3a, in refluxing water.

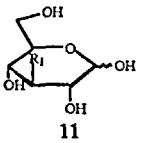
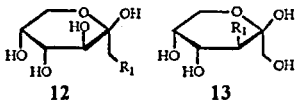
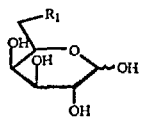
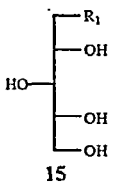
	R_1	compd	solvent	acid catalyst	time (h)	yield (%)
 8	$OP(O)(OEt)_2$	8 a	H_2O	---	0.2	72
	$OP(S)(OEt)_2$	8 b	H_2O	---	0.8	45
			[a] H_2O 1,4-Dioxane	HCl (0.4 N)	0.5	72
 9  10	$OP(O)(OEt)_2$	9 a	H_2O	---	1.2	61
	$OP(O)(OEt)_2$	10a	H_2O	---	3	60

a. T=40°C

Total deprotection.

The di-*O*-isopropylidene derivatives **1a, 1b, 2a, 4a** and **5f** were fully deprotected by refluxing in water for 1-7 h to give **11a, 11b, 12a, 14a** and **15f** respectively in yields ranging from 50 to 69 % (Table 3). However, under these conditions, **4b** remained

Table 3 : Total deprotection of diethoxy-*O*-phosphono esters 1-4a, 1b, 5b and 5f in refluxing water.

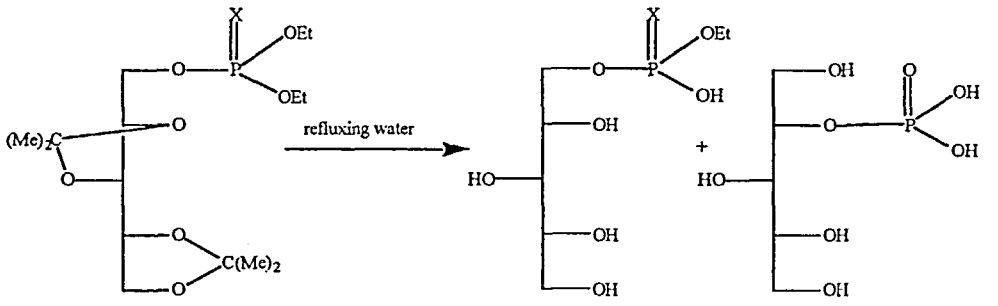
	R_1	compd	solvent	acid catalyst	time (h)	yield (%)
 11	$OP(O)(OEt)_2$	11 a	H_2O	---	3	63
	$OP(S)(OEt)_2$	11 b	H_2O	---	1	68
 12 13	$OP(O)(OEt)_2$	12 a	H_2O	---	7	69
	$OP(O)(OEt)_2$	13 a	H_2O	---	5	0 [a]
 14	$OP(O)(OEt)_2$	14 a	H_2O	---	4	63
	$OP(S)(OEt)_2$	14 b	H_2O	---	5	0 [b]
			^cH_2O 1,4-Dioxane	HCl (0.4 N)	3	43
 15	$OP(O)(OEt)_2$	15 a	H_2O	---	1	0 [d]
	$OP(S)(OEt)_2$	15 b	H_2O	---	2	0 [d]
			^cH_2O 1,4-Dioxane	HCl (0.4 N)	0.5	82
	$SP(S)(OEt)_2$	15 f	H_2O	---	5	50

a. initial product was decomposed ; b. initial product was recovered ; c. T=60°C ; d. monoethoxy deprotected derivatives and acidic ester were observed.

undissolved after 5 h. Solubility was effected using 1,4-dioxane-H_2O (4:1) but neither partial nor total deprotection was achieved after refluxing for 5 h.

Alternatively, treatment of **4b** with 1,4-dioxane-H_2O-HCl for 3 h afforded the fully deprotected derivative **14b** in 43% yield (Table 2). Reaction of the di-*O*-isopropylidene-D,L-xylitol esters **5a** in refluxing water gave a mixture of the fully deprotected monoethoxy ester **15'a** (95% yield in 1 h) and the rearrangement product **15"** (Scheme 1). Similarly deprotection of **5b** gave **15'b** (95% yield in 2 h) and **15"**. Also, **15"** could be obtained by longer refluxing (6-15 h) of either **5a** or **5b** in water. The structure of **15"** was determined by ^{13}C and ^{31}P NMR spectroscopy and mass spectrometry. In comparison with the parent diacetone xylitol **5a**, the derivative **15"** showed a downfield shift for the resonance of both C-2 (ca. +11.5 ppm) and C-1 (ca. 4.1

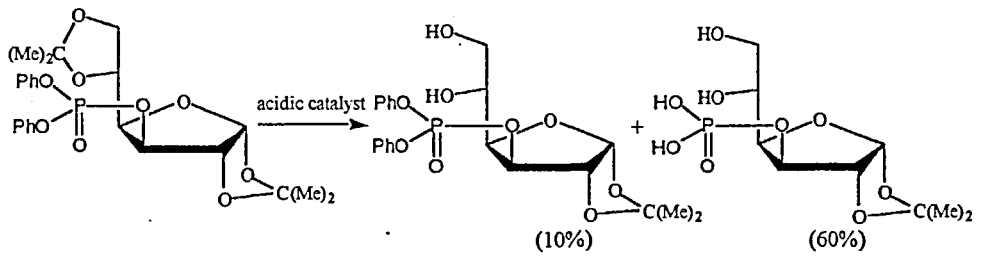
ppm). The absence of sulfur in **15"** was confirmed by an upfield shift of ^{31}P NMR (- 1,9 *vs* + 60 ppm) and mass spectrometry (M-H+ : 230.8).



Scheme 1

Similarly deprotection of **5a** with the addition of an acid catalyst (wet acidic resin or 1,4-dioxane-H_2O-HCl), gave **15'a** and **15"**. The main advantage of the autocatalytic method is the convenience of workup. In the case of the thioester **5b** both diacetal groups remained intact following deprotection using an added acid catalyst to give **15b** as the main product (82%). All attempts to fully deprotect the di-*O*-isopropylidene fructose ester **3a** using refluxing water, HCl-dioxane and acidic resin resulted in decomposition. Also, the attempted autocatalytic cleavage of the diphenyl phosphate and diphenyl thiophosphate derivatives proved unsuccessful. In most cases, over the range of compounds **1-5**, reaction with an added acid catalyst resulted in decomposition. However, limited success was obtained in the case of the conversion of **1c** to **8c** with 1,4-dioxane-HCl or acidic resin in yields of 10% and 7% respectively. Each of these reactions also gave **8'** in about 60% yield. Attempts to effect total deprotection of **1c** using similar conditions resulted in decomposition (Scheme 2).

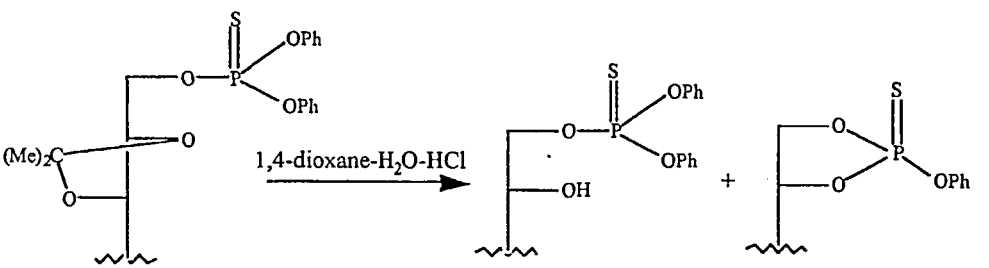
The diphenyl thionophosphates of xylitol (**5d**) and glycerol (**6d**) were fully deprotected using 1,4-dioxane-H_2O-HCl to give **7d** and **15d**, respectively, in modest



1c 8c 8'

Scheme 2

yields (25% and 15%) (Scheme 3). Each of these reactions also gave the respective phenyl thionophosphates **15'd** (20%) and **7'd** (5%) as byproducts. These results are similar to those observed for the corresponding diethoxyphosphoryl analogues (Scheme 1), with the exception that the cyclic phenyl thionophosphates **15'd** and showed no tendency to cleave and thereby give the corresponding 2-*O*- phosphoryl derivative (**15"**).



5 d
6 d

15 d
7 d

15'd
7'd

Scheme 3

Biological activity.

Preliminary investigations to detect antifungal activity against *Fusarium oxysporum* f. sp. *Lini* and *Botrytis cinerea*, which usually contaminate flax cultures, were conducted *in vitro* using solid media (Czapek Yeast Agar and glycine agar)[21] and a

liquid medium (Fayret).[22] Among the products tested, compounds **8b**, **11b** and **14b** caused significant mycelium alterations for the two fungi, without growth inhibition. The optical microscopic analysis of spores revealed hyphea deformation which was characterized by an increase in cell size. Sporulation inhibition was observed for *Fusarium* with 3-*O*-(diethoxythionophosphoryl)-D-glucopyranose (**11b**) at 500 ppm. In addition the 6-*O*-(dithiophenoxyphosphoryl) ester of di-*O*-isopropylidene galactose (**4e**) showed a competitive inhibition of acetylcholinesterase at 2.4 mM , indicating their potential for use as insecticides.[23]

EXPERIMENTAL

General Procedure. Melting points were determined on a digital melting-point apparatus (Electrothermal) and are uncorrected. Optical rotations were recorded at 22 °C in $CHCl_3$ or MeOH solutions with a digital polarimeter DIP-370 (JASCO) using a 1 dm cell. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or Me_2SO-d_6 (internal Me_4Si), respectively, at 300.13 MHz and at 75.47 MHz (Bruker AM WB-300). TLC was performed on Silica F254 (Merck) and detection by UV light at 254 nm or by charring with phosphomolybdic-H_2SO_4 reagent. Column chromatography was effected on Silica Gel 60 (Merck, 230 mesh). Me_2CO, hexane, ether and each industrial grade were supplied by CINAS. Elemental analyses were performed by the Service Central de Micro-Analyse du Centre National de Recherche Scientifique (Vernaison, France), bases and solvents were supplied by ACROS or ALDRICH. Diethoxyphosphoroester of di-*O*-isopropylidene glucose (**1a**) and the diphenoxyphosphoroesters of di-*O*-isopropylideneglucose (**1c**) and di-*O*-isopropylidenegalactose (**4c**) were obtained using the following methodologies in 70, 90 and 98% respectively. The physical chemical data are in accordance with values reported.[7,8]

1-*O*-(Diethoxyphosphoryl)-2,3:4,5-di-*O*-isopropylidene-α-D-fructopyranose (2a). *t*-BuOK (3.1 g, 28 mmol) was added to a stirred solution of 2,3:4,5-di-*O*-isopropylidene-α-D-fructopyranose (5.0 g, 19 mmol) and diethoxyphosphoryl chloride (4.1 g, 24 mmol) in CH_2Cl_2 (56 mL) at room temperature for 1 h. A saturated aqueous solution of NH_4Cl was added and the mixture stirred for a further 10 min. The aqueous phase was extracted with CH_2Cl_2, the organic phase was dried (Na_2SO_4) and the solvent

was evaporated under reduced pressure. The crude product was purified on a silica gel column eluted with hexane-ether (1:4) to give 5.2 g (68%) of **2a**. $[\alpha]_D^{22}$ -50° (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 4.29 (dd, 1H, $J_{4,5}$ = 7.8 Hz, H-4), 4.05 (d, 1H, $J_{3,4}$ = 2.3 Hz, H-3), 3.91 (d, 1H, $J_{5,6}$ = 0 Hz, H-5), 3.83 (m, 4H, OCH_2), 3.75 (dd, 1H, $J_{1,1'}$ = 11.0 Hz, $J_{H\text{-}1,P}$ = 5.3 Hz, H-1), 3.68 (dd, 1H, $J_{H\text{-}1',P}$ = 4.8 Hz, H-1'), 3.59 (d, 1H, $J_{6,6'}$ = 13.0Hz, H-6), 3.39 (d, 1H, $J_{5,6'}$ = 0 Hz, H-6'), 1.03 (m, 6H, CH_2CH_3), 1.33, 1.22, 1.09, 1.02 (s, 12H, $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 109.2, 108.7 (2C, $C(CH_3)_2$), 101.3 (d, $J_{C\text{-}2,P}$ = 10.1 Hz, C-2), 70.6 (C-5), 69.9 (C-4), 69.7 (C-3), 67.0 (C-1), 63.6 (2C, OCH_2), 61.1 (C-6), 26.3, 25.6, 25.1, 23.9 (4C, $C(CH_3)_2$), 15.9 (2C, CH_2CH_3).

Anal. Calcd for $C_{16}H_{29}O_9P$ (396.47): C, 48.48; H, 7.37; P, 7.81. Found: C, 48.51; H, 7.31; P, 7.83.

3-*O*-(Diethoxyphosphoryl)-1,2:4,5-di-*O*-isopropylidene-α-D-fructopyranose (3a). Likewise, 1,2:4,5-di-*O*-isopropylidene-α-D-fructopyranose (5.0 g, 19mmol) gave, after 1 h, 2.8 g (36%) of **3a**. $[\alpha]_D^{22}$ -169° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 4.32 (dd, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 4.25 (d, 1H, $J_{1,1'}$ =9.3 Hz, H-1), 4.19 (d, 1H, $J_{3,4}$ =7.7 Hz, $J_{H\text{-}3,P}$ = 5.2 Hz, H-3), 4.13 (m, 1H, $J_{5,6}$ = 2.2 Hz, H-5), 4.08 (m, 4H, OCH_2), 4.05 (d, 1H, H-1'), 4.02 (H-6), 3.98 (H-6'), 1.48, 1.39, 1.33, 1.27 (s, 12H, $C(CH_3)_2$), 1.25 (m, 6H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 111.5, 108.8 (2C, $C(CH_3)_2$), 103.4 (C-2), 75.4 (d, $J_{C\text{-}3,P}$ = 2.9 Hz, C-3), 75.2 (d, $J_{C\text{-}4,P}$ = 5.3 Hz, C-4), 73.5 (C-5), 71.3 (C-1), 59.9 (C-6), 63.4 (d, 1C, $J_{CH_2\text{-}P}$ = 5.3 Hz, OCH_2), 63.2 (d, 1C, $J_{CH_2\text{-}P}$ = 7.1 Hz, OCH_2), 29.3, 27.5, 25.9, 25.6 (4C, $C(CH_3)_2$), 15.3 (d, 1C, $J_{CH_3\text{-}P}$ = 6.9 Hz, CH_2CH_3), 15.2 (d, 1C, $J_{CH_3\text{-}P}$ = 7.2 Hz, CH_2CH_3).

Anal. Calcd for $C_{16}H_{29}O_9P$ (396.47): C, 48.48; H, 7.37; P, 7.81. Found: C, 48.44; H, 7.61; P, 7.80.

6-*O*-(Diethoxyphosphoryl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (4a). Likewise, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5.0 g, 19 mmol) gave, after 1 h, 6.8 g (89%) of **4a**. $[\alpha]_D^{22}$ -274° (*c* 1.4, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 5.37 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 4.50 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 4.17 (dd, 1H, $J_{2,3}$= 2.5 Hz, H-2), 4.11 (dd, 1H, $J_{4,5}$ = 1.7 Hz, H-4), 4.05 (dd, 1H, $J_{6,6'}$ = 9.4 Hz, H-6), 3.98 (m, 4H, CH_2CH_3), 3.89 (dd, 1H, $J_{5,6'}$ = 6.5 Hz, H-6'), 3.88 (ddd, 1H, $J_{5,6}$ = 5.2Hz, H-5), 1.18-1.17 (m, 6H, 1.32 CH_2CH_3), 1.38, 1.28, 1.23, 1.15 (s, 12H, $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 108.5,107.7 (2C, $C(CH_3)_2$), 95.2 (C-1), 70.5 (2C, C-3, C-4), 70.3 (C-2), 66.8 (d, $J_{C\text{-}5,P}$ = 6.2 Hz, C-5), 65.7 (d, $J_{C\text{-}6,P}$ = 3.8 Hz, C-6), 63.7 (d, 2C, $J_{CH_2\text{-}P}$ =4.5 Hz, OCH_2), 24.7, 23.7, 23.4 (4C, $C(CH_3)_2$), 15.0 (d, 2C, $J_{CH_3\text{-}P}$ = 5.1 Hz, CH_2CH_3).

Anal. Calcd for $C_{16}H_{29}O_9P$ (396.47): C, 48.48; H, 7.37; P, 7.81. Found: C, 47.94; H, 7.31; P, 7.97.

1-*O*-(Diethoxyphosphoryl)-2,3:4,5-di-*O*-isopropylidene-D,L-xylitol (5a). Likewise, 2,3:4,5-di-*O*-isopropylidene-D,L-xylitol (4.4 g, 19 mmol) gave, after 1 h, 4.8 g

(70%) of **5a**. ^{1}H NMR ($CDCl_3$) δ 3.99-3.89 (m, 4H, H-4, H-2, H-1, H-1'), 3.92 (m, 4H, OCH_2), 3.85 (dd, 1H, $J_{4,5}$ = 6.7 Hz, H-5), 3.82 (dd, 1H, $J_{2,3}$ = 7.2 Hz, $J_{3,4}$ = 4.4Hz, H-3), 3.66 (dd, 1H, $J_{4,5'}$ = 7.2 Hz, $J_{5,5'}$ = 8.2 Hz, H-5') , 1.38, 1.32, 1.30 (s, 12H, $C(CH_3)_2$), 1.21 (m, 6H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 110.0,109.6 (2C, $C(CH_3)_2$), 77.1 (C-3), 75.7 (d, $J_{C\text{-}2,P}$ = 7.0 Hz C-2), 74.8 (C-4), 66.6 (C-1), 65.4 (C-5), 63.8 (2C, OCH_2), 26.9, 26.0, 25.2 (4C, $C(CH_3)_2$), 15.9 (2C, CH_2CH_3).

Anal. Calcd for $C_{15}H_{29}O_8P$ (348.67): C, 48.90; H, 7.93; P, 8.40. Found: C, 48.57; H, 8.10; P, 8.28.

1-*O*-(Diethoxyphosphoryl)-2,3-*O*-isopropylidene-D,L-glycerol (6a). Likewise, 2,3-*O*-isopropylidene-D,L-glycerol (2.5 g, 19 mmol) gave, after 1 h, 4.5 g (89%) of **6a**. ^{1}H NMR ($CDCl_3$) δ 4.17 (m, 1H, $J_{1,2}$ = 5.8 Hz, H-2), 3.99 (m, 4H, OCH_2), 3.88 (dd, 1H, $J_{3,3'}$ = 8.6 Hz, H-3), 3.84 (dd, 1H, H-1), 3.79 (dd, 1H, $J_{1',2}$ = 5.7Hz, H-1'), 3.71 (dd, 1H, $J_{2,3'}$ = 2.0 Hz, H-3'), 1.21 (m, 6H, CH_2CH_3), 1.29, 1.21 (s, 6H, $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 108.7 ($C(CH_3)_2$), 73.0 (d, $J_{C\text{-}2,P}$ = 7.4 Hz,C-2), 68.2 (C-1), 65.1 (d, $J_{C\text{-}3,P}$ = 4.7 Hz, C-3), 62.8 (2C, OCH_2), 25.6, 24.2 (2C, $C(CH_3)_2$), 15.0 (d, 2C, $J_{CH_3\text{-}P}$ = 6.0 Hz, CH_2CH_3).

Anal. Calcd for $C_{10}H_{21}O_6P$ (268.25): C, 44.77; H, 7.89; P, 11.54. Found: C, 43.80; H, 8.54; P, 11.44.

3-*O*-(Diethoxythionophosphoryl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (1b). Likewise, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (5.0 g, 19 mmol) and diethoxythionophosphoryl chloride (4.5 g, 24 mmol) gave, after 1 h, 6.8 g (85%) of **1b**. $[\alpha]_D^{22}$ -12° (*c* 1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 5.77 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.78 (dd, 1H, $J_{3,4}$ = 2.5 Hz, $J_{H\text{-}3,P}$ = 10.3 Hz, H-3), 4.60 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 4.14 (m, 1H, $J_{5,6'}$ = 5.4 Hz, H-5), 4.02 (m, 2H, OCH_2), 4.01 (dd, 1H, $J_{4,5}$ = 1.7 Hz, H-4), 4.00 (m, 2H, OCH_2), 3.94 (dd, 1H, $J_{5,6}$ = 5.9 Hz, H-6), 3.85 (dd, 1H, $J_{6,6'}$ = 9.2 Hz, H-6'), 1.28 (m, 6H, CH_2CH_3), 1.17 (s, 12H, $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ111.2,108.1 (2C, $C(CH_3)_2$), 103.9 (C-1), 82.5 (C-2), 79.3 (d, $J_{C\text{-}4,P}$ = 8.3 Hz, C-4), 79.2 (C-3), 71.2 (C-5), 66.0 (C-6), 65.5 (2C, OCH_2), 25.7, 25.2, 24.2 (4C, $C(CH_3)_2$), 14.8 (d, 2C, $J_{CH3,P}$ = 6.0 Hz, CH_2CH_3).

Anal. Calcd for $C_{16}H_{29}O_8PS$ (412.53): C, 46.59; H, 7.08; P, 7.50; S, 7.77. Found: C, 46.10; H, 7.06; P, 7.65; S, 7.65.

6-*O*-(Diethoxythionophosphoryl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (4b). Likewise, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5.0 g, 19 mmol) gave, after 1 h, 6.4 g (80%) of **4b**. $[\alpha]_D^{22}$ -8° (*c* 1.0, $CHCl_3$). mp 42.5-44.0 °C. ^{1}H NMR ($CDCl_3$) δ 5.40 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 4.49 (dd, 1H, $J_{3,4}$ = 7.9Hz, H-3), 4.20 (dd, 1H, $J_{2,3}$ = 2,4 Hz, H-2), 4.14 (dd, 1H, $J_{4,5}$ = 1.7 Hz, H-4), 4.10-3.98 (m, 3H, H-6, H-6', H-5), 4.04 (m, 4H, OCH_2), 1.32 (m, 3H, CH_2CH_3), 1.22 (m, 3H, CH_2CH_3), 1.42, 1.23, 1.21, 1.18 (s, 12H, $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 108.5, 107.7 (2C, $C(CH_3)_2$), 95.2 (C-1), 69.7 (2C, C-3, C-4), 69.5 (C-2), 66.8 (d, $J_{C\text{-}5,P}$ = 6.7Hz, C-5), 65.4 (C-6), 63.3 (2C, OCH_2), 25.0, 24.9, 23.9, 23.4 (4C, $C(CH_3)_2$), 14.7 (d, 2C, $J_{CH3,P}$ = 8.3 Hz, CH_2CH_3).

Anal. Calcd for $C_{16}H_{29}O_8PS$ (412.53): C, 46.59; H, 7.08; P, 7.50; S, 7.77. Found: C, 46.67; H, 7.37; P, 7.37; S, 7.65.

1-*O*-(Diethoxythionophosphoryl)-2,3:4,5-di-*O*-isopropylidene-D,L-xylitol (5b). Likewise, 2,3:4,5-di-*O*-isopropylidene-D,L-xylitol (4.4 g, 19 mmol) gave, after 1 h, 4.8 g (94%) of **5b**. ^{1}H NMR ($CDCl_3$) δ 4.05 (m, 1H, $J_{3,4}$ = 4.4 Hz, H-4), 4.01-3.98 (m, 4H, OCH_2), 3.99-3.96 (m, 3H, H-1, H-1', H-2), 3.88 (dd, 1H, $J_{4,5}$ = 6.7 Hz, H-5), 3.83 (dd, 1H, $J_{2,3}$ = 7.1 Hz, H-3), 3.72 (dd, 1H, $J_{4,5'}$ = 7.4 Hz, $J_{5,5'}$ = 8.2 Hz, H-5'), 1.21 (m, 6H, CH_2CH_3), 1.26, 1.25, 1.22, 1.18 (s, 12H, $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 110.0,109.6 (2C, $C(CH_3)_2$), 77.4 (C-3), 75.7 (d, $J_{C\text{-}2,P}$ = 8.5 Hz C-2), 75.0 (C-4), 67.1 (C-1), 65.5 (C-5), 64.3 (2C, OCH_2), 26.9, 26.1, 25.3 (4C, $C(CH_3)_2$), 15.8 (d, 2C, $J_{CH3,P}$ = 6.0 Hz, CH_2CH_3).

Anal. Calcd for $C_{15}H_{29}O_7PS$ (384.43): C, 48.86; H, 7.60; P, 8.05; S, 8.34. Found: C, 48.45; H, 7.49; P, 8.00; S, 8.27.

1-*O*-(Diethoxythionophosphoryl)-2,3-*O*-isopropylidene-D,L-glycerol (6b). Likewise, 2,3-*O*-isopropylidene-D,L-glycerol (2.5 g, 19 mmol) gave, after 1 h, 5.1 g (94%) of **6b**. ^{1}H NMR ($CDCl_3$) δ 4.12 (dd, 1H, $J_{2,3'}$ = 5.5 Hz, H-2), 3.93 (m, 4H, OCH_2), 3.88 (dd, 1H, $J_{1,2}$ = 6.2 Hz, H-1), 3.84 (dd, 1H, $J_{2,3}$ = 5.9 Hz, H-3), 3.79 (dd, 1H, $J_{3,3'}$ = 10.6 Hz, H-3'), 3.64 (dd, 1H, $J_{1,1'}$ = 8,5 Hz, H-1'), 1.19 (m, 6H, CH_2CH_3), 1.28, 1.21 (s, 6H, $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 109.6 ($C(CH_3)_2$), 73.5 (d, $J_{C\text{-}2,P}$ = 9.1Hz,C-2), 67.5 (d, $J_{C\text{-}1,P}$ = 4.5 Hz, C-1), 66.1 (C-3), 64.2 (2C, d, $J_{CH2,P}$ = 4.1 Hz, OCH_2), 26.5, 25.1 (2C, $C(CH_3)_2$), 15.7 (d, 2C, $J_{CH_3,P}$ = 6.8 Hz, CH_2CH_3).

Anal. Calcd for $C_{10}H_{21}O_5PS$ (284.31): C, 42.24; H, 7.44; P, 10.89; S, 11.27. Found: C, 42.42; H, 7.69; P, 11.00; S, 11.15.

1-*O*-(Diphenoxyphosphoryl)-2,3:4,5-di-*O*-isopropylidene-D,L-xylitol (5c). Diphenoxyphosphoryl chloride (10.2 g, 38 mmol), 4-DMAP (9.28 g, 76 mmol) and pyridine (6.1 mL, 76 mmol) were successively added to a stirred solution 2,3:4,5-di-*O*-isopropylidene-D,L-xylitol (4.4 g, 19 mmol) in CH_2Cl_2 (190 mL) at room temperature for 1h. A saturated aqueous solution of NH_4Cl was added and the mixture stirred for a further10 min. The aqueous phase was extracted with CH_2Cl_2, the organic phase was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The crude product waspurified on a silica gel column eluted with hexane-ether (1:4) to give 6.1 g (69%) of **5c**, mp 62-66 °C. ^{1}H NMR ($CDCl_3$) δ 7.32-7.13 (m, 10H, OPh), 4.35 (dd, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.27 (m, 1H, $J_{1',2}$ = 4.5 Hz, H-1'), 4.16 (m, 1H, $J_{4,5'}$ = 7.0 Hz, H-4), 4.09 (m, 1H, $J_{2,3}$ = 7.9Hz H-2), 3.95 (dd, 1H, $J_{4,5}$ = 6.8 Hz, H-5), 3.88 (dd, 1H, $J_{3,4}$ = 4.2 Hz, H-3), 3.78 (dd, 1H, $J_{5,5'}$ = 8.3 Hz, H-5'), 1.38, 1.36, 1.33, 1.32 (s, 12H, $C(CH_3)_2$) ; ^{13}C NMR ($CDCl_3$) δ 149.5 (2C, C*ipso*), 128.7 (4C, C*m*), 124.4 (2C, C*p*), 119.1 (4C, C*o*), 110.3,109.8 (2C, $C(CH_3)_2$), 76.0 (C-3), 74.6 (d, $J_{C\text{-}2,P}$ = 8.1 Hz, C-2), 73.7 (C-4), 67.2 (C-1), 64.5 (C-5), 26.0, 25.5, 24.3 (4C, $C(CH_3)_2$).

Anal. Calcd for $C_{23}H_{29}O_8P$ (465.45): C, 59.48; H, 6.29; P, 6.67. Found: C, 59.33; H, 6.19; P, 6.71.

1-*O*-(Diphenoxyphosphoryl)-2,3-*O*-isopropylidene-D,L-glycerol (6c). Likewise , 2,3-*O*-isopropylidene-D,L-glycerol (2.5 g, 19 mmol) gave, after 1 h, 4.9 g (75%) of 6c. ^{1}H NMR ($CDCl_3$) δ 7.26-7.02 (m, 10H, OPh), 4.15 (m, 3H, H-1,H-1',H-2), 3.90 (dd, 1H, $J_{3,2}$ = 5.2 Hz, H-3), 3.68 (dd, 1H, $J_{2,3'}$ = 6.1 Hz, , $J_{3,3'}$ = 8.7 Hz, H-3'), 1.30, 1.25 (s, 6H, $C(CH_3)_2$) ; ^{13}C NMR ($CDCl_3$) δ 151.4 (2C, C*ipso*), 129.7 (4C, C*m*), 125.3 (2C, C*p*), 120.0 (4C, C*o*), 109.8 ($C(CH_3)_2$), 73.7 (d, $J_{C\text{-}2,P}$ = 7.4 Hz,C-2), 68.6 (d, $J_{C\text{-}1,P}$ = 4.9 Hz, C-1), 65.7 (C-3), 26.6, 25.1 (2C, $C(CH_3)_2$).

Anal. Calcd for $C_{18}H_{21}O_6P$ (364.33): C, 59.34; H, 5.81; P, 8.50. Found: C, 59.12; H, 5.77; P, 8.60.

3-*O*-(Diphenoxythionophosphoryl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (1d). Employed the same methodology used for **1a**, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (5.0 g, 19 mmol) and diphenoxythionophosphoryl chloride (6.8 g, 24 mmol) gave, after 1 h, 5.9 g (60%) of **1d**. $[\alpha]_D^{22}$ +4.3° (*c* 1.3, $CHCl_3$), mp 38 °C. ^{1}H NMR ($CDCl_3$) δ 7.36-7.16 (m, 10H, OPh), 5.80 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.13 (dd, 1H, $J_{3,4}$ = 2.7 Hz, H-3), 4.60 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 4.32 (m, 1H, $J_{5,6}$ = 6.0 Hz, H-5), 4.19 (m, 1H, H-4), 4.05 (dd, 1H, $J_{6,6'}$ = 8.7 Hz, H-6), 4.03 (dd, 1H, $J_{5,6'}$ = 5.1 Hz, H-6'), 1.48, 1.41, 1.27, 1.24 (s, 12H, $C(CH_3)_2$);.^{13}C NMR ($CDCl_3$) δ 150.3 (2C, C*ipso*), 128.7 (4C, C*m*), 124.7 (2C, C*p*), 120.2 (4C, C*o*), 111.5, 108.4 (2C, $C(CH_3)_2$), 104.0 (C-1), 82.5 (C-2), 80.7 (C-3), 79.5 (d, $J_{C\text{-}4,P}$ = 8.6 Hz, C-4), 71.1 (C-5), 66.2 (C-6), 25.9, 25.7, 25.3, 25.2 (4C, $C(CH_3)_2$).

Anal. Calcd for $C_{24}H_{29}O_8PS$ (508.53): C, 56.69; H, 5.75; P, 6.09; S, 6.30. Found: C, 56.10; H, 5.56; P, 6.19; S, 6.23.

6-*O*-(Diphenoxythionophosphoryl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (4d). Likewise, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5.0 g, 19 mmol) gave, after 1 h, 7.3 g (75%) of **4d**. $[\alpha]_D^{22}$ -78° (*c* 1.4, $CHCl_3$), mp 78-79 °C. ^{1}H NMR ($CDCl_3$) δ 7.32-7.17 (m, 10H, OPh), 5.55 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 4.60 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 4.45 (m, 1H, $J_{6,6'}$ = 10.7 Hz, H-6), 4.38 (dd, 1H, $J_{5,6'}$ = 7.2 Hz, H-6'), 4.32 (dd, 1H, $J_{2,3}$ = 2,5 Hz, H-2), 4.24 (dd, 1H, $J_{4,5}$ = 1.9 Hz, H-4), 4.15 (ddd, 1H, $J_{5,6}$ = 5.4 Hz, H-5), 1.47, 1.44, 1.41, 1.31 (s, 12H, $C(CH_3)_2$),; ^{13}C NMR ($CDCl_3$) δ 150.8 (2C, C*ipso*), 129.5 (4C, C*m*), 125.4 (2C, C*p*), 121.1 (4C, C*o*), 109.6, 108.8 (2C, $C(CH_3)_2$), 96.2 (C-1), 70.6 (3C, C-2, C-3, C-4), 67.8 (d, $J_{C\text{-}6,P}$ = 3.5 Hz, C-6), 66.7 (d, $J_{C\text{-}5,P}$ = 7.5 Hz, C-5), 26.0, 24.9, 24.4 (4C, $C(CH_3)_2$).

Anal. Calcd for $C_{24}H_{29}O_8PS$ (508.53): C, 56.69; H, 5.75; P, 6.09; S, 6.30. Found: C, 56.26; H, 5.67; P, 6.16; S, 6.21.

1-*O*-(Diphenoxythionophosphoryl)-2,3:4,5-di-*O*-isopropylidene-D,L-xylitol(5d). Likewise, 2,3:4,5-di-*O*-isopropylidene-D,L-xylitol (4.4 g, 19 mmol) gave, after 1 h, 5.5 g (60%) of **5d**. ^{1}H NMR ($CDCl_3$) δ 7.34-7.15 (m, 10H, OPh), 4.39 (dd, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 4.29 (m, 1H, $J_{1,1'}$ = 8.4 Hz, H-1'), 4.19 (dd, 1H, $J_{2,3}$ = 7.8Hz H-2), 4.13 (m, 1H, $J_{4,5'}$ = 7.1 Hz, H-4), 3.95 (dd, 1H, $J_{4,5}$ = 6.9 Hz, H-5), 3.93 (dd, 1H, $J_{3,4}$ = 4.2 Hz, H-3), 3.82 (dd, 1H, $J_{5,5'}$ = 8.3 Hz, H-5'), 1.42, 1.39, 1.34 (s, 12H, $C(CH_3)_2$),; ^{13}C NMR ($CDCl_3$) δ 150.2 (2C, C*ispo*), 129.7 (4C, C*m*), 125.6 (2C, C*p*), 121.1 (4C, C*o*), 110.2, 109.6 (2C, $C(CH_3)_2$), 77.1 (C-3), 75.6 (d, $J_{C\text{-}2,P}$ = 8.8 Hz, C-2), 74.8 (C-4), 68.5 (C-1), 65.5 (C-5), 27.0, 26.1, 25.4 (4C, $C(CH_3)_2$).

Anal. Calcd for $C_{23}H_{29}O_7PS$ (480.51): C, 57.49; H, 6.08; P, 6.45; S, 6.67. Found: C, 57.57; H, 6.10; P, 6.28; S, 6.50.

1-*O*-(Diphenoxythionophosphoryl)-2,3-*O*-isopropylidene-D,L-glycerol (6d). Likewise, 2,3-*O*-isopropylidene-D,L-glycerol (2.5 g, 19 mmol) gave, after 1 h, 5.4 g (75%) of **6d**. ^{1}H NMR ($CDCl_3$) δ 7.37-7.25 (m, 10H, OPh), 4.38 (m, 3H, H-1,H-1',H-2), 4.06 (m, 1H, H-3), 3.90 (m, 1H, H-3'), 1.55, 1.45 (s, 6H, $C(CH_3)_2$),; ^{13}C NMR ($CDCl_3$) δ 150.0 (2C, C*ispo*), 129.0 (4C, C*m*), 125.0 (2C, C*p*), 120.4 (4C, C*o*), 109.8 ($C(CH_3)_2$), 73.1 (C-2), 68.4 (C-1), 65.1 (C-3), 26.0, 24.6 (2C, $C(CH_3)_2$).

Anal. Calcd for $C_{18}H_{21}O_5PS$ (380.39): C, 56.84; H, 5.56; P, 8.14; S, 8.43. Found: C, 56.80; H, 6.54; P, 8.44; S, 8.52.

3-*O*-(Dithiophenoxyphosphoryl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (1e). Dithiophenoxyphosphoryl chloride was prepared from thiophenol (96 mmol), NaOH (96 mmol) and $POCl_3$ (32 mmol) in toluene at room temperature. After 1.5 h, saturated $NaHCO_3$ aqueous solution was added, the organic phase was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure to give a residue which was recrystallized in Et_2O to give 3.4 g of the acid chloride. Using methodology described for **1c**, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (5.0 g, 19 mmol) and dithiophenoxyphosphoryl chloride (11.6 g, 38 mmol) gave, after 2 h, 1.5g (15%) of **1e**. $[\alpha]_D^{22}$ -50° (*c* 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.55-7.21 (m, 10H, SPh), 5.70 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.99 (dd, 1H, $J_{3,4}$ = 2.5 Hz, $J_{H\text{-}3,P}$ = 9.3 Hz, H-3), 4.51 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 4.15 (dd, 1H, $J_{4,5}$ = 4.8 Hz, H-4), 4.06 (m, 1H, $J_{5,6}$ = 5.8 Hz, H-5), 3.99 (dd, 1H, $J_{6,6'}$ = 8.2 Hz, H-6), 3.93 (dd, 1H, $J_{5,6'}$ = 5.3 Hz, H-6'), 1.47, 1.39, 1.28, 1.20 (s, 12H, $C(CH_3)_2$) ; ^{13}C NMR ($CDCl_3$) δ 134.7 (4C, C*o*), 128.7 (2C, C*p*), 128.4 (4C, C*m*), 125.8, 125.1 (2C, C*ipso*), 112.4,109.3 (2C, $C(CH_3)_2$), 104.0 (C-1), 82.6 (C-2), 79.7 (d, $J_{C\text{-}3,P}$ = 9.0 Hz, C-3), 79.5 (d, $J_{C\text{-}4,P}$ = 7.8 Hz, C-4), 71.2 (C-5), 66.0 (C-6), 26.7, 26.5, 26.1 (4C, $C(CH_3)_2$).

Anal. Calcd for $C_{24}H_{29}O_7PS_2$ (524.59): C, 54.95; H, 5.57; P, 5.90; S, 12.12. Found: C, 54.58; H, 5.51; P, 5.75; S, 12.10.

6-*O*-(Dithiophenoxyphosphoryl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (4e). Likewise, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5.0 g, 19 mmol) gave, after 2 h, 1.6 g (16%) of **4e**. $[\alpha]_D^{22}$ +111° (*c* 1.2, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 7.47-7.22 (m, 10H, SPh), 5.43 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 4.48 (dd, 1H, $J_{4,5}$ = 1.8 Hz, H-4), 4.25 (m, 2H, H-6, H-6'), 4.20 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 4.03 (dd, 1H, $J_{2,3}$ = 2,5 Hz, H-2), 3.98 (m, 1H, H-5), 1.48, 1.35, 1.22 (s, 12H, $C(CH_3)_2$) ; ^{13}C NMR ($CDCl_3$) δ 135.2 (4C, C*o*), 129.3 (6C, C*m*, C*p*), 125.0 (2C, C*ipso*), 109.5, 108.7 (2C, $C(CH_3)_2$), 96.1 (C-1), 70.5 (C-4), 70.4 (2C, C-2, C-3), 66.8 (d, $J_{C\text{-}5,P}$ = 6.8 Hz, C-5), 66.3 (d, $J_{C\text{-}6,P}$ = 7.6 Hz, C-6), 25.8, 24.8, 24.3 (4C, $C(CH_3)_2$).

Anal. Calcd for $C_{24}H_{29}O_7P\ S_2$ (524.59): C, 54.95; H, 5.57; P, 5.90; S, 12.12. Found: C, 54.78; H, 5.50; P, 5.81; S, 12.08.

1-*O*-(Dithioethoxyphosphoryl)-2,3-*O*-isopropylidene-D,L-glycerol (6e). Likewise, 2,3-*O*-isopropylidene-D,L-glycerol (2.5 g, 19 mmol) gave, after 2 h, 0.7 g (9%) of **6e** and the two by-products **6'e** (1.2g (21%)) and **6''e** (0.5g (12%)).

6e: ^1H NMR ($CDCl_3$) δ 7.53-7.21 (m, 10H, SPh), 4.18 (m, 2H, H-1,H-1'), 4.10 (m, 1H, H-2), 3.92 (dd, 1H, $J_{2,3}$ = 6.2 Hz, H-3), 3.69 (dd, 1H, $J_{2,3'}$ = 5.1 Hz, , $J_{3,3'}$ = 8.7 Hz, H-3'), 1.33 (s, 6H, $C(CH_3)_2$) ; ^{13}C NMR ($CDCl_3$) δ 134.4 (4C, C*o*), 128.4 (4C, C*m*), 125.3 (4C, C*ipso*, C*p*), 109.0 ($C(CH_3)_2$), 72.9 (d, $J_{C\text{-}2,P}$ = 7.5 Hz,C-2), 66.4 (d, $J_{C\text{-}1,P}$ = 8.2 Hz, C-1), 65.2 (C-3), 25.8, 24.3 (2C, $C(CH_3)_2$).

Anal. Calcd for $C_{18}H_{21}O_4PS_2$ (396.46): C, 54.53; H, 5.34; P, 7.81; S, 16.17. Found: C, 54,48; H, 5.29; P, 7.92; S, 16.33.

6'e: ^1H NMR ($CDCl_3$) δ 7.49-7.20 (m, 5H, Sph), 4.15 (m, 1H, H-2), 3.98 (m, 2H, H-1,H-1'), 3.89 (dd, 1H, $J_{2,3}$ = 6.2 Hz, H-3), 3.63 (dd, 1H, $J_{2,3'}$ = 2.2 Hz, $J_{3,3'}$ = 7.7 Hz, H-3'), 1.33 (s, 6H, $C(CH_3)_2$) ; ^{13}C NMR ($CDCl_3$) δ 133.8 (2C, C*o*), 128.5 (C*p*), 128.3 (2C, C*m*), 124.7 (C*ipso*), 108.9 ($C(CH_3)_2$), 72.8 (C-2), 66.7 (C-1), 65.1 (C-3), 25.7, 24.2 (2C, $C(CH_3)_2$).

Anal. Calcd for $C_{12}H_{17}O_5PS$ (304.30): C, 47.37; H, 5.63; P, 10.18; S, 10.54. Found: C, 47.43; H, 5.66; P, 10.35; S, 11.02.

6''e: ^1H NMR ($CDCl_3$) δ 4.15 (m, 1H, H-2), 3.89 (dd, 1H, $J_{2,3}$ = 5.6 Hz, H-3), 3.80 (m, 2H, H-1,H-1'), 3.63 (dd, 1H, $J_{2,3'}$ = 8.6 Hz, $J_{3,3'}$ = 8.4 Hz, H-3'), 1.33 (s, 6H, $C(CH_3)_2$) ; ^{13}C NMR ($CDCl_3$) δ 108.6 ($C(CH_3)_2$), 72.8 (d, $J_{C\text{-}2,P}$ = 7.2 Hz, C-2), 66.7 (d, $J_{C\text{-}1,P}$ = 2.7 Hz, C-1), 64.8 (C-3), 25.7, 24.2 (2C, $C(CH_3)_2$).

Anal. Calcd for $C_6H_{13}O_6P$ (212.14): C, 33.97; H, 6.18; P, 14.60. Found: C, 33.80; H, 6.24; P, 14.24.

6-*S*-(Diethoxythionophosphoryl)-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (4f). 6-Deoxy-6-iodo-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5.0 g, 13.5 mmol) was added to a stirred solution of ammonium diethyl dithiophosphate (2.7

g , 13.5 mmol) and LiOH (0.32 g , 13.5 mmol) in refluxing acetonitrile (50 mL). After 4 h the solvent was evaporated under reduced pressure. The crude product was extracted with $CHCl_3$ and saturated aqueous NH_4Cl. The organic phase was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The crude product was purified on a silica gel column eluted with hexane-ether (85:15) to give 0.7g (12%) of **4f**. $[\alpha]_D^{22}$ -50 ° (*c* 1.2, $CHCl_3$), mp 86-88 °C. ^{1}H NMR ($CDCl_3$) δ 5.37 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 4.49 (dd, 1H, $J_{3,4}$ = 7.7 Hz, H-3), 4.18 (dd, 1H, $J_{2,3}$ = 2.3 Hz, H-2), 4.15 (d, 1H, $J_{4,5}$ = 0 Hz, H-4), 4.07 (m, 4H, OCH_2), 3.85 (dd, 1H, $J_{5,6}$ = 6.8 Hz, H-5), 2.97 (dd, 1H, $J_{6,6'}$ = 7.5 Hz, H-6), 2.91 (dd, 1H, $J_{5,6'}$ = 7.0 Hz, H-6'), 1.22 (m, 6H, CH_2CH_3), 1.42, 1.37, 1.25, 1.21 (s, 12H, $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 109.3, 108.6 (2C, $C(CH_3)_2$), 96.4 (C-1), 71.6 (C-4), 70.9 (C-3), 70.4 (C-2), 67.3 (C-5), 63.8 (d, 1C, $J_{CH_2,P}$ = 6.0 Hz, OCH_2), 63.7 (d, 1C, $J_{CH_2,P}$ = 5.9 Hz, OCH_2), 33.1 (C-6), 25.9, 24.8, 24.4 (4C, $C(CH_3)_2$), 15.7 (d, 2C, $J_{CH_3,P}$ = 7.7 Hz, CH_2CH_3).

Anal. Calcd for $C_{16}H_{29}O_7PS_2$ (428.50): C, 44.85; H, 6.82; P, 7.23; S, 14.96. Found: C, 44.94; H, 6.51; P, 7.34; S, 14.76.

1-*S*-(Diethoxythionophosphoryl)-1-deoxy-2,3:4,5-di-*O*-isopropylidene-D,L-xylitol (5f). Likewise, 2,3:4,5-di-*O*-isopropylidene-D,L-xylitol (5.0 g, 14.6 mmol) gave, after 4 h, 3.5 g (60%) of **5f**. ^{1}H NMR ($CDCl_3$) δ 4.15 (m, 1H, H-4), 4.12 (m, 1H, H-2), 4.10 (m, 4H, OCH_2), 3.98 (dd, 1H, $J_{4,5}$ = 6.7 Hz, H-5), 3.79 (1H, $J_{5,5'}$ = 8.1 Hz, H-5'), 3.77 (m, 1H, H-3), 3.12 (dd, 1H, $J_{1,2}$ = 4.4 Hz, H-1), 2.96 (m, 1H, $J_{1,1'}$ = 13.7 Hz, H-1'), 1.25 (m, 6H, CH_2CH_3), 1.32, 1.29, 1.28 (s, 12H, $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 108.9, 108.7 (2C, $C(CH_3)_2$), 78.5 (C-3), 75.0 (C-2), 73.9 (C-4), 64.7 (C-5), 63.1 (2C, OCH_2), 34.9 (C-1), 26.3, 26.0, 25.2, 24.5 (4C, $C(CH_3)_2$), 14.9 (d, 2C, $J_{CH_3,P}$ = 8.1 Hz, CH_2CH_3).

Anal. Calcd for $C_{15}H_{29}O_6PS_2$ (400.49): C, 44.98; H, 7.29; P, 7.73; S, 16.01. Found: C, 45.26; H, 7.74; P, 7.75; S, 15.61.

1-*S*-(Diethoxythionophosphoryl)-1-deoxy-2,3-*O*-isopropylidene-D,L-glycerol (6f). Likewise, 2,3-*O*-isopropylidene-D,L-glycerol (3.7 g, 15.3 mmol) gave, after 4 h, 2.2 g (51%) of **6f**. ^{1}H NMR ($CDCl_3$) δ 4.28 (m, 1H, H-3), 4.16 (m, 1H, H-3'), 4.13 (m, 4H, OCH_2), 3.73 (m, 1H, H-2), 3.03 (m, 1H, H-1), 3.00 (m, 1H, H-1'), 1.40, 1.23 (s, 6H. $C(CH_3)_2$); 1.32 (m, 6H, CH_2CH_3). ^{13}C NMR ($CDCl_3$) δ 108.9 ($C(CH_3)_2$), 73.8 (C-2), 67.3 (C-3), 63.2 (2C, OCH_2), 35.3 (C-1), 25.9, 24.4 (2C, $C(CH_3)_2$), 14.9 (d, 2C, $J_{CH_3,P}$ = 7.8 Hz, CH_2CH_3).

Anal. Calcd for $C_{10}H_{21}O_4PS_2$ (300.37): C, 39.99; H, 7.05; P, 5.32; S, 21.35. Found: C, 40.20; H, 6.95; P, 5.09; S, 21.88.

1-*O*-(Diethoxyphosphoryl)-D,L-glycerol (7a). A suspension of 1-*O*-(diethoxyphosphoryl)-2,3-*O*-isopropylidene-D,L-glycerol (**6a**) (2.0 g; 7.5 mmol) was stirred in water (18 mL) under reflux. After 1 h, 1,4-dioxane was added and the mixture

concentrated under reduced pressure. The residue was dissolved in THF, dried (Na_2SO_4) and the solvent evaporated under reduced pressure. The crude product was purified on a silica gel column eluted with hexane-acetone (1:4) to give 1.6g (94%) of **7a**. ^1H NMR ($CDCl_3$) δ 4.06 (m, 4H, OCH_2), 4.03-4.00 (m, 2H, H-1, H-1'), 3.83 (m, 1H, $J_{2,3}$ = 4.2 Hz, H-2), 3.62 (dd, 1H, $J_{3,3'}$ = 11.5 Hz, H-3), 3.56 (dd, 1H, $J_{2,3'}$ = 5.5 Hz, H-3'), 1.27 (m, 6H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 69.6 (d, $J_{C\text{-}2,P}$ = 5.4 Hz,C-2), 67.3 (C-1, $J_{C\text{-}1,P}$ = 4.9 Hz), 63.2 (d, $J_{C\text{-}3,P}$ = 5.1 Hz, C-3), 61.8 (2C, OCH_2), 15.0 (d, 2C, $J_{CH_3,P}$ = 6.0 Hz, CH_2CH_3).

Anal. Calcd for $C_7H_{17}O_6P$ (228.24): C, 36.84; H, 7.51; P, 13.57. Found: C, 36.76; H, 7.73; P, 13.31.

3-*O*-(Diethoxyphosphoryl)-1,2-*O*-isopropylidene-α-D-glucofuranose (8a). Likewise, 3-*O*-(diethoxyphosphoryl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1a**) (2.0 g, 5.0 mmol) gave, after 0.2 h, 1.3 g (72%) of **8a**. $[\alpha]_D^{24}$ +20° (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 5.68 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.59 (dd, 1H, $J_{3,4}$ = 2.4 Hz, $J_{H\text{-}3,P}$ = 8.7 Hz, H-3), 4.44 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 3.93 (m, 1H, H-4), 3.89 (m, 2H, OCH_2), 3,61 (m, 1H, $J_{5,6'}$ = 5.7 Hz, H-5), 3.42 (dd, 1H, $J_{5,6}$ = 6.0 Hz, H-6), 3.29 (dd, 1H, $J_{6,6'}$ = 11.9 Hz, H-6'), 1.26, 1.09 (s, 2H, $C(CH_3)_2$) 1.14 (m, 6H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 111.2 (C, $C(CH_3)_2$), 104.8 (C-1), 83.1 (C-2), 79.5 (C-4), 79.4 (C-3), 67.9 (C-5), 64.5 (2C, OCH_2), 63.9 (C-6), 26.4, 26.0 (2C, $C(CH_3)_2$), 15.8 (2C, CH_2CH_3).

Anal. Calcd for $C_{13}H_{25}O_9P$ (357.40): C, 43.82; H, 7.07; P, 8.69. Found: C, 43.69; H, 7.51; P, 8.61.

1-*O*-(Diethoxyphosphoryl)-2,3-isopropylidene-α-D-fructopyranose (9a). Likewise, 2,3:4,5-di-*O*-isopropylidene-α-D-fructopyranose (**2a**) (2.0 g, 5 mmol) gave, after 1.2 h, 1.1 g (61%) of **9a**. $[\alpha]_D^{24}$ -6° (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 4.18 (d, 1H, $J_{3,4}$ = 4.6 Hz, H-3), 4.17 (m, 2H, H-1, H-1'), 4.12 (dd, 1H, $J_{4,5}$ = 2.8 Hz, H-4), 4.06 (m, 4H, OCH_2), 3.93 (m, 1H, $J_{5,6}$ = 4.7 Hz, H-5), 3.73 (dd, 1H, $J_{6,6'}$ = 11.6 Hz, H-6), 3.62 (dd, 1H, $J_{5,6'}$ = 8.1 Hz, H-6'), 1.44, 1.29 (s, 6H, $C(CH_3)_2$), 1.26 (m, 6H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 110.2 ($C(CH_3)_2$), 100.9 (d, $J_{C\text{-}2,P}$ = 8.3 Hz, C-2), 75.9 (C-1), 66.5 (C-4), 65.4 (C-3), 64.2 (d, 2C, $J_{C\text{-}2,P}$ = 5.4 Hz, OCH_2), 63.7 (C-5), 63.3 (C-6), 27.4, 25.8 (2C, $C(CH_3)_2$), 15.9 (2C, CH_2CH_3).

Anal. Calcd for $C_{13}H_{25}O_9P$ (357.40): C, 43.82; H, 7.07; P, 8.69. Found: C, 43.46 ; H, 7.22 ; P, 8.30.

3-*O*-(Diethoxyphosphoryl)-1,2-*O*-isopropylidene-α-D-fructopyranose (10a). Likewise, 1,2:4,5-di-*O*-isopropylidene-α-D-fructopyranose (**3a**) (2.0 g, 5 mmol) gave, after 3 h, 1.1 g (60%) of **10a**. $[\alpha]_D^{23}$ -120° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 4.28 (H-4), 4.13 (m, 4H, OCH_2), 4.12-3.96 (m, 3H, H-1, H-3, H-5), 3.82-3.68 (m, 2H, H-6, H-6'), 3.54 (d, 1H, $J_{1,1'}$ = 12.2 Hz, H-1'), 1.34, 1.28 (s, 6H, $C(CH_3)_2$), 1.26 (m, 6H, CH_2CH_3) ; ^{13}C NMR ($CDCl_3$) δ 110.7 (1C, $C(CH_3)_2$), 104.5 (C-2), 74.5 (C-3), 71.1 (C-1), 68.9 (C-4),

64.5 (2C, C-5, C-6), 63.4 (d, 1C, $J_{CH_2,P}$ = 4.9 Hz, OCH_2), 63.1 (d, 1C, $J_{CH_2,P}$ = 4.9 Hz, OCH_2), 26.1, 25.8 (2C, $C(CH_3)_2$), 15.7 (2C, CH_2CH_3).

Anal. Calcd for $C_{13}H_{25}O_9P$ (357.40): C, 43.82; H, 7.07; P, 8.69 Found: C, 43.44; H, 7.21; P, 8.72.

3-*O*-(Diethoxyphosphoryl)-D-glucofuranose (11a). Likewise, 3-*O*-(diethoxyphosphoryl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1a**) (2.0 g, 5.0 mmol) gave, after 3 h, 1.0 g (63%) of **11a** (α/β : 1/1). $[\alpha]_D^{23}$ +43° (*c* 1.1, MeOH). ^{13}C NMR (Me_2SO-*d6*) α form : δ 92.1 (C-1), 81.7 (d, $J_{C-3,P}$ = 6.0 Hz, C-3), 71.9 (C-2), 70.9 (C-5), 68.8 (C-4), 63.1 (2C, OCH_2), 60.8 (C-6), 15.8 (d, 2C, $J_{CH3,P}$ = 6.1 Hz, CH_2CH_3). β form : δ 96.4 (C-1), 83.8 (C-3), 76.0 (C-5), 73.4 (C-2), 68.8 (C-4), 63.1 (2C, OCH_2), 60.8 (C-6), 15.8 (d, 2C, $J_{CH3,P}$ = 6.1 Hz, CH_2CH_3).

Anal. Calcd for $C_{10}H_{21}O_9P$ (316.24): C, 37.98; H, 6.69; P, 9.79 Found: C, 37.50; H, 6.95; P, 9.38.

1-*O*-(Diethoxyphosphoryl)-D-fructopyranose (12a). Likewise, 1-*O*-(diethoxyphosphoryl)-2,3:4,5-di-*O*-isopropylidene-α-D-fructopyranose (**2a**) (2.0 g, 5.0 mmol) gave, after 7 h, 1.1 g (69%) of **12a** (α/β : 3/2). $[\alpha]_D^{24}$ +30° (*c* 1.4, MeOH). ^{13}C NMR (Me_2SO-*d6*) α form : δ 100.1 (C-2), 75.8 (C-1), 69.4 (C-4), 67.5 (C-3), 63.1 (2C, OCH_2), 62.0 (C-5), 61.9 (C-6), 15.8 (2C, CH_2CH_3). β form : δ 96.7 (d, J_{C-P} = 9.0 Hz, C-2), 74.8 (C-1), 69.4 (C-4), 68.9 (C-5), 67.1 (C-3), 63.4 (C-6), 63.1 (2C, OCH_2), 15.8 (2C, CH_2CH_3).

Anal. Calcd for $C_{10}H_{21}O_9P$ (316.24): C, 37.98; H, 6.69; P, 9.79 Found: C, 37.62; H, 6.88; P, 9.41.

6-*O*-(Diethoxyphosphoryl)-D-galactopyranose (14a). Likewise, 6-*O*-(diethoxy - phosphoryl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**4a**) (2.0 g, 5.0 mmol) gave, after 4 h, 1.0 g (63%) of **14a** (α/β : 3/2). $[\alpha]_D^{28}$ +29° (*c* 1.3, MeOH), mp 46 °C. ^{13}C NMR (Me_2SO-*d6*) α form : δ 92.5 (C-1), 68.8 (C-4), 68.4 (C-5), 68.2 (C-3), 68.0 (C-2), 66.7 (C-6), 63.2 (d, 2C, $J_{CH2,P}$ = 3.9 Hz, OCH_2), 15.8 (d, 2C, $J_{CH3,P}$ = 6.9 Hz, CH_2CH_3). β form : δ 97.2 (C-1), 72.9 (C-3), 72.6 (d, J_{C-P} = 7.5 Hz, C-5), 71.7 (C-2), 68.8 (C-4), 66.7 (C-6), (d, 2C, $J_{CH2,P}$ = 3.9 Hz, OCH_2), 15.8 (d, 2C, $J_{CH3,P}$ = 6.9 Hz, CH_2CH_3).

Anal. Calcd for $C_{10}H_{21}O_9P$ (316.24): C, 37.98; H, 6.69; P, 9.79 Found: C, 37.56; H, 6.95; P, 9.21.

1-*O*-(Diethoxythionophosphoryl)-D,L-glycerol (7b). Likewise, 1-*O*-(diethoxythionophosphoryl)-2,3-*O*-isopropylidene-D,L-glycerol (**6b**) (2.0 g, 7.0 mmol) gave, after 2 h, 1.4 g (81%) of **7b**. ^{1}H NMR ($CDCl_3$) δ 3.96 (dd, 1H, $J_{1,2}$ = 5.4 Hz, H-1), 3.93 (m, 4H, OCH_2), 3.91 (m, 1H, $J_{1,1'}$ = 8.5 Hz, H-1'), 3.82 (m, 1H, $J_{2,3}$ = 3.7 Hz, H-2), 3.59 (dd, 1H, $J_{3,3'}$ = 11.6 Hz, H-3), 3.49 (dd, 1H, $J_{2,3'}$ = 5.6 Hz, H-3'), 1.20 (m, 6H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 70.4 (d, $J_{C-2,P}$ = 7.5 Hz, C-2), 68.2 (d, $J_{C-1,P}$ = 4.3 Hz, C-1), 64.6 (OCH_2), 62.8 (C-3), 15.8 (d, 2C, $J_{CH_3,P}$ = 6.3 Hz, CH_2CH_3).

Anal. Calcd for $C_7H_{17}O_5PS$ (244.24) : C, 34.42; H, 7.01; P, 12.68; S, 13.25. Found: C, 34.21; H, 6.94; P, 12.81; S, 13.25.

3-*O*-(Diethoxythionophosphoryl)-1,2-*O*-isopropylidene-α-D-glucofuranose (8b). 3-*O*-(Diethoxythionophosphoryl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1b**) (2.0 g, 5.0 mmol) was dissolved in a stirred mixture of dioxane-HCl (37% aqueous solution) (25:1) at 40 °C. After 0.5 h $NaHCO_3$ was added and the mixture concentrated under reduced pressure. The residue was dissolved in THF, dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The crude product was purified on a silica gel column eluted with hexane-acetone (7:3) to give 1.3 g (72%) of **8b**. $[\alpha]_D^{23}$ -37° (*c* 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 5.78 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.80 (dd, 1H, $J_{3,4}$ = 2.3 Hz, $J_{H\text{-}3,P}$ = 10.1 Hz, H-3), 4.54 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 4.05 (m, 5H, H-4, OCH_2), 3,75 (m, 1H, $J_{5,6'}$ = 5.7 Hz, H-5), 3.70 (m, 1H, H-6), 3.56 (dd, 1H, $J_{6,6'}$ = 11.5 Hz, H-6'), 1.37, 1.19 (s, 6H, $C(CH_3)_2$) 1.25-1.23 (m, 6H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 111.1 (1C, $C(CH_3)_2$), 104.2 (C-1), 82.4 (C-2), 80.3 (d, $J_{C\text{-}3,P}$ = 5.4 Hz, C-3), 78.4 (d, $J_{C\text{-}4,P}$ = 9.0 Hz, C-4), 68.0 (C-5), 63.2 (C-6), 64.1 (2C, OCH_2), 26.3, 26.0 (2C, $C(CH_3)_2$), 15.6 (2C, CH_2CH_3).

Anal. Calcd for $C_{13}H_{25}O_8PS$ (372.37): C, 41.93; H, 6.77; P, 8.32; S, 8.61 Found: C, 41.80; H, 6.90; P, 8.58; S, 8.58.

3-*O*-(Diethoxythionophosphoryl)-D-glucofuranose (11b). Applying the methodology used for **7a**, 3-*O*-(diethoxythionophosphoryl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1b**) (2.0 g, 5.0 mmol) gave, after 1 h, 1.1 g (68%) of **11b** (α/β : 3/2). $[\alpha]_D^{23}$ +52° (*c* 1.1, MeOH). ^{13}C NMR (Me_2SO-*d6*) α form : δ 92.1 (C-1), 82.5 (d, $J_{C\text{-}3,P}$ = 6.0 Hz, C-3), 71.7 (C-2), 70.8 (C-5), 68.7 (C-4), 63.2 (2C, $J_{CH2,P}$ = 4.6 Hz, OCH_2), 60.6 (C-6), 15.8 (d, 2C, $J_{CH3,P}$ = 5.6 Hz, CH_2CH_3). β form : δ 96.5 (C-1), 84.5 (C-3), 76.0 (C-5), 73.3 (C-2), 68.7 (C-4), 63.0 (2C, $J_{CH2,P}$ = 4.6 Hz, OCH_2), 60.6 (C-6), 15.5 (d, 2C, $J_{CH3,P}$ = 7.5 Hz, CH_2CH_3)

Anal. Calcd for $C_{10}H_{21}O_8PS$ (332.31): C, 36.14; H, 6.37; P, 9.32; S, 9.65 Found: C, 35.50; H, 6.45; P, 9.84; S, 9.81.

6-*O*-(Diethoxythionophosphoryl)-D-galactopyranose (14b). Applying the methodology used for **8b**, 6-*O*-(diethoxythionophosphoryl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**4b**) (2.0 g, 5.0 mmol) gave, after 3 h, at 60 °C, 0.7 g (43%) of **14b** (α/β : 2/3). $[\alpha]_D^{28}$ -217° (*c* 1.2, MeOH), mp 74 °C. ^{13}C NMR (Me_2SO-*d6*) α form : δ 92.5 (C-1), 68.9 (C-4), 68.4 (3C, C-2, C-3, C-5), 66.7 (C-6), 63.9 (2C, OCH_2), 15.6 (d, 2C, $J_{CH3,P}$ = 6.2 Hz, CH_2CH_3). β form : δ 97.2 (C-1), 72.9 (C-3), 72.6 (d, $J_{C\text{-}P}$ = 8.6 Hz, C-5), 71.7 (C-2), 69.0 (C-4), 66.7 (C-6), 63.9 (2C, OCH_2), 15.6 (d, 2C, $J_{CH3,P}$ = 6.2 Hz, CH_2CH_3).

Anal. Calcd for $C_{10}H_{21}O_8PS$ (332.31): C, 36.14; H, 6.37; P, 9.32; S, 9.65 Found: C, 36.30; H, 6.45; P, 9.84; S, 9.81.

1-*O*-(Diethoxythionophosphoryl)-D,L-xylitol (15b). Likewise, 1-*O*-(diethoxythionophosphoryl)-2,3:4,5-di-*O*-isopropylidene-D,L-xylitol **(5b)** (2.0 g, 5.0 mmol) gave, after 0.5 h, 1.3 g (82%) of **15b**. ^{13}C NMR (Me_2SO-*d6*) δ 72.6 (C-3), 70.8 (d, $J_{C\text{-}2,P}$ = 8.0 Hz, C-2), 70.4 (C-4), 68.4 (C-1), 64.6 (d, $J_{CH2,P}$ = 3.3 Hz, OCH_2), 63.4 (C-5), 15.9 (d, $J_{CH3,P}$ = 6.8 Hz, CH_2CH_3).

Anal. Calcd for $C_9H_{21}O_7PS$ (304.29): C, 35.52; H, 6.96; P, 10.18; S, 10.54. Found: C, 35.57; H, 7.10; P, 10.28; S, 10.32.

3-*O*-(Diphenoxyphosphoryl)-1,2-*O*-isopropylidene-α-D-glucofuranose (8c). Using methodology for **8b**, 3-*O*-(diphenoxyphosphoryl)-1,2:5,6-*O*-isopropylidene-α-D-glucofuranose **(1c)** (3.0 g, 5.6 mmol) gave, after 5 h, 0.3 g (10%) of **8c** and 1.0g (58%) of 3-*O*-phosphoryl-1,2-*O*-isopropylidene-α-D-glucofuranose (**8'**).

8c: $[\alpha]_D^{22}$ +33° (*c* 1.5, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 7.34-7.12 (m, 10H, OPh), 5.81 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.02 (dd, 1H, $J_{3,4}$ = 2.0 Hz, H-3), 4.48 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 3.69 (m, 1H, $J_{5,6}$ = 5.2 Hz, H-5), 4.12 (d, 1H, $J_{4,5}$ = 9.1 Hz, H-4), 3.73 (dd, 1H, $J_{6,6'}$ = 11.4 Hz, H-6), 3.57 (dd, 1H, $J_{5,6'}$ = 5.8 Hz, H-6'), 1.42, 1.21 (s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ 149.8 (2C, C*ipso*), 129.0 (4C, C*m*), 124.9 (2C, C*p*), 119.1 (4C, C*o*), 111.6 ($C(CH_3)_2$), 103.9 (C-1), 82.2 (C-2), 80.2 (d, $J_{C\text{-}3,P}$ = 3.5 Hz, C-3), 78.7 (C-4), 66.8 (C-5), 63.1 (C-6), 25.6, 25.3 (2C, $C(CH_3)_2$).

Anal. Calcd for $C_9H_{21}O_7PS$ (304.29): C, 55.75; H, 5.57; P, 6.85. Found: C, 55.67; H, 5.60; P, 6.78.

8': $[\alpha]_D^{22}$ +77° (*c* 0.9, $CHCl_3$) mp 34 °C ; . ^{13}C NMR ($CDCl_3$) δ 115.7 ($C(CH_3)_2$), 106.5 (C-1), 86.3 (C-2), 81.6 (d, $J_{C\text{-}3,P}$ = 13.4 Hz, C-3), 79.2 (C-4), 70.9 (C-5), 65.5 (C-6), 28.1, 27.8 (2C, $C(CH_3)_2$).

1-*O*-(Diphenoxythionophosphoryl)-D,L-glycerol (7d). Likewise, 1-*O*-(diphenoxythionophosphoryl)-2,3-*O*-isopropylidene-D,L-glycerol **(6d)** (5.0 g, 13.0 mmol) gave, after 2.0 h, 0.7 g (15%) of **7d** and 0.2 g (5%) of 1,2-(phenoxythionophsphoryl)-D,L-glycerol (**7'd**) as a by-product.

7d: ^1H NMR ($CDCl_3$) δ 7.35-7.17 (m, 10H, OPh), 4.32 (dd, 1H, $J_{1,2}$ = 5.1 Hz, H-1), 4.28 (dd, 1H, $J_{1,1'}$ = 9.3 Hz, H-1'), 3.96 (dd, 1H, $J_{1',2}$ = 5.2 Hz, H-2), 3.68 (dd, 1H, $J_{2,3}$ = 3.7 Hz, H-3), 3.59 (m, 1H, $J_{3,3'}$ = 11.4 Hz, H-3') ; ^{13}C NMR (Me_2SO-*d6*) δ 150.4 (2C, C*ipso*), 129.7 (4C, C*m*), 125.7 (2C, C*p*), 121.0 (4C, C*o*), 70.4 (d, $J_{C\text{-}2,P}$ = 7.4 Hz, C-2), 69.6 (d, $J_{C\text{-}1,P}$ = 6.3 Hz C-1), 62.8 (C-3).

Anal. Calcd for $C_{15}H_{17}O_5PS$ (340.33): C, 52.94; H, 5.03; P, 9.10; S, 9.42. Found: C, 52.57; H, 5.10; P, 8.58; S, 9.22.

7'd: ^{13}C NMR (Me_2SO-*d6*) δ 149.7 (C, *Cipso*), 128.8 (2C, C*m*), 124.8 (1C, C*p*), 120.1 (2C, C*o*), 78.8 (C-2), 67.0 (C-1), 61.3 (C-3).

Anal. Calcd for $C_9H_{11}O_4PS$ (246.22): C, 43.90; H, 4.50; P, 12.58; S, 13.02. Found: C, 43.71; H, 4.61; P, 12.10; S, 12.95.

1-*O*-(Diphenoxythionophosphoryl)-D,L-xylitol (15d). Likewise, 1-*O*-(diphenoxythionophosphoryl)-2,3:4,5-di-*O*-isopropylidene-D,L-xylitol **(5d)** (2.0 g, 4.2 mmol) gave, after 3.0 h, 0.4 g (25%) of **15d** and 0.2 g (20%) of **15'd** as by-product.

15d: ^{13}C NMR (Me_2SO-*d6*) δ 150.2 (2C, *Cipso*), 129.3 (4C, C*m*), 125.5 (2C, C*p*), 120.7 (4C, C*o*), 71.2 (2C, C-1, C-3), 70.3 (2C, C-2, C-4), 62.6 (C-5).

Anal. Calcd for $C_{17}H_{21}O_7PS$ (400.07): C, 51.00; H, 5.29; P, 7.74; S, 8.01. Found: C, 49.27; H, 5.10; P, 7.28; S, 7.88.

15'd: ^{13}C NMR (Me_2SO-*d6*) δ 151.3 (1C, *Cipso*), 129.8 (2C, C*m*), 124.2 (1C, C*p*), 120.7 (2C, C*o*), 81.0 (C-2), 76.7 (C-3), 76.1 (C-4), 72.7 (C-1), 59.5 (C-5).

Anal. Calcd for $C_{11}H_{15}O_6PS$ (306.27): C, 43.14; H, 4.94; P, 10.11; S, 10.47. Found: C, 42.57; H, 4.64; P, 10.25; S, 10.67.

1-*S*-(Diethoxythionophosphoryl)-1-deoxy-D,L-glycerol (7f). Applying the methodology described for **7a**, 1-*S*-(diethoxythionophosphoryl)-1-deoxy-2,3-*O*-isopropylidene-D,L-glycerol (**6f**) (2.0 g, 6.7 mmol) gave, after 2.5 h, 1.2 g (70%) of **7f**. ^{1}H NMR ($CDCl_3$) δ 4.05 (m, 4H, OCH_2), 3.57 (dd, 1H, $J_{3,3'}$ = 11.6 Hz, H-3), 3.43 (dd, 1H, $J_{2,3'}$ = 6.4 Hz, H-3'), 2.90 (m, 1H, H-1), 2.81 (m, 1H, H-1'), 2.09 (m, 1H, $J_{2,3}$ = 3.3 Hz, H-2), 1.23 (m, 6H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 70.2 (C-2), 63.8 (C-3), 63.3 (d, 2C, $J_{CH_2,P}$ = 5.6 Hz OCH_2), 36.1 (C-1), 14.9 (d, 2C, $J_{CH_3,P}$ = 7.4 Hz, CH_2CH_3).

Anal. Calcd for $C_7H_{17}O_4PS_2$ (260.31): C, 32.30; H, 6.58; P, 11.90; S, 24.63. Found: C, 32.09; H, 7.01; P, 11.78; S, 24.47.

1-*S*-(Diethoxythionophosphoryl)-1-deoxy-D,L-xylitol (15f). Likewise, 1-*S*-(diethoxythionophosphoryl)-1-deoxy-2,3:4,5-di-*O*-isopropylidene-D,L-xylitol (**5f**) (2.0 g, 5.0 mmol) gave, after 5 h, 0.8 g (50%) of **15f**. ^{13}C NMR (Me_2SO-*d6*) δ 71.9 (C-2), 71.7 (C-3), 70.6 (C-4), 63.3 (d, $J_{CH2,P}$ = 4.1 Hz, OCH_2), 62.4 (C-5), 36.1 (C-1), 15.4 (d, $J_{CH3,P}$ = 7.3 Hz, CH_2CH_3).

Anal. Calcd for $C_9H_{21}O_6PS_2$ (320.36): C, 33.74; H, 6.60; P, 9.67; S, 20.02. Found: C, 33.52; H, 6.75; P, 9.75; S, 20.23.

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