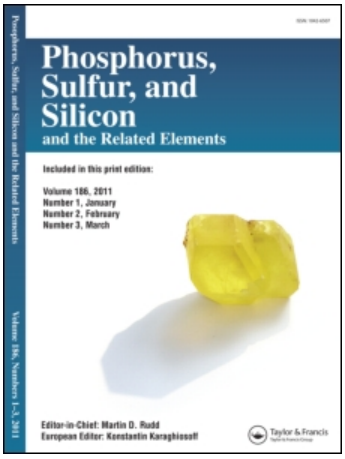

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SYNTHESIS OF *S*-α- AND -β-D-GLYCOSYL PHOSPHOROTHIOATES AND Se-α-D-GLYCOSYL PHOSPHOROSELENOATES FROM PERACETYLATED MONOSACCHARIDES

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SYNTHESIS OF *S*-α- AND -β-D-GLYCOSYL PHOSPHOROTHIOATES AND *Se*-α-D-GLYCOSYL PHOSPHOROSELENOATES FROM PERACETYLATED MONOSACCHARIDES

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Ambident anions derived from phosphorothioates **5**, **5a** and phosphoroselenoates **6–7** were glycosylated by per-*O*-acetylated β-D-hexopyranoses **1–2** in the presence of boron trifluoride etherate to yield *S*-α-D-glycosyl phosphorothioates **12–13** and *Se*-α-D-glycosyl phosphoroselenoates **14–16**. The reaction of aliphatic phosphorothioates **3–4a** with **1–2** leads to *S*-β-D-glycosyl phosphorothioates **8–11** with high yield.

Keywords: Glycosylation of phosphorothioates and phosphoroselenoates promoted by $BF_3{\cdot}Et_2O$; S-α-D-glycosyl and S-β-D-glycosyl phosphorothioates; Se-α-D-glycosyl phosphoroselinoates

INTRODUCTION

This paper constitutes a part of the studies on thio- and seleno analogues of sugar phosphates which are both useful in the synthesis of modified monosaccharides and as glycosyl donors.

The glycosyl phosphorothioates and phosphoroselenoates were prepared by condensation of the corresponding glycosyl halides[1–5] with phosphorothioates and phosphoroselenoates. This reaction led to a mixture of thiolo and thiono (or selenolo—selenono) isomers, the former predominating, having β-D-configuration. From the biochemical point of view α-D-glycosyl phosphates are

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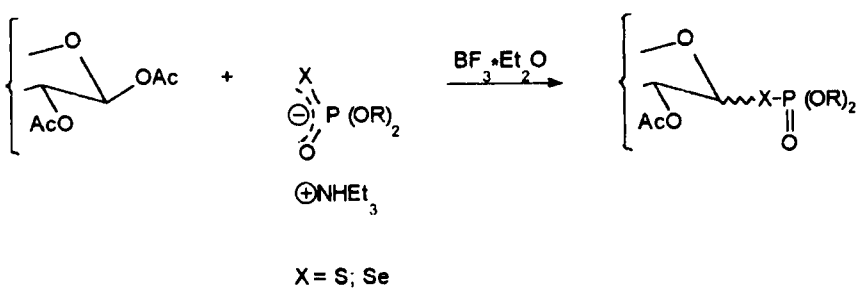
far more interesting than glycosyl phosphates having β-D-configuration. Chmielewski and BeMiller have pointed out[5] that di-*tert*-butyl phosphorothioate with glycosyl halides produce derivatives of *S*-α-glycosyl phosphorothioates, but the yield of reaction is low and the products are unstable. It has been reported[3] that the β-glycosylated selenolophosphates, derived only from neopentyl glycol, can be thermally and catalytically anomerized into the thermodynamically more stable α-isomers.

We now report on the reaction peracetylated sugars with phosphorothioate and phosphoroselenoate in the presence of boron trifluoride diethyl ether complex.

RESULTS AND DISCUSSION

Previously we have found[6] that the reaction of peracetylated sugars, stable and easily accessible glycosyl donors, with *O,O*-dialkylphosphorodithioates in the presence of boron trifluoride etherate allows the synthesis of *S*-glycosyl phosphorodithioates with high yield and stereoselectivity. The present research is a continuation of the investigations on the reaction catalysed by $BF_3 \cdot Et_2O$ involving peracetylated sugars and is now extended to ambident anions: phosphorothioates and phosphoroselenoates. Depending on the nature of the phosphorus reagents and the reaction conditions, *S*-β- or *S*-α,β-glycosyl phosphorothioates or *Se*-α,β-glycosyl phosphoroselenoates were obtained.



SCHEME 1

It is worth to emphasize that anomers having α-D-configuration predominated in crude reaction mixture and were easily isolated.

In this study, per-*O*-acetylated β-D-glucopyranose (**1**) and β-D-galactopyranose (**2**) as the representative 1,2-trans-*O*-acetates of sugars were examined and two types of organophosphorus reagents, *O,O*-dialkylphosphorothioates **3–5a** and *O,O*-dialkylphosphoroselenoates **6–7** were employed (Figure 1).

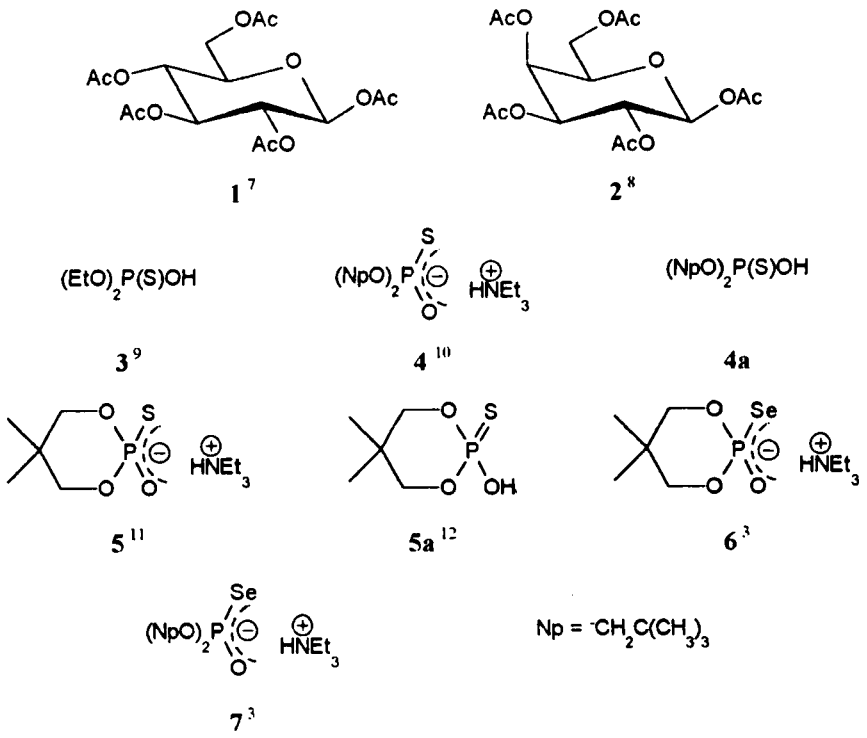


FIGURE 1 Starting materials for the *Synthesis of S-glycosyl phosphorothioates* and *Se-glycosyl phosphoroselenoates.*

Per-*O*-acetylated β-hexopyranoses **1,2**, organophosphorus reagents **3–7**, and boron trifluoride etherate were brought to react in 1,2-dichloroethane solvent at 20°C. Depending on the nature of substrates, 3–5 mmol equivalents of $BF_3{\cdot}Et_2O$ were used. Reactions were monitored by ^1H and ^{31}P NMR spectroscopy. As the formation of the complexes $(RO)_2P(X)\ O^-....BF_3$, seriously interfered with the appearance of ^{31}P NMR spectra, it was necessary to remove $BF_3{\cdot}Et_2O$ from the reaction mixture before testing the sample.

The reaction of equimolar amounts of peracetylated sugars **1** or **2** with *O,O*-dialkylphosphorothioates **3** or **4** gave *S*-β-D-glycosyl phosphorothioates **8–11** with high yield (Table I). The same results were obtained when both triethylammonium salt **4a** or acid **4** were employed as thiophosphorylated agents. When the reaction (**1** with **3**) time was extended to several days, a ^{31}P NMR spectrum of a crude reaction mixture showed that the β-product **8** predominated, and a small amount of α-product was present, accompanied by the decomposition

TABLE I Reaction Conditions and ^{31}P NMR data for compounds **8–16**[a].

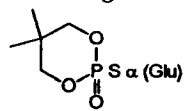
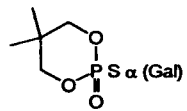
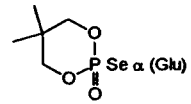
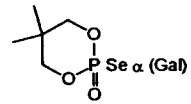
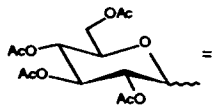
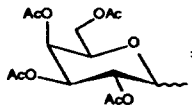
Entry	*Sugar*	*Substrates*		*Time*	*^{31}P NMR of the crude mix. δ ($CDCl_3$)*	*Ratio α/β anomers*	*Products*		*^{31}P NMR δ ($CDCl_3$)*
		Phosph reagent	*$BF_3 \cdot Et_2O$ [mmol]*						
1	**1**	**3**	5	4 h	28,66, 22,91	1:10	**8**[2]	$(EtO)_2P(O)S\beta$ (Glu)	22,91
2	**2**	**3**	5	10 min	28,74, 22,31	1:10	**9**	$(EtO)_2P(O)S\beta$ (Gal)	22,31
3	**1**	**4**	5	48 h	23,62, 23,03	1:10	**10**[2]	$(NpO)_2P(O)S\beta$ (Glu)	23,03
4	**2**	**4**	5	24 h	23,78, 23,38	1:20	**11**	$(NpO)_2P(O)S\beta$ (Gal)	23,38
5	**1**	**5**	3	7 days	15,51, 16,16	4:1	**12**		15,51
6	**2**	**5**	3	7 days	15,53, 16,41	5:1	**13**		15,53

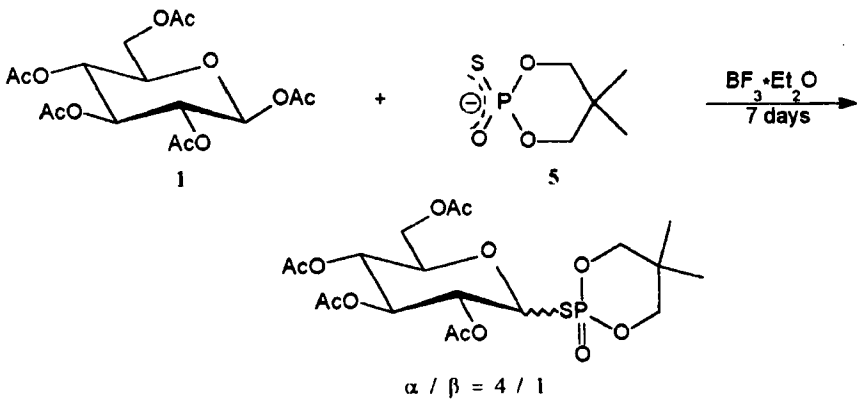
TABLE I (Continued)

Entry	*Sugar*	*Substrates*		*Time*	*^{31}P NMR of the crude mix. δ ($CDCl_3$)*	*Ratio α/β anomers*		*Products*	*^{31}P NMR δ ($CDCl_3$)*
		Phosph reagent	*$BF_3{\cdot}Et_2O$ [mmol]*						
7	**1**	**6**	5	48 h	8,9, 10,36	8:1	**14**[3]		8,9
8	**2**	**6**	5	24 h	8,9, 10,36	10:1	**15**[3]		8,9
9	**1**	**7**	3	6 days	17,03, 17,53	2,3:1	**16**	$(NpO)_2$ P Se α (Glu) ‖ O	17,03

a  = Glu  = Gal

products. The β-products **8–11** were isolated and characterised by means of ^{1}H; ^{13}C and ^{31}P NMR spectra, including other physical data (Table I and Experimental).

The reaction of **1** or **2** with phosphorothioate **5** in the presence of $BF_3 \cdot Et_2O$ was more complex and gave α/β mixtures of *S*-glycosyl phosphorothioates (Scheme 2). After 7 days the α/β isomers ratio was 4/1 (reaction **1** with **5**) and 5/1 (reaction **2** with **5**), as found by ^{31}P NMR spectroscopy (Table I, entry 5,6).



SCHEME 2

2Similarly, the reaction of **1** or **2** with phosphoroselenoate **6** (selenoic analogue of **5**) led to α/β mixtures of *Se*-glycosyl phosphoroselenoates, where the α-product predominated in the crude reaction mixture (Table I, entry 7,8). Selenophosphorylation of peracetate **1** with **7** (which has neopentyl groups) was less stereoselective than the other reactions investigated (α/β ratio 2,3/1 after 6 days). All experiments leading to α/β mixtures of products were carefully monitored by ^{31}P and ^{1}H NMR spectroscopy as follows. Phosphorus substrates and $BF_3 \cdot Et_2O$ were washed out from reaction mixtures by means of saturated $NaHCO_3$ and then water. The residues after drying and evaporating the organic solvent, were examined by both ^{1}H and ^{31}P NMR every few hours. At the beginning ^{31}P NMR spectra showed the presence of only one ^{31}P NMR signal, indicating the thiolo- or selenolophosphates structure of products. In the course of the reaction the second ^{31}P NMR signal appeared and its intensity gradually increased, until the reaction equilibrium was established (Table I). The major product was isolated and characterised as α-anomer. The results of ^{31}P NMR observations indicated that during the first step of reaction β-glycosyl phosphoroesthers were formed, due to the anchimeric assistance of C-2 acetyl group in

formation of acyloxonium ion, which favoured the attack of phosphoric nucleophile from the β-side. In the second step, β-glycosyl phosphates were anomerized to thermodynamically more stable α-glycosyl isomers.

The structure of *S*-α-D-hexopyranosyl phosphorothioates and *Se*-α-D-hexopyranosyl phosphorothioates was confirmed by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. A significant downfield shift of the anomeric proton in **12–16** together with its splitting pattern (dd) confirms the α-arrangement of C^{1}-S-P(O)$(OR)_2$ and C^{1}-SeP(O)$(OR)_2$. The α-D-configuration of products was further confirmed by the highly positive $[\alpha]_D$ values.

In conclusion, it was found that the glycosylation of phosphorothioates and phosphoroselenoates under the action of $BF_3 \cdot Et_2O$ was accompanied by anomerisation. The β-glycosyl phosphoroselenoates derived from neopentyl glycol and neopentyl alcohol underwent anomerisation faster than the corresponding sulfur analogues (derived from neopentyl glycol). It offers a novel approach to *S*-α-glycosyl phosphorothioates and *Se*-α-glycosyl phosphoroselenoates, hardly accessible glycosyl donors.

EXPERIMENTAL

General Methods

Melting points were determined with a Boethius PHMK 05 apparatus and are uncorrected. Optical rotations values were determined with a Polamat A polarimeter. IR spectra were obtained by using a Unicam SP-200G spectrophotometer. ^{31}P NMR spectra were measured with H_3PO_4 as external standard (Bruker 200AC operating at 81.01 MHz), ^{1}H NMR spectra were measured in $CDCl_3$ with Me_4Si as the internal standard (Bruker 300 MSL spectrometer). ^{13}C NMR spectra were determined in $CDCl_3$ solutions with a Bruker 300 MSL spectrometer operating at 75.46 MHz. Chemical shifts are given in parts per million, the coupling constants are expressed as J value in Hertz. Elemental analyses were performed at the Microanalitycal Laboratory, Institute of Chemistry, Medical University, Łódź. Column chromatography was carried on Kieselgel 60, 0.040–0.063 mm (230–400 Mesh) ASTM, Merck with benzene, acetone, chloroform 3 : 1 : 1 mixture as eluent. Detection was effected by exposure to iodine vapors. Petroleum ether was dried and distilled at the temp. 98–102°C, light petroleum ether within 35–55°C.

Starting Materials

The peracetates of sugars **1** and **2** were prepared according to known procedures[7,8]. The organophosphorus substrates **3–7** were obtained by the procedures described in literature: *O,O*-diethylphosphorothioic acid (**3**)[9], triethylammonium salt of *O,O*-dineopentylphosphorothioic acid (**4**)[10], 2-mercapto-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-oxide (**5a**)[12] and the triethylammonium salt of **5a** (**5**)[11], triethylammonium salt of 2-hydroxy-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-selenide (**6**)[3] triethylammonium salt of *O,O*-dineopentylphosphoroselenoic acid (**7**)[3].

Preparation of S-glycosyl Phosphorothioates 8–13 and Se-glycosyl Phosphoroselenoates 14–16—General Procedure

Boron trifluoride etherate (amount in Table I) was added to a stirred solution of peracetates **1–2** (1 mmol) and organophosphorus substrate **3,4,4a** (1 mmol) or **5,5a,6,7** (1.5 mmol) in 1,2-dichloroethane (25 mL). The mixture was kept at ambient temperature, for the time indicated in Table I. The reaction mixture was then washed with saturated $NaHCO_3$ (3 × 15 mL) and water (15 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The products were isolated by column chromatography (**8–9**) or crystallization (**10–16**). The following compounds were prepared in this manner.

O,O-Diethyl-S-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-phosphorothioate (8)[2]

Column chromatography gave **8** as an oil (0.21 g, 42.0%), $|\alpha|_D^{25}$ + 12.4° (c 1.29, $CHCl_3$); lit. + 13.9 (c 4.09)[2]. IR, ^{31}P, ^1H NMR data of the product **8** were identical with the reported values[2].

O,O-Diethyl-S-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-phosphorothioate (9)

Column chromatography gave **9** as an oil (0.39 g, 77.9%), $|\alpha|_D^{25}$ + 20.16° (c 1.16, $CHCl_3$); IR (CCl_4): ν 1275 (P=O), 1750 cm^{-1} (acetyl); ^1H NMR ($CDCl_3$): δ 5.44 (dd, 1H, $J_{3,4}$ 3.3 Hz, $J_{4,5} \approx 1$ Hz, H-4), 5.24 (t, 1H, $J_{1,2}$=$J_{2,3}$=10 Hz, H-2), 5.13–4.92 (m, 2H, H-1, H-3), 4.24–3.90 (m, 7H, 2xOCH_2, H-6, H-6, H-5), 2.11, 2.03, 1.99, 1.93 (4s, 12H, 4xOAc), 1.28 (t, J 7, 6H, 2xCH_3); ^{13}C NMR ($CDCl_3$): δ 83.53 (d, $^2J_{C,P} \sim 3$ Hz, C-1), 67.39 (d, $^3J_{C,P}$

10.0 Hz, C-2), 74.46 (C-5), 71.02 (C-3), 66.81 (C-4), 61.09 (C-6), 63.41 (2d, 2xOCH_2, $^2J_{C,P}$ 5.2 Hz), 20.03, 19.92 (2s, 4xAc), 15.39 (2xCH_3). Anal. Calcd for $C_{18}H_{29}O_{12}PS$: C, 43.20; H, 5.84. Found: C, 43.50; H, 5.76.

O,O-Di-neo-pentyl-S-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-phosphorothioate (10)[2]

Two crystallisations from CCl_4 and petroleum ether gave **10** as needles (0.32 g, 54.8%): mp 116–7°C, lit. mp 116–7°C[2]; $|\alpha|_D^{25}$ + 6.6° (c 1.78, $CHCl_3$), lit. +6.6° (c 1.8, $CHCl_3$)[2]. IR, ^{31}P, ^1H NMR data of the product **10** were identical with the reported values[2].

O,O-Di-neo-pentyl-S-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-phosphorothioate (11)

Two crystallisations from CCl_4 and petroleum ether gave **11** as needles (0.33 g, 56.5%): mp 96–7°C; $|\alpha|_D^{25}$ +25.04° (c 1.15, $CHCl_3$); IR (KBr): ν 1270 (P═O), 1750 cm^{-1} (acetyl); ^1H NMR ($CDCl_3$): δ 5.44 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,5} < 1$ Hz, H-4), 5.29 (t, $J_{1,2}$ 10 Hz, $J_{2,3}$ 9.9 Hz, 1H, H-2), 5.12–5.05 (m, 2H, H-1, H-3), 4.21–3.99 (m, 3H, H-6, H-6, H-5, H-5), 2.15, 2.07, 2.03, 1.98 (4s, 12H, 4xOAc), 0.96, 0.94 (2s, 18H, 6xCH_3), 3.96–3.64 (m, 4H, 2xOCH_2); ^{13}C NMR ($CDCl_3$): δ 83.79 (d, $^2J_{C,P} \sim 3$ Hz, C-1), 67.84 (d, $^3J_{C,P}$ 10.4 Hz, C-2), 74.84 (C-5), 71.66 (C-3), 67.02 (C-4), 61.02 (C-6), 31.97 (d, $^3J_{C,P}$ 6.8 Hz, CCH_3), 26.00, (6xCH_3), 20.61, 20.49 (4xCH_3CO), 170.21–169.80 (C═O). Anal. Calcd for $C_{24}H_{41}O_{12}PS$: C, 49.35; H, 7.17. Found: C, 49.37; H, 7.20.

5,5-Dimethyl-2-oxo-2-S-(2′,3′,4′,6′-tetra-O-acetyl-α-D-glucopyranosyl)-2-thio-1,3,2-dioxaphosphorinane (12)

Two crystallisations from diethyl ether gave **12** as needles (0.23 g, 44.92%): mp 123–4°C; $|\alpha|_D^{25}$ +187.25° (c 1.02, $CHCl_3$); IR (KBr): ν 1270 (P═O), 1750 cm^{-1} (acetyl); ^1H NMR ($CDCl_3$): δ 6.20 (dd, 1H, $J_{1,2}$ 5.2 Hz, $J_{I,P}$ 8.3 Hz, H-1), 5.36 (t, 1H, $J_{2,3}$ 9.8 Hz, H-3), 5.16 (dd, 1H, $J_{1,2}$ 5.2 Hz, $J_{2,3}$ 9.8 Hz, H-2), 5.10 (t, 1H, $J_{4,5}$ 9.5 Hz, $J_{3,4}$ 9.9 Hz, H-4), 4.37–3.84 (m, 7H, 2xOCH_2, H-6, H-6, H-5′), 2.07, 2.06, 2.03, 2.02 (4s, 12H, 4xOAc), 1.28, 0.92 (2s, 6H, 2xCH_3); ^{13}C NMR ($CDCl_3$): δ 82.61 (C-1), 70.07 (C-5), 69.94 (C-3), 69.52 (d, $^3J_{C,P}$ 5.9 Hz, C-2), 67.82 (C-4), 61.27 (C-6), 32.31 (d, $^3J_{C,P}$ 6.4 Hz, CCH_3), 21.74-20.43 (4xAc), 21.74–20.30 (2xCH_3), 170.41–169.20 (4xC═O). Anal. Calcd for $C_{19}H_{29}O_{12}PS$: C, 44.53; H, 5.70. Found: C, 44.29; H, 5.68.

5,5-Dimethyl-2-oxo-2-S-(2′,3′,4′,6′-tetra-O-acetyl-α-D-galactopyranosyl)-2-thio-1,3,2-dioxaphosphorinane (13)

Two crystallisations from CCl_4 gave **13** as needles (0.21 g, 41.1%): mp 166–8°C; $|\alpha|_D^{25}$ +197.52° (c 1.21, $CHCl_3$); IR (KBr): ν 1270 (P═O), 1750 cm^{-1} (acetyl); ^1H NMR ($CDCl_3$): δ 6.27 (dd, 1H, $J_{1,2}$ 5.1 Hz, $J_{1,P}$ 8.0 Hz, H-1), 5.47 (dd, 1H, $J_{4,5}$ 1.1 Hz, $J_{3,4}$ 3.1 Hz, H-4), 5.44 (dd, 1H, $J_{1,2}$ 5.1 Hz, $J_{2,3}$ 10.7 Hz, H-2), 5.14 (dd, 1H, $J_{3,4}$ 3.1 Hz, H-3), 4.39 (t, 1H, $J_{5,6}$ 6.9 Hz, H-5), 4.19 3.80 (m, 6H, 2 × OCH_2, H-6, H-6′), 2.12, 2.06, 2.01, 1.98 (4s, 12H, 4 × OAc), 1.28, 0.90 (2s, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$): δ 83.61 (C-), 68.63 (C-5), 67.96 (C-3), 67.04 (C-4), 66.74 (d, $^3J_{C,P}$ 6.4 Hz, C-2), 60.68 (C-6), 32.39 (d, $^3J_{C,P}$ 6.8 Hz, CCH_3), 21.86 (CH_3, ax), 20.44 (CH_3, eq), 20.61, 20.54 (4 × Ac), 170.32–169.50 (4 × C═O). Anal. Calcd for $C_{19}H_{29}O_{12}PS$: C, 44.53; H, 5.70. Found: C, 44.41; H, 5.73.

5,5-Dimethyl-2-oxo-2-Se-(2′,3′,4′,6′-tetra-O-acetyl-α-D-glucopyranosyl)-2-seleno-1,3,2-dioxaphosphorinane (14)[3].

Two crystallisations from CCl_4 and petroleum ether gave **14** as needles (0.34 g, 60.8 %): mp 146–8°C, lit. mp 146–8°C[3]; $|\alpha|_D^{25}$ +222.2° (c 0.8, $CHCl_3$), lit. +199.8°[3]. Ir, ^{31}P, ^1H NMR data of the product **14** were identical with the described values[3].

5,5-Dimethyl-2-oxo-2-Se-(2′,3′,4′,6′-tetra-O-acetyl-α-D-galactopyranosyl)-2-seleno-1,3,2-dioxaphosphorinane (15)[3]

Two crystallisations from CCl_4 and petroleum ether gave **15** as needles (0.32 g, 57.24 %): mp 168–70°C, lit. mp 168–70°C[3]; $|\alpha|_D^{25}$ +221.66° (c 1.68, $CHCl_3$), lit. +225° (c 1.8, $CHCl_3$)[3]. IR, ^{31}P, ^1H, NMR data of the product **15** were identical with the reported values[3].

O,O-Di-neo-pentyl-Se-(2′,3′,4′,6′-tetra-O-acetyl-α-D-galactopyranosyl)-phosphoro-selenoate (16)

Two crystallisations from light petroleum ether gave **16** as needles (0.32 g, 50.71 %): mp 89–91°C; $|\alpha|_D^{25}$ +179.45° (c 0.99, $CHCl_3$); IR (KBr): ν 1270 (P═O), 1750 cm^{-1} (acetyl); ^1H NMR ($CDCl_3$): δ 6.39 (dd, 1H, $J_{1,2}$ 5.2 Hz, $J_{1,P}$ 8.9′ Hz, H-1), 5.73–5.14 (m, 2H, H-3, H-4), 5.08 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{1,2}$ 5.1 Hz, H-2), 4.18 (dd, 1H, $J_{5,6}$ 2.Hz, $J_{6,6}$ 12 Hz, H-6′), 4.38–4.20 (m, 2H, H-5, H-6), 3.85–3.63 (m, 4H, 2 × OCH_2), 2.08, 2.07, 2.03, 2.02 (4s, 12H, 4 × OAc), 0.95 (s, 9

× CH_3); ^{13}C NMR ($CDCl_3$): δ 83.65 (d, $^2J_{C,P}$ 2.6 Hz, C-1), 71.65 (C-5), 71.15 (C-3), 70.15 (d, $^3J_{C,P}$ 5.2 Hz, C-2), 67.70 (C-4), 61.32 (C-6), 32.24 (d, $^2J_{C,P}$ 6.7 Hz, CCH_3), 26.16 (9 × CH_3), 20.65, 20.78 (4 × Ac), 170.59–169.35 (4 × C=O). Anal. Calcd for $C_{24}H_{41}O_{12}PSe$: C, 45.65; H, 6.54. Found: C, 46.05; H, 6.92.

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References

[1] M. Michalska, J. Michalski and I. Orlich, *Bull. Acad. Pol. Sci.*; *Ser. Sci., Chim.*, **22**, 1053, (1974); *Chem. Abstr.*, **82**, 140430h, (1975).
[2] M. Michalska, I. Orlich-Krężel and J. Michalski, *Tetrahedron*, **34**, 617, (1978).
[3] M. Michalska, J. Michalski and I. Orlich-Krężel, *Pol. J. Chem.*, **53**, 253, (1979).
[4] P. Lipka and M. Michalska, *Carbohydr. Res.*, **113**, 317, (1983).
[5] M. Chmielewski and J. N. BeMiller, *Carbohydr. Res.*, **96**, 73, (1981).
[6] W. Kudelska and M. Michalska, *Synthesis*, 1539, (1995).
[7] A. I. Vogel, *Textbook of Practical Organic Chemistry*, (Longmans, London, 1954) pp 438–439.
[8] E. Erwig and W. Koenigs, *Ber. Dtsch. Chem. Ges.*, **22**, 2207, (1889).
[9] T. W. Mastin and A. M. Khaletskii, *Zh. Obshch. Khim.*, **31**, 2508, (1961).
[10] S. Bluj, B. Borecka, A. Łopusiñski and J. Michalski, *Rocz. Chem.*, **48**, 329, (1974); *Chem. Abstr.*, **81**, 63085z, (1974).
[11] R. S. Edmundson, *Tetrahedron*, **21**, 2379, (1965).
[12] K. Bruzik and W. Stec, *J. Org. Chem.*, **46**, 1618, (1981).