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## Synthesis of β-D-Xylopyranoside Thiophosphate Derivatives

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Abstract—A method of synthesis of  $\beta$ -D-xylopyranoside thiophosphate derivatives was developed. Biological testing revealed a high insecticidal activity in the synthesized compounds.

Keywords: xylose, organophosphorus pesticides, thiophosphates, insecticide activity

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Organophosphorus pesticides are among the most widely used agricultural pesticides [1–6]. This is due to a number of advantages they offer over other pesticides: high insecticidal, acaricidal, and fungicidal activity and broad-spectrum action on noxious pest arthropods; metabolism products are almost nontoxic for humans and animals; relatively fast metabolism in vertebrates and lack of tendency to accumulate in their tissues, as well as fairly low, if any, chronic toxicity; systemic effect of some insecticides and fungicides; and low consumption and fast action on plant pests [3, 7–9]. Moreover, most organophosphorus pesticides readily degrade in soil to form phosphoric acid and other simple products, leaving almost no harmful residues in the environment [10–14].

At present the list of organophosphorus pesticides used in agriculture includes more than 200 organophosphorus compounds of different classes [3–5, 15–17]; among them thiophosphate and thiophosphonate derivatives are the most efficient fungicides and insecticides [3, 7, 18–21]. However, this list of agricultural crop protection agents includes almost no carbohydrates, in particular, organophosphorus mono- and oligosaccharides [22–25]. In this connection, we considered of interest to synthesize thiophosphate derivatives of monosaccharides and to test their pesticidal activity.

The aim of the present work was the synthesis of thiophoshate derivatives of xylose and testing their insecticidal activity.

In the first step we performed acetylation of D-(+)xylose with acetic anhydride in anhydrous pyridine in the presence of a 4-(dimethylamino)pyridine (DMAP) catalyst. The resulting xylose tetraacetate 1 was treated with HBr (33% solution in acetic acid) in anhydrous dichloromethane by the procedure described in [26] to obtain 2,3,4-tri-O-acetyl-α-D-xylopyranoside bromide 2. The latter compound is unstable, and, therefore, it was reacted without additional purification with potassium thioacetate in a 4 : 1 mixture of anhydrous CH<sub>2</sub>Cl<sub>2</sub> and DMF. The reaction product, 2,3,4-tri-O-acetyl-1-S-acetyl- $\beta$ -D-xylopyranoside **3**, was treated with sodium methylate in anhydrous methanol to remove the acetate groups, after which the reaction medium was neutralized to pH 7.2 with Dowex H<sup>+</sup>, and intermediate 4 was reacted with dialkyl(diaryl)phosphoryl chlorides (dimethylphosphoryl chloride, diethylphosphoryl chloride, or diphenylphosphoryl chloride) in anhydrous pyridine in the presence of DMAP (catalyst) to obtain thiophoshate  $\beta$ -D-xylo-pyranoside derivatives 5-7.

The structure of compounds 5–7 was confirmed by NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P). Protons at the anomeric carbon atom in the <sup>1</sup>H NMR spectra of these compounds give doublet signals at 5.74–5.81 ppm ( $J_{1,2} = 8.6-8.8$  Hz), which provides evidence for the  $\beta$  configuration of monosaccharides 5–7 and is consistent with the <sup>1</sup>H NMR parameters of xylose derivatives reported in [26, 27]. The methoxy protons appear as doublets at 3.37–3.39 ppm (5), and the ethoxy protons



 $R = CH_3 (5), C_2H_5 (6), C_6H_5 (7). a, (CH_3CO)_2O, C_5H_5N, DMAP, 0-20^{\circ}C; b, HBr (33\% CH_3COOH), CH_2Cl_2, 0^{\circ}C; c, KSAc, CH_2Cl_2-DMF (4 : 1), 20^{\circ}C; d, NaOCH_3, CH_3OH, 0^{\circ}C; e, Dowex H^+, CH_3OH, 0^{\circ}C; f, (RO)_2P(O)Cl, C_5H_5N, DMAP, 0-20^{\circ}C.$ 

appear as methyl triplets at 1.09–1.17 ppm and methylene quartets at 3.87 ppm (6). The  $J_{\rm HP}$  constant was 10.2 Hz. The  $J_{\rm HP}$  = constant for the (O)P(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> fragment in compound 6 could not be estimated, probably, because of its small value.

In the <sup>13</sup>C NMR spectra of compound **5** the methyl carbons give a doublet at 52.67 ppm ( $J_{CP} = 6.8$  Hz). The <sup>13</sup>C NMR spectrum of compound **6** displays EtO doublets at 16.60 ppm ( $J_{CP} = 6.8$  Hz), and OCH<sub>2</sub> doublets at 62.07 ppm ( $J_{CP} = 5.5$  Hz), which is consistent with published data [28–30]. The phosphorus chemical shifts of  $\beta$ -D-xylopyranoside thiophosphate derivatives **5**–7 were 24.5–28.3 ppm; such  $\delta_P$  values are characteristic of [(RO)<sub>2</sub>P(O)SR] thiophosphates with a tetracoordinate phosphorus atom [29, 31, 32].

Earlier we synthesized mono- and disaccharides with S-Hg-R functional groups (R = alkyl or phenyl) at the anomeric carbon atom and studied their fungicidal and herbicidal activity [27]. According to the testing results, such functionally substituted monoand disaccharides showed a pronounced fungicidal and herbicidal activity and even excelled in biological activity such known agents as Delsene [2-(methoxycarbonylamino)benzimidazole], Vectra (bromoconazole), and Rubigan  $[(\pm)-\alpha-(pyrimidin-5-yl)-2,4'-dichlorobenz$ hydryl alcohol], which are used as efficient phytofungicides. However, the presence of mercury atoms in the synthesized saccharides sets a limit to their practical application as pesticides. As known, mercury accumulates in living bodies and can transform into stable methylmercury derivatives which are

highly toxic and carcinogenic compounds [12, 33, 34]. In this connection, even though mercury compounds are potent pesticides, they are no longer used in most countries in the world. At present the design of new pesticides is required to ensure, along with a high efficiency, low toxicity, easy degradation in soil, and environmental safety [35–40].

Taking these requirements into account, we previously synthesized aryl-substituted xylose derivatives which exhibited a high activity against a series of phytopathogenic fungi [41]. As mentioned above, organophosphorus pesticides containing thiophosphate moieties were found to be potent insecticides. *S*-Trifluoromethyl thiophosphates and halocyclobutyl thiophosphates [42], dihaloethyl thiophosphates [44], as well as thiophosphate derivatives of organic compounds of different classes [3, 7, 20, 45–47] were described, which show a high insecticidal activity and are widely used in agriculture. Therefore, we focused our further research on the search for new potentially high-efficiency thiophosphate insecticides derived from mono- and disaccharides.

Insecticidal activity testing  $\beta$ -D-xylopyranoside thiophosphate derivatives **5–7** established their high activity against suctorial insects. The test object was the vetch aphid species *Medoura viciae* Buckt. (see the table). It was shown that compound **5** in a concentration of 0.1% killed 90% of aphides within 2 h after treatment. Compounds **6** and **7** showed a high insecticidal activity at the same concentration, and in this case the mortality of aphides was 100% within 6–

## BELAKHOV et al.

Comp. no.	Insecticidal activity, % mortality					
	0.1%			0.05%		
	2 h	6 h	24 h	2 h	6 h	24 h
Control (water)	0	0	10	0	0	0
Control (water + Neonol AF 9-10)	0	0	10	0	0	0
5	90	95	100	35	40	100
6	50	90	100	10	10	30
7	75	100	_	85	100	_

Insecticidal activity of thiophosphate β-D-xylopyranoside derivatives 5-7 against vetch aphid (Medoura viciae Buckt.)

24 h. Compounds **5** and **7** in a concentration of 0.05% killed 100% of test objects within 6–24 h. The insecticidal activity of compound **6** under similar conditions was much lower (mortality 30%).

Thus, we synthesized thiophosphate  $\beta$ -D-xylopyranoside derivatives having a high insecticidal activity. It should be noted that the search for new pesticides among mono- and disaccharides is a promising direction in view of the fact that the research needs to be extended to other types of pesticidal activity, such as fungicidal, acaricidal, and nematicidal. Furthermore, of undeniable interest is to explore the growth control effect of mono- and disaccharide pesticides, taking into account that agricultural plants can use carbohydrates as a source of carbon nutrition for herbage mass build-up. In the latter case, such potential pesticides not only provide a multitargeted positive effect, but also are almost completely consumed, not forming by-products that would require to be utilized, and, therefore, are more environmentally friendly.

## EXPERIMENTAL

Regents purchased from Sigma–Aldrich (USA) or Fluka (Switzerland) were used as received. Organic solvents were purified before use by the procedures described in [48].

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker Avance III instrument (Germany) at 600 MHz in CDCl<sub>3</sub> or CD<sub>3</sub>OD, internal reference TMS. The <sup>31</sup>P NMR spectra were measured on a Bruker AC-200 instrument (Germany) at 200 MHz, external reference 85% H<sub>3</sub>PO<sub>4</sub>. The mass spectra (MALDI TOF) were run on a MALDI Micromass spectrometer (USA), matrix  $\alpha$ -cyano-4-hydroxycynnamic acid. The IR spectra were registered on a Bruker Vector 22 instrument (Germany) in KBr pellets. Reactions were monitored and the product purity was controlled by TLC on Silica Gel 60  $F_{254}$  (0.25 mm, Merck, Gernamy), eluents ethyl acetate–hexane (1 : 1) and methanol–chloroform (1 : 4). Spots were visualized by charring with a special solution containing 120 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and 5 g of (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> in 10% H<sub>2</sub>SO<sub>4</sub>. Column chromatography was performed on Silica Gel 60 (63-200 µm, Merck, Gernamy). Dowex 50Wx8 in the H<sup>+</sup>form (200–400 µm, Sigma– Aldrich, USA) was used for pH adjustment. The melting points were measured on an Electrothermal IA9300 apparatus (Great Britain).

1,2,3,4-Tetra-*O*-acetyl-β-D-xylopyranoside (1). The DMAP catalyst was added to a solution of 30.0 g (0.2 mol) D-(+)-xylose in 150 mL of anhydrous pyridine, after which 81.7 g (0.8 mol) of acetic anhydride was added dropwise with vigorous stirring at 0°C under argon over the course of 20 min. The reaction mixture was stirred at 0°C for 1 h and then for an additional 3 h at 20°C. The reaction progress was monitored by TLC in ethyl acetate-hexane, 1 : 1. When the reaction was complete, the mixture was cooled to 0°C and diluted with ethyl acetate. The organic phase was treated in succession with 5% H<sub>2</sub>SO<sub>4</sub> and concentrated solutions of NaHCO<sub>3</sub> and NaCl, and then dried with anhydrous MgSO<sub>4</sub> and concentrated at a reduced pressure. The resulting amorphous substance was purified by column chromatography on silica gel, eluent ethyl acetatehexane, 1 : 9. A 1.5 : 1 mixture of the  $\beta$  and  $\alpha$  anomers was obtained. B-Anomer 1 was isolated as colorless crystals after double recrystallization of the anomers mixture from ethanol. Yield 57%, mp 127-128°C,  $[\alpha]_D^{20}$ -38.7 (c 2.3, CH<sub>2</sub>Cl<sub>2</sub>) {mp 126-127°C,  $[\alpha]_D^{20}$ 

-38.5 (*c* 2.3, CH<sub>2</sub>Cl<sub>2</sub>) [49]},  $R_f$  0.56 (ethyl acetate-hexane, 1 : 1). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm (*J*, Hz): 2.02 s, 2.03 s, 2.04 s, 2.06 s (12H, acetyl groups), 3.52 d.d (1H, H<sup>5a</sup>,  $J_{4,5a} = 8.5$ ,  $J_{5a,5b} = 11.9$ ), 4.12 d.d (1H, H<sup>5b</sup>,  $J_{4,5b} = 5.0$ ,  $J_{5b,5a} = 12.0$ ), 4.91 d.d.d (1H, H<sup>4</sup>,  $J_{4,5a} = 8.4$ ,  $J_{4,5b} = 4.8$ ), 4.99 t (1H, H<sup>2</sup>,  $J_{2,3} = 7.8$ ), 5.18 t (1H, H<sup>3</sup>,  $J_{3,4} = 7.8$ ), 5.34 d (1H, H<sup>1</sup>,  $J_{1,2} = 8.7$ ). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_C$ , ppm: 20.65, 20.68, 20.71, 20.74 [C(O)O<u>CH<sub>3</sub></u>], 65.69 (C<sup>5</sup>), 68.25 (C<sup>4</sup>), 69.08 (C<sup>3</sup>), 71.64 (C<sup>2</sup>), 80.34 (C<sup>1</sup>), 169.30, 169.58, 169.71, 169. 85 [<u>C</u>(O)OCH<sub>3</sub>]. Mass spectrum (MALDI TOF), *m/z*: 341.17 [*M* + Na]<sup>+</sup> (calculated for C<sub>13</sub>H<sub>18</sub>O<sub>9</sub>Na: 341.12).

1,3,4-Tri-O-acetyl-α-D-xylopyranoside bromide (2). A solution of 13.2 g (0.162 mol) HBr in 30% acetic acid was added at  $-5^{\circ}$ C under argon to a solution of 17.1 g (0.054 mol) of compound 1 in 100 mL of anhydrous dichloromethane. The reaction mixture was stirred at 5°C for 1.5 h and then an additional 3 h at 20°C. Reaction progress was monitored by TLC, eluent ethyl acetate-hexane, 1:1. When the reaction was complete, the mixture was cooled to 0°C and diluted with cold dichloromethane, after which pieces of frozen 5% solution of NaHCO3 were added. The aqueous layer was washed with 3 portions of cold dichloromethane, the combined extracts were dried with anhydrous MgSO<sub>4</sub> and concentrated at a reduced pressure. Compound 2 readily decomposed on storage and on column chromatography on silica gel and, therefore, it was used in the subsequent reaction without additional purification. An analytical sample of bromide 2 was prepared by recrystallization from ethyl acetate-hexane, 2 : 3. Yield 80%, mp 102-103°C (mp 101–102°C [50]),  $R_{\rm f}$  0.67 (ethyl acetate–hexane, 1 : 1). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm (J, Hz): 2.03 s, 2.04 s, 2.06 s (9H, acetyl groups), 3.58 d.d (1H,  $H^{5a}$ ,  $J_{4,5a} = 8.7$ ,  $J_{5a,5b} = 12.0$ ), 4.17 d.d (1H,  $H^{5b}$ ,  $J_{4,5b} =$ 5.0,  $J_{5b,5a} = 12.0$ ), 4.96 d.d.d (1H, H<sup>4</sup>,  $J_{4,5a} = 8.6$ ,  $J_{4,5b} =$ 5.2), 5.04 t (1H, H<sup>2</sup>,  $J_{2,3} = 7.9$ ), 5.18 t (1H, H<sup>3</sup>,  $J_{3,4} =$ 7.9), 5.34 d (1H, H<sup>1</sup>,  $J_{1,2} = 4.2$ ). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 20.70, 20.73, 20.76 [C(O)O<u>CH</u><sub>3</sub>],  $65.74 (C^5), 68.25 (C^4), 69.15 (C^3), 72.03 (C^2), 80.60$ (C<sup>1</sup>), 169.62, 169.79, 169. 88 [C(O)OCH<sub>3</sub>]. Mass spectrum (MALDI TOF), m/z: 340.12  $[M + H]^+$ (calculated for  $C_{11}H_{16}BrO_7$ : 340.09).

**2,3,4-Tri-***O***-acetyl-1**-*S***-acetyl-** $\beta$ **-D-xylopyranoside** (3) was prepared by the modified procedure described in [27]. A solution of 13.2 g (0.091 mol) of potassium thioacetate in 25 mL of DMF–dichlorometane, 1 : 4, was added dropwise at –70°C under argon to a solution of 15.5 g (0.046 mol) of compound 2 in 75 mL of a

1:4 mixture of anhydrous DMF and dichloromethane. The reaction temperature was gradually raised over the course of 3 h to 20°C and then the mixture was stirred at this temperature for 12 h. The reaction progress was monitored by TLC, eluent ethyl acetate-hexane, 1:1. When the reaction was complete the mixture was cooled to 0°C and diluted with cold ethyl acetate, after which ice was added. The organic phase was washed with water, dried with anhydrous MgSO<sub>4</sub>, and concentrated at a reduced pressure. The dry amorphous substance was purified by column chromatography on silica gel, eluent ethyl acetate-hexane, 1 : 9. Yield 75%, yellow crystals, mp 97–98°C,  $[\alpha]_D^{20}$ –8.5 (c 1.0, CHCl<sub>3</sub>) {mp 95–98°C,  $[\alpha]_D^{20}$ –8.4 (*c* 1.0, CHCl<sub>3</sub>) [27]},  $R_{\rm f}$  0.51 (ethyl acetate-hexane, 1 : 1). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm (J, Hz): 2.04 s, 2.06 s, 2.08 s (9H, acetyl groups), 2.36 s (3H, S-acetyl group). 3.54 d.d (1H,  $H^{5a}$ ,  $J_{4,5a} = 8.5$ ,  $J_{5a,5b} = 11.9$ ), 4.16 d.d (1H,  $H^{5b}$ ,  $J_{4,5b} = 5.0$ ,  $J_{5b,5a} = 12.0$ ), 4.87 d.d.d (1H, H<sup>4</sup>,  $J_{4,5a} = 8.4$ ,  $J_{4,5b} = 4.8$ ), 5.03 t (1H, H<sup>2</sup>,  $J_{2,3} = 7.8$ ), 5.21 t (1H,  $H^{3}$ ,  $J_{3,4} = 7.8$ ), 5.37 d (1H,  $H^{1}$ ,  $J_{1,2} = 8.7$ ). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 20.65, 20.65, 20.69, 20.73 [C(O)O<u>CH<sub>3</sub></u>], 30.84 (S-acetyl group), 65.72 (C<sup>5</sup>), 68.29  $(C^4)$ , 69.11  $(C^3)$ , 71.59  $(C^2)$ , 80.38  $(C^1)$ , 169.32, 169.54, 169.67 [C(O)OCH<sub>3</sub>]. Mass spectrum (MALDI TOF), m/z: 357.13  $[M + Na]^+$  (calculated for C13H18O8NaS: 357.10).

[1-(Dialkoxy(diphenoxy)phosphoryl)sulfanyl]-β-**D-xylopyranosides (5–7).** Sodium methylate (3.5 g, 0.016 mol) was added at 0°C under argon to a solution of 1.3 g (0.004 mol) of compound 3 in 30 mL of anhydrous methanol. The reaction progress was monitored by TLC, eluent methanol-chloroform, 1:4. The reaction was performed for 4 h at 0°C, after which the reaction mixture was neutralized with the Dowex  $H^+$  cationite in anhydrous methanol to pH 7.2 and filtered. The filtrate was concentrated at a reduced pressure, and the residue was dried for 5 h in a vacuum at 20°C. The resulting pyranoside 4 was dissolved in 50 mL of anhydrous pyridine, and 4-(dimethylamino) pyridine and 0.006 mol of the corresponding dialkyl (diphenyl)phosphoryl chloride were added to the solution at 0°C under argon. The reaction was performed at 0°C for 1 h and then for an additional 4 h at 20°C. The reaction progress was monitored by TLC, eluent methanol-chloroform, 1:4. When the reaction was complete the mixture was cooled to 0°C and diluted with ethyl acetate. The organic phase was treated in succession with 5% H<sub>2</sub>SO<sub>4</sub> and concentrated solutions of NaHCO<sub>3</sub> and NaCl, and then dried with

anhydrous MgSO<sub>4</sub> and concentrated at a reduced pressure. The resulting amorphous substance was purified by column chromatography on silica gel, eluent methanol–chloroform, 1 : 9. The eluates containing the target product were combined and concentrated at a reduced pressure. The residue was dried in a vacuum at 20°C for 5 h and recrystallized from methanol–chloroform, 1 : 3. Compounds 5–7 were isolated as fine white crystals.

**[1-(Dimethoxyphosphoryl)sulfanyl]-β-D-xylopyra**noside (5). Yield 72%, mp 131–132°C,  $R_f$  0.57 (methanol–chloroform, 1 : 4). <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD), δ, ppm (*J*, Hz): 3.37 d [6H, (O)P(OCH<sub>3</sub>)<sub>2</sub>, *J*<sub>HP</sub> = 10.2], 3.52 d.d (1H, H<sup>5a</sup>, *J*<sub>4,5a</sub> = 8.5, *J*<sub>5a,5b</sub> = 11.9), 4.13 d.d (1H, H<sup>5b</sup>, *J*<sub>4,5b</sub> = 5.0, *J*<sub>5b,5a</sub> = 12.0), 4.85 d.d.d (1H, H<sup>4</sup>, *J*<sub>4,5a</sub> = 8.4, *J*<sub>4,5b</sub> = 4.8), 5.01 t (1H, H<sup>2</sup>, *J*<sub>2,3</sub> = 7.8), 5.18 t (1H, H<sup>3</sup>, *J*<sub>3,4</sub> = 7.8), 5.74 d (1H, H<sup>1</sup>, *J*<sub>1,2</sub> = 8.7). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_C$ , ppm (*J*, Hz): 52.67 d [*J*<sub>CP</sub> = 6.8, (O)P(OCH<sub>3</sub>)<sub>2</sub>], 65.69 (C<sup>5</sup>), 68.25 (C<sup>4</sup>), 69.14 (C<sup>3</sup>), 71.56 (C<sup>2</sup>), 80.41 (C<sup>1</sup>). <sup>31</sup>P NMR spectrum (CD<sub>3</sub>OD):  $\delta_P$  26.4 ppm. Mass spectrum (MALDI TOF), *m/z*: 297.07 [*M* + Na]<sup>+</sup> (calculated for C<sub>7</sub>H<sub>15</sub>O<sub>7</sub>NaPS: 297.03).

[1-(Diethoxyphosphoryl)sulfanyl]-β-D-xylopyranoside (6). Yield 76%, mp 138–139°C, R<sub>f</sub> 0.54 (methanol-chloroform, 1 : 4). <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD), δ, ppm (J, Hz): 1.09 d.t and 1.17 d.t [6H, (O)P(OCH<sub>2</sub><u>CH<sub>3</sub></u>)<sub>2</sub>, J = 7.4 Hz], 3.50 d.d (1H, H<sup>5a</sup>,  $J_{4,5a} =$ 8.5,  $J_{5a,5b} = 11.9$ ), 3.87 d.q [4H,  $J_{HP} = 10.2$ ,  $J_{HH} = 7.4$ , (O)P(O<u>CH</u><sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 4.17 d.d (1H, H<sup>5b</sup>,  $J_{4,5b} = 5.0, J_{5b,5a} =$ 12.0),  $\overline{4.81}$  d.d.d (1H, H<sup>4</sup>,  $J_{4,5a} = 8.4$ ,  $J_{4,5b} = 4.8$ ), 4.97 t  $(1H, H^2, J_{2,3} = 7.8), 5.14 t (1H, H^3, J_{3,4} = 7.8), 5.77 d$ (1H, H<sup>1</sup>,  $J_{1,2} = 8.6$ ). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{C}$ , ppm (J, Hz): 16.69 d  $[J_{CP} = 6.8, (O)P(OCH_2CH_3)_2],$ 62.07 d  $[J_{CP} = 5.5, (O)P(OCH_2CH_3)_2], 65.63 (C^5),$ 68.21 (C<sup>4</sup>), 69.18 (C<sup>3</sup>), 71.60 (C<sup>2</sup>), 80.37 (C<sup>1</sup>).  $^{31}P$ NMR spectrum (CD<sub>3</sub>OD): δ<sub>P</sub> 28.3 ppm. Mass spectrum (MALDI TOF), m/z: 325.09  $[M + Na]^+$  (calculated for C<sub>9</sub>H<sub>19</sub>O<sub>7</sub>NaPS: 325.06).

**[1-(Diphenoxyphosphoryl)sulfanyl]-β-D-xylopyranoside (7).** Yield 70%, mp 143–144°C,  $R_f$  0.49 (methanol–chloroform, 1 : 4). <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD), δ, ppm (*J*, Hz): 3.57 d.d (1H, H<sup>5a</sup>, *J*<sub>4,5a</sub> = 8.5, *J*<sub>5a,5b</sub> = 11.9), 4.17 d.d (1H, H<sup>5b</sup>, *J*<sub>4,5b</sub> = 5.0, *J*<sub>5b,5a</sub> = 12.0), 4.87 d.d.d (1H, H<sup>4</sup>, *J*<sub>4,5a</sub> = 8.4, *J*<sub>4,5b</sub> = 4.8), 5.10 t (1H, H<sup>2</sup>, *J*<sub>2,3</sub> = 7.8), 5.21 t (1H, H<sup>3</sup>, *J*<sub>3,4</sub> = 7.8), 5.81 d (1H, H<sup>1</sup>, *J*<sub>1,2</sub> = 8.8), 7.25–7.37 m [10H, (O)P(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 65.69 (C<sup>5</sup>), 68.28 (C<sup>4</sup>), 69.24 (C<sup>3</sup>), 71.63 (C<sup>2</sup>), 80.42 (C<sup>1</sup>), 121.64, 123.41, 132.75, 148.92 [(O)P(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]. <sup>31</sup>P NMR spectrum (CD<sub>3</sub>OD):  $\delta_P$  24.5 ppm. Mass spectrum (MALDI TOF), *m/z*: 421.11 [*M* + Na]<sup>+</sup> (calculated for C<sub>17</sub>H<sub>19</sub>O<sub>7</sub>NaPS: 421.07).

Insecticidal activity assay was performed under laboratory conditions on aphid Medoura viciae Buckt. by contact toxicity method [51]. The test object was chosen in view of the high nocuity of sucking insects, associated with their high reproductive potential, high abundance, and broad polyphagy. Laboratory pest populations isolated in natural conditions were used in the experiments. The aphid populations were bred and maintained on young bean plants. Toxicity testing against aphid was performed in Petri dishes 40 mm in diameter, containing filter paper treated with a (0.1-0.05)% aqueous solution of Neonol AF 9-10 [ $\alpha$ -(isononylphenyl)-ω-hydroxypoly(oxy-1,2-ethanediyl)] [52] dosed at 0.3 mL/dish. Test insects were placed on the treated substrates (20–30 insects per replication; a total of 5 replications per sample were performed). The dishes left to stand at 23-25°C, and after 2, 4, 6, and 24 h the mortality of suctorial insects was estimated in the test and control samples. Filter paper in control Petri dishes was treated with tap water or a solution of Neonol AF 9-10 in tap water of the same concentration as in the test experiments. Neonol AF 9-10 is widely used in microbiological industry in the production of preparative forms [53, 54].

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