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Synthesis of *O*-Aryl N^4-Glycosyl(thiosemicarbazido)phosphonothioates

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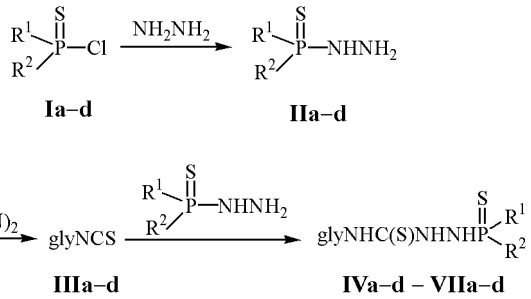
Abstract—A reaction of aryl(aryloxy)thiophosphonic acids hydrazides with glycosyl isothiocyanates was studied. Amides of *N*-(glycosylthioureylene)aryl(aryloxy)thiophosphonic acids were synthesized. The structure and composition of the new compounds were confirmed by the data of IR, ^{1}H and ^{31}P NMR and mass spectra, and by results of elemental analyses.

Phosphoric acids hydrazides and their derivatives possess cytostatic, pesticidal, and other bioregulator properties. For instance, thiosemicarbazide is an efficient insecticide [1].

In view of above we studied the modification of these compounds with glycosyl isothiocyanates and obtained the first representatives of glycosylated thiosemicarbazides. The introduction of a carbohydrate fragment into the structure of phosphohydrazides would evidently diminish their toxicity and increase the solubility in water.

The glycosyl isothiocyanates constitute a large class of accessible organic substances which can serve as intermediate products in the organic synthesis [2, 3].



Ia, IIa, IV: R^1 = Ph, R^2 = PhO; **Ib, IIb, V**: R^1 = Ph, R^2 = *n*-MePhO; **Ic, IIc, VI**: R^1 = Ph, R^2 = *t*-BuPhO; **Id, IId, VII**: R^1 = *p*-EtPh, R^2 = PhO; **III**–**VII**, gly: tetra-*O*-acetyl-β-D-glucosyl isothiocyanate (**a**), tetra-*O*-acetyl-β-D-mannosyl isothiocyanate (**b**), tri-*O*-acetyl-β-D-xylosyl isothiocyanate (**c**), hepta-O-acetyl-D-lactosyl isothiocyanate (**d**).

As initial sugars for preparation of glycosyl isothiocyanates were used glucose, mannose, xylose, and lactose. We established that reaction of acylhalogenoses of the above carbohydrates with lead(II) thiocyanate afforded glycosyl isothiocyanates. The hydrazides of aryl(aryloxy)thiophosphonic acids **IIa–d** were obtained by treating with hydrazine aryl(aryloxy)thiophosphonic chlorides. The study of reactions between phosphorus-containing hydrazides **IIa–d** with carbohydrates isothiocyanates **IIIa–d** revealed that the process occurred readily. Evidently the anomeric effect operating through the semiacetal bond C^1–O_{cycle} reduced the electron density on the carbon atom of the isothiocyanate group and thus significantly increased the electrophilicity of NCS group attached to the glycoside center of the monosaccharide. Therefore glycosyl isothiocyanates **IIIa–d** turned out to be more reactive than common isothiocyanates.

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In the IR spectra of compounds **IV–VII** lacks the characteristic band of NCS group (2100 cm^{-1}) and appear absorption bands of the following groups: NH–CS–NH (1510–1490 cm^{-1}) and C=S (1240–1220 cm^{-1}), P=S (705–685 cm^{-1}), P–N (915–905 cm^{-1}).

In the ^1H NMR spectra of compounds **IVa–VIIa** signals are observed in the region δ 5.5–3.2 ppm corresponding to the protons of glucose fragment. The coupling of anomeric proton of glucose H^1 with protons H^2 and N^4H gives rise to a doublet of doublets at δ 5.61 ppm ($^2J_{H^1H^2}$ = $^2J_{H^1N^4H}$ 8.7 Hz). The proton of N^1H group also appears as a doublet of doublets at δ 7.75 ppm with coupling constants $^2J_{HN^1,P}$ 16 Hz and $^2J_{HN^1,HN^2}$ 4.6 Hz. To determine the chemical shifts of NH protons the compounds under study were subjected to the exchange with D_2O. Actually, on replacing the labile hydrogen by deuterium in the spectrum, for instance, of compound **Va** disappeared doublets of doublets at δ 7.36, 7.43, and 7.55 ppm, whereas the doublet of doublets of the anomeric proton an δ 5.60 ppm transformed into a doublet of triplets (since for deuterium I = 1). Thus it was confirmed that the fragment $N^4HCSN^2HN^1HPSRR.'$ was actually linked to carbon C^1 of the monosaccharide skeleton and that it contained labile hydrogen atoms attached to nitrogens.

In the ^{31}P NMR spectra of compounds **IV–VII** characteristic signals of the P=S moiety appear in the region δ_P 64–78 ppm, $^2J_{HN^1,P}$ 12–20 Hz (see EXPERIMENTAL).

In the mass spectra of all reaction products molecular ion peaks are observed evidencing the stability of compounds **IV–VII** under electron impact.

EXPERIMENTAL

All synthesis were carried out in anhydrous solvents. The TLC analyses were performed on GF-254 plates (China). As eluent was used a mixture benzene–ethyl acetate, 2:1. Melting points were measured on heating block Yanaco MP-S3 (Japan). Optical activity of compounds was determined on Perkin-Elmer-241 MC instrument. Elemental analyses were performed on analyzers MT-3 and Perkin-Elmer-2400. IR spectra were recorded on spectrophotometer Perkin-Elmer-325 from samples pelletized with KBr. ^1H and ^{31}P NMR spectra were registered on spectrometer Bruker AC 80 at operating frequencies 80 and 32.4 MHz respectively using TMS as internal reference (^1H) and 85% phosphoric acid as external reference (^{31}P), solvents $CDCl_3$ or D_2O. Mass spectra were measured on VG-ZAB-HS instrument.

Glycosyl isothiocyanates **IIIa–d** were prepared by procedure [2]. Tetra-*O*-acetyl-β-D-glucosyl isothiocyanate (**IIIa**), yield 54%, mp 109–110°C. Tetra-*O*-acetyl-β-D-mannosyl isothiocyanate (**IIIb**), yield 55%, syrupy substance, R_f 0.84. Tri-*O*-acetyl-β-D-xylosyl isothiocyanate (**IIIc**), yield 41%, mp 88–90°C. Hepta-*O*-acetyl-D-lactosyl isothiocyanate (**IIId**), yield 50%, mp 169–171°C.

Aryl(aryloxy)thiophosphonic chlorides. To a solution of 0.079 mol of $PhP(S)Cl_2$ in 20 ml of anhydrous ether at 20–25°C was added dropwise with stirring 0.079 mol of an appropriate phenol and 0.079 mol of pyridine in 5 ml of anhydrous pyridine. The solution was heated at reflux for 2 h, the precipitated pyridine hydrochloride was filtered off, the filtrate was concentrated under reduced pressure and left standing in a refrigerator for 12 h. Then it was filtered, the syrupy residue was distilled in a vacuum collecting the appropriate fraction.

Phenyl(phenoxy)thiophosphonic chloride (**Ia**), yield 51%, bp 214–218°C (0.5 mm Hg). Phenyl(*p*-tolyloxy)thiophosphonic chloride (**Ib**), yield 30%, bp 180–188°C (0.3 mm Hg). Phenyl(*p*-*tert*-butylphenyloxy)thiophosphonic chloride (**Ic**), yield 45%, bp 218–220°C (0.5 mm Hg). *p*-Ethylphenyl(phenoxy)-thiophosphonic chloride (**Id**), yield 38%, bp 205–209°C (0.5 mm Hg).

Aryl(aryloxy)thiophosphonic acids hydrazides IIa–d. To 0.3 mol of hydrazine hydrate at cooling below –12°C with vigorous stirring was added dropwise 0,022 mol of an appropriate aryl(aryloxy)thiophosphonic chloride **Ia–d,** the reaction mixture was stirred for 5 h, the precipitate was filtered off, washed with ethanol and ether, and recrystallized from a mixture tetrachloromethane–petroleum ether, 3:1. The corresponding compounds **IIa–d** were thus obtained.

Phenyl(phenoxy)thiophosphonic acid hydrazide (IIa), yield 62%, mp 123–125°C. Phenyl(*p*-tolyloxy)-thiophosphonic acid hydrazide (**IIb**), yield 82%, mp 10–112°C. Phenyl(*p*-*tert*-butylphenyloxy)thiophosphonic acid hydrazide (**IIc**), yield 56%, mp 92–94°C. *p*-Ethylphenyl(phenoxy)thiophosphonic acid hydrazide (**IId**), yield 72%, mp 107–108.5°C.

***N*-(glycosylthioureylene)aryl(aryloxy)thiophosphonic acids amides.** A mixture of 1 mmol of an appropriate aryl(aryloxy)thiophosphonic acid hydrazide **IIa–d** and 1 mmol of glycosyl isothiocyanate **IIIa–d** in 10 ml of chloroform was heated at reflux under TLC monitoring. On cooling the separated precipitate was filtered off, the solvent was distilled

off in a vacuum, and 2 ml of anhydrous ether was added to the residue. The separated precipitate was filtered off and recrystallized from a mixture of 95% ethanol and water.

4-[2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl]-1-[phenyl(phenoxy)thiophosphoryl]thiosemicarbazide (IVa). Yield 81%, mp 165–168°C. IR spectrum, ν, cm^{-1}: 1754 (C=O), 1505 (NH–C=S), 1460 (P–Ph), 1225 (P–O–Ar), 920 (P–N), 696 (P=S). ^1H NMR spectrum, δ, ppm: 1.79–2.13 m (12H, CH_3), 3.25– 3.98 m (2H, H^6 of sugar), 4.71–5.71 m (5H, H^{1-5} of sugar), 7.27– 8.16 m (13H, H arom, NH). ^{31}P NMR spectrum, δ, ppm (*J*, Hz): 66.7 d ($^2J_{PH}$ 14). Mass spectrum, *m/z* (I_{rel}, %): 653 ($[M]^+$, 100), 331 (57). Found, %: C 50.01; H 4.89; N 6.47; P 4.78. $C_{27}H_{32}N_3O_{10}PS_2$. Calculated, %: C 49.61; H 4.93; N 6.43; P 4.74.

4-[2,3,4,6-Tetra-*O*-acetyl-β-D-mannopyranosyl]-1-[phenyl(phenoxy)thiophosphoryl]thiosemicarbazide (IVb). Yield 38%, R_f 0.54. IR spectrum, ν, cm^{-1}: 1755 (C=O), 1498 (NH–C=S), 1447 (P–Ph), 1210(P–O–Ar), 909 (P–N), 695 (P=S). ^1H NMR spectrum, δ, ppm: 1.77–2.12 m (12H, CH_3), 3.24–3.96 m (2H, H^6 of sugar), 4.68–5.70 m (5H, H^{1-5} of sugar), 7.15–8.17 m (13H, H arom, NH). ^{31}P NMR spectrum, δ, ppm (*J*, Hz): 66 " ($^2J_{PH}$ 14.5). Mass spectrum, *m/z* (I_{rel}, %): 653 ($[M]^+$, 100), 331 (38). Found, %: C 50.11; H 4.90; N 6.57; P 4.82. $C_{27}H_{32}N_3O_{10}PS_2$. Calculated, %: C 49.61; H 4.93; N 6.43; P 4.74.

4-[2,3,4,6-Tetra-*O*-acetyl-β-D-xylopyranosyl]-1-[phenyl(phenoxy)thiophosphoryl]thiosemicarbazide (IVc). Yield 44%, mp 97–99°C. IR spectrum, ν, cm^{-1}: 1750 (C=O), 1492 (NH–C=S), 1458 (P–Ph), 1234 (P–O–Ar), 910 (P–N), 690 (P=S). ^1H NMR spectrum, δ, ppm: 1.81–2.12 m (9H, CH_3), 3.20–5.69 m (5H, H^{1-5} of sugar), 7.10–8.15 m (13H, H arom, NH). ^{31}P NMR spectrum, δ, ppm (*J*, Hz): 66 d ($^2J_{PH}$ 12.5). Mass spectrum, *m/z* (I_{rel}, %): 697 ($[M]^+$, 100), 259 (48). Found, %: C 51.22; H 4.91; N 7.31; P 5.39. $C_{24}H_{28}N_3O_8PS_2$. Calculated, %: C 49.56; H 4.85; N 7.22; P 5.33.

4-[2,3,4,6-Tetra-*O*-acetyl-β-D-lactosyl]-1-[phenyl-(phenoxy)thiophosphoryl]thiosemicarbazide (IVd). Yield 60%, R_f 0.37. IR spectrum, ν, cm^{-1}: 1751 (C=O), 1506 (NH–C=S), 1440 (P–Ph), 1210 (P–O–Ar), 911 (P–N), 701 (P=S). ^1H NMR spectrum, δ, ppm: 1.79–2.01 m (21H, CH_3), 3.18–5.64 m (13H, H of sugar), 7.08–8.09 m (13H, H arom, NH). ^{31}P NMR spectrum, δ, ppm (*J*, Hz): 67 d ($^2J_{PH}$ 15.5). Mass spectrum, *m/z* (I_{rel}, %): 941 ($[M]^+$, 100), 331 (41). Found, %: C 49.67; H 5.10; N 4.49; P 3.32. $C_{39}H_{48}N_3O_{18}PS_2$. Calculated, %: C 49.73; H 5.14; N 4.46; P 3.29.

4-[2,3;4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl]-1-[phenyl(*p*-tolyloxy)thiophosphoryl]thiosemicarbazide (Va). Yield 47%, mp 193–194°C. IR spectrum, ν, cm^{-1}: 1754 (C=O), 1506 (NH–C=S), 1220 (P–O–Ar), 907 (P–N), 697 (P=S). ^1H NMR spectrum, δ, ppm: 1.80–2.06 q (12H, CH_3), 2.02–2.10 s (3H, CH_3), 3.68–4.35 m (2H, H^6 of sugar), 4.79–5.61 m (5H, H^{1-5} of sugar), 7.04–7.55 m (10H, H arom, NH), 8.17 br.s (1H, NH). ^{31}P NMR spectrum, ppm (*J*, Hz): 75 " ($^2J_{PH}$ 16) . Mass spectrum, *m/z* (I_{rel}, %): 667 ($[M]^+$, 100), 331 (10). Found, %: C 50.44; H 5.16; N 6.31; P 4.59. $C_{28}H_{34}N_3O_{10}PS_2$. Calculated, %: C 50.37; H 5.13; N 6.29; P 4.64.

4-[2,3,4,6-Tetra-*O*-acetyl-β-D-mannopyranosyl]-1-[phenyl(*p*-tolyloxy)thiophosphoryl]thiosemicarbazide (Vb). Yield 62%, R_f 0.42. IR spectrum, ν, cm^{-1}: 1751 (C=O), 1507 (NH–C=S), 1119 (P–O–Ar), 914 (P–N), 690 (P=S). ^1H NMR spectrum, δ, ppm: 1.77–2.04 q (12H, CH_3), 2.28 s (3H, CH_3), 3.70–4.32 m (2H, H^6 of sugar), 4.81–5.62 m (5H, H^{1-5} of sugar), 7.06–7.58 m (10H, H arom, NH); 8.15 br.s (1H, NH). ^{31}P NMR spectrum, δ, ppm (*J*, Hz): 75 d ($^2J_{PH}$ 16). Mass spectrum, *m/z* (I_{rel}, %): 667 ($[M]^+$, 100), 331 (24). Found, %: C 50.41; H 5.10; N 6.25; P 4.61. $C_{28}H_{34}N_3O_{10}PS_2$. Calculated, %: C 50.37; H 5.13; N 6.29; P 4.64.

4-[2,3,4-Triacetyl-*O*-δ-D-xylopyranosyl]-1-[phenyl(*p*-tolyloxy)thiophosphoryl]thiosemicarbazide (Vc). Yield 90%, mp 109–111°C. IR spectrum, ν, cm^{-1}: 1753 (C=O), 1504 (NH–C=S), 1221 (P–O–Ar), 910 (P–N), 692 (P=S). ^1H NMR spectrum, δ, ppm: 1.87–2.10 m (9H, CH_3), 2.27 s (3H, CH_3), 3.68–4.35 m (2H, H^5 of sugar), 4.79–5.61 m (4H, H^{1-4} of sugar), 7.06–7.53 m (10H, H arom, NH), 8.20 br.s (1H, NH). ^{31}P NMR spectrum, δ, ppm (*J*, Hz): 75 d ($^2J_{PH}$ 16). Mass spectrum, *m/z* (I_{rel}, %): 596 ($[M]^+$, 100), 259 (15). Found, %: C 50.35; H 5.10; N 7.11; P 5.25. $C_{25}H_{30}N_3O_8PS_2$. Calculated, %: C 50.41; H 5.08; N 7.05; P 5.20.

4-[Hepta-*O*-acetyl-β-D-lactosyl]-1-[(*p*-tolyloxy)thiophosphoryl]thiosemicarbazide (Vd). Yield 56%, R_f 0.25. IR spectrum, ν, cm^{-1}: 1748 (C=O), 1505 (NH–C=S), 1220 (P–O–Ar), 912 (P–N), 689 (P=S). ^1H NMR spectrum, δ, ppm: 1.75–2.04 m (21H, CH_3), 2.18 s (3H, CH_3), 3.50–5.41 m (13H, H of sugar), 6.97–8.19 m (11H, H arom, NH). ^{31}P NMR spectrum, δ, ppm (*J*, Hz): 78 d ($^2J_{PH}$ 15).

Mass spectrum, *m/z* (I_{rel}, %): 955 ([*M*]$^+$, 100), 331 (30). Found, %: C 50.70; H 5.32; N 4.38; P 3.21. $C_{40}H_{50}N_3O_{18}PS_2$. Calculated, %: C 50.26; H 5.27; N 4.40; P 3.24.

4-[2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl]-1-[phenyl(*p*-*tert*-butylphenoxy)thiophosphoryl]thiosemicarbazide (VIa). Yield 82%, mp 196–197°C. IR spectrum, ν, cm^{-1}: 1751 (C=O), 1508 (NH–C=S), 1438 (P–Ph), 1220 (P– O–Ar), 912 (P–N), 692 (P=S). ^{1}H NMR spectrum, δ, ppm: 1.28 s (9H, CH_3), 1.77–2.04 q (12H, CH_3), 3.25–5.57 m (7H, H of sugar), 6.80– 8.29 m (11H, H arom, NH). ^{31}P NMR spectrum, δ, ppm, (*J*, Hz): 77.5 d ($^2J_{PH}$ 20). Mass spectrum, *m/z* (I_{rel}, %): 710 ([*M*]$^+$, 100), 652 (80), 331 (24). Found, %: C 51.90; H 5.57; N 5.96; P 4.39. $C_{31}H_{40}N_3O_{10}PS_2$. Calculated, %: C 52.46; H 5.68; N 5.92; P 4.36.

4-[2,3,4,6-Tetra-*O*-acetyl-β-D-mannopyranosyl]-1-[phenyl(*p*-*tert*-butylphenoxy)thiophosphoryl]-thiosemicarbazide (VIb). Yield 52%, mp 135–136°C. IR spectrum, ν, cm^{-1}: 1755 (C=O), 1506 (NH–C=S), 1437 (P–Ph), 1220 (P–O–Ar), 911 (P–N), 690 (P=S). ^{1}H NMR spectrum, δ, ppm: 1.27 s (9H, CHd3), 1.77–2.02 q (12H, CH_3), 3.25–5.54 m (7H, H of sugar), 6.81–8.28 m (11H, H arom, NH). ^{31}P NMR spectrum, δ, ppm, (*J*, Hz): 77 d ($^2J_{PH}$ 19). Mass spectrum, *m/z* (I_{rel}, %): 710 ([*M*]$^+$, 100), 652 (63), 331 (38%). Found, %: C, 51.38; H, 5.57; N 5.83; P 4.48. $C_{31}H_{30}N_3O_{10}PS_2$. Calculated, %: C 52.46; H 5.68; N 5.92; P 4.36.

4-[2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl]-1-[phenyl(*p*-*tert*-butylphenoxy)thiophosphoryl]thiosemicarbazide (VIc). Yield 74%, mp 102–104°C. IR spectrum, ν, cm^{-1}: 1757 (C=O), 1508 (NH–C=S), 1438 (P–Ph), 1221 (P–O–Ar), 912 (P–N), 693 (P=S). ^{1}H NMR spectrum, δ, ppm: 1.26 s (9H, CH_3), 1.28–2.00 q (9H, CH_3), 3.26–5.54 m (6H, H of sugar), 6.78– 8.30 m (11H, H arom, NH). ^{31}P NMR spectrum, δ, ppm, (*J*, Hz): 78 d ($^2J_{PH}$ 21). Mass spectrum, *m/z* (I_{rel}, %): 637 ([*M*]$^+$, 100), 580 (77), 259 (48%). Found, %: C 52.51; H 5.71; N 6.63; P 4.81. $C_{28}H_{36}N_3O_8PS_2$. Calculated, %: C 52.74; H 5.69; N 6.59; P 4.86.

4-[Hepta-O-acetyl-β-D-lactosyl]-1-[phenyl(*p*-*tert*-butylphenoxy)thiophosphoryl]thiosemicarbazide (VId). Yield 71%, R_f 0.39. IR spectrum, ν, cm^{-1}: 1756 (C=O), 1507 (NH–C=S), 1437 (P–Ph), 1224 (P–O– Ar), 910 (P–N), 705 (P=S). ^{1}H NMR spectrum, δ, ppm): 1.20–2.00 m (21H, CH_3), 1.25 s (9H, CH_3), 3.20–5.48 m (13H, H of sugar), 6.77–8.24 m (11H, H arom, NH). ^{31}P NMR spectrum, δ, ppm (*J*, 75 d ($^2J_{PH}$ 19.5) . Mass spectrum, *m/z* (I_{rel}, %): 998 Hz): ([*M*]$^+$, 100), 973 (54), 331 (17%). Found, %: C 50.26; H 5.53; N 4.26; P 3.14. $C_{43}H_{56}N_3O_{18}PS_2$. Calculated, %: C 51.75; H 5.66; N 4.21; P 3.10.

4-[2,3,5,6-Tetra-O-acetyl-β-D-glucopyranosyl]-1-[*p*-ethylphenyl(phenoxy)thiophosphoryl]thiosemicarbazide (VIIa). Yield 56%, mp 147–149°C. IR spectrum, ν, cm^{-1}: 1756 (C=O), 1501 (NH–C=S), 1440 (P–Ph), 1221 (P–O–Ar), 910 (P–N), 700 (P=S). ^{1}H NMR spectrum, δ, ppm: 1.30 t (3H, CH_3), 1.77–2.07 q (12H, CH_3), 2.81 m (2H, CH_2), 3.20–3.82 m (2H, H^6 of sugar), 4.72–5.74 m (5H, H^{1-5} of sugar), 7.00–8.15 m (12H, H arom, NH). ^{31}P NMR spectrum, δ, ppm (*J*, Hz): 68 d ($^2J_{PH}$ 17). Mass spectrum, *m/z* (I_{rel}, %): 681 ([*M*]$^+$, 100), 331 (61). Found, %: C 50.88; H 5.29; N 6.20; P 4.56. $C_{29}H_{36}N_3O_{10}PS_2$. Calculated, %: C 51.09; H 5.32; N 6.16; P 4.54.

4-[2,3,5,6-Tetra-O-acetyl-β-D-mannopyranosyl]-1-[*p*-ethylphenyl(phenoxy)thiophosphoryl]thiosemicarbazide (VIIb). Yield 45%, R_f 0.66. IR spectrum, ν, cm^{-1}: 1751 (C=O), 1495 (NH–C=S), 1412 (P–Ph), 1220 (P–O–Ar), 915 (P–N), 687 (P=S). ^{1}H NMR spectrum, δ, ppm: 1.30 t (3H, CH_3), 1.78–2.09 q (12H, CH_3), 2.82 m (2H, CH_2), 3.20–3.81 m (2H, H^6 of sugar), 4.69–5.76 m (5H, H^{1-5} of sugar), 7.01–8.14 m (12H, H arom, NH). ^{31}P NMR spectrum, δ, ppm (*J*, Hz): 64.5 d ($^2J_{PH}$ 16) . Mass spectrum, *m/z* (I_{rel}, %): 681 ([*M*]$^+$, 100), 331 (14). Found, %: C 50.79; H 5.35; N 6.11; P 4.51. $C_{29}H_{36}N_3O_{10}PS_2$. Calculated, %: C 51.09; H 5.32; N 6.16; P 4.54.

4-[2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl]-1-[*p*-ethylphenyl(phenoxy)thiophosphoryl]thiosemicarbazide (VIIc). Yield 67%, R_f 0.57. IR spectrum, ν, cm^{-1}: 1754 (C=O), 1502 (NH–C=S), 1440 (P–Ph), 1216 (P–O–Ar), 908 (P–N), 701 (P=S). ^{1}H NMR spectrum, δ, ppm: 1.30 t (3H, CH_3), 1.81–2.10 t (9H, CH_3), 2.79 m (2H, CH_2), 3.21–5.70 m (6H, H^{1-5} of sugar), 7.04–8.10 m (12H, H arom, NH). ^{31}P NMR spectrum, δ, ppm, (*J*, Hz): 67 d ($^2J_{PH}$ 16.5) . Mass spectrum, *m/z* (I_{rel}, %): 610 ([*M*]$^+$, 100), 259 (22). Found, %: C 50.89; H 5.24; N 6.92; P 5.10. $C_{26}H_{32}N_3O_8PS_2$. Calculated, %: C 51.22; H 5.29; N 6.89; P 5.08.

4-[Hepta-*O*-acetyl-β-D-lactosyl]-1-[*p*-ethylphenyl-(phenoxy)thiophosphoryl]thiosemicarbazide (VIId). Yield 41%, R_f 0.35. IR spectrum, ν, cm^{-1}: 1755 (C=O), 1506 (NH–C=S), 1450 (P–Ph), 1220 (P–O–Ar), 910 (P–N), 707 (P=S). ^{1}H NMR spectrum, δ,

ppm: 1.29 t (3H, CH_3), 1.75–2.03 m (21H, CH_3), 2.77 m (2H, CH_2), 3.19–5.61 m (13H, H of sugar), 6.94–8.07 m (12H, H arom, NH). ^{31}P NMR spectrum, δ, ppm, (*J*, Hz): 66 d ($^2J_{PH}$ 17) . Mass spectrum, *m/z* (I_{rel}, %): 970 ($[M]^+$, 100), 331 (14). Found, %: C 51.20; H 5.44; N 4.29; P 3.21. $C_{41}H_{52}N_3O_{18}PS_2$. Calculated, %: C 50.77; H 5.40; N 4.33; P 3.19.

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