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Structure of Aldoses Condensation Products with *SH*-Containing Hydrazides

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Abstract

The structure of the condensation products of thiobenzohydrazide, 2-sulfanylacetohydrazide, 3-sulfanylpropiohydrazide, and 2-sulfanylbenzohydrazide with a series of aldoses (L-arabinose, D-ribose, L-rhamnose, D-galactose, D-glucose, and D-mannose) was studied by ^{1}H- and ^{13}C-NMR spectroscopy.

Keywords

Aldoses *SH*-Acylhydrazones, 1,3,4-Thiadiazolines, 1,3,4-Thiadiazines, 1,3,4-Thiadiazepines, Ring-Chain-Ring Tautomerism

Subject Areas: **Organic Chemistry**

1. Introduction

Condensation products of aldoses with acylhydrazines attracted attention due to their high biological activity. Some of them exhibited an antimicrobial [1] and antifungal [2] activity. Among aldoses acylhydrazones, containing in their structure, a functional sulfohydryl group is known only thiobenzohydrazones of arabinose, glucose and mannose [3], as well as 2-sulfonylbenzohydrazones of arabinose and glucose [4], the structure of which is not proved. The presence of a functional nucleophilic SH-group in the aldosohydrazone fragment could give rise in appearance of new structural possibilities in further transformations. Intermolecular nucleophilic at-

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tacks of SH-fragments at the C=N polar bond contained in the linear structure can lead to repeated cyclization with the formation of new cyclic forms.

The aim of the present work was to study of the structure of the condensation products of aldoses with hydrazides of thiobenzoic ($PhCSNHNH_2$), sulfanylacetic ($HSCH_2CONHNH_2$), 3-sulfanylpropionic ($HSCH_2CH_2CONHNH_2$), and 2-sulfanylbenzoic ($2\text{-}HSC_6H_4CONHNH_2$) acids by ^1H- and ^{13}C-NMR spectroscopy methods (**Figure 1**, **Figure 2**, **Figure 3** and **Figure 4**).

2. Results and Discussion

Compounds **1-4** were synthesized in yields 55% - 90% by heating equimolar amounts of the corresponding aldose (L-arabinose, D-xylose, D-ribose, L-rhamnose, D-galactose, D-glucose, D-mannose) and corresponding sulfur-containig hydrazide (thiobenzohydrazide, 2-sulfanylacetohydrazide, 3-sulfanylpropiohydrazide, 2-sulfanylbenzohydrazide) in boiling methanol for a short time (**Table 1**, **Table 2**, **Table 3**, and **Table 4**).

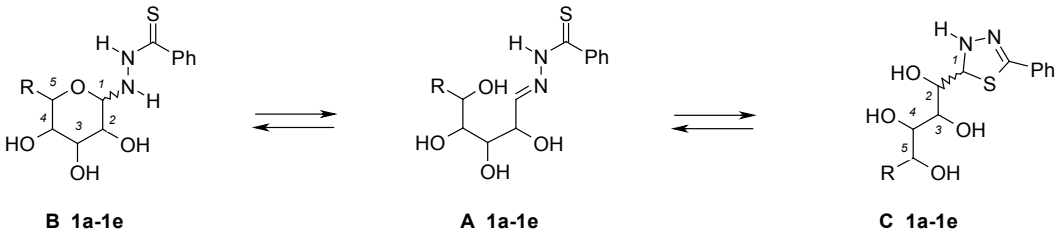

Figure 1. Aldoses thiobenzoylhydrazones **1a-1e**.

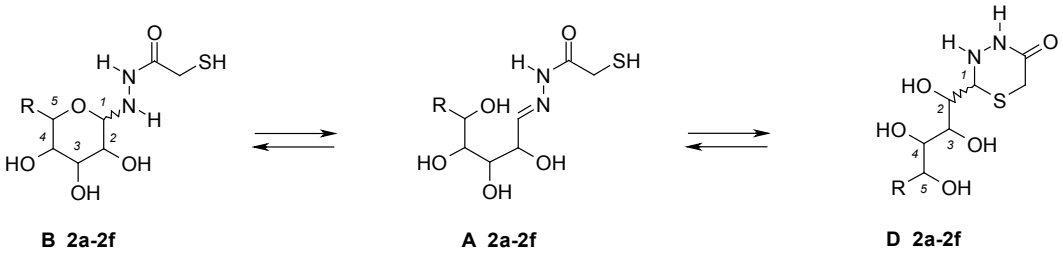

Figure 2. Aldoses 2-sulfanylacetylhydrazones **2a-2f**.

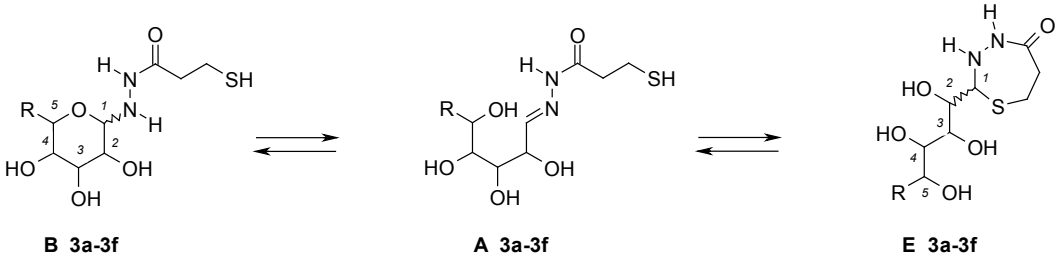

Figure 3. Aldoses 3-sulfanypropionyhydrazones **3a-3f**.

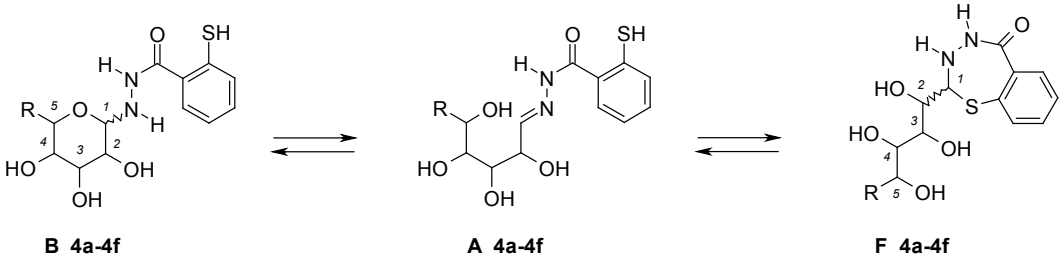

Figure 4. Aldoses 2-sulfanylbenzoylhydrazones **4a-4f**.

Table 1. Tautomeric composition of aldoses thiobenzoylhydrazones **1a-1e** (72 h after dissolution).

Compound	R	Initial aldose	Form in crystals	Tautomeric composition (%) in DMSOd_6		
				Form **B**	Form **A**	Form **C**
1a	H	L-Arabinose	**C**	-	40	60
1b	CH_3	L-Rhamnose	**C**	-	30	70
1c	CH_2OH	D-Galactose	**C**	-	35	65
1d	CH_2OH	D-Glucose	**C**	10	45	45
1e	CH_2OH	D-Mannose	**C**	-	20	80

Table 2. Tautomeric composition of aldoses 2-sulfanylacetylhydrazones **2a-2f** (72 h after dissolution).

Compound	R	Initial aldose	Form in crystals	Tautomeric composition (%) in D_2O		
				Form **B**	Form **A**	Form **C**
2a	H	L-Arabinose	**D**	10	-	90
2b	H	D-Xylose	**D**	25	-	75
2c	CH_3	L-Rhamnose	**B**	100	-	-
2d	CH_2OH	D-Galactose	**D**	15	-	85
2e	CH_2OH	D-Glucose	**B**	70	-	30
2f	CH_2OH	D-Mannose	**D**	10	-	90

Table 3. Tautomeric composition of aldoses 3-sulfanypropionyhydrazones **3a-3f** (72 h after dissolution).

Compound	R	Initial aldose	Form in crystals	Tautomeric composition (%) in D_2O		
				Form **B**	Form **A**	Form **C**
3a	H	L-Arabinose	**E**	65	5	30
3b	H	D-Xylose	**E**	50	10	40
3c	H	D-Ribose	**E**	70	10	20
3d	CH_2OH	D-Galactose	**B**	70	5	25
3e	CH_2OH	D-Glucose	**B**	85	5	10
3f	CH_2OH	D-Mannose	**B**	75	5	20

Table 4. Tautomeric composition of aldoses 2-sulfanylbenzoylhydrazones **4a-4f** (72 h after dissolution).

Compound	R	Initial aldose	Form in crystals	Tautomeric composition (%) in DMSOd_6		
				Form **B**	Form **A**	Form **C**
4a	H	L-Arabinose	**F**	-	-	100
4b	H	D-Ribose	**F**	-	-	100
4c	CH_3	L-Rhamnose	**F**, **B**	35	20	45
4d	CH_2OH	D-Galactose	**F**	-	-	100
4e	CH_2OH	D-Glucose	**F**, **B**	45	-	55
4f	CH_2OH	D-Mannose	**F**	35	15	50

In all experiments, the ^{1}H- and ^{13}C-NMR spectra were recorded at definite time intervals starting from the moment of dissolution until the end of transformations. In addition, the structure of the compounds under study in the crystalline state was confirmed by solid-phase high-resolution ^{13}C-NMR spectroscopy (CPMAS). For example, pyranose form **B** was expected to give a signal from the anomeric C-1 atom at δ 85 - 90 ppm; analogous signals from five-membered 1,3,4-thiadiazoline **C** form, six-membered 1,3,4-thiadiazine **D** form, or seven-membered 1,3,4-thiadiazepine **E** and **F** forms should appear in a stronger field, at δ 70 - 75 ppm. It is typical of sp^3-hybridized carbon atom for saturated ring systems, located between sulfur and nitrogen atoms [5] [6]. Hydrazone structure **A** should give rise to a downfield signal at δ 145 - 155 ppm (C=N) in the ^{13}C-NMR spectrum.

One set of signals belonging to 1,3,4-thiadiazoline form **C** is observed in ^{1}H- and ^{13}C-NMR spectra of the products of the condensation of aldoses with thiobenzohydrazide **1a-1e** (Table 1). This finding suggests that compounds **1a-1e** has the same structure in the crystalline state. Solid-phase ^{13}C-NMR spectrum was recorded for arabinose condensation product **1a**. When the spectral patterns of solutions of compounds **1a-1e** to in DMSOd_6 no longer changed indicating the achievement of an equilibrium state (72 h after the dissolution), signals corresponding to linear hydrazone structure **A** were fixed. In the case of glucose tiobenzoylhydrazone **1d** about 10% of the pyranose form **B** can be detected.

In the ^{1}H- and ^{13}C-NMR spectra of solutions of aldoses sulfanylacetylhydrazones **2a**, **2b**, **2d**, and **2f** in D_2O (other solvents proved to be unsuitable due to the low solubility) the observed signals corresponded to cyclic tautomeric forms **B** and **D**, and mainly each of these forms was present as two stereoisomers: α,β-**B** and (2*R*,*S*)-**D** or (**D** and **D′**) (Table 2). The relative intensity of signals belonging to forms **B** and **D** in the ^{13}C-NMR spectra changed with time; after 72 h these variations finished indicating the attainment of the equilibrium state. Therewith in the ^{13}C NMR spectra of compounds **2a**, **2b**, **2d**, and **2f** taken just after the dissolution the intensity of signals belonging to the thiadiazine form **D** was significantly higher than in the spectra registered after the establishment of the equilibrium. This fact suggests that in the crystalline state compounds **2a**, **2b**, **2d**, and **2f** exist in the thiadiazine structure **D**, and in solution they are partially converted in the pyranose form **B**. On the contrary, at recording of the ^{13}C-NMR spectra of the glucose derivative **2e** the intensity of signals of pyranose form **B** decreased with time and the intensity of the signals of thiadiazine form **D** grew, suggesting that in the crystalline state this compound had the pyranose structure **A**. Finally, in the ^{13}C-NMR spectra of rhamnose derivative **2c** both just after dissolution and 72 h later only the signals of pyranose form **B** were observed. In neither example we could detect the hydrazone form **A**; consequently the name "sulfanylacetylhydrazone" could be applied to these systems only tentatively.

Compounds **3a-3f** were expected to exhibit complicated tautomeric behavior due to their ability to undergo cyclization with formation of both six-membered pyranose form **B** and seven-membered 1,3,4-thiadiazepin form **E** (Table 3). According to ^{13}C-NMR spectra taken off in solid phase, the condensation products of 3-sulfanylpropionylhydrazine with arabinose, xylose, and ribose (compounds **3a-3c** respectively) exist in crystalline state as thiadiazepins **E**. Two sets of the signals belonging to the configurational isomers of thiadiazepin forms **E** and **E′** appeared in the solid phase ^{13}C-NMR spectrum of compound 3**a**. It was impossible to determine the 2*R*- or 2*S*-configuration of these forms. Unlike pentose derivatives **3a-3c**, the condensation products **3d-f** derived from 3-sulfanylpropionylhydrazine and hexoses do not give rise to cyclic thiadiazepin form **E** in crystals. Compounds **3d-3f** in the crystalline state has cyclic structure **B**. The ^{1}H-NMR spectra of solutions of 3-sulfanylpropanoylhydrazones **3a-3f** in D_2O, recorded immediately after dissolution, contained signals assignable to pyranose structure **B**. After 72 h, *i.e.*, when the spectral patterns of solutions of **3a-3f** in D_2O no longer changed (equilibrium was attained), signals corresponding to both cyclic tautomers **B** and **E** and linear hydrazone structure **A** were present, and each cyclic tautomer was a mixture of two stereoisomers: α,β-**B** and (2*R*,*S*)-**E** or (**E** and **E′**). The equilibrium position varies over a wide range: from **B**:**A**:**E** ratio 85:5:10 for glucose derivative **3e** to 50:10:40 for xylose derivative **3b** respectively.

A different situation was observed with the condensation products obtained from aldoses and 2-sulfanylbenzohydrazide (Table 4). Judging by variation of their ^{1}H- and ^{13}C-NMR spectra, compounds **4a-4f** in the crystalline state have cyclic 1,3,4-benzothiadiazepin structure **F**. Solid-phase ^{13}C-NMR spectrum was recorded for glucose condensation product **4e**. With the lapse of time, signals belonging to the second configurational isomer of benzothiadiazepin form **F′** appeared in the ^{1}H- and ^{13}C-NMR spectra of solutions of **4a-4f** in DMSOd_6, but it was impossible to assign these signals to particular (2*R*)- or (2*S*)-isomer. The ^{1}H- and ^{13}C-NMR spectra of condensation products **4a**, **4b**, and **4d** derived from arabinose, ribose, and galactose no longer change in 15 - 20 days, indicating the absence of linear structure **A** and cyclic form **B** in the equilibrium mixture. Compounds **4c** and **4e** ob-

tained by condensation of 2-sulfanylbenzohydrazide with rhamnose and glucose behaved differently. After keeping their solutions in DMSOd_6 for 72 h, the ^{1}H- and ^{13}C-NMR data indicated formation of cyclic pyranose form **B** (two sets of signals were observed due to the presence of several stereoisomers). Up to 20% of linear hydrazone tautomer **A** was detected for rhamnose derivative **4c**. After 30 days, the ^{1}H- and ^{13}C-NMR spectra of compounds **4c** and **4e** contained only signals belonging to pyranose form **B**. We succeeded in isolating tautomer **B** of compound **4c** in the crystalline state, and its structure was confirmed by the solid-phase ^{13}C-NMR spectrum. In other words, compounds **4c** and **4e** demonstrated irreversible transformation of benzo-1,3,4-thiadiazepin tautomer **F** into tetrahydropyran structure **B**, which can be observed spectrally. The ^{1}H- and ^{13}C-NMR spectra of the condensation product of 2-sulfanylbenzohydrazide with mannose (compound **4f**) finished to change in 72 h. The equilibrium mixture consisted of 50% of benzothiadiazepin tautomer **F**, 15% of linear structure **A**, and 35% of pyranose **B** form; in addition, each cyclic tautomer was a mixture of two stereoisomers.

3. Conclusion

Thus, the study noted the general tendency of the condensation products of aldoses with thiobenzoic, sulfanylacetic, 3-sulfanylpropionic, and 2-sulfanylbenzoic acids hydrazides to undergo ring-chain-ring tautomeric transformation involving two different cyclic structures via intramolecular nucleophilic addition of the SH group at the hydrazone C=N bond. The results of the present study may be interesting from the practical viewpoint, e.g., for the design of new radioprotective agents as well as of polymeric materials for techniques, medicine, and biology. The condensation products of SH-acylhydrazides with aldoses may also be applied for complexing the colloid species of the noble metals controlling their structure and the size of the forming nanoparticles and thus governing the process of their self-organization into supramolecular structures [7] [8]. This will be the subject of our future investigations.

4. Experimental Part

^{1}H- and ^{13}C-NMR spectra were registered on a spectrometer Bruker AV-400 at operating frequencies 400 and 100 MHz respectively (internal reference hexamethyldisiloxane). The solid-phase ^{13}C-NMR spectra were obtained on a Bruker AM-500 spectrometer (125 MHz) using a standard procedure utilizing cross polarization and magic angle spinning (CPMAS) technique (frequency 4.5 kHz; internal reference hexamethylbenzene). The tautomeric composition of obtained compounds was estimated by the integration of the appropriate signals in the ^{1}H NMR spectra. Elemental analysis of previously unknown compounds was carried out on a CHN Analyzer Hewlett Packard 185B. The purity of prepared compounds was checked by TLC on Silufol UV-254 plates, eluent butanol-water-acetone, 8:1:1.

Synthesis of aldoses SH-acylhydrazones (1-4)

To a solution of 0.01 mol of SH-containing hydrazide in 25 ml of methanol 0.01 mol of an appropriate aldose was added, and the mixture was boiled for a period of 1-3 h. The solvent was removed at a reduced pressure, and the residue was washed with ether (3 × 50 ml), and the colorless crystalline substance was filtered off on a glass filter funnel (40 - 100 μm), dried and stored in a desiccator over P_2O_5.

L-Arabinose thiobenzoylhydrazone (1a)

Yield 70%, m.p. 161˚C - 162˚C (lit. [3] m.p. 163˚C - 164˚C). ^{13}C-NMR spectrum (solid phase): δ = form **C**(100%): 64.23 (C-5), 70.21 (C-2), 71.15 (C-3), 73.11 (C-4), 76.07 (C-1), 118.96, 122.78, 128.11, 130.90 (Ar), 134.05 (ArC-S), 143.18 (C=N) ppm. ^{13}C-NMR spectrum (DMSOd_6): δ = form **A**(40%): 63.91 (C-5), 70.87 (C-2), 71.22 (C-3), 72.29 (C-4), 131.81 (ArC-S), 144.50 (C-1), 183.48 (C=S); form **C**(60%): 63.62 (C-5), 69.90 (C-2), 71.08 (C-3), 72.73 (C-4), 75.91 (C-1), 131.54 (ArC-S), 142.69 (C=N), 121.27 - 131.41 (Ar in **A** and **C**) ppm. Found, %: C 50.73; H 5.61; N 9.79. $C_{12}H_{16}N_2O_4S$. Calculated, %: C 50.69; H 5.67; N 9.85.

L-Arabinose 2-sulfanylacetylhydrazone (2a)

Yield 75%, m.p. 120˚C - 121˚C. ^{13}C-NMR spectrum (D_2O): δ = α-**B**(10%): 25.52 (CH_2SH), 62.38 (C-5), 67.31 (C-4), 68.09 (C-2), 72.71 (C-3), 90.40 (C-1), 172.36 (C=O); form **D**(55%): 26.90 (CH_2S), 63.02 (C-5), 65.58 (C-1), 69.60 (C-2), 70.57 (C-3), 71.12 (C-4), 177.19 (C=O); form **D**′(35%): 27.04 (CH_2S), 62.88 (C-5), 64.40 (C-1), 69.72 (C-2), 70.04 (C-3), 70.87 (C-4), 176.63 (C=O) ppm. Found, %: C 35.34; H 5.88; N 11.80. $C_7H_{14}N_2O_5S$. Calculated, %: C 35.29; H 5.92; N 11.76.

L-Arabinose 3-sulfanylpropionylhydrazone (3a)

Yield 55%, m.p. 146˚C - 148˚C. ^{13}C-NMR spectrum (solid phase): δ = forms **E**, **E**′(100%): 23.74 and 30.14

(CH_2S), 35.95 and 39.48 ($\underline{C}H_2CO$), 63.23 and 64.70 (C-5), 69.78 (C-2), 70.79 (C-3), 71.17 (C-4), 77.34 (C-1), 170.81 (C=O) ppm. ^{13}C-NMR spectrum (D_2O): δ = form **A**(5%): 152.03 (C-1), 169.78 (C=O); forms **E**, **E′**(30%): 24.48 and 25.04 (CH_2S), 33.41 and 34.16 (CH_2CO), 63.70 (C-5), 67.48 (C-1), 69.57 (C-4), 70.23 (C-3), 70.49 (C-2), 172.11 (C=O); α-**B**(10%): 19.32 (CH_2SH), 36.77 (CH_2CO), 61.82 (C-5), 68.24 (C-2), 69.07 (C-3), 70.03 (C-4), 85.98 (C-1), 172.63 (C=O); β-**B**(55%): 19.34 (CH_2S), 37.05 (CH_2CO), 62.46 (C-5), 68.83 (C-4), 70.29 (C-2), 72.04 (C-3), 89.83 (C-1), 172.57 (C=O) ppm. Found, %: C 38.03; H 6.44; N 11.06. $C_8H_{16}N_2O_5S$. Calculated, %: C 38.09; H 6.39; N 11.10.

L-Arabinose 2-sulfanylbenzoylhydrazone (4a)

Yield 60%, m.p. 177˚C - 178˚C (lit. [4] m.p. 175˚C - 176˚C). ^{1}H-NMR spectrum (DMSOd_6): δ = form **F**(75%): 9.24 (br.s, NHCO); form **F′**(25%): 9.24 (br.s, NHCO) ppm. ^{13}C-NMR spectrum (DMSOd_6): δ = form **F**: 63.37 (C-5), 69.40 (C-2), 70.08 (C-3), 71.51 (C-4), 75.40 (C-1), 140.13 (ArC-S), 175.40 (C=O); form **F′**: 63.61 (C-5), 69.40 (C-2), 70.38 (C-3), 71.01 (C-4), 74.24 (C-1), 140.13 (ArC-S), 172.75 (C=O), 127.90 - 133.47 (Ar in **F** and **F′**) ppm. Found, %: C 48.06; H 5.29; N 9.41. $C_{12}H_{16}N_2O_5S$. Calculated, %: C 47.99; H 5.37; N 9.33.

Spectral characteristics of compounds **1b-1e**, **2b-2f**, **3b-2f**, and **4b-4f** were described previously [9]-[12].

Acknowledgements

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