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Synthesis pathway to carbohydrate-derived salicylidene hydrazides as ligands for oxovanadium complexes

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Abstract—Salicylidene hydrazides represent important ligands forming oxovanadium complexes. Carbohydrate-derived chiral salicylidene hydrazides as ligands for metal ion complexation were synthesized for the first time. The pathway of the mild and selective synthesis starts from commercial saccharides like methyl-α-D-glucopyranoside and methyl-α-D-mannopyranoside. All synthesized carbohydrate-derived salicylidene hydrazides are able to form oxovanadium complexes. The mononuclear structure proposed for the complex of 1,2,3,4-tetra-*O*-methyl-α-D-glucopyranuronic acid salicylidene hydrazide is consistent with the analytical data (NMR, IR and MS).

1. Introduction

Salicylidene hydrazides are versatile structural units that can act as mono- or dianionic ONO tridentate donors. Oxovanadium complexes of these ligands have been used as enzyme models for the active site of vanadium dependent haloperoxidases.[1–3] Similar complexes, which have an additional coordination site bound at a side chain also offer good haloperoxidase activity.[4,5]

Since haloperoxidases are known to catalyze enantioselective sulfoxidation[6–9] as well as oxovanadium complexes of tri- or tetradentate Schiff base ligands,[10–13] such complexes of salicylidene hydrazides with a chiral backbone should be a good catalysts for enantioselective sulfoxidation (Fig. 1).

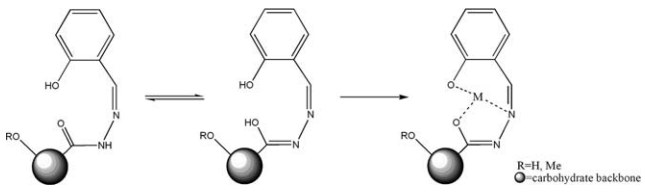

Figure 1. Salicylidene hydrazides with a chiral carbohydrate backbone.

Recently, we described the first structurally characterized prototypes of copper complexes from aminodeoxysugars and its efficient catalytic activity in catechol oxidation.[14–17] Moreover, carbohydrate-derived chiral Mn(III)–salen complexes are potent catalysts in enantiomeric epoxidation of alkenes.[18]

The aim of the present paper is to extend and to confirm the carbohydrate-based structure design of chiral transition metal complexes with catalytic activity using salicylidene hydrazides as ONO ligands and carbohydrates with or without additional free hydroxyl groups. Therefore, an important topic of the work was a concept for an easy synthesis of a large variety of carbohydrate-derived salicylidene hydrazides and its exemplification by typical examples.

Furthermore the complexation behaviour of these ligands with vanadate was investigated.

2. Results and discussion

Carbohydrates as polyfunctional and chiral natural compounds are—with growing importance—starting materials and ligands for the synthesis of catalytic active transition metal complexes.[19–26] Due to the broad variety of configurational and conformational principles of carbohydrates a tuning of the complex structure and also of its catalytic activity can be achieved by varying the carbohydrate moiety. Moreover, the introduction of substituents into the carbohydrate skeleton may influence complex properties like

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solubility and magnetic behaviour as well as the catalytic activity—even if the substituent is not directly coordinated to the metal.[16]

In order to investigate the structural design in the field of carbohydrate-based salicylidene hydrazides and their oxovanadium complexes we have synthesized a set of pyranosides and open chain analogue (Fig. 2, **11** and **23**), respectively. Besides, the stereochemistry of the ligands (glucose and mannose, see Fig. 2, **14** and **5**) and the kind and amount of functional substituents (ketal groups, ethers) at the carbohydrate have been modified.

We developed a synthetic route that allows a selective conversion to salicylidene hydrazides starting from any purchasable saccharide with a primary OH-group. Scheme 1 shows this synthetic pathway considering methyl-2,3-*O*-isopropylidene-α-D-mannuronic acid salicylidene hydrazide **5** starting from methyl-α-D-mannopyranoside **1** as an example.

First, an isopropylidene ketal **2** is formed in order to increase the solubility of the educt **1**. In the next step, which is the key step, the primary OH-group is oxidized selectively using TEMPO-reagent. The carboxyl group is transformed into the corresponding methylester **3** and then converted into the hydrazide **4**. Finally, the Schiff base **5** with salicylaldehyde is formed.

For transferring this pathway to other saccharides just the introduction of the functional substituents has to be adapted to the respective carbohydrate and its stereochemistry.

The ability of this type of ligands to form oxovanadium complexes was demonstrated primarily using the salicylidene hydrazide **20** without free OH donor groups. Therefore, a solution of the ligand and equimolar amount of KVO_3 in methanol was refluxed for 24 h. After purification potassium [1,2,3,4-tetra-*O*-methyl-α-D-glucopyranuronic acid salicylidene hydrazidato] dioxo vanadate **24** could be obtained as a yellow powder in 63% yield. The structure proposed for the vanadium complex **24**, which is consistent with the analytical data (quod infra), is shown in Figure 3. The ^{1}H NMR data of the complex verify the absence of the signals of the aromatic OH-group and of the amide N–H proton (9.19 and 10.87 ppm, respectively). The ^{51}V NMR spectrum recorded in MeOD shows a single resonance in the expected range for *cis*-dioxovanadium(v) complexes, i.e., at $\delta=-544$ ppm with a peak width at half height of $\Delta\nu_{1/2}=526$ Hz. Mass spectrometry experiments have confirmed the formation of the named complex. Infrared spectra show a deprotonation of the ligand amide function since the C=O and N–H stretches of the free ligand at 1711 and 3206 cm^{-1}, respectively, can not be observed in the complex spectrum. Instead a strong signal at 1617 cm^{-1} occurs that can be assigned to the –C=N–N=C-structural unit of the metal-bound salicylidene hydrazide. It indicates a coordination of the enolate form of the amide moiety.[2,27] Furthermore two strong bands are observed at 910 and 918 cm^{-1} belonging to the stretching vibrations of the *cis*-dioxovanadium moiety of the complex.

Attempts to form oxovanadium complexes of the ligands **5**, **11** and **23** lead to mixtures of different coordination compounds, that we were not able to separate up to now. But ^{51}V NMR experiments show a formation of two species in

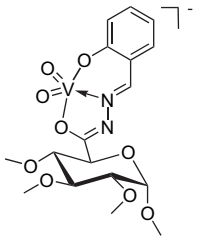


Figure 3. Proposed structure of the complex anion **24**.

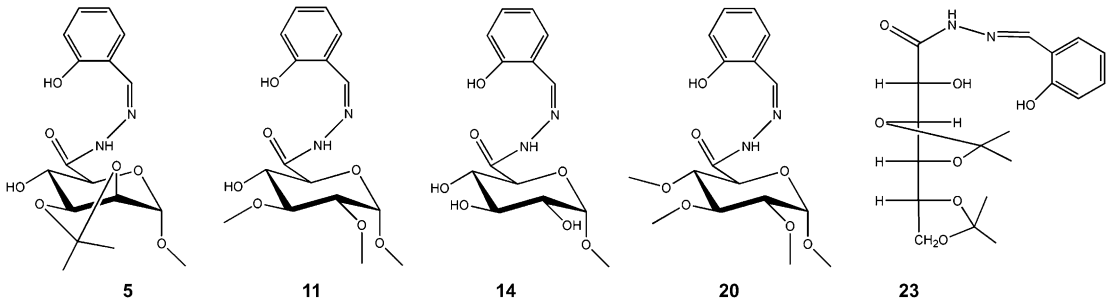
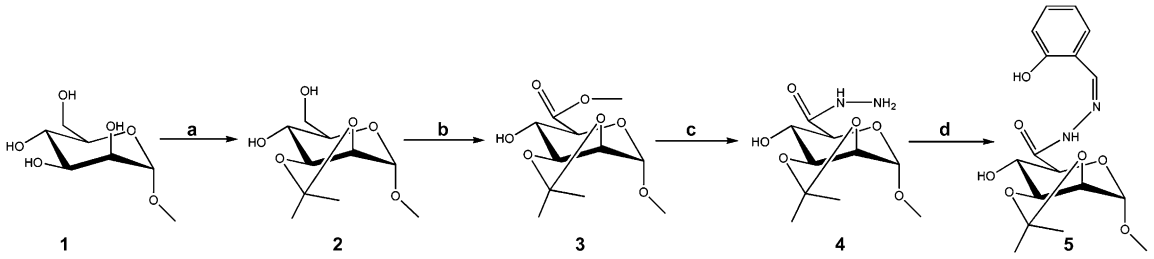


Figure 2. Set of carbohydrate-based salicylidene hydrazides.



Scheme 1. Reagents and conditions: (a) dimethoxy propane, *p*-toluene sulfonic acid, DMF, rt, 24 h; (b) TEMPO oxidation, rt, 2 h; methyl iodide, DMF, rt, 24 h; (c) hydrazine monohydrate, ethanol, reflux, 3 h and (d) salicylaldehyde, ethanol, reflux, 6 h.

each case. This suggests that the free OH-group at these carbohydrates is able to participate in the complex formation.

A first test in catalytic sulfoxidation reaction with **24** showed a complete and selective conversion of the substrate to the corresponding sulfoxide within 90 min. Therefore thioanisole was reacted with 1 mol % of **24** at room temperature in CH_2Cl_2/MeOH (7:3) with 1.2 equiv of H_2O_2 as oxidation agent. No enantioselectivity was observed, which may be caused by the use of the protic solvent methanol, as described in lit.[10]

3. Conclusion

The paper reports the preparation of the first carbohydrate-derived chiral salicylidene hydrazides and its oxovanadium complexes. An important topic of the work was the development of an easy pathway to a large variety of chiral ligands of this type starting from commercial carbohydrates. The ligands **5**, **11**, **14**, **20** and **23** form oxovanadium complexes with VO_3^-. The proposed mononuclear structure of complex **24** can be proved by NMR, IR and MS and it is an active catalyst for sulfoxidation.

Further investigations are concentrated on structure determination of the oxovanadium complexes and their catalytic activity in sulfoxidation reactions.

4. Experimental

4.1. General

NMR spectra were recorded on a Bruker AC-200 spectrometer. IR spectra were measured on a Perkin–Elmer 2000 spectrometer. Mass spectra were carried out on a Finnigan MAT SSQ710 or a Finnigan MAT 95XLTRAP. Elemental analyses were acquired by use of a Leco CHNS 932. The UV–vis data were recorded with a Cary 5000 from Varian. Chemicals were obtained from Fluka and Aldrich, respectively. TLC was conducted on Merck glass plates coated with silica gel 60. Chromatography was performed using silica gel 60 (Particle size 0.063–0.2 mm) from Fluka Chemie GmbH.

4.1.1. Methyl-2,3-*O*-isopropylidene-α-D-mannopyranoside (2). Compound **2** was synthesized according to the lit.[28] starting from methyl-α-D-mannopyranoside **1**.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.36, 1.45 (2s, 6H, 2× –$C(CH_3)_2$), 3.36 (s, 3H, –OCH_3), 3.50–4.11 (m, 6H, H-2, H-3, H-4, H-5, H-6), 4.88 ppm (s, 1H, H-1); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.01, 27.83 (2×–$C(CH_3)_2$), 54.99 (–OCH_3), 62.28 (C-6), 69.29 (C-4), 69.54 (C-2), 75.40 (C-3), 78.25 (C-5), 98.38 (C-1), 109.65 ppm (–$C(CH_3)_2$). Anal. Calcd for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75. Found: C, 51.36; H, 7.60.

4.1.2. Methyl-2,3-*O*-isopropylidene-α-D-mannuronic acid methylester (3). Compound **2** 2.5 g (10.6 mmol) was dissolved in 55 ml ethyl acetate, 31 ml of a saturated aqueous solution of $NaHCO_3$, 0.3 g (1.6 mmol) TBAF trihydrate and 0.445 g (2.8 mmol) TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl radical) were added. After cooling to 0 °C a cooled mixture of 55 ml sodium hypochloride (6% in water), 27 ml of a saturated solution of $NaHCO_3$ and 55 ml of a saturated solution of NaCl in water was added slowly. The reaction mixture was stirred vigorously for 2 h at 0 °C until completion (TLC control, eluent ethyl acetate/methanol 1:1). After evaporation in vacuum the product was dissolved in methanol and filtered over silica gel suspended in methanol in order to remove the inorganic salts. The crude acid was converted into the methylester as described.[29] Yield: 1.72 g (62%) colourless oil.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.33, 1.49 (2s, 6H, 2× –$C(CH_3)_2$), 3.45 (s, 3H, –OCH_3), 3.80 (s, 3H, –$COOCH_3$), 3.95–4.35 (m, 4H, H-2, H-3, H-4, H-5), 4.94 ppm (s, 1H, H-1); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 25.31, 26.89 (2× –$C(CH_3)_2$), 52.22 (–$COOCH_3$), 55.33 (–OCH_3), 69.01 (C-4), 69.87 (C-2), 74.16 (C-3), 76.05 (C-5), 98.53 (C-1), 109.59 (–$C(CH_3)_2$), 170.25 ppm (–$COOCH_3$). Anal. Calcd for $C_{11}H_{18}O_7$: C, 50.38; H, 6.92%. Found: C, 49.69; H, 6.89.

4.1.3. Methyl-2,3-*O*-isopropylidene-α-D-mannuronic acid hydrazide (4). Compound **3** 3.3 g (12.5 mmol) and 1.25 g (25 mmol) hydrazine hydrate were refluxed in dry ethanol (50 ml) for 3 h. After evaporation the crude product was crystallized from methanol/ethyl acetate/*n*-hexane. Yield: 1.91 g (58%) colourless needles.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.31, 1.47 (2s, 6H, 2× –$C(CH_3)_2$), 3.40 (s, 3H, –OCH_3), 3.81 (dd, J=9.0 Hz, J=6.2 Hz, 1H, H-4), 3.89 (s, 1H, –NH_2), 4.03–4.21 (m, 3H, H-5, H-3, H-2), 4.34 (s, 1H, –OH), 4.93 (s, 1H, H-1), 7.86 ppm (s, 1H, –N*H*NH_2); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 25.75, 27.50 (–$C(CH_3)_2$), 55.70 (–OCH_3), 68.42 (C-4), 70.12 (C-2), 74.29 (C-3), 76.62 (C-5), 98.53 (C-1), 109.74 (–$C(CH_3)_2$), 171.18 ppm (–CO–NH–). Anal. Calcd for $C_{10}H_{18}N_2O_6$: C, 45.80; H, 6.92%; N, 10.68. Found: C, 45.81; H, 6.85; N, 10.81.

4.1.4. Methyl-2,3-*O*-isopropylidene-α-D-mannuronic acid salicylidene hydrazide (5). Compound **4** 1.0 g (3.8 mmol) was suspended in dry methanol (30 ml) and refluxed after adding 0.46 g (3.8 mmol) salicylaldehyde. After 6 h reaction was completed (TLC control ethyl acetate/methanol 1:1). The solvent was removed and the crude product was washed with ethanol. Yield: 1.25 g (90%).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.26, 1.36 (s, 3H, –$C(CH_3)_2$), 3.50 (s, 3H, –OCH_3), 4.00 (m, 1H, H-4), 4.17–4.32 (m, 4H, H-5, H-3, H-2, –OH), 5.03 (s, 1H, H-1), 6.87–7.03 (m, 2H, H-3_{Ar}, H-5_{Ar}), 7.21 (dd, J=7.7 Hz, J=1.7 Hz, 1H, H-4_{Ar}), 7.29–7.37 (m, 1H, H-6_{Ar}), 8.41 (s, 1H, –CH=N–), 9.54 (s, 1H, Ar–OH), 10.80 ppm (s, 1H, –CO–NH–); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 25.26, 27.05 (–$C(CH_3)_2$), 55.70 (–OCH_3), 69.18 (C-4), 69.48 (C-2), 73.70 (C-3), 75.86 (C-5), 98.38 (C-1), 109.87 (–$C(CH_3)_2$), 116.66 (C-3_{Ar}), 117.05 (C-1_{Ar}), 119.09 (C-5_{Ar}), 130.83 (C-6_{Ar}), 132.07 (C-4_{Ar}), 152.21 (–CH=N–), 158.41 (C-2_{Ar}), 166.17 ppm (–CO–NH–). Anal. Calcd for $C_{17}H_{22}N_2O_7$: C, 55.73; H, 6.05; N, 7.65. Found: C, 55.74; H, 5.71; N, 7.51.

4.1.5. Methyl-4,6-*O*-benzylidene-α-D-glucopyranoside (6). Methyl-α-D-glucopyranoside was reacted as described in lit.[30] to give **6**.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 3.42–3.83 (m, 5H, H-2, H-3, H-5, H-6), 3.42 (s, 3H, –OCH_3), 4.27 (dd, *J*=8.8 Hz, *J*=3.0 Hz, 1H, H-4), 4.74 (d, *J*=3.8 Hz, 1H, H-1), 5.50 (s, 1H, Ph–CH), 7.34–7.37 (m, 3H, H-3$_{Ar}$, H-4$_{Ar}$, H-5$_{Ar}$), 7.47–7.53 ppm (m, 2H, H-2$_{Ar}$, H-6$_{Ar}$); ^{13}C NMR ($CDCl_3$, 60 MHz): δ 55.49 (–OCH_3), 62.35 (C-5), 68.90 (C-6), 71.53 (C-3), 72.79 (C-2), 80.93 (C-4), 99.82 (C-1), 101.90 (Ph–CH), 126.33 (C-2$_{Ar}$ C-6), 127.03 (C-3$_{Ar}$ C-5$_{Ar}$), 128.97 (C-4$_{Ar}$), 137.06 ppm (C-1$_{Ar}$). Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.70; H, 6.32.

4.1.6. 4,6-*O*-Benzylidene-1,2,3-tri-*O*-methyl-α-D-glucopyranoside (7). Synthesis was carried out according to Ref. 31 starting from **6**.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.23 (dd, *J*=9.1 Hz, *J*=3.6 Hz, 1H, H-2), 3.50–3.83 (m, 4H, H-6, H-5, H-3), 3.44, 3.55, 3.64 (3s, 9H, 3×–OCH_3), 4.28 (dd, *J*=9.3 Hz, *J*=4.0 Hz, 1H, H-4), 4.86 (d, *J*=3.6 Hz, 1H, H-1), 5.45 (s, 1H, Ph–CH), 7.33–7.4 (m, 3H, H-3$_{Ar}$, H-4$_{Ar}$, H-5$_{Ar}$), 7.46–7.53 ppm (m, 2H, H-2$_{Ar}$, H-6$_{Ar}$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 54.93, 59.00, 60.65 (3×–OCH_3), 61.92 (C-5), 68.74 (C-6), 79.53 (C-4), 81.11 (C-3), 81.84 (C-2), 98.10 (C-1), 101.05 (Ph–CH), 125.75 (C-2$_{Ar}$ C-6), 127.86 (C-3$_{Ar}$ C-5$_{Ar}$), 128.59 (C-4$_{Ar}$), 137.06 ppm (C-1$_{Ar}$). Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.96; H, 7.15. Found: C, 62.20; H, 7.28.

4.1.7. 1,2,3-Tri-*O*-methyl-α-D-glucopyranoside (8). Compound **8** was prepared by conversion of **7** as described.[32]

^{1}H NMR (methanol-d_3, 200 MHz): δ 3.29–3.37 (m, 2H, H-2, H-3), 3.41, 3.46, 3.48 (3s, 9H, 3×–OCH_3), 3.67–3.83 (m, 4H, H-4, H-5, H-6), 4.85 ppm (d, *J*=3.4 Hz, 1H, H-1); ^{13}C NMR (methanol-d_3, 50 MHz): δ 55.34, 58.67, 61.21 (3×–OCH_3), 62.48 (C-5), 71.31 (C-6), 73.43 (C-3), 82.82 (C-2), 84.45 (C-4), 98.52 ppm (C-1). Anal. Calcd for $C_9H_{18}O_6$: C, 48.64; H, 8.16. Found: C, 48.72; H, 8.15.

4.1.8. 1,2,3-Tri-*O*-methyl-α-D-glucopyranuronic acid methylester (9). Oxidation of 2.0 g (9 mmol) **8** was performed like **3**. The crude acid was treated as describe to obtain the methylester.[33] Yield: 1.94 g (86%) of a colourless oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 3.21 (dd, *J*=9.2 Hz, *J*=3.4 Hz, 1H, H-2), 3.45–3.70 (m, 2H, H-3, H-4), 3.43, 3.46, 3.58 (3s, 9H, 3×–OCH_3), 3.77 (1s, 3H, –COO*C*H$_3$), 4.08 (d, *J*=9.5 Hz, 1H, H-5), 4.86 ppm (d, *J*=3.4 Hz, 1H, H-1); ^{13}C NMR ($CDCl_3$, 60 MHz): δ 52.64 (COO*C*H$_3$), 55.82, 58.97, 61.07 (3×–OCH_3), 70.52 (C-5), 71.63 (C-3), 80.74 (C-2), 81.67 (C-4), 97.96 (C-1), 170.69 ppm (*C*OOCH$_3$). Anal. Calcd for $C_{10}H_{18}O_7$: C, 48.00; H, 7.25. Found: C, 47.93; H, 7.00.

4.1.9. 1,2,3-Tri-*O*-methyl-α-D-glucopyranuronic acid hydrazide (10). Procedure like that of **4**. The product precipitated, was filtered and washed with ethyl acetate. Compound **9** 1.64 g (6.55 mmol) gave 1.40 g (85%) as colourless needles.

^{1}H NMR (DMSO-d_6, 200 MHz): δ 3.07 (dd, *J*=9.6 Hz, *J*=3.2 Hz, 1H, H-2), 3.18–3.69 (m, 2H, H-3, H-4), 3.28, 3.31, 3.42 (3s, 9H, 3×–OCH_3), 4.27 (s 2H, –NH_2), 4.79 (d, *J*=3.2 Hz, 1H, H-5), 5.27 (d, *J*=5.6 Hz, 1H, H-1), 9.35 ppm (s, 1H, –N*H*NH$_2$); ^{13}C NMR (DMSO-d_6, 50 MHz): δ 54.55, 57.24, 59.73 (3×–OCH_3), 70.14 (C-5), 70.27 (C-3), 80.18 (C-2), 82.14 (C-4), 97.08 (C-1), 167.51 ppm (–CO–NH–). Anal. Calcd for $C_9H_{18}O_6N_2$: C, 43.20; H, 7.25; N, 11.19. Found: C, 43.24; H, 7.34; N, 11.11.

4.1.10. 1,2,3-Tri-*O*-methyl-α-D-glucopyranuronic acid salicylidene hydrazide (11). The reaction was carried out like **5**. The crude product was purified by column chromatography (eluent: ethyl acetate). Compound **10** 0.60 g (2.4 mmol) gave 0.68 g (80%) **11**.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.20 (dd, *J*=9.6 Hz, *J*=3.5 Hz, 1H, H-2), 3.47–3.75 (m, 2H, H-3, H-4), 3.47, 3.52, 3.65 (3s, 9H, 3×–OCH_3), 4.17 (d, *J*=9.8 Hz, 1H, H-5), 4.91 (d, *J*=3.6 Hz, 1H, H-1), 6.83–6.99 (m, 2H, H-3$_{Ar}$, H-5$_{Ar}$), 7.16 (dd, *J*=7.7 Hz, *J*=1.7 Hz, 1H, H-4$_{Ar}$), 7.26–7.34 (m, 1H, H-6$_{Ar}$), 8.35 (s, 1H, –CH=N–), 9.41 (s, 1H, Ar–OH), 10.75 ppm (s, 1H, –CO–NH–); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 56.10, 59.32, 61.24 (3×–OCH_3), 69.15 (C-5), 73.02 (C-3), 80.44 (C-2), 81.80 (C-4), 98.27 (C-1), 116.94 (C-3$_{Ar}$), 117.39 (C-1$_{Ar}$), 119.46 (C-5$_{Ar}$), 131.16 (C-6$_{Ar}$), 132.47 (C-4$_{Ar}$), 152.72 (–CH=N–), 158.74 (C-2$_{Ar}$), 166.99 ppm (–CO–NH–). Anal. Calcd for $C_{16}H_{22}N_2O_7$: C, 54.23; H, 6.26; N, 7.91. Found: C, 53.61; H, 6.43; N, 7.46.

4.1.11. 1-*O*-Methyl-α-D-glucopyranuronic acid methylester (12). Procedure like that of **9**. Methyl-α-D-glucopyranoside 3.88 g (20 mmol) gave 3.19 g (72%) as a colourless oil.

^{1}H NMR (DMSO-d_6, 200 MHz): δ 3.15 (d, *J*=5.2 Hz, 1H, H-2), 3.27 (s, 3H, –OCH_3), 3.47 (s, 1H, –OH), 3.65 (s, 3H, –COO*C*H$_3$), 3.78 (s, 1H, –OH), 3.84 (s, 1H, –OH), 4.58 (d, *J*=3.4 Hz, 1H, H-3), 4.88 (d, *J*=6.2 Hz, 1H, H-4), 4.95 (d, *J*=4.6 Hz, 1H, H-5), 5.27 ppm (d, *J*=5.8 Hz, H-1); ^{13}C NMR (DMSO-d_6, 50 MHz): δ 51.90 (–COO*C*H$_3$), 54.97 (–OCH_3), 71.49 (H-4), 71.61 (H-2), 71.75 (H-3), 72.71 (H-5), 100.67 (H-1), 170.01 ppm (–*C*OOCH$_3$). Anal. Calcd for $C_8H_{14}O_7$: C, 43.24; H, 6.35. Found: C, 42.87; H, 6.85.

4.1.12. 1-*O*-Methyl-α-D-glucopyranuronic acid hydrazide (13). Compound **12** 3.13 g (14.1 mmol) was treated like **4**. Crystallization from methanol gave 2.29 g (73%) as colourless needles.

^{1}H NMR (DMSO-d_6, 200 MHz): δ 3.16 (m, 1H, H-2), 3.36 (s, 3H, –OCH_3), 3.47, 3.65, 3.70 (3s, 3H, 3×–OH), 4.25 (s, 2H, –NH_2), 4.51 (d, *J*=3.6 Hz, 1H, H-3), 4.77 (d, *J*=6.2 Hz, 1H, H-4), 4.81 (d, *J*=4.4 Hz, 1H, H-5), 5.02 (d, *J*=4.2 Hz, H-1), 9.29 ppm (–N*H*NH$_2$); ^{13}C NMR (DMSO-d_6, 50 MHz): δ 54.88 (–OCH_3), 70.68 (H-4), 71.24 (H-2), 71.56 (H-3), 72.98 (H-5), 100.45 (H-1), 167.88 ppm (–CO–NH–). Anal. Calcd for $C_7H_{14}N_2O_6$: C, 37.84; H, 6.35; N, 12.61. Found: C, 37.76; H, 6.38; N, 12.48.

4.1.13. 1-*O*-Methyl-α-D-glucopyranuronic acid salicylidene hydrazide (14). Procedure like that of **5**. The crude

product was crystallized from ethyl acetate/methanol (2:1). Compound **13** 0.50 g (2.3 mmol) gave 0.59 g (78%) **14**.

^{1}H NMR (acetone-d_6, 200 MHz): δ 3.31 (d, J=5.0 Hz, 1H, H-2), 3.43 (s, 3H, –OCH_3), 3.62–3.70 (m, 2H, H-3, H-4), 3.83 (d, J=7.4 Hz, 1H, –OH), 4.10 (d, J=9.2 Hz, 1H, H-5), 4.26 (d, J=3 Hz, 1H, –OH), 4.51 (d, J=3 Hz, 1H, –OH), 4.77 (d, J=3.6 Hz, 1H, H-1), 6.87–6.95 (m, 2H, H-3_{Ar}, H-5_{Ar}), 7.27–7.36 (m, 2H, H-4_{Ar}, H-6_{Ar}), 8.54 (s, 1H, –CH=N–), 10.96 (s, 1H, Ar–OH), 11.38 ppm (s, 1H, –CO–NH–); ^{13}C NMR (acetone-d_6, 50 MHz): δ 55.77 (–OCH_3), 71.06 (H-4), 72.45 (H-2), 73.22 (H-3), 74.05 (H-5), 101.14 (H-1), 117.29 (C-3_{Ar}), 118.46 (C-1_{Ar}), 119.75 (C-5_{Ar}), 131.63 (C-6_{Ar}), 132.15 (C-4_{Ar}), 151.51 (–CH=N–), 159.19 (C-2_{Ar}), 167.02 ppm (–CO–NH–). Anal. Calcd for $C_{14}H_{18}N_2O_7$: C, 51.53; H, 5.56; N, 8.59. Found: C, 50.74; H, 6.61; N, 7.41.

4.1.14. 1-*O*-Methyl-6-*O*-triphenylmethyl-α-D-glucopyranose (15). Synthesized according to lit.[34]

^{1}H NMR (DMSO-d_6, 250 MHz): δ 3.03 (t, J=8.2 Hz, 2H, H-6), 3.26 (d, J=9.6 Hz, 1H, H-4), 3.42 (d, J=9.4 Hz, 1H, H-3), 3.60 (t, J=7.6 Hz, 1H, H-2), 4.07 (m, 1H, H-5), 3.37 (s, 3H, –OCH_3), 4.61 (d, J=3.5 Hz, 1H, H-1), 7.15–7.38 (m, 15H, –$C(Ph)_3$); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 55.11 (–OCH_3), 63.89 (C-6), 70.20 (C-5), 71.43 (C-3), 72.05 (C-2), 74.48 (C-4), 86.82 (–$C(Ph)_3$), 99.12 (C-1), 127.18 (C-4_{Ar}), 127.91 (C-3_{Ar}), 128.68 (C-2_{Ar}), 143.83 ppm (C-1_{Ar}). Anal. Calcd for $C_{26}H_{28}O_6$: C, 71.54; H, 6.47. Found: C, 72.14; H, 6.89.

4.1.15. 1,2,3,4-Tetra-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranose (16). Compound **15** 12.25 g (28.1 mmol) was treated like **7**. Crystallization of the crude product in methanol gave 10.08 g (75%) as colourless needles.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 3.13 (dd, J=4.4 Hz, J=10.0 Hz, 1H, H-2), 3.33–3.65 (m, 5H, H-3, H-4, H-5, H-6), 3.33, 3.48, 3.59, 3.65 (4s, 12H, 4×–OCH_3), 4.94 (d, J=3.5 Hz, 1H, H-1), 7.26–7.54 ppm (m, 15H, –$C(Ph)_3$); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 54.95, 59.04, 60.38, 60.96 (4×–OCH_3), 62.44 (C-6), 70.10 (C-5), 79.98 (C-3), 81.90 (C-2), 83.74 (C-4), 86.25 (–OC(Ph)$_3$), 97.32 (C-1), 126.94 (C-4_{Ar}), 127.74 (C-2_{Ar}), 128.78 (C-3_{Ar}), 144.06 ppm (C-1_{Ar}). Anal. Calcd for $C_{29}H_{34}O_6$: C, 72.78; H, 7.16. Found: C, 72.99; H, 7.30.

4.1.16. 1,2,3,4-Tetra-*O*-methyl-α-D-glucopyranose (17). Treating of **16** as shown in Ref. 35 gave **17**.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 3.09 (dd, J=3.6 Hz, J=9.6 Hz, 1H, H-2), 3.44–3.58 (m, 2H, H-3, H-4), 3.66 (dd, J=11.7 Hz, J=4.0 Hz, 1H, H-6), 3.76 (dd, J=11.7 Hz, J=2.9 Hz, 1H, H-5), 3.34, 3.45, 3.50, 3.56 (4s, 12H, 4×–OCH_3), 4.73 ppm (d, J=3.6 Hz, 1H, H-1); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 55.13, 59.02, 60.54, 60.83 (4×–OCH_3), 61.91 (C-6), 70.54 (C-5), 79.61 (C-3), 81.82 (C-2), 83.37 (C-4), 97.48 ppm (C-1). Anal. Calcd for $C_{10}H_{20}O_6$: C, 50.84; H, 8.53. Found: C, 52.08; H, 8.93.

4.1.17. 1,2,3,4-Tetra-*O*-methyl-α-D-glucopyranuronic acid methylester (18). Oxidation of 5.00 g (21 mmol) **17** and formation of the corresponding methylester was performed like **3**. Purification of the crude product by column chromatography with ethyl acetate gave 3.91 g (70%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.15 (dd, J=14.6 Hz, J=3.4 Hz, 1H, H-2), 3.33–3.53 (m, 2H, H-3, H-4), 4.01 (d, J=12.3 Hz, 1H, H-5), 3.41, 3.47, 3.48, 3.58 (4s, 12H, 4×–OCH_3), 3.78 (s, 3H, –$COOCH_3$), 4.81 ppm (d, J=3.6 Hz, 1H, H-1); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 52.51 (–COOCH$_3$), 55.58, 59.14, 60.46, 60.94 (4×–OCH_3), 69.90 (C-5), 81.18 (C-3), 81.21 (C-2), 82.86 (C-4), 98.06 (C-1), 170.11 ppm (–COOCH$_3$). Anal. Calcd for $C_{11}H_{20}O_7$: C, 49.99; H, 7.63. Found: C, 50.16; H, 7.53.

4.1.18. 1,2,3,4-Tetra-*O*-methyl-α-D-glucopyranuronic acid hydrazide (19). Procedure like that of **4**. The product precipitated, was filtered and washed with ethyl acetate. Yield: 3.90 g (14.7 mmol) **18** gave 3.57 g (92%) **19**.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.18 (dd, J=3.6 Hz, J=9.7 Hz, 1H, H-2), 3.24–3.36 (m, 2H, H-3, H-4), 3.87 (d, J=10.0 Hz, 1H, H-5), 3.38, 3.47, 3.47, 3.57 (4s, 12H, 4×–OCH_3), 4.82 (d, J=3.4 Hz, 1H, H-1), 7.44 ppm (s, 1H, –NHNH$_2$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 55.76, 59.13, 60.62, 60.95 (4×–OCH_3), 69.47 (C-5), 81.06 (C-3), 81.63 (C-2), 83.04 (C-4), 97.87 (C-1), 169.81 ppm (–CO–NH–NH$_2$). Anal. Calcd for $C_{10}H_{20}N_2O_6$: C, 45.45; H, 7.63; N, 10.60. Found: C, 44.56; H, 7.81; N, 10.37.

4.1.19. 1,2,3,4-Tetra-*O*-methyl-α-D-glucopyranuronic acid salicylidene hydrazide (20). Compound **19** 0.5 g (1.9 mmol) was treated like **5**. Crystallization in methanol/ethyl acetate (1:4) gave 0.53 g (74%) as a colourless solid.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.22 (dd, J=3.4 Hz, J=6.2 Hz, 1H, H-2), 3.29–3.60 (m, 2H, H-4, H-3), 3.46, 3.54, 3.57, 3.64 (4s, 12H, 4×–OCH_3), 4.10 (d, J=12.5 Hz, 1H, H-5), 4.92 (d, J=3.4 Hz, 1H, H-1), 6.87–7.03 (m, 2H, H-3_{Ar}, H-5_{Ar}), 7.20–7.32 (m, 2H, H-4_{Ar}, H-6_{Ar}), 8.47 (s, 1H, –CH=N–), 9.19 (s, 1H, Ar–OH), 10.87 ppm (s, 1H, –CO–NH–); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 55.64, 58.89, 60.42, 60.71 (4×–OCH_3), 69.32 (C-5), 80.74 (C-3), 81.60 (C-2), 82.77 (C-4), 97.66 (C-1), 116.89 (C-3_{Ar}), 116.99 (C-1_{Ar}), 119.02 (C-5_{Ar}), 130.71 (C-6_{Ar}), 131.83 (C-4_{Ar}), 151.72 (–CH=N–), 158.34 (C-2_{Ar}), 164.57 ppm (–CO–NH–). Anal. Calcd for $C_{17}H_{24}N_2O_7$: C, 55.43; H, 6.57; N, 7.60. Found: C, 55.51; H, 6.51; N, 7.64.

4.1.20. 3,4,5,6-Di-*O*-isopropylidene-D-gluconic acid methylester (21). Synthesis was carried out according to lit.[36] starting from D-gluconic acid-δ-lactone.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.37, 1.39 (2s, 6H, –$C(CH_3)_2$), 1.41, 1.45 (2s, 6H, –$C(CH_3)_2$), 2.44 (s, –OH), 3.86 (s, 3H, –COOCH$_3$), 3.99–4.24 (m, 5H, H-3, H-4, H-5, H-6), 4.37 ppm (dd, J=9.1 Hz, J=2.3 Hz, 1H, H-2); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 25.27, 26.53, 26.69, 27.16 (2×–C(CH$_3$)$_2$), 52.73 (–COOCH$_3$), 67.89 (C-6), 69.43 (C-5), 76.45 (C-4), 77.27 (C-3), 80.89 (C-2), 109.87, 110.09 (2×–C(CH$_3$)$_2$), 173.02 ppm (–COOCH$_3$). Anal. Calcd for $C_{13}H_{22}O_7$: C, 53.78; H, 7.64. Found: C, 53.48; H, 7.79.

4.1.21. 3,4,5,6-Di-*O*-isopropylidene-D-gluconic acid hydrazide (22). Compound **21** 4.11 g (14.2 mmol) was treated like **4**. Crystallization from ethyl acetate/*n*-hexane gave 3.81 g (92%) **22**.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.30, 1.35 (2s, 6H, –C(CH_3)$_2$), 1.38 (s, 6H, –C(CH_3)$_2$), 3.83–3.99 (m, 2H, H-6), 4.03–4.15 (m, 2H, H-5, H-4), 4.29 (d, J=1.4 Hz, 1H, H-3), 4.42 (dd, J=8.0 Hz, J=1.6 Hz, 1H, H-2), 7.84 ppm (s, 1H, –N*H*NH$_2$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 25.14, 26.66 (–C(*C*H$_3$)$_2$), 26.82, 27.02 (–C(*C*H$_3$)$_2$), 67.71 (C-6), 69.87 (C-5), 76.89 (C-4), 76.94 (C-3), 79.72 (C-2), 109.91, 110.07 (2×–*C*(CH$_3$)$_2$), 171.75 ppm (–CO–NH–). Anal. Calcd for $C_{12}H_{22}N_2O_6$: C, 49.65; H, 7.64; N, 9.65. Found: C, 48.86; H, 7.77; N, 9.53.

4.1.22. 3,4,5,6-Di-*O*-isopropylidene-D-gluconic salicylidene hydrazide (23). Procedure like that of **5**. The product was washed with ethanol. The conversion of 1.14 g (4.0 mmol) **22** gave 1.12 g (70%) **23**.

^{1}H NMR (DMSO-d_6, 200 MHz): δ 1.28, 1.35 (2s, 12H, 2× –C(CH_3)$_2$), 3.80–3.86 (m, 1H), 3.95–4.19 (m, 3H, H-6, H-5, H-4), 4.16 (s, 1H, H-3), 4.31 (dd, J=7.6 Hz, J=1.8 Hz, 1H, H-2), 6.08 (d, J=6.4 Hz, 1H, –OH), 6.86–6.93 (m, 2H, H-3$_{Ar}$, H-5$_{Ar}$), 7.24–7.32 (m, 1H, H-4$_{Ar}$), 7.39–7.44 (m, 1H, H-6$_{Ar}$), 8.67 (s, 1H, –CH=N–), 11.34 (s, 1H, Ar–OH), 11.59 ppm (s, 1H, –CO–NH–); ^{13}C NMR (DMSO-d_6, 50 MHz): δ 25.25, 26.48 (–C(*C*H$_3$)$_2$), 26.74, 27.06 (–C(*C*H$_3$)$_2$), 66.59 (C-6), 69.90 (C-5), 75.1 (C-4), 76.45 (C-3), 80.32 (C-2), 108.91, 109.07 (2×–*C*(CH$_3$)$_2$), 116.41 (C-3$_{Ar}$), 118.44 (C-1$_{Ar}$), 119.29 (C-5$_{Ar}$), 129.83 (C-6$_{Ar}$), 131.32 (C-4$_{Ar}$), 149.12 (–CH=N–), 157.50 (C-2$_{Ar}$), 168.16 ppm (–CO–NH–). Anal. Calcd for $C_{19}H_{26}N_2O_7$: C, 57.86; H, 6.64; N, 7.10. Found: C, 57.98; H, 6.59; N, 7.13.

4.1.23. Potassium [1,2,3,4-tetra-*O*-methyl-α-D-glucopyranuronic acid salicylidene hydrazidato] dioxo vanadate (24). KVO_3 0.190 g (1.36 mmol) was added to a solution of 0.500 g (1.36 mmol) **20** in 75 ml methanol. The mixture was refluxed for 24 h and filtered hot. After removing the solvent the solid residue was washed with CH_2Cl_2. Yield: 0.42 g (63%) of a yellow powder.

MS (Micro-ESI neg. in MeOH): m/z=937 (18%, 2(VO$_2$L)$^-$+K$^+$), 921 (20%, 2(VO$_2$L)$^-$+Na$^+$), 449.3 (100%, (VO$_2$L)$^-$); FTIR (KBr): 2939 ($\nu_{as\ C-H}$ –CH_3), 2839 (ν_{C-H} –OCH_3), 1617 ($\nu_{C=N-N=C}$), 1570+1546 ($\nu_{C=C}$ Ar), 1476+1449 ($\delta_{as\ C-H}$ –CH_3), 1356+1362 ($\delta_{sy\ C-H}$ –CH_3), 1157+1093+1071+1045 ($\nu_{as\ C-O-C}$), 918+910 (ν_{VO_2}), 760 cm^{-1} (γ_{OOP} amide); UV–vis (MeOH): λ_{max} (log ε)=228 (3.19), 290 (3.07), 381 (2.63) nm; ^{1}H NMR (methanol-d_3, 400 MHz): δ 3.38–3.57 (m, 3H, H-2, H-3, H-4), 3.38, 3.39, 3.44, 3.54 (4s, 12H, 4×–OCH_3), 4.13 (d, J=9.65 Hz, 1H, H-5), 4.90 (d, J=3.36 Hz, 1H, H-1), 6.84–6.91 (m, 2H, H-3$_{Ar}$, H-5$_{Ar}$), 7.38–7.41 (m, 1H, H-4$_{Ar}$), 7.49 (dd, J=7.60 Hz, J=1.60 Hz, 1H, H-6$_{Ar}$), 8.79 ppm (s, 1H, –CH=N–); ^{13}C NMR (methanol-d_3, 100 MHz): δ 55.65, 58.78, 60.65, 60.90 (4×–OCH_3), 70.25 (C-5), 82.14 (C-3), 82.53 (C-2), 83.70 (C-4), 99.03 (C-1), 119.48 (C-3$_{Ar}$), 120.15 (C-1$_{Ar}$), 120.74 (C-5$_{Ar}$), 133.76 (C-6$_{Ar}$), 135.40 (C-4$_{Ar}$), 158.83 (–CH=N–), 165.74 (C-2$_{Ar}$), 173.31 ppm (–CO–N–); ^{51}V NMR (methanol-d_3, 105 MHz): δ −544 ppm ($\nu_{½}$=526 Hz). Anal. Calcd for $C_{17}H_{22}N_2O_9VK\cdot H_2O$: C, 40.32; H, 4.78; N, 5.53. Found: C, 40.34; H, 4.58; N, 5.95.

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