Facile Syntheses of Novel Acyclic Polycarboxylic Acids

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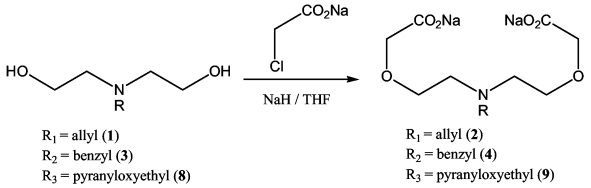
The synthesis of novel di- and tricarboxylic acids is described. Starting from diethanolamine, a series of *N*-substituted diethanol derivatives were prepared which were converted in the subsequent reaction step into the corresponding carboxylic acids by treatment with chloroacetic acid. *N*,*N*-bis[2-(carboxymethoxy)ethyl]glycine was obtained by *N*-alkylation of glycine ethylester with ethyl 2-(2-bromoethoxy)acetate.

Key words: Carboxylic Acids, Environmentally Benign Ligands, Complexones

Introduction

Aminopolycarboxylic acids have found widespread applications as complexation ligands (complexones) in numerous industrial, medical and agricultural processes. Among them, ethylenediaminetetraacetic acid (EDTA) and diethylene triaminepentaacetic acid (DTPA) are used as chelating agents in a vast number of large-scale industrial applications. Indiscriminate use of these ligands, however, has recently been called into question due to their virtual non-biodegradability, their accumulation in the environment and their propensity to mobilize toxic heavy metal ions from the soil [1]. Furthermore, the two principal manufacturing processes for EDTA and related chelating agents are both based on cyanomethylation of the parent polyamine [2], which utilizes either highly toxic sodium cyanide [3] or hydrogen cyanide [4] and formaldehyde. As a part of our current efforts regarding the design and development of more environmentally benign chelating agents, we recently reported complexation studies of the pentadentate *N*,*O* chelating ligand iminodisuccinate (ISA) [5, 6]. In this paper we describe the synthesis of a new class of diethanolamine-derived carboxylic acids which are potential candidates for complexation studies in aqueous solution.



R_1 = allyl (**1**)
R_2 = benzyl (**3**)
R_3 = pyranyloxyethyl (**8**)

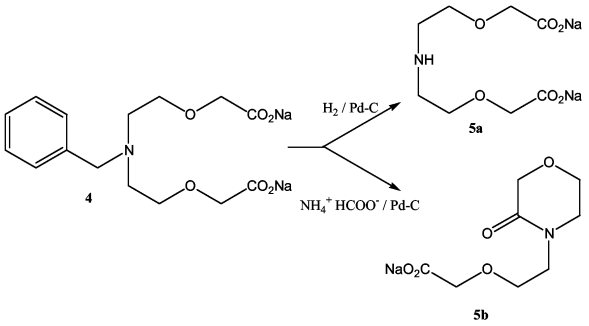
R_1 = allyl (**2**)
R_2 = benzyl (**4**)
R_3 = pyranyloxyethyl (**9**)

Scheme 1. Synthesis of diethanolamine derived dicarboxylic acids.

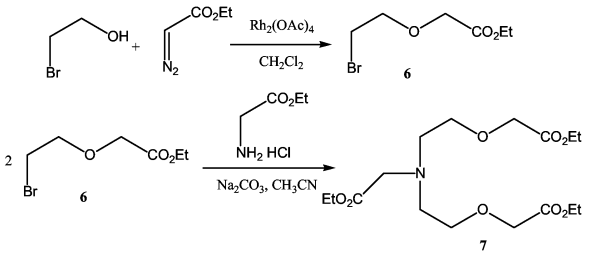
Results and Discussion

The syntheses of *N*-substituted diethanolamine derived dicarboxylic acids were performed as outlined in Scheme 1, starting from known *N*-substituted diethanolamine derivatives [7 – 9]. For the *N*-allyl- (**1**) and the *N*-benzyl substituted diethanolamine (**3**) the formation of the alkoxide and carboxylate was accomplished in one pot by use of four equivalents of sodium hydride to yield the corresponding dicarboxylates **2** and **4** in excellent yields. Because of the presence of the acid-labile pyranyloxy-protecting group in **9**, the alkoxide and carboxylate were prepared in separate reaction vessels. These afforded, after combination, the corresponding pyranyloxy-protected dicarboxylate **10** in high yield.

We envisaged that the *N*-benzyl-substituted diacid **4** would be a promising candidate for the grafting of a further acid side arm onto the nitrogen atom. To this end, the benzyl group was removed by catalytic hydrogenation on Pd/charcoal. Interestingly, the formation of the product is dependent on the hydrogen source (Scheme 2). The desired diacid **5a** is exclusively



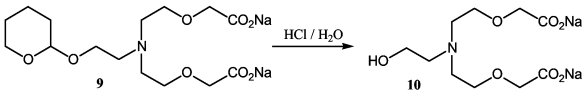
Scheme 2. Cleavage of *N*-benzyl group leading to different products depending on the hydrogen source.



Scheme 3. Synthesis of *N*,*N*-bis[2-(carboxymethoxy)ethyl] glycine triethyl ester (**7**).

formed when the benzyl group is removed under an atmosphere of hydrogen. However, if ammonium formate is used as an alternative hydrogen source [10, 11], the lactame **5b** is predominantly formed accompanied by traces of the diacid **5a** as evidenced by ^{13}C NMR spectroscopy and CI-mass spectrometry (signals at 178.2 and 170.1 ppm in the ^{13}C NMR and the observation of the molecular $[M + H]^+$-peak at 204).

The lactame **5b** could not be obtained analytically pure, since it was impossible to separate it from the diacid contaminate. However, lactame **5b** and diacid **5a** are fully interconvertible into each other. Treatment of lactame **5b** with aqueous HCl at elevated temperature yields the diacid **5a**; conversely, the lactame **5b** is formed in an appreciable amount from the diacid **5a** upon prolonged heating under vacuum. It was found that the dicarboxylate **5a** is extremely reluctant towards reaction with chloroacetic acid even when various solvents and bases are employed. Instead of the desired tricarboxylic acid, the lactame **5b** was formed. This is presumably attributable to a significant pH-change in the reaction medium, rendering the lone-pair on the nitrogen atom more reactive towards intramolecular cyclisation rather than intermolecular nucleophilic attack. In order to obtain a derivative of *N*,*N*-bis[2-(carboxymethoxy)ethyl]glycine (**7**), ethyl 2-(2-



Scheme 4. Removal of the THP protecting group.

bromoethoxy)acetate (**6**), prepared by rhodium(II) catalysed *O*-alkylation of 2-bromoethanol with ethyl diazoacetate, was reacted with glycine ethylester hydrochloride in refluxing acetonitrile in the presence of anhydrous sodium carbonate, yielding **7** as its triethylester after purification on silica gel in moderate yields (Scheme 3).

This compound exhibits in the ^{13}C NMR spectrum two signals at 169.9 ppm and 172.4 ppm for the inequivalent ester carbonyl carbon atoms.

The *N*-pyranyloxy substituted dicarboxylic **9** acid was cleanly converted into the hydroxyethyl dicarboxylic acid **10** by cleavage of the pyranyloxy group in HCl/H_2O. The compound was obtained quantitatively as a highly hygroscopic salt (Scheme 4).

All the syntheses reported so far were repeated using redistilled THF without compromising yield of the products. This aspect may be attractive for large scale industrial applications.

Conclusion

In our present studies, we provide a series of novel di- and tricarboxylic acids. We were also capable to use redistilled THF in our ligand syntheses without significantly lowering the yield of the products. Current and future studies in our laboratories are focused on the complexation behaviour of these novel ligands with various transition and main group metal ions.

Experimental Section

General

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 200 FT-NMR spectrometer. ^{1}H and ^{13}C data are listed in parts per million [ppm] relative to tetramethylsilane and were referenced using the residual proton solvent peak (^{1}H) or the carbon resonance (^{13}C). ^{13}C NMR spectra in which D_2O was used as solvent were calibrated using 1,4-dioxane as an external standard ($\delta = 66.66$ ppm). The following abbreviations were used to express the multiplicities of the ^{1}H NMR signals: s = singlet; d = doublet; t = triplet; m = multiplet; b = broad. ESI mass spectra and high-resolution mass spectra (HRMS) were recorded on a Micromass LCT instrument (capillary voltage 3.5 kV, sample cone 35 V, source temperature 120 °C, desolvation temperature 150 °C). Elemental analyses were recorded

on a Perkin Elmer 2400 Series II CHNS/O Analyzer. THF was freshly distilled from sodium benzophenone ketyl prior to use. All other solvents employed in the syntheses were of HPLC-grade and used directly as purchased. *N*-benzyl-diethanolamine [7], *N*-2-(pyranyloxyethyl)-diethanolamine [8, 9], *N*-allyl-diethanolamine [8] and rhodium(II) acetate [12] were prepared according to published procedures. All other chemicals were obtained commercially and used without further purification. All reactions employing sodium hydride were performed under a positive atmosphere of dry argon in oven-dried glassware by using Schlenk techniques.

N-Allyl-2,8-dioxa-5-aza-1,9-nonanedicarboxylic acid (**2**)

To a vigorously stirred solution of *N*-allyl-diethanolamine (**1**) (11.24 g, 77.4 mmol) and α-chloroacetic acid (14.63 g, 154.8 mmol) in THF (500 ml) was added sodium hydride (325.1 mmol, 13.00 g of a 60% dispersion in mineral oil) at 0 °C in small portions. After complete addition the cloudy reaction mixture was heated to reflux for 24 h during which the color of the reaction mixture changed from white to reddish. The solution was cooled to ambient temperature and water (2 ml) was added dropwise in order to destroy the excess of employed sodium hydride. The solvent was removed on a rotary evaporator and the purple oily residue was dissolved in hot water (200 ml) and subsequently extracted with petroleum ether (3×150 ml). The volume of the aqueous phase was reduced until a glutinous red residue has formed. This was subsequently dissolved in hot anhydrous ethanol (300 ml), the NaCl precipitate filtered off, washed with hot ethanol (5×50 ml) and the solution was evaporated again to total dryness, by placing the flask into boiling water. In order to remove any remaining traces of NaCl, the residue was subjected to a Soxhlet extraction for 12 h using anhydrous ethanol as solvent (300 ml). After complete removal of the solvent 21.00 g (89%) of **2** were obtained as reddish crystals. – ^{1}H NMR (200 MHz, D_2O, 295 K): $\delta = 2.77$ (t, $^3J_{HH} = 5.8$ Hz, 4 H, N-CH_2), 3.23 (d, $^3J_{HH} = 6.8$ Hz, 2 H, N-CH_2-CH=CH_2), 3.63 (t, $^3J_{HH} = 5.8$ Hz, 4 H, O-CH_2), 3.87 (s, 4 H, O-CH_2CO_2), 5.20 – 5.30 (m, 2 H, N-CH_2-CH=CH_2), 5.78 – 5.94 (m, 1 H, N-CH_2-CH=CH_2). – ^{13}C{^{1}H} NMR (50 MHz, D_2O, 295 K): $\delta = 52.2$ (O-*C*H_2CO_2), 56.9 (N-*C*H_2-CH=CH_2), 67.6 (N-*C*H_2), 69.8 (O-*C*H_2), 119.7, 133.4 (olefinic carbons), 178.1 (CO_2Na). – MS (ESI): *m/z* (%) = 328(100) [M^+ + Na]. – HRMS: *m/z* 306.0927 [M + H^+] ($C_{11}H_{18}NO_6Na_2$ requires 306.09295).

N-Benzyl-2,8-dioxa-5-aza-1,9-nonanedicarboxylic acid (**4**)

The synthesis was performed analogously to that of **2**, employing *N*-benzyl-diethanolamine (**3**) (10.00 g, 51.2 mmol), α-chloroacetic acid (9.68 g, 102.4 mmol) and sodium hydride (208 mmol, 8.40 g of a 60% dispersion in mineral oil) in THF (300 ml). After extraction with petroleum ether (3×100 ml) and complete removal of the solvent 15.1 g (83%) of **4** were obtained as off-white crystals. – ^{1}H NMR (200 MHz, D_2O, 295 K): $\delta = 2.73$ (t, $^3J_{HH} = 5.6$ Hz, 4 H, N-CH_2), 3.58 (t, $^3J_{HH} = 5.6$ Hz, 4 H, O-CH_2), 3.66 (s, 2 H, C_6H_5CH_2), 3.81 (s, 4 H, O-CH_2CO_2), 7.35 (br s, 5 H, C_6H_5). – ^{13}C{^{1}H} NMR (50 MHz, D_2O, 295 K): $\delta = 52.1$ (O-*C*H_2CO_2), 57.3 (N-*C*$H_2$$C_6H_5$), 66.4 (N-*C*$H_2$), 69.5 (O-*C*$H_2$), 127.9, 128.5, 130.1, 134.9 (aromatic carbons), 177.6 (CO_2Na). – MS (ESI): *m/z* (%) = 378(100) [M^+ + Na]. – HRMS: *m/z* 356.1063 [M^+ + H] ($C_{15}H_{20}NO_6Na_2$ requires 356.1086). – $C_{15}H_{19}NNa_2O_6 \cdot H_2O$ (373.31): calcd. C 48.26, H 5.67, N 3.75; found C 48.36, H 5.94, N 3.70.

2,8-Dioxa-5-aza-1,9-nonanedicarboxylic acid (**5**)

Method A (employing H_2-gas)

To solution of *N*-benzyl-2,8-dioxa-5-aza-1,9-nonanedicarboxylic acid disodium salt (**4**) (10.0 g, 28.1 mmol) in EtOH / H_2O (100 ml, 1:1) was added palladium-charcoal (1.00 g, 10% Pd). The reaction apparatus, comprising a three-necked flask and a reflux condenser was thoroughly flushed with argon and subsequently connected to a hydrogen cylinder. The mixture was refluxed for 16 h under an atmosphere of hydrogen while the progress of the reaction was monitored by ^{13}C NMR spectroscopy (disappearance of the aromatic carbons). The solution was filtered through a Büchner funnel and the solvent was removed in vacuum. The residual water was removed in vacuum by immersing the flask into boiling water. The disodium salt **5a** was obtained as a white powder (7.40 g). – ^{1}H NMR (200 MHz, D_2O, 295 K): $\delta = 3.25$ (t, $^3J_{HH} = 4.7$ Hz, 4 H, N-CH_2), 3.77 (t, $^3J_{HH} = 4.7$ Hz, 4 H, O-CH_2), 3.96 (s, 4 H, O-CH_2CO_2). – ^{13}C{^{1}H} NMR (50 MHz, D_2O, 295 K): $\delta = 47.0$ (O-*C*H_2CO_2), 65.8 (N-*C*H_2), 69.9 (O-*C*H_2), 178.1 (CO_2Na). – MS (ESI): *m/z* (%) = 244(40) [M^+ + Na], 222(100) [M^+ + H]. – $C_8H_{13}NNa_2O_6$(265.17): calcd. C 36.24, H 4.94, N 5.28; found C 36.26, H 5.25, N 4.95.

Method B (employing ammonium formate)

To solution of **4** (5.00 g, 14.1 mmol) and ammonium formate (5.00 g, 79.3 mmol) in ethanol (100 ml) was added palladium-charcoal (0.50 g, 10% Pd). The solution was refluxed for 6 h and subsequently filtered through a Büchner funnel, and the solution was concentrated on a rotary evaporator to about 30 ml. After cooling to room temperature the precipitated inorganic salts were removed by filtration. According to the ^{13}C NMR and CI-mass spectrum the lactame **5b** was formed. However, the observation of additional signals at 178.5, 66.5 and 47.5 ppm in the ^{13}C NMR spectrum were indicative of the formation of traces of the diacid **5a**. – ^{13}C{^{1}H} NMR (50 MHz, D_2O,

295 K): $\delta = 46.6, 46.9, 64.2, 66.5, 67.7, 70.6$ (aliphatic carbons), 170.1, 178.2 (CO_2H and CON). – MS (CI, NH_3): *m/z* (%) = 204(10) [M^+ + H], 146(12) [M^+-$C_2H_2O_2$], 128(100) [M^+-$C_2H_4O_3$]. – MS (ESI): *m/z* (%) = 248(100) ([M^+-H + Na_2], 226(90) [M^+ + Na].

The aqueous lactame solution **5b** was refluxed with concentrated HCl (2 ml) for 30 min. Reaction control indicated the formation of the diacid **5a**. The solution was concentrated to about 10 ml and acetone (50 ml) was added. The formed inorganic salts were filtered off and the solvent was completely removed in vacuum to yield the diacid **5a** as a brownish oil (2.31 g, 74 %). – ^{1}H NMR (200 MHz, D_2O, 295 K): $\delta = 3.32$ (t, $^3J_{HH} = 4.8$ Hz, 4 H, N-C*H*$_2$), 3.84 (t, $^3J_{HH} = 4.8$ Hz, 4 H, O-C*H*$_2$), 4.15 (s, 1 H, N-*H*), 4.20 (s, 4 H, O-C*H*$_2$CO$_2$); the resonance for the carboxylic proton was not found. – ^{13}C{^{1}H} NMR (50 MHz, D_2O, 295 K): $\delta = 46.9$ (O-*C*H$_2$CO$_2$), 65.9 (N-*C*H$_2$), 67.7 (O-*C*H$_2$), 174.5 (CO_2H). – HRMS: *m/z* 222.0983 [M^+ + H] ($C_8H_{16}NO_6$ requires 222.0978).

Ethyl 2-(2-bromoethoxy)acetate (**6**)

To a solution of 2-bromoethanol (5.03 g, 40.2 mmol) in methylene chloride (50 ml) was added dirhodium tetraacetate (200 mg, 1.1 mol%) at 0 °C. The ice bath was removed and a solution of ethyl diazoacetate (4.70 g, 41.2 mmol) in methylene chloride (50 ml) was added dropwise over a period of 30 min while the evolution of N_2-gas could be detected. The catalyst was removed by filtration and solvent was removed in vacuum. Distillation of the greenish crude product (115 – 122 °C, 1 Torr) yielded the desired product as colorless oil (6.91 g, 78%). – ^{1}H NMR (200 MHz, $CDCl_3$, 295 K): $\delta = 1.21$ (t, $^3J_{HH} = 7.1$ Hz, 3 H, O-CH$_2$-C*H*$_3$), 3.43 (t, $^3J_{HH} = 6.2$ Hz, 2 H, C*H*$_2$), 3.81 (t, $^3J_{HH} = 6.2$ Hz, 2 H, C*H*$_2$), 4.07 (s, 2 H, OC*H*$_2$-CO$_2$Et), 4.13 (q, $^3J_{HH} = 7.1$ Hz, 3 H, O-C*H*$_2$-CH$_3$). – ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 295 K): $\delta = 14.2$ (O$_2$C-CH$_2$-*C*H$_3$), 30.0 (*C*H$_2$Br), 60.9 (O-*C*H$_2$-CH$_2$Br), 68.4 (CO$_2$-*C*H$_2$-CH$_3$), 71.4 (O-*C*H$_2$-CO$_2$Et), 170.0 (*C*O$_2$Et).

N,N-Bis[2-(carboxymethoxy)ethyl]glycine triethyl ester (**7**)

A suspension of glycine ethyl ester hydrochloride (1.57 g, 11.3 mmol), ethyl 2-(2-bromoethoxy)acetate (5.00 g, 23.7 mmol) and anhydrous sodium carbonate (6.00 g, 56.6 mmol) was refluxed in acetonitrile (50 ml) for 24 h. The pale yellow solution was filtered and the residual inorganic salts were washed with methylene chloride (3 × 25 ml). After removal of the solvent an yellow oil was obtained, which was subsequently purified by column chromatography on silica gel employing ethyl acetate as eluent. After drying of the colorless fraction in vacuum 2.36 g (6.50 mmol, 58%) of **7** were obtained as a off-white oil. – ^{1}H NMR (200 MHz, $CDCl_3$, 295 K): $\delta = 1.23 - 1.34$ (m, 9 H, CO$_2$CH$_2$C*H*$_3$), 2.68 (t, $^3J_{HH} = 4.8$ Hz, 4 H, OC*H*$_2$), 3.23 (s, 2 H, NC*H*$_2$CO$_2$Et), 3.59 (t, $^3J_{HH} = 4.8$ Hz, 4 H, NC*H*$_2$), 4.05 (s, 4 H, OC*H*$_2$CO$_2$Et), 4.16 – 4.24 (m, 6 H, CO$_2$C*H*$_2$CH$_3$). – ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 295 K): $\delta = 14.1$, 54.0, 55.4, 60.4, 60.8, 68.3, 69.7, 170.4, 172.4. MS (ESI): *m/z* (%) = 364 (100) [M^+ + H]. – $C_{16}H_{29}NO_8$ (363.40): calcd. C 52.88, H 8.04, N 3.85, found C 53.03, H 7.98, N 3.91.

N-2-(Pyranyloxyethyl)-2,8-dioxa-5-aza-1,9-nonanedicarboxylic acid (**9**)

To a suspension of sodium hydride (125 mmol, 5.00 g of a 60% dispersion in mineral oil) in THF (100 ml) was added dropwise a solution of **8** (14.53 g, 62.3 mmol) in THF (100 ml). After complete addition, the reaction mixture was refluxed for 2 h while the initially white reaction mixture turned yellow. A suspension of chloroacetic acid, sodium salt (124.5 mmol) in THF (200 ml) [prepared from chloroacetic acid (11.75 g, 124 mmol) and sodium hydride (125 mmol, 5.00 g of a 60% dispersion in mineral oil) in THF (200 ml) followed by subsequent reflux for 1 h] was added and the reaction mixture was allowed to reflux for further 16 h. Water (0.5 ml) was carefully added and the solvent was removed on a rotary evaporator. The tan residue was dissolved in water (200 ml) and subsequently extracted with chloroform (3 × 150 ml; to remove of the mineral oil arising from the NaH dispersion). The aqueous phase was evaporated to such an extent that a glutinous residue formed, which was subsequently taken up in hot anhydrous ethanol (300 ml). The NaCl precipitate was filtered off, washed with hot ethanol (5 × 50 ml) and the solution was evaporated again to total dryness, by placing the flask into boiling water. After complete removal of the solvent 21.32 g (87%) of **9** were obtained as orange crystals. – ^{1}H NMR (200 MHz, [D_6]-DMSO, 343 K): $\delta = 1.54 - 1.83$ (m, 8 H, py-C*H*$_2$), 2.60 – 2.90 (m, 6 H, C*H*$_2$N), 3.53 – 3.63 (m, 6 H, C*H*$_2$O), 3.77 (s, 4 H, O*H*$_2$CO$_2$Na) 3.82 – 3.93 (m, 1 H, OC*H*O). – ^{13}C{^{1}H} NMR (50 MHz, D_2O, 295 K): $\delta = 19.4, 24.6, 30.1, 52.6, 53.3, 63.7, 64.4, 66.8, 69.7, 100.0, 177.9$ (CO_2Na). – MS (ESI): *m/z* (%) = 416 (100) [M^+ + Na]. – HRMS: *m/z* 394.1447 [M^+ + H] ($C_{15}H_{26}NO_8Na_2$ requires 394.1457).

N-2-(Hydroxyethyl)-2,8-dioxa-5-aza-1,9-nonanedicarboxylic acid (**10**)

To a solution of **9** (3.00 g, 7.63 mmol) in H_2O (30 ml) was added under vigorous stirring concentrated HCl until a pH value of 2 of the reaction solution was reached. The solution was stirred for 4 h at room temperature and subsequently extracted with chloroform (3 × 50 ml) in order to remove the formed THP-acetal. The pH value was then adjusted to 8 by addition of solid $NaHCO_3$. The solvent was completely removed under vacuum and the tan colored residue was subsequently extracted with hot ethanol (500 ml) and filtered.

After complete removal of the ethanol the disodium salt of **10** was obtained in quantitative yield (2.02 g) as tan colored, highly hygroscopic crystals. Crystals of **10** readily deliquesced when exposed to air. – ^{1}H NMR (200 MHz, [D$_6$]-DMSO, 343 K): $\delta = 2.60$ (t, $^3J_{HH} = 4.9$ Hz, 2 H), 2.69 (t, $^3J_{HH} = 4.9$ Hz, 2 H), 2.77 (t, $^3J_{HH} = 5.6$ Hz, 4 H), 3.61 (t, $^3J_{HH} = 5.6$ Hz, 4 H), 3.81 (s, 4 H, O-CH_2CO$_2$), 6.24 (s br 3 H, OH and CO$_2$H). – ^{13}C{^{1}H} NMR (50 MHz, D$_2$O, 295 K): $\delta = 53.8$, 55.5, 56.4, 65.3, 70.1, 178.2 (CO$_2$H). – MS (ESI): *m/z* (%) = 332(83) [M$^+$ + Na$_3$-H$_2$], 310 (12) [M$^+$ + Na$_2$-H], 288(100) ([M$^+$ + Na]. – HRMS: *m/z* 310.0865 [M$^+$ + H] (C$_{10}$H$_{18}$NO$_7$Na$_2$ requires 310.0879). – C$_{10}$H$_{17}$NNa$_2$O$_7$ (309.22): calcd. C 38.84, H 5.54, N 4.53; found C 38.52, H 5.88, N 4.27.

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