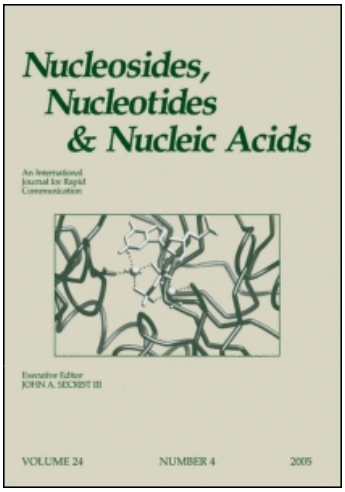

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Synthesis of Double Headed Imidazoline Acyclo C-Nucleosides: 1,4-bis[1-Amino-5-oxo-4-Substituted-(Imidazolin-2-yl)]galacto-tetritols

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ABSTRACT

Condensation of 2,3,4,5-tetra-*O*-acetyl-galactaroyl dichloride **(1)** with two equivalents of the α-amino esters **2a–c** gave the corresponding 2,3,4,5-tetra-*O*-acetyl-galactaric acid diamides **3a–c**. Heterocyclization of **3a–c** by heating with hydrazine hydrate took place with concomitant de-*O*-acetylation of the poly-acetoxyalkyl chain to give 1,4-bis[1-amino-5-oxo-4-substituted(imidazolin-2-yl)] *galacto*-tetritols **(5a–c)** and not the theoretically possible 1,2,4-triazinones **4** as indicated by spectral data. Compounds **5a–c** readily reacted with *p*-nitrobenz-aldehyde to give the corresponding *p*-nitrobenzylideneamino derivatives **6a-c**. Acetylation of **5a–c** afforded the 2,3,4,5-tetra-*O*-acetyl-1,4-bis[1-acetamido-5-oxo-4-substituted(imidazolin-2-yl)]*galacto*-tetritols **(7a,b,d)**. De-*O*-acetylation of **7a,b,d** gave 1,4-bis[1-acetamido-5-oxo-4-substituted (imidazolin-2-yl)]*galacto*-tetritols **(8a–c)**.

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INTRODUCTION

Imidazole acyclo *C*-nucleosides constitute an important class of acyclo C-nucleosides[1–6] especially after the isolation and characterization of the naturally occurring imidazole acyclo *C*-nucleoside antibiotic CV-1 [5-hydroxy-(D-*arabino*-tetritol-1-yl)imidazolidin-2-one] from a strain of S*treptomyces* sp.II.[7] Accordingly, considerable efforts have been directed toward the synthesis of many imidazole acyclo *C*-nucleosides seeking their diverse biological activities.[1–6] Members of imidazole acyclo *C*-nucleosides were found to produce lymphopenia,[8] depress blood lymphocyte counts in both mice and rats,[9] prevent spontaneous and cyclophosphamide-induced diabetes in non-obese diabetic mice[10] as well as possess protein kinase inhibition.[11] Moreover, multitudinous pharmaceutical activities[12–18] and agrochemical applications[19–21] were attributed to compounds comprising imidazole rings. These aspects prompted us to investigate a novel approach for the synthesis of the title double headed imidazoline acyclo *C*-nucleosides as a part of a program directed towards the synthesis of acyclo *C*-nucleosides.[22–25]

RESULTS AND DISCUSSION

Condensation of one molar equivalent of 2,3,4,5-tetra-*O*-acetyl-galactaroyl dichloride **(1)**[26] with two molar equivalents of three α-amino esters, namely: glycine ethyl ester **(2a)**, L-phenylalanine methyl ester **(2b)** and L-tyrosine methyl ester **(2c)** hydrochlorides gave products which showed three IR absorptions characteristic of NH, ester and amide corbonyls. The products correctly analysed for the 2,3,4,5-tetra-*O*-acetyl-galactaric acid diamide structures **3a–c**. Each product exhibited ^{1}H NMR signals of two exchangeable NH protons, four tetritolyl chain protons and four *O*-acetyl group protons. Compound **3a** showed in addition, two ethyl group protons and two methylene protons while compounds **3b** and **3c** showed the expected two benzyl group protons, two CH protons and two methyl group protons (compound **3c** showed also two broad exchangeable OH protons).

Subjecting compound **3a** to heterocyclization by heating with hydrazine hydrate, gave a single crystalline product which revealed IR absorptions at 3310 (OH and NH), 1663 (CON) and 1618 cm^{-1} (C=N) and lacked the ester carbonyl absorptions of the parent **3a**. The cyclization product correctly analysed for the molecular formula $C_{10}H_{16}N_6O_6$ indicating that heterocyclization took place with concomitant hydrazinolytic de-*O*-acetylation of the sugar chain. Accordingly, it may possess the 1,4-bis[2,5-dihydro-6-oxo-1H-(1,2,4-triazin-3-yl)]*galacto*-tetritol **(4)** or the 1,4-bis[1-amino-5-oxo-(imidazolin-2-yl)]*galacto*-tetritol **(5a)** structure. However the product was assigned the imidazolinone structure **5a** rather than the 1,2,4-triazinone structure **4** on the bases of the following evidence. First, the appearance of the two amino groups of **5a** as one singlet signal at δ 8.61. Had structure **4** been obtained, two separate NH proton signals would have appeared as double one-proton signals at δ 10–11.5 and δ 6.9–7.5 ppm.[27–29] Second, the ease of condensation of the amino group of **5a** with *p*-nitrobenzaldehyde to afford the corresponding *p*-nitrobenzylideneamino derivative **6a**. The alternative 1,2,4-triazinone structure **4** would not undergo such a reaction.

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Similarly, the diamides **3b,c** were heterocyclized by heating with hydrazine hydrate to the corresponding double headed acyclo *C*-nucleosides **5b,c**. The mass spectrum of **5b** did not show its molecular ion peak, yet revealed peaks for the alditolyl chain C1–C2 cleavage. The spectrum showed a fragment at m/z 217 corresponding to the heterocyclic base carrying a protonated formyl group characterising *C*-nucleoside structures.[30] Condensation of compounds **5b** or **5c** with *p*-nitrobenzaldehyde afforded the corresponding *p*-nitro-benzylideneamino derivatives **6b** and **6c**.

Treatment of **5a**–**c** with acetic anhydride in the presence of pyridine at room temperature caused acetylation of the hydroxy groups as well as the imidazoline amino group to give the 2,3,4,5-tetra-*O*-acetyl-1,4-bis[1-acetamido-5-oxo-4-substituted(imidazolin-2-yl)]*galacto*-tetritols **7a,b,d**. IR spectra of the latter compounds showed OAc, CON and C=N absorptions. The ^{1}H NMR spectra of the prepared compounds showed two exchangeable NH protons, four tetritolyl chain protons, two acetamido methyl protons and four acetoxy methyl protons (compound **7d** showed two additional aryloxy acetyl group protons), in addition compound **7a** showed two imidazolinyl CH_2 protons while compounds **7b** and **7d** showed the expected two benzyl group protons and two imidazolinyl CH protons. The mass spectrum of **7b** showed the characteristic protonated formyl heterocylic fragment at m/z 260.

De-*O*-acetylation of **7a,b,d** with a solution of ammonium hydroxide and methanol gave the corresponding 1,4-bis[1-acetamido-5-oxo-4-substituted (imidazolin-2-yl)]*galacto*-tetritols **8a**–**c** which showed (OH and NH), (CON) and (C=N) IR absorptions.

EXPERIMENTAL

Melting points were determined on MEL-TEMP II melting point apparatus in open glass capillaries and are uncorrected. The infrared spectra IR were recorded for potassium bromide discs on a Pye-Unicam SP1025 spectrophotometer. Proton magnetic resonance ^{1}H NMR spectra were carried out at ambient temperature (~25°C) with a Varian EM-390 or with a Brucker AC-250 spectrometers using tetramethylsilane (TMS) as an internal standard. Mass spectra (MS) were performed on a Hewlett-Packard 5995 gas chromatography-mass spectrometer system. Homogeneity of the products and follow up of the reactions were checked by ascending thin-layer chromatography TLC on plates precoated with silica gel G (E. Merck; layer thickness 0.25 mm), used without pretreatment. All ratios of the used solvent systems were volume to volume V/V, the solvent system used were: (A) $CHCl_3$/MeOH (9:1) and (B) $CHCl_3$/MeOH (1:1); the distance of the solvent travel was 5 cm and the spots were visualised by exposure to iodine vapour for a few minutes. Elemental microanalyses were performed at the Microanalytical Unit, Cairo University, Cairo, Egypt.

General Procedure for the Preparation of 2,3,4,5-Tetra-O-acetyl-galactaric acid diamides (3a–c). A solution of **1** (5 mmol) in dry benzene (30 mL) was gradually added to a stirred solution of the appropriate α-amino ester hydrochloride

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(**2a–c**, 10 mmol) in dry pyridine (15 mL) at ambient temperature. After stirring for 3 h, the solvents were evaporated under reduced pressure and the syrupy residue was crystallised from EtOH. The following compounds were prepared:

2,3,4,5-Tetra-O-acetyl-galactaric acid di(glycine ethyl ester)amide(3a). Colorless crystals; Yield: 70%; m.p.: 198–200°C; TLC: (A), R_f: 0.51; IR: 3244 (NH), 1755 (ester C=O) and 1678 cm^{-1} (CON); ^1H NMR ($CDCl_3$): δ 9.61 (s, 2 H, exchangeable, 2 NH), 6.26, 5.50 (2s, 2 H each, tetritoldi-1,4-yl 4 H), 4.78 (q, 4 H, 2 CH_2CH_3), 3.31 (s, 4 H, 2 CH_2), 2.18, 2.15 (2 s, 6 H each, 4 OAc), 1.24 (t, 6 H, 2 CH_2CH_3).

Anal. Calcd. for $C_{22}H_{32}N_2O_{14}$: C, 48.2; H, 5.8; N, 5.1. Found: C, 48.3; H, 5.9; N, 5.1.

2,3,4,5-Tetra-O-acetyl-galactaric acid di(phenylalanine methyl ester)amide(3b). Colorless crystals; Yield: 78%; m.p.: 206–208°C; TLC: (A), R_f: 0.53; IR: 3277 (NH), 1759 (ester C=O) and 1665 cm^{-1} (CON); ^1H NMR (CD_3): δ 9.86 (s, 2 H, exchangeable, 2 NH), 7.66–7.14 (m, 10 H, ArH), 5.65, 5.37 (2 s, 2 H each, tetritoldi-1,4 yl 4H), 5.06–4.81 (m, 2 H, CONHC*H*). 4.16–3.98 (m, 4 H, 2 benzyl CH_2), 3.75 (s, 6 H, 2 OCH_3), 2.28, 2.19 (2 s, 6H, 4 OAc).

Anal. Calcd. for $C_{34}H_{40}N_2O_{14}$: C, 58.3; H, 5.7; N, 4.0. Found: C, 58.4; H, 5.6; N, 4.0.

2,3,4,5-Tetra-O-acetyl-galactaric acid di(Tyrosine methyl ester)amide (3c). Colorless crystals; Yield: 75%; m.p.: 220–222°C. TLC: (A), R_f: 0.49; IR: 3430 (OH), 3319 (NH). 1764 (ester C=O), and 1676 cm^{-1} (C=N); ^1H NMR [$(CD_3)_2SO$]: δ 9.93 (s, 2 H, exchangeable, 2 NH), 7.23–6.85 (m, 8 H, ArH), 5.85, 5.45 (2 d, 2 H each, tetritoldi-1,4-yl, 5.16–4.99, (m, 2 H, CONHC*H*), 4.46 (s, broad, 2 H, exchangeable, 2 OH) 4.11–3.92 (m, 4 H, 2 benzy CH_2), 3.74 (s, 6 H, 2OCH_3), 2.28, 2.09 (2 s, 6 H, 4 OAc).

Anal. Calcd. for $C_{34}H_{40}N_2O_{16}$: C, 55.7; H, 5.5; N, 3.8. Found: C, 55.7; H, 5.4; N, 3.9.

General Procedure for the Preparation of 1,4-Bis(1-amino-5-oxo-4-substituted (imidazolin-2-yl)]galacto-tetritols (5a–c). A mixture of the particular diamide **(3a–c**, 1 mmol) and hydrazine hydrate (50 mL) was heated at reflux for 4 h and then evaporated under reduced pressure. The obtained residue was crystallized from a H_2O/MeOH-mixture. The following compounds were prepared:

1,4-Bis[1-amino-5-oxo-(imidazolin-2-yl)]galacto-tetritol(5a). Colorless crystals; Yield: 61%; m.p.: 266–270°C/dec.; TLC: (B), R_f: 0.52; IR: 3310 (broad, OH + NH), 1663 (CON), and 1618 cm^{-1} (C=N); ^1H NMR [$(CD_3)_2SO$]: δ 8.61 (s, 4 H, exchangeable, 2 NH_2), 5.10, 4.40 (2 s, broad, exchangeable, 2 OH each), 4.18, 3.76 (2 d, 2 H each, tetritoldi-1,4-yl 4 H), 3.29 (s, 4 H, 2 imidazolinyl CH_2).

Anal. Calcd. for $C_{10}H_{16}N_6O_6$: C, 38.0; H, 5.1; N, 26.6. Found: C, 38.2; H, 5.0; N, 26.5.

1,4-Bis[1-amino-4-benzyl-5-oxo-(imidazolin-2-yl)]galacto-tetritol (5b). Colorless crystals; Yield: 67%; m.p.: 238–240°C/dec.; TLC: (B), R_f: 0.49; IR: 3376, 3320

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(OH), 3182 (NH), 1661 (CON), and 1604 cm^{-1} (C=N); ^1H NMR [$(CD_3)_2SO$]: δ 8.79 (s, 4 H, exchangeable, 2 NH_2), 7.91–6.61 (m, 12 H, 10 ArH, 2 imidazolinyl H), 5.71, 5.39 (2 d, exchangeable, 2 OH each), 4.97, 4.61 (2 s, 2 H each, tetritoldi-1,4-yl 4 H), 4.52 (s, 4 H, 2 benzyl CH_2).

Anal. Calcd. for $C_{24}H_{28}N_6O_6$: C, 58.1; H, 5.7; N, 16.9. Found: C, 58.2; H, 5.7; N, 16.9.

1,4-Bis[1-amino-4-(p-hydroxybenzyl)-5-oxo-(imidazolin-2-yl)]galacto-tetritol (5c). Colorless crystals; Yield: 63%; m.p.: 300–304°C/dec; TLC: (B), R_f: 0.47; IR: 3327 (broad, OH + NH), 1665 (CON), and 1618 cm^{-1} (C=N); ^1H NMR [$(CD_3)_2SO$]: δ 8.81 (s, 4 H, exchangeable, 2 NH_2), 7.84–6.53 (m, 10 H, 8 ArH, 2 imidazolinyl H), 5.51, 5.23 (2 d, exchangeable, 2 OH each), 4.99 (s, board, 2 H, exchangeable 2 OH), 4.81, 4.69 (2 s, 2 H each, tetritold 1,4-yl 4 H), 4.41 (s, 4 H, 2benzyl CH_2).

Anal. Calcd. for $C_{24}H_{28}N_6O_8$: C, 54.5; H, 5.3; N, 15.9. Found: C, 54.6; H, 5.2; N, 15.8.

General Procedure for the Preparation of p-Nitrobenzylideneamino derivatives(6a–c). A solution of the particular **5a–c** (0.5 mmol) in H_2O (15 mL) was treated with a solution of *p*-nitrobenzaldehyde (0.5 mmol) in ethanol (25 mL) and the mixture was heated at 100°C for 30 min. The product which separated after attaining ambient temperature was filtered and crystallized from a H_2O/MeOH – mixture. The following compounds were prepared:

1,4-Bis[1-(p-nitrobenzylideneamino)-5-oxo-(imidazolin-2-yl)]galacto-tetritol(6a). Pale yellow crystals; Yield: 72%; m.p.: 238–240°C; TLC: (B), R_f: 0.50; IR: 3361 (broad, OH), 1681 (CON), 1645, and 1629 cm^{-1} (C=N); ^1H NMR [$(CD_3)_2SO$]: δ 8.20–7.81 (m, 10 H, 8 ArH, 2 CH=N), 5.23, 4.64 (2 d, exchangeable 2 OH each), 4.59, 4.19 (2 d, 2 H each, tetritoldi-1,4-yl 4 H), 3.49 (s, 4 H, 2 imidazolinyl CH_2).

Anal. Calcd. for $C_{24}H_{22}N_8O_{10}$: C, 49.5; H, 3.8; N, 19.2. Found: C, 49.5; H, 3.9; N, 19.3.

1,4-Bis[1-(p-nitrobenzylideneamino)-4-benzyl-5-oxo-(imidazolin-2-yl)] galacto-tetritol(6b). Pale yellow crystals; Yield: 68%; m.p. 226–228°C/dec.; TLC: (B), R_f: 0.47; IR: 3393 (broad, OH), 1679 (CON), 1645, and 1627 cm^{-1} (C=N); ^1H NMR [$(CD_3)_2SO$]: δ 8.37–7.82 (m, 18 H, ArH), 7.32–6.84 (m, 4 H, 2 CH=N, 2 imidozolinyl H), 5.74, 5.34 (2 d, exchangeable 2 OH each), 4.93, 4.54 (2 s, 2 H each, tetritoldi-1,4-yl 4 H), 4.31 (s, 4 H, 2 benzyl CH_2).

Anal. Calcd. for $C_{38}H_{34}N_8O_{10}$: C, 59.8; H, 4.5; N, 14.7. Found: C, 59.9; H, 4.4; N, 14.8.

1,4-Bis[1-(p-nitrobenzylideneamino)-4-(p-hydroxybenzyl)-5-oxo-(imidazolin-2-yl)] galacto-tetritol (6c). Pale yellow crystals; Yield: 62%; m.p. 268–270°C/dec.; TLC: (B), R_f: 0.45; IR: 3329 (broad, OH), 1678 (CON), 1646, and 1628 cm^{-1} (C=N); ^1H NMR [$(CD_3)_2SO$]: δ 8.54–7.58 (m, 16 H, ArH), 7.21–6.90 (m, 4 H, 2 CH=N, 2 imidazolinyl H), 5.67, 5.29 (2 d, exchangeable 2 OH each), 5.01 (s, broad, 2 H, exchangeable, 2 OH), 4.88, 4.39 (2 s, 2 H each, tetritoldi-1,4-yl 4 H), 4.21 (s, 4 H, 2 benzyl CH_2).

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Anal. Calcd. for $C_{38}H_{34}N_8O_{12}$: C, 57.4; H, 4.3; N, 14.1. Found: C, 57.4; H, 4.3; N, 14.0.

General Procedure for the Preparation of 2,3,4,5-Tetra-O-acetyl-1,4-bis [1-acetamido-5-oxo-4-substituted(imidazolin-2-yl)]galacto-tetritols (7a,b,d). A mixture of the respective **5a–c** (5 mmol) in pyridine (5 mL) and acetic anhydride (25 mL) was stirred for 24 h at ambient temperature. The mixture was evaporated under reduced pressure and the residue was crystallized from EtOH. The following compounds were prepared:

2,3,4,5-Tetra-O-acetyl-1,4-bis[1-acetamido-5-oxo-(imidazolin-2-yl)] galacto-tetritol (7a). Colorless crystals; Yield: 71%; m.p.: 260–261°C/dec.; TLC: (A), R_f: 0.55; IR: 3459 (NH), 1741 (OAc), 1662 (CON), and 1645 cm^{-1} (C=N); ^1H NMR ($CDCl_3$): δ 13.20 (s, 2 H, exchangeable, 2 NH), 6.47, 5.87 (2 s, 2 H each, tetritoldi-1,4-yl-4 H), 3.33 (s, 4 H, 2 imidazolinyl CH_2), 2.47 (s, 6 H, 2 NAc), 2.19, 2.09 (2 s, 6 H each, 4 OAc).

Anal. Calcd. for $C_{22}H_{28}N_6O_{12}$: C, 46.5; H, 4.9; N, 14.8. Found: C, 46.6; H, 4.8; N, 14.7.

2,3,4,5-Tetra-O-acetyl-1,4-bis[1-acetamido-4-benzyl-5-oxo-(imidazolin-2-yl)]galacto-tetritol (7b). Colorless crystals; Yield: 68%; m.p.: 250–251°C/dec.; TLC: (A), R_f: 0.53; IR: 3440 (OH), 1740 (OAc), 1675 (CON), and 1642 cm^{-1} (C=N); ^1H NMR ($CDCl_3$): δ 13.09 (s, 2 H, exchangeable, 2 NH), 7.42–6.98 (m, 12 H, 10 ArH, 2 imidazolinyl H), 6.54, 5.73 (2 s, 2 H each, tetritoldi- 1,4-yl 4 H), 4.11 (d, 4 H, 2 benzyl CH_2), 2.54 (s, 6 H, 2 NAC), 2.13, 2.01 (2 s, 5 H each, 4 OAc).

Anal. Calcd. for $C_{36}H_{40}N_6O_{12}$:C, 57.8; H, 5.4; N, 11.2. Found: C, 57.7; H, 5.4; N, 11.1.

2,3,4,5-Tetra-O-acetyl-1,4-bis[1-acetamido-4-(p-acetoxybenzyl)-5-oxo-(imidazolin-2-yl)]galacto-tetritol (7d). Colorless crystals; Yield: 65%; m.p.: 254–255°C/dec.; TLC: (A), R_f: 0.51; IR: 3460 (NH), 1741 (OAc), 1663 (CON), and 1644 cm^{-1} (C=N); ^1H NMR ($CDCl_3$): δ 13.31(s, 2 H, exchangeable, 2 NH), 7.62–7.27 (m, 10 H, 8 ArH, 2 imidazolinyl H), 6.67, 5.65 (2 s, 2 H each, tetritoldi-1,4-yl 4 H), 4.40 (d, 4 H, 2 benzyl CH_2), 2.20 (s, 6 H, 2NAc), 2.11, 2.08, 2.04 (3 s, 6 H each, 6 OAc).

Anal. Calcd. for $C_{40}H_{44}N_6O_{10}$: C, 55.6; H, 5.1; N, 9.7. Found: C, 55.7; H, 5.0; N, 9.8.

General Procedure for the Preparation of 1,4-Bis[1-acetamido-5-oxo-4-substituted-(imidazolin-2-yl)]galacto-tetritols (8a–c). A solution of the appropriate **7a,b,d** (2 mmol) in methanol (50 mL) was treated with 20% aqueous NH_3 solution (15 mL) and kept at ambient temperature for 24 h. Evaporation of the solvent under reduced pressure gave a residue which crystallized from a H_2O/MeOH – mixture. The Following compounds were prepared:

1,4-Bis[1-acetamido-5-oxo-(imidazolin-2-yl)]galacto-tetritol (8a). Colorless crystals; Yield: 57%; m.p.: 328–330°C/dec.; TLC: (B), R_f: 0.58; IR: 3439 (broad OH + NH), 1694 (CON) and 1645 cm^{-1} (C=N); ^1H NMR [$(CD_3)_2SO$]: δ 13.14

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(s, 2 H, exchangeable, 2 NH), 5.53, 4.91 (2 d, exchangeable, 2 OH each), 4.77, 3.80 (2 d, 2 H each, tetritoldi-1,4-yl 4 H), 3.53 (s, 4 H, 2 imidazolinyl CH_2), 2.89 (s, 6 H, 2 NAc).

Anal. Calcd. for $C_{14}H_{20}N_6O_8$: C, 42.0; H, 5.0; N, 21.0. Found: C, 42.1; H, 5.0; N, 21.1.

1,4-Bis[1-acetamido-4-benzyl-5-oxo-(imidazolin-2-yl)]galacto-tetritol(8b). Colorless crystals; Yield: 61%; m.p.: >350°C; TLC: (B), R_f: 0.56; IR: 3301 (broad OH + NH), 1694 (CON), and 1600 cm^{-1} (C=N); ^1H NMR [$(CD_3)_2SO$]: δ 13.04 (s, 2 H, exchangeable, 2 NH), 7.37–6.82 (m, 12 H, 10 ArH, 2 imidozolinyl H), 5.84, 5.17 (2 d, exchangeable, 2 OH each), 4.83, 4.59 (2 s, 2 H each, tetritoldi-1,4-yl 4 H), 4.39 (s, 4 H, 2 benzyl CH_2), 2.94 (s, 6 H, 2 NAc).

Anal. Calcd. for $C_{28}H_{32}N_6O_8$: C, 57.9; H, 5.5; N, 14.5. Found: C, 57.9; H, 5.4; N, 14.5.

1,4-Bis[1-acetamido-4-(p-hydroxybenzyl)-5-oxo-imidazolin-2-yl)galacto-tetritol (8c). Colorless crystals; Yield: 64%; m.p.: > 350°C; TLC: (B), 0.53; IR: 3442 (broad OH + NH), 1685 (CON), and 1614 cm^{-1} (C=N); ^1H NMR [$(CD_3)_2SO$]: δ 13.21 (s, 2 H, exchangeable), 7.21–6.73 (m, 10 H, 8 ArH, 2 imidazolinyl H), 5.73, 5.22 (2 d, exchangeable, 2 OH each), 4.92 (s, broad, 2 H, exchangeable 2 OH), 4.71, 4.21 (2 s, 2 H each, tetritoldi-1,4-yl 4 H), 4.09 (s, 4 H, 2 benzyl CH_2), 2.89 (s, 6 H, 2 NAc). Anal. Calcd. for $C_{28}H_{32}N_6O_{16}$: C, 54.9; H, 5.2; N, 13.7. Found: C, 54.8; H, 5.2; N, 13.8.

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