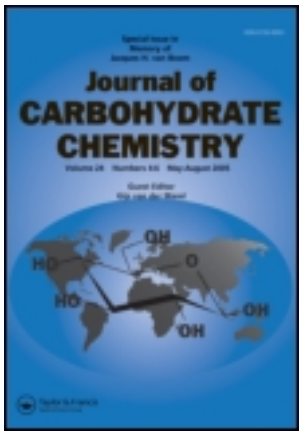

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Diastereoselective Synthesis of Galactopyranosyl Amino Esters and Their Transformation into C-Nucleosides

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Diastereoselective Synthesis of Galactopyranosyl Amino Esters and Their Transformation into C-Nucleosides

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ABSTRACT

Galactopyranosylated olefinic ester (**4**) on conjugate addition of amines yielded stereoselectively galactopyranosylated amino esters (**5**–**18**) in fair to good yield. The selected amino esters (**5**, **6**, **13**, and **15**–**17**) on reaction with isocyanates resulted in ureido galactopyranosyl amino esters (**19**–**24**) in very good yields. Lactamization of compounds **19**–**24** with DBU, 4 Å MS, and tetrabutylammonium bromide in refluxing toluene gave respective C-galactopyranosyl dihydropyrimidine-2,4-diones (**25**–**30**) in respectable yields.

Key Words: Amino esters; Diastereoselection; Nucleosides; Galactopyranose.

INTRODUCTION

Sugar amino acids one of the important construction elements in nature and important constituent of naturally occurring nucleoside antibiotics serve as versatile synthons in organic synthesis.[1,2] Due to structural importance and involvement in many biological processes chemical synthesis of amino sugar derivatives has been a fertile area in bio-organic chemistry.[2] Glycosylated amino acids having amino and carboxyl functionalities

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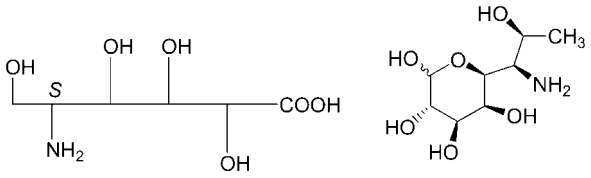
either in rings or as appendages serve as very good scaffold for the combinatorial synthesis, of the library of glycoconjugates and glycopeptides of biological importance particularly as peptido mimics.[3,4]

We have very recently embarked upon a program to the synthesis of biologically important compounds from glycosyl amino acids particularly for antitubercular,[5] antiparasitic,[6] and antidiabetic activities.[7] Because of the importance of galactose sugars in *M. tuberculosis*[8,9] and presence of galactopyranosyl skeleton in destomic acid (**1**)[10] and lincosamine (**2**),[11] the important constituents of the antibiotics, we were interested in the synthesis of galactopyranosyl amino esters, which could be transformed into C-nucleosides. Galactopyranosyl dialdoses have successfully been used for chain elongation to synthesize a variety of biologically significant compounds.[12,13] Different approaches have been adopted for the synthesis of galactopyranosyl amino sugars from time to time.[14] In general N-functionality has been introduced at C-5 or C-6 in furanoses and pyranoses, respectively, utilizing corresponding dialdose and 2-aminothiazole aldehydes.[15] Stereoselective introduction of N- or heteronucleophiles to the glycosylated olefinic esters has recently also been reported by others[16] and our group.[6] However, reports on stereoselective synthesis of galactopyranosyl amino sugars by asymmetric induction in Michael type reactions are very scanty.[17] The present work describes the synthesis of the β-galactopyranosyl amino esters and their conversion into C-nucleosides.



1 **2**

RESULTS AND DISCUSSION

Synthetic strategy (Schs. 1 and 2) begins with 1,2 : 3,4-di-*O*-isopropylidene-α-D-*galacto*pyranose which on oxidation with pyridinium chlorochromate in presence of 4 Å MS yielded 1,2 : 3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose **3** in 80% yield. Dialdose **3** on lithium hydroxide catalyzed olefination with triethyl phosphonoacetate resulted in (*E*)-ethyl 6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-α-D-*galacto*-6-eno-octopyranuronate **4** exclusively in quantitative yield. The structure and geometry of the olefinic ester **4** was decided on the basis of ^{1}H NMR spectral data where the coupling constant ($J_{6,7} = 15.6$ Hz) of vinylic protons H-6 and H-7 confirmed a trans (*E*) relationship between the two protons.

Conjugate addition of ethanolic ammonia to the olefinic ester **4** led to the formation of two diastereoisomers in 52 : 48 ratios. The ratio of isomers was determined by ^{1}H NMR spectrum of crude reaction mixture where H-1 appeared as "d" with different chemical shifts in the two isomers. The conversion into amino esters was more than 90% at 25°C. The two isomers (**5** and **5a**) were separated by flash column chromatography over silica gel

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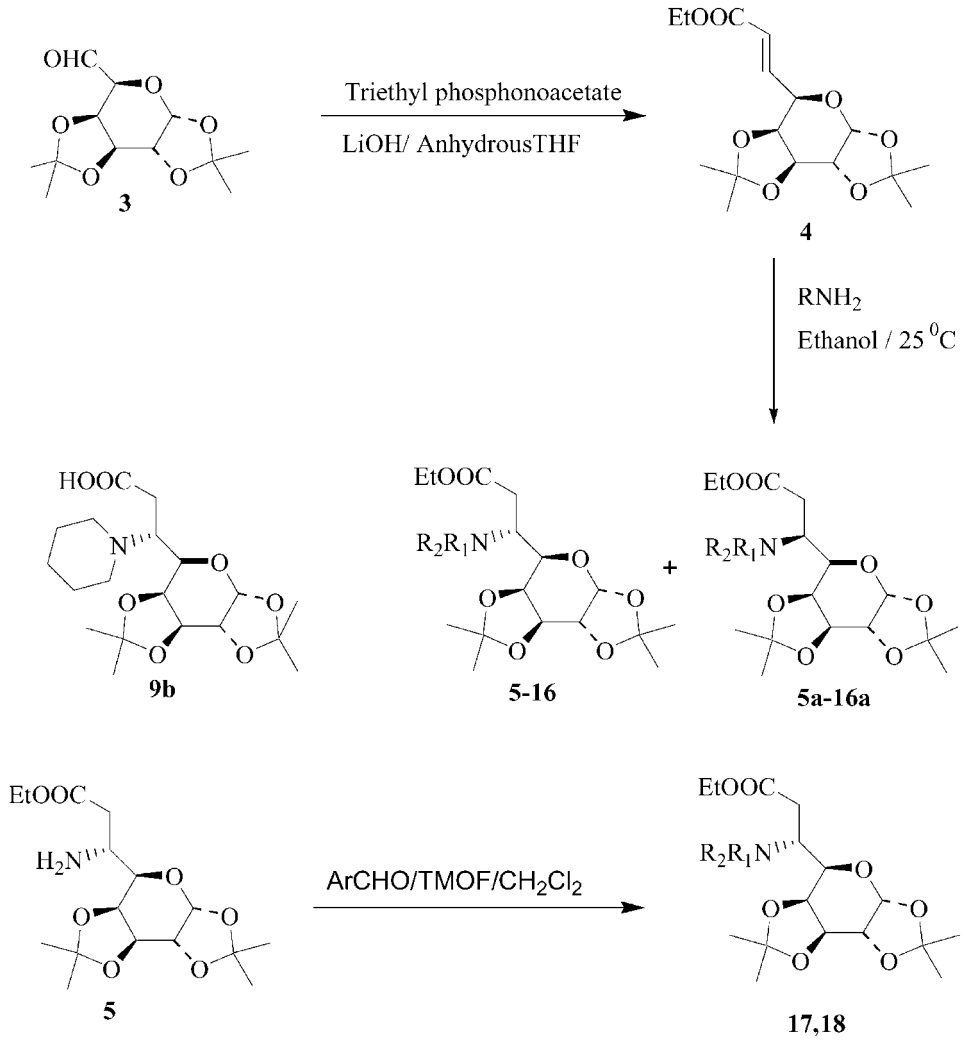

Scheme 1. Synthesis of galactopyranosyl amino esters.

and the structures were elucidated on the basis of spectral data. MS spectrum of the above compounds showed $[M + H]^+$ at 346 while in ^1H NMR spectrum H-1 appeared as "d" at δ 5.56 and δ 5.51 in compounds **5** and **5a**, respectively. Two "dd" signals at δ 4.31 and at around δ 4.60 accounted for H-2 and H-3, respectively, in both the isomers. H-5 adjacent to the newly generated stereogenic center C-6 appeared as "dd" at δ 3.63 and 3.55 in compounds **5** and **5a**, respectively, while the proton attached to C-6 appeared as "m" at around δ 3.40 in **5** and as "ddd" at δ 3.36 in compound **5a**. The methylene protons at C-7 appeared as two "dd" at δ 2.67 and 2.46 in **5** and at δ 2.84 and 2.36 in compound **5a** besides other usual signals.

Similarly, conjugate addition of different amines including butylamine, heptylamine, octylamine, dodecylamine, hexadecylamine and oleylamine, pyrrolidine, and

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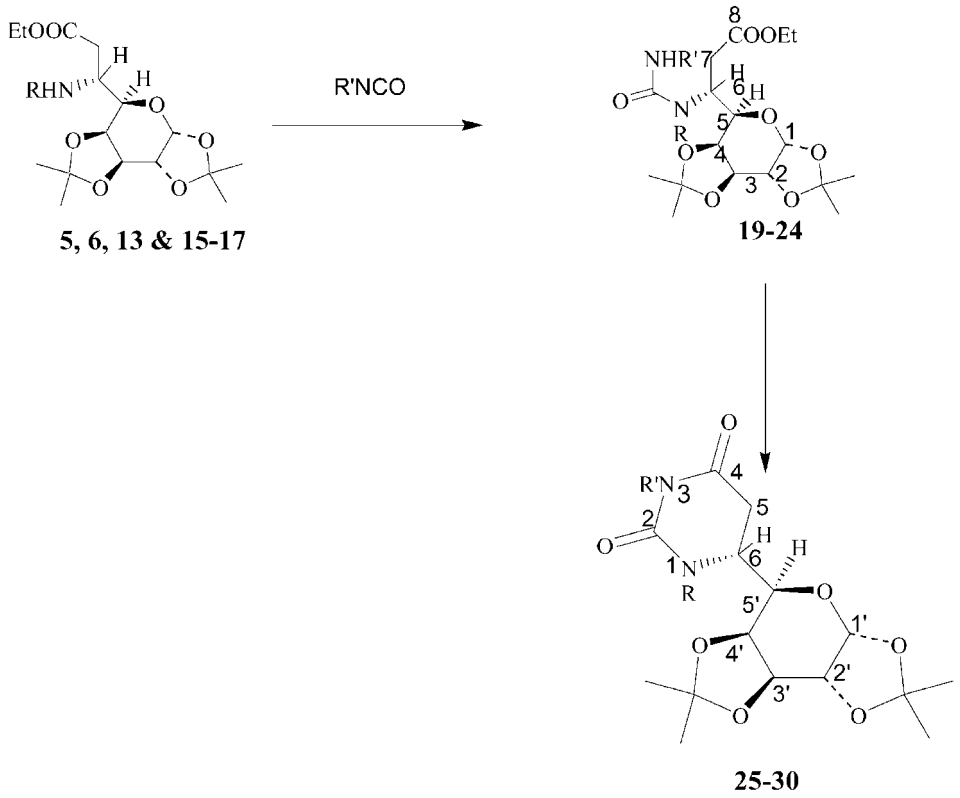

Scheme 2. Synthesis of galactopyranosyl C-nucleosides.

piperidine, cyclopropyl amine and cyclohexyl amine and benzyl amine to the above olefinic ester **4** was carried out successfully to give a diastereomeric mixture of galactopyranosylated amino esters (Table 1). As evident from the table diastereoselection varies with the nature of amines used. Conjugate addition of ammonia resulted in almost no diastereoselection (52 : 48). With alkyl-substituted amines including *n*-butylamine (60 : 40) and long chain alkyl substituted amines a low diastereoselection was observed. A considerable diastereoselection was observed with benzylamine (84 : 16), pyrrolidine (93 : 07), and piperidine (95 : 05). However, with piperidine as nucleophile reaction was very slow and a longer reaction time resulted in glycosylated amino acid (**9b**) along with the amino esters (**9** and **9a**). Different reaction conditions for better diastereoselection, including lowering of temperature and change in solvents resulted in no improvement in diastereoselectivity. In most of the cases the minor diastereoisomers (**6a**, **7a**, **8a**, **9a**, **10a**, **13a**, and **15a**) formed could not be separated even by repeated column chromatography and were found to be contaminated with starting olefinic ester. However, minor isomers **5a**, **14a**, and **16a** formed in their respective reactions were separated by flash column chromatography in pure form. Compounds **11a** and **12a** could only be separated in minor amount for the purpose of NMR spectroscopy by repeated column chromatography over SiO_2. Galactopyranosylated amino esters **17** and **18** were obtained by reductive arylation of compound **5**,

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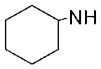
Table 1. Galactopyranosylated amino esters synthesized either by conjugate addition of amines to the olefinic ester **4** (**5**–**16**) or by reductive amination (**17** and **18**).

Compound	R_1R_2N	Time (hr)	Ratio of isomers S : R	Yield (%)
5, **5a**	NH_2	24	52 : 48	90[a]
6, **6a**		16	85 : 15	82[b]
7, **7a**	$CH_3(CH_2)_3NH$	18	60 : 40	79[b]
8, **8a**		16	93 : 07	70[b]
9, **9a**		24	95 : 05	65[b]
10, **10a**		22	62 : 38	90[b]
11, **11a**	$CH_3(CH_2)_6NH$	24	53 : 47	80[b]
12, **12a**	$CH_3(CH_2)_7NH$	18	67 : 33	84[b]
13, **13a**	$CH_3(CH_2)_{11}NH$	14	70 : 30	90[b]
14, **14a**	$CH_3(CH_2)_{15}NH$	18	64 : 36	88[a]
15, **15a**	$CH_3(CH_2)_8CH{=}CH(CH_2)_7CH_3$	16	75 : 25	82[b]
16, **16a**	$C_6H_5CH_2NH$	16	84 : 16	86[a]
17	$C_6H_3(OCH_3)_2CH_2NH$	16	—	80[a]
18	$C_6H_4(OH)CH_2NH$	16	—	70[a]

[a]Isolated yields.
[b]Yields calculated on the basis of integration of ^{1}H NMR signal (H-1).

whereas compound **16** could be obtained by both the methods. Thus, reaction of compound **5** with benzaldehyde, 3,4-dimethoxy benzaldehyde and 2-hydroxy benzaldehyde separately in the presence of trimethyl orthoformate followed by reduction of the intermediates with sodium cyanoborohydride afforded galactopyranosyl aryl amino esters **16**, **17**, and **18**, respectively, in fair to good yield.

Next we aimed at the synthetic utility of galactopyranosylated amino esters in the preparation of C-nucleoside analogs. Few of the amino esters were selected keeping in mind the structural diversity. Thus, the galactopyranosyl amino ester (**5**) on reaction with 4-chlorophenyl isocyanate gave ureido galactopyranosyluronate (**19**) in 69% yield. Similar reaction of compounds (**6**, **13**, **15**–**17**) with benzyl or 4-chlorophenyl isocyanates resulted in ureido galactopyranosyl amino esters **20**–**24** (Sch. 2, Table 2) in very good yields.

The structural assignments of the above compounds were based on spectroscopic data and analysis. Absorption bands in the IR spectrum of **19** at 3341 (NH stretch), 1657 (CONH I band) and 1545 (CONH II band) indicated the formation of urea derivative. In ^{1}H NMR spectrum, four aromatic protons appeared as "m" at around δ 7.24 and a "d" at δ 5.44 accounted for –N*H*CO. H-1, H-2, H-3, and H-4 appeared as "dd" at δ 5.56, 4.32, 4.60, and 4.25, respectively. While H-5, $-OCH_2$, and H-6 appeared as "m" at around δ 4.10 besides other usual ^{1}H NMR signals. The formation of urea derivative was further substantiated by ^{13}C NMR spectrum where a signal at δ 155.8 showed a –CONH group besides other usual signals. The urea derivatives, so

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Table 2. Galactopyranosylated ureidyl derivatives **19**–**24** and C-nucleosides **25**–**30**.

Compound	*R*	*R′*	Reaction time (hr)	Yield (%)
19	H	4-Cl-phenyl	7.0	69
20	Cyclopropyl	Benzyl	4.0	95
21	Dodecyl	Benzyl	4.0	95
22	Oleyl	4-Cl-phenyl	4.0	95
23	Benzyl	4-Cl-phenyl	4.0	98
24	3,4-Dimethoxyphenylmethyl	Benzyl	3.0	98
25	H	4-Cl-phenyl	2.0	70
26	Cyclopropyl	Benzyl	6.0	75
27	Dodecyl	Benzyl	4.0	89
28	Oleyl	4-Cl-phenyl	4.0	90
29	Benzyl	4-Cl-phenyl	4.5	92
30	3,4-Dimethoxyphenylmethyl	Benzyl	3.5	95

obtained, on reaction with our recently discovered lactamization reagent[18] (DBU, 4 Å molecular sieve and tetrabutyl ammonium bromide) in refluxing toluene gave corresponding nucleosides **25**–**30** (Sch. 2, Table 2) in fair to good yields. The structures of the nucleosides were determined on the basis of spectroscopic data and analysis. In ^{1}H NMR spectrum absence of signals corresponding to $-OCH_2CH_3$ at around δ 4.10 and 1.20, respectively, was indication for cyclization. H-6 was shifted to downfield and appeared as "m" at around δ 4.06–3.62, while in ^{13}C NMR appearance of two signals at around δ 165 (–NCON–) and δ 152 (–CON–) besides other usual signals confirm the structure.

The stereochemistry at C-6 in galactopyranosyl amino esters obtained by conjugate addition of amines to the galactopyranosyl olefinic esters has tentatively been predicted on the basis of literature precedent and mechanistic grounds. It is documented that conjugate addition of nucleophiles to galactopyranosylated olefins gives two epimers the major one "*S*" while the minor isomer has "*R*" stereochemistry at C-6.[19] The above stereochemistry at C-6 has been rationalized based on transition state models and the extent of approach of the nucleophile to the prochiral center. Looking into the transition state models **A** (Cram) and **B** (Felkin-Anh), the major attack of nucleophilic amines to C-6 in olefin would take place from the side of the least bulky group (hydrogen attached to C-5 of the pyranose ring, the "si" diastereoface), and hence the major reaction product has "*S*" configuration at C-6 while that of the minor one is "*R*" (Fig. 1). This "*S*" configuration is maintained in ureidyl derivatives as well as in cyclization products as no inversion is taking place during the course of these reactions. The *threo* relationship between protons at C-5′ and at C-6 in nucleosides has been substantiated by ^{1}H NMR spectrum of a prototype dihydropyrimidin-2,4-dione (**29**), where $J_{5',6}$ was found to be 9.0 Hz indicating a dihedral angle of either about 0° or 180°. To confirm the spatial relationship between H-5′ and H-6 in compound **29** NOE experiment was done which did not show any interaction between H-5′ (δ 4.05) and H-6 (at around δ 3.86) confirming trans relationship between these two protons and hence the compound has "*S*" configuration at C-6.

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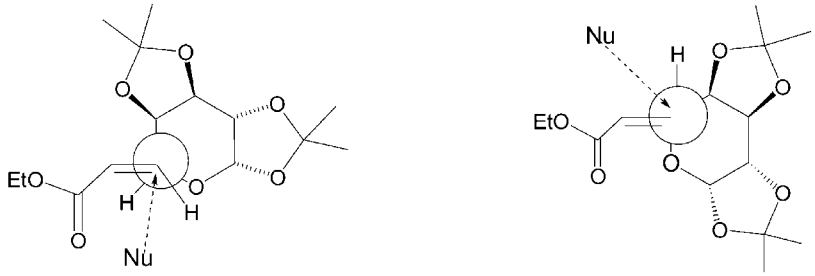

Cram Open chain model
A

Felkin-Anh model
B

Figure 1. Transition state models for the reaction.

EXPERIMENTAL

General Methods

Thin-layer chromatography was carried out on silica gel (Kiesel 60-F254, Merck, Darmstadt, Germany) and spots were developed in iodine vapors and also by spraying with 5% sulfuric acid in alcohol followed by heating at 100°C. Column chromatography was carried out on flash silica gel (230–400 mesh, Merck) using the indicated eluent. IR spectra were recorded as thin films on KBr plates with a Perkin Elmer 881 spectrophotometer (Beaconsfield, Buckinghamshire, England). NMR spectra were recorded on Bruker spectrometers 200 and 300 MHz (Fallanden, Switzerland) and reference used was $CDCl_3$. Chemical shifts were given as δ ppm values and "*J*" values were given in Hertz (Hz). Elemental analyses were performed on a Perkin–Elmer 2400 II elemental analyzer (Rodano, Milan, Italy). The optical rotations were measured in a 1.0 dm tube with Jasco dip-140 polarimeter (Rudolph Research, Flanders, NJ, USA) in chloroform, methanol, or ethyl acetate. The excess of the reagents or solvents were evaporated under reduced pressure at a bath temperature between the ranges 55–60°C.

1,2 : 3,4-Di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (3)

To a magnetically stirred slurry of anhydrous 4 Å molecular sieve (10.0 g) and pyridinium chlorochromate (20.5 g, 96.2 mmol) in dry CH_2Cl_2 (250 mL), solution of 1,2 : 3,4-di-*O*-isopropylidene-α-D-galactopyranose (10.0 g, 38.76 mmol) in dry CH_2Cl_2 (50 mL) was added and stirred for 2 hr. Reaction mixture filtered using Celite pad, solid cake washed with more CH_2Cl_2 and evaporated under reduced pressure to give a crude product. It was purified by column chromatography over SiO_2 using hexane : ethyl acetate (7 : 3) as eluent to give **3**[20] as colorless oil. Yield: 5.6 g (56.4%), R_f 0.5 (hexane : ethyl acetate, 3 : 2); $[\alpha]_D^{20}$ −57.6° (*c* 0.187, chloroform); MS (FAB) = m/z 259 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 1741, 1614; ^1H NMR (200 MHz, $CDCl_3$): δ 9.62 (s, 1H, CHO), 5.67 (d, $J = 4.8$ Hz, 1H, H-1), 4.65 (dd, $J = 7.8$ and 2.1 Hz, 1H, H-3), 4.60 (dd, $J = 7.8$ and

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1.7 Hz, 1H, H-4), 4.38 (dd, $J = 4.8$ and 2.1 Hz, 1H, H-2), 4.19 (d, $J = 1.7$ Hz, 1H, H-5), 1.51, 1.44, 1.35, 1.32 [each s, each 3H, $2 \times C(CH_3)_2$]; ^{13}C NMR (50 MHz, $CDCl_3$): δ 200.5, 110.4, 109.4, 96.6, 73.6, 72.1, 70.9, 68.3, 26.4, 26.2, 25.2.

(*E*)-Ethyl 6,7-Dideoxy-1,2 : 3,4-di-*O*-isopropylidene-α-D-*galacto*-6-eno-octopyranuronate (4)

The solution of compound **3** (2 g, 7.75 mmol) in anhydrous THF (15 mL) and triethyl phosphono acetate (1.53 mL, 7.75 mmol) was magnetically stirred at 25°C. To the stirring reaction mixture $LiOH{\cdot}H_2O$ (0.33 g, 7.75 mmol) was added and stirring continued for 10 hr. The solvent evaporated under reduced pressure to give a residual mass. The latter was dissolved in dichloromethane (50 mL) and washed with water (2×10 mL). The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure to give a crude mass, which was chromatographed over SiO_2 using hexane : ethyl acetate (4 : 1) as eluent to give **4** as colorless oil. Yield: 2.16 g (85%); R_f 0.6 (hexane : ethyl acetate, 3 : 2); $[\alpha]_D^{20}$ −45.5° (*c* 0.2, chloroform); MS (FAB): $m/z = 329$ $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 1720; ^1H NMR (200 MHz, $CDCl_3$): δ 6.88 (dd, $J = 15.7$ and 4.4 Hz, 1H, H-6), 6.13 (dd, $J = 15.7$ Hz, 1H, H-7), 5.59 (d, $J = 5.0$ Hz, 1H, H-1), 4.63 (dd, $J = 7.7$ and 2.3 Hz, 1H, H-3), 4.45 (dd, $J = 4.4$ and 2.0 Hz, 1H, H-5), 4.35 (dd, $J = 5.0$ and 2.3 Hz, 1H, H-2), 4.29 (dd, $J = 7.7$ and 2.0 Hz, 1H, H-4), 4.16 (q, $J = 7.1$ Hz, 2H, $-OCH_2$), 1.51, 1.43, 1.34, 1.32 [each s, each 3H, $2 \times C(CH_3)_2$], 1.26 (t, $J = 7.1$ Hz, 3H, $-OCH_2CH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.0, 146.6, 120.6, 109.7, 109.3, 96.8, 74.5, 71.4, 70.6, 65.9, 60.7, 26.8, 25.5, 24.8, 14.6.

Anal. Calcd for $C_{16}H_{24}O_7$: C, 58.53; H, 7.31. Found: C, 58.52; H, 7.30.

Ethyl 6-Amino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-α-D-*galacto*-octopyranuronate (5)

A solution of compound **4** (3.0 g, 9.1 mmol) in ethanolic ammonia (30 mL) was magnetically stirred at 30°C for 24 hr. Solvent evaporated and the residue was chromatographed over SiO_2 column using chloroform : methanol (9 : 1) as eluent to give compound **5** as colorless oil. R_f 0.43 (chloroform : methanol, 9 : 1); MS (FAB) = m/z 346 $(M + H)^+$; $[\alpha]_D^{20}$ −65.1° (*c* 0.18, chloroform); IR (Neat) ν_{max} cm^{-1}: 3387, 1727; ^1H NMR (200 MHz, $CDCl_3$): δ 5.56 (d, $J = 5.0$ Hz, 1H, H-1), 4.60 (dd, $J = 8.1$ and 2.2 Hz, 1H, H-3), 4.44 (dd, $J = 8.1$ and 1.7 Hz, 1H, H-4), 4.31 (dd, $J = 5.0$ and 2.2 Hz, 1H, H-2), 4.14 (q, $J = 7.1$ Hz, 2H, $-OCH_2$), 3.63 (dd, $J = 6.9$ and 1.7 Hz, 1H, H-5), 3.43–3.35 (m, 1H, H-6), 2.67 and 2.46 (each dd, $J = 16.4$ and 5.0 Hz, 2H, H-7_A and H-7_B), 1.67 (bs, 2H, NH_2), 1.51, 1.44, 1.35 [each s, 3H, 3H, 6H, $2 \times C(CH_3)_2$], 1.25 (t, $J = 7.2$ Hz, 3H, $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.4, 109.7, 109.0, 96.9, 72.0, 71.3, 71.1, 70.7, 60.8, 48.9, 38.1, 26.3, 25.3, 24.8, 24.7, 14.57.

Anal. Calcd for $C_{16}H_{27}NO_7$: C, 55.65; H, 7.82; N, 4.05. Found: C, 55.67; H, 7.88; N, 4.05.

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Ethyl 6-Amino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-octopyranuronate (5a)

R_f 0.54 (chloroform : methanol, 9 : 1); MS (FAB) = m/z 346 $(M + H)^+$; $[\alpha]_D^{20}$ −64.4° (*c* 0.22, chloroform); IR (Neat) ν_{max} cm^{-1}: 3429, 1654; ^1H NMR (200 MHz, $CDCl_3$): δ 5.51 (d, J = 5.0 Hz, 1H, H-1), 4.62 (dd, J = 7.9 and 2.4 Hz, 1H, H-3), 4.44 (dd, J = 7.9 and 1.8 Hz, 1H, H-4), 4.31 (dd, J = 5.0 and 2.4 Hz, 1H, H-2), 4.10 (q, J = 7.1 Hz, 2H, $-OCH_2$), 3.55 (dd, J = 8.8 and 1.8 Hz, 1H, H-5), 3.36 (ddd, J = 8.8, 8.5, and 3.2 Hz, 1H, H-6), 2.84 (dd, J = 16.4 and 3.2 Hz, 1H, $H\text{-}7_A$), 2.36 (dd, J = 16.4 and 8.5 Hz, 1H, $H\text{-}7_B$), 1.67 (bs, 2H, NH_2), 1.51, 1.44, 1.35 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.25 (t, J = 7.2 Hz, 3H, $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 173.0, 109.6, 108.9, 96.8, 71.1, 70.9, 70.7, 69.2, 60.6, 48.7, 38.9, 26.3, 25.3, 24.9, 24.6, 14.6.

Anal. Calcd for $C_{16}H_{27}NO_7$: C, 55.65; H, 7.82; N, 4.05. Found: C, 55.60; H, 7.90; N, 3.89.

Ethyl 6-Cyclopropylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-α-D-*galacto*-octopyranuronate (6)

A solution of compound **4** (3 g, 9.1 mmol) and cyclopropyl amine (0.63 mL, 9.1 mmol) in alcohol (30 mL) was magnetically stirred at 30°C for 16 hr. Solvent evaporated and the residue was chromatographed over SiO_2 column using hexane : ethyl acetate (4 : 1) as eluent to give title compound. Colorless solid, mp 70–72°C; R_f 0.51 (hexane : ethyl acetate, 4 : 1); $[\alpha]_D^{20}$ −43.3° (*c* 0.15, chloroform); MS (FAB) = m/z 386 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3371, 1727; ^1H NMR (200 MHz, $CDCl_3$): δ 5.56 (d, J = 5.0 Hz, 1H, H-1), 4.59 (dd, J = 8.0 and 2.0 Hz, 1H, H-3), 4.37 (d, J = 8.0 Hz, 1H, H-4), 4.33 (dd, J = 5.0 and 2.0 Hz, 1H, H-2), 4.12 (q, J = 7.1 Hz, 2H, $-OCH_2$), 3.94 (d, J = 7.3 Hz, 1H, H-5), 3.41–3.31 (m, 1H, H-6), 2.75 and 2.62 (each dd, 2H, J = 15.7 and 5.4 Hz, $H\text{-}7_A$ and $H\text{-}7_B$), 2.14 (m, 2H, NH and NCH), 1.51, 1.45, 1.32 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.25 (t, J = 7.1 Hz, OCH_2CH_3), 0.44–0.38 (m, 4H, cyclopropyl ring protons); ^{13}C NMR ($CDCl_3$): δ 172.7, 109.5, 108.9, 97.1, 72.0, 71.5, 71.0, 68.6, 60.6, 56.6, 36.0, 29.0, 26.4, 25.3, 24.7, 14.5, 7.5, 5.8.

Anal. Calcd for $C_{19}H_{31}NO_7$: C, 59.22; H, 8.05; N, 3.63. Found: C, 59.25; H, 8.11; N, 3.63.

Ethyl 6-Butylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (7)

Colorless oil; R_f 0.56 (hexane : ethyl acetate, 3 : 2); $[\alpha]_D^{20}$ −60.0° (*c* 0.15, chloroform); MS (FAB) = m/z 402 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3344, 1733; ^1H NMR (200 MHz, $CDCl_3$): δ 5.55 (d, J = 5.0 Hz, 1H, H-1), 4.59 (dd, J = 7.9 and 2.3 Hz, 1H, H-3), 4.36 (dd, J = 7.9 and 1.5 Hz, 1H, H-4), 4.31 (dd, J = 5.0 and 2.3 Hz, 1H, H-2), 4.12 (q, J = 7.1 Hz, 2H, $-OCH_2$), 3.86 (dd, J = 7.1 and 1.5 Hz, 1H, H-5), 3.27–3.18 (m, 1H, H-6), 2.72–2.45 (m, 4H, $NHCH_2$ and H-7), 1.76 (bs, 1H, NH), 1.51, 1.45, 1.32 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.29–1.22 (m, 7H, 2 × CH_2 and $-OCH_2CH_3$), 0.89 (t, J = 7.2 Hz,

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3H, $-CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.7, 109.6, 108.9, 97.0, 72.0, 71.5, 71.0, 68.8, 60.6, 56.0, 47.0, 35.8, 32.6, 26.3, 25.3, 24.7, 20.8, 14.5, 14.4.

Anal. Calcd for $C_{20}H_{35}NO_7$: C, 59.85; H, 8.72; N, 3.49. Found: C, 60.02; H, 9.07; N, 3.46.

Ethyl 6-(Pyrrolidin-1-yl)-6,7-Dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (8)

Colorless oil; R_f 0.58 (hexane : ethyl acetate, 3 : 2); $[\alpha]_D^{20}$ -110.6° (*c* 0.15, chloroform), MS (FAB) = m/z 400 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 2986, 2930, 1721; ^1H NMR (200 MHz, $CDCl_3$): δ 5.56 (d, $J = 5.0$ Hz, 1H, H-1), 4.57 (dd, $J = 8.0$ and 2.2 Hz, 1H, H-3), 4.32 (d, $J = 8.0$ Hz, 1H, H-4), 4.26 (dd, $J = 5.0$ and 2.2 Hz, 1H, H-2), 4.12 (q, $J = 7.2$ Hz, 2H, $-OCH_2$), 3.77–3.67 (m, 2H, H-5 and H-6), 2.73–2.40 (m, 6H, 2 × NCH_2 and H-7), 1.68 (m, 4H, pyrrolidine protons), 1.58, 1.51, 1.43, 1.32 [each s, each 3H, 2 × $C(CH_3)_2$], 1.23 (t, $J = 7.1$ Hz, $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 173.1, 109.2, 108.6, 96.1, 72.2, 71.2, 70.6, 67.6, 60.5, 55.4, 50.2, 36.5, 26.2, 25.6, 24.7, 23.2, 14.5.

Anal. Calcd for $C_{20}H_{33}NO_7$: C, 60.15; H, 8.27; N, 3.50. Found: C, 60.21; H, 8.27; N, 3.22.

Ethyl 6-(Piperidin-1-yl)-6,7-Dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (9)

Colorless oil; R_f 0.54 (hexane : ethyl acetate, 3 : 2); $[\alpha]_D^{20}$ -108.4° (*c* 0.113, chloroform); MS (FAB) = m/z 414 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 2987, 2932, 1721; ^1H NMR (200 MHz, $CDCl_3$): δ 5.57 (d, $J = 5.1$ Hz, 1H, H-1), 4.64 (dd, $J = 7.7$ and 2.1 Hz, 1H, H-3), 4.35 (dd, $J = 5.1$ and 2.1 Hz, 1H, H-2), 4.29 (dd, $J = 7.7$ and 1.4 Hz, 1H, H-4), 4.15 (q, $J = 7.0$ Hz, 2H, $-OCH_2$), 3.78 (d, $J = 8.7$ Hz, H-5), 3.41–3.31 (m, 1H, H-6), 2.81 and 2.31 (m, 6H, H-7 and 2 × $N{\cdot}CH_2$), 1.51, 1.51, 1.33 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.32–1.24 (m, 9H, piperidine protons and $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172, 109.2, 108.3, 96.5, 73.2, 71.7, 70.5, 68.1, 67.4, 61.4, 60.3, 50.4, 35.5, 27.1, 26.0, 25.9, 24.8, 24.1, 14.2.

Anal. Calcd for $C_{21}H_{35}NO_7$: C, 61.01; H, 8.47; N, 3.39. Found: C, 60.92; H, 8.49; N, 3.37.

Ethyl 6-(Piperidin-1-yl)-6,7-Dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronic acid (9b)

Yield: 30%, Colorless solid, mp 158–60°C; R_f 0.45 (chloroform : methanol, 9 : 1); $[\alpha]_D^{20}$ -101.4° (*c* 0.138, chloroform); MS (FAB) = m/z 386 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3432, 1661; ^1H NMR (200 MHz, $CDCl_3$): δ 5.55 (d, $J = 5.1$ Hz, 1H, H-1), 4.61 (dd, $J = 7.9$ and 2.5 Hz, 1H, H-3), 4.35 (dd, $J = 5.1$ and 2.5 Hz, 1H, H-2), 4.08 (d, $J = 7.9$ and 1.5 Hz, 1H, H-4), 3.78 (dd, $J = 9.8$ and 1.5 Hz, H-5), 3.40–2.94 (m, 5H, H-6, 2 × $N{\cdot}CH_2$), 2.62 and 2.24 (each dd, $J = 13.0$ and 4.1 Hz, 2H, H-7), 1.76 (m, 6H, piperidine protons),

1.51, 1.41, 1.34, 1.32 [each s, each 3H, 2 × $C(CH_3)_2$]; ^{13}C NMR ($CDCl_3$): δ 173, 109.8, 108.8, 96.3, 70.7, 70.5, 70.0, 67.7, 61.5, 53.0, 29.7, 25.9, 25.8, 24.7, 24.3, 23.4.

Anal. Calcd for $C_{19}H_{31}NO_7$: C, 59.22; H, 8.05; N, 3.63. Found: C, 58.98; H, 7.84; N, 3.71.

Ethyl 6-Cyclohexylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (10)

Colorless oil; R_f 0.52 (hexane : ethyl acetate, 7 : 3); $[\alpha]_D^{20}$ −72.2° (*c* 0.175, chloroform); MS (FAB) = m/z 428 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3340, 1730; ^1H NMR (200 MHz, $CDCl_3$): δ 5.55 (d, J = 5.1 Hz, 1H, H-1), 4.56 (dd, J = 7.9 and 2.1 Hz, 1H, H-3), 4.37 (dd, J = 7.9 and 1.5 Hz, 1H, H-4), 4.28 (dd, J = 5.0 and 2.1 Hz, 1H, H-2), 4.11 (q, J = 7.1 Hz, 2H, $-OCH_2$), 3.82 (dd, J = 6.6 and 1.5 Hz, 1H, H-5), 3.40–3.31 (m, 1H, H-6), 2.68 (dd, J = 15.5 and 5.7 Hz, 1H, H-7_A), 2.51–2.41 (m, 2H, NHC*H* and H-7_B), 1.88–1.67 (m, 5H, 2 × $NHCH_2$ and NH), 1.50, 1.45, 1.32 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.28–1.15 (m, 9H, cyclohexyl ring protons and $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.6, 109.1, 108.4, 96.7, 71.6, 71.1, 70.7, 68.6, 60.1, 54.6, 53.0, 37.1, 34.4, 33.5, 25.9, 25.2, 24.9, 24.3, 14.2.

Anal. Calcd for $C_{22}H_{37}NO_7$: C, 61.8; H, 8.66; N, 3.27. Found: C, 61.76; H, 8.67; N, 3.22.

Ethyl 6-Heptylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (11)

Colorless oil; R_f 0.47 (hexane : ethyl acetate, 7 : 3); $[\alpha]_D^{20}$ −42.2° (*c* 0.138, chloroform); MS (FAB) = m/z 444 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3429, 1732; ^1H NMR (200 MHz, $CDCl_3$): δ 5.55 (d, J = 5.0 Hz, 1H, H-1), 4.59 (dd, J = 8.0 and 2.2 Hz, 1H, H-3), 4.35 (dd, J = 8.0 and 1.4 Hz, 1H, H-4), 4.30 (dd, J = 5.0 and 2.2 Hz, 1H, H-2), 4.12 (q, J = 7.1 Hz, 2H, $-OCH_2$), 3.86 (d, J = 7.2 Hz, 1H, H-5), 3.27–3.18 (m, 1H, H-6), 2.72–2.45 (m, 4H, $NHCH_2$ and H-7), 1.85 (bs, 1H, NH), 1.51, 1.45, 1.32 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.29–1.22 (m, 13H, 5 × CH_2 and $-OCH_2CH_3$), 0.87 (t, J = 6.6 Hz, 3H, $-CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.3, 109.2, 108.5, 96.6, 71.6, 71.1, 70.6, 68.4, 60.2, 55.6, 47.1, 35.6, 31.8, 30.2, 29.2, 27.3, 25.9, 24.9, 24.3, 22.6, 14.1, 14.0.

Anal. Calcd for $C_{23}H_{41}NO_7$: C, 62.30; H, 9.25; N, 3.16. Found: C, 62.31; H, 9.25; N, 3.16.

Ethyl 6-Heptylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-octopyranuronate (11a)

Colorless oil; R_f 0.65 (hexane : ethyl acetate, 7 : 3); $[\alpha]_D^{20}$ −53.9° (*c* 0.375, chloroform), MS (FAB) = m/z 444 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3346, 1725; ^1H NMR (200 MHz, $CDCl_3$): δ 5.49 (d, J = 5.0 Hz, 1H, H-1), 4.57 (dd, J = 7.9 and 2.1 Hz, 1H, H-3), 4.45 (dd, J = 7.9 and 1.5 Hz, 1H, H-4), 4.26 (dd, J = 5.0 and 2.1 Hz, 1H, H-2),

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4.12 (q, $J = 7.1$ Hz, 2H, $-OCH_2$), 3.68 (d, $J = 8.4$ Hz, 1H, H-5), 3.26–3.16 (m, 1H, H-6), 2.79 (dd, $J = 15.9$ and 4.0 Hz, 1H, H-7_A), 2.61 (t, $J = 6.8$ Hz, 2H, NCH_2), 2.45 (dd, $J = 15.9$ and 7.4 Hz, 1H, H-7_B), 1.58 (s, 1H, NH), 1.49, 1.44, 1.33 [each s, 3H, 3H, 6H, $2 \times C(CH_3)_2$], 1.30–1.21 (m, 13H, $5 \times CH_2$ and $-OCH_2CH_3$), 0.87 (t, $J = 6.7$ Hz, 3H, $-CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 173.1, 109.3, 108.7, 96.9, 71.4, 71.0, 69.1, 67.8, 60.4, 54.5, 47.3, 35.6, 32.2, 30.8, 29.6, 27.6, 26.3, 25.3, 24.8, 22.9, 14.6, 14.4.

Anal. Calcd for $C_{23}H_{41}NO_7$: C, 62.30; H, 9.25; N, 3.16. Found: C, 62.11; H, 8.93; N, 3.26.

Ethyl 6-Octylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (12)

Colorless oil; R_f 0.46 (hexane : ethyl acetate, 7 : 3); $[\alpha]_D^{20}$ -43.4° (c 0.175, chloroform); MS (FAB) = m/z 458 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3369, 1732; ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.56 (d, $J = 5.0$ Hz, 1H, H-1), 4.60 (dd, $J = 8.0$ and 2.0 Hz, 1H, H-3), 4.36 (d, $J = 8.0$ Hz, 1H, H-4), 4.30 (dd, $J = 5.0$ and 2.0 Hz, 1H, H-2), 4.12 (q, $J = 7.1$ Hz, 2H, $-OCH_2$), 3.86 (d, $J = 7.1$ Hz, 1H, H-5), 3.27–3.18 (m, 1H, H-6), 2.72–2.46 (m, 4H, $NHCH_2$ and H-7), 1.95 (bs, 1H, NH), 1.51, 1.45, 1.32 [each s, 3H, 3H, 6H, $2 \times C(CH_3)_2$], 1.29–1.22 (m, 15H, $6 \times CH_2$ and $-OCH_2CH_3$), 0.87 (t, $J = 6.6$ Hz, 3H, $-CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.7, 109.6, 108.9, 97.0, 72.0, 71.5, 71.0, 68.7, 60.6, 56.0, 47.5, 36.0, 32.2, 30.5, 29.8, 29.6, 27.7, 26.3, 25.3, 24.7, 23.0, 14.5, 14.4.

Anal. Calcd for $C_{24}H_{43}NO_7$: C, 63.01; H, 9.40; N, 3.06. Found: C, 63.0; H, 9.32; N, 2.89.

Ethyl 6-Octylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-octopyranuronate (12a)

Colorless oil; R_f 0.63 (hexane : ethyl acetate, 7 : 3); $[\alpha]_D^{20}$ -56.7° (c 0.275, chloroform); MS (FAB) = m/z 458 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3399, 1725; ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.50 (d, $J = 4.9$ Hz, 1H, H-1), 4.60 (dd, $J = 7.7$ and 2.0 Hz, 1H, H-3), 4.45 (d, $J = 7.7$ Hz, 1H, H-4), 4.27 (dd, $J = 4.9$ and 2.0 Hz, 1H, H-2), 4.12 (q, $J = 7.0$ Hz, 2H, $-OCH_2$), 3.68 (d, $J = 8.4$ Hz, 1H, H-5), 3.26–3.17 (m, 1H, H-6), 2.79 (dd, $J = 16.0$ and 4.0 Hz, 1H, H-7_A), 2.61 (t, $J = 6.7$ Hz, 2H, NCH_2), 2.45 (dd, $J = 16.0$ and 7.5 Hz, 1H, H-7_B), 1.63 (bs, 1H, NH), 1.49, 1.44, 1.34 [each s, 3H, 3H, 6H, $2 \times C(CH_3)_2$], 1.30–1.22 (m, 15H, $6 \times CH_2$ and $-OCH_2CH_3$), 0.87 (t, $J = 6.6$ Hz, 3H, $-CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 173.2, 109.3, 108.7, 96.9, 71.4, 70.9, 69.1, 67.9, 60.5, 54.5, 47.3, 35.6, 32.2, 30.9, 29.9, 29.7, 27.7, 26.4, 25.3, 24.7, 23.0, 14.6, 14.4.

Anal. Calcd for $C_{24}H_{43}NO_7$: C, 63.01; H, 9.40; N, 3.06. Found: C, 62.89; H, 9.40; N, 3.10.

Ethyl 6-Dodecylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (13)

Colorless oil; R_f 0.45 (hexane : ethyl acetate, 4 : 1); $[\alpha]_D^{20}$ -48.6° (c 0.175, chloroform); MS (FAB) = m/z 514 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3340, 1730;

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^{1}H NMR (200 MHz, $CDCl_3$): δ 5.55 (d, $J = 5.1$ Hz, 1H, H-1), 4.58 (dd, $J = 7.9$ and 2.1 Hz, 1H, H-3), 4.35 (d, $J = 7.9$ Hz, 1H, H-4), 4.30 (dd, $J = 5.1$ and 2.1 Hz, 1H, H-2), 4.12 (q, $J = 7.1$ Hz, 2H, $-OCH_2$), 3.85 (d, $J = 7.1$ Hz, 1H, H-5), 3.23–3.20 (m, 1H, H-6), 2.71–2.46 (m, 4H, NHCH_2 and H-7), 2.09 (bs, 1H, NH), 1.51, 1.44, 1.32 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.25–1.21 (m, 23H, 10 × CH_2 and $-OCH_2CH_3$), 0.88 (t, $J = 6.6$ Hz, 3H, $-CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.7, 109.5, 108.9, 97.1, 72.0, 71.2, 71.1, 68.8, 60.6, 56.0, 47.5, 36.0, 35.6, 32.3, 30.9, 30.6, 30.0, 29.9, 29.8, 29.7, 27.7, 26.4, 25.3, 24.7, 23.0, 14.6, 14.4.

Anal. Calcd for $C_{28}H_{51}NO_7$: C, 65.49, H, 9.94, N, 2.72. Found: C, 65.50, H, 10.01, N, 2.74.

Ethyl 6-Hexadecylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (14)

Colorless oil; R_f 0.46 (hexane : ethyl acetate, 4 : 1); $[\alpha]_D^{20}$ -26.4° (c 0.125, chloroform); MS (FAB) = m/z 570 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3347, 1726; ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.55 (d, $J = 5.1$ Hz, 1H, H-1), 4.58 (dd, $J = 8.0$ and 2.2 Hz, 1H, H-3), 4.35 (dd, $J = 8.0$ and 1.4 Hz, 1H, H-4), 4.30 (dd, $J = 5.1$ and 2.2 Hz, 1H, H-2), 4.12 (q, $J = 7.1$ Hz, 2H, $-OCH_2$), 3.85 (dd, $J = 7.2$ and 1.4 Hz, 1H, H-5), 3.25–3.16 (m, 1H, H-6), 2.71–2.44 (m, 4H, NHCH_2 and H-7), 1.72 (bs, 1H, NH), 1.51, 1.44, 1.32 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.28–1.21 (m, 31H, 14 × CH_2 and $-OCH_2CH_3$), 0.87 (t, $J = 6.6$ Hz, 3H, $-CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 173.1, 109.3, 108.7, 96.9, 71.3, 69.1, 60.4, 54.5, 47.3, 35.6, 32.3, 30.8, 30.0, 29.9, 29.7, 27.6, 26.4, 25.3, 24.7, 23.0, 20.4, 14.6, 14.4.

Anal. Calcd for $C_{32}H_{59}NO_7$: C, 67.48, H, 10.36, N, 2.46. Found: C, 67.48, H, 10.41, N, 2.45.

Ethyl 6-Hexadecylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-octopyranuronate (14a)

Colorless oil; R_f 0.63 (hexane : ethyl acetate, 4 : 1); $[\alpha]_D^{20}$ -35.9° (c 0.287, chloroform); MS (FAB) = m/z 570 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3350, 1727; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.49 (d, $J = 5.1$ Hz, 1H, H-1), 4.57 (dd, $J = 8.1$ and 2.1 Hz, 1H, H-3), 4.43 (dd, $J = 8.1$ and 1.2 Hz, 1H, H-4), 4.26 (dd, $J = 5.1$ and 2.1 Hz, 1H, H-2), 4.12 (q, $J = 7.2$ Hz, 2H, $-OCH_2$), 3.68 (d, $J = 8.4$ Hz, 1H, H-5), 3.24–3.18 (m, 1H, H-6), 2.78 (dd, $J = 16.4$ and 4.2 Hz, 1H, H-7_A), 2.61 (t, $J = 6.9$ Hz, 2H, NHCH_2), 2.45 (dd, $J = 16.4$ and 7.5 Hz, 1H, H-7_B), 1.57 (bs, 1H, NH), 1.49, 1.44, 1.34, 1.30 [each s, each 3H, 2 × $C(CH_3)_2$], 1.27–1.23 (m, 31H, 14 × CH_2 and $-OCH_2CH_3$), 0.87 (t, $J = 6.9$ Hz, 3H, $-CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.7, 109.5, 108.9, 97.1, 72.0, 71.4, 71.0, 68.8, 60.6, 56.0, 47.5, 36.0, 32.3, 30.6, 30.0, 29.9, 29.8, 27.7, 27.3, 26.4, 25.4, 24.7, 23.0, 14.6, 14.4.

Anal. Calcd for $C_{32}H_{59}NO_7$: C, 67.48, H, 10.36, N, 2.46. Found: C, 67.47, H, 9.96, N, 2.65.

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Ethyl 6-Oleylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (15)

Colorless oil; R_f 0.51 (hexane : ethyl acetate, 3 : 2); $[\alpha]_D^{20}$ −28.5° (*c* 0.625, chloroform); MS (FAB) = *m*/*z* 596 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3367, 1734, 1660; ^1H NMR (200 MHz, $CDCl_3$): δ 5.55 (d, *J* = 5.0 Hz, 1H, H-1), 5.36–5.32 (m, 2H, CH═CH), 4.59 (dd, *J* = 7.9 and 2.1 Hz, 1H, H-3), 4.35 (d, *J* = 7.9 Hz, 1H, H-4), 4.30 (dd, *J* = 5.0 and 2.1 Hz, 1H, H-2), 4.12 (q, *J* = 7.2 Hz, 2H, $-OCH_2$), 3.85 (d, *J* = 7.1 Hz, 1H, H-5), 3.24–3.20 (m, 1H, H-6), 2.71–2.49 (m, 4H, $NHCH_2$ and H-7), 2.0 (m, 4H, $CH_2CH{=}CHCH_2$), 1.68 (bs, 1H, NH), 1.51, 1.48, 1.32 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.28–1.21 (m, 27, 12 × CH_2 and $-OCH_2CH_3$), 0.88 (t, *J* = 7.1Hz, 3H, $-CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.7, 130.7, 130.3, 109.6, 108.9, 97.1, 72.0, 71.5, 71.2, 68.8, 60.6, 56.1, 47.5, 36.0, 32.9, 32.3, 30.8, 30.6, 30.1, 30.1, 29.9, 29.7, 29.5, 27.7, 27.6, 26.4, 25.4, 24.7, 23.0, 14.6, 14.4.

Anal. Calcd for $C_{34}H_{61}NO_7$: C, 68.57, H, 10.25, N, 2.35. Found: C, 68.57, H, 10.26, N, 2.36.

Ethyl 6-Benzylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (16)

Colorless oil; R_f 0.45 (hexane : ethyl acetate, 3 : 2); $[\alpha]_D^{20}$ −45.1° (*c* 0.375, chloroform); MS (FAB) = *m*/*z* 436 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3345, 1726, 1599; ^1H NMR (200 MHz, $CDCl_3$): δ 7.34–7.20 (m, 5H, ArH), 5.55 (d, *J* = 5.0 Hz, 1H, H-1), 4.60 (dd, *J* = 7.8 and 2.2 Hz, 1H, H-3), 4.37 (dd, *J* = 7.8 and 1.5 Hz, 1H, H-4), 4.21 (dd, *J* = 5.0 and 2.2 Hz, 1H, H-2), 4.13 (q, *J* = 7.1 Hz, 2H, $-OCH_2CH_3$), 3.95–3.71 (m, 3H, H-5 and $CH_2C_6H_5$), 3.35–3.25 (m, 1H, H-6), 2.71 and 2.53 (each, dd, *J* = 15.3 and 5.6 Hz, each 1H, H-7_A and H-7_B), 1.83 (bs, 1H, NH), 1.51, 1.41, 1.32 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.25 (t, *J* = 7.1 Hz, 3H, $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.5, 141.0, 128.6, 128.5, 127.1, 109.6, 109.0, 97.0, 71.9, 71.5, 71.0, 69.0, 60.7, 55.2, 51.4, 35.9, 26.4, 25.4, 24.7, 14.6.

Anal. Calcd for $C_{23}H_{33}NO_7$: C, 63.44, H, 7.58, N, 3.21. Found: C, 63.41, H, 7.60, N, 3.22.

Ethyl 6-Benzylamino-6,7-dideoxy-1,2 : 3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-octopyranuronate (16a)

Colorless oil; R_f 0.65 (hexane : ethyl acetate, 3 : 2); $[\alpha]_D^{20}$ −78.2° (*c* 0.225, chloroform); MS (FAB) = *m*/*z* 436 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3350, 1728, 1600; ^1H NMR (300 MHz, $CDCl_3$): δ 7.34–7.21 (m, 5H, ArH), 5.50 (d, *J* = 5.0 Hz, 1H, H-1), 4.59 (dd, *J* = 8.0 and 2.0 Hz, 1H, H-3), 4.53 (dd, *J* = 8.0 and 1.2 Hz, 1H, H-4), 4.26 (dd, *J* = 5.0 and 2.0 Hz, 1H, H-2), 4.11 (q, *J* = 7.2 Hz, 2H, $-OCH_2CH_3$), 3.85 (s, 2H, $CH_2C_6H_5$), 3.75 (d, *J* = 8.4 Hz, 1H, H-5), 3.32–3.28 (m, 1H, H-6), 2.81 (dd, *J* = 15.9 and 3.9 Hz, 1H, H-7_A), 2.49 (dd, *J* = 15.9 and 7.2 Hz, 1H, H-7_B), 1.65 (bs, 1H, NH), 1.50, 1.43, 1.35, 1.31 [each s, each 3H, 2 × $C(CH_3)_2$], 1.25 (t, *J* = 7.2 Hz, 3H, $-OCH_2CH_3$);

^{13}C NMR ($CDCl_3$): δ 173.0, 141.2, 128.6, 127.2, 109.3, 108.7, 96.9, 71.4, 69.2, 60.5, 54.3, 51.8, 35.6, 26.4, 25.4, 24.7, 14.6.

Anal. Calcd for $C_{23}H_{33}NO_7$: C, 63.44, H, 7.58, N, 3.21. Found: C, 63.55, H, 7.68, N, 3.30.

Ethyl 6-(3,4-Dimethoxyphenylmethyl)amino-6,7-Dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (17)

General Method

Ethyl-6,7-dideoxy-6-amino-β-L-*glycero*-1,2 : 3,4-di-*o*-isopropylidene-α-D-*galacto*-octopyranuronate **5** (1.5 g, 4.34 mmol) was dissolved in a mixture of trimethyl orthoformate and dichloromethane (2 : 5) and stirred magnetically at 0°C. 3,4 dimethoxybenzaldehyde (0.5 mL, 4.5 mmol) was added and stirring continued for another 4 hr at the same temperature. $NaCNBH_3$ (0.26 g, 4.34 mmol) was added to the stirring reaction mixture and stirring continued for 12 hr at 30°C. Solvent evaporated under reduced pressure and the residue was dissolved in ethyl acetate and washed with aqueous NH_4Cl (2 × 25 mL) followed by water (2 × 20 mL). It was dried (Na_2SO_4) and evaporated under reduced pressure to give the crude mass, which was chromatographed over SiO_2 column using hexane : ethyl acetate (4 : 1) as eluent to give title compound. Yield: (80%); Colorless oil; R_f 0.35 (hexane : ethyl acetate, 4 : 1); $[\alpha]_D^{20}$ −48.3° (*c* 0.087, chloroform); MS (FAB) = m/z 496 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 1726; ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.93–6.80 (m, 3H, ArH), 5.56 (d, J = 5.0 Hz, 1H, H-1), 4.59 (dd, J = 8.0 and 2.0 Hz, 1H, H-3), 4.37 (d, J = 8.0 Hz, 1H, H-4), 4.31 (dd, J = 5.0 and 2.0 Hz, 1H, H-2), 4.13 (q, J = 7.1 Hz, 2H, $-OCH_2$), 3.96–3.68 (m, 9H, NCH_2, 2 × Ar-OCH_3 and H-5), 3.32–3.29 (m, 1H, H-6), 2.70 and 2.52 (each dd, J = 16.8 and 5.5 Hz, each 1H, H-7_A and H-7_B), 1.87 (bs, 1H, NH), 1.52, 1.41, 1.32 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.25 (t, J = 7.2 Hz, 3H, $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 172.5, 149.3, 148.3, 133.6, 120.7, 112.0, 111.4, 109.6, 109.0, 97.0, 71.9, 71.5, 71.0, 69.0, 60.7, 56.3, 56.1, 55.0, 51.0, 35.8, 26.3, 25.3, 24.8, 14.6.

Anal. Calcd for $C_{25}H_{37}NO_9$: C, 60.60, H, 7.47, N, 2.82. Found: C, 60.58, H, 7.47, N, 2.81.

Ethyl 6-(2-Hydroxyphenylmethyl)amino-6,7-Dideoxy-1,2 : 3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-octopyranuronate (18)

Yield: (70%); Colorless oil; R_f 0.40 (hexane : ethyl acetate, 4 : 1); $[\alpha]_D^{20}$ −24.9° (*c* 0.125, chloroform); MS (FAB) m/z = 436 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 1726; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.41 (bs, 1H, Ar-OH), 7.31–7.24 and 6.94–6.81 (each m, each 2H, ArH), 5.47 (d, J = 4.9 Hz, 1H, H-1), 4.63 (dd, J = 7.9 and 2.3 Hz, 1H, H-3), 4.39 (d, J = 7.9 Hz, 1H, H-4), 4.29 (dd, J = 4.9 and 2.3 Hz, 1H, H-2), 4.16–3.81 (m, 6H, $-OCH_2$, $-NCH_2$,, H-5, H-6), 2.92–2.70 (m, 2H, H-7), 1.55 (bs, 1H, NH), 1.50, 1.47, 1.35 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.19 (t, J = 7.2 Hz, 3H, $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 171.9, 168.8, 161.5, 132.9, 132.3 119.1, 117.3, 109.6, 109.1, 97.0, 71.2, 71.1, 70.7, 69.3, 65.3, 60.7, 38.2, 26.5, 26.4, 25.3, 24.8, 14.6.

Anal. Calcd for $C_{23}H_{33}NO_8$: C, 61.19, H, 7.31, N, 3.10. Found: C, 61.20, H, 7.31, N, 3.08.

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(1*R*, 2*R*, 3S, 4S, 5R, 6*S*) Ethyl [6,7-Dideoxy-6-{N^3-(4-Chlorophenyl)-(1-Ureidyl)}-1,2 : 3,4-di-*O*-Isopropylidene-tetrahydro-1,5-octopyranos-5-yl]-uronate (19)

The amino ester **5** (0.50 g, 1.44 mmol) and *p*-chlorophenyl isocyanate (0.23 g, 1.5 mmol) in anhydrous dichloromethane (15.0 mL) was magnetically stirred at 25°C for 7 hr. Solvent was evaporated and the reaction mixture was chromatographed over SiO_2 column using a gradient of hexane : ethyl acetate (4 : 1) as eluent to give title compound. yield: 0.50 g (69%); colorless oil; R_f 0.40 (hexane : ethyl acetate, 7 : 3); $[\alpha]_D^{20}$ −20.6° (*c* 0.087, chloroform); MS (FAB) = m/z 500, $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3341, 1726, 1657, 1545; ^1H NMR (200 MHz, $CDCl_3$): δ 7.30–7.18 (m, 4H, ArH), 6.74 (s, 1H, –NHAr), 5.56 (d, $J = 4.9$ Hz, 1H, H-1), 5.44 (d, $J = 7.7$ Hz, 1H, –NHCO), 4.60 (dd, $J = 7.8$ and 2.3 Hz, 1H, H-3), 4.32 (dd, $J = 4.9$ and 2.3 Hz, 1H, H-2), 4.25 (dd, $J = 7.8$ and 1.6 Hz, 1H, H-4), 4.17–4.02 (m, 4H, $-OCH_2$, H-5 and H-6), 2.85 and 2.75 (each dd, $J = 17.0$ and 5.2 Hz, each 1H, H-7_A and H-7_B), 1.52, 1.41, 1.32 [each s, 3H, 3H, 6H, 2 × $C(CH_3)_2$], 1.20 (t, $J = 7.2$ Hz, 3H, $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 173.0, 155.8, 138.3, 129.3, 128.3, 121.8, 109.8, 109.2, 96.8, 71.8, 71.2, 71.1, 68.1, 61.0, 48.4, 35.9, 26.3, 25.3, 24.8, 14.5.

Anal. Calcd for $C_{23}H_{31}N_2O_8Cl$: C, 55.31, H, 6.21, N, 5.61. Found: C, 55.44, H, 6.21, N, 5.59.

(1*R*, 2*R*, 3S, 4S, 5R, 6*S*) Ethyl [6,7-Dideoxy-6-{N^3-Benzyl-N^1-cyclopropyl-(1-Ureidyl)}-1,2 : 3,4-di-*O*-Isopropylidene-tetrahydro-1,5-octopyranos-5-yl]-uronate (20)

It was obtained by the reaction of **6** (250 mg, 0.65 mmol) with benzyl isocyanate (86.4 mg, 0.65 mmol) as described above. Yield: 0.33 g (95%); Colorless solid, mp 108–110°C; R_f 0.51 (hexane : ethyl acetate, 7 : 3); $[\alpha]_D^{20}$ −49° (*c* 0.20, chloroform); MS (FAB) = m/z 519 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3452, 1731, 1656, 1515; ^1H NMR (200 MHz, $CDCl_3$): δ 7.31–7.22 (m, 5H, ArH), 5.48 (d, $J = 5.0$ Hz, 1H, H-1), 4.60 (dd, $J = 8.0$ and 2.5 Hz, 1H, H-3), 4.45 and 4.39 (each d, $J = 6.0$ Hz, each 1H, NCH_A and NCH_B), 4.28 (dd, $J = 5.0$ and 2.5 Hz, 1H, H-2), 4.20–4.08 (m, 4H, H-4, $-OCH_2$ and H-5), 3.77–3.74 (m, 1H, H-6), 3.44–3.37 (m, 1H, NCH), 2.74–2.58 (m, 2H, H-7), 1.60 (s, 1H, NH), 1.46, 1.32, 1.29 [each s, 6H, 3H, 3H, 2 × $C(CH_3)_2$], 1.22 (t, $J = 7.1$ Hz, OCH_2CH_3), 0.78–0.48 (m, 4H, cyclopropyl ring protons); ^{13}C NMR ($CDCl_3$): δ 172.5, 159.0, 140.6, 129.0, 127.6, 127.2, 110.0, 109.7, 97.0, 71.6, 71.5, 70.9, 68.0, 60.6, 44.4, 35.4, 26.4, 25.6, 25.0, 14.6, 9.9, 8.8.

Anal. Calcd for $C_{27}H_{38}N_2O_8$: C, 62.54; H, 7.33; N, 5.40. Found: C, 62.52; H, 7.23; N, 5.40.

(1*R*, 2*R*, 3S, 4S, 5R, 6*S*) Ethyl [6,7-Dideoxy-6-{N^3-Benzyl-N^1-dodecyl-(1-Ureidyl)}-1,2 : 3,4-di-*O*-Isopropylidene-tetrahydro-1,5-octopyranos-5-yl]-uronate (21)

It was obtained by the reaction of **13** (0.70 g, 1.36 mmol) with benzyl isocyanate (0.19 g, 1.45 mmol) as described above. Yield: 0.84 g (95%); colorless foam; R_f 0.65

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(hexane : ethyl acetate, 3 : 2); $[\alpha]_D^{20}$ -29.7° (*c* 0.0875, chloroform); MS (FAB) = m/z 647 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 2927, 1727, 1645, 1536, 1460; ^1H NMR (200 MHz, $CDCl_3$): δ 7.31–7.26 (m, 5H, ArH), 5.48 (d, $J = 5.0$ Hz, 1H, H-1), 4.59 (dd, $J = 7.7$ and 2.0 Hz, 1H, H-3), 4.45 and 4.35 (each d, $J = 5.7$ Hz, each 1H, NCH_A and NCH_B), 4.28 (dd, $J = 5.0$ and 2.0 Hz, 1H, H-2), 4.19–4.06 (m, 5H, H-4, $-OCH_2$, H-5 and H-6), 3.21–3.13 (m, 3H, NCH_2 and H-7_A), 2.71 (dd, $J = 15$ and 4.0 Hz, 1H, H-7_B), 1.62 (s, 1H, N*H*), 1.47, 1.39, 1.30 [each s, 3H, 3H, 6H, $2 \times C(CH_3)_2$], 1.28–1.20 (m, 23H, CH_2s and $-OCH_2CH_3$), 0.88 [t, $J = 6.7$ Hz, 3H, $-(CH_2)_{11}CH_3$].

Anal. Calcd for $C_{36}H_{58}N_2O_8$: C, 66.87, H, 8.98, N, 4.33. Found: C, 67.12, H, 9.0, N, 4.25.

(1*R*, 2*R*, 3S, 4S, 5R, 6*S*) Ethyl [6,7-Dideoxy-6-{N^3-(4-Chlorophenyl), N^1-Oleyl-(1-Ureidyl)}-1,2 : 3,4-di-*O*-Isopropylidene-tetrahydro-1,5-octopyranos-5-yl]-uronate (22)

It was obtained by the reaction of **15** (0.60 g, 1.00 mmol) with 4-Cl-phenyl isocyanate (0.16 g, 1.1 mmol) as described above. Yield: 0.72 g (95%), colorless foam; R_f 0.55 (hexane : ethyl acetate, 7 : 3); $[\alpha]_D^{20}$ -30° (*c* 0.15, chloroform); MS (FAB) = m/z 750 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3019, 2928, 1724, 1663, 1520; ^1H NMR (200 MHz, $CDCl_3$): δ 7.30–7.17 (m, 4H, ArH), 5.53 (d, $J = 5.0$ Hz, 1H, H-1), 5.36–5.34 (m, 2H, CH═CH), 4.62 (dd, $J = 7.7$ and 2.3 Hz, 1H, H-3), 4.34–4.31 (m, 2H, H-2 and H-4), 4.22–4.11 (m, 4H, $-OCH_2$, H-5 and H-6), 2.76–2.71 (m, 2H, H-7), 1.90–2.10 (m, 4H, CH_2CH═$CHCH_2$), 1.50, 1.42, 1.32 [each s, 3H, 3H, 6H, $2 \times C(CH_3)_2$], 1.26–1.21 (m, 26H, CH_2s and $-OCH_2CH_3$), 0.87 [t, $J = 6.7$ Hz, 3H, $(CH_2)_7CH_3$].

Anal. Calcd for $C_{41}H_{65}N_2O_8Cl$: C, 65.68, H, 8.68, N, 3.74. Found: C, 66.65, H, 8.66, N, 3.72.

(1*R*, 2*R*, 3S, 4S, 5R, 6*S*) Ethyl [6,7-Dideoxy-6-{N^3-(4-Chlorophenyl)-N^1-Benzyl-(1-Ureidyl)}-1,2 : 3,4-di-*O*-Isopropylidene-tetrahydro-1,5-octopyranos-5-yl]-uronate (23)

It was obtained by the reaction of **16** (0.70 g, 1.61 mmol) with 4-Cl-phenyl isocyanate (0.25 g, 1.64 mmol) as described above. Yield: 0.93 g (98%); colorless foam; R_f 0.40 (hexane : ethyl acetate, 4 : 1); $[\alpha]_D^{20}$ -42.2° (*c* 0.175, chloroform); MS (FAB) = m/z 590 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 2990, 2931, 1725, 1598, 1527; ^1H NMR (200 MHz, $CDCl_3$): δ 7.33–7.16 (m, 9H, ArH), 5.58 (d, $J = 5.0$ Hz, 1H, H-1), 4.80 (bs, 1H, Ar-NH), 4.63 (dd, $J = 7.8$ and 2.3 Hz, 1H, H-3), 4.34 (dd, $J = 5.0$ and 2.3 Hz, 1H, H-2), 4.22 (d, $J = 7.8$ Hz, 1H, H-4), 4.03–4.13 (m, 6H, $-OCH_2$, $-NCH_2$, H-5 and H-6), 2.89–2.51 (m, 2H, H-7), 1.53, 1.42, 1.33 [each s, 3H, 3H, 6H, $2 \times C(CH_3)_2$], 1.18 (t, $J = 7.1$ Hz, 3H, $-OCH_2CH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.0, 157.7, 139.1, 138.7, 129.1, 128.9, 127.5, 120.9, 110.1, 109.2, 96.9, 71.69, 71.63, 70.92, 67.8, 61.3, 53.8, 49.2, 35.3, 26.4, 26.3, 25.3, 14.4.

Anal. Calcd for $C_{30}H_{37}N_2O_8Cl$: C, 61.17, H, 6.28, N, 4.75. Found: C, 61.20, H, 6.31, N, 4.72.

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(1*R*, 2*R*, 3S, 4S, 5R, 6*S*) Ethyl [6,7-Dideoxy-6-{N^3-Benzyl-N^1-(3,4-Dimethoxyphenyl methyl)-(1-Ureidyl)}-1,2 : 3,4-di-*O*-Isopropylidene-tetrahydro-1,5-octopyranos-5-yl]-uronate (24)

It was obtained by the reaction of **17** (0.50 g, 1.01 mmol) with benzyl isocyanate (0.16 g, 1.1 mmol) as described above. Yield: 0.62 g (98%); colorless foam; R_f 0.40 (hexane : ethyl acetate 4 : 1); $[\alpha]_D^{20}$ −40.7° (*c* 0.15, chloroform); MS (FAB) = m/z 629 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3422, 1728, 1644, 1518, 1459, 1254; ^1H NMR (200 MHz, $CDCl_3$): δ 7.35–7.19 (m, 5H, ArH), 6.79–6.76 (m, 2H, ArH), 5.54 (d, $J = 5.0$ Hz, 1H, H-1), 4.61 (dd, $J = 7.9$ and 2.3 Hz, 1H, H-3), 4.53–4.40 (m, 4H, N^1CH_2 and $NHCH_2$), 4.34 (d, $J = 7.9$ Hz, 1H, H-4), 4.30 (dd, $J = 5.0$ and 2.3 Hz, 1H, H-2), 4.23 (d, $J = 7.9$ Hz, 1H, H-5), 4.06 (q, $J = 7.2$ Hz, 2H, $-OCH_2$), 3.88–3.78 (m, 9H, 2 × $ArOCH_3$, N^3CH_2 and H-6), 3.0 and 2.7 (each d, $J = 16.5$ Hz, each 1H, H-7_A and H-7_B), 1.47, 1.41, 1.31 [each s, 3H, 3H, and 6H, 2 × $(CH_3)_2$], 1.18 (t, $J = 7.4$ Hz, 3H, OCH_2CH_3).

Anal. Calcd for $C_{33}H_{44}N_2O_{10}$: C, 63.06, H, 7.06, N, 4.46. Found: C, 63.12, H, 7.10, N, 4.48.

(1′*R*, 2′*R*, 3′*S*, 4′S, 5′*R*, 6*S*) N^3-(4-Chlorophenyl)-5,6-Dihydro-6-(1′,2′ : 3′,4′-di-*O*-Isopropylidene-1′,2′,3′,4′-tetrahydro-1′,5′-Pyranos-5′-yl)-pyrimidin-2,4-dione (25)

A mixture of compound **19** (0.30 g, 0.60 mmol), 4 Å MS (0.03 g), TBAB (0.03 g, 0.093 mmol) and DBU (0.086 mL, 0.564 mmol) in anhydrous toluene (15 mL) was refluxed for 2 hr. Solvent was evaporated and the residue was chromatographed over a SiO_2 column using a gradient of hexane : ethyl acetate (3 : 1) as eluent to give title compound. Yield: 0.19 g (70%); colorless foam; R_f 0.30 (hexane : ethyl acetate, 3 : 2); $[\alpha]_D^{25}$ −51.8° (*c* 0.3125, chloroform); MS (FAB) $m/z = 454$ $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 3393, 1661, 1598, 1554, 1495, 1384; ^1H NMR (200 MHz, $CDCl_3$): δ 7.26–7.11 (m, 4H, ArH), 5.54 (d, $J = 4.4$ Hz, 1H, H-1′), 4.57 (d, $J = 7.1$ Hz, 1H, H-3′), 4.28–4.06 (m, 4H, H-2′, H-4′, H-5′, H-6), 2.71–2.76 (m, 2H, H-5), 1.47, 1.38, 1.29 [each s, 3H, 3H, and 6H, 2 × $(CH_3)_2$]; ^{13}C NMR (50 MHz, $CDCl_3$): δ 172, 168, 137.9, 121.6, 120.7, 109.9, 109.4, 96.8, 71.6, 71.3, 71.0, 53.7, 34.1, 26.3, 25.3, 24.6.

Anal. Calcd for $C_{21}H_{25}N_2O_7Cl$: C, 55.62, H, 5.52, N, 6.18. Found: C, 55.70, H, 5.72, N, 6.14.

(1′*R*, 2′*R*, 3′*S*, 4′S, 5′*R*, 6*S*) N^3-Benzyl-N^1-cyclopropyl-5,6-dihydro-6-(1′,2′ : 3′,4′-di-*O*-Isopropylidene-1′,2′,3′,4′-tetrahydro-1′,5′-pyranos-5′-yl)-Pyrimidin-2,4-dione (26)

It was obtained from **20** (0.20 g, 0.39 mmol) as described in general procedure. Yield: 0.14 g (75%); colorless solid, mp 123–125°C; R_f 0.54 (hexane : ethyl acetate 3 : 2); $[\alpha]_D^{25}$ +3.2° (*c* 0.125, chloroform); MS (FAB) = m/z 473 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 1713, 1671, 1436; ^1H NMR (200 MHz, $CDCl_3$): δ 7.26–7.19 (m, 5H, ArH), 5.47 (d, $J = 5.0$ Hz, 1H, H-1), 4.89 (s, 2H, NCH_2Ar), 4.56 (dd, $J = 7.8$ and 2.4 Hz, 1H, H-3),

4.25 (dd, $J = 5.0$ and 2.4 Hz, 1H, H-2), 4.18 (d, $J = 7.8$ Hz, 1H, H-4), 3.85–3.73 (m, 2H, H-5 and H-6), 3.01–2.82 (m, 2H, H-5_A and NCH), 2.71 (dd, $J = 17.0$ and 5.8 Hz, 1H, H-5_B), 1.57, 1.44, 1.29 [each s, 3H, 3H, 6H, 2 × C(CH_3)$_2$], 0.97–0.52 (m, 4H, cyclopropyl ring protons); ^{13}C NMR ($CDCl_3$): δ 168.9, 154.2, 138.0, 129.7, 128.7, 127.6, 110.2, 109.2, 96.7, 71.2, 71.0, 70.6, 68.8, 54.0, 44.4, 34.3, 32.2, 26.2, 25.2, 24.7, 10.3, 6.6.

Anal. Calcd for $C_{25}H_{32}N_2O_7$: C, 63.56; H, 6.78; N, 5.93. Found: C, 63.52; H, 6.78; N, 5.90.

(1′*R*, 2′*R*, 3′*S*, 4′S, 5′*R*, 6*S*)-N^3-Benzyl-N^1-dodecyl-5,6-dihydro-6-(1′,2′ : 3′,4′-di-*O*-Isopropylidene-1′,2′,3′,4′-tetrahydro-1′,5′-pyranos-5′-yl)-Pyrimidin-2,4-dione (27)

It was obtained from **21** (0.40 g, 0.62 mmol) as described in general procedure. Yield: 0.33 g (89%); colorless foam; R_f 0.55 (hexane : ethyl acetate 3 : 2); $[\alpha]_D^{25}$ −20.5° (*c* 0.4, chloroform); MS (FAB) = *m*/*z* 601 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 1727, 1648, 1518, 1461, 1379; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.45–7.42 (m, 2H, ArH), 7.26–7.22 (m, 3H, ArH), 5.43 (d, $J = 5.0$ Hz, 1H, H-1′), 4.90 (s, 2H, NCH_2Ar), 4.61 (dd, $J = 7.6$ and 2.3 Hz, 1H, H-3′), 4.33 (dd, $J = 5.0$ and 2.3 Hz, 1H, H-2′), 3.95 (d, $J = 7.6$ Hz, 1H, H-4′), 3.81 (m, 1H, NCH_A), 3.69–4.10 (m, 2H, H-5′ and H-6), 3.30–2.90 (m, 1H, NCH_B), 2.89–2.70 (m, 2H, H-5), 1.50 (m, 2H, $-NCH_2$ CH_2), 1.44, 1.29 [each s, each 3H, C(CH_3)$_2$], 1.25 (m, 18H, 9 × CH_2), 1.09 [s, 6H, C(CH_3)$_2$], 0.87 (t, $J = 7.6$ Hz, 3H, CH_2CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.1, 152.9, 138.1, 129.5, 128.7, 127.6, 110.1, 109.2, 96.5, 71.1, 70.9, 70.5, 69.4, 52.5, 50.0, 44.4, 34.2, 32.1, 30.0, 29.9, 29.7, 29.7, 28.6, 27.3, 26.3, 26.1, 25.2, 24.7, 14.5.

Anal. Calcd for $C_{34}H_{52}N_2O_7$: C, 68.0, H, 8.67, N, 4.67. Found: C, 68.23, H, 8.91, N, 4.68.

(1′*R*, 2′*R*, 3′*S*, 4′S, 5′*R*, 6*S*)-N^3-(4-Chlorophenyl)-N^1-Oleyl-5,6-dihydro-6-(1′,2′ : 3′,4′-di-*O*-Isopropylidene-1′,2′,3′,4′-tetrahydro-1′,5′-pyranos-5′-yl)-Pyrimidin-2,4-dione (28)

It was obtained from **22** (0.50 g, 0.67 mmol) as described in general procedure. Yield: 0.42 g (90%); colorless foam; R_f 0.40 (hexane : ethyl acetate 3 : 2); $[\alpha]_D^{25}$ −10.9° (*c* 0.2375, chloroform); MS (FAB) = *m*/*z* 704 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 1710, 1593, 1473, 1351; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.37 (d, $J = 8.4$ Hz, 2H, ArH), 7.10 (d, $J = 8.4$ Hz, 2H, ArH), 5.55 (d, $J = 5.0$ Hz, 1H, H-1′), 5.37–5.34 (m, 2H, CH═CH), 4.61 (dd, $J = 8.0$ and 2.2 Hz, 1H, H-3′), 4.33 (dd, $J = 5.0$ and 2.2 Hz, 1H, H-2′), 4.25(d, $J = 8.0$ Hz, 1H, H-4′), 4.02–3.81 (m, 3H, H-5′, NCH_A and H-6), 3.24–2.96 (m, 2H, H-5_B and NCH_B), 2.02–1.99 (m, 4H, CH_2CH═$CHCH_2$), 1.63–1.61 (m, 2H, NCH_2), 1.46 and 1.34 (each s, each 6H, 2 × (CH_3)$_2$), 1.33–1.16 (m, 13 × CH_2), 0.88 (t, $J = 7.2$ Hz, 3H, CH_2CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.8, 152.6, 134.4, 130.4, 129.4, 110.2, 109.2, 96.8, 71.2, 70.9, 70.5, 68.0, 52.4, 50.1, 34.5, 32.3, 30.1, 29.7, 28.4, 27.7, 26.7, 26.3, 25.1, 14.5.

Anal. Calcd for $C_{39}H_{59}N_2O_7Cl$: C, 66.57, H, 8.4, N, 3.98. Found: C, 66.95, H, 8.44, N, 3.92.

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(1′*R*, 2′*R*, 3′*S*, 4′S, 5′*R*, 6*S*)-N^1-Benzyl-N^3-(4-Chlorophenyl)-5,6-Dihydro-6-(1′,2′ : 3′,4′-di-*O*-Isopropylidene-1′,2′,3′,4′-tetrahydro-1′,5′-pyranos-5′-yl)-Pyrimidin-2,4-dione (29)

It was obtained from **23** (0.40 g, 0.68 mmol) as described above. Yield: 0.34 g (92%); Colorless foam; R_f 0.55 (hexane : ethyl acetate, 3 : 2); $[\alpha]_D^{25}$ +4° (*c* 0.075, chloroform); MS (FAB) = m/z 544 $(M + H)^+$; IR (Neat) ν_{max} cm^{-1}: 1685, 1593, 1373; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.39 (dd, J = 11.3 and 2.6 Hz, 2H, ArH), 7.41–7.33 (m, 5H, ArH), 7.18–7.12 (m, 3H, ArH), 7.15 (dd, J = 11.3 and 2.6 Hz, 2H, ArH), 5.62 (d, J = 5.1 Hz, 1H, H-1′), 5.42 and 4.24 (two d, J = 14.9 Hz, each 1H, NCH_A and NCH_B), 4.62 (dd, J = 7.8 and 2.4 Hz, 1H, H-3′), 4.36 (dd, J = 5.1 and 2.4 Hz, 1H, H-2′), 4.20 (dd, J = 7.8 and 1.8 Hz, 1H, H-4′), 4.05 (dd, J = 9.0 and 1.8 Hz, 1H, H-5′), 3.89–3.84 (m, 1H, H-6), 2.90–2.82 (m, 2H, H-5), 1.48, 1.44, 1.34, 1.31 [each s, each 3H, 2 × $(CH_3)_2$]; ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.7, 153.2, 137.6, 134.5, 134.4, 130.4, 129.5, 129.2, 128.9, 128.2, 110.2, 109.3, 96.8, 71.2, 70.9, 70.5, 69.2, 52.4, 50.5, 34.6, 26.7, 26.3, 25.1, 24.9.

Anal. Calcd for $C_{28}H_{31}N_2O_7Cl$: C, 61.87, H, 5.71, N, 5.16. Found: C, 62.26, H, 5.91, N, 5.03.

(1′*R*, 2′*R*, 3′*S*, 4′S, 5′*R*, 6*S*)-N^3-Benzyl-N^1-(3,4-Dimethoxy phenylmethyl)-5,6-Dihydro-6-(1′,2′ : 3′,4′-di-*O*-Isopropylidene-1′,2′,3′,4′-tetrahydro-1′,5′-pyranos-5′-yl)-Pyrimidin-2,4-dione (30)

It was obtained from **24** (0.50 g, 0.80 mmol) as described in general procedure. Yield: 0.44 g (95%); colorless foam; R_f 0.35 (hexane : ethyl acetate, 3 : 2); MS (FAB) = m/z 583 $(M + H)^+$; $[\alpha]_D^{25}$ −8.34° (*c* 0.285, chloroform); IR (Neat) ν_{max} cm^{-1}: 1710, 1596, 1461, 1355; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.47 (dd, J = 8.4 and 1.2 Hz, 2H, ArH), 7.30–7.24 (m, 3H, ArH), 6.84–6.81 (m, 3H, ArH), 5.52 (d, J = 5.0 Hz, 1H, H-1′), 5.30 and 4.96 (two d, J = 14.8 Hz, each 1H, NCH_2Ar), 4.60 (dd, J = 7.8 and 1.6 Hz, 1H, H-3′), 4.36 (dd, J = 5.0 and 1.6 Hz, 1H, H-2′), 4.12 (dd, J = 7.8 and 1.8 Hz, 1H, H-4′), 3.83 and 3.86 (each s, each 3H, Ar-OCH_3), 3.75–3.62 (m, 1H, H-6), 2.80 (dd, J = 16.8 and 5.6 Hz, 1H, H-5_A), 2.70 (dd, J = 16.8 and 5.6 Hz, 1H, H-5_B), 1.46, 1.26, 1.12 [each s, 3H, 3H, 6H, 2 × $(CH_3)_2$]; ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.0, 153.2, 130.4, 138.1, 149.1, 149.7, 129.5, 128.8, 127.7, 121.3, 112.1, 111.6, 109.3, 110.1, 96.6, 71.1, 70.5, 69.7, 56.3, 52.0, 50.3, 44.6, 34.2, 26.3, 26.1, 25.2, 24.8.

Anal. Calcd for $C_{31}H_{38}N_2O_9$: C, 63.91, H, 6.53, N, 4.81. Found: C, 64.05, H, 6.52, N, 4.73.

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