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Synthesis and ring opening reactions of 2-glyco-1,4-dimethyl-3-nitro-7-oxabicyclo[2.2.1]hept-5-enes

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ABSTRACT

The high-pressure asymmetric Diels–Alder reactions of D-*galacto*- (**1a**) and D-*manno*-3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-nitrohept-1-enitol (**1b**) with 2,5-dimethylfuran (**2**) afforded mixtures of cycloadducts, from which the (2*S*,3*R*)-3-*exo*-nitro (**3a** and **3b**), (2*R*,3*S*)-3-*exo*-nitro (**4a** and **4b**), and (2*R*,3*S*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(1,4-dimethyl-3-*endo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl)-D-*galacto*-pentitol (**5b**) were isolated pure. Deacetylation of these compounds led to new chiral mono-, bi-, and tricyclic ethers, being their asymmetric centers arising from the chiral inductor used in the cycloaddition reaction. A ring opening mechanism through a 1-nitro-1,3-cyclohexadiene intermediate has been proposed.

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1. Introduction

Racemic 7-oxabicyclo[2.2.1]hept-5-ene-*trans*-3-nitro-2-carboxylates[1] are very useful compounds for the preparation of natural products bearing multisubstituted cyclohexanol units after regioselective cleavage of the ethereal C–O bond.[2] However, although the access to chiral derivatives of 7-oxabicyclo[2.2.1]heptenes seems also promising, references about this type of compounds are rather scarce,[3] probably due to difficulties related to their asymmetric synthesis. In particular, apart from papers of our group,[4] we have not found any reference about the preparation of chiral 7-oxanitronorbornenes; attempts to prepare these compounds by using chiral nitroacrylates as dienophiles have failed, being obtained chiral amino derivatives by reduction from racemic 7-oxanitronorbornenes, followed by enzymatic resolution or chiral HPLC.[2c]

In recent years, the seven-membered oxacycles and other medium size rings have received a considerable attention.[5] This fact is mainly due to their biological and synthetic interest as well as their occurrence in a wide variety of natural products, such as zoapatanol,[6] hemibrevetoxin B,[7] or ciguatoxins and brevetoxins A and B.[8] Among the methods described for their preparation, we reported in a preliminary communication,[4b] a new one-pot ring opening reaction where the cycloadduct **3a** led to an optically pure oxocine and undecul-2-ose derivatives. These latter compounds could be considered as higher sugars,[9] being identified as fragments of biologically interesting compounds, such as octosylic acids A and C,[10] antifungal C-glycoside malayamycin A,[10] and ezomycins.[11]

Following our research work on asymmetric synthesis with sugar-derived nitro compounds,[12] we describe in full details about Diels–Alder reactions between nitroalkenes **1a**[13] and **1b**[14] with 2,5-dimethylfuran (**2**). It is noteworthy that, by changing the solvent, we have observed variations in both the rate and stereoselectivity of the cycloadditions with **1a**. In addition, we describe the ring opening reactions and the products obtained from the new cycloadducts.

2. Results and discussion

The high-pressure Diels–Alder reactions between the D-*galacto*-nitroalkene **1a** and 2,5-dimethylfuran **2** afforded mixtures[4b] of cycloadducts **3a**, **4a**, and **5a**, in ratios that were dependent both on the solvent and on the reaction time (Scheme 1 and Table 1, entries 1–8). After fractional crystallization from the crude product, the *exo*-nitro stereoisomers **3a** and **4a** were isolated pure. Similarly, D-*manno*-nitroalkene **1b** and 2,5-dimethylfuran led, after 3 days, to a 6.8:3.5:1.0 mixture of **3b**, **4b**, and **5b** (Scheme 1 and Table 1, entry 11), that was separated by column chromatography and semi-preparative HPLC. Neither in this reaction nor in the previous, ^{1}H NMR signals were observed for the *endo*-nitro product **6**.

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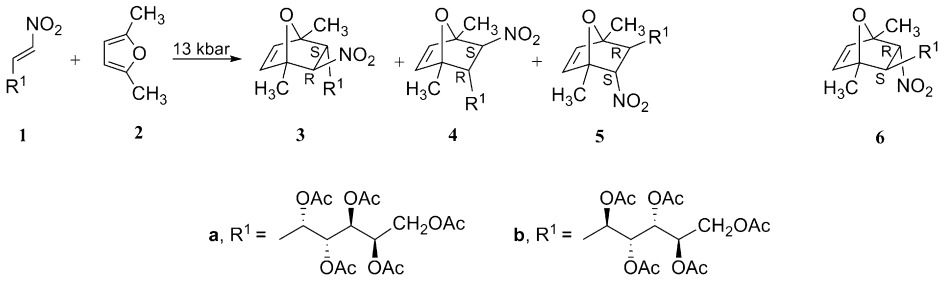


Scheme 1.

Table 1
Solvents, relative ratios between cycloadducts, facial diastereoselectivity, *exo*/*endo* ratios, and reaction times for reactions of nitroalkenes **1a** and **1b** with 2,5-dimehtylfuran[a]

Entry	Nitroalkene	Solvent	Ratio of adducts[b]			(2*R*,3*S*)/(2*S*,3*R*) Ratio[c]	*exo*/*endo* Ratio	Time (days)	% Conv.
			3	**4**	**5**				
1	**1a**	CH_3CN	7.1	7.3	1.0	1.17	14.4	2	93
2	**1a**	Acetone	5.2	4.4	1.0	1.04	9.6	3	75
3	**1a**	Acetone	7.7	9.4	1.0	1.35	17.1	4	88
4	**1a**	Acetone	5.7	3.3	1.0	0.75	9.0	6	91
5	**1a**	THF	8.1	10.0	1.0	1.35	18.0	4.5	94
6	**1a**	CH_2Cl_2	6.7	5.8	1.0	1.01	12.5	3	95
7	**1a**	CH_2Cl_2	47.0	10.0	1.0	0.23	57.0	4.5	100
8	**1a**	$CHCl_3$	3.3	4.7	1.0	1.73	8.0	2	97
9	**1b**	Acetone	6.3	3.2	1.0	0.66	9.5	3	100
10	**1b**	THF	6.6	3.7	1.0	0.71	10.3	3	100
11	**1b**	CH_2Cl_2	6.8	3.5	1.0	0.66	10.6	3	100
12	**1b**	CH_2Cl_2	6.5	3.1	1.0	0.63	9.6	4	100

[a] All experiments were carried out at rt, under 13 kbar pressure.
[b] Determined by integration of the pertinent peaks in the ^{1}H NMR spectra.
[c] Facial diastereoselectivity: (2*R*,3*S*)- and (2*S*,3*R*)-adducts arise, respectively, from cycloadditions at the C1-*re* and C1-*si* faces of the nitroalkene **1a** or **1b**.

As observed for cycloadditions between the same nitroalkenes and furan[4a] or 2-methylfuran,[4c] it is noteworthy that none of these reactions occurred under atmospheric pressure, both at room temperature and at reflux, even for prolonged periods. In addition, no reaction was observed when these processes were carried out in 1:1 CH_2Cl_2–water, or with the same solvent mixture and 5 M LiCl under mechanical stirring.[15]

Since solubility of nitroalkene **1a** in CH_2Cl_2 was rather low (ca. 0.15 g/mL), we tested other solvents for cycloadditions between this dienophile and 2,5-dimethylfuran. Thus, we observed that some parameters as reaction time, diastereoselectivity, or *endo*/*exo* ratio were dependent on the solvent. As shown in Table 1, the *exo*-nitro **3a** was the major adduct in those reactions with acetone (3 or 6 days) or CH_2Cl_2 (entries 2, 4, 6, and 7), whereas the *exo*-nitro **4a** preponderate with acetonitrile, acetone (4 days), tetrahydrofuran or chloroform (entries 1, 3, 5, and 8). It is noticeable the change that occurs in diastereoselectivity with acetone (entries 2–4), as well as the high percentage of **3a** with CH_2Cl_2 (entry 7). The diastereoselectivity changed from 0.23, after 4.5 days in CH_2Cl_2 (entry 7), being the 2*S*,3*R* adduct **3a** predominant, to 1.73 in $CHCl_3$ after 2 days (entry 8), with 2*R*,3*S* adduct **4a** as the major product. Fluctuation of diastereoselectivity with reaction time has been previously observed for the reaction between methyl nitroacrylate and 2-methylfuran.[16] Regarding time needed for each one of the cycloadditions, it is noticeable that after 2 days with $CHCl_3$ or acetonitrile, were achieved reaction completion percentages (% conv.) that in acetone required 6 days. From a synthetic point of view, data indicate that the best reaction conditions to prepare the adduct **3a** would be those indicated in entry 7, whereas those specified in entry 8 would give a better yield of **4a**.

Unlikely to what was observed for **1a**, the cycloaddition of **1b** and 2,5-dimethylfuran with solvents or reaction times indicated in Table 1 (entries 9–12) did not show significative changes of the results.

The preference for the *exo*-nitro adducts in both cycloadditions agrees with previous findings in similar processes between furans and (*E*)-1,1,1-trichloro-3-nitro-2-propene;[17] an increase toward those adducts was observed with increasing substitution at the terminal positions of the furan diene.

In previous publications,[4a,c] and following a rule stated by Franck,[18] we reported that the facial selectivity in cycloadditions with **1a** or **1b**, using dichloromethane as solvent, was dependent on the configuration of the chiral center adjacent to the dienophilic double bond. Thus, the major adducts were those resulting of the attack by the diene at the C1-*si* face of **1a** and at the C1-*re* face of **1b**. Now, when the same solvent and reaction time were used (Table 1, entries 7 and 11), we found that the attack by 2,5-dimethylfuran on both sugar nitroolefins occurred predominantly at the C1-*si* face, thus leading to (2*S*,3*R*)-cycloadducts; i.e., the facial stereoselectivity in these reactions did not show dependence on the configuration of chiral center adjacent to the dienophilic double bond.

Structures for **3**–**5** were supported by spectroscopic data, as well as on their comparison with those for similar adducts from furan[4a] and 2-methylfuran.[4c] Absolute configuration at the new chiral centers at C-2 and C-3 were based on X-ray powder diffractometry[4b] for **3a** and chemical correlations (see below).

Treatment of **3a** with aqueous methanolic K_2CO_3, followed by acidification to ca. pH 6 with Amberlite IR-120 (H^+) resin, led to a mixture, from which undecul-2-ose **8b** and oxocine **9c** were obtained. Conventional reacetylation of the crude mixture and separation by column chromatography afforded **7d**, **8a**, and **9e** (Fig. 1). Although bicycle **7f** was not isolated, it was characterized as the corresponding acetyl derivative **7d** and the *O*-methylglycoside **7g**.[4b] The formation of compounds **7**–**9** from cycloadduct **3a**, under the deacetylation conditions could be justified through a ring opening reaction leading to a proposed 1-nitro-1,3-cyclohexadiene intermediate, followed by intramolecular nucleophilic additions from hydroxy groups of the sugar side-chain on the diene system and, finally, carbon–carbon bond heterolytic rupture.[4b]

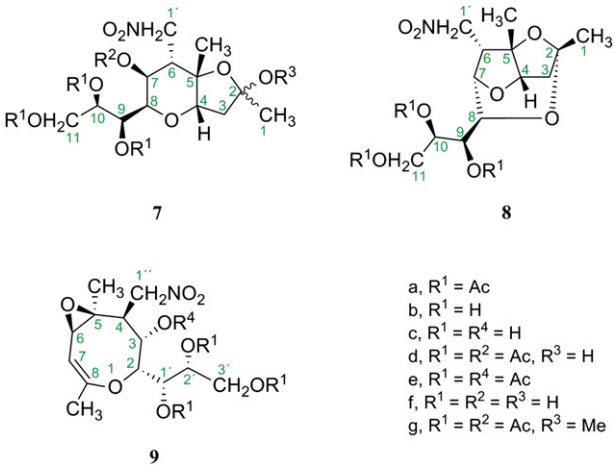


Figure 1. Structures of compounds **7**–**9**.

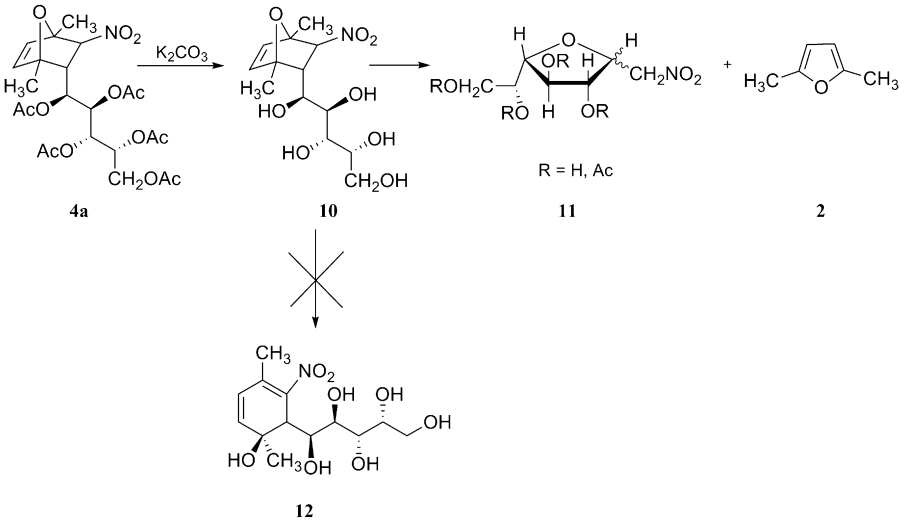
The reaction of cycloadduct **4a** with K_2CO_3 and resin, under identical conditions to those used for **3a**, led to different results. Thus the ^{1}H NMR spectrum of the crude mixture from **4a** showed two doublet signals for a major product (at 6.24 and 6.42 ppm) that were assigned to olefinic H-5 and H-6; also, a doublet at 4.67 ppm, and a double doublet at 2.80 ppm suggest the deacetylated structure **10** (Scheme 2). This compound could not be isolated due to its transformation, complete after 3 days in the NMR tube, into 2,5-dimethylfuran and the diastereomeric sugars **11** (R=H); conventional acetylation of this crude product led to a mixture of two tetraacetates **11** (R=Ac) whose ^{1}H and ^{13}C NMR spectra were different to those described for 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-1-desoxi-1-nitro-D-*glycero*-L-*manno*-heptitol.[19a] The ^{1}H NMR spectrum of the mixture **11** (R=Ac) showed that by irradiation at 5.36 ppm (H-6), collapsed six signals between 4.39 and 4.06 ppm that were assigned to protons H-7a, H-7b, and H-5 of both anomers. These data, and the ^{13}C NMR shift for C-5 (82.1 ppm), typical for furanoside derivatives,[19b] agree with structures of 2,5-anhydro-1-deoxy-1-nitroalditols **11**, formed through retro Diels–Alder reaction, by cyclization between C-2 and C-5 from deacetylated derivative of the nitroalkene **1a**.

hypothetical carbanion because of steric hindrance. As described,[20] removal of the H-3 proton would be at the origin of the opening of the bicyclic system to the corresponding 1-nitro-1,3-cyclohexadiene intermediate **12** (Scheme 2).

The reaction with K_2CO_3 and acid resin, either from **3b** or a mixture **3b**–**5b** led to an oily residue, from which crystallized the oxepine **14** (Scheme 3). Similarly to described,[2e,20c] the formation of this compound can be justified considering that besides deprotection of the sugar chain, the intermediate **13** should be formed; then, a tandem process involving nucleophilic attacks[21a,b] from hydroxy groups of the sugar chain (Scheme 3, path a), followed by the marked carbon–carbon heterolytic bond rupture would lead to **14**. Through this mechanism, that is analogous to that described by us for **3a**,[4b] the oxepine **14** (with the nitromethyl group and the sugar fragment in a trans-relationship), could only be derived from cycloadduct **3b**. The ^{1}H NMR spectrum of **14** showed four D_2O exchangeable signals (three doublets and a triplet) for hydroxy groups; on the contrary, a triplet assigned to H-2 did not change, as would have happened if it were the H-3 of the possible alternative isomer **17** (Scheme 3). The structure of the oxepine **14** was also confirmed through its corresponding tetraacetate **19** (Fig. 2); for both compounds, the coupling constant values between H-2 and H-3 (8.8 and 9.2 Hz, respectively) support a trans-relationship for nitromethyl group and the sugar side-chain.

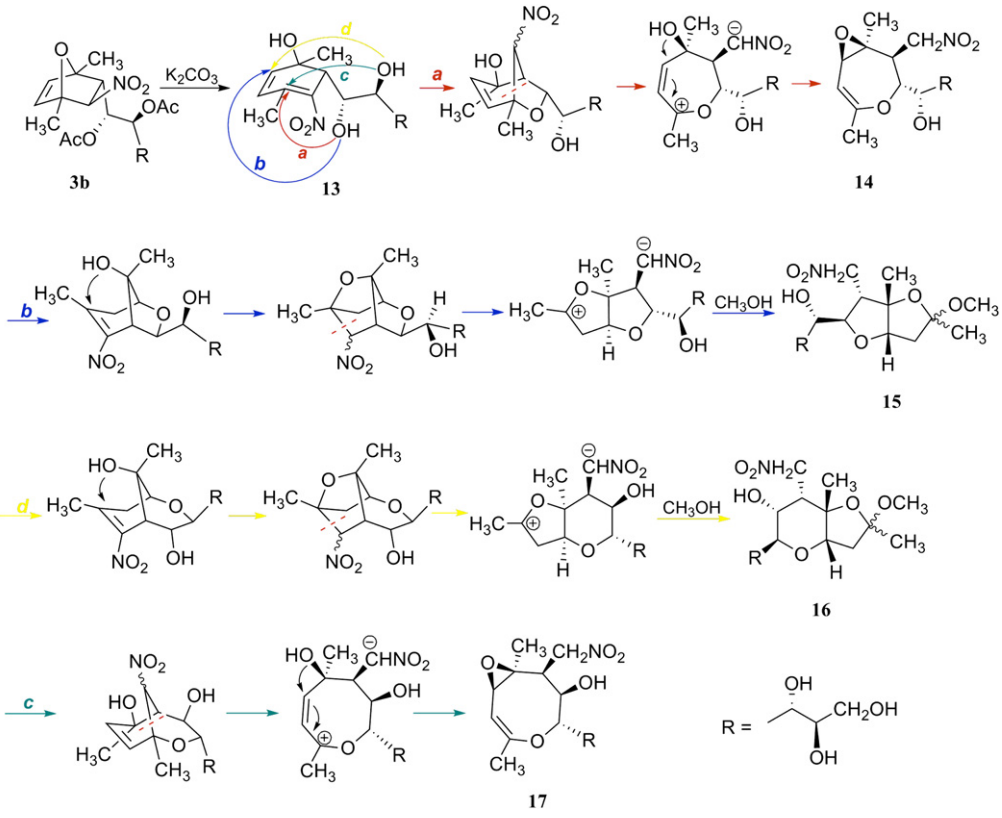
From the mother liquor of crystallization of **14**, 2,5:4,7-dianhydroundecul-2-ose **15** (Scheme 3) was obtained as a solid anomeric mixture of methylglycosides, probably as a result of the presence of methanol under the acid conditions. Besides ^{1}H and ^{13}C NMR signals supporting the methoxy group (at 3.08 and 48.8 ppm, respectively), the major anomer of **15** showed three doublets and one triplet that disappeared by D_2O exchange; noticeably, this exchange did not alter the triplet H-7, as it should be expected for its isomer **16** (Scheme 3). Conventional acetylation of **15** led to tetraacetate **18**, also isolated as the major product from **3b**, after treatment with methanolic K_2CO_3/resin and reacetylation. Therefore, both **14** and **15** arise from **3b**, probably through the 1-nitro-1,3-cyclohexadiene **13**, following mechanisms indicated in Scheme 3, paths a and b.

Deacetylation of **3b** led to an oil from which methyl glycoside **16** was isolated by PTLC. Formation of **16** could be justified as indicated in Scheme 3 (path d), by a mechanism involving intramolecular



Scheme 2.

The difference in behavior of cycloadducts **3a** and **4a** could be justified by (a), difficulty of access by the base to the *endo* H-3 proton in **4a**, located between the sugar side-chain and methyl group on C-4 and/or (b), the difficulty of stabilizing as nitronate the nucleophilic addition from OH-2′ on the terminal carbon of the intermediate **13**, followed by the marked carbon–carbon bond rupture and glycosidation with methanol and the acid resin. Conventional acetylation of the crude mixture from **3b** yielded the



Scheme 3.

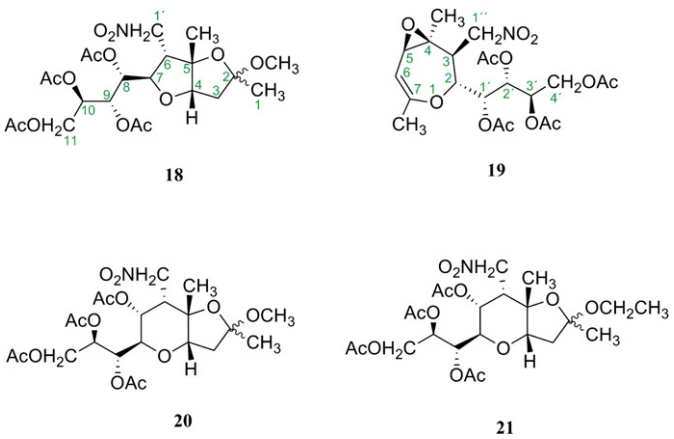


Figure 2. Structures of compounds **18**–**21**.

methyl and ethyl glycoside tetraacetates **20** and **21**, being the formation of the latter due to the presence of absolute ethanol, used to remove residual water by coevaporation before the reacetylation.

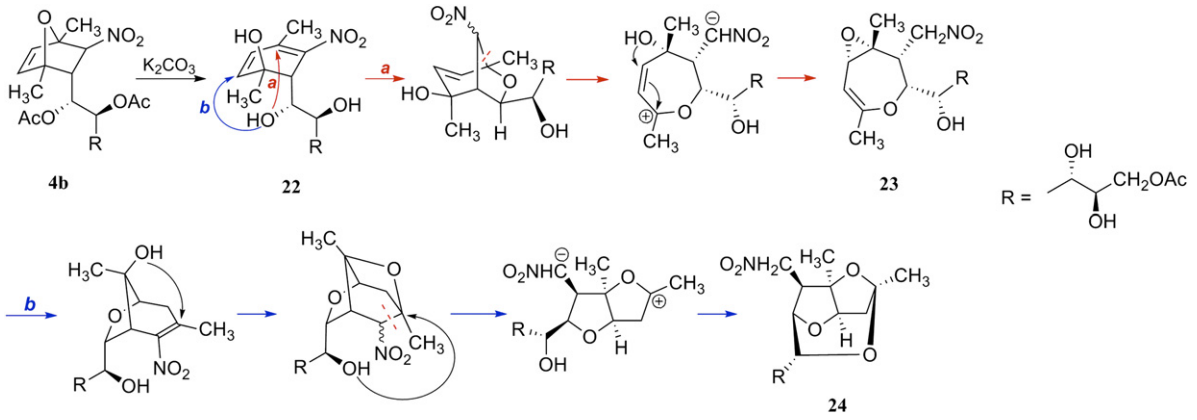
The ^{1}H NMR spectra of compounds **7**–**9**, **14**–**16**, and **18**–**21** showed typical AB systems for both protons of their respective nitromethyl groups; in all cases, the protons that appear at lower field underwent a more rapid D_2O exchange than those at higher field. The signals for the sugar side-chain protons of **18** and **19** were almost superimposable, thus supporting identity between these fragments.

Treatment of **4b** with K_2CO_3 and Amberlite IR-120 (H^+) yielded oxepine **23** and tricycle **24**. As it is showed in Scheme 4, the formation of these both compounds could be justified through intramolecular nucleophilic attacks from OH-1′ on the unsaturated system of 1-nitro-1,3-cyclohexadiene **22**, then followed by the marked carbon–carbon bond ruptures. Path a would lead to **23** where, in contrast to its analogue **14**, the nitromethyl group and the acyclic sugar fragment showed a cis-relationship ($J_{2,3}$ 5.7 Hz). In a similar way, path b would lead to 4,7:2,8-dianhydroundecul-2-ulo-2,5-furanoside **24**; in this case, after the heterolytic rupture, the first hydroxy group of the sugar fragment would be very close to the carbocationic center, thus facilitating the subsequent cyclization.

Compounds **25**–**28** were obtained by K_2CO_3 deacetylation and subsequent Ac_2O/Py reacetylation from **4b**. Also, conventional acetylation of an analytical sample of **23** led to tetraacetyl derivative **25** ($J_{2,3}$ 6.0 Hz), whereas tricyclic **24** yielded a mixture of triacetate **26** and diacetate **27** (Fig. 3). The ^{1}H NMR spectrum of tricyclic oxime **28** did not show the characteristic AB system for CH_2NO_2 group, but a singlet (11.24 ppm) that was assigned to C*H*=N oxyminic proton; also, at 2.25 ppm appeared a singlet attributable to the methyl acetate group on the nitrogen, whereas those at 2.11, 2.07, and 2.04 ppm were assigned to methyl acetate groups on the sugar side-chain. Because of their structural analogy, the formation of **28** could be justified from **26** through conversion of its nitro group into oxime,[21] probably due to silica gel of the chromatographic plate.

Treatment of **5b** with K_2CO_3 and resin yielded oxepine **30** (Scheme 5). The structure of this compound was supported on its ^{1}H and ^{13}C NMR spectra, which were very similar to those of **14** and **23**. Formation of **30** could be explained through the intermediate **29** (Scheme 5), with subsequent attack from the first hydroxy group to the nitroalkenic double bond and rupture of the marked carbon–carbon bond. The value for the coupling constant $J_{2,3}$ (4.8 Hz) agrees with a cis-relationship between substituents at C-2 and C-3. Conventional acetylation of **30** led to tetraacetate **31** (Fig. 4) with $J_{2,3}$=4.2 Hz, thus supporting the proposed structures.

For compounds **23**–**27** and **30**,**31** we observed ^{1}H NMR signals for protons corresponding to AB systems in their respective



Scheme 4.

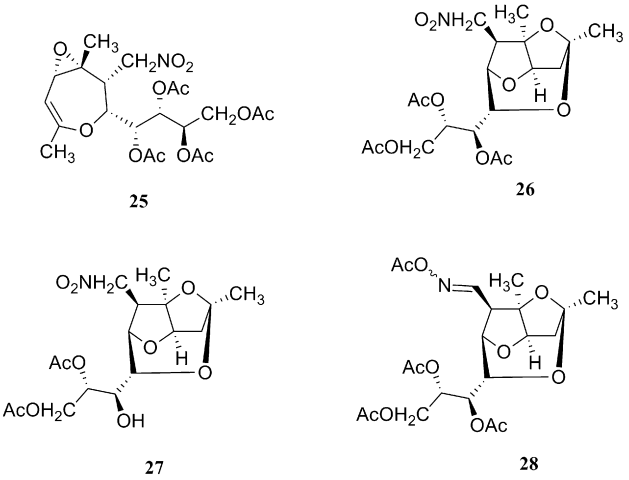
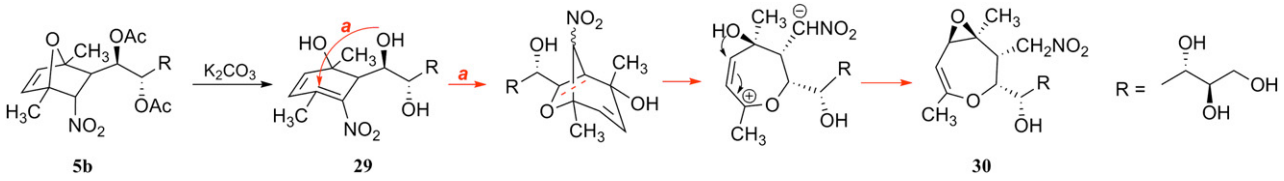


Figure 3. Structures of compounds **25**–**28**.

acid–base properties of its geminal protons and the inductive and resonance effects of this group. As far as we are aware, there is no antecedent about these new opening reactions of 7-oxanitronorbornenic systems under very mild and ecofriendly conditions.

3. Conclusions

In summary, by using high-pressure asymmetric cycloaddition between α-nitroalkenes derived from D-galactose or D-mannose and 2,5-dimethylfuran, we have obtained new optically pure 2-glyco-1,4-dimethyl-3-nitro-7-oxabicyclo[2.2.1]hept-5-enes. Their structures are based on spectroscopic data, including X-ray powder diffractometry, as well as on chemical correlations. In addition, we describe a new mild procedure for the ring opening reaction of the cycloadducts, proposing mechanisms to justify the spontaneous formation of new chiral mono-, bi-, and tricyclic ethers.



Scheme 5.

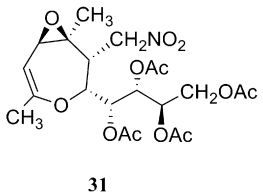


Figure 4. Structure of oxepine–epoxyde **31**.

–CH_2NO_2 groups; as cited above, these protons were exchangeable with D_2O, being this faster for those appearing at lower field.

It is noteworthy that tandem reactions here described involve up to seven processes (in the case of the formation of **24**) of rupture and formation of bonds in a single synthetic step. Once the sugar side-chain has been deacetylated, the driving force for the reactions is the activating effect of the nitro group, which affects both the

4. Experimental

4.1. General

All chemicals were purchased from commercial sources and were used directly, without further purification. Preparative TLC was performed using silica gel (Merck 60 GF_{254}). TLC was performed on precoated Merck Kieselgel 60 GF_{254} aluminum backed plates; bands were visualized by UV light, iodine vapor or *p*-anisaldehyde. NMR spectra were taken on a Bruker AC/PC (400 MHz for ^1H and 100 MHz for ^{13}C) instruments. All chemical shifts were expressed in parts per million on the respect of the residual solvent signal. Coupling constant values are recorded in hertz. Optical rotations were measured with a Perkin–Elmer 241 polarimeter in a 1 dm tube. HRMS were recorded on an AutoSpec spectrometer. High-pressure reactions were carried out by using a high-pressure apparatus U-101 (Unipress Equipment Division, High Pressure Research Center, Polish Academy of Sciences). HPLC separation was carried out using Zorbax RX-Sil

USHL001118 column (9.4×250 mm^2), following by UV-detection (Diode-Array G1315B detector).

4.2. (2*S*,3*R*)-1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-(1,4-dimethyl-3-*exo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl)-D-*galacto*-pentitol (3a), (2*R*,3*S*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(1,4-dimethyl-3-*exo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl)-D-*galacto*-pentitol (4a), and (2*R*,3*S*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(1,4-dimethyl-3-*endo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl)-D-*galacto*-pentitol (5a)

Method (A). To a solution of (*E*)-3,4,5,6,7-penta-*O*-acetyl-D-*galacto*-1-nitrohept-1-enitol[13] **1a** (1.0 g, 2.3 mmol) in CH_2Cl_2 (7.5 mL) was added 2,5-dimethylfuran **2** (1.12 mL, 11.6 mmol). After 4.5 days at room temperature under 13 kbar pressure, the solvent was evaporated, leading to an oil that consisted of a 47:10:1 mixture of cycloadducts **3a**, **4a**, and **5a**, respectively. This mixture was dissolved in the minimum quantity of ethyl acetate at room temperature and, after standing in the refrigerator, the pure adduct **3a** crystallized as a white powder (two crops; 0.43 g, 43%).

Method (B). To a solution of **1a**,[13] (0.75 g, 1.7 mmol) in $CHCl_3$ (8.0 mL) was added 2,5-dimethylfuran **2** (0.80 mL, 8.3 mmol). After 2 days at room temperature under 13 kbar pressure, the solvent was evaporated, leading to an oil that consisted of a 3.3:4.7:1.0 mixture of **3a**, **4a**, and **5a**, respectively. Working-up as described in method A yielded two crops of pure **3a** (0.21 g, 30%), together with a third crop (32 mg) containing this same cycloadduct slightly contaminated with nitroalkene **1a**. Then, the mother liquor was evaporated and the resulting residue was crystallized from methanol, yielding 0.17 g (24%) of pure **4a** and then 0.10 g of a 1:1 mixture of **4a** and **5a**.

Compound **3a**: white solid; mp 189–190 °C; $[\alpha]_D$ −37.4 (*c* 0.5, $CHCl_3$); IR (KBr): ν_{max} 2969 (C–H), 1741 (C=O), 1552, 1379 (NO_2), 1211, 1046 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 6.40 (d, 1H, $J_{5,6}$=5.5 Hz, H-6), 6.25 (d, 1H, H-5), 5.23 (dd, 1H, $J_{2',3'}$=9.5 Hz, $J_{1',2'}$=1.4 Hz, H-2′), 5.12 (dd, 1H, $J_{3',4'}$=1.8 Hz, H-3′), 5.09 (m, 1H, H-4′), 4.78 (dd, 1H, $J_{1',2}$=11.3 Hz, H-1′), 4.35 (d, 1H, $J_{2,3}$=3.4 Hz, H-3), 4.27 (dd, 1H, $J_{4',5'a}$=4.8 Hz, $J_{5'a,5'b}$=11.6 Hz, H-5′a), 3.75 (dd, 1H, $J_{4',5'b}$=7.2 Hz, H-5′b), 2.97 (dd, 1H, H-2), 2.15 (s, 3H, OAc), 2.08 (s, 6H, 2×OAc), 2.05 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.57 (s, 3H, CH_3-1), 1.49 (s, 3H, CH_3-4); ^{13}C NMR ($CDCl_3$) δ: 170.4, 170.2, 169.9, 169.8, 169.4 (O–*C*O–CH_3), 143.1 (C-6), 136.6 (C-5), 92.8 (C-3), 88.5, 87.9 (C-1,4), 71.3, 68.3, 67.8, 67.5 (C-1′,2′,3′,4′), 62.1 (C-5′), 51.3 (C-2), 21.0, 20.8, 20.7, 20.6, 20.2 (O–CO–*C*H$_3$), 18.7 (CH_3-1), 14.9 (CH_3-4); FABMS *m*/*z* (rel int.): 552 (M+Na, 7), 456 (M−CH_2OAc, 28), 311 (M−$C_9H_{13}O_6$−H, 13), 239 (M−$C_{12}H_{17}O_8$−H, 21), 237 (32), 221 (M−$C_{12}H_{17}O_8$−OH, 23), 153 (M−$C_{15}H_{21}O_{10}$−CH_3, 13), 131 (100), 91 (M−$C_{15}H_{21}O_{10}$−NO_2H−2CH_3, 42), 73 (21); HRMS (FAB) calcd for $C_{23}H_{31}NO_{13}$+Na 552.1693. Found (M+Na)$^+$ 552.1689. Compound **4a**: white solid; mp: 181–183 °C; $[\alpha]_D$=+101.9 (*c* 0.5, $CHCl_3$); IR (KBr): ν_{max} 2986 (C–H), 1748 (C=O), 1553, 1371 (NO_2), 1217, 1041 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 6.19 (d, 1H, $J_{5,6}$=5.6 Hz, H-6), 6.16 (d, 1H, H-5), 5.36 (dd, 1H, $J_{1',2'}$=2.4 Hz, $J_{2',3'}$=9.6 Hz, H-2′), 5.23 (dd, 1H, $J_{1',2}$=2.4 Hz, H-1′), 5.13 (dd, 1H, $J_{3',4'}$=2.0 Hz, H-3′), 5.06 (ddd, 1H, H-4′), 4.70 (d, 1H, $J_{2,3}$=4.0 Hz, H-3), 4.25 (dd, 1H, $J_{4',5'a}$=5.2 Hz, $J_{5'a,5'b}$=12.0 Hz, H-5′a), 3.76 (dd, 1H, $J_{4',5'b}$=7.2 Hz, H-5′b), 2.80 (dd, 1H, H-2), 2.10 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.01 (s, 9H, 3×OAc), 1.70 (s, 3H, CH_3-1), 1.48 (s, 3H, CH_3-4); ^{13}C NMR ($CDCl_3$) δ: 170.8, 170.6, 170.3, 170.2, 169.8 (O–*C*O–CH_3), 140.6 (C-6), 136.8 (C-5), 90.8 (C-3), 88.9, 87.2 (C-1,4), 70.4, 67.3, 66.7, 64.8 (C-1′,2′,3′,4′), 62.0 (C-5′), 51.8 (C-2), 21.1, 21.0, 20.9, 20.8, 20.4 (O-CO-*C*H$_3$), 17.2 (CH_3-1), 14.6 (CH_3-4); FABMS *m*/*z* (rel int.):[22] 552 (M+Na, 3), 457 (M+H−CH_2OAc, 20), 456 (M−CH_2OAc, 100), 374 (M*+H−HOAc, 40), 261 (10), 201 (22), 95 (57), 96 (75); HRMS (FAB) calcd for $C_{23}H_{31}NO_{13}$+Na 552.1693. Found 552.1698. Compound **5a**: oil; ^{1}H NMR ($CDCl_3$) δ: 6.38 (d, 1H, $J_{5,6}$=5.6 Hz, H-6), 6.04 (d, 1H, H-5), 5.50 (dd, 1H, $J_{1',2}$=4.8 Hz, $J_{1',2'}$=2.4 Hz, H-1′), 5.41 (dd, 1H, $J_{2',3'}$=9.6 Hz, H-2′), 5.23 (dd, 1H, H-3′), 5.17 (m, 1H, $J_{3',4'}$=2.0 Hz, H-4′), 4.79 (d, 1H, $J_{2,3}$=3.2 Hz, H-3), 4.28 (dd, 1H, $J_{4',5'a}$=4.8 Hz, H-5′a), 3.80 (dd, $J_{4',5'b}$=7.2 Hz, $J_{5'a,5'b}$=11.6 Hz, H-5′b), 2.51 (dd, 1H, H-2), 2.13 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.73 (s, 3H, CH_3-1), 1.69 (s, 3H, CH_3-4).

4.3. (2*S*,3*R*)-1′,2′,3′,4′,5′-Penta-*O*-acetyl-1′-*C*-(1,4-dimethyl-3-*exo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl)-D-*manno*-pentitol (3b), (2*R*,3*S*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(1,4-dimethyl-3-*exo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl)-D-*manno*-pentitol (4b), and (2*R*,3*S*)-1′,2′,3′,4′,5′-penta-*O*-acetyl-1′-*C*-(1,4-dimethyl-3-*endo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl)-D-*manno*-pentitol (5b)

To a solution of (*E*)-3,4,5,6,7-penta-*O*-acetyl-D-*manno*-1-nitrohept-1-enitol[14] **1b** (1.56 g, 3.5 mmol) in CH_2Cl_2 (2.5 mL) was added 2,5-dimethylfuran **2** (1.49 mL, 14 mmol). After 3 days at room temperature under 13 kbar pressure, the solvent was evaporated to an oily 6.8:3.5:1.0 mixture of cycloadducts **3b**, **4b**, and **5b**, respectively, from which pure **5b** (0.11 g, 7%) was isolated by column chromatography (Et_2O–light petroleum 1.5:1). A fraction (0.15 g) of the crude product was subjected to semipreparative HPLC (EtOAc–hexane 1:1, 3 mL/min, λ=270 nm), affording cycloadducts **3b** (t_R=11.6 min, 35 mg) and **4b** (t_R=10.7 min, 75 mg). Compound **3b**: oil; $[\alpha]_D$ +99.5 (*c* 0.5, $CHCl_3$); IR (NaCl): ν_{max} 2923 (C–H), 1749 (C=O), 1553, 1371 (NO_2), 1217, 1046 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 6.24 (d, 1H, $J_{5,6}$=5.6 Hz, H-6), 6.23 (d, 1H, H-5), 5.41 (dd, 1H, $J_{2',3'}$=1.6 Hz, $J_{3',4'}$=9.2 Hz, H-3′), 5.05 (dd, 1H, $J_{1',2'}$=4.8 Hz, H-2′), 5.00 (m, 1H, H-4′), 4.88 (dd, 1H, $J_{1',2}$=9.9 Hz, H-1′), 4.51 (d, 1H, $J_{2,3}$=4.0 Hz, H-3), 4.20 (dd, $J_{4',5'a}$=2.4 Hz, $J_{5'a,5'b}$=12.4 Hz, H-5′a), 4.11 (dd, 1H, $J_{4',5'b}$=4.0 Hz, H-5′b), 3.25 (dd, 1H, $J_{2,3}$=3.8 Hz, H-2), 2.12 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.64 (s, 3H, CH_3-1), 1.53 (s, 3H, CH_3-4); ^{13}C NMR ($CDCl_3$) δ: 170.7, 170.1, 169.8, 169.4, 169.1 (O–*C*O–CH_3), 141.8 (C-6), 137.3 (C-5), 94.0 (C-3), 88.7, 87.9 (C-1,4), 72.2, 69.4, 67.8, 66.5 (C-1′,2′,3′,4′), 61.0 (C-5′), 51.2 (C-2), 20.9, 20.8, 20.6, 20.3 (O–CO–*C*H$_3$), 18.6 (CH_3-1), 14.6 (CH_3-4); CIMS *m*/*z*[22] (rel int.): 530 (M+H, 1), 375 (M*+H−OAc, 25), 374 (M*+H−OAc, 100), 187 (48), 97 (35), 96 (43), 61 (42); HRMS (CI) calcd for $C_{23}H_{31}NO_{13}$+H 530.1874. Found 530.1847. Compound **4b**: oil; $[\alpha]_D$ −24.8 (*c* 0.5, $CHCl_3$); IR (NaCl): ν_{max} 2922 (C–H), 1748 (C=O), 1554, 1371 (NO_2), 1216, 1046 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 6.18 (d, 1H, $J_{5,6}$=5.5 Hz, H-6), 6.13 (d, 1H, H-5), 5.41 (dd, 1H, $J_{2',3'}$=3.0 Hz, $J_{3',4'}$=8.4 Hz, H-3′), 5.26 (dd, 1H, H-2′), 5.14 (dd, 1H, $J_{1',2'}$=4.4 Hz, $J_{1',2}$=1.8 Hz, H-1′), 4.99 (m, 1H, H-4′), 4.64 (d, 1H, $J_{2,3}$=4.1 Hz, H-3), 4.23 (dd, 1H, $J_{4',5'a}$=2.8 Hz, $J_{5'a,5'b}$=12.7 Hz, H-5′a), 4.09 (dd, 1H, $J_{4',5'b}$=5.0 Hz, H-5′b), 2.98 (dd, 1H, H-2), 2.15 (s, 3H, OAc), 2.07 (s, 6H, 2×OAc), 2.06 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.67 (s, 3H, CH_3-1), 1.52 (s, 3H, CH_3-4); ^{13}C NMR ($CDCl_3$) δ: 170.6, 169.9, 169.8, 169.7 (O–*C*O–CH_3), 140.8 (C-6), 136.9 (C-5), 91.5 (C-3), 89.2, 87.1 (C-1,4), 70.1, 68.3, 67.8, 67.6 (C-1′,2′,3′,4′), 61.2 (C-5′), 50.9 (C-2), 20.9, 20.8, 20.7, 20.6, 20.3 (O–CO–*C*H$_3$), 17.0 (CH_3–1), 14.6 (CH_3-4); CIMS *m*/*z*[22] (rel int.): 530 (M+H, 10), 375 (M*+H−OAc, 15), 374 (M*+H−HOAc, 100), 332 (M*+H−HOAc−C_2H_2O, 25), 219 (25), 187 (25), 95 (17), 61 (30); HRMS (CI) calcd for $C_{23}H_{31}NO_{13}$+H 530.1874. Found 530.1867. Compound **5b**: oil; $[\alpha]_D$=+20.8 (*c* 0.24, $CHCl_3$); IR (NaCl): ν_{max} 2917 (C–H), 1748 (C=O), 1544, 1368 (NO_2), 1218, 1033 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 6.38 (d, 1H, $J_{5,6}$=5.6 Hz, H-6), 6.07 (d, 1H, H-5), 5.50 (dd, 1H, H-3′), 5.50 (dd, 1H, H-1′), 5.28 (dd, 1H, $J_{2',3'}$=2.4 Hz, $J_{1',2'}$=9.6 Hz, H-2′), 5.06 (m, 1H, $J_{3',4'}$=9.2 Hz, H-4′), 4.92 (d, 1H, $J_{2,3}$=3.6 Hz, H-3), 4.20 (dd, 1H, $J_{4',5'a}$=2.8 Hz, $J_{5'a,5'b}$=12.8 Hz, H-5′a), 4.07 (dd, 1H, $J_{4',5'b}$=4.8 Hz, H-5′b), 2.61 (dd, 1H, $J_{1',2}$=2.8 Hz, H-2), 2.11 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.06 (s, 3H, OAc), 1.75 (s, 3H, CH_3-1), 1.73 (s, 3H, CH_3-4); ^{13}C NMR ($CDCl_3$) δ: 170.6, 170.5, 169.9, 169.6 (O–*C*O–CH_3), 143.8 (C-6), 135.9 (C-5), 91.0 (C-3), 88.1, 86.6 (C-1,4), 69.0, 68.4, 67.7, 67.3 (C-1′,2′,3′,4′), 61.8 (C-5′), 48.8 (C-2), 21.0, 20.9, 20.8, 20.7, 20.6 (O–CO–*C*H$_3$), 17.4 (CH_3-1), 16.3 (CH_3-4). CIMS *m*/*z*[22]

(rel int.): 530 (M+H, 1), 375 (M*+H−OAc, 10), 374 (M*+H−HOAc, 50), 201 (17), 187 (30), 97 (50), 96 (100), 61 (37); HRMS (CI) calcd for $C_{23}H_{31}NO_{13}$+H 530.1874. Found 530.1885.

4.4. 4,7:2,8-Dianhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitromethyl-α-D-lyxo-D-*galacto*-undec-2-ulo-2,5-furanoside (8b) and (2*R*,3*S*,4*S*,5*S*,6*R*)-5,6-epoxy-3-hydroxy-5,8-dimethyl-4-nitromethyl-2-(D-*threo*-triitol-1′-yl)-3,4-dihydro-2*H*-oxocine (9c)

To a solution of **3a** (0.40 g, 0.76 mmol) in 90% methanol (10.2 mL) was added K_2CO_3 (0.46 g) and the mixture was stirred at 0 °C for 2 h. After treatment with Amberlite IR-120 (H^+) resin until ca. pH 6, the mixture was filtered, and the solvent evaporated to an oily residue from which compound **8b** (15 mg, 8%) was isolated by PTLC (CH_2Cl_2–MeOH 7:1, three elutions). The oxocine **9c** (37 mg, 15%) was obtained by extraction of the residue with $CDCl_3$. Compound **8b**: oil; ^{1}H NMR (DMSO-d_6) δ: 4.94 (dd, 1H, $J_{1'a,1'b}$=14.5 Hz, $J_{1'a,6}$=4.8 Hz, H-1′a), 4.62 (dd, 1H, $J_{6,7}$=6.6 Hz, $J_{7,8}$=1.9 Hz, H-7), 4.61 (dd, 1H, $J_{1'b,6}$=9.2 Hz, H-1′b), 4.36 (d, 1H, $J_{3a,4}$=5.6 Hz, $J_{3b,4}$<1 Hz, H-4), 3.71 (dd, 1H, $J_{9,10}$<1 Hz, $J_{8,9}$=10.0 Hz, H-9), 3.64 (t, 1H, $J_{10,11a}$=$J_{10,11b}$=6.8 Hz, H-10), 3.63 (dd, 1H, H-8), 3.38 (dd, 1H, H-11a), 3.32 (dd, 1H, $J_{11a,11b}$=10.3 Hz, H-11b), 2.82 (ddd, 1H, $J_{6,7}$=6.6 Hz, H-6), 2.04 (dd, 1H, H-3a), 1.92 (br d, 1H, $J_{3a,3b}$=14.0 Hz, H-3b), 1.37, 1.35 (s, 3H, H-1a,1b,1c and s, 3H, CH_3-5); ^{13}C NMR (DMSO-d_6) δ: 108.4 (C-2), 89.4 (C-5), 85.5 (C-8), 77.2, 76.4 (C-7,4), 72.9 (CH_2NO_2), 69.3, 68.2 (C-9,10), 62.9 (C-11), 49.8 (C-6), 44.7 (C-3), 25.8 (C-1), 21.2 (CH_3-5). Compound **9c**: oil; ^{1}H NMR ($CDCl_3$) δ: 4.94 (br s, 1H, H-7), 4.68 (dd, 1H, $J_{1''a,1''b}$=13.6 Hz, $J_{1''a,4}$=6.0 Hz, H-1″a), 4.67 (br s, 1H, $J_{6,7}$ 1.0 Hz, $J_{6,CH3\text{-}8}$=1.2 Hz, H-6), 4.38 (dd, 1H, $J_{1''b,4}$=6.4 Hz, H-1″b), 3.99 (ddd, 1H, H-2′), 3.95 (dd, 1H, $J_{2,3}$=1.2 Hz, $J_{3,4}$=10.4 Hz, H-3), 3.82 (d, 1H, H-2), 3.82 (d, 1H, $J_{1',2'}$=4.8 Hz, H-1′), 3.70 (dd, 1H, $J_{2',3'a}$=2.4 Hz, $J_{3'a,3'b}$=7.6 Hz, H-3′a), 3.63 (dd, 1H, $J_{2',3'b}$=1.2 Hz, H-3′b), 2.98 (ddd, 1H, H-4), 1.84 (s, 3H, CH_3-8), 1.49 (s, 3H, CH_3-5); CIMS *m*/*z* (rel int.): 320 (M+H, 62), 302 (M−OH, 18), 255 (M−OH−NO_2H, 15), 242 (M−OH−CH_2NO_2, 23), 237 (M−OH−H_2O−NO_2H, 21), 228 (M−$C_3H_7O_3$, 18), 224 (M−OH−CH_2NO_2−H_2O, 18), 198 (M−$C_3H_7O_3$−NO, 30), 197 (23), 188 (26), 183 (M−$C_3H_7O_3$−NO−CH_3, 23), 181 (M−$C_3H_7O_3$−NO−OH, 18), 153 (M−$C_3H_7O_3$−CH_2NO_2−CH_3, 45), 123 (43), 113 (100), 103 (58), 97 (30), 91 (37), 87 (67), 85 (37), 84 (25), 73 (50), 69 (25), 57 (29), 48 (41); HRMS (CI) calcd for $C_{13}H_{21}NO_8$+H 320.1345. Found $(M+H)^+$ 320.1354.

4.5. (9,10,11-Tri-*O*-acetyl)-7-acetoxy-4,8-anhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitromethyl-D-lyxo-D-*galacto*-undec-2-ulo-2,5-furanose (7d), (9,10,11-tri-*O*-acetyl)-4,7:2,8-dianhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitromethyl-α-D-lyxo-D-*galacto*-undec-2-ulo-2,5-furanoside (8a), and (2*R*,3*S*,4*S*,5*S*,6*R*)-2-(1′,2′,3′-tri-*O*-acetyl-D-*threo*-triitol-1′-yl)-3-acetoxy-5,6-epoxy-5,8-dimethyl-4-nitromethyl-3,4-dihydro-2*H*-oxocine (9e)

Following the procedure described in Section 4.4, a solution of **3a** (0.30 g, 0.57 mmol) in 90% methanol (16 mL) was treated with K_2CO_3 (0.34 g), affording 0.15 g of an oily residue that was dissolved in pyridine (1.2 mL) and acetic anhydride (1.2 mL). After 12 h at −15 °C and 1 h at room temperature, the mixture was poured onto ice-cold water (30 mL), extracted with CH_2Cl_2 (3×30 mL) and washed successively with 1 M HCl (1×30 mL), saturated aqueous $NaHCO_3$ (1×30 mL), and water (1×30 mL). The organic layer was dried ($MgSO_4$) and the solvent evaporated to an oil (0.21 g) that was subjected to flash column chromatography (EtOAc–hexane 1:1), affording compounds **7d** (0.12 g, 60%), **8a** (40 mg, 20%), and **9e** (30 mg, 15%). Compound **7d**: oil; $[\alpha]_D$ +29.4 (*c* 0.54, $CHCl_3$); IR (NaCl): ν_{max} 3479, 2977 (C–H), 1746 (C=O), 1556, 1373 (NO_2), 1217, 1037 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 5.57 (dd, 1H, $J_{9,10}$=2.4 Hz, H-9), 5.37 (ddd, 1H, H-10), 5.11 (dd, 1H, $J_{7,8}$=1.6 Hz, $J_{8,9}$=9.6 Hz, H-8), 4.76 (dd, 1H, $J_{1'a,6}$=6.8 Hz, H-1′a), 4.49 (dd, 1H, $J_{1'a,1'b}$=13.6 Hz, $J_{1'b,6}$=6.0 Hz, H-1′b), 4.41 (dd, 1H, $J_{3b,4}$=4.4 Hz, H-4), 4.29 (dd, 1H, $J_{10,11a}$=5.6 Hz, H-11a), 4.27 (dd, 1H, $J_{6,7}$=8.8 Hz, H-7), 3.93 (dd, 1H, $J_{10,11b}$=7.2 Hz, $J_{11a,11b}$=11.2 Hz, H-11b), 2.58 (ddd, 1H, H-6), 2.29 (br d, 1H, $J_{3a,3b}$=14.8 Hz, H-3a), 2.09 (dd, 1H, H-3b), 2.16 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.50 (s, 3H, H-1a,1b,1c), 1.27 (s, 3H, CH_3-5); ^{13}C NMR ($CDCl_3$) δ: 170.5, 170.4, 170.1, 169.8 (O–*C*O–CH_3, C-7–O–*C*O–CH_3), 106.8 (C-2), 91.7 (C-5), 88.7 (C-4), 79.0 (C-8), 72.7 (CH_2NO_2), 68.9, 68.6, 67.9 (C-7,9,10), 62.0 (C-11), 47.3 (C-6), 44.1 (C-3), 28.2 (C-1), 22.8 (CH_3-5), 20.7, 20.6 (O–CO–*C*H_3, C-7–O–CO–*C*H_3); FABMS *m*/*z* (rel int.): 528 (M+Na, 19), 489 (M−O, 24), 488 (M−OH, 100), 446 (M−OH−C_2H_2O, 35), 428 (M−OH−HOAc, 68), 370 (M−OH-2×OAc, 34), 221 (28), 219 (37), 198 (M−$C_9H_{13}O_6$−NO−HOAc, 44), 151 (97), 123 (19), 123 (68), 109 (50), 97 (58), 96 (74), 95 (63), 81 (43), 73 (95); HRMS (FAB) calcd for $C_{21}H_{31}NO_{13}$+Na 528.1693. Found 528.1706. Compound **8a**: oil; $[\alpha]_D$ +68.0 (*c* 0.50, $CHCl_3$); IR (NaCl): ν_{max} 3455, 2936 (C–H), 1744 (C=O), 1554, 1375 (NO_2), 1223, 1049 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 5.45 (ddd, 1H, H-10), 5.23 (dd, 1H, $J_{9,10}$=1.6 Hz, H-9), 4.74 (dd, 1H, $J_{1'a,1'b}$=13.6 Hz, $J_{1'a,6}$=4.8 Hz, H-1′a), 4.56 (dd, 1H, $J_{1'b,6}$=9.6 Hz, H-1′b), 4.48 (dd, 1H, $J_{3b,4}$=4.0 Hz, $J_{3a,4}$<1.0 Hz, H-4), 4.23 (dd, 1H, $J_{11a,11b}$=12.0 Hz, $J_{10,11a}$=4.8 Hz, H-11a), 4.09 (br d, 1H, $J_{6,7}$=6.4 Hz, $J_{7,8}\approx$0 Hz, H-7), 4.06 (dd, 1H, $J_{10,11b}$=8.0 Hz, H-11b), 3.36 (d, 1H, $J_{8,9}$=9.2 Hz, H-8), 3.05 (ddd, 1H, H-6), 2.29 (br d, 1H, $J_{3a,3b}$=14.4 Hz, H-3a), 2.18 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 (dd, 1H, H-3b), 1.46 (s, 3H, H-1a,1b,1c), 1.33 (s, 3H, CH_3-5); ^{13}C NMR ($CDCl_3$) δ: 172.3, 170.5, 170.1 (O–*C*O–CH_3), 106.7 (C-2), 92.3 (C-5), 89.4 (C-4), 81.1 (C-7), 74.8 (CH_2NO_2), 70.8, 70.2, 69.6 (C-8,9,10), 62.6 (C-11), 47.9 (C-6), 43.8 (C-3), 27.4 (C-1), 22.4 (CH_3-5), 20.7, 20.6 (O–CO–*C*H_3); CIMS *m*/*z* (rel int.): 446 (M+H, 35), 428 (M+H−H_2O, 25), 386 (M+H−HOAc, 58), 331 (22), 326 (M+H−2HOAc, 20), 228 (M−$C_9H_{13}O_6$, 11), 219 (13), 198 (M−$C_9H_{13}O_6$−NO, 100), 187 (25), 169 (M−$C_9H_{13}O_6$−NO−COH, 13), 153 (M−$C_9H_{13}O_6$−HNO_2−CO, 30), 151 (21), 123 (M−$C_9H_{13}O_6$−HNO_2−CO−$2CH_3$, 27), 96 (42), 95 (63), 61 (26); HRMS (CI) calcd for $C_{19}H_{27}NO_{11}$+H 446.1662. Found 446.1642. Compound **9e**: oil; $[\alpha]_D$ +24.5 (*c* 0.51, $CHCl_3$); IR (NaCl): ν_{max} 3024 (=C–H), 2972 (C–H), 1747 (C=O), 1668 (C=C), 1559, 1373 (NO_2), 1216, 1032 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 5.54 (dd, 1H, $J_{1',2'}$=2.4 Hz, H-1′), 5.35 (m, 1H, H-2′), 5.19 (dd, 1H, $J_{1',2}$=9.6 Hz, H-2), 4.84 (br s, 1H, H-7), 4.61 (dd, 1H, $J_{1''a,4}$=7.6 Hz, H-1″a), 4.57 (br s, 1H, $J_{6,\ CH3\text{-}8}$=1.2 Hz, $J_{6,7}$<1.0 Hz, H-6), 4.43 (dd, 1H, $J_{1''b,4}$=4.4 Hz, $J_{1''a,1''b}$=14.4 Hz, H-1″b), 4.24 (dd, 1H, $J_{2',3'a}$=5.6 Hz, H-3′a), 3.94 (dd, 1H, $J_{3'a,3'b}$=11.6 Hz, $J_{2',3'b}$=7.2 Hz, H-3′b), 3.64 (dd, 1H, $J_{2,3}$=2.4 Hz, $J_{3,4}$=10.8 Hz, H-3), 2.58 (ddd, 1H, H-4), 2.12 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.81 (s, 3H, CH_3-8), 1.41 (s, 3H, CH_3-5); ^{13}C NMR ($CDCl_3$) δ: 170.4, 170.3, 170.1 (O–*C*O–CH_3), 169.2 (C-3–O–*C*O–CH_3), 160.5 (C-8), 95.1 (C-7), 91.7 (C-5), 90.4 (C-6), 75.1 (C-2), 71.4 (CH_2NO_2), 68.7, 68.0 (C-1′,2′), 66.3 (C-3), 61.9 (C-3′), 47.1 (C-4), 22.0 (CH_3-8), 20.6, 20.5 (O–CO–*C*H_3, C-3–O–CO–*C*H_3), 13.5 (CH_3-5); CIMS *m*/*z* (rel int.): 488 (M+H, 19), 429 (M+H−OAc, 20), 428 (M−HOAc, 100), 386 (M−HOAc−C_2H_2O, 14), 383 (M+H−OAc−NO_2, 14), 370 (M+H-2OAc, 26), 326 (M+H−2HOAc−C_2H_2O, 10), 325 (M−2HOAc−C_2H_2O, 18), 266 (M+H−3HOAc−C_2H_2O, 13), 265 (M−3HOAc−C_2H_2O, 40), 263 (M+H−OAc−2HOAc−NO_2, 18), 257 (39), 243 (18), 229 (M+H−$C_9H_{13}O_6$−C_2H_2O, 14), 221 (13), 203 (13), 198 (M−$C_9H_{13}O_6$−C_2H_2O−NO, 37), 153 (M−$C_9H_{13}O_6$−C_2H_2O−CH_2NO_2−CH_3, 36), 123 (15), 96 (15); HRMS (CI) calcd for $C_{21}H_{29}NO_{12}$+H 488.1768. Found 488.1754.

4.6. Methyl (9,10,11-tri-*O*-acetyl)-7-acetoxy-4,8-anhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitromethyl-D-lyxo-D-*galacto*-undec-2-ulo-2,5-furanoside (7g)

To a solution of **7d** (60 mg, 0.12 mmol) in methanol (3 mL) was added Dowex 50Wx8-100 (H^+) resin (0.3 g) and kept at 3 °C for 5

days. Then, filtration of the resin and evaporation of the solvent led to a chromatographically pure oil (52 mg, 87%) consisting of compound **7g** as a 1:1 mixture of the α and β anomers; 8.2 mg of one of these anomers could be isolated pure by PTLC (Et_2O–light petroleum 1:1); oil; IR (NaCl): ν_{max} 2920 (C–H), 1747 (C=O), 1556, 1375 (NO_2), 1218, 1057 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.55 (dd, 1H, $J_{9,10}$=2.4 Hz, H-9), 5.35 (ddd, 1H, H-10), 5.11 (dd, 1H, $J_{7,8}$=2.0 Hz, $J_{8,9}$=9.6 Hz, H-8), 4.71 (dd, 1H, $J_{1'a,6}$=8.0 Hz, H-1′a), 4.41 (dd, 1H, $J_{1'a,1'b}$=13.6 Hz, $J_{1'b,6}$=4.0 Hz, H-1′b), 4.35 (dd, 1H, $J_{3b,4}$=5.6 Hz, H-4), 4.27 (dd, 1H, $J_{10,11a}$=4.8 Hz, H-11a), 4.15 (dd, 1H, $J_{6,7}$=10.8 Hz, H-7), 3.92 (dd, 1H, $J_{10,11b}$=7.2 Hz, $J_{11a,11b}$=11.6 Hz, H-11b), 3.24 (s, 3H, OCH_3), 2.47 (ddd, 1H, H-6), 2.23 (br d, 1H, $J_{3a,3b}$=14.8 Hz, H-3a), 2.05 (dd, 1H, H-3b), 2.13 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.43 (s, 3H, H-1a,1b,1c), 1.29 (s, 3H, CH_3-5); ^{13}C NMR ($CDCl_3$) δ: 170.5, 170.4, 170.2 (O–*C*O–CH_3), 169.3 (C-7–O–*C*O–CH_3), 109.8 (C-2), 92.4 (C-5), 87.7 (C-4), 77.5 (C-8), 71.4 (CH_2NO_2), 68.7, 68.2, 66.9 (C-7,9,10), 62.2 (C-11), 49.6 (C-6), 46.8 (O–CH_3), 46.1 (C-3), 23.7, 23.5 (C-1, CH_3-5), 20.7, 20.6, 20.5, 20.3 (O–CO–*C*H_3, C-7–O–CO–*C*H_3); FABMS *m*/*z* (rel int.): 542 (M+Na, 13), 413 (M−HOAc−NO_2, 35), 385 (M−HOAc−OAc−CH_3, 20), 371 (M−HOAc−C_2H_2O−NO_2, 18), 357 (M−2HOAc−C_2H_2O, 14), 281 (M−2HOAc−C_2H_2O−2CH_3−NO_2, 13), 221 (M−3HOAc−C_2H_2O−2CH_3−NO_2, 11), 207 (18), 149 (100), 147 (57), 133 (13), 105 (19), 95 (23), 91 (29); HRMS (FAB) calcd for $C_{22}H_{33}NO_{13}$+Na 542.1849. Found 542.1853.

4.7. (2*R*,3*S*)-1′-*C*-(1,4-dimethyl-3-*exo*-nitro-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl)-D-*galacto*-pentitol (10) and 2,5-anhydro-1-deoxy-1-nitro-D-*glycero*-L-*manno*- or D-*glycero*-L-*gluco*-heptitol (11)

Following the procedure described in Section 4.4, a solution of **4a** (0.30 g, 0.57 mmol) in 90% methanol (8.4 mL) was treated with K_2CO_3 (0.33 g), affording 0.16 g (88%) of an oil with deacetylated cycloadduct **10** as the major product. After 5 days at room temperature, the ^1H NMR spectrum of the reaction crude showed the absence of **10**, and the formation of deacetylated anhydro **11** (R=H) and 2,5-dimethylfuran. Then, evaporation of the solvent and conventional acetylation of the resulting residue (0.15 g), led to an oil from which 91 mg (51%) of a 1.0:0.8 diastereoisomeric mixture of **11** (R=Ac) was isolated by PTLC (Et_2O–hexane 1:1). Compound **10**: ^1H NMR (DMSO-d_6) δ: 6.42 (d, 1H, $J_{5,6}$=5.2 Hz, H-6), 6.24 (d, 1H, H-5), 4.67 (d, 1H, $J_{2,3}$=4.0 Hz, H-3), 2.80 (dd, 1H, $J_{1',2}$=6.8 Hz, H-2), 1.55 (s, 3H, CH_3-1), 1.34 (s, 3H, CH_3-4). Compound **11** (R=Ac). Major diasteroisomer: ^1H NMR ($CDCl_3$) δ: 5.36 (m, 1H, H-6), 5.24 (t, 1H, H-4), 5.11 (dd, 1H, H-3), 4.77–4.65 (m, 3H, H-1a,1b,2), 4.34 (dd, 1H, H-7a), 4.23 (dd, 1H, H-5), 4.19 (dd, 1H, H-7b), 2.16 (s, 3H, OAc), 2.15 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.12 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$) δ: 170.6–169.4 (O–*C*O–CH_3, eight signals), 82.1 (C-5), 80.2 (C-2), 78.8 (C-3), 78.1 (C-4), 76.2 (C-1), 69.5 (C-6), 62.4 (C-7), 20.9, 20.8, 20.7 (O–CO–*C*H_3). Compound **11** (R=Ac). Minor diasteroisomer: ^1H NMR ($CDCl_3$) δ: 5.39 (dd, 1H, H-3), 5.3 (m, 1H, H-6), 5.13 (t, 1H, H-4), 4.87 (m, 1H, H-2), 4.58 (m, 2H, H-1a,1b), 4.39 (dd, 1H, H-7a), 4.12 (dd, 1H, H-7b), 4.06 (dd, 1H, H-5), 2.17 (s, 3H, OAc), 2.15 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$): δ: 170.6–169.4 (O–*C*O–CH_3, eight signals), 82.2 (C-5), 77.4 (C-4), 76.4 (C-3), 76.1 (C-2), 73.8 (C-1), 69.5 (C-6), 62.6 (C-7), 20.9, 20.8, 20.7 (O–CO–*C*H_3).

4.8. (2*R*,3*S*,4*S*,5*R*)-4,5-Epoxy-4,7-dimethyl-3-nitromethyl-2-(D-*arabino*-tetritol-1′-yl)-2,3-dihydrooxepine (14) and methyl 4,7-anhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitromethyl-D-*arabino*-L-*altro*-undec-2-ulo-2,5-furanoside (15)

Following the procedure described in Section 4.4, a solution of a mixture of **3b**, **4b**, and **5b** (3.0 g, 5.6 mmol; 6.8:3.5:1.0 ratio) in 90% methanol (75 mL) was treated with K_2CO_3 (3.3 g), affording 2.5 g of an oily residue which, by crystallization from methanol, yielded 0.2 g (8%) of the oxepine **14** as a white solid. Concentration of the solvent afforded two crops of compound **15** (0.17 g, 7%). By the same method, an analytical sample of **14** was obtained from **3b**, after PTLC (Et_2O–hexane 1:1) of the crude product. Compound **14**: $[\alpha]_D$ +1.2 (*c* 0.5, CH_3OH); IR (KBr): ν_{max} 3349, 3235 (O–H), 2936, 2849 (C–H), 1671 (C=C), 1549, 1376 (NO_2), 1077, 1034 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6) δ: 4.82 (br s, 1H, H-6), 4.75 (dd, 1H, $J_{1''a,1''b}$=14.5 Hz, $J_{1''a,3}$=5.0 Hz, H-1″a), 4.66 (br s, 1H, H-5), 4.57 (dd, 1H, $J_{1''b,3}$=7.7 Hz, H-1″b), 4.46 (d, 1H, $J_{H,OH}$=7.6 Hz, OH), 4.45 (d, 1H, $J_{H,OH}$=4.4 Hz, OH), 4.35 (t, 1H, $J_{H\text{-}4',OH}$=5.6 Hz, OH-4′), 4.32 (d, 1H, $J_{H,OH}$=7.2 Hz, OH), 3.69 (t, 1H, $J_{1',2}$=8.4 Hz, $J_{1',2'}\approx$1 Hz, H-1′), 3.56 (ddd, 1H, $J_{3',4'a}$=2.6 Hz, $J_{4'a,4'b}$=10.6 Hz, H-4′a), 3.49 (t, 1H, $J_{2,3}$=8.8 Hz, H-2), 3.34 (m, 3H, H-2′,3′,4′b), 2.75 (ddd, 1H, H-3), 1.78 (s, 3H, CH_3-7), 1.36 (s, 3H, CH_3-4). ^{13}C NMR (DMSO-d_6) δ: 159.0 (C-7), 96.5 (C-6), 92.7 (C-4), 90.1 (C-5), 77.2 (C-2), 73.7 (CH_2NO_2), 71.7, 70.9, 70.4 (C-1′,2′,3′), 63.8 (C-4′), 51.2 (C-3), 22.8 (CH_3-7), 13.6 (CH_3-4); ClMS *m*/*z* (rel int.): 320 (M+H, 100), 304 (M+H−O, 12), 302 (M+H−H_2O, 28), 284 (M+H−2H_2O, 9), 237 (M−2H_2O−NO_2, 5), 198 (M−$C_4H_9O_4$, 19), 28 (11). HRMS (CI) calcd for $C_{13}H_{21}NO_8$+H−O 304.1396. Found 304.1381. Compound **15** (major anomer): white solid; ^1H NMR (DMSO-d_6) δ: 4.68 (d, 1H, $J_{1'a,6}$=5.6 Hz, $J_{1'a,1'b}$=15.2 Hz, H-1′a), 4.67 (d, 1H, $J_{1'b,6}$=7.6 Hz, H-1′b), 4.48 (d, 1H, $J_{H,OH}$=6.8 Hz, OH), 4.42 (dd, 1H, H-4), 4.40 (d, 1H, $J_{H,OH}$=7.2 Hz, OH), 4.34 (t, 1H, $J_{H\text{-}11,OH}$=5.2 Hz, OH-11), 4.32 (d, 1H, OH), 3.69 (t, 1H, $J_{6,7}$=8.0 Hz, $J_{7,8}$=9.2 Hz, H-7), 3.68 (m, 1H, H-8), 3.57 (m, 1H, H-11a), 3.37 (m, 3H, H-9,10,11b), 3.08 (s, 3H, OCH_3), 2.69 (ddd, 1H, H-6), 2.26 (dd, 1H, $J_{3a,4}$=6.8 Hz, $J_{3a,3b}$=14.0 Hz, H-3a), 1.93 (dd, 1H, $J_{3b,4}$=4.0 Hz, H-3b), 1.36 (s, 3H, CH_3-5), 1.35 (s, 3H, H-1a,1b,1c). ^{13}C NMR (DMSO-d_6) δ: 110.0 (C-2), 91.6 (C-5), 88.2 (C-4), 79.5 (C-7), 74.3 (CH_2NO_2), 71.7, 71.1, 70.4 (C-8,9,10), 64.0 (C-11), 51.2 (C-6), 48.8 (OCH_3), 45.0 (C-3), 24.7 (C-1), 22.5 (CH_3-5).

4.9. Methyl 4,8-anhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitromethyl-D-*arabino*-L-*altro*-undec-2-ulo-2,5-furanoside (16)

Following the procedure described in Section 4.4, a solution of **3b** (0.11 g, 0.21 mmol) in 90% methanol (2.8 mL) was treated with K_2CO_3 (0.12 g), affording 53 mg of an oily mixture containing compounds **14**, **15**, and **16**. Pure **16** (6.6 mg, 12%) was isolated by PTLC (EtOAc–EtOH 16:1). Compound **16**: oil; ^1H NMR (DMSO-d_6) δ: 4.81 (dd, $J_{1'a,1'b}$=14.8 Hz, $J_{1'a,6}$=6.4 Hz, H-1′a), 4.56 (dd, 1H, $J_{1'b,6}$=10.0 Hz, H-1′b), 4.25 (dd, 1H, H-4), 4.06 (dd, 1H, $J_{6,7}$=6.8 Hz, H-7), 3.74 (br d, 1H, $J_{7,8}$=10.0 Hz, H-8), 3.58 (ddd, $J_{10,11a}$=2.4 Hz, $J_{11a,11b}$=10.8 Hz, H-11a), 3.40 (m, 1H, H-10), 3.35 (d, 1H, $J_{9,10}$=8.4 Hz, $J_{8,9}\approx$0 Hz, H-9), 3.35 (dd, 1H, $J_{10,11b}$=3.6 Hz, H-11b), 3.03 (s, 3H, OCH_3), 2.86 (ddd, 1H, H-6), 2.31 (dd, 1H, $J_{3a,3b}$=14.0 Hz, $J_{3a,4}$=7.6 Hz, H-3a), 1.92 (dd, 1H, $J_{3b,4}$=3.6 Hz, H-3b), 1.40 (s, 3H, H-1a,1b,1c), 1.32 (s, 3H, CH_3-5).

4.10. Methyl (8,9,10,11-tetra-*O*-acetyl)-4,7-anhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitromethyl-D-*arabino*-L-*altro*-undec-2-ulo-2,5-furanoside (18)

Conventional acetylation of **15** (48 mg, 0.15 mmol) with 1:1 Ac_2O–pyridine (0.8 mL) led to an oil from which oily compound **18** (27 mg, 38%) was isolated by PTLC (EtOAc–hexane 2:1); $[\alpha]_D$ −22.5 (*c* 0.4, $CDCl_3$); IR (NaCl): ν_{max} 2964 m, 2926 m (C–H), 1748 f (C=O), 1556 m, 1374 m (NO_2), 1219 f, 1048 m (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.50 (dd, 1H, $J_{9,10}$=8.8 Hz, H-9), 5.16 (dd, 1H, $J_{8,9}$=2.4 Hz, H-8), 5.10 (ddd, 1H, H-10), 4.71 (dd, $J_{1'a,1'b}$=14.0 Hz, $J_{1'a,6}$=5.2 Hz, H-1′a), 4.48 (dd, 1H, H-4), 4.37 (dd, 1H, $J_{1'b,6}$=7.2 Hz, H-1′b), 4.26 (dd, $J_{10,11a}$=2.8 Hz, H-11a), 4.11 (dd, 1H, $J_{10,11b}$=5.2 Hz, $J_{11a,11b}$=12.0 Hz, H-11b), 3.86 (dd, 1H, $J_{6,7}$=8.0 Hz, $J_{7,8}$=6.8, H-7), 3.19 (s, 3H, OCH_3), 2.72 (ddd, 1H, H-6), 2.40 (dd, 1H, $J_{3a,3b}$=14.4 Hz, $J_{3a,4}$=6.4 Hz, H-3a), 2.02 (dd, 1H, $J_{3b,4}$=2.0 Hz, H-3b), 2.11 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 1.47 (s, 3H, H-1a,1b,1c), 1.39 (s, 3H, CH_3-5). ^{13}C NMR ($CDCl_3$) δ: 170.7, 170.4, 170.0, 169.6 (O–*C*O–

CH_3), 109.8 (C-2), 91.5 (C-5), 88.3 (C-4), 79.4 (C-7), 73.4 (CH_2NO_2), 70.2, 68.2, 68.1 (C-8,9,10), 61.7 (C-11), 50.3 (C-6), 48.8 (OCH_3), 46.1 (C-3), 22.9, 22.3 (C-1, CH_3-5), 20.8, 20.7, 20.6 (O–CO–CH_3). ESI MS *m*/*z* (rel int.): 504 (M−CH_3, 10), 488 (M−OCH_3, 100), 489 (M−NO, 41), 473 (M−NO_2, 29), 472 (M−HNO_2, 47), 461 (28), 460 (M+H−HOAc, 80), 446 (M−OCH_3−C_2H_2O, 36), 429 (M−NO−HOAc, 18), 428 (M−OCH_3−HOAc, 68), 370 (M−OCH_3−HOAc−NO−CO, 14), 369 (11), 355 (M−OCH_3−HOAc−NO−CO−CH_3, 14), 329 (12), 289 (11), 198 (M−$HOCH_3$−$C_{12}H_{17}O_8$, 20), 183 (M−$C_{12}H_{17}O_8$−NO_2H, 22), 151 (M−$HOCH_3$−$C_{12}H_{17}O_8$−HNO_2, 11), 127 (19), 123 (11); HRMS (ESI) calcd for $C_{21}H_{30}NO_{12}$ 488.1763. Found 488.1765.

4.11. (2*R*,3*S*,4*S*,5*R*)-(1′,2′,3′,4′-Tetra-*O*-acetyl-D-*arabino*-tetritol-1′-yl)-4,5-epoxy-4,7-dimethyl-3-nitromethyl-2,3-dihydrooxepine (19)

Conventional acetylation of **14** (40 mg, 0.13 mmol) with 1:1 Ac_2O–pyridine (0.6 mL) led to an oil from which oily compound **19** (34 mg, 63%) was isolated by PTLC (EtOAc–hexane 2:1); IR (NaCl): ν_{max} 2919 (C–H), 1747 (C=O), 1661 (C=C), 1557, 1373 (NO_2), 1219, 1043 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.51 (dd, 1H, $J_{1',2'}$=2.0 Hz, $J_{2',3'}$=8.8 Hz, H-2′), 5.16 (dd, 1H, $J_{1',2}$=5.7 Hz, H-1′), 5.11 (m, 1H, H-3′), 4.82 (br s, 1H, H-6), 4.66 (br s, 1H, H-5), 4.65 (dd, 1H, $J_{1''a,1''b}$=14.3 Hz, $J_{1''a,3}$=5.3 Hz, H-1″a), 4.33 (dd, 1H, $J_{1''b,3}$=6.8 Hz, H-1″b), 4.26 (dd, 1H, $J_{3',4'a}$=2.5 Hz, $J_{4'a,4'b}$=12.4 Hz, H-4′a), 4.11 (dd, 1H, $J_{3',4'b}$=5.1 Hz, H-4′b), 3.71 (dd, 1H, $J_{2,3}$=9.2 Hz, H-2), 2.92 (m, 1H, H-3), 2.11 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.80 (s, 3H, CH_3-7), 1.26 (s, 3H, CH_3-4); ^{13}C NMR ($CDCl_3$) δ: 170.7, 170.4, 170.0, 169.7 (O–*C*O–CH_3), 160.1 (C-7), 95.8 (C-6), 92.3 (C-4), 91.1 (C-5), 78.2 (C-2), 73.1 (CH_2NO_2), 69.9, 68.1, 67.7 (C-1′,2′,3′), 61.8 (C-4′), 49.5 (C-3), 22.6 (CH_3-7), 20.8, 20.7 (O–CO–*C*H_3), 13.7 (CH_3-4); FABMS *m*/*z* (rel int.): 470 (M−OH, 1), 468 (M−OH−H_2, 15), 355 (M−HOAc−C_2H_2O−NO, 1), 300 (M−OH−H_2−2HOAc−NO_2, 15), 281 (5), 221 (M−OH−H_2−3HOAc−NO_2, 5), 207 (61), 193 (2), 147 (15), 133 (100), 108 (2); HRMS (FAB) calcd for $C_{21}H_{29}NO_{12}$−OH 470.1662. Found 470.1674.

4.12. Methyl (9,10,11-tri-*O*-acetyl)-7-acetoxy-4,8-anhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitromethyl-D-*arabino*-L-*altro*-undec-2-ulo-2,5-furanoside (20) and ethyl (9,10,11-tri-*O*-acetyl)-7-acetoxy-4,8-anhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitromethyl-D-*arabino*-L-*altro*-undec-2-ulo-2,5-furanoside (21)

Following the procedure described in Section 4.5, treatment of the mixture **3b**–**5b** (0.15 g, 0.28 mmol) led to an oil from which the pure compounds **20** (14.1 mg, 13%) and **21**(11.7 mg, 10%) were isolated by PTLC (EtOAc–hexane 2:1). Compound **20**: oil; $[\alpha]_D$ +46.4 (*c* 0.56, $CDCl_3$); IR (NaCl): ν_{max} 2964, 2926 (C–H), 1747 (C=O), 1557, 1372 (NO_2), 1215, 1057 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.48 (dd, 1H, $J_{9,10}$=8.8 Hz, H-9), 5.45 (dd, 1H, $J_{8,9}$=2.4 Hz, H-8), 5.00 (ddd, 1H, H-10), 4.65 (dd, $J_{1'a,1'b}$=15.2 Hz, $J_{1'a,6}$=6.4 Hz, H-1′a), 4.47 (dd, 1H, $J_{1'b,6}$=9.2 Hz, H-1′b), 4.34 (dd, 1H, H-4), 4.24 (dd, $J_{10,11a}$=2.8 Hz, H-11a), 4.09 (dd, 1H, $J_{6,7}$=6.0 Hz, $J_{7,8}$=7.6, H-7), 4.05 (dd, 1H, $J_{10,11b}$=5.6 Hz, $J_{11a,11b}$=12.4 Hz, H-11b), 3.15 (s, 3H, OCH_3), 2.82 (ddd, 1H, H-6), 2.47 (dd, 1H, $J_{3a,3b}$=14.0 Hz, $J_{3a,4}$=6.0 Hz, H-3a), 1.99 (dd, 1H, $J_{3b,4}$=3.6 Hz, H-3b), 2.13 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.47 and 1.46 (s, 3H, H-1a,1b,1c and s, 3H, CH_3-5). ^{13}C NMR ($CDCl_3$) δ: 170.6, 170.1, 169.9, 169.4 (O–*C*O–CH_3), 111.5 (C-2), 92.3 (C-5), 88.5 (C-4), 78.9 (C-8), 71.6 (CH_2NO_2), 69.2, 68.3, 68.0 (C-7,9,10), 61.8 (C-11), 48.7, 48.6 (C-6, OCH_3), 47.1 (C-3), 24.6 (C-1), 21.6 (CH_3-5), 20.9, 20.7 (O–CO–CH_3); ESI MS *m*/*z* (rel int.): 504 (M−CH_3, 8), 489 (M−NO, 59), 488 (M−OCH_3, 100), 473 (M−NO_2, 17), 472 (M−HNO_2, 24), 460 (M+H−HOAc, 33), 446 (M−OCH_3−C_2H_2O, 8), 428 (M−OCH_3−HOAc, 25), 355 (M−OCH_3−HOAc−NO−CO−CH_3, 9), 329 (10), 198 (M−$HOCH_3$−$C_9H_{13}O_6$−HOAc−CH_3, 10), 183 (M−$HOCH_3$−$C_9H_{13}O_6$−HOAc−NO, 12), 127 (26); HRMS (ESI) calcd for $(M-OCH_3)^+$ $C_{21}H_{30}NO_{12}$ 488.1763. Found 488.1753. Compound **21**: oil; ^1H NMR ($CDCl_3$) δ: 5.48 (dd, 1H, $J_{9,10}$=8.8 Hz, H-9), 5.45 (dd, 1H, $J_{8,9}$=2.4 Hz, H-8), 5.00 (ddd, 1H, H-10), 4.64 (dd, $J_{1'a,1'b}$=15.2 Hz, $J_{1'a,6}$=6.4 Hz, H-1′a), 4.47 (dd, 1H, $J_{1'b,6}$=8.8 Hz, H-1′b), 4.34 (dd, 1H, H-4), 4.24 (dd, $J_{10,11a}$=2.8 Hz, H-11a), 4.10 (dd, 1H, $J_{6,7}$=6.4 Hz, $J_{7,8}$=8.4 Hz, H-7), 4.05 (dd, 1H, $J_{10,11b}$=5.6 Hz, $J_{11a,11b}$=12.4 Hz, H-11b), 3.48 (dt, 1H, J_{gem}=9.2 Hz, $J_{H,CH3}$=7.2 Hz, OCH_2CH_3), 3.40 (dt, 1H, OCH_2CH_3), 2.88 (ddd, 1H, H-6), 2.48 (dd, 1H, $J_{3a,3b}$=14.8 Hz, $J_{3a,4}$=7.2 Hz, H-3a), 1.99 (dd, 1H, $J_{3b,4}$=3.6 Hz, H-3b), 2.13 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.48 (s, 6H, H-1a,1b,1c, CH_3-5), 1.10 (t, 3H, OCH_2CH_3).

4.13. (2*R*,3*R*,4*R*,5*S*)-4,5-Epoxy-4,7-dimethyl-3-nitromethyl-2-(D-*arabino*-tetritol-1′-yl)-2,3-dihydrooxepine (23) and 4,7:2,8-dianhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitro-methyl-β-D-*arabino*-L-*galacto*-undec-2-ulo-2,5-furanoside (24)

Following the procedure described in Section 4.4, treatment of **4b** (0.10 g, 0.19 mmol) in 90% methanol (2.8 mL) with K_2CO_3 (0.11 g), afforded 0.049 g of an oily residue from which the pure compounds **23** (5.2 mg, 10%) and **24** (3.2 mg, 7%) were isolated by PTLC (EtOAc–EtOH 16:1). Compound **23**: oil; ^1H NMR (DMSO-d_6) δ: 4.83 (br s, 1H, H-6), 4.82 (dd, 1H, $J_{1''a,1''b}$=14.8 Hz, $J_{1''a,3}$=5.4 Hz, H-1″a), 4.54 (br s, 1H, H-5), 4.36 (dd, 1H, $J_{1''b,3}$=10.0 Hz, H-1″b), 3.93 (dd, 1H, $J_{2,3}$=5.7 Hz, H-2), 3.67 (br d, 1H, $J_{1',2}$=9.6 Hz, $J_{1',2'}\approx$1 Hz, H-1′), 3.57 (dd, 1H, $J_{3',4'a}$=2.9 Hz, $J_{4'a,4'b}$=11.2 Hz, H-4′a), 3.35 (m, 3H, H-2′,3′,4′b), 3.05 (ddd, 1H, H-3), 1.70 (s, 3H, CH_3-7), 1.38 (s, 3H, CH_3-4). Compound **24**: oil; ^1H NMR (DMSO-d_6) δ: 5.13 (dd, 1H, $J_{1'a,1'b}$=16.4 Hz, $J_{1'a,6}$=10.0 Hz, H-1′a), 4.71 (dd, 1H, $J_{1'b,6}$=3.6 Hz, H-1′b), 4.70 (d, 1H, $J_{H\text{-}9,OH}$=6.8 Hz, OH-9), 4.48 (d, 1H, $J_{H\text{-}10,OH}$=5.6 Hz, OH-10), 4.38 (d, 1H, $J_{3b,4}$=6.8 Hz, H-4), 4.31 (t, 1H, $J_{H\text{-}11,OH}$=3.2 Hz, OH-11), 4.30 (d,1H, $J_{6,7}$=6.4 Hz, $J_{7,8}\approx$0 Hz, H-7), 4.29 (d, 1H, H-8), 3.50 (dd, 1H, $J_{10,11a}$=3.2 Hz, H-11a), 3.39 (m, 1H, H-10), 3.33 (dd, 1H, $J_{11a,11b}$=11.2 Hz, $J_{10,11b}$=2.0 Hz, H-11b), 3.27 (dd, 1H, $J_{9,10}$=8.8 Hz, $J_{8,9}$=2.4 Hz, H-9), 2.62 (ddd, 1H, H-6), 2.28 (d, 1H, $J_{3a,3b}$=14.8 Hz, $J_{3a,4}\approx$0 Hz, H-3a), 1.98 (dd, 1H, H-3b), 1.40 (s, 3H, H-1a,1b,1c), 1.37 (s, 3H, CH_3-5); CIMS *m*/*z* (rel int.): 322 (M+3, 36), 321 (M+2, 100), 320 (M+1, 93), 319 (M^+, 9), 303 (M−O, 24), 302 (M−OH, 19), 279 (18), 259 (19), 258 (18), 229 (M+H−$C_3H_7O_3$, 19), 228 (M−$C_3H_7O_3$, 23), 199 (M+H−$C_3H_7O_3$−NO, 20), 198 (M−$C_3H_7O_3$−NO, 22), 153 (20), 151 (21), 139 (24), 124 (55), 123 (76), 113 (27), 97 (40), 96 (33), 85 (34); HRMS (CI) calcd for $C_{13}H_{21}NO_8$+H 320.1345. Found 320.1346.

4.14. (2*R*,3*R*,4*R*,5*S*)-(1′,2′,3′,4′-Tetra-*O*-acetyl-D-*arabino*-tetritol-1′-yl)-4,5-epoxy-4,7-dimethyl-3-nitromethyl-2,3-dihydrooxepine (25), (9,10,11-tri-*O*-acetyl)-4,7:2,8-dianhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitromethyl-β-D-*arabino*-L-*galacto*-undec-2-ulo-2,5-furanoside (26), (10,11-di-*O*-acetyl)-4,7:2,8-dianhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-nitromethyl-β-D-*arabino*-L-*galacto*-undec-2-ulo-2,5-furanoside (27), and (9,10,11-tri-*O*-acetyl)-4,7:2,8-dianhydro-1,3,6-trideoxy-5-*C*-methyl-6-*C*-(*N*-acetoxy-oxime)-β-D-*arabino*-L-*galacto*-undec-2-ulo-2,5-furanoside (28)

Following the same procedure described in Section 4.5, compound **4b** (0.12 g, 0.23 mmol) led to an oily mixture, from which **25** (3.3 mg, 4%), **26** (13 mg, 17%), **27** (5.6 mg, 7%), and **28** (3.6 mg, 5%) were isolated pure by PTLC (EtOAc–hexane 2:1). Compound **25**: oil; IR (NaCl): ν_{max} 2926 (C–H), 1747 (C=O), 1665 (C=C–O), 1557, 1372 (NO_2), 1217, 1042 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.49 (dd, 1H, $J_{1',2'}$=2.0 Hz, $J_{2',3'}$=8.4 Hz, H-2′), 5.34 (dd, 1H, $J_{1',2}$=9.2 Hz, H-1′), 5.01 (m, 1H, H-3′), 4.91 (br s, 1H, H-6), 4.72 (br s, 1H, $J_{3,5}\approx$1 Hz, H-5), 4.58 (dd, 1H, $J_{1''a,1''b}$=15.2 Hz, $J_{1''a,3}$=8.0 Hz, H-1″a), 4.44 (dd, 1H, $J_{1''b,3}$=6.8 Hz, H-1″b), 4.21 (dd, 1H, $J_{3',4'a}$=2.8 Hz, $J_{4'a,4'b}$=12.4 Hz, H-

4′a), 4.10 (dd, 1H, $J_{2,3}$=6.0 Hz, H-2), 4.04 (dd, 1H, $J_{3',4'b}$=6.0 Hz, H-4′b), 3.08 (ddd, 1H, H-3), 2.11 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.05 (s, 6H, 2×OAc), 1.85 (s, 3H, CH_3-7), 1.43 (s, 3H, CH_3-4); FABMS *m*/*z* (rel int.): 489 (M+2, 25), 488 (M+H, 100), 428 (M+H−HOAc, 39), 383 (M+H−HOAc−NO−CH_3, 22), 368 (M+H−2HOAc, 24), 322 (M+H−2HOAc−NO_2, 17), 308 (M+H−3HOAc, 16), 263 (M+H−2HOAc−NO_2−OAc, 25), 261 (M−3HOAc−NO_2, 32), 221 (M−OH−H_2−3HOAc−NO_2, 26), 219 (M−3HOAc−NO_2−C_2H_2O, 23), 201 (M−4HOAc−NO_2, 10), 198 (M−$C_{12}H_{17}O_8$, 77), 151 (M−$C_{12}H_{17}O_8$−HNO_2, 15), 149 (39), 129 (18), 123 (M−$C_{12}H_{17}O_8$−CO−HNO_2, 35), 113 (21), 109 (26), 97 (32), 96 (86), 95 (48); HRMS (FAB) calcd for $C_{21}H_{29}NO_{12}+H^+$ 488.1768. Found 488.1784. Compound **26**: oil; $[\alpha]_D$ +18.6 (*c* 0.36, $CHCl_3$); IR (NaCl): ν_{max} 2964 (C–H), 1745 (C═O), 1552, 1371 (NO_2), 1217, 1041 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.38 (t, 1H, $J_{9,10}$=$J_{8,9}$=5.6 Hz, H-9), 5.21 (ddd, 1H, H-10), 5.07 (dd, 1H, $J_{1'a,1'b}$=16.0 Hz, $J_{1'a,6}$=8.8 Hz, H-1′a), 4.67 (dd, 1H, $J_{1'b,6}$=3.6 Hz, H-1′b), 4.55 (d, 1H, $J_{6,7}$=6.0 Hz, $J_{7,8}\approx$0 Hz, H-7), 4.44 (d, 1H, $J_{3b,4}$=6.8 Hz, H-4), 4.43 (dd, 1H, $J_{10,11a}$=2.8 Hz, H-11a), 4.33 (d, 1H, $J_{8,9}$=5.6 Hz, H-8), 4.08 (dd, 1H, $J_{11a,11b}$=12.4 Hz, $J_{10,11b}$=6.8 Hz, H-11b), 2.72 (ddd, 1H, H-6), 2.36 (d, 1H, $J_{3a,3b}$=15.2 Hz, $J_{3a,4}\approx$0 Hz, H-3a), 2.10 (dd, 1H, H-3b), 2.08 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.47 (s, 3H, H-1a,1b,1c), 1.46 (s, 3H, CH_3-5); ^{13}C NMR ($CDCl_3$) δ: 170.7, 170.0, 169.8 (O–*C*O–CH_3), 108.7 (C-2), 88.8 (C-5), 85.6 (C-4), 80.9, 79.9 (C-7,8), 71.5 (CH_2NO_2), 70.6, 70.5 (C-9,10), 61.8 (C-11), 51.3 (C-6), 42.3 (C-3), 24.4 (C-1), 21.7 (CH_3-5), 20.8, 20.7, 20.3 (O–CO–*C*H_3). ESI MS *m*/*z* (rel int.): 447 (M+2, 38), 446 (M+H, 100), 428 (M+H−H_2O, 29), 388 (11), 386 (M+H−HOAc, 28), 326 (M+H−2HOAc, 11), 228 (M−$C_9H_{13}O_6$, 6), 198 (M−$C_9H_{13}O_6$−NO, 6), 187 (9), 169 (M−$C_9H_{13}O_6$−NO−CO−H, 10), 123 (M−$C_9H_{13}O_6$−HNO_2−CO−$2CH_3$, 67); HRMS (ESI) calcd for $C_{21}H_{29}NO_{13}$+Na 468.1476. Found 468.1465. Compound **27**: oil; $[\alpha]_D$=−7.8 (*c* 0.4, $CHCl_3$); IR (NaCl): ν_{max} 3473 (O–H), 2967 (C–H), 1745 (C═O), 1554, 1376 (NO_2), 1223, 1048 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.18 (dd, 1H, $J_{1'a,1'b}$=15.6 Hz, $J_{1'a,6}$=9.6 Hz, H-1′a), 5.06 (dd, 1H, H-10), 4.57 (dd, 1H, $J_{1'b,6}$=3.6 Hz, H-1′b), 4.52 (d, 1H, $J_{6,7}$=6.0 Hz, $J_{7,8}\approx$0 Hz, H-7), 4.45 (d, 1H, $J_{3b,4}$=7.2 Hz, H-4), 4.42 (dd, 1H, $J_{10,11a}$=2.8 Hz, H-11a), 4.36 (dd, 1H, $J_{11a,11b}$=13.2 Hz, $J_{10,11b}$=3.6 Hz, H-11b), 4.16 (d, 1H, $J_{8,9}$=2.4 Hz, H-8), 3.76 (ddd, 1H, $J_{9,10}$=8.0 Hz, H-9), 2.87 (d, 1H, $J_{H\text{-}9,OH}$=6.4 Hz, OH-9), 2.81 (ddd, 1H, H-6), 2.31 (d, 1H, $J_{3a,3b}$=15.2 Hz, $J_{3a,4}\approx$0 Hz, H-3a), 2.03 (dd, 1H, H-3b), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.46 and 1.49 (s, 3H, H-1a,1b,1c) and (s, 3H, CH_3-5); ^{13}C NMR ($CDCl_3$) δ: 171.5, 169.7 (O-*C*O-CH_3), 108.8 (C-2), 88.9 (C-5), 85.6 (C-8), 81.8, 80.8 (C-7,4), 71.9 (CH_2NO_2), 71.5, 70.1 (C-9,10), 62.5 (C-11), 51.1 (C-6), 42.6 (C-3), 24.6 (C-1), 21.7 (CH_3-5), 21.0, 20.9, 20.8 (O–CO–*C*H_3); ESI MS *m*/*z* (rel int.): 405 (M+2, 7), 404 (M+H, 38), 386 (M+H−H_2O, 8), 344 (M+H−HOAc, 8), 326 (M+H−H_2O−HOAc, 6), 258 (8), 228 (M−$C_7H_{11}O_5$, 29), 169 (M−$C_7H_{11}O_5$−NO−CO−H, 8), 139 (12), 123 (M−$C_7H_{11}O_5$−HNO_2−CO−$2CH_3$, 100), 113 (11), 97 (10), 81 (12); HRMS (ESI) calcd for $C_{17}H_{25}NO_{11}$+H 404.1551. Found 404.1545. Compound **28**: oil; ^1H NMR ($CDCl_3$) δ: 11.24 (s, 1H, C*H*═NOAc), 5.35 (dd, 1H, $J_{9,10}$=6.4 Hz, H-9), 5.26 (ddd, 1H, H-10), 4.54 (d, 1H, H-7), 4.46 (d, 1H, $J_{3b,4}$=6.4 Hz, H-4), 4.37 (dd, 1H, $J_{10,11a}$=2.8 Hz, H-11a), 4.35 (d, 1H, $J_{8,9}$=4.4 Hz, H-8), 4.06 (dd, 1H, $J_{11a,11b}$=12.4 Hz, $J_{10,11b}$=6.4 Hz, H-11b), 3.01 (d, 1H, $J_{6,7}$=6.4 Hz, H-6), 2.37 (d, 1H, $J_{3a,3b}$=13.2 Hz, $J_{3a,4}\approx$0 Hz, H-3a), 2.08 (dd, 1H, H-3b), 2.25 (s, 3H, NOAc), 2.11 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.60 (s, 6H, H-1a,1b,1c, CH_3-5); ^{13}C NMR ($CDCl_3$) δ: 170.7, 170.4, 169.7 (O–*C*O–CH_3), 167.6 (N–O–*C*O–CH_3), 163.0 (*C*H–N–OAc), 109.1 (C-2), 87.5 (C-5), 86.3 (C-4), 81.2, 80.9 (C-7,8), 70.2, 70.1 (C-9,10), 62.0 (C-11), 59.8 (C-6), 42.0 (C-3), 24.4 (C-1), 22.5 (CH_3-5), 21.1, 20.9, 20.7 (O–CO–*C*H_3), 18.3 (N–O–CO–*C*H_3); ESI MS *m*/*z* (rel int.): 471 (M^+, 20), 470 (M−H, 84), 428 (M−C_2H_3O, 42), 427 (M−H−C_2H_3O, 67), 414 (14), 413 (M−C_2H_3O−CH_3, 67), 358 (15), 353 (M−C_2H_3O−CH_3−HOAc, 13), 238 (M−$C_9H_{13}O_6$−O, 10), 210 (M−$C_9H_{13}O_6$−H−C_2H_3O, 12), 195 (M−$C_9H_{13}O_6$−OAc, 12), 187 (13), 181 (M−$C_9H_{13}O_6$−C_2H_3O−CH_3, 15), 139 (100), 138 (14), 123 (14), 115 (15), 109 (11), 97 (23), 96 (49), 95 (23); HRMS (ESI) calcd for $C_{21}H_{29}NO_{11}$−H 470.1657. Found 470.1659.

4.15. (2*R*,3*R*,4*S*,5*R*)-4,5-Epoxy-4,7-dimethyl-3-nitromethyl-2-(D-*arabino*-tetritol-1′-yl)-2,3-dihydrooxepine (30)

Following the procedure described in Section 4.4, a solution of **5b** (0.10 g, 0.19 mmol) in 90% methanol (2.8 mL) was treated with K_2CO_3 (0.11 g), affording compound **30** (53 mg, 87%) as a chromatographically pure oil; $[\alpha]_D$ +8.8 (*c* 0.5, DMSO); IR (NaCl): ν_{max} 3368 (O–H), 2935 (C–H), 1658 (C═C–O), 1554, 1376 (NO_2), 1076, 1034 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6) δ: 4.92 (dd, 1H, $J_{1''a,1''b}$=15.2 Hz, $J_{1''a,3}$=4.0 Hz, H-1″a), 4.74 (br s, 1H, H-6), 4.66 (br s, 1H, H-5), 4.60 (dd, 1H, $J_{1''b,3}$=10.0 Hz, H-1″b), 3.98 (dd, 1H, $J_{2,3}$=4.8 Hz, $J_{1',2}$=9.6 Hz, H-2), 3.68 (br d, 1H, H-1′), 3.58 (dd, 1H, $J_{3',4'a}$=3.2 Hz, $J_{4'a,4'b}$=10.8 Hz, H-4′a), 3.5–3.2 (m, 3H, H-2′,3′,4′b), 3.08 (m, 1H, H-3), 1.80 (s, 3H, CH_3-7), 1.25 (s, 3H, CH_3-4); ^{13}C NMR (DMSO-d_6) δ: 159.3 (C-7), 95.3 (C-6), 94.1 (C-4), 88.7 (C-5), 75.9 (C-2), 72.7 (CH_2NO_2), 70.7, 70.2, 66.8 (C-1′,2′,3′), 63.6 (C-4′), 47.3 (C-3), 18.3 (CH_3-7), 13.5 (CH_3-4); ClMS *m*/*z* (rel int.): 320 (M+H, 17), 302 (M+H−H_2O, 10), 224 (18), 198 (M−$C_4H_9O_4$, 44), 188 (18), 153 (M+H−$C_4H_8O_4$−NO_2, 46), 151 (M−$C_4H_9O_4$−NO_2H, 44), 139 (24), 127 (26), 123 (M+H−$C_4H_9O_4$−NO_2−$2CH_3$, 48), 113 (46), 109 (40), 103 (36), 97 (100), 96 (86), 95 (48), 87 (42), 85 (60), 81 (34), 73 (68), 69 (76), 61 (96), 57 (67), 55 (36); HRMS (CI) calcd for $C_{13}H_{21}NO_8$+H 320.1345. Found 320.1338.

4.16. (2*R*,3*R*,4*S*,5*R*)-(1′,2′,3′,4′-Tetra-*O*-acetyl-D-*arabino*-tetritol-1′-yl)-4,5-epoxy-4,7-dimethyl-3-nitromethyl-2,3-dihydrooxepine (31)

Conventional acetylation of **30** (41 mg, 0.13 mmol) with 1:1 Ac_2O–pyridine (0.6 mL) led to an oil from which oily compound **31** (8 mg, 13%) was isolated by PTLC (EtOAc–hexane 2:1); ^1H NMR ($CDCl_3$): δ 5.44 (dd, 1H, $J_{1',2'}$=3.5 Hz, $J_{2',3'}$=9.0 Hz, H-2′), 5.29 (dd, 1H, $J_{1',2}$=8.9 Hz, H-1′), 5.09 (m, 1H, H-3′), 4.88 (dd, 1H, $J_{1''a,1''b}$=18.5 Hz, $J_{1''a,3}$=2.8 Hz, H-1″a), 4.73 (br s, 1H, H-6), 4.60 (br s, 1H, H-5), 4.30 (dd, 1H, $J_{1''b,3}$=10.8 Hz, H-1″b), 4.24 (dd, 1H, $J_{3',4'a}$=2.7 Hz, $J_{4'a,4'b}$=12.5 Hz, H-4′a), 4.03 (dd, 1H, $J_{3',4'b}$=5.3 Hz, H-4′b), 3.87 (dd, 1H, $J_{2,3}$=4.2 Hz, H-2), 2.98 (dt, 1H, H-3), 2.11 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.06 (s, 6H, 2×OAc), 1.90 (s, 3H, CH_3-7), 1.40 (s, 3H, CH_3-4).

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22. Besides the respective fragmentation signals from adducts **4a**, **3b**, **4b**, and **5b**, also were observed those corresponding to nitroalkene **1a** or **1b**, being indicated these latter with the symbol M*.