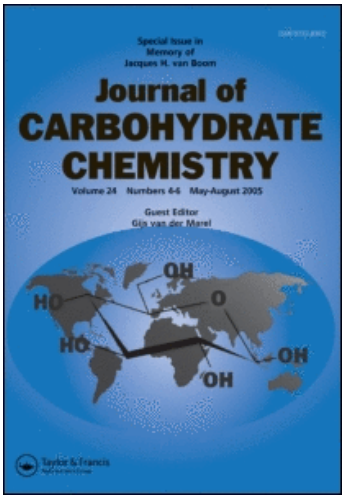

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SYNTHESIS OF ACYCLIC UNSATURATED SUGAR DERIVATIVES

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ABSTRACT

Starting from the new (2*E*)-4,5,6,7-tetra-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*arabino*-hept-2-enose (**2**), or the previously described (2*E*)-4,5,6-tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (**4**), a series of acyclic unsaturated sugar derivatives have been synthetized. Compounds **2** and **4** reacted with DBU, leading to 9:1 (2*E*,4*Z*)- and (2*E*,4*E*)-4-acetoxydienal mixtures. The unsaturated aldimines **10-12** were obtained by reaction of **4** or the dienals **8+9** with primary amines. Selective reduction of aldimines afforded their corresponding allylamines.

INTRODUCTION

Cyclic and acyclic unsaturated sugar derivatives[2] are useful as reactive intermediates for the synthesis of numerous natural products[3] or as substrates for Diels-Alder reactions.[4] More specifically, the α,β-unsaturated aldehydo-sugars have been used in the preparation of a variety of products, including branched-chain higher ketoses,[5] polyhydroxy unsaturated acids,[6] and *N*-nucleosides.[7] In connection with

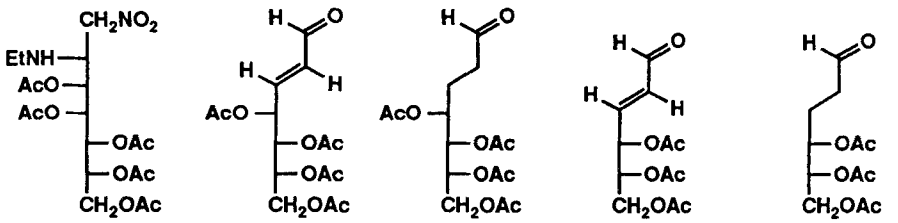
this, we describe here a number of compounds that have been obtained from the new (2*E*)-4,5,6,7-tetra-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*arabino*-hept-2-enose (**2**) or from the previously known[8] (2*E*)-4,5,6-tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (**4**).

RESULTS AND DISCUSSION

Following the methodology developed for the conversion of the nitro group into carbonyl,[9] treatment of previously described[10] **1** with $TiCl_3$ in THF under nitrogen led to the crystalline *trans*-α,β-unsaturated aldehyde **2**. The IR spectrum of **2** showed absortions characteristic of the α,β-unsaturated aldehyde group, and the 200 MHz ^1H NMR spectrum in deuteriochloroform was readily interpretable, showing a wide doublet ($J_{1,2}$ = 7.7 Hz) at δ 9.55 ppm for the aldehydic proton; the H-2 signal (at δ 6.18 ppm) was strongly coupled ($J_{2,3}$ = 15.8 Hz) to H-3, and displayed a small, long-range coupling ($J_{2,4}$ = 1.7 Hz) with H-4, indicative of the *trans*-alkene structure. The H-3 signal resonated at a somewhat lower field (δ 6.70 ppm) than H-2, and showed moderate coupling ($J_{3,4}$ = 4.0 Hz) to H-4. This overall pattern is typical of similar, *trans*-2,3-unsaturated aldehydes.[8,11]

Both **2** and its dihydro derivative **3** gave crystalline (2,4-dinitrophenyl)hydrazones having analytical and spectroscopic data (UV, IR and ^1H and ^{13}C NMR) agreeing with their expected structures.

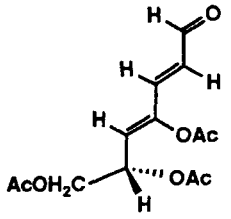
The α,β-unsaturated aldehyde **4**, its dihydro derivative **5**, and their respective (2,4-dinitrophenyl)hydrazones have been obtained as described,[8,12] but their previously unreported ^1H and ^{13}C NMR data, are given here.



1 **2** **3** **4** **5**

Reaction of **2** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry CH_2Cl_2 at room temperature prompted the loss of acetic acid[13] (from H-4

and OAc-5), leading to 4-acetoxydienals 6 (2*E*,4*Z*) and 7 (2*E*,4*E*) as a 9:1 mixture.[14] A similar treatment for the α,β-unsaturated aldehyde 4 gave dienals 8 (2*E*,4*Z*) and 9 (2*E*,4*E*) in the same 9:1 ratio.[14] This result was also achieved when compounds 2 and 4 were dissolved in pyridine, although, in this case, the elimination proceeded more slowly.



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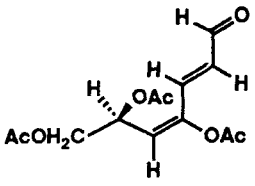

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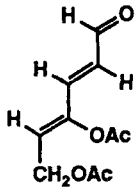

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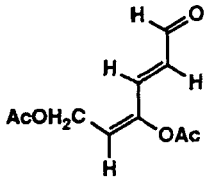

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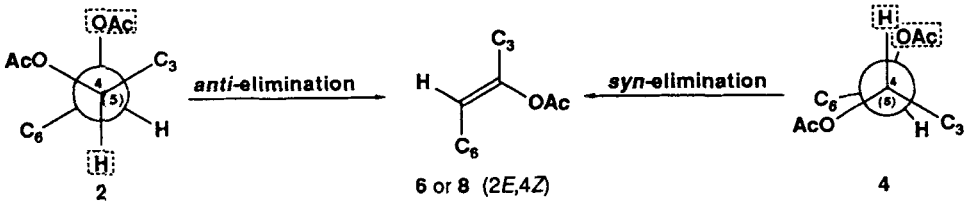
Concerning the reaction mechanism, facile elimination of acetic acid is probably due to the acidity of the proton on C-4, which is enhanced by the aldehyde group (C-1). We think that the nearly equal ratio (*E*,*Z*:*E*,*E*) of dienals from 2 and 4 indicates a common pathway. Since we have not observed deuterium-hydrogen exchange (thus excluding a $E1cB_R$ process) and a E2 mechanism would require a predominant *anti* elimination from 2 and a predominant *syn*-elimination from 4 (Scheme 1), we suggest that these reactions could occur mainly through an irreversibly formed carbanion ($E1cB_I$ mechanism).[15]

The structures of the new dienals were determined on the basis of their spectroscopic data (UV, IR, ^1H and ^{13}C NMR) and by means of the preparation of crystalline (2,4-dinitrophenyl)hydrazones of the major products (2*E*,4*Z*). The UV spectra of dienals in ethanolic solution showed an intense maximum at *ca.* 264 nm, which indicates a batochromic shift if it is compared with those of their respective precursors. In all cases, the geometries about the C4-C5 double bonds were deduced from NOE NMR experiments. Irradiation on H-5 of the major products 6 and 8 (2*E*,4*Z*)



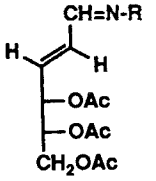
2 6 or 8 (2*E*,4*Z*) 4

SCHEME 1

led to an increase of their respective H-3 signals. In contrast, this change was not observed for the same protons of the minor products 7 and 9 (2*E*,4*E*). The shape of H-3 (a doublet) and H-5 signals (a doublet in 6 and 7 or a triplet in 8 and 9) support the proposed structures in which there is no proton on C-4.

Treatment of (2*E*)-4,5,6-tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (**4**) with equimolar quantities of several primary aliphatic or aromatic amines led to the corresponding 2,3-unsaturated aldimines **10a-10f**. The reactions were performed in dry ethyl ether at 0 °C. We have observed that the 1:1 molar ratio is crucial because slight amounts of amine in excess promote side reactions, especially deacetylation of the sugar chain. The formation of aldimines was completed in 15 min for aliphatic and in 1 h for aromatic amines; this could be due to the lesser nucleophicility of a nitrogen bonded to an aromatic ring, when it is compared with the same atom bonded to an alkyl substituent.

Similarly as above, 9:1 mixtures[14] of (2*E*,4*Z*) and (2*E*,4*E*) α,β,γ,δ-unsaturated aldimines (**11+12**; **a**,**c**,**d**,**e**) were formed, by condensation of (**8**+**9**, 9:1) with the corresponding amines; in this case, reactions proceeded more slowly, probably as the result of the lesser electrophilicity of the aldehydic carbon in **8** or **9** as compared with the same carbon in **4**.



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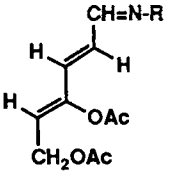

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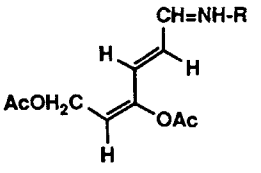

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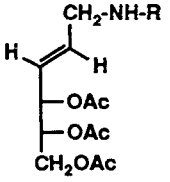

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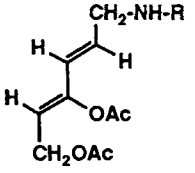

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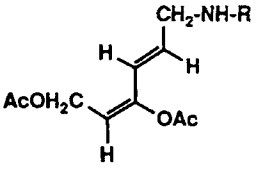

15

a), R=*i*-propyl
b), R=*n*-propyl
c), R=cyclohexyl
d), R=benzyl
e), R=*p*-methoxyphenyl
f), R=1-naphtyl

In the ^{1}H NMR spectra of all aldimines (**10-12**), the signal at lower field (8.16-7.84 ppm) was assigned to the iminic proton that appears as a doublet with $J_{1,2}$ values of 6.9-8.8 Hz, indicative[16] of a *s-trans* conformation for the N=C1-C2=C3 fragment; the rest of signals, together with the ^{13}C NMR and IR spectra, support their proposed structures.

Selective reduction of C=N bond of the α,β-unsaturated aldimines **10a-10f** with one molar equivalent of methanolic sodium borohydride, yielded their corresponding allylamines **13a-13f**. In a similar way, from the 9:1 mixtures of **11+12,a,c**, we obtained their respective 9:1 mixtures[14] of (2*E*,4*Z*) and (2*E*,4*E*) $\alpha,\beta,\gamma,\delta$-unsaturated amines (**14+15,a,c**).

The spectra of all unsaturated amines (**13-15**) showed clearly that the reduction occurred only on the iminic bond. In the ^{1}H NMR spectra the two protons on C-1 appear at 3.2-3.3 ppm as a broad doublet due to their couplings with H-2 (5.6-5.8 Hz), H-3, and the aminic proton ($\simeq$ 1 Hz); the aminic proton gave a broadened signal (1-3 ppm) that disappeared by addition of deuterium oxide.

We have not found direct precedence for sugar-allylamines as being stable products.[17] In the non-carbohydrate field, allylamines have been objects of interest[18] because of their synthetic potential, their presence in natural products,[19] and their activity as antifungal agents.[20]

EXPERIMENTAL

General Procedures. Solvents were evaporated under reduced pressure below 40 °C bath temperature. Melting points were determined with a Electrothermal 8100 apparatus and are uncorrected. Optical rotations were obtained at 20±2 °C with a Perkin-Elmer 141 polarimeter. UV spectra were recorded with a Beckman DU-50 spectrophotometer. IR spectra were taken as potassium bromide pellets or as a liquid film inserted between NaCl plates using a Perkin-Elmer 399 spectrophotometer. ^{1}H NMR (200.13 MHz) and ^{13}C NMR (50.33 MHz) were obtained on Brucker AC 200 E instrument with tetramethylsilane as internal reference and deuteriochloroform as solvent. NMR assignments were facilitated by addition of deuterium oxide and decoupling methods. TLC was performed on

silica gel 60 GF_{254} (Merck), with visualization of spots by UV light or iodine vapour; solvents were a) benzene-methanol, 10:1 and b) chloroform-acetone, 9:1. Elemental analyses were determined by the Servicio de Microanálisis de la Universidad de Extremadura with a Perkin-Elmer 240 C Elemental Analyser.

3,4,5,6,7-Penta-*O*-acetyl-1,2-dideoxy-2-ethylamino-1-nitro-D-*glycero*-D-*talo*-heptitol (1). This compound was prepared as previously described.[10] To a stirred suspension of (*E*)-3,4,5,6,7-penta-*O*-acetyl-D-*galacto*-1-nitrohept-1-ene[21] (2.0 g, 4.47 mmol) in methanol (8 mL) was added, dropwise, a solution of ethylamine (0.29 mL, 4.47 mmol) in methanol (0.5 mL). After stirring for 30 min, the solid **1** was filtered and washed on the filter with cold methanol (overall yield from D-mannose, 22%). Recrystallized from methanol, it had mp 120-122 °C; $[\alpha]_D$ +36° (*c* 0.5, chloroform); IR (KBr) 3400 (N-H), 1740, 1720 (C=O ester), 1550, 1360 (NO_2). Lit.[10] mp 120-122 °C; $[\alpha]_D$ +36.4° (*c* 0.5, chloroform).

(2*E*)-4,5,6,7-Tetra-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*arabino*-hept-2-enose (2). A buffered $TiCl_3$ solution was prepared by adding NH_4OAc (7.69 g, 99.9 mmol) in 25 mL of H_2O to 15% aqueous $TiCl_3$ (17.2 mL, 16.7 mmol) under nitrogen. 3,4,5,6,7-Penta-*O*-acetyl-1,2-dideoxy-2-ethylamino-1-nitro-D-*glycero*-D-*talo*-heptitol[10] (**1**, 2.0 g, 4.18 mmol) in THF was added rapidly and the two-phase system was stirred for 30 min at room temperature. The reaction mixture was then poured into ether and the phases separated. The aqueous layer was extracted several times with ether; the organic extracts were combined, washed with 5% $NaHCO_3$ and with brine, then dried (Na_2SO_4) and concentrated. The title compound crystallized by adding light petroleum and was recrystallized from ethanol (0.43 g, 30%): mp 103-104 °C; $[\alpha]_D$ +36° (*c* 0.5, chloroform); UV (EtOH) 219 nm; IR (KBr) 2830, 2730 (CH aldehyde), 1735 (C=O ester), 1700 (C=O aldehyde), 1640 (C=C); ^1H NMR δ 9.55 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 6.70 (dd, 1H, $J_{2,3}$ = 15.8 Hz, H-3), 6.18 (ddd, 1H, $J_{2,4}$ = 1.7 Hz, H-2), 5.83 (m, 1H, H-4), 5.47 (dd, 1 H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 9.1 Hz, H-5), 5.24 (ddd, 1H, H-6), 4.28 (dd, 1H, $J_{6,7}$ = 2.7 Hz, $J_{7,7'}$ = 12.6 Hz, H-7), 4.18 (dd, 1H, $J_{6,7'}$ = 4.2 Hz, H-7'), 2.16 (s, 3H, 1 OAc), 2.08 (s, 3H, 1 OAc), 2.07 (s, 3H, 1 OAc), 2.06 (s, 3H, 1 OAc); ^{13}C NMR δ 192.2 (CHO), 170.4, 169.6, 169.5 ($OCOCH_3$), 149.3 (C-3), 132.8 (C-2), 69.6 (C-4), 69.1 (C-5), 67.9 (C-6), 61.6 (C-7), 20.7, 20.6, 20.4 ($OCOCH_3$).

Anal. Calcd for $C_{15}H_{20}O_9$: C, 52.32; H, 5.85. Found: C, 52.05; H, 5.99.

The product (**2**) afforded a (2,4-dinitrophenyl)hydrazone having mp 172-174 °C after recrystallization from 3:1 benzene-ethanol; R_F 0.63 (solvent a); $[\alpha]_D$ -19° (*c* 0.5, chloroform); UV (EtOH) 370 nm; IR (KBr) 3300 (NH), 1745 (C=O ester), 1625 (C=C, C=N), 1520, 1350 (NO_2); ^{1}H NMR δ 11.16 (s, 1H, NH), 9.12 (d, 1H, $J_{3Ar,5Ar}$ = 2.5 Hz, H-3arom.), 8.33 (dd, 1H, $J_{5Ar,6Ar}$ = 9.6 Hz, H-5arom.), 7.94 (d, 1H, H-6arom.), 7.79 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 6.52 (ddd, 1H, $J_{2,3}$ = 15.7 Hz, $J_{2,4}$ = 1.5 Hz, H-2), 6.10 (dd, 1H, $J_{3,4}$ = 5.2 Hz, H-3), 5,74 (m, 1H, H-4), 5.42 (dd, 1H, $J_{4,5}$ = 3.1 Hz, $J_{5,6}$ = 8.5 Hz, H-5), 5.24 (m, 1H, H-6), 4.30 (dd, 1H, $J_{6,7}$ = 2.3 Hz, $J_{7,7'}$ = 12.4 Hz, H-7), 4.18 (dd, 1H, $J_{6,7'}$ = 4.0 Hz, H-7'), 2.17 (s, 3H, 1 OAc), 2.10 (s, 6H, 2 OAc), 2.08 (s, 3H, 1 OAc); ^{13}C NMR δ 170.4, 169.7, 169.5 ($OCOCH_3$), 147.4 (C-1), 144.4 (C-1arom.), 138.4 (C-4arom.), 135.6 (C-3), 125.9 (C-5arom.), 129.5 (C-5arom.), 128.7 (C-2), 123.2 (C-3arom.), 116.6 (C-6arom.), 70.2 (C-4), 69.8 (C-5), 68.2 (C-6), 61.6 (C-7), 20.7, 20.6, 20.5 ($OCOCH_3$).

Anal. Calcd for $C_{21}H_{24}N_4O_{12}$: C, 48.09; H, 4.61; N, 10.68. Found: C, 48.45; H, 4.60; N, 10.67.

4,5,6,7-Tetra-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*arabino*-heptose (3). A solution of (2*E*)-4,5,6,7-tetra-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*arabino*-hept-2-enose (**2**, 0.46 g, 1.33 mmol) in ethanol (50 mL) was hydrogenated at atmospheric pressure and room temperature in the presence of 10% palladized carbon (0.07 g). After 17 h, TLC (solvent b) revealed the absence of (**2**) and the formation of one single product with R_F 0.48. The catalyst was filtered off and the filtrate was concentrated to yield the title compound as an oil (0.45 g, 98 %); $[\alpha]_D$ +33° (*c* 1.37, chloroform); IR (film) 1750 (C=O); ^{1}H NMR δ 9.73 (s, 1H, H-1), 5.31 (dd, 1H, $J_{4,5}$ = 2.7 Hz, $J_{5,6}$ = 8.7 Hz, H-5), 5.18 (m, 1H, H-4), 5.13 (m, 1H, H-6), 4.24 (dd, 1H, $J_{6,7}$ = 2.7 Hz, $J_{7,7'}$ = 12.6 Hz, H-7), 4.14 (dd, 1H, $J_{6,7'}$ = 4.6 Hz, H-7'), 2.57 (dt, 1H, $J_{2,2'}$ = 17.9 Hz, $J_{2,3}$ = $J_{2,3'}$ = 7.5 Hz, H-2), 2.46 (dt, 1H, $J_{2',3}$ = $J_{2',3'}$ = 6.3 Hz, H-2'), 2.15 (s, 3H, 1 OAc), 2.05 (s, 9H, 3 OAc), 1.85 (m, 2H, H-3,3'); ^{13}C NMR δ 200.3 (CHO), 170.6, 170.5, 169.8 ($OCOCH_3$), 70.1 (C-4), 69.6 (C-5), 68.2 (C-6), 61.7 (C-7), 39.4 (C-2), 23.1 (C-3), 20.7, 20.6 ($OCOCH_3$).

The (2,4-dinitrophenyl)hydrazone of **3** showed mp 124-126 °C after recrystallization from ethanol-benzene; R_F 0.80 (solvent a); $[\alpha]_D$ +19°

(*c* 0.65, chloroform); UV (EtOH) 355 nm; IR (KBr) 3290 (NH), 1745 (C=O ester), 1620, 1600 (C=N, C=C), 1510, 1345 (NO_2); ^{1}H NMR δ 11.05 (s, 1H, NH), 9.10 (d, 1H, $J_{3Ar,5Ar}$ = 2.6 Hz, H-3arom.), 8.31 (dd, 1H, $J_{5Ar,6Ar}$ = 9.6 Hz, H-5arom.), 7.94 (d, 1H, H-6arom.), 7.56 (t, 1H, $J_{1,2}$ = 4.7 Hz, H-1), 5.39-5.12 (m, 3H, H-4,5,6), 4.27 (dd, 1H, $J_{6,7}$ = 2.5 Hz, $J_{7,7'}$ = 12.6 Hz, H-7), 4.17 (dd, 1H, $J_{6,7'}$ = 4.6 Hz, H-7'), 2.48 (m, 2H, H-2,2'), 2.17 (s, 3H, 1 OAc), 2.10 (s, 3H, 1 OAc), 2.06 (s, 3H, 1 OAc), 2.05 (s, 3H, 1 OAc), 1.89 (m, 2H, H-3, 3'); ^{13}C NMR δ 170.4, 170.2, 169.7, 169.6 ($OCOCH_3$), 150.0 (C-1), 144.8 (C-1arom.), 137.7 (C-4arom.), 129.8 (C-5arom.), 128.7 (C-2arom.), 123.1 (C-3arom.), 116.3 (C-6arom.), 69.9 (C-4), 69.4 (C-5), 68.2 (C-6), 61.6 (C-7), 28.0 (C-2), 23.1 (C-3), 20.5, 20.4 ($OCOCH_3$).

Anal. Calcd for $C_{21}H_{26}N_4O_{12}$: C, 47.91; H, 4.98; N, 10.64. Found: C, 48.06; H, 5.04; N, 10.50.

(2*E*)-4,5,6-Tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (4). This compound has been prepared as previously described,[8] R_F 0.7 (solvent b); UV (EtOH) 217 nm; IR (film) 1750 (C=O ester), 1700 (C=O aldehyde); ^{13}C NMR δ 192.3 (CHO), 170.4, 169.9, 169.3 ($OCOCH_3$), 148.1 (C-3), 133.6 (C-2), 70.9 (C-5), 70.4 (C-4), 61.3 (C-3), 20.7, 20.6 ($OCOCH_3$).

The (2,4-dinitrophenyl)hydrazone of **4** showed mp 110-112 °C; lit.[12] mp 108-109 °C; ^{1}H NMR δ 11.20 (s, 1H, NH), 9.10 (d, 1H, $J_{3Ar,5Ar}$ = 2.5 Hz, H-3arom.), 8.33 (d, 1H, $J_{5Ar,6Ar}$ = 9.6 Hz, H-5arom.), 7.95 (d, 1H, H-6arom.), 7.87 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 6.60 (dd, 1H, $J_{2,3}$ = 15.8 Hz, H-2), 6.18 (dd, 1H, $J_{3,4}$ = 6.3 Hz, H-3), 5.69 (dd, 1H, $J_{4,5}$ = 5.0 Hz, H-4), 5.29 (ddd, 1H, H-5), 4.32 (dd, 1H, $J_{5,6}$ = 3.6 Hz, $J_{6.6'}$ = 12.1 Hz, H-6), 4.21 (dd, 1H, $J_{5,6'}$ = 6.6 Hz, H-6'), 2.17 (s, 3H, 1 OAc), 2.12 (s, 3H, 1 OAc), 2.09 (s, 3H, 1 OAc); ^{13}C NMR δ 170.5, 169.9, 169.4 ($OCOCH_3$), 147.5 (C-1), 144.4 (C-1arom.), 138.3 (C-4arom.), 134.9 (C-3), 129.9 (C-2 and C-5arom.), 129.4 (C-2arom.), 123.2 (C-3arom.), 116.6 (C-6arom.), 71.3, 71.2 (C-4,5), 61.5 (C-6), 20.7, 20.6 ($OCOCH_3$).

Hydrogenation of **4** with 10% Pd/C led to its dihydro derivative[12] **5** as an oil; ^{1}H NMR δ 9.76 (t, 1H, $J_{1,2} = J_{1,2'}$ = 0.8 Hz, H-1), 5.20-5.06 (m, 2H, H-4,5), 4.31 (dd, 1H, $J_{5.6}$ = 3.3 Hz, $J_{6,6'}$ = 12.1 Hz, H-6), 4.17 (dd, 1H, $J_{5,6'}$ = 6.2 Hz, H-6'), 2.53 (td, 2H, $J_{2,3}$ = 7.9 Hz, H-2,2'), 2.12 (s, 3H, 1 OAc), 2.09 (s, 6H, 2 OAc), 1.97 (m, 2H, H-3,3'); ^{13}C NMR δ 200.3 (CHO), 170.1, 169.8, 169.7 ($OCOCH_3$), 71.0, 70.4 (C-4,5), 61.4 (C-6), 39.1 (C-2), 21.9 (C-3), 20.4, 20.2 ($OCOCH_3$).

Compound **4** was characterized as its (2,4-dinitrophenyl)hydrazone, mp 124-126 °C; lit.[12] mp 123-124 °C; ^{1}H NMR δ 11.05 (s, 1H, NH), 9.06 (d, 1H, $J_{3Ar,5Ar}$ = 2.5 Hz, H-3arom.), 8.30 (dd, 1H, $J_{5Ar,6Ar}$ = 9.6 Hz, H-5arom.), 7.91 (d, 1H, H-6arom.), 7.62 (t, 1H, $J_{1,2} = J_{1,2'}$ = 4.5 Hz, H-1), 5.31-5.18 (m, 2H, H-4,5), 4.37 (dd, 1H, $J_{5,6}$ = 3.1 Hz, $J_{6,6'}$ = 12.2 Hz, H-6), 4.19 (dd, 1H, $J_{5,6'}$ = 6.7 Hz, H-6'), 2.50 (m, 2H, H-2,2'), 2.11 (s, 6H, 2 OAc), 2.08 (s, 3H, 1 OAc), 1.97 (m, 2H, H-3,3'); ^{13}C NMR δ 170.5, 170.1, 170.0 ($OCOCH_3$), 150.4 (C-1), 144.9 (C-1arom.), 137.7 (C-4arom.), 129.8 (C-5arom.), 128.7 (C-2arom.), 123.2 (C-3arom.), 116.4 (C-6arom.), 71.5, 70.7 (C-4,5), 61.7 (C-6), 28.1 (C-2), 26.3 (C-3), 20.7, 20.6 ($OCOCH_3$).

(2*E*,4*Z*)-4,6[*R*],7-Tri-*O*-acetyl-2,4-heptadienal (6) and its (2*E*,4*E*) isomer (7). To a solution of 2 (2.0 g, 5.8 mmol) in dry CH_2Cl_2 (20 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.90 mL, 5.8 mmol). After stirring at room temperature for 16 h, ^{1}H NMR of the reaction mixture showed that the starting material was completely converted into a 9:1 mixture of **6** and **7**. The solution was washed with 0.1M HCl, saturated $NaHCO_3$, and water, and dried ($MgSO_4$). Filtration through charcoal and concentration gave 1.3 g (79%) of **6** and **7** as an oily unseparable mixture; UV (EtOH) 264 nm; IR (film) 2850, 2750 (CH aldehyde), 1755 (C=O ester), 1625 (C=C); ^{1}H NMR (2*E*,4*Z* isomer, **6**) δ 9.62 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 6.96 (d, 1H, H-3), 6.14 (dd, 1H, $J_{2,3}$ = 15.6 Hz, H-2), 5.84 (d, 1H, $J_{5,6}$ = 8.7 Hz, H-5), 5.76 (m, 1H, H-6), 4.32 (dd, 1H, $J_{6.7}$ = 3.6 Hz, $J_{6,7'}$ = 12.0 Hz, H-7), 4.08 (dd, 1H, $J_{6,7'}$ = 6.0 Hz, H-7'), 2.33 (s, 3H, 1 OAc-4), 2.08 (s, 3H, 1 OAc), 2.07 (s, 3H, 1 OAc); (2*E*,4*E* isomer, **7**) δ 9.70 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 7.49 (d, 1H, H-3), 6.22 (dd, 1 H, $J_{2,3}$ = 15.6 Hz, H-2), 5.92 (m, 1 H, H-6), 5.65 (d, 1H, $J_{5,6}$ = 8.7 Hz, H-5), 4.29 (dd, 1H, $J_{6,7}$ = 3.6 Hz, $J_{6,7'}$ = 12.0 Hz, H-7), 4.14 (dd, 1H, $J_{6,7'}$ = 6.0 Hz, H-7'), 2.24 (s, 3H, 1 OAc-4), 2.12 (s, 3H, 1 OAc), 2.08 (s, 3H, 1 OAc); ^{13}C NMR (2*E*,4*Z* isomer, **6**) δ 192.2 (CHO), 170.3, 169.6 ($OCOCH_3$), 167.9 ($OCOCH_3$-4), 147.1 (C-4), 144.1 (C-3), 129.8 (C-2), 124.3 (C-5), 66.1 (C-6), 63.7 (C-7), 20.6, 20.5, 20.1 ($OCOCH_3$); (2*E*,4*E* isomer, **7**) δ 192.2 (CHO), 148.1 (C-4), 145.4 (C-3), 130.5 (C-2), 123.4 (C-5), 66.6 (C-6), 64.0 (C-7).

Treatment of the 9:1 mixture of **6** and **7** with (2,4-dinitrophenyl)hydrazine yielded crystalline (2,4-dinitrophenyl)hydrazone of the

major isomer **6** (2*E*,4*Z*); mp 165-167 °C (from EtOH); UV (EtOH) 385 nm; IR (KBr) 3300 (NH), 1750 (C=O ester), 1630 (C=C, C=N), 1520, 1350 (NO_2); ^1H NMR δ 11.23 (s, 1H, NH), 9.11 (d, 1H, $J_{3Ar,5Ar}$ = 2.3 Hz, H-3arom.), 8.32 (dd, 1H, $J_{5Ar,6Ar}$ = 9.6 Hz, H-5arom.), 7.95 (d, 1H, H-6arom.), 7.83 (d, 1H, $J_{1,2}$ = 7.0 Hz, H-1), 6.50 (m, 2H, H-2,3), 5.79 (ddd, 1H, $J_{5,6}$ = 8.9 Hz, H-5), 4.31 (dd, 1H, $J_{6,7}$ = 3.7 Hz, $J_{7,7'}$ = 11.9 Hz, H-7), 4.07 (dd, 1H, $J_{6,7}$ = 6.9 Hz, H-7'), 2.39 (s, 3H, 1 OAc-4), 2.08 (s, 6H, 2 OAc); ^{13}C NMR δ 170.6, 169.9 ($OCOCH_3$), 168.4 ($OCOCH_3$-4), 148.3 (C-1), 147.6 (C-4), 144.3 (C-1arom.), 138.6 (C-4arom.), 133.0 (C-3), 130.0 (C-5arom.), 129.7 (C-2arom.), 126.7 (C-2), 123.3 (C-3arom.), 119.6 (C-5), 116.8 (C-6arom.), 66.4 (C-6), 64.2 (C-7), 20.9, 20.8, 20.5 ($OCOCH_3$).

Anal. Calcd for $C_{19}H_{20}N_4O_{10}$: C, 49.14; H, 4.34; N, 12.06. Found: C, 48.79; H, 4.33; N, 11.50.

(2*E*,4*Z*)-4,6-Di-*O*-acetyl-2,4-hexadienal (8) and its (2*E*,4*E*) isomer (9). A 9:1 mixture of **8** and **9** was prepared, according to the above given procedure for the mixture of **6** and **7**. Yield: 81%; oil; UV (EtOH) 264 nm; IR (film) 2840, 2750 (CH aldehyde), 1750 (C=O ester), 1610 (C=C); ^1H NMR (2*E*,4*Z* isomer, **8**) δ 9.62 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 6.97 (d, 1H, H-3), 6.14 (dd, 1H, $J_{2,3}$ = 15.5 Hz, H-2), 6.00 (t, 1H, J = 6.7 Hz, H-5), 4.65 (d, 2H, H-6,6'), 2.30 (s, 3H, 1 OAc-4), 2.08 (s, 3H, 1 OAc-6); (2*E*,4*E* isomer, **9**) δ 9.69 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 7.37 (d, 1H, H-3), 6.20 (dd, 1H, $J_{2,3}$ = 15.5 Hz, H-2), 5.87 (t, 1H, $J_{5,6}$ = 7.8 Hz, H-5), 4.86 (d, 2H, H-6,6'), 2.26 (s, 3H, 1 OAc-4), 2.12 (s, 3H, 1 OAc-6); ^{13}C NMR (2*E*,4*E* isomer, **8**) δ 192.5 (CHO), 170.5 ($OCOCH_3$-6), 167.6 ($OCOCH_3$-4), 146.1 (C-4), 144.6 (C-3), 129.2 (C-2), 125.2 (C-5), 58.7 (C-6), 20.7, 20.3 ($OCOCH_3$); (2*E*,4*Z* isomer, **9**) δ 192.7 (CHO), 146.5 (C-4), 139.3 (C-3), 130.3 (C-2), 123.9 (C-5), 58.6 (C-6), 20.8 ($OCOCH_3$).

Treatment of the 9:1 mixture of **8** and **9** with (2,4-dinitrophenyl)-hydrazine yielded crystalline (2,4-dinitrophenyl)hydrazone of the major isomer **8** (2*E*,4*Z*); mp 217-219 °C (from EtOH); UV ($CHCl_3$) 382 nm; IR (KBr) 3300 (NH), 1750 (C=O ester), 1625 (C=C, C=N), 1515, 1340 (NO_2); ^1H NMR δ 11.23 (s, 1H, NH), 9.13 (d, 1H, $J_{3Ar,5Ar}$ = 2.6 Hz, H-3arom.), 8.33 (dd, 1H, $J_{5Ar,6Ar}$ = 9.6 Hz, H-5 arom.), 7.95 (d, 1H, H-6arom.), 7.82 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1), 6.50 (m, 2H, H-2,3), 5.78 (t, 1H, $J_{5,6}$ = 7.0 Hz, H-5), 4.63 (d, 2H, H-6,6'), 2.36 (s, 3H, 1 OAc-4), 2.08 (s, 3H, 1 OAc-6); ^{13}C NMR δ 170.6 ($OCOCH_3$-6), 167.9 ($OCOCH_3$-4), 147.7 (C-1), 147.2

(C-4), 144.3 (C-1arom.), 138.5 (C-4arom.), 133.4 (C-3), 130.0 (C-5arom.), 129.6 (C-2arom.), 125.6 (C-2), 123.4 (C-3arom.), 120.1 (C-5), 116.7 (C-6arom.), 58.7 (C-6), 20.7, 20.4 ($OCOCH_3$).

Anal. Calcd for $C_{16}H_{16}N_4O_8$: C, 48.98; H, 4.11; N, 14.28. Found: C, 48.91; H, 4.07; N, 14.04.

(2*E*)-4,5,6-Tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose isopropylimine (10a). To a solution of (2*E*)-4,5,6-tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (**4**, 0.93 g, 3.40 mmol) in dry ethyl ether (7 mL) was added isopropylamine (0.28 mL, 3.40 mmol) and molecular sieve (Merck, 4 Å). After 15 min at 0 °C, ^1H NMR of the reaction mixture showed that the starting material was completely converted into the title product. Filtration of the molecular sieve and concentration yielded **10a** as an oil (0.91 g, 86%); $[\alpha]_D$ +26° (*c* 0.96, chloroform); IR (film) 1750 (C=O ester), 1660, 1620 (C=N, C=C); ^1H NMR δ 7.98 (d, 1H, $J_{1,2}$ = 8.7 Hz, H-1), 6.41 (ddd, 1H, $J_{2,3}$ = 15.7 Hz, $J_{2,4}$ = 1.5 Hz, H-2), 6.07 (dd, 1H, $J_{3,4}$ = 4.5 Hz, H-3), 5.64 (t, 1H, $J_{4,5}$ = 4.6 Hz, H-4), 5.25 (m, 1H, H-5), 4.27 (dd, 1H, $J_{5,6}$ = 4.0 Hz, $J_{6,6'}$ = 12.1 Hz, H-6), 4.18 (dd, 1H, $J_{5,6'}$ = 6.5 Hz, H-6'), 3.35 (m, 1H, N-C*H*), 2.10 (s, 3H, 1 OAc), 2.08 (s, 3H, 1 OAc), 2.05 (s, 3H, 1 OAc), 1.18 (d, 6H, J = 6.2 Hz, CH*Me*$_2$); ^{13}C NMR δ 170.5, 170.1, 169.5 ($OCOCH_3$), 158.3 (C-1), 135.3 (C-3), 133.5 (C-2), 71.3, 71.2 (C-4,5), 61.6 (C-5), 61.3 (N-*C*H), 23.9 (CH*Me*$_2$), 20.8, 20.7 ($OCOCH_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose *n*-propylimine (10b). The title compound was prepared using *n*-propylamine according to the above given procedure for **10a**; oil, 76% yield; $[\alpha]_D$ +28° (*c* 0.34, chloroform); IR (film) 1750 (C=O ester), 1635 (C=C, C=N); ^1H NMR δ 7.87 (d, 1H, $J_{1,2}$ = 8.7 Hz, H-1), 6.44 (ddd, 1H, $J_{2,3}$ = 15.8 Hz, $J_{2,4}$ = 1.2 Hz, H-2), 6.01 (dd, 1H, $J_{3,4}$ = 5.8 Hz, H-3), 5.65 (t, 1H, $J_{4,5}$ = 4.6 Hz, H-4), 5.26 (m, 1H, H-5), 4.27 (dd, 1H, $J_{5,6}$ = 4.1 Hz, $J_{6,6'}$ = 12.1 Hz, H-6), 4.18 (dd, 1H, $J_{5,6'}$ = 6.7 Hz, H-6'), 3.43 (t, 2H, J = 7.3 Hz, N-*C*H$_2$), 2.11 (s, 3H, 1 OAc), 2.08 (s, 3H, 1 OAc), 2.08 (s, 3H, 1 OAc), 2.05 (s, 3H, 1 OAc), 1.65 (m, 2H, N-CH$_2$-*C*H$_2$), 0.91 (t, 3H, CH$_2$-*C*H$_3$); ^{13}C NMR δ 170.5, 170.1, 169.5 ($OCOCH_3$), 160.9 (C-1), 135.6 (C-3), 133.3 (C-2), 71.3, 71.2 (C-4,5), 63.1 (C-6), 61.9 (N-*C*H$_2$), 23.8 (N-CH$_2$-*C*H$_2$), 20.8, 20.7 ($OCOCH_3$), 11.8 (CH$_2$-*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose cyclohexylimine (10c). The title compound was prepared using cyclo-

hexylamine, according to the above given procedure for **10a**; oil, 78% yield; $[\alpha]_D$ +22° (*c* 1.0, chloroform); IR (film) 1750 (C=O ester), 1670, 1640 (C=N, C=C); ^{1}H NMR δ 7.90 (d, 1H, $J_{1,2}$ = 8.7 Hz, H-1), 6.42 (ddd, 1H, $J_{2,3}$ = 15.7 Hz, $J_{2,4}$ 1,3 Hz, H-2), 6.07 (dd, 1H, $J_{3,4}$ = 5.7 Hz, H-3), 5.64 (t, 1H, $J_{4,5}$ = 4.5 Hz, H-4), 5.25 (m, 1H, H-5), 4.27 (dd, 1H, $J_{5,6}$ = 4.0 Hz, $J_{6,6'}$ = 12.1 Hz, H-6), 4.18 (dd, $J_{5,6'}$ = 5.7 Hz, H-6'), 3.02 (m, 1H, J = 5.9 Hz, N-C*H*), 2.10 s, 3H, 1 OAc), 2.08 (s, 3H, 1 OAc), 2.05 (s, 3H, 1 OAc), 1.82-1.10 (m, 10H, cyclohexyl); ^{13}C NMR δ 170.4, 170.0, 169.4 (OCOCH$_3$), 158.5 (C-1), 135.1 (C-3), 133.5 (C-2), 72.2, 72.1 (C-4,5), 69.5 (N-*C*H), 61.5 (C-6), 34.0, 25.3, 24.5 (cyclohexyl), 20.7, 20.6 (OCO*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose N-benzylimine (10d). The title compound was prepared using benzylamine, according to the above given procedure for **10a**; oil, 80% yield; $[\alpha]_D$ +21° (*c* 0.48, chloroform); IR (film) 1750 (C=O ester), 1655, 1630 (C=N, C=C); ^{1}H NMR δ 7.99 (dt, 1H, $J_{1,2}$ = 8.7 Hz, $J_{1,CHPh}$ ≃ 1 Hz, H-1), 7.38-7.20 (m, 5H, phenyl), 6.49 (ddd, 1H, $J_{2,3}$ = 15.7 Hz, $J_{2,4}$ = 1.2 Hz, H-2), 6.14 (dd, 1H, $J_{3,4}$ = 5.7 Hz, H-3), 5.65 (t, 1H, $J_{4,5}$ = 4.6 Hz, H-4), 5.26 (m, 1H, H-5), 4.66 (br s, 2H, C*H*$_2$-Ph), 4.27 (dd, 1H, $J_{5,6}$ = 4.0 Hz, $J_{6,6'}$ = 12.1 Hz, H-6), 4.18 (dd, 1H, $J_{5,6}$ = 6.5 Hz, H-6'), 2.10 (s, 3H, 1 OAc), 2.08 (s, 3H, 1 OAc), 2.05 (s, 3H, 1 OAc); ^{13}C NMR δ 170.5, 170.0, 169.4 (OCOCH$_3$), 161.6 (C-1), 138.6, 128.5, 128.0, 127.1 (phenyl), 136.2 (C-3), 133.3 (C-2), 71.2 , 71.1 (C-4,5), 65.0 (*C*H$_2$-Ph), 61.6 (C-6), 20.8, 20.7 (OCO*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (*p*-methoxy)phenylimine (10e). The title compound was prepared using (*p*-methoxy)phenylamine, according to the above given procedure for **10a**. In this case, the time reaction was 1 h; oil, 93% yield; $[\alpha]_D$ +24° (*c* 1.0, chloroform); IR (film) 1750 (C=O ester), 1655, 1620 (C=N, C=C); ^{1}H NMR δ 8.13 (d, 1H, $J_{1,2}$ = 8.8 Hz, H-1), 7.15 (d, 2H, J = 6.9 Hz, 2Harom.), 6.88 (d, 2Harom.), 6.62 (dd, 1H, $J_{2,3}$ = 15.6 Hz, $J_{2,4}$ = 1.2 Hz, H-2), 6.27 (dd, 1H, $J_{3,4}$ = 5.8 Hz, H-3), 5.71 (t, 1H, $J_{4,5}$ = 4.4 Hz, H-4), 5.30 (m, 1H, H-5), 4.30 (dd, 1H, $J_{5,6}$ = 4.0 Hz, $J_{6,6'}$ = 12.1 Hz, H-6), 4,21 (dd, 1H, $J_{5,6'}$ = 6.5 Hz, H-6'), 3.80 (s, 3H, OC*H*$_3$), 2.13 (s, 3H, 1 OAc), 2.09 (s, 3H, 1 OAc), 2.06 (s, 3H, 1 OAc); ^{13}C NMR δ 170.4, 170.0, 169.4 (OCOCH$_3$), 158.5, 143.6, 122.1, 114.6 (phenyl), 157.5 (C-1), 136.9 (C-3), 133.7 (C-2), 71.1 (C-4,5), 61.6 (C-6), 55.3 (OC*H*$_3$), 20.6, 20,5 (OCO*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose 1-naphtylimine (10f). The title compound was prepared using 1-naphtylamine, according to the above given procedure for **10a**. The time reaction was 1 h; oil, 80% yield; $[\alpha]_D$ +10° (*c* 1.0, chloroform); IR (film) 1750 (C=O ester), 1650, 1610 (C=N, C=C); ^{1}H NMR δ 8.21 (m, 1Harom.), 8.12 (d, 1H, $J_{1,2}$ = 8.8 Hz, H-1), 7.85-7.20 (m, 5H arom.), 6.90 (d, 1H, J = 7.1 Hz, 1Harom.), 6.79 (dd, 1H, $J_{2,3}$ = 15.1 Hz, H-2), 6.30 (dd, 1H, $J_{3,4}$ = 5.7 Hz, H-3), 5.76 (t, 1H, $J_{4,5}$ = 4.5 Hz, H-4), 5.33 (m, 1H, H-5), 4.32 (dd, 1H, $J_{5,6}$ = 4,5 Hz, $J_{6.6'}$ = 12.2 Hz, H-6), 4.23 (dd, 1H, $J_{5,6'}$ = 6.9 Hz, H-6'), 2.14 (s, 3H, 1 OAc), 2.09 (s, 3H, 1 OAc), 2.04 (s, 3H, 1 OAc); ^{13}C NMR δ 170.3, 169.8, 169.3 ($OCOCH_3$), 160.2 (C-1), 148.4, 133.6, 128.2, 127.4, 126.3, 126.1, 125.7, 125.5, 123.5, 112.5 (naphtyl), 138.1 (C-3), 133.5 (C-2), 71.1, 71.0 (C-4,5), 61.4 (C-6), 20.6, 20.5 ($OCOCH_3$).

(2*E*,4*Z*)-4,6-Di-*O*-acetyl-1-isopropylimino-2,4-hexadiene (11a) and its (2*E*,4*E*) isomer (12a). Treatment of 9:1 mixture of **8** and **9** with isopropylamine, as indicated above for **10a** afforded to the 9:1 mixture of **11a** and **12a**. The time reaction was 2 h 20 min; oil, 71% yield; IR (film) 1735 (C=O ester), 1645, 1625 (C=N, C=C); ^{1}H NMR (2*E*,4*Z* isomer, **11a**) δ 7.90 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 6.46 (d, 1H, H-3), 6.33 (dd, 1H, $J_{2,3}$ = 15.5 Hz, H-2), 5.70 (t, 1H, $J_{5,6}$ = 6.9 Hz, H-5), 5.60 (d, 2H, H-6,6'), 3.37 (m, 1H, N-C*H*), 2.26 (s, 3H, 1 OAc-4), 2.05 (s, 3H, 1 OAc-6), 1.18 (d, 6H, J = 6.2 Hz, CH*Me*$_2$); (2*E*,4*E* isomer, **12a**) δ 7.97 (d, 1H, $J_{1,2}$ = 9.4 Hz, H-1), 6.81 (d, 1H, $J_{2,3}$ = 15.6 Hz, H-3), 5.59 (t, 1H, H-5), 4.79 (d, 2H, $J_{5,6}$ = 7.8 Hz, H-6,6'); ^{13}C NMR (2*E*,4*Z* isomer, **11a**) δ 170.6 ($OCOCH_3$-6), 167.9 ($OCOCH_3$-4), 158.5 (C-1), 147.4 (C-4), 133.9 (C-3), 129.9 (C-2), 119.1 (C-5), 61.4 (N-*C*H), 58.7 (C-6), 24.0 (CH-*Me*$_2$), 20.7, 20.3 ($OCOCH_3$).

(2*E*,4*Z*)-4,6-Di-*O*-acetyl-1-cyclohexylimino-2,4-hexadiene (11c) and its (2*E*,4*E*) isomer (12c). Treatment of a 9:1 mixture of **8** and **9** with cyclohexylamine, as indicated above for **10a**, afforded to the 9:1 mixture of **11c** and **12c**. The time reaction was 2 h 20 min; oil, 67% yield; IR (film) 1735 (C=O ester), 1645, 1625 (C=N, C=C); ^{1}H NMR (2*E*,4*Z* isomer, **11c**) δ 7.93 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 6.46 (d, 1H, $J_{2,3}$ = 15.5 Hz, H-3), 6.32 (dd, 1H, H-2), 5.71 (t, 1H, $J_{5,6}$ = 6.9 Hz, H-5), 4.60 (d, 2H, H-6,6'), 3.03 (m, 1H, N-C*H*), 2.26 (s, 3H, 1 OAc-4), 2.06 (s, 3H, 1

OAc-6), 1.93-1.10 (m, 10H, cyclohexyl); (2*E*,4*E* isomer, **12c**) δ 7.97 (d, 1H, $J_{1,2}$ = 9.3 Hz, H-1), 6.81 (d, 1H, $J_{2,3}$ = 15.5 Hz, H-3), 5.59 (t, 1H, H-5), 4.79 (d, 2H, $J_{5,6}$ = 7.9 Hz, H-6,6'); ^{13}C NMR (2*E*,4*Z* isomer, **11c**) δ 170.5 (*O*C*O*CH$_3$-6), 167.8 (*O*C*O*CH$_3$-4), 158.8 (C-1), 147.3 (C-4), 133.7 (C-3), 129.9 (C-2), 119.0 (C-5), 69.7 (N-C*H*), 58.6 (C-6), 34.1, 25.3, 24.5 (cyclohexyl), 20.6, 20.2 (OCO*C*H$_3$).

(2*E*,4*Z*)-4,6-Di-*O*-acetyl-1-benzylimino-2,4-hexadiene (11d) and its (2*E*,4*E*) isomer (12d). Treatment of a 9:1 mixture of **8** and **9** with benzylamine, as indicated above for **10a**, afforded to the 9:1 mixture of **11d** and **12d**. The time reaction was 2 h 20 min; oil, 68% yield; IR (film) 1735 (C=O ester), 1635 (C=N, C=C); ^{1}H NMR (2*E*,4*Z* isomer, **11d**) δ 8.00 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 7.40-7.15 (m, 5H, phenyl), 6.25 (d, 1H, $J_{2,3}$ = 15.5 Hz, H-3), 6.20 (dd, 1H, H-2), 5.73 (t, 1H, $J_{5,6}$ = 6.9 Hz, H-5), 4.67 (br s, 2H, N-C*H*$_2$), 4.60 (d, 2H, H-6,6'), 2.25 (s, 3H, 1 OAc-4), 2.05 (s, 3H, 1 OAc-6); (2*E*,4*E* isomer, **12d**) δ 8.08 (d, 1H, $J_{1,2}$ = 8.4 Hz, H-1), 6.87 (d, 1H, $J_{2,3}$ = 15.3 Hz, H-3), 5.62 (t, 1H, H-5), 4.79 (d, 2H, $J_{5,6}$ = 7.9 Hz, H-6,6'); ^{13}C NMR (2*E*,4*Z* isomer, **11d**) δ 170.5 (*O*C*O*CH$_3$-6), 167.7 (*O*C*O*CH$_3$-4), 161.9 (C-1), 147.1 (C-4), 138.5, 128.4, 127.9, 127.0 (phenyl), 134.7 (C-3), 129.4 (C-2), 119.6 (C-5), 65.0 (N-*C*H$_2$), 58.5 (C-6), 20.5, 20.2 (OCO*C*H$_3$).

(2*E*,4*Z*)-4,6-Di-*O*-acetyl-1-(*p*-methoxy)phenylimino-2,4-hexadiene (11e) and its (2*E*,4*E*) isomer (12e). Treatment of 9:1 mixture of **8** and **9** wit (*p*-methoxy)phenylamine, as indicated above for **10a**, afforded to the 9:1 mixture of **11e** and **12e**. The time reaction was 2 h 20 min; oil, 66% yield; IR (film) 1730 (C=O ester), 1635, 1610 (C=N, C=C); ^{1}H NMR (2*E*,4*Z* isomer, **11e**) δ 8.16 (dd, 1H, $J_{1,2}$ = 6.9 Hz, $J_{1,3}$ = 1.5 Hz, H-1), 7.16 (d, 2H, J = 6.9 Hz, 2Harom.), 6.88 (d, 2Harom.), 6.63 (dd, 1H, $J_{2,3}$ = 14.5 Hz, H-2), 6.57 (d, 1H, H-3), 5.77 (t, 1H, $J_{5,6}$ = 6.9 Hz, H-5), 4.62 (d, 2H, H-6,6'), 3.80 (s, 3H, OC*H*$_3$), 2.30 (s, 3H, 1 OAc-4), 2.05 (s, 3H, 1 OAc-6); (2*E*,4*E* isomer, **12e**) δ 8.23 (d, 1H, $J_{1,2}$ = 9.0 Hz, H-1), 5.65 (t, 1H, $J_{5,6}$ 7.9 Hz, H-5), 4.82 (d, 2H, H-6,6'); ^{13}C NMR (2*E*,4*Z* isomer, **11e**) δ 170.5 (*O*C*O*CH$_3$-6), 167.7 (*O*C*O*CH$_3$-4), 158.6 (C-1), 157.6, 143.6, 122.1, 114.2 (phenyl), 147.2 (C-4), 135.4 (C-3), 129.8 (C-2), 119.8 (C-5), 58.6 (C-6), 55.2 (O*C*H$_3$), 20.6, 20.2 (OCO*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-1,2,3-trideoxy-1-isopropylamino-D-*erythro*-hex-2-enose (13a). Sodium borohydride (0.11 g, 2.91 mmol) was added to a stirred solution of (2*E*)-4,5,6-tri-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-

erythro-hex-2-enose isopropylimine (**10a**, 0.91 g, 2.91 mmol) in methanol (5 mL) at 0 °C. After 15 min, ^{1}H NMR showed the complete conversion of the starting material. The solution was filtered and the filtrate was diluted with dichloromethane (20 mL), then was washed successively with saturated aqueous $NaHCO_3$ and water, dried with magnesium sulfate, and concentrated, yielding the title product (0.89 g, 97%) as an oil; $[\alpha]_D$ +29° (*c* 1.0, chloroform); IR (film) 1740 (C=O ester), 1640 (C=C); ^{1}H NMR δ 5.91 (dt, 1H, $J_{1,2}$ = 5.8 Hz, H-2), 5.60 (dd, 1H, $J_{2,3}$ = 15.3 Hz, H-3), 5.47 (dd, 1H, $J_{3,4}$ = 6.9 Hz, $J_{4,5}$ = 4.4 Hz, H-4), 5.21 (m, 1H, H-5), 4.25 (dd, 1H, $J_{5,6}$ = 3.7 Hz, $J_{6,6'}$ = 12.1 Hz, H-6), 4.10 (dd, 1H, $J_{5,6'}$ = 7.0 Hz, H-6'), 3.26 (d, 2H, H-1,1'), 2.80 (m, 1H, J = 6.1 Hz, N-C*H*), 2.07 (s, 3H, 1 OAc), 2.06 (s, 3H, 1 OAc), 2.05 (s, 3H, 1 OAc), 1.47 (m, 1H, N*H*), 1.06 (d, 6H, CH*Me*$_2$); ^{13}C NMR δ 170.2, 169.8, 169.3 (O*C*OCH$_3$), 134.9 (C-2), 123.9 (C-3), 71.4, 71.3 (C-4,5), 61.6 (C-6), 48.2 (C-1), 47.8 (N-*C*H), 22.5 (CH*Me*$_2$), 20.7, 20.6, 20.4 (OCO*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-1,2,3-trideoxy-1-(*n*-propylamino)-D-*erythro*-hex-2-enose (13b). The title compound was prepared from **10b**, according to the above given procedure for **13a**; oil, 82 % yield; $[\alpha]_D$ +14° (*c* 1.0, chloroform); IR (film) 1750 (C=O ester), 1630 (C=C); ^{1}H NMR δ 5.90 (dt, $J_{1,2}$ = 5.6 Hz, H-2), 5.60 (dd, 1H, $J_{2,3}$ = 15.1 Hz, H-3), 5.47 (dd, 1H, $J_{3,4}$ = 6.8 Hz, H-4), 5.21 (m, 1H, H-5), 4.26 (dd, 1H, $J_{5,6}$ = 4.0 Hz, $J_{6,6'}$ = 12.1 Hz, H-6), 4.16 (dd, 1H, $J_{5,6'}$ = 7.0 Hz, H-6'), 3.26 (d, 2H, H-1,1'), 2.56 (t, 2H, J = 7.1 Hz, N-C*H*$_2$), 2.39 (m, 1H, N*H*), 2.08 (s, 3H, 1 OAc), 2.07 (s, 3H, 1 OAc), 2.06 (s, 3H, 1 OAc), 1.51 (m, 2H, N-CH$_2$-C*H*$_2$), 0.92 (t, 3H, J = 7.1 Hz, CH$_2$-C*H*$_3$); ^{13}C NMR δ 170.5, 170.0, 169.6 (O*C*OCH$_3$), 134.8 (C-2), 124.3 (C-3), 72.2 (C-4), 71.5 (C-5), 61.8 (C-6), 51.0 (N-*C*H$_2$), 50.1 (C-1), 22.9 (N-CH$_2$-*C*H$_2$), 20.8, 20.7, 20.6 (OCO*C*H$_3$), 11.6 (CH$_2$-*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-1,2,3-trideoxy-1-cyclohexylamino-D-*erythro*-hex-2-enose (13c). The title compound was prepared from **10c**, according to the above given procedure for **13a**; oil, 86% yield; $[\alpha]_D$ +24° (*c* 0.5, chloroform); IR (film) 1740 (C=O ester), 1640 (C=C); ^{1}H NMR δ 5.90 (dt, 1H, $J_{1,2}$ = 5.8 Hz, H-2), 5.60 (dd, 1H, $J_{2,3}$ = 15.2 Hz, H-3), 5.45 (dd, 1H, $J_{3,4}$ = 6.9 Hz, $J_{4,5}$ = 4.4 Hz, H-4), 5.20 (m, 1H, H-5), 4.25 (dd, 1H, $J_{5,6}$ = 3.7 Hz, $J_{6,6'}$ = 12.0 Hz, H-6), 4.14 (dd, 1H, $J_{5,6'}$ = 7.0 Hz, H-6'), 3.27 (d, 2H, H-1,1'), 2.42 (m, 1H, N-C*H*), 2.07 (s, 3H, 1 OAc), 2.05 (s, 3H, 1 OAc), 2.04 (s, 3H, 1 OAc), 1.9-1.0 (m, 10H, cyclohexyl),

1.45 (m, 1H, N*H*); ^{13}C NMR δ 169.7, 169.3, 168.8 (OCOCH$_3$), 134.7 (C-2), 123.5 (C-3), 71.6, 71.0 (C-4,5), 61.2 (C-6), 55.4 (N-*C*H), 47.3 (C-1), 32.8, 25.5, 24.3 (cyclohexyl), 20.2, 20.1, 19.9 (OCO*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-1,2,3-trideoxy-1-benzylamino-D-*erythro*-hex-2-enose (13d). The title compound was prepared from **10d**, according to the above given procedure for **13a**; oil, 79% yield; $[\alpha]_D$ +28° (*c* 0.5, chloroform); IR (film) 1740 (C=O ester), 1635 (C=C); ^{1}H NMR δ 7.28 (m, 5H, phenyl), 5,89 (dt, 1H, $J_{1,2}$ = 5.7 Hz, H-2), 5.61 (dd, $J_{2,3}$ = 15.3 Hz, H-3), 5.47 (dd, 1H, $J_{3,4}$ = 6.9 Hz, $J_{4,5}$ = 4.4 Hz, H-4), 5.21 (m, 1H, H-5), 4.25 (dd, 1H, $J_{5,6}$ = 3.7 Hz, $J_{5,6'}$ = 12.1 Hz, H-6), 4.14 (dd, 1H, $J_{5,6'}$ = 7.0 Hz, H-6'), 3.73 (br s, 2H, N-C*H*$_2$), 3.24 (d, 2H, H-1,1'), 2.69 (m, 1H, N*H*), 2.04 (s, 3H, 1 OAc), 2.03 (s, 3H, 1 OAc), 2.00 (s, 3H, 1 OAc); ^{13}C NMR δ 169.9, 169.4, 168.9 (OCOCH$_3$), 139.3, 127.9, 127.8, 127.6 (phenyl), 134.0 C-2), 124.3 (C-3), 71.6, 71.0 (C-4,5), 61.3 (C-6), 52.4 (N-*C*H), 49.3 (C-1), 20.3, 20.2, 20.0 (OCO*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-1,2,3-trideoxy-1-(*p*-methoxy)phenylamino-D-*erythro*-hex-2-enose (13e). The title compound was prepared from **10e**, according to the above given procedure for **13a**; oil, 71% yield; $[\alpha]_D$ +21° (*c* 0.5, chloroform); IR (film) 1740 (C=O ester), 1645 (C=C); ^{1}H NMR δ 6.74 (d, 1H, J = 7.0 Hz, 2Harom.), 6.53 (d, 2Harom.), 5.89 (dt, 1H, $J_{1,2}$ = 4.8 Hz, H-2), 5.65 (dd, 1H, $J_{2,3}$ = 15.5 Hz, H-3), 5.47 (dd, 1H, $J_{3,4}$ = 6.7 Hz, $J_{4,5}$ = 4.6 Hz, H-4), 5.18 (m, 1H, H-5), 4.20 (dd, 1H, $J_{5,6}$ = 3.7 Hz, $J_{6,6'}$ = 12.0 Hz, H-6), 4.10 (dd, 1H, $J_{5,6'}$ = 6.9 Hz, H-6'), 3.72 (br s, 2H, H-1,1'), 3.70 (s, 3H, OC*H*$_3$), 2.03 (s, 3H, 1 OAc), 2.01 (s, 3H, 1 OAc), 2.00 (s, 3H, 1 OAc); ^{13}C NMR δ 170.1, 169.7, 169.3 (OCOCH$_3$), 151.8, 141.6, 114.4, 113.9 (phenyl), 133.4 (C-2), 124.3 (C-3), 71.7, 71.2, (C-4,5), 61.4 (C-6), 55.0 (OCH$_3$), 45.5 (C-1), 20.5, 20.3, 20.2 (OCO*C*H$_3$).

(2*E*)-4,5,6-Tri-*O*-acetyl-1,2,3-trideoxy-1-(1-naphtylamino)-D-*erythro*-hex-2-enose (13f). The title compound was prepared from **10f**, according to the above given procedure for **13a**; oil, 67% yield; $[\alpha]_D$ +21° (*c* 1.0, chloroform); IR (film) 1740 (C=O ester), 1630 (C=C); ^{1}H NMR δ 7.78 (m, 2Harom.), 7.40-7.20 (m, 4Harom.), 6.52 (dd, 1H, J = 7.2 Hz, J = 1.1 Hz, 1Harom.), 5.99 (dt, 1H, $J_{1,2}$ = 5.0 Hz, H-2), 5.72 (dd, 1H, $J_{2,3}$ = 15.2 Hz, H-3), 5.51 (dd, 1H, $J_{3,4}$ = 6.8 Hz, $J_{4,5}$ = 4.8 Hz, H-4), 5.20 (m, 1H, H-5), 4.24 (dd, 1H, $J_{5,6}$ = 3.7 Hz, $J_{6,6'}$ = 12.1 Hz, H-6), 4.13 (dd, 1H, $J_{5,6'}$ = 6.9 Hz, H-6'), 3.92 (d, 2H, H-1,1'), 2.04 (s, 3H,

1 OAc), 2.01 (s, 3H, 1 OAc), 1.99 (s, 3H, 1 OAc); ^{13}C NMR δ 170.5, 169.9, 169.6 ($OCOCH_3$), 142.6, 134.1, 128.5, 126.4, 125.7, 119.8, 117.6, 104.7 (naphtyl), 132.7 (C-3), (124.6 (C-2), 71.9, 71.5 (C-4,5), 61.7 (C-6), 45.2 (C-1), 20.8, 20.7, 20.6 ($OCOCH_3$).

(2*E*,4*Z*)-4,6-Di-*O*-acetyl-1-isopropylamino-2,4-hexadiene (14a) and its (2*E*,4*E*) isomer (15a). Treatment of a 9:1 mixture of **11a** and **12a** with sodium borohydride, as indicated above for **13a**, afforded the 9:1 mixture of **14a** and **15a**. The time reaction was 20 min; oil, 82% yield; IR (film) 1745 (C=O ester), 1640 (C=C); ^{1}H NMR (2*E*,4*Z* isomer **14a**) δ 6.10 (d, 1H, $J_{2,3}$ = 15.3 Hz, H-3), 5.84 (dt, 1H, $J_{1,2}$ = 6.2 Hz, H-2), 5.48 (t, 1H, $J_{5,6}$ = 7.2 Hz, H-5), 4.56 (d, 2H, H-6,6'), 3.32 (d, 2H, H-1,1'), 2.82 (m, 1H, J = 6.2 Hz, N-C*H*), 2.26 (s, 3H, 1 OAc-4), 2.05 (s, 3H, 1 OAc-6), 1.77 (m, 1H, N*H*), 1.06 (d, 6H, $CHMe_2$); (2E,4*E* isomer, **15a**) δ 6.43 (d, 1H, $J_{2,3}$ = 15.6 Hz, H-3), 5.38 (t, 1H, $J_{5,6}$ = 7.5 Hz, H-5), 4,75 (d, 2H, H-6,6'); ^{13}C NMR (2*E*,4*Z* isomer, **14a**) δ 170.7 ($OCOCH_3$-6), 168,2 ($OCOCH_3$-4), 148.0 (C-4), 131.0 (C-3), 124.8 (C-2), 114.2 (C-5), 58.7 (C-6), 48.5 (C-1), 48.2 (N-C*H*), 22.7 ($CHMe_2$), 20.8, 20.4 ($OCOCH_3$).

(2*E*,4*Z*)-4,6-Di-*O*-acetyl-1-cyclohexylamino-2,4-hexadiene (14c) and its (2*E*,4*E*) isomer (15c). Treatment of a 9:1 mixture of **11c** and **12c** with sodium borohydride, as indicated above for **13a**, afforded the 9:1 mixture of **14c** and **15c**. The time reaction was 20 min; oil, 86% yield; IR (film) 1750 (C=O ester), 1640 (C=C); ^{1}H NMR (2*E*,4*Z* isomer, **14c**) δ 6.10 (d, 1H, $J_{2,3}$ = 15.3 Hz, H-3), 5.84 (dt, 1H, $J_{1,2}$ = 6.0 Hz, H-2), 5.48 (t, 1H, $J_{5,6}$ = 7.2 Hz, H-5), 4.55 (d, 2H, H-6,6'), 3.35 (d, 2H, H-1,1'), 2.39 (m, 1H, N-C*H*), 2.26 (s, 3H, 1 OAc-4), 2.05 (s, 3H, 1 OAc-6), 1.9-1.0 (m, 10H, cyclohexyl), 1.69 (m, 1H, N*H*); (2*E*,4*E* isomer, **15c**) δ 6.41 (d, 1H, $J_{2,3}$ = 15.6 Hz, H-3), 5.37 (t, 1H, $J_{5,6}$ = 7.6 Hz, H-5), 4.74 (d, 2H, H-6,6'); ^{13}C NMR (2*E*,4*Z* isomer, **14c**) δ 170.7 ($OCOCH_3$-6), 168.1 ($OCOCH_3$-4), 148.0 (C-4), 131.2 (C-3), 124.7 (C-2), 114.2 (C-5), 58.7 (C-6), 56.2 (N-C*H*), 47.9 (C-1), 33.3, 26.0, 24.9 (cyclohexyl), 20.8, 20.4 ($OCOCH_3$).

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