Carbohydrate Research, 128 (1984) 227–234
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

N-ARYL-D-LYXOPYRANOSYLAMINES, THEIR ACYL DERIVATIVES, AND SELECTIVE BENZOYLATION OF *N*-ACETYL-*N*-ARYL-α-D-LYXOPYRANOSYLAMINES

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(Received April 18th, 1983; accepted for publication, November 23rd, 1983)

ABSTRACT

N-*p*-Chlorophenyl- and *N*-*p*-methoxyphenyl-D-lyxopyranosylamines have been synthesised, and also their tri-*O*-acetyl, *N*-acetyl-tri-*O*-acetyl, and *N*-acetyl derivatives. The configurations and conformations of these compounds have been established. Some derivatives of the *N*-aryl-D-lyxopyranosylamines were obtained as two stable, crystalline $^4C_1$ and $^1C_4$ isomers. The effect of steric factors on $N \rightarrow O$ acetyl migration has been ascertained. Selective benzoylation of *N*-acetyl-*N*-aryl-α-D-lyxopyranosylamines afforded partially esterified derivatives in which the reactivity of the hydroxyl groups followed the sequence HO-4 > HO-3 > HO-2.

INTRODUCTION

Previous studies have been concerned with the synthesis, elucidation of the structure, and the properties of esters of some *N*-aryl- and *N*-acetyl-*N*-aryl-β-D-xylo-[1], -β-D-ribo-[2], and -α-L-arabino-pyranosylamines[3], and with establishment of the relative reactivity of the hydroxyl groups in these compounds. We now report on some *N*-aryl-D-lyxopyranosylamines and their derivatives.

RESULTS AND DISCUSSION

N-Aryl-D-lyxopyranosylamines (**1**, **2**) are colourless, crystalline, laevorotatory compounds. Mutarotation occurs rapidly in methanol or ethanol, and the value of $[\alpha]_D$ increases. Attempts to determine the anomeric configuration by using ^{1}H-n.m.r. spectroscopy (80 or 100 MHz) with acetone-d_6, methanol-d_4 , or pyridine-d_5 as solvents failed because the H-sugar's signals were complex multiplets at δ 4–5. The ^{13}C-n.m.r. spectra were also of no value. Crystalline **3** was the sole product obtained on acetylation of **1**, but acetylation of **2** gave the β-$^4C_1$ (**4**) and α-$^1C_4$ (**7**) isomers of 2,3,4-tri-*O*-acetyl-*N*-*p*-methoxyphenyl-D-lyxopyranosylamine, which were isolated by fractional crystallisation. The different behaviour of **1** and **2** on acetylation may be associated with the basicity of the amines. The pK_b values [4] of *p*-chloro- and *p*-methoxy-aniline are 10.02 and 8.71, respectively. The configu-

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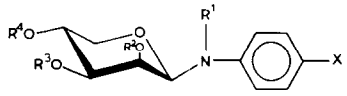
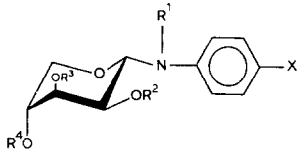


1 X = Cl, 2 X = OMe } , $R^1 = R^2 = R^3 = R^4 = H$

3 X = Cl, 4 X = OMe } , $R^1 = H, R^2 = R^3 = R^4 = Ac$

5 X = Cl, 6 X = OMe } , $R^1 = R^2 = R^3 = R^4 = Ac$



7 X = OMe, $R^1 = H, R^2 = R^3 = R^4 = Ac$

8 X = Cl, 9 X = OMe } , $R^1 = R^2 = R^3 = R^4 = Ac$

10 X = Cl, 11 X = OMe } , $R^1 = Ac, R^2 = R^3 = R^4 = H$

12 X = Cl, 13 X = OMe } , $R^1 = Ac, R^2 = R^3 = R^4 = Bz$

14 X = Cl, 15 X = OMe } , $R^1 = Ac, R^2 = H, R^3 = R^4 = Bz$

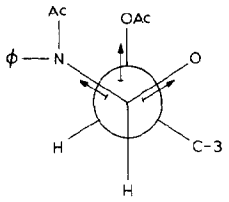
16 X = Cl, 17 X = OMe } , $R^1 = Ac, R^3 = H, R^2 = R^4 = Bz$

18 X = Cl, 19 X = OMe } , $R^1 = Ac, R^2 = R^3 = H, R^4 = Bz$

rations and conformations of **3**, **4**, and **7** were assigned on the basis of ^{1}H-n.m.r. data. In the spectra of **3** and **4**, the coupling constants ($J_{1,2} = J_{2,3} = 2$, $J_{4,5e}$ 2, $J_{4,5a}$ 9 Hz) together with the $[\alpha]_D$ value indicate the β-$^4C_1$ structure. Also, the $\Delta\delta_{H\text{-}5e,H\text{-}5a}$ value of ~0.7 p.p.m. is characteristic of this conformation[1,5,6]. On the other hand, the data for **7** ($J_{1,2}$ 9, $J_{2,3} = J_{3,4} = 2$, $J_{4,5e} = J_{4,5a} = 2$ Hz; $\Delta\delta_{H\text{-}5e,H\text{-}5a}$ 0.12 p.p.m.)[1,5,6] reveal the α-$^1C_4$ structure. The direction of changes of the chemical shift values on going from **4** to **7** accords with the rule of Lemieux and Stevens[7].

N-Acetylation of **3**, **4**, and 7 by the Frérejacque method[8] afforded *N*-acetyl-2,3,4-tri-*O*-acetyl-*N*-aryl-D-lyxopyranosylamines as mixtures of the $^4C_1$ and $^1C_4$ isomers. Each isomer was obtained homogeneous by chromatography or fractional crystallisation of the crude reaction products. The configurations and conformations of **5**, **6**, **8**, and **9** were established on the basis of ^{1}H-n.m.r. data. The β-$^4C_1$ structure of **5** and **6** follows from the signal structure for H-1(s), H-2(s) (the $J_{1,2}$ and $J_{2,3}$ values were not discernible), H-5*e*(dd), and H-5*a*(dd), the coupling constants $J_{4,5e}$ 3 and $J_{4,5a}$ 9 Hz, and the magnitude (~0.65 p.p.m.) of $\Delta\delta_{H\text{-}5e,H\text{-}5a}$. For **8** and **9**, the structure of the signals and the numerical values of the coupling constants [H-1(d), $J_{1,2}$ 10 Hz; H-2(dd), $J_{2,3}$ 3 Hz; H-5*e*(dd) and H-5*a*(dd), $J_{4,5e} = J_{4,5a} = 3$ Hz] reveal the α-$^1C_4$ structure. The $\Delta\delta_{H\text{-}5e,H\text{-}5a}$ value of 0.75 p.p.m. likewise supports this structure[1,5,6].

Although some pyranoses and their derivatives exist in solution in both chair conformations at equilibrium[9], the isolation of two "conformational" isomers in the solid state is rarely observed[10,11]. Presumably, two isomers of *N*-acetyl-*N*-aryl and *N*-aryl derivatives of 2,3,4-tri-*O*-acetyl-D-lyxopyranosylamine were obtained because the energies of the β-$^4C_1$ and α-$^1C_4$ structures are similar, as for the β-$^4C_1$ and α-$^1C_4$ forms (10.4 and 10.8 kJ.mol^{-1}, respectively[12]) of D-lyxopyranose. The stability of the β-$^4C_1$ and α-$^1C_4$ derivatives of the *N*-acetyl-*N*-aryl- and *N*-aryl-D-



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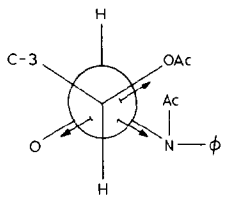

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lyxopyranosylamines can be compared on the basis of stereoelectronic interactions. For **3–6** (β-$^4C_1$), the $\Delta 2$ effect[13,14] and dipole interactions[15] are involved (C-1-N, C-1-O, C-2-OAc dipoles shown in the projection **20** along the C-1–C-2 bond). On the other hand, in the α-$^1C_4$ structure (**7–9**), AcO-2,3 are axial, but there is no $\Delta 2$ effect and the dipole–dipole interactions are more favourable, because the direction of the C-1-O dipole is opposite to the resultant dipole of the C-1-N and C-2-OAc bonds (projection **21**).

Taking into account the yield of the β-$^4C_1$ and α-$^1C_4$ isomers formed on acetylation, it appears that *N*-acetylation favours the formation of the α-$^1C_4$ isomer, which could reflect an increase in the $\Delta 2$ effect in β-$^4C_1$ *N*-acetyl-tri-*O*-acetyl-D-lyxopyranosylamines in comparison with the corresponding *O*-acetyl derivatives.

Treatment of the *N*-acetyl-tri-*O*-acetyl-D-lyxopyranosylamines **8** and **9** (α-$^1C_4$) with dimethylamine in methanol effected *O*-deacetylation only, to afford the *N*-acetyl-*N*-aryl-α-D-lyxopyranosylamines **10** and **11**, respectively, whereas **5** and **6** (β-$^4C_1$) underwent both *O*- and *N*-deacetylation, to give *N*-aryl-D-lyxopyranosylamines **1** and **2**, respectively. In both groups of compounds, *O*-deacetylation occurs first, but for **5** and **6**, because HO-2 and N-Ac are *cis*, 1→2 acetyl migration occurs followed by *O*-deacetylation.

The relative reactivity of the hydroxyl groups in the *N*-acetyl-*N*-aryl-α-D-lyxopyranosylamines **10** and **11** was determined by benzoylation at $\sim -30°$, using 1 mol of sugar derivative and 2.5 mol of benzoyl chloride. Under these conditions, the products were *N*-acetyl-*N*-aryl-2,3,4-tri- (**12**, **13**), -3,4-di- (**14**, **15**), -2,4-di- (**16**, **17**), and -4- (**18**, **19**) -*O*-benzoyl-α-D-lyxopyranosylamines, and each was isolated by chromatography. Inspection of the ^{1}H-n.m.r. data (Table I) reveals the α-$^1C_4$ structure of each of these benzoates.

The positions of the unsubstituted hydroxyl groups in **14–19** were determined by comparing their ^{1}H-n.m.r. data with those (Table I) of the corresponding tribenzoate (**12** or **13**). The unsubstituted hydroxyl group in **14** and **15** was located at C-2 on the basis of the downfield shift (~1.40 p.p.m.) of the H-2 signal compared with those of **12** and **13**. Both the direction and magnitude of this shift displacement corresponds to the C-OH→COBz transition. Likewise, for **16** and **17**, the only shift (~1.43) was associated with the H-3 signals, thus indicating the unsubstituted hydroxyl group to be attached to C-3. The benzoyl group in **18** and **19** must be at C-4,

TABLE I

^{1}H-N M R. DATA[a] FOR COMPOUNDS **3–19**

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*e	*H-5*a	$\Delta\delta_{H\text{-}5e,H\text{-}5a}$	*NAc*	OCH_3	*OAc*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5c}$	$J_{4,5a}$
3	5.35d	5.05t	4.77m		3.95dd	3.30dd	0.65	—	—	1.87(2×) 2.02	2	2	—	2	9
4	5.35d	5.05t	4.77m		3.97dd	3.27dd	0.70	—	3.67	1.95(2×) 2.07	2	2	—	2	9
5	5.92s	5.40s	5.07–4.82m		4.10dd	3.35dd	0.65	1.35	—	1.62 1.75 1.87	—	—	—	3	9
6	5.90s	5.40s	5.02–4.77m		4.07dd	3.35dd	0.68	1.32	3.63	1.60 1.77 1.87	—	—	—	3	9
7	5.22d	4.24dd	5.02t	4.75m	3.87dd	3.75dd	0.12	—	3.62	1.90 1.95 2.00	9	2	2	2	2
8	6.10d	4.37dd	5.25t	4.62m	3.95dd	3.80dd	0.15	1.70	—	1.82 1.87 2.00	10	3	3	3	3
9	6.05d	4.37dd	5.22t	4.60m	3.97dd	3.80dd	0.17	1.70	3.65	1.82 1.85 2.00	10	3	3	3	3
10	5.92d	4.60dd	5.17t	4.92m	—	—	—	1.82	—	—	10	3	3	—	—
11	5.95d	4.55dd	5.15t	4.90m	—	—	—	1.85	3.60	—	10	3	3	—	—
12	6.55d	4.92dd	5.75t	5.10m	4.27dd	4.05dd	0.22	1.72	—	—	10	3	3	2	2
13	6.57d	4.92dd	5.77t	5.07m	4.25dd	4.02dd	0.23	1.70	3.60	—	10	3	3	3	3
14	6.10d	3.50dd	5.35t	4.95m	4.02dd	3.87dd	0.15	1.67	—	—	10	3	3	2.5	2.5
15	6.15d	3.45dd	5.35d	5.00m	4.02dd	3.87dd	0.15	1.67	3.65	—	10	3	3	2.5	2.5
16	6.42d	4.62dd	4.32t	4.92m	4.02dd	3.87dd	0.15	1.62	—	—	9	3	3	2	2
17	6.47d	4.65dd	4.32t	4.90m	4.02dd	3.82dd	0.20	1.57	3.60	—	9	3	3	2	2
18	5.95d	3.25dd	3.85m	4.95m	4.15dd	3.95dd	0.20	1.75	—	—	10	3	3	2	2.5
19	5.97d	3.32dd	3.82m	4.95m	4.15dd	3.97dd	0.18	1.75	3.65	—	10	3	3	2	2.5

[a]Chemical shifts (δ scale): s, singlet; d, doublet; m, multiplet; t, triplet. Coupling constants (±0.5 Hz) were determined by first-order analysis.

because the H-2 signals are shifted by ~1.65 p.p.m., and the H-3 signals by ~1.95 p.p.m.

The products obtained after selective benzoylation indicate the reactivity sequence for **10** and **11** to be HO-4 > HO-3 > HO-2.

EXPERIMENTAL

Melting points are uncorrected. Optical rotations were determined (Hilger–Watt instrument) for solutions (*c* 0.5) in ethanol (**1** and **2**) or chloroform (**3–19**) at 22°. T.l.c. was performed on silica gel G with *A*, carbon tetrachloride–acetone (3:1); or *B*, di-isopropyl ether–benzene (4:1). Column chromatography was performed on Kieselgel (<0.08 mm). ^{1}H-N.m.r. spectra ($CDCl_3$, internal Me_4Si) were recorded with a Tesla-BS 487C (80 MHz) spectrometer. I.r. spectra were recorded for Nujol mulls with a Perkin–Elmer 257 spectrophotometer.

N-*Aryl*-D-*lyxopyranosylamines*. — A mixture of 0.1 mol of D-lyxose, the amine (*p*-chloro- or *p*-methoxy-aniline), and dry ethanol (75 mL) was heated at ~100° for 1 h, cooled, and diluted with ether (10 mL).

The *N*-*p*-chlorophenyl derivative **1** (95%) had m.p. 155–158°, $[\alpha]_D$ −133→ −1°.

Anal. Calc. for $C_{11}H_{14}ClNO_4$: C, 50.86; H, 5.39; N, 5.39. Found: C, 50.64; H, 5.39; N, 5.41.

The *N*-*p*-methoxyphenyl derivative **2** (84%) had m.p. 115–120°, $[\alpha]_D$ −160→ −5°.

Anal. Calc. for $C_{12}H_{17}NO_5$: C, 56.47; H, 6.66; N, 5.50. Found: C, 56.72; H, 6.91; N, 5.47.

2,3,4-Tri-O-*acetyl*-N-*aryl*-D-*lyxopyranosylamines* (**3**, **4**, *and* **7**). — Conventional acetylation of **1** (0.05 mol) with acetic anhydride in pyridine afforded **3** (90%), m.p. 150° (from methanol), $[\alpha]_D$ −64→ −37°, R_F (solvent *A*) 0.75.

Anal. Calc. for $C_{17}H_{20}ClNO_7$: C, 52.91; H, 5.18; N, 3.63. Found: C, 52.47; H, 5.10; N, 3.70.

Similar acetylation of **2** gave (t.l.c., solvent *A*) a mixture of two compounds in the ratio ~2:1. Fractional crystallisation from ether–light petroleum gave the β anomer **4** (first fraction, 55%), m.p. 135°, $[\alpha]_D$ −88→ −54°, R_F (solvent *A*) 0.74; ν_{max} 3330 (NH) and 1750 cm^{-1} (ester CO).

Anal. Calc. for $C_{18}H_{23}NO_8$: C, 56.69; H, 6.03; N, 3.67. Found: C, 56.41; H, 6.07; N, 3.86.

The second fraction was the α anomer **7** (25%), m.p. 104°, $[\alpha]_D$ −44→ −30°, R_F (solvent *A*) 0.76; ν_{max} 3370 (NH) and 1750 cm^{-1} (ester CO).

Anal. Found: C, 56.74; H, 5.98; N, 3.72.

N-*Acetyl-2,3,4-tri*-O-*acetyl*-N-*aryl*-D-*lyxopyranosylamines* (**5**, **6**, **8**, **9**). — A mixture of **3**, **4**, or **7** (0.03 mol), acetic anhydride (30 mL), and zinc chloride (0.2 g) was heated at ~100° for 10 min, cooled, and poured into ice and water. The crude product from **3** (two components) was fractionally crystallised from ether–

light petroleum (2:1) or ethanol, to furnish the α anomer **8** (first fraction, 55%), m.p. 192°, $[\alpha]_D$ −101°, R_F (solvent *A*) 0.55; ν_{max} 1750 (ester CO) and 1675 cm^{-1} (amide CO).

Anal. Calc. for $C_{19}H_{22}ClNO_8$: C, 53.33; H, 5.14; N, 3.27. Found: C, 53.07; H, 5.00; N, 3.35.

The second fraction was the β anomer **5** (22%), m.p. 129°, $[\alpha]_D$ +4°, R_F (solvent *A*) 0.60; ν_{max} 1750 (ester CO) and 1660 cm^{-1} (amide CO).

Anal. Found: C, 53.21; H, 4.98; N, 3.46.

Column chromatography of the products from **4** gave the β anomer **6** as a syrup (25%), $[\alpha]_D$ +6°, R_F (solvent *A*) 0.58; ν_{max} 1750 (ester CO) and 1680 cm^{-1} (amide CO).

Anal. Calc for $C_{20}H_{25}NO_9$: C, 56.73; H, 5.91; N, 3.30. Found: C, 56.47; H, 5.82; N, 3.45.

Likewise, **7** gave the α anomer **9** (53%), m.p. 143°, $[\alpha]_D$ −104°, R_F (solvent *A*) 0.52; ν_{max} 1750 (ester CO) and 1680 cm^{-1} (amide CO).

Anal. Calc. for $C_{20}H_{25}NO_9$: C, 56.73; H, 5.91; N, 3.30. Found: C, 56.77; H, 5.92; N, 3.58.

N-*Acetyl*-N-*aryl*-α-D-*lyxopyranosylamines* (**10**, **11**). — A solution of 0.05 mol of **8** in dry methanol (100 mL) containing 0.5 mol of dimethylamine was kept at 20° for 14 h and then concentrated, and the residue was crystallised from ether to give **10** (80%), m.p. 53°, $[\alpha]_D$ −46°, R_F (solvent *A*) 0.03; ν_{max} 3300 (OH) and 1650 cm^{-1} (amide CO).

Anal. Calc. for $C_{13}H_{16}ClNO_5$: C, 51.74; H, 5.31; N, 4.64. Found: C, 51.58; H, 5.46; N, 4.52.

Likewise, **9** gave **11** (94%), m.p. 208°, $[\alpha]_D$ −51°, R_F (solvent *A*) 0.03; ν_{max} 3310 (OH) and 1630 cm^{-1} (amide CO).

Anal. Calc. for $C_{14}H_{19}NO_6$: C, 56.56; H, 6.39; N, 4.71. Found: C, 56.65; H, 6.49; N, 4.89.

Under the above conditions, **5** or **6** gave only **1** or **2**, respectively.

Selective benzoylation of N-*acetyl*-N-*aryl*-α-D-*lyxopyranosylamines*. — To a solution of **10** (0.03 mol) in dry pyridine (50 mL) at −30° was added benzoyl chloride (0.075 mol) dropwise during 30 min. The mixture was kept for 3 h at ~ −25° and for 1 h at +20°. T.l.c. (solvent *B*) then indicated almost complete conversion into four products. Chloroform (150 mL) was added, and the mixture was poured into ice and water. The chloroform layer was washed with 2–3% sulfuric acid and aqueous 5% sodium hydrogencarbonate, dried (Na_2SO_4), and concentrated. Column chromatography (solvent *B*) of the syrupy residue gave, first, *N*-acetyl-2,3,4-tri-*O*-benzoyl-*N*-*p*-chlorophenyl-α-D-lyxopyranosylamine (**12**, 19%), m.p. 248°, $[\alpha]_D$ −31°, R_F (solvent *B*) 0.7; ν_{max} 1725 (ester CO) and 1670 cm^{-1} (amide CO).

Anal. Calc. for $C_{34}H_{28}ClNO_8$: C, 66.50; H, 4.56; N, 2.28. Found: C, 66.55; H, 4.70; N, 2.35.

Eluted second was *N*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-chlorophenyl-α-D-lyxo-

pyranosylamine (**14**, 18%), m.p. 200°, $[\alpha]_D$ −78°, R_F 0.40; ν_{max} 3280 (OH), 1725 (ester CO), and 1660 cm^{-1} (amide CO).

Anal. Calc. for $C_{27}H_{24}ClNO_7$: C, 63.69; H, 4.71; N, 2.75. Found: C, 63.61; H, 4.92; N, 3.04.

Eluted third was *N*-acetyl-2,4-di-*O*-benzoyl-*N*-*p*-chlorophenyl-α-D-lyxopyranosylamine (**16**, 14%), m.p. 50°, $[\alpha]_D$ −85°, R_F 0.28; ν_{max} 3350 (OH), 1725 (ester CO), and 1665 cm^{-1} (amide CO).

Anal. Calc. for $C_{27}H_{24}ClNO_7$: C, 63.69; H, 4.71; N, 2.75. Found: C, 63.82; H, 5.09; N, 2.56.

Eluted fourth was *N*-acetyl-4-*O*-benzoyl-*N*-*p*-chlorophenyl-α-D-lyxopyranosylamine (**18**, 34%), m.p. 225°, $[\alpha]_D$ −128°, R_F 0.10; ν_{max} 3420, 3490 (OH), 1725 (ester CO), and 1650 cm^{-1} (amide CO).

Anal. Calc. for $C_{20}H_{20}ClNO_6$: C, 59.18; H, 4.93; N, 3.45. Found: C, 59.23; H, 4.80; N, 3.68.

Similar treatment of **11** gave the following four products.

N-Acetyl-2,3,4-tri-*O*-benzoyl-*N*-*p*-methoxyphenyl-α-D-lyxopyranosylamine (**13**, 21%), m.p. 247°, $[\alpha]_D$ −44°, R_F (solvent *B*) 0.65; ν_{max} 1725 (ester CO) and 1675 cm^{-1} (amide CO).

Anal. Calc. for $C_{35}H_{31}NO_9$: C, 68.96; H, 5.09; N, 2.29. Found: C, 68.94; H, 5.16; N, 2.55.

N-Acetyl-3,4-di-*O*-benzoyl-*N*-*p*-methoxyphenyl-α-D-lyxopyranosylamine (**15**, 19%), m.p. 206°, $[\alpha]_D$ −82°, R_F 0.36; ν_{max} 3300 (OH), 1725 (ester CO), and 1645 cm^{-1} (amide CO).

Anal. Calc. for $C_{28}H_{27}NO_8$: C, 66.53; H, 5.34; N, 2.77. Found: C, 66.30; H, 5.24; N, 3.00.

N-Acetyl-2,4-di-*O*-benzoyl-*N*-*p*-methoxyphenyl-α-D-lyxopyranosylamine (**17**, 14%), m.p. 105°, $[\alpha]_D$ −87°, R_F 0.32; ν_{max} 3400 (OH), 1725 (ester CO), and 1660 cm^{-1} (amide CO).

Anal. Calc. for $C_{28}H_{27}NO_8$: C, 66.53; H, 5.34; N, 2.77. Found: C, 66.43; H, 5.16; N, 2.78.

N-Acetyl-4-*O*-benzoyl-*N*-*p*-methoxyphenyl-α-D-lyxopyranosylamine (**19**, 35%), m.p. 182°, $[\alpha]_D$ −133°, R_F 0.08; ν_{max} 3490 (OH), 1725 (ester CO), and 1650 cm^{-1} (amide CO).

Anal. Calc. for $C_{21}H_{23}NO_7$: C, 62.84; H, 5.73; N, 3.49. Found: C, 62.72; H, 6.00; N, 3.31.

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