*Carbohydrate Research*, 210 (1991) 327–332
Elsevier Science Publishers B.V., Amsterdam



# Note

## Stereoselective synthesis of nitropyrazolines: 1,3-dipolar cycloaddition of diazoalkanes to (*E*)-4,5,6,7,8-penta-*O*-acetyl-1,2,3-trideoxy-2-*C*-nitro-D-*manno*-oct-2-enitol

Manuel Mancera, Enrique Rodriguez, Isaac Roffé, Juan A. Galbis*,
*Departamento de Química Orgánica y Farmacéutica, Universidad de Sevilla, Apartado 874, 41080 Sevilla (Spain)*

Clara F. Conde, and Alejandro Conde
*Departamento de Física de la Materia Condensada, Universidad de Sevilla, Apartado 1065, 41080 Sevilla (Spain)*

(Received February 16th, 1990; accepted for publication, August 1st, 1990)

We have described a stereoselective synthesis of 3-nitro-4-(D-*galacto*-penta-acetoxypentyl)pyrazolines by cycloaddition of diazoalkanes to sugar nitro-olefins that have the D-*galacto* configuration[1]. Baer and Gilron[2] have also reported the preparation of a nitropyrazoline, in moderate yield (29%), by the addition of diazomethane to 3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-nitro-D-*manno*-hept-1-enitol, but the stereochemistry of the product was not discussed.

We now report the preparation of (*E*)-4,5,6,7,8-penta-*O*-acetyl-1,2,3-trideoxy-2-*C*-nitro-D-*manno*-oct-2-enitol (**1**), and its reaction with diazoalkanes has been studied in order to ascertain the influence of the configuration of the sugar chain on the stereoselectivity. The products are of interest because they are acyclonucleosides, and compounds of this type have received attention as antiviral drugs[3,4].

As with D-galactose[1], the reaction of D-mannose with nitroethane in the presence of sodium methoxide gave only two (84:16 ratio) of the four possible stereoisomeric 1,2-dideoxy-2-*C*-nitro-octitols ($^1$H- and $^{13}$C-n.m.r. data), treatment of the hexa-acetates of which with sodium hydrogen carbonate gave 81% of **1**. The *E* configuration was assigned to **1** on the basis of the $^1$H-n.m.r. data. Thus, the allylic coupling ($J_{1,3}$ 1.1 Hz) indicated the *E* configuration[5] and the chemical shift of the resonance of the olefinic proton (6.87 p.p.m.) was closer to that (6.91 p.p.m.) expected for the *E* configuration than to that (6.29 p.p.m.)[6] for the *Z* configuration. The $J_{3,4}$ value of 7.4 Hz is also indicative of an *anti* disposition of H-3,4. Hence, the conformation **1**(*E*) must preponderate in solution with H-4 eclipsed with the ethylenic bond and no 1,3-parallel interactions of acetoxyl groups.

* Author for correspondence.

0008-6215/91/$ 03.50 

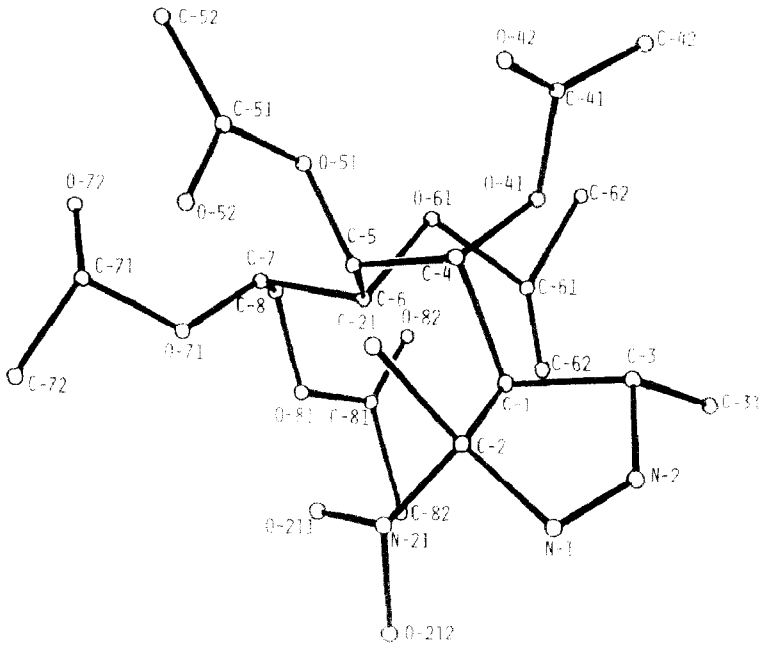
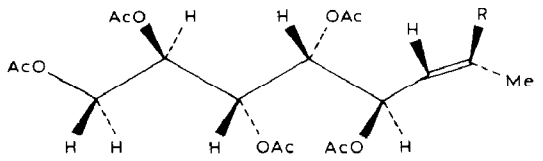



Fig. 1. An ORTEP drawing of **2** ($C_{30}H_{39}N_3O_{12}$). Only non-hydrogen atoms are represented.

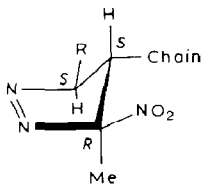
The cycloaddition reaction of **1** with diazoethane at 0° in 1,4-dioxane gave the nitropyrazoline **2** (95%). The $^1$H- and $^{13}$C-n.m.r. spectra indicated the presence of only one stereoisomer. The addition of the diazoalkane to the less hindered face of the nitro-olefin yielded the 3*R*,4*S* diastereomer. The $J_{4,5}$ value of 7.8 Hz indicated an *anti* arrangement of H-4,5 in agreement with a 5*S* configuration in a $^4E$ conformation of the heterocycle. This assignation was proved by X-ray analysis (see Experimental). Figure 1 shows a drawing of the molecule of **2** in which only the non-H atoms are represented. As the absolute stereochemistry of the sugar chain atoms is known, the 3*R*,4*S*,5*S* configuration can be assigned to the new chiral centres.

Aromatisation of **2**, effected with hydrogen chloride, gave the pyrazole **4** (90%), the structure of which was proved by elemental analysis and spectral data.

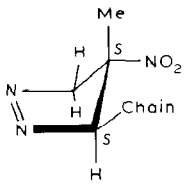
When **1** was treated with diazomethane, a mixture (quantitative) of the two possible regioisomers **3** (86%) and **3′** (14%) was obtained (n.m.r. data), which could not be resolved by chromatography. Although the absolute stereochemistry of **3** was not determined, the 3*R*,4*S* configuration was assigned by analogy with the results with diazoethane. The regioisomer **3′** must also arise by addition to the less hindered face of the olefin and the 3*S*,4*S* configuration was assigned. The aromatisation of the mixture of **3** and **3′** gave a syrupy major product (**5**, 45% after column chromatography). Compounds **3** and **3′** are probably regioisomers because, in the reaction[3] of diazomethane with (*E*)-4,5,6,7,8-penta-*O*-acetyl-1,2,3-trideoxy-2-*C*-nitro-D-*galacto*-oct-2-enitol, the two pyrazolines obtained were transformed into two regioisomeric pyrazoles. However, since only the pyrazole **5** was isolated, **3′** could be a diastereomer of **3**, formed by addition of diazomethane to the other face of the nitro olefin.



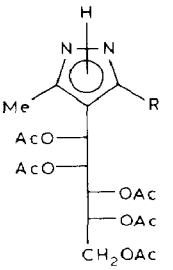
1 (*E*) R = $NO_2$



2 R = Me
3 R = H



3′



4 R = Me
5 R = H
6 R = $CO_2Et$

Chain = D-*manno*-pentitol-1-yl

Compound **1** failed to react with ethyl diazoacetate under conditions employed with the diazoalkanes. However, when the reaction was carried out in dichloromethane, under reflux, the syrupy pyrazole **6** was obtained.

## EXPERIMENTAL

*General methods.* — Solutions were concentrated *in vacuo* at <40°. Melting points were determined with an Electrothermal apparatus and are uncorrected. Optical rotations were measured at 20–25° with a Perkin–Elmer 241 polarimeter (10-cm cell). I.r. spectra were recorded with a Perkin–Elmer 1310 spectrophotometer. F.t.-n.m.r. spectra (in $CDCl_3$) were obtained with Bruker WP-80-SY and Varian XL-200 spectrometers. T.l.c. was performed on Silica Gel $60F_{254}$ (Merck) with detection with u.v. light or by charring with sulfuric acid. Ascending p.c. was carried out on Whatman No. 1 paper, using *A*, butan-1-ol–pyridine–water (1:1:1); and *B*, butan-1-ol–acetone–water (2:7:1); and detection with alkaline silver nitrate.

*1,2-Dideoxy-2-C-nitro-octitols.* — To a stirred suspension of D-mannose (8.00 g, 44.41 mmol) in dry methanol (35 mL) and nitroethane (45.00 mL) was added cold methanolic sodium methoxide prepared from sodium (2.00 g) and methanol (46 mL). The mixture was stirred for 24 h, and the sodium aci-nitroalcohols were collected and washed with cold methanol, ether, and light petroleum. An aqueous solution was treated with an excess of Dowex 50 ($H^+$) resin, then concentrated to yield a syrup that was crystallised from ethanol to afford a mixture (6.2 g, 55%) of two octitols in the ratio 86:14, m.p. 168–169°; $\nu_{max}$ 3350 (OH) and 1550 $cm^{-1}$ ($NO_2$). N.m.r. data [$(CD_3)_2SO$]: major product, $^1H$, $\delta$ 1.50 (d, 3 H, $J_{1,2}$ 6.7 Hz, H-1,1,1), 3.20–3.80 (m, 6 H, H-4/8), 4.12

(dd, 1 H, $J_{3,4}$ 1.9 Hz, H-3), 4.76 (m, 1 H, $J_{2,3}$ 6.3 Hz, H-2); $^{13}$C, $\delta$ 15.40 (C-1), 64.40 (C-8), 69.40–70.30 (C-4/7), 72.20 (C-3), 88.20 (C-2); minor product, $^1$H, $\delta$ 1.41 (d, 3 H, $J_{1,2}$ 7.7 Hz, H-1), 3.20–3.80 (m, 7 H, H-3/8), 4.85 (m, 1 H, H-2); $^{13}$C, $\delta$ 16.60 (C-1), 64.40 (C-8), 69.40–70.30 (C-4/7), 73.10 (C-3), 86.20 (C-2).

*Anal.* Calc. for $C_8H_{15}NO_8$: C, 37.65; H, 6.71; N, 5.49. Found: C, 37.83; H, 6.69; N, 5.14.

*3,4,5,6,7,8-Hexa-*O*-acetyl-1,2-dideoxy-2-*C*-nitro-octitols.* — A solution of the above nitroalcohols (0.81 g, 3.17 mmol) in acetic anhydride (5 mL) was treated with one drop of conc. sulfuric acid. After 24 h at room temperature, the mixture was poured onto ice, and the resulting solid was recrystallised from ethanol to afford a mixture (1.25 g, 78%) of hexa-acetates, m.p. 80–81°, $R_f$ 0.44 and 0.43 (3:1 ether–hexane); $\nu_{max}$ 1760 (C=O) and 1560 cm$^{-1}$ ($NO_2$). N.m.r. data ($CDCl_3$): major product, $^1$H, $\delta$ 1.48 (d, 3 H, $J_{1,2}$ 6.9 Hz, H-1,1,1), 2.09 (s, 15 H, 5 OAc), 3.99 (dd, 1 H, $J_{7,8'}$ 5.0 Hz, H-8'), 4.24 (dd, 1 H, $J_{7,8}$ 3.0, $J_{8,8'}$ –12.5 Hz, H-8), 4.63 (dq, 1 H, $J_{2,3}$ 6.0 Hz, H-2), 4.99 (m, 1 H, H-7), 5.21–5.56 (m, 3 H, H-4,5,6), 5.50 (dd, 1 H, $J_{3,4}$ 1.6 Hz, H-3); $^{13}$C, $\delta$ 14.70 (C-1), 20.50 (OAc), 61.80 (C-8), 67.10–68.40 (C-4/7), 69.70 (C-3), 81.20 (C-2), 169.80 (OAc); minor product, $^1$H, $\delta$ 1.63 (d, 3 H, $J_{1,2}$ 6.7 Hz, H-1,1,1), 2.09 (s, 15 H, 5 OAc), 3.99 (dd, 1 H, $J_{7,8'}$ 5.0 Hz, H-8'), 4.24 (dd, 1 H, $J_{7,8}$ 3.0, $J_{8,8'}$ –12.5 Hz, H-8), 4.62 (dq, 1 H, H-2), 4.99 (m, 1 H, H-7), 5.21–5.56 (m, 4 H, H-3/6); $^{13}$C, $\delta$ 16.00 (C-1), 20.40 (OAc), 61.80 (C-8), 67.10–68.70 (C-4/7), 70.40 (C-3), 83.00 (C-2), 169.80 (OAc).

*Anal.* Calc. for $C_{30}H_{39}NO_{14}$: C, 47.34; H, 5.76; N, 2.76. Found: C, 47.45; H, 5.54; N, 2.49.

*4,5,6,7,8-Penta-*O*-acetyl-1,2,3-trideoxy-2-*C*-nitro-*D*-manno-oct-2-enitol* (**1**). — A solution of the above mixture of hexa-acetates (0.70 g, 1.38 mmol) in dry benzene (5 mL) was boiled under reflux (2.5 h) in the presence of sodium hydrogen carbonate (5.00 g), then cooled, filtered, and concentrated. The solid residue was recrystallised from ethanol to give **1** (0.50 g, 81%), m.p. 104–106°, $[\alpha]_D$ +49° (*c* 0.5, dichloromethane); $\nu_{max}$ 1750 (C=O) and 1545 cm$^{-1}$ ($NO_2$). N.m.r. data ($CDCl_3$): $^1$H, $\delta$ 2.02 (s, 15 H, 5 OAc), 2.27 (d, 3 H, $J_{1,3}$ 1.1 Hz, H-1,1,1), 4.06 (dd, 1 H, $J_{7,8'}$ 4.4, $J_{8,8'}$ –12.5 Hz, H-8'), 4.25 (dd, 1 H, $J_{7,8}$ 2.5 Hz, H-8), 5.36–5.94 (m, 4 H, H-4/7), 6.87 (m, 1 H, $J_{3,4}$ 7.4 Hz, H-3); $^{13}$C, $\delta$ 13.00 (C-1), 20.25 (OAc), 61.60 (C-8), 67.00–69.30 (C-4/7), 127.20 (C-3), 152.20 (C-2), 169.35 (OAc).

*Anal.* Calc. for $C_{18}H_{25}NO_{12}$: C, 48.32; H, 5.63; N, 3.13. Found: C, 48.29; H, 5.68; N, 2.83.

*(3R,4S,5S)-3,5-Dimethyl-3-nitro-4-(penta-*O*-acetyl-*D*-manno-pentitol-1-yl)-1-pyrazoline* (**2**). — To a solution of **1** (0.31 g, 0.69 mmol) in 1,4-dioxane (15 mL) at 0° was added dropwise a solution of diazoethane (0.10 g, 1.78 mmol) in ether (5 mL). The mixture was stored for 48 h at 0°, then concentrated, and the residue was crystallised from ethanol to give **2** (0.33 g, 95%), m.p. 99–100°, $[\alpha]_D$ +80° (*c* 0.5, dichloromethane), $R_f$ 0.40 (ether–hexane, 3:1); $\nu_{max}$ 1750 (C=O) and 1550 cm$^{-1}$ ($NO_2$). N.m.r. data ($CDCl_3$): $^1$H, $\delta$ 1.66 (d, 3 H, $J_{Me,5}$ 7.1 Hz, Me), 1.84 (s, 3 H, Me), 2.08 (s, 15 H, 5 OAc), 2.87 (t, 1 H, $J_{4,5} = J_{4,1'}$ 7.8 Hz, H-4), 3.81 (dd, 1 H, $J_{4',5'}$ 4.4, $J_{5',5'}$ –13.3 Hz, H-5'), 4.28 (dd, 1 H, $J_{4',5'}$ 3.3 Hz, H-5'), 4.48 (dq, 1 H, H-5), 5.07–5.22 (m, 3 H, H-2',3',4'), 5.57 (dd, 1

H, H-1'); $^{13}C$, $\delta$ 16.60 (Me), 17.90 (Me), 20.15 (OAc), 47.10 (C-4), 61.10 (C-5'), 67.10–69.60 (C-1'/4'), 87.50 (C-5), 124.10 (C-3), 169.70 (OAc).

*Anal.* Calc. for $C_{20}H_{29}N_3O_{12}$: C, 47.71; H, 5.81; N, 8.35. Found: C, 47.80; H, 5.84; N, 8.26.

*(3R,4S)-3-Methyl-3-nitro-4-(penta-*O*-acetyl-*D*-manno-pentitol-1-yl)-1-pyrazoline* (**3**) *and (3S,4S)-4-methyl-4-nitro-3-(penta-*O*-acetyl-*D*-manno-pentitol-1-yl)-1-pyrazoline* (**3'**). — A solution of **1** (1.80 g, 4.02 mmol) in 1,4-dioxane (15 mL) was treated with diazomethane (0.39 g, 9.28 mmol) as described in the preparation of **2**. The resulting solution was stored at 0° for 1 h, then concentrated to dryness. Crystallisation of the solid residue from methanol gave a mixture (1.96 g) of **3** and **3'**, m.p. 88–90°; $\nu_{max}$ 1750 (C=O) and 1550 $cm^{-1}$ ($NO_2$). N.m.r. data ($CDCl_3$): **3**, $^1H$, $\delta$ 1.83 (s, 3 H, Me), 2.02–2.12 (s, 15 H, 5 OAc), 3.06 (m, 1 H, H-4), 4.04 (dd, 1 H, $J_{4',5''}$ 4.4, $J_{5',5''}$ −12.8 Hz, H-5''), 4.26 (dd, 1 H, $J_{4',5'}$ 3.1 Hz, H-5'), 4.57 (dd, 1 H, $J_{4,5b}$ 6.9, $J_{5a,5b}$ −18.2 Hz, H-5b), 4.96 (dd, 1 H, $J_{4,5a}$ 8.7 Hz, H-5a), 5.03–5.40 (m, 4 H, H-1'/4'); $^{13}C$, $\delta$ 16.50 (Me), 20.40 (OAc), 40.20 (C-4), 61.30 (C-5'), 68.10–70.10 (C-1'/4'), 78.70 (C-5), 123.20 (C-3), 169.40 (OAc); **3'**, $^1H$, $\delta$ 1.66 (s, 3 H, Me), 2.02–2.12 (s, 15 H, 5 OAc), 4.04 (dd, 1 H, $J_{4',5''}$ 4.4, $J_{5',5''}$ −12.8 Hz, H-5''), 4.26 (dd, 1 H, $J_{4',5'}$ 3.1 Hz, H-5'), 5.03–5.40 (m, 4 H, H-1'/4'); $^{13}C$, $\delta$ 14.80 (Me), 20.40 (OAc), 42.50 (C-3), 61.30 (C-5'), 67.50–70.10 (C-1'/4'), 75.10 (C-5), 122.10 (C-4), 169.50 (OAc).

*Anal.* Calc. for $C_{19}H_{27}N_3O_{12}$: C, 46.63; H, 5.56; N, 8.59. Found: C, 46.82; H, 5.60; N, 8.48.

*3,5-Dimethyl-4-(penta-*O*-acetyl-*D*-manno-pentitol-1-yl)pyrazole* (**4**). — Dry hydrogen chloride was bubbled through a solution of **2** (1.50 g, 2.98 mmol) in chloroform (10 mL). T.l.c. indicated the rapid formation of **4**, $R_f$ 0.50 (ethyl acetate–hexane, 5:1), as the sole product. The solvent was evaporated to give syrupy **4** (1.02 g, 90%), $[\alpha]_D$ +18° (*c* 0.5, dichloromethane); $\lambda_{max}$ 236 nm ($\varepsilon_{mM}$ 3.01); $\nu_{max}$ 3250 (NH) and 1730 $cm^{-1}$ (C=O). N.m.r. data ($CDCl_3$): $^1H$, $\delta$ 1.79–2.13 (s, 15 H, 5 OAc), 2.31 (s, 6 H, 2 Me), 4.06 (dd, 1 H, $J_{4',5''}$ 4.8 Hz, H-5''), 4.27 (dd, 1 H, $J_{4',5'}$ 3.0, $J_{5',5''}$ −12.6 Hz, H-5'), 4.99–5.65 (m, 4 H, H-1'/4'), 8.35 (bs, 1 H, NH); $^{13}C$, $\delta$ 10.70 (Me), 20.20 (OAc), 61.90 (C-5'), 64.30–69.20 (C-1'/4'), 110.20 (C-4), 143.60 [C-3(5)], 169.60 (OAc).

*Anal.* Calc. for $C_{20}H_{28}N_2O_{10}$: C, 52.63; H, 6.14; N, 6.14. Found: C, 52.38; H, 6.07; N, 6.23.

*3(5)-Methyl-4-(penta-*O*-acetyl-*D*-manno-pentitol-1-yl)pyrazole* (**5**). — A stream of hydrogen chloride was passed through the mixture (2.00 g, 4.08 mmol) of **3** and **3'** in chloroform (15 mL). Evaporation of the solvent and column chromatography (ethyl acetate–hexane, 1:2) of the syrupy residue afforded the major product **5** as a syrup (0.81 g, 45%), $R_f$ 0.40 (ethyl acetate–hexane, 4:1), $[\alpha]_D$ +12° (*c* 0.5, dichloromethane); $\lambda_{max}$ 235 nm ($\varepsilon_{mM}$ 2.58); $\nu_{max}$ 3290 (NH) and 1740 $cm^{-1}$ (C=O). N.m.r. data ($CDCl_3$): $^1H$, $\delta$ 1.92 (s, 15 H, 5 OAc), 2.28 (s, 3 H, Me), 3.99 (dd, 1 H, $J_{4',5''}$ 5.0 Hz, H-5''), 4.20 (dd, 1 H, $J_{4',5'}$ 3.2, $J_{5',5''}$ −12.8 Hz, H-5'), 5.42–5.65 (m, 4 H, H-1'/4'), 7.50 (s, 1 H, H-3), 9.27 (bs, 1 H, NH); $^{13}C$, $\delta$ 10.30 (Me), 20.40 (OAc), 61.90 (C-5'), 64.90–70.10 (C-1'/4'), 113.30 (C-4), 135.30 [C-5(3)], 142.30 [C-3(5)], 169.40 (OAc).

*Anal.* Calc. for $C_{19}H_{26}N_2O_{10}$: C, 51.58; H, 5.92; N, 6.33. Found: C, 51.42; H, 6.02; N, 6.43.

*3(5)-Ethoxycarbonyl-5(3)-methyl-4-(penta-O-acetyl-D-manno-pentitol-1-yl)-py-razole* (**6**). — A solution of **1** (1.00 g, 2.23 mmol) and ethyl diazoacetate (1.13 mL, 11.00 mmol) in dichloromethane (35 mL) was heated under reflux (72 h), then concentrated. Column chromatography of the residue afforded **6** as a syrup (0.60 g, 52%), $R_f$ 0.35 (hexane–ethyl acetate, 2:1), $[\alpha]_D$ +9° (*c* 0.5, dichloromethane); $\lambda_{max}$ 237 nm ($\varepsilon_{mM}$ 3.12); $\nu_{max}$ 3330 (NH) and 1750 cm$^{-1}$ (C=O). N.m.r. data ($CDCl_3$): $^1$H, $\delta$ 1.41 (t, 3 H, $J_{Me,CH}$ 7.1 Hz, $CH_3CH_2$), 2.00 (s, 15 H, 5 OAc), 2.41 (s, 3 H, Me), 4.10 (dd, 1 H, $J_{4',5'}$ 4.8, $J_{5',5''}$ −12.4 Hz, H-5″), 4.26 (dd, 1 H, $J_{4',5'}$ 3.1 Hz, H-5′), 4.40 (q, 2 H, $CH_3CH_2$), 5.12 (m, 1 H, $J_{3',4'}$ 9.2 Hz, H-4′), 5.63 (dd, 1 H, $J_{2',3'}$ 2.0 Hz, H-3′), 5.87 (dd, 1 H, H-2′), 6.24 (dd, 1 H, $J_{1',2'}$ 10.2 Hz, H-1′), 9.70 (bs, 1 H, NH); $^{13}$C, $\delta$ 11.10 (Me), 14.20 (Et), 20.36 (OAc), 61.00 (Et), 62.20 (C-5′), 63.70–69.50 (C-1′/4′), 115.80 (C-4), 138.10 [C-5(3)], 144.80 [C-3(5)], 160.70 ($CO_2$Et), 169.57 (OAc).

*Anal.* Calc. for $C_{22}H_{30}N_2O_{12}$: C, 51.36; H, 5.88; N, 5.44. Found: C, 51.39; H, 5.88; N, 5.24.

*X-Ray crystallography**. — Only poor quality crystals of **2** could be obtained, which limited the accuracy of the X-ray analysis. Single crystals of **2** at room temperature are orthorhombic, space group $P2_12_12_1$, with $a$ = 15.042(9) Å, $b$ = 21.463(12) Å, $c$ = 7.701(8) Å, $V$ = 2486.2(12) Å$^3$, and $Z$ = 4. A total of 2537 independent reflections with $\sin\Theta/\lambda < 0.60$ were collected on an Enraf–Nonius CAD4 diffractometer, using the $\omega-2\Theta$ scan method. Only 553 reflections were considered as observed by the usual criterion $I > 2\sigma(I)$. The solution of the structure by direct methods (MULTAN 80) was not straightforward because of the low resolution of the diffraction data, but all of the non-H atoms were located. Full-matrix least-squares refinement was carried out in the overall isotropic temperature factor approach, using a weighting scheme based on statistical counts ($w = 1/\sigma^2(F)$), to a final convergence $R$ = 0.12. The structural model obtained in this way did not allow an accurate description of the bonding geometry in the molecule, but revealed the stereochemistry.

ACKNOWLEDGMENTS

We thank the CICYT for financial support (Grant PA86-0218C03-01).

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* Lists of bond lengths and angles, structure factors, and atomic co-ordinates of the non-hydrogen atoms have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA DD 454/*Carbohydr. Res.*, 210 (1991) 327–332.