Carbohydrate Research
Elsevier Publishing Company, Amsterdam
Printed in Belgium

AMINO SUGARS: ADDITION OF ACYL NITRITES TO 3,4,6-TRI-*O*-ACETYL-D-GLUCAL

JOHANNES H. JORDAAN
Life Sciences Division, Atomic Energy Board, Pretoria (South Africa)

(Received June 24th, 1969)

ABSTRACT

Acyl nitrites, either preformed or generated *in situ*, add to 3,4,6-tri-*O*-acetyl-D-glucal in a *cis* fashion to give dimeric 2-deoxy-2-nitroso adducts having the α-D-*gluco* configuration. Adducts of acetyl, benzoyl, phenylacetyl, and propionyl nitrite were obtained. Partial, catalytic hydrogenation, or reduction with sodium hydrosulfite, afforded the corresponding azoxy derivatives. Prolonged reduction with a zinc–copper couple in acetic acid, followed by acetylation, and hydrolysis with sodium methoxide in methanol, gave 2-acetamido-2-deoxy-D-glucose.

INTRODUCTION

The stereoselective *cis*-addition of nitrosyl chloride to acetylated glycals[1,2] presents a facile route for the synthesis of 2-amino-2-deoxyglycosides[3,4]. The reported *cis*-addition of nitrosyl formate to certain olefins[4,5] prompted an investigation of the addition of acyl nitrites to tri-*O*-acetyl-D-glucal (**1**), in order to find a direct and convenient route for the synthesis of 1-*O*-acyl derivatives of 2-amino-2-deoxy-D-glucose. This report describes the addition of four acyl nitrites, generated *in situ* or preformed, to 3,4,6-tri-*O*-acetyl-D-glucal and some studies on reduction of the adducts.

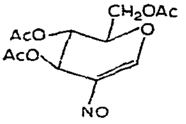
It is known that addition of nitrosyl chloride to acetate **1** gives a readily isolable, dimeric, nitroso *cis*-adduct **3**, having the α-D-*gluco* configuration[1,2]. It was shown[3] that this adduct could be readily dehydrochlorinated to give an intermediate 2-nitroso-D-glucal triacetate **2**, which rapidly added carboxylic acids or alcohols. In the latter case, 2-oximinoglycosides were obtained[4], which, in turn, could be reduced to 2-amino-2-deoxy-α-D-glycosides. Addition of a carboxylic acid to **2** produces a mixture of products, even under carefully controlled conditions; this route for synthesis of derivatives of 2-acylamino-2-deoxy-D-glucose is unattractive, because of the extreme sensitivity to moisture of the intermediate nitrosoglucal.

It has been shown[5] that some acyl nitrites add to olefins to give either monomeric or dimeric nitroso adducts. Evidence available indicated that the addition might proceed through a four-center transition state, leading to a *cis* product. As in the case of nitrosyl chloride addition, it seemed reasonable to expect that addition of acyl nitrites to **1** might lead to *cis* adducts, unless equilibrium displacement of acylate by acylate occurred.

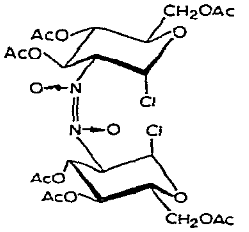
RESULTS AND DISCUSSION

Solutions of acetyl, benzoyl, phenylacetyl, and propionyl nitrites in methylene chloride were prepared by treatment of the corresponding silver salts of the carboxylic acids with nitrosyl chloride[6] at low temperature. These solutions were each treated with **1** for several days at −5°. The products **4a–d** were obtained in yields of 49–62%. Elemental analyses were in agreement with the structures shown, and ultraviolet absorption maxima at 300 nm corresponded to that of nitroso groups in other *trans*-nitroso dimers[5-7]. Assignments of the infrared spectra in the region characteristic for *trans*-nitroso dimers[5,8] were complicated by other absorption bands

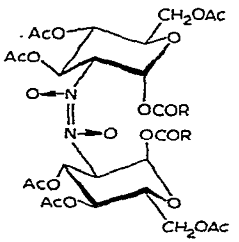
1



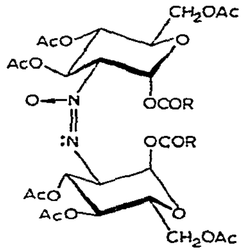
2



3



4a R = Me
b R = Et
c R = Ph
d R = PhCH$_2$



5a R = Me
b R = Ph

The mass spectra of compounds **4a–d** did not contain peaks for the molecular ions of either the monomeric or dimeric structures. In each case, the observed peak of highest mass had *m/e* 301, and an accurate mass consistent with the formula $C_{12}H_{15}NO_8$, which corresponds to the nitrosoglucal **2**. Superimposed on the spectrum of **2**, peaks were obtained which originated from the carboxylic acid that would be thermally eliminated from C-1 and C-2. Thus, apart from the peak of *m/e* 301 and its derived ions, the spectrum of **4b** contained a peak of *m/e* 74, representing propionic acid, that of **4c** showed a strong peak of *m/e* 122 (benzoic acid), and that of **4d** had an intense *m/e* 136 peak (phenylacetic acid). Since no peaks of mass above *m/e* 301 were obtained, and a probe temperature of *ca.* 190° was employed, thermal elimination of carboxylic acid from **4** is suggested.

The n.m.r. spectra of **4a–d** indicated the presence of protons on all of the ring carbon atoms (Table I). The splitting of 3.0–3.5 Hz for H-1 and H-2, and of *ca.* 11 Hz for H-2 and H-3 require the compounds to be in the α-D-*gluco* configuration; these data are in agreement with those obtained[1,2] for the corresponding product **3** from addition of nitrosyl chloride. Signals for all of the other protons were in agreement with the structures shown.

Generation[5] of the required acyl nitrites, *in situ*, in methylene chloride, or in

TABLE I

N.M.R. DATA[a] OF DIMERIC 3,4,6-TRI-*O*-ACETYL-1-*O*-ACYL-2-DEOXY-2-NITROSO-α-D-GLUCOPYRANOSES

Compound	*H-1 (d)*	*H-2 (q)*	*H-3 (q)*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$
4a	6.48	5.43	6.02	3.5	11.0	9.1
4b	6.41	5.42	5.98	3.5	11.0	9.2
4c	6.53	5.60	6.14	3.3	10.7	9.3
4d	6.43	5.37	5.90	3.1	10.7	9.1

[a]Chemical shifts in p.p.m. and splittings in Hz.

ether, by the use of isopentyl nitrite, the relevant carboxylic acid, and 70% perchloric acid as catalyst, in the addition reactions to **1**, were only marginally successful. Since the rate of the addition reaction was found to be relatively slow, acid-catalyzed elimination of carboxylic acid from the addition products appeared to become competitive. Periodic examination of the reaction mixtures by t.l.c. showed a gradual disappearance of **1**, with concomitant appearance of the required **4** as well as several other products. Final yields varied considerably, and, after work-up of the reaction mixtures following the complete disappearance of **1**, maximal yields of 18% for **4a**, 17% for **4b**, 0.3% for **4c**, and 9.4% for **4d** were obtained.

The possibility of converting **3** into a 1-*O*-acyl derivative was investigated; treatment with silver acetate in glacial acetic acid gave a syrup that showed several spots on t.l.c. (silica gel; benzene–acetone, 85:15). The major, slow-moving component corresponded to authentic **4a** on co-chromatography in several solvent systems. Similar treatment of **3** with silver acetate in methylene chloride produced a syrup which, among several spots (t.l.c.), showed one major, fast-moving component. Isolation of this component by preparative chromatography on silica gel plates gave a chromatographically pure oil that had elemental analysis, t.l.c. behaviour, and n.m.r. and mass spectra identical with those of 3,4,6-tri-*O*-acetyl-D-glucal. It therefore seems that, after an initial electrophilic attack of silver on chlorine, the incipient positive charge on C-1 could be neutralized either by loss of nitrosonium ion from C-2 in a *cis* elimination to give **1**, or by loss of a proton from C-2 to produce **2** in a *trans* elimination. In the latter case, free acetic acid could add[2] to **2** to give **4a**. From the available data, it is uncertain whether the elimination reaction proceeds through an ionic intermediate, or concertedly.

Reduction of **4a** in refluxing ethanol–acetone with sodium hydrosulfite produced crystalline 2,2′-azoxy-bis(1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose) (**5a**) in 60% yield. The product showed an i.r. peak at 1500 cm^{-1}, due to an azoxy group[10]. The mass spectrum of **5a** had a highest mass peak of *m/e* 647, which had an accurate mass corresponding to $C_{26}H_{35}N_2O_{17}$. The required molecular ion peak with *m/e* 706 was not obtained, but facile loss of 59 mass units ($CH_3COO^{\cdot}$) could be expected in peracetylated carbohydrates[9]. Similarly, sodium hydrosulfite reduction of **4b** produced crystalline 2,2′-azoxy-bis(3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-deoxy-α-D-glucopyranose) (**5b**) in 67% yield. The product showed i.r. peaks at 1500 and 1490 cm^{-1} which could be attributed to a phenyl group and a *trans*-azoxy group[10]. The ultraviolet spectrum showed diminished absorption in the region of 300 nm. The mass spectrum of **5b** showed a peak of highest mass at *m/e* 710, with an accurate mass corresponding to $C_{34}H_{34}N_2O_{15}$, which indicates the loss of two molecules of acetic acid from the expected molecular ion having *m/e* 830.

In symmetrically substituted azoxides, neighboring protons of the substituent on the oxygen-bearing nitrogen atom would be expected to be slightly deshielded, relative to the protons of the substituent on the other nitrogen atom[10]. As anticipated, the n.m.r. spectra of **5a** and **5b** showed two sets of signals for H-1, H-2, and H-3 of the two identical substituents in each of the azoxides. It is clear from Table II that the α-D-*gluco* configuration had been retained during reduction. All other signals in the spectra were in agreement with the structures shown. Hydrogenation of **4a** and **4b** in ethyl acetate, using 10% palladium–charcoal catalyst, gave products identical with **5a** and **5b**.

TABLE II

N.M.R. DATA[a] OF AZOXY COMPOUNDS, $R_1\overset{\overset{O}{\uparrow}}{N} = NR_2$

Compound	*H-1* (*d*)	*H-2* (*q*)	*H-3* (*q*)	*H-4* (*t*)	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$
5a, R_1	6.43	4.78	6.03	5.12	3.8	10.8	9.3
R_2	6.28	4.43	5.73	5.12	3.5	10.6	9.3
5b, R_1	6.55	4.89	6.18	5.16	3.5	10.7	9.6
R_2	6.53	4.53	5.88	5.16	3.4	10.6	9.6

[a] Chemical shifts in p.p.m. and splittings in Hz.

Reduction of **4a** with excess of a zinc–copper couple in acetic acid for 4 days, followed by treatment with acetic anhydride, produced a syrup that showed two spots on t.l.c. The major, fast-moving component was collected from preparative layer chromatograms. After *O*-deacetylation with sodium methoxide in methanol, the product proved to be identical with 2-acetamido-2-deoxy-D-glucose in co-chromatography on silica gel.

Attempts are being made to extend the addition reaction to the use of carboxylic acids having functional side-chains, and to find improved procedures for reduction of the nitroso dimers to 1-*O*-acyl derivatives of 2-amino-2-deoxy-α-D-glucose.

EXPERIMENTAL

General. — Melting points were taken in capillary tubes in a Büchi silicone bath apparatus, and are corrected. Infrared spectra were determined for KBr discs with a Perkin–Elmer 257 grating spectrophotometer. Ultraviolet spectra were determined in 2-methoxyethanol with a Beckman DK-2A ratio recording spectrophotometer. N.m.r. spectra were recorded in deuteriochloroform on a Varian A-60A spectrometer with tetramethylsilane as internal standard. Mass spectra were obtained with an AEI MS-9 mass spectrometer. Optical rotations were determined with a Perkin–Elmer 141 polarimeter. Thin-layer chromatograms were run on pre-coated, silica gel F plates (Merck), and spots were detected with alkaline hydroxylamine followed by ferric nitrate sprays[11], unless otherwise indicated. Preparative layer chromatograms were run on pre-coated, preparative, silica gel plates (Merck). Microanalyses were performed by Dr. Franz Pascher, Bonn, Western Germany.

Silver salts were conveniently prepared by addition of excess of aqueous silver nitrate to an aqueous solution of the sodium salt of the particular acid, followed by filtration, washing with water, and drying *in vacuo*.

*1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-nitroso-α-*D*-glucopyranose dimer* (**4a**). — (*a*) To a stirred suspension of 18.26 g (110 mmoles) of dry, powdered silver acetate in 200 ml of anhydrous methylene chloride at −15°, was added a solution of 6.55 g (100 mmoles) of nitrosyl chloride in 50 ml of methylene chloride, previously cooled to −15°. The mixture was stirred for 1 h at ambient temperature and then filtered through a sintered-glass funnel in a dry-box. The salts on the filter were washed with 50 ml of methylene chloride, and the yellow filtrate was cooled to −50° and added to a solution of 27.2 g (100 mmoles) of **1** in 100 ml of methylene chloride. The mixture was kept for 4 days at −5° and then poured into 250 ml of ice–water. The blue, organic layer was washed with water (3 × 250 ml), dried over magnesium sulfate, filtered, and then evaporated to dryness *in vacuo* at a bath temperature below 40°. The blue, solid residue was triturated with 200 ml of ether and cooled to −10°, and the crystalline precipitate was collected. The product was washed with 50 ml of ether and recrystallized from acetone–hexane to give 16.7 g (62%) of colorless crystals that showed one spot on t.l.c. (benzene–acetone, 85:15) and had m.p. 144–145°, $[\alpha]_D^{20}$ +151° (*c* 1.19, chloroform); λ_{max} 300 nm (ε 9200)*; n.m.r. data (Table I): δ 1.94–2.13 (4 peaks, CH_3CO_2-); 3.95–4.30, 3-proton signal.

Anal. Calc. for $C_{14}H_{19}NO_{10}$ (monomer): C, 46.54; H, 5.30; N, 3.88. Found: C, 46.62; H, 5.30; N, 3.81.

(*b*) A solution of 5.44 g (20 mmoles) of **1** in a mixture of 4.7 g (40 mmoles) of isopentyl nitrite and 10 ml of dry tetrahydrofuran was added dropwise during 30 min to a stirred solution of 5 ml glacial acetic acid in 20 ml of dry methylene chloride containing 0.1 ml of 70% perchloric acid at −10°. The mixture was kept for 48 h at 0°, washed with water (3 × 50 ml), dried over magnesium sulfate, filtered, and spin-evaporated to dryness *in vacuo* at a bath temperature below 40°. The blue residue was triturated with 20 ml of ether. Colorless crystals separated on cooling; yield, 1.3 g (18%), after recrystallization from acetone–hexane. The product showed one spot on t.l.c. and was identical with **4a** in all aspects described in (*a*).

*3,4,6-Tri-*O*-acetyl-2-deoxy-2-nitroso-1-*O*-propionyl-α-*D*-glucopyranose dimer* (**4b**) — (*a*) A suspenson of 9.95 g (55 mmoles) of dry, powdered silver propionate in 100 ml of methylene chloride was treated with a solution of 3.23 g (50 mmoles) of

---

*Calc. by using the molecular weight of the dimer.

nitrosyl chloride in 25 ml of methylene chloride (to obtain a solution of propionyl nitrite), followed by treatment with 13.6 g (50 mmoles) of **1**, as described for **4a**. Two recrystallizations from ethyl acetate–hexane gave 9.7 g (52%) of colorless needles that showed one spot on t.l.c. (benzene–acetone, 85:15) and had m.p. 136–137°, $[\alpha]_D^{20}$ +140° (*c* 1.19, chloroform); λ_{max} 300 nm (ε 9000); n.m.r. data (Table I): δ 2.38 (2-proton quartet, *J* 7.3 Hz, CH_3CH_2), 1.11 (3-proton triplet, *J* 7.3 Hz, CH_3CH_2), 1.9–2.1, 3 signals for CH_3CO_2.

Anal. Calc. for $C_{15}H_{21}NO_{10}$ (monomer): C, 48.00; H, 5.64; N, 3.73. Found: C, 48.27; H, 5.37; N, 3.55.

(*b*) A solution of 6 g of propionic acid in 20 ml of methylene chloride containing 0.1 ml of 70% perchloric acid was treated with a solution of 5.44 g (20 mmoles) of **1** in a mixture of 4.7 g of isopentyl nitrite and 5 ml of dry tetrahydrofuran, as described for **4a**. Recrystallization of the product from ethyl acetate–hexane gave 1.31 g (17%) of colorless needles that were identical with **4b** described in (*a*).

3,4,6-Tri-O-acetyl-1-O-benzoyl-2-deoxy-2-nitroso-α-D-glucopyranose dimer (**4c**). — (*a*) Treatment of a suspension of 28.5 g (125 mmoles) of silver benzoate in 100 ml of dry methylene chloride with a solution of 10 g (150 mmoles) of nitrosyl chloride in 100 ml of methylene chloride (to obtain a solution of benzoyl nitrite), followed by treatment with 27.2 g (100 mmoles) of **1** in 100 ml of methylene chloride, as described for **4a**, gave a blue residue after work-up and evaporation of the solvent *in vacuo*. A solution of the residue in boiling ether was cooled to −50°, and the crystalline precipitate was collected after 1 h; yield, 23.4 g. Evaporation of the mother liquor *in vacuo*, followed by trituration with a small volume of ether, gave 2.1 g of product. Two recrystallizations from acetone–hexane gave 23.9 g (56%) of colorless crystals that showed one spot on t.l.c. (benzene–acetone, 85:15) and had m.p. 140–141°, $[\alpha]_D^{20}$ +203° (*c* 1.03, chloroform); λ_{max} 300, 288 nm (ε 9600, 8400); n.m.r. data (Table I): δ 1.9–2.2 (4 peaks, CH_3CO_2), 4.1–4.4 (3-proton signal), 7.4–7.6 and 7.9–8.2 (5 phenyl protons).

Anal. Calc. for $C_{19}H_{21}NO_{10}$ (monomer): C, 53.90; H, 5.00; N, 3.31. Found: C, 53.67; H, 4.84; N, 3.58.

(*b*) Treatment of a solution of 6.1 g (50 mmoles) of benzoic acid in 20 ml of methylene chloride containing 0.1 ml of 70% perchloric acid with a solution of 5.44 g (20 mmoles) of **1** in a mixture of 4.7 g of isopentyl nitrite and 10 ml of dry tetrahydrofuran, as described for **4a**, gave a white solid. Recrystallization from acetone–hexane gave 265 mg (0.3%) of colorless crystals that were identical with **4c** described in (*a*).

3,4,6-Tri-O-acetyl-2-deoxy-2-nitroso-1-O-phenylacetyl-α-D-glucopyranose dimer (**4d**). — (*a*) Treatment of a suspension of 14.5 g (60 mmoles) of dry, powdered silver phenylacetate in 100 ml of methylene chloride with a solution of 3.23 g (50 mmoles) of nitrosyl chloride in 100 ml of methylene chloride, followed by treatment of the filtered solution of phenylacetyl nitrite with 13.6 g (50 mmoles) of **1**, and work-up as described for **4a**, gave a crystalline product. Two recrystallizations from acetone–hexane gave 10.7 g (49%) of colorless crystals that showed one spot on t.l.c. (benzene–

acetone, 85:15) and had m.p. 135–136°, $[\alpha]_D^{20}$ +133° (*c* 1.06, chloroform); λ_{max} 300 nm (ε 9000); n.m.r. data (Table I): δ 1.9–2.1, three CH_3CO_2 signals; 3.5–4.2, multiple peaks for 5 protons; 7.26 (5-proton singlet).

Anal. Calc. for $C_{20}H_{23}NO_{10}$ (monomer): C, 54.92; H, 5.30; N, 3.20. Found: C, 54.71; H, 5.38; N, 3.26.

(*b*) A solution of 7.8 g (50 mmoles) of phenylacetic acid in 20 ml of methylene chloride, containing 0.2 ml of 70% perchloric acid, was treated with a solution of 5.44 g (20 mmoles) of **1** in a mixture of 4.7 g of isopentyl nitrite and 10 ml of dry tetrahydrofuran, as described for **4a**. Two recrystallizations of the product from acetone–hexane gave 820 mg (9.4%) of colorless crystals that were identical with **4d** in (*a*).

*2,2'-Azoxy-bis(1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-*D*-glucopyranose)* (**5a**). — To a solution of 3.61 g (10 mmoles of monomer) of **4a** in a mixture of 75 ml of ethanol and 25 ml of acetone was added a solution of 1 g of sodium hydrosulfite in 10 ml of water. The mixture was stirred under reflux, and enough water was added to clarify the solution. Refluxing was continued for 6 h; the mixture was then cooled and poured, with stirring, into 600 ml of ice–water. The mixture was extracted with chloroform (5 × 25 ml), and the combined extracts were washed with water, dried over magnesium sulfate, and evaporated *in vacuo*. The residue was recrystallized twice from aqueous ethanol to give 2.13 g (60%) of colorless crystals that showed one spot on t.l.c. (benzene–ethyl acetate, 3:2; or benzene–acetone, 7:3) and had m.p. 224–225°, $[\alpha]_D^{20}$ +160° (*c* 1.18, chloroform); ν_{max} 1500 cm^{-1} (*trans* N=NO); n.m.r. data (Table II): δ 1.9–2.2 (8 CH_3CO_2 signals), 3.8–4.15 (6 protons).

Anal. Calc. for $C_{28}H_{38}N_2O_{19}$: C, 47.60; H, 5.42; N, 3.96. Found: C, 47.52; H, 5.28; N, 4.03.

*2,2'-Azoxy-bis(3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-deoxy-α-*D*-glucopyranose)* (**5b**). — Reduction of 4.23 g (10 mmoles as monomer) of **4b** with sodium hydrosulfite, as described for **5a**, gave 2.78 g (67%) of colorless crystals, after an additional recrystallization from chloroform–light petroleum (60–80° fraction). The product showed one spot on t.l.c., as described for **5a**, and had m.p. 211–212°, $[\alpha]_D^{20}$ +209° (*c* 1.25, chloroform); λ_{max} 270, 276, 283 nm (ε 2000, 2100, 1700); ν_{max} 1515 cm^{-1} (N=NO); n.m.r. data (Table II): δ 1.85–2.15 (6 CH_3CO_2 signals), 4.05–4.37 (six protons), 7.4–8.2 (10 phenyl protons).

Anal. Calc. for $C_{38}H_{42}N_2O_{19}$: C, 54.94; H, 5.10; N, 3.37. Found: C, 55.10; H, 5.14; N, 3.41.

Reduction of **4a** *with zinc in acetic acid.* — A mixture of 5 g of zinc dust and 1.5 g of hydrated copper sulfate was stirred at room temperature in a mixture of 40 ml of glacial acetic acid and 10 ml of water. To the mixture was added a solution of 1.8 g (5 mmoles, as monomer) of **4a** in 25 ml of glacial acetic acid. Stirring was continued during 72 h, with the addition of 1-g portions of zinc dust at 12-h intervals, and the addition of 5 ml of acetic anhydride after 60 h. The mixture was filtered, diluted with 600 ml of water, and extracted with chloroform (5 × 20 ml). The extracts were washed with water, dried over sodium sulfate, and evaporated to give 1.5 g of a colorless glass. The product showed two spots on t.l.c. (benzene–acetone, 2:1); the faster-moving spot was the major component. The mixture was fractionated on ten preparative plates of silica gel (benzene–acetone, 2:1), to give the faster-moving (700 mg) and slower-moving components (190 mg) as homogeneous (t.l.c.) glasses. Hydrolysis of each component with sodium methoxide in anhydrous methanol gave products of which only that obtained from the faster-moving component was identical with authentic 2-acetamido-2-deoxy-D-glucose (t.l.c., ethyl acetate–pyridine–acetic acid–water, 5:5:1:3).

*Reaction of 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-*D*-glucopyranosyl chloride dimer with silver acetate.* — (*a*) *In benzene.* To a stirred solution of 3.3 g (10 mmoles as monomer) of **3**[1,2] in 25 ml of glacial acetic acid was added 2.5 g (15 mmoles) of dry, powdered silver acetate, and stirring was continued for 24 h at room temperature. The mixture was filtered, the residue washed with 10 ml of glacial acetic acid, and the filtrate diluted with 250 ml of water. The solution was extracted with chloroform (5 x 20 ml), and the combined extracts were washed well with water. The solution was dried over magnesium sulfate, filtered, and evaporated *in vacuo*, to leave 3 g of a syrupy product that showed several spots on t.l.c. (benzene–acetone, 85:15), with one major, slower-moving component. Co-chromatography of the product with authentic **4a** on silica gel, using either benzene–acetone (85:15), chloroform–acetone (9:1), or benzene–methanol (95:5), showed that the major component was identical with **4a**.

(*b*) *In dichloromethane.* Treatment of 3.3 g (10 mmoles) of **3** with silver acetate in methylene chloride, as described above, followed by filtration, washing with water, and drying over magnesium sulfate, gave 3.5 g of a syrup on evaporation *in vacuo*. The product showed several spots on t.l.c. (benzene–acetone, 85:15), but one major, fast-moving spot predominated. A 1-g portion of the product was fractionated on ten preparative plates of silica gel (benzene–acetone, 85:15), to give the faster-moving component (540 mg) as an oil, which was indistinguishable from 3,4,6-tri-*O*-acetyl-D-glucal (**1**) by t.l.c. (benzene–methanol, 95:5; or benzene–acetone, 85:15), elemental analysis, and i.r., n.m.r., and mass spectra.

ACKNOWLEDGMENT

The South African Council for Scientific and Industrial Research is thanked for the n.m.r. and mass spectra.

REFERENCES

1 W. J. Serfontein, J. H. Jordaan, and J. White, *Tetrahedron Lett.*, (1964) 1069.
2 R. U. Lemieux, T. L. Nagabhushan, and I. K. O'Neill, *Tetrahedron Lett.*, (1964) 1909.
3 R. U. Lemieux and T. L. Nagabhushan, *Tetrahedron Lett.*, (1965) 2143.
4 R. U. Lemieux, S. W. Gunner, and T. L. Nagabhushan, *Tetrahedron Lett.*, (1965) 2149.
5 (*a*) H. C. Hamann and D. Swern, *Tetrahedron Lett.*, (1966) 3303; (*b*) H. C. Hamann and D. Swern, *J. Amer. Chem. Soc.*, 90 (1968) 6481.

6 W. Pritzkow and H. Nitzer, *J. Prakt. Chem.*, 25 (1964) 69.
7 B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, (1956) 1670.
8 B. G. Gowenlock, H. Spedding, J. Trotman, and D. H. Whiffen, *J. Chem. Soc.*, (1957) 3927.
9 K. Biemann, D. C. De Jongh, and H. K. Schnoes, *J. Amer. Chem. Soc.*, 85 (1963) 1763.
10 F. D. Greene and S. S. Hecht, *Tetrahedron Lett.*, (1969) 575.
11 M. E. Tate and C. T. Bishop, *Can. J. Chem.*, 40 (1962) 1043.