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STUDIES RELATED TO THE SYNTHESIS OF DERIVATIVES OF 2,6-DIAMINO-2,3,4,6-TETRADEOXY-D-*erythro*-HEXOSE (PURPUROSAMINE C), A COMPONENT OF GENTAMICIN C_{1a}*

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ABSTRACT

Reduction of 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (levoglucosenone) with lithium aluminium hydride afforded principally 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**3**), which was converted into 3,4-dihydro-2(*S*)-hydroxymethyl-2*H*-pyran (**8**) following acid-catalysed methanolysis and reductive rearrangement of the resulting α-glycoside **4** with lithium aluminium hydride. 1,6-Anhydro-3,4-dideoxy-2-*O*-toluene-*p*-sulphonyl-β-D-*threo*-hexopyranose, prepared from **3**, reacted slowly with sodium azide in hot dimethyl sulphoxide to give 1,6-anhydro-2-azido-2,3,4-trideoxy-β-D-*erythro*-hexopyranose, which was transformed into a mixture of methyl 2-acetamido-6-*O*-acetyl-2,3,4-trideoxy-α-D-*erythro*-hexopyranoside (**10**) and the corresponding β anomer following acid-catalysed methanolysis, catalytic reduction, and acetylation. Acid treatment of methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*erythro*-hexopyranosid-2-ulose yielded the enone **15**, which was readily transformed into methyl 6-*O*-acetyl-3,4-dideoxy-α-D-*glycero*-hexopyranosid-2-ulose (**19**). Procedures for the conversions of DL-**8**, **10**, and **19** into methyl 2,6-diacetamido-2,3,4,6-tetradeoxy-α-D-*erythro*-hexopyranoside (methyl *N*,*N*′-diacetyl-α-purpurosaminide C) have already been described.

INTRODUCTION

Syntheses of the *N*,*N*′-diacetyl-α-glycoside **1** of 2,6-diamino-2,3,4,6-tetradeoxy-D-*erythro*-hexose (purpurosamine C), a component[1] of the aminoglycoside antibiotic gentamicin C_{1a}, have recently been reported by this[2] and other[3] laboratories. In seeking alternative synthetic routes to **1** and derivatives of purpurosamines[1] A and B, we have examined the possibilities of using levoglucosenone (**2**) as a starting material. Levoglucosenone (**2**) has been detected as a minor component of the pyrolysis of cellulose in the presence of acid catalysts[4,5], and Shafizadeh and Chin[6] have recently reported a laboratory-scale preparation of **2** by pyrolysis of Kraft waste-paper in the presence of a dilute solution of phosphoric acid. We have found that pyrolysis of

*Dedicated to Professor Kurt Heyns on the occasion of his 70th birthday.

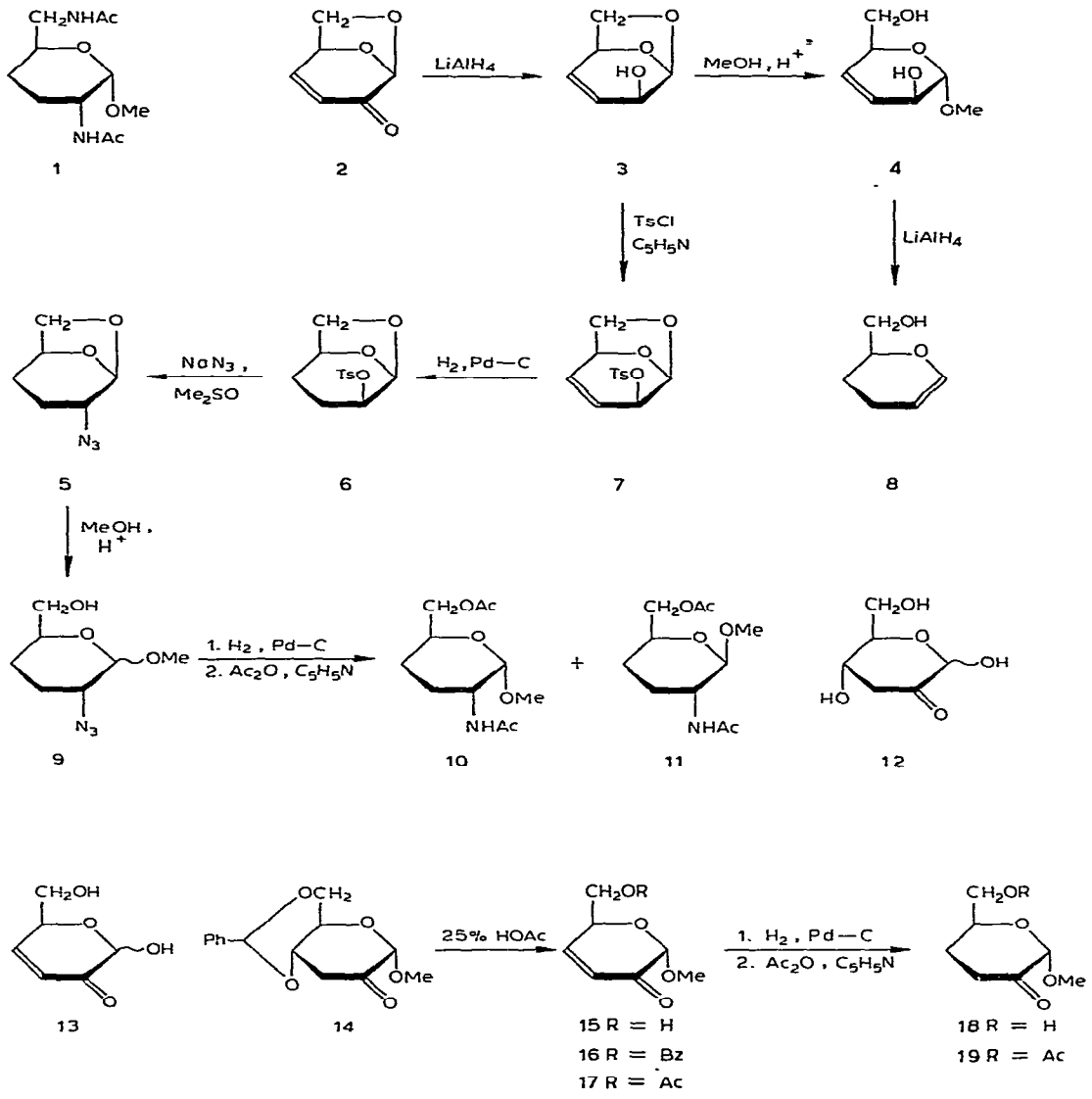
microgranular cellulose powder in the presence of M potassium hydrogensulphate solution affords **2** in 2–3% yield, following chromatography of the pyrolysate on silica gel. Although the yield of **2** obtained by the pyrolytic method is inevitably low, relatively large quantitites of **2** can be amassed quickly and without too much difficulty. Köll *et al.*[7] have recently prepared **2** by an alternative route from 1,6:2,3-dianhydro-4-deoxy-β-D-*ribo*-hexopyranose.

RESULTS AND DISCUSSION

Reduction of **2** with lithium aluminium hydride in ether gave, as the principal product, 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**3**), which was isolated in crystalline form. We have already discussed[8] the chemical evidence on which the structure assigned to **3** is based, and it suffices to point out that we dispute the claim made by Shafizadeh and Chin[6] that the reduction product is the C-2 epimer of **3**, *viz.* 1,6-anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose. Not unexpectedly, reduction of **2** with either sodium borohydride[7] or lithium aluminium hydride[8] yields **3** stereoselectively by the addition of hydride ion from the less-hindered side of the carbonyl group.

Acid-catalysed methanolysis of **3** afforded mainly methyl 3,4-dideoxy-α-D-*threo*-hex-3-enopyranoside (**4**), whose physical constants and ^{1}H-n.m.r. spectrum were identical with those of an authentic compound prepared by another route[2]. This evidence also establishes the *threo* configuration for **3**. On heating with lithium aluminium hydride in 1,4 dioxane, **4** was slowly transformed into 2(*S*)-hydroxymethyl-3,4-dihydro-2*H*-pyran (**8**), which was identified by comparison of its i.r. and ^{1}H-n.m.r. spectra with those of the racemic compound[9]. The reductive rearrangement **4** → **8** is analogous to a number of rearrangements studied by Fraser-Reid *et al.*[10], who have also commented on the mechanism of the rearrangement. Previous work[11] in our laboratory has shown that racemic **8** can be transformed into methyl *N*,*N*′-diacetyl-α-DL-purpurosaminide C (DL-**1**) by way of the addition of nitrosyl chloride, *etc.*, and a similar approach should enable optically pure **8** to be used in the synthesis of pseudo-disaccharides and -trisaccharides related to gentamicin[1] C_{1a}.

Levoglucosenone (**2**) might be transformed into methyl *N*,*N*′-diacetyl-α-purpurosaminide (**1**) by another route which was of particular interest to us, since several of the intermediates should be capable of further elaboration to give 2,6-diamino-2,3,4,6,7-pentadeoxyheptoses related to purpurosamines A and B, whose complete structures have still to be assigned[1]. Catalytic hydrogenation of the toluene-*p*-sulphonate **7** derived from **3** afforded the saturated analogue **6**, which reacted slowly with sodium azide in dimethyl sulphoxide at 110° to give 1,6-anhydro-2-azido-2,3,4-trideoxy-β-D-*erythro*-hexopyranose (**5**) in about 50% yield. Alternative synthetic routes to **6** have been reported by Černý's group[12,13], who found[13] that **6** does not undergo direct displacement of the sulphonyloxy group on heating with sodium benzoate in *N*,*N*-dimethylformamide. The difficulties encountered in effecting the direct displacement of sulphonyloxy groups at C-2 of glycopyranosides are well



known[14], although such displacements have been achieved[15] when the transition state for the displacement is not encumbered by torsional strain and dipolar interactions between the incoming nucleophile or the departing anion and the anomeric substituent. The sluggishness of the azide displacement on **6** is no doubt due to the development of unfavourable torsional strain and dipolar interactions in the transition state[14,15], although the severity of these interactions may be reduced by distortions inherent to the fused bicyclic system. The absence of an electronegative substituent at C-3 may also enhance the reactivity of the sulphonyloxy group of **6** towards direct

displacement[14,16], which appears to be achieved only with highly nucleophilic species such as an azide ion.

Acid-catalysed methanolysis of the azide **5** furnished a mixture containing the α- and β-glycosides **9**, which ^{1}H-n.m.r. spectroscopy indicated to be present in roughly equal amounts. Reduction and acetylation of **9** gave methyl 2-acetamido-6-*O*-acetyl-2,3,4-trideoxy-α-D-*erythro*-hexopyranoside[2] (**10**) and the corresponding β-glycoside **11**. The mixture of **10** and **11** could not be resolved satisfactorily by column chromatography, whereas fractional crystallisation afforded only small amounts of the pure compounds. The α-glycoside **10** has already been converted[2] into methyl *N*,*N*′-diacetyl-α-purpurosaminide C (**1**) but, because of the difficulties encountered in separating the glycosides **10** and **11**, this route to **10** is far less convenient than the one described later, which is based on acid-catalysed rearrangement of methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*erythro*-hexopyranosid-2-ulose (**14**).

Acid-catalysed rearrangement of the 3-deoxyglycosulose **12** is known[17] to yield the glycosulos-3-ene **13**, presumably *via* the corresponding 2,3-enol, and then 5-hydroxymethyl-2-furaldehyde. We reasoned that treatment of **14** with dilute acid would likewise give **15**, following removal of the benzylidene group, and that the presence of the glycosidic substituent would ensure that **15** is not degraded further, *via* the furanoid form, in the same way as **13**. This expectation was realised when **14** was transformed into **15** in high yield on heating with 25% aqueous acetic acid. Holder and Fraser-Reid[18] have developed alternative preparations of the enone **15** in which reductive elimination of vicinal sulphonyloxy groups was used to introduce the 3,4-alkenic bond, prior to oxidation of the resulting allylic alcohol with manganese dioxide. The enone **15** was characterised as the crystalline benzoate **16** and as the syrupy acetate **17**, both derivatives having physical constants or spectroscopic data in agreement with recorded values[18,19]. Hydrogenation of **15** over palladised charcoal yielded **18**, which was acetylated to give **19** (ref. 2). Alternatively, catalytic hydrogenation of the acetate **17** gave **19**, together with some saturated alcohol formed by concomitant reduction of the carbonyl group. The contaminating alcohol was oxidized to **19** with ruthenium tetraoxide in dichloromethane, prior to the isolation of **19** by distillation. The conversion of **19** into **10**, and thereafter into methyl *N*,*N*′-diacetyl-α-purpurosaminide C (**1**), has been described previously[2].

EXPERIMENTAL

General methods. — T.l.c. was performed on Kieselgel G, and detection was effected with vanillin–sulphuric acid[20]. I.r. spectra were recorded for Nujol mulls or liquid films with a Perkin–Elmer Infracord spectrometer, and ^{1}H-n.m.r. spectra were routinely recorded for solutions in deuteriochloroform by use of a Perkin–Elmer R10 (60 MHz) spectrometer; in all cases, the spectra were compatible with the structures assigned. Optical rotations were measured with a Perkin–Elmer 141 automa'ic polarimeter. Light petroleum refers to the fraction having b.p. 60–80°, unless otherwise indicated. Melting points are uncorrected.

1,6-Anhydro-3,4-dideoxy-β-D-glycero-*hex-3-enopyranos-2-ulose* (*levoglucosenone*) (**2**). — Microgranular cellulose powder (100 g, Whatman CC41) was mixed to a stiff paste with M potassium hydrogensulphate solution (150 ml) and the mixture was pyrolysed (in two batches) in a 500-ml round-bottom flask at ~15 mm Hg by direct heating with a Bunsen burner. The pyrolysates were collected, combined, and extracted with dichloromethane (5 × 50 ml). Removal of the solvent left a mobile tar (9.3 g), which, after chromatography on silica gel (elution with dichloromethane) and distillation, yielded levoglucosenone (**2**) (1.96 g, 2.5%), b.p. 108–110° (bath) at ~15 mm Hg, $[\alpha]_D^{25}$ −435° (*c* 1, chloroform); lit.[5] $[\alpha]_D$ −460° (*c* 1, chloroform); lit.[6] $[\alpha]_D$ −458° (*c* 3.97, chloroform). The ^{1}H-n.m.r. spectrum of **2** was identical with that appearing in the literature[5].

1,6-Anhydro-3,4-dideoxy-β-D-threo-*hex-3-enopyranose* (**3**). — Lithium aluminium hydride (0.9 g) was gradually added to a stirred solution of **2** (0.9 g) in dry ether (50 ml), and, after 10 min, the excess of the reagent was decomposed by the careful addition of water. The suspension was filtered, insoluble material was washed thoroughly with ether, and the combined filtrate and washings were concentrated to a syrup, from which benzene was distilled several times. Crystallisation from ether–light petroleum gave **3** (0.61 g), m.p. 67–69°, $[\alpha]_D^{25}$ −34° (*c* 1, chloroform); lit.[7] m.p. 65–66.5°, $[\alpha]_D$ −35.3° (*c* 1, chloroform). The ^{1}H-n.m.r. spectrum of **3** was identical with published data[7].

Methyl 3,4-dideoxy-α-D-threo-*hex-3-enopyranoside* (**4**). — A solution of **3** (1.8 g) in dry methanol (50 ml) containing conc. sulphuric acid (1 ml) was set aside for 4 days, when t.l.c. (ethyl acetate) showed that no starting material remained. The solution was then neutralised with conc. ammonia solution (3 ml) and concentrated. Toluene was evaporated several times from the residue, which was afterwards dissolved in ethyl acetate and the solution was filtered and concentrated. Chromatography on silica gel (elution with ethyl acetate) and distillation gave **4** (1.3 g, 58%), b.p. 90–97° (bath) at ~9 mm Hg, which after crystallisation from ether–light petroleum (b.p. 40–60°) had m.p. 70–71.5°, $[\alpha]_D^{25}$ +204° (*c* 1, chloroform); lit.[2] m.p. 71–72°, $[\alpha]_D^{25}$ +205° (*c* 1, chloroform). The ^{1}H-n.m.r. spectrum of **4** was indistinguishable from that of a sample prepared previously in our laboratories.

3,4-Dihydro-2(S)-*hydroxymethyl-2*H-*pyran* (**8**). — A solution of **4** (1.3 g) in 1,4-dioxan (50 ml) containing lithium aluminium hydride (0.78 g) was heated under gentle reflux for 3 days, whereafter the excess of hydride was destroyed by the careful addition of water. Insoluble material was filtered off and washed with ether, and the combined filtrate and washings were dried (magnesium sulphate) and concentrated. Chromatography of the residue on silica gel (elution with ethyl acetate) gave **8** (0.45 g, 49%), b.p. 85–90° (bath) at ~0.9 mm Hg, $[\alpha]_D^{25}$ +77° (*c* 1, chloroform). The ^{1}H-n.m.r. and i.r. spectra of **8** were indistinguishable from those of a sample of racemic **8** (kindly provided by Dr. I. Da'aboul).

1,6-Anhydro-3,4-dideoxy-2-O-toluene-p-*sulphonyl-β*-D-threo-*hex-3-enopyranose* (**7**). — To a cooled (0°) solution of **3** (0.64 g) in pyridine (5 ml) was added toluene-*p*-sulphonyl chloride (1.9 g) and, after 1 h at room temperature, the reaction mixture

was partitioned between toluene and water. The toluene layer was separated, washed with M hydrochloric acid solution and water, and dried (magnesium sulphate). Removal of the solvent and recrystallisation of the residue from aqueous methanol, and then from ether–light petroleum, gave **7** (1.1 g, 72%), m.p. 81.5–82.5°, $[\alpha]_D^{25}$ −29° (*c* 1, chloroform)* (Found: C, 55.6; H, 5.2; S, 11.4. $C_{13}H_{14}O_5S$ calc.: C, 55.3; H, 5.0; S, 11.3%.)

The corresponding methanesulphonate, prepared from **3** in the usual way, had m.p. 109–110° (from aqueous methanol), $[\alpha]_D^{25}$ −45° (*c* 1.4, chloroform) (Found: C, 41.0; H, 4.9; S, 15.2. $C_7H_{10}O_5S$ calc.: C, 40.8; H, 4.9; S, 15.5%).

*1,6-Anhydro-3,4-dideoxy-2-*O*-toluene-*p*-sulphonyl-β-*D-threo-*hexopyranose* (**6**). — A solution of **7** (1 g) in methanol (50 ml) containing 5% palladised carbon (0.1 g) was shaken with a slight overpressure of hydrogen for 15 min at room temperature. The catalyst and solvent were then removed and the residue was recrystallised from aqueous methanol to give **6** (0.75 g), m.p. 85–86°, $[\alpha]_D^{25}$ −80° (*c* 1, chloroform); lit.[12] m.p. 83–85°, $[\alpha]_D$ −82° (*c* 0.66, chloroform).

*1,6-Anhydro-2-azido-2,3,4-trideoxy-β-*D-erythro-*hexopyranoside* (**5**). — A solution of **6** (1 g) in dimethyl sulphoxide (20 ml) containing sodium azide (2.6 g) was heated at 110° for 48 h, whereupon the cooled reaction mixture was poured into water (100 ml) and the aqueous solution was extracted with ether (4 × 50 ml). The combined ethereal extracts were evaporated and the residue was chromatographed on silica gel (elution with dichloromethane) and distilled to give **5** (0.28 g, 50%), b.p. 106–107° (bath) at ~15 mm Hg, $[\alpha]_D^{25}$ −28° (*c* 1, methanol); ν_{max}^{film} 2090 cm^{-1} (N_3) (Found: C, 46.8; H, 6.1; N, 27.1. $C_6N_9N_3O_2$ calc.: C, 46.5; H, 5.8; N, 27.1%).

*Methyl 2-acetamido-6-*O*-acetyl-2,3,4-trideoxy-α-*D-erythro-*hexopyranoside* (**10**) *and the corresponding β anomer* **11**. — A solution of **5** (0.155 g) in methanol (10 ml) containing conc. sulphuric acid (1 ml) was heated under gentle reflux for 4 h before the solution was neutralised with solid calcium carbonate. Removal of the insoluble residue and solvents left a syrup, which gave a mixture (0.13 g) containing roughly equal amounts of the α- and β-glycosides **9** following chromatography over silica gel (elution with ethyl acetate); n.m.r.: τ 5.25 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of the α anomer) 5.76 (d, 1 H, $J_{1,2}$ 8 Hz, H-1 of the β anomer), and 6.52 and 6.41 (3 H, s, each OMe).

The mixture of the glycosides **9** (0.13 g) in methanol (10 ml) containing 5% palladised carbon (0.1 g) was shaken with a slight overpressure of hydrogen for 2 h at room temperature. Removal of the catalyst and solvent left a thick syrup, which was acetylated with acetic anhydride (1 ml) and pyridine (1 ml) in the usual way. Repeated fractional crystallisation of the acetylated products (0.15 g) from ether or ether–light petroleum gave the β-glycoside **11** (11 mg), m.p. 182–183°, $[\alpha]_D^{25}$ −64.5° (*c* 1, chloroform) (Found: C, 53.1; H, 7.6; N, 5.9. $C_{11}H_{19}NO_5$ calc.: C, 53.9; H, 7.8; N, 5.7%), and the α-glycoside **10** (25 mg), m.p. 99–100°, $[\alpha]_D^{25}$ +90 ±2° (*c* 1, chloroform); lit.[2] m.p. 99–100°, $[\alpha]_D$ +98° (*c* 0.8, chloroform). The ^{1}H-n.m.r. spectra of the

*The physical constants reported earlier[8] for **7** are in error, because they were measured using a sample that had slightly decomposed on storage.

α-glycoside **10** was identical with that of an authentic sample (kindly provided by Dr. I. Da'aboul), while the ^{1}H-n.m.r. spectrum of the β-glycoside **11** exhibited signals, *inter alia*, at τ 5.63 (d, 1 H, $J_{1,2}$ 8 Hz, H-1) and 6.48 (s, 3 H, OMe).

*Methyl 3,4-dideoxy-α-*D-glycero-*hex-3-enopyranosid-2-ulose* (**15**). — A suspension of the benzylidene derivative[21] **14** (3 g) in 25% acetic acid (100 ml) was heated under reflux for 5 h, whereafter the solvents were removed. The residue was extracted with ether (3 × 60 ml), and the combined ethereal extracts were dried (magnesium sulphate) and evaporated to yield **15** (1.5 g, 83.5%), $[\alpha]_D^{25}$ +55° (*c* 1.2, chloroform), as a chromatographically homogenous syrup that could not be induced to crystallise; lit.[18] m.p. 60.5–61°, $[\alpha]_D$ +54.65° (*c* 0.5, chloroform).

The benzoate **16**, prepared from **15** in the usual way, had m.p. 89–89.5° (from ethanol), $[\alpha]_D^{25}$ −19° (*c* 1.7, chloroform), in agreement with values [m.p. 87–88° (ref. 18), m.p. 85.5–86° (ref. 19)] reported in the literature.

*Methyl 6-*O*-acetyl-3,4-dideoxy-α-*D-glycero-*hexopyranosid-2-ulose* (**19**). — *Method* (*a*). The enone **15** (7.6 g) was acetylated, according to the procedure of Holder and Fraser-Reid[18], to give an oily acetate **17** (8 g, 83%) that exhibited ^{1}H-n.m.r. parameters identical with those reported. A solution of **17** (8 g) in dry methanol (45 ml) containing 5% palladised charcoal (0.5 g) and a little calcium carbonate was shaken under a slight overpressure of hydrogen for 20 min at room temperature; t.l.c. (acetone–light petroleum, 1:2, v/v) then showed the presence of **19** (the more-mobile component) and a minor component, presumably formed by reduction of the ketone group. The catalyst and solvent were removed, and the residue was oxidized with ruthenium tetraoxide in dichloromethane until a single component only was detected by t.l.c. The excess of oxidant was then destroyed with propan-2-ol. Removal of the spent oxidant and solvents gave **19** (5 g, 62%), b.p. 65–70° (bath) at 0.1 mm Hg, $[\alpha]_D^{25}$ +82° (*c* 1, chloroform); ν_{max}^{film} 1750 cm^{-1} (broad, C=O); lit.[2] b.p. 65–68° (bath) at ~0.2 mm Hg, $[\alpha]_D^{25}$ +83° (*c* 0.9, chloroform). The n.m.r. spectrum of **19** was indistinguishable from that of the authentic compound[2].

Method (*b*). A solution of **15** (4.4 g) in dry methanol (25 ml) containing 5% palladised charcoal (~0.1 g) and a little calcium carbonate was shaken under a slight overpressure of hydrogen for 20 min at room temperature; t.l.c. (acetone–light petroleum, 1:2, v/v) then revealed the presence of **18** and minor components of lower mobility. After removal of the catalyst and solvent, the residue was chromatographed on silica gel (elution with acetone–light petroleum, 1:2, v/v) to give **18** (2.7 g, 61%), ν_{max}^{film} 3400 (OH) and 1750 cm^{-1} (C=O), as a syrup that was used in the next step without further purification.

To a solution of **18** (2.6 g) in dry pyridine (40 ml) was added acetic anhydride (~2 mol), and the mixture was set aside overnight at room temperature. Work-up in the usual way afforded **19** (1.8 g, 55%), b.p. 65–69° (bath) at 0.1 mm Hg, $[\alpha]_D^{25}$ +82° (*c* 0.5, chloroform). This material was identical (i.r. and ^{1}H-n.m.r. spectra) with that obtained in (*a*).

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