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IMPROVED SYNTHESIS OF 2,5-ANHYDRO-D-ALLONONITRILE

HASSAN S. EL KHADEM AND JOSHUA KAWAI

Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, Michigan 49931 (U.S.A.)

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ABSTRACT

Two types of mixed ester of β-D-ribofuranose were synthesized. The first had the same groups attached to O-1, 2, and 3, and the second had the same groups attached to O-2, 3, and 5. The three esters obtained in the highest yields, starting from D-ribose, were then converted into the halides and nitriles. Of the esters studied, the best suited for conversion into the nitrile was 1-*O*-acetyl-2,3,5-tri-*O*-*p*-toluyl-β-D-ribofuranose, which afforded 2,5-anhydro-3,4,6-tri-*O*-*p*-toluyl-D-allononitrile in 60% yield.

INTRODUCTION

A number of *C*-nucleosides having the D-*ribo* configuration have been obtained from 2,5-anhydro-D-allononitrile or 2,5-anhydro-D-allonic acid[1–5]. The aim of the present work was to prepare a number of mixed esters of D-ribofuranose, and to convert them into 2,5-anhydro-D-allononitrile, in order to determine which ester was best suited for the synthesis of this *C*-nucleoside precursor. Our work was prompted by the fact that none of the known, simple tetraacyl or tetraaroyl esters of D-ribose can be converted into a crystalline nitrile in satisfactory yield. Thus, tetra-*O*-acetyl-β-D-ribofuranose[6] (**12**), which is commercially available, is not suitable, because the resulting 3,4,6-tri-*O*-acetyl-2,5-anhydro-D-allononitrile (**29**) is not crystalline, and would require purification by chromatography. Tetra-*O*-benzoyl-β-D-ribofuranose (**13**) affords a crystalline nitrile, namely, 3,4,6-tri-*O*-benzoyl-2,5-anhydro-D-allononitrile (**30**), but is obtained from D-ribose in only 40% yield[7]. Furthermore, the same nitrile (**30**) may be prepared in higher yield from the commercially available 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose[8] (**21**), as will be discussed later. Similarly, tetra-*O*-*p*-nitrobenzoyl-[9] and tetra-*O*-*p*-toluyl-β-D-ribofuranose[10] (**14** and **15**) are obtained in poor yield (9 and 14%, respectively) from D-ribose, and are therefore not useful starting-materials.

DISCUSSION

Two types of ester were studied. In the first, identical groups were attached to

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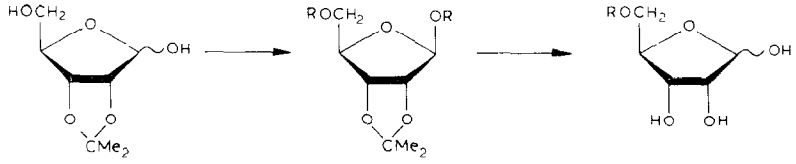
O-1, 2, and 3, and a different group to O-5. The second type had the same aroyl group attached to O-2, 3, and 5, and a different group to O-1. To prepare the first type of ester, 2,3-*O*-isopropylidene-D-ribofuranose (**1**), which is obtainable from D-ribose in almost quantitative yield[11], was treated with *p*-nitrobenzoyl chloride in pyridine, to afford 2,3-*O*-isopropylidene-1,5-di-*O*-*p*-nitrobenzoyl-β-D-ribofuranose (**2**) in 76% yield[12]. Compound **2** underwent acetolysis with acetic acid–acetic anhydride–sulfuric acid, to give 1,2,3-tri-*O*-acetyl-5-*O*-*p*-nitrobenzoyl-β-D-ribofuranose (**4**) in low yield (21%, based on D-ribose). When compound **2** was partially deblocked with trifluoroacetic acid at room temperature, it yielded 5-*O*-*p*-nitrobenzoyl-D-ribofuranose (**6**) in high yield (70%, based on D-ribose). However, **6** afforded 5-*O*-*p*-nitrobenzoyl-1,2,3-tri-*O*-*p*-toluyl-β-D-ribofuranose (**8**) and 1,2,3-tri-*O*-benzoyl-5-*O*-*p*-nitrobenzoyl-β-D-ribofuranose (**9**) in low yields when treated with *p*-toluyl chloride or benzoyl chloride in pyridine, which lowered their overall yields, based on D-ribose, to 25 and 23%, respectively.

Similarly, when 2,3-*O*-isopropylidene-D-ribofuranose (**1**) was treated with *p*-toluyl chloride in pyridine, it afforded 2,3-*O*-isopropylidene-1,5-di-*O*-*p*-toluyl-β-D-ribofuranose (**3**) in 76% yield. When this was subjected to acetolysis, it gave 1,2,3-tri-*O*-acetyl-5-*O*-*p*-toluyl-β-D-ribofuranose (**5**) in 23% yield (based on D-ribose). *O*-Deisopropylidenation of **3** with trifluoroacetic acid gave compound **7** which, on treatment with *p*-nitrobenzoyl chloride or benzoyl chloride, afforded 1,2,3-tri-*O*-*p*-nitrobenzoyl-5-*O*-*p*-toluyl-β-D-ribofuranose (**10**) in 8% yield, and 1,2,3-tri-*O*-benzoyl-5-*O*-*p*-toluyl-β-D-ribofuranose (**11**) in 40% yield (based on D-ribose), respectively.

Because none of these esters proved useful for conversion into nitriles, owing to the low yields, we turned our attention to another type of mixed ester, namely, those in which similar aroyl groups are attached to O-2, 3, and 5, and another ester group to O-1. Four mixed esters were investigated, namely, 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (**21**) and 2,3,5-tri-*O*-*p*-benzoyl-1-*O*-*p*-nitrobenzoyl-β-D-ribofuranose[13] (**22**) both of which are commercially available, as well as the new 1-*O*-acetyl-2,3,5-tri-*O*-*p*-nitrobenzoyl-β-D-ribofuranose (**23**) and 1-*O*-acetyl-2,3,5-tri-*O*-*p*-toluyl-β-D-ribofuranose (**24**).

The new mixed esters were prepared from methyl D-ribofuranoside (**16**), obtained by the Fischer method[14,15], by treatment with the corresponding aroyl chloride, followed by acetolysis by the Recondo–Rinderknecht method[8]. Thus, when methyl D-ribofuranoside (**16**) was treated with *p*-nitrobenzoyl chloride or *p*-toluyl chloride in pyridine, it yielded crystalline methyl 2,3,5-tri-*O*-*p*-nitrobenzoyl-D-ribofuranoside (**18β**), and syrupy methyl 2,3,5-tri-*O*-*p*-toluyl-D-ribofuranoside (**19**), in 86 and 100% yield, respectively. These two compounds (**18β** and **19**) underwent acetolysis, to give amorphous 1-*O*-acetyl-2,3,5-tri-*O*-*p*-nitrobenzoyl-α,β-D-ribofuranose (**23**) and crystalline 1-*O*-acetyl-2,3,5-tri-*O*-*p*-toluyl-β-D-ribofuranose (**24**) in 89 and 62% yield, respectively. Thus, although acetolysis was useful in converting the syrupy methyl glycoside **19** into a crystalline ester in the case of the *p*-toluyl derivative, it afforded no advantage with the *p*-nitrobenzoic ester **18β**.

Accordingly, for the next stage of the investigation, the crystalline methyl



1

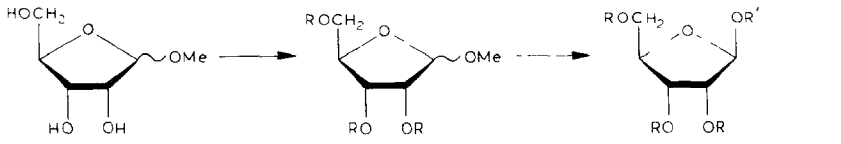
2 R = pNBz
3 R = pTol

pNBz = $COC_6H_4NO_2$-*p*
pTol = COC_6H_4Me-*p*

6 R = pNBz
7 R = pTol

4 R = pNBz
5 R = pTol

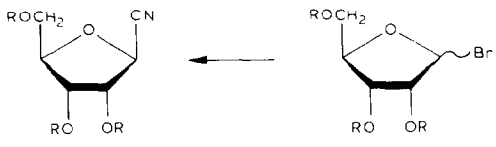
8 R = pNBz, R′ = pTol
9 R = pNBz, R′ = Bz
10 R = pTol, R′ = pNBz
11 R = pTol, R′ = Bz
12 R = R′ = Ac
13 R = R′ = Bz
14 R = R′ = pNBz
15 R = R′ = pTol



16

17 R = Bz
18 R = pNBz
19 R = pTol

20 R = R′ = Ac
21 R = Bz, R′ = Ac
22 R = Bz, R′ = pNBz
23 R = pNBz, R′ = Ac
24 R = pTol, R′ = Ac



29 R = Ac
30 R = Bz
31 R = pNBz
32 R = pTol

25 R = Ac
26 R = Bz
27 R = pNBz
28 R = pTol

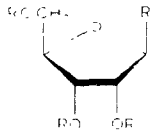


TABLE I

YIELDS OF 3,4,6-TRI-*O*-AROYL-2,5-ANHYDRO-D-ALLONONITRILES (**30**–**32**)

R	*R'*	*R'* → *Br* yield (%)	*R'* → *CN* yield (%)	D-*Ribose* → *nitrile* yield (%)
Bz	OAc	not isolated	60[a]	30
pNBz	OMe	79	14	9
pTol	OAc	100	60	37

[a]The yield reported in ref. 16 is 88%; however, this yield has seldom been duplicated. The yield reported here is the average of five experiments

2,3,5-tri-*O*-*p*-nitrobenzoyl-β-D-ribofuranoside (**18β**) was converted directly into the bromide (**27**), whereas methyl 2,3,5-tri-*O*-*p*-toluyl-D-furanoside **19** was first converted by acetolysis into the crystalline acetate (**24**), and this treated with HBr, to afford bromide **28**. Furthermore, as the *p*-nitrobenzoyl group is bulkier than the acetyl group, and as both groups are removed during halide formation, it was decided to use, in the next step, 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (**21**), instead of 2,3,5-tri-*O*-benzoyl-1-*O*-*p*-nitrobenzoyl-β-D-ribofuranose (**22**).

For the final stages of the study, *i.e.*, conversion into the halide, and this into the nitrile, the three most promising compounds selected were 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (**21**), methyl 2,3,5-tri-*O*-*p*-nitrobenzoyl-β-D-ribofuranoside (**18β**), and 1-*O*-acetyl-2,3,5-tri-*O*-*p*-toluyl-β-D-ribofuranose (**24**). These were converted into bromides **26**, **27**, and **28** with HBr in dichloromethane, and these into nitriles **30**, **31**, and **32** with mercuric cyanide in nitromethane by the Bobek–Farkas method[16].

Table I shows the yields of the corresponding 2,3,5-tri-*O*-aroyl bromides obtained from these compounds, and the overall yields of 2,5-anhydro-tri-*O*-aroyl-D-allononitriles, based on D-ribose. From Table I, it may be seen that 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (**21**) affords 2,5-anhydro-2,3,6-tri-*O*-benzoyl-D-allononitrile[16] (**30**) in 30% yield (based on D-ribose). However, this nitrile is quite difficult to crystallize, and requires repeated column chromatography to isolate it in this yield.

Methyl 2,3,5-tri-*O*-*p*-nitrobenzoyl-β-D-ribofuranoside (**18β**) gives a very low yield (14%) of nitrile **31**, even though its conversion into bromide **27** proceeds in high yield (79%). Finally, 1-*O*-acetyl-2,3,5-tri-*O*-*p*-toluyl-β-D-ribofuranose (**24**) gives crystalline nitrile **32** in >37% yield (based on D-ribose). This yield is achieved with-

out chromatography, and may be improved if the mother liquors are chromatographed. Accordingly, we recommend the use of 1-*O*-acetyl-2,3,5-tri-*O*-*p*-toluyl-β-D-ribofuranose (**24**) as a precursor for synthesis of 2,5-anhydro-D-allononitrile and 2,5-anhydro-D-allonic acid.

EXPERIMENTAL

General. — Melting points were determined on a Kofler block apparatus and are not corrected. Specific rotations were measured, in a 0.2-dm tube, with a Bendix-NPL 1100 polarimeter. P.m.r. spectra were recorded with a Varian EM-360 spectrometer with Me_4Si as the internal standard. Microanalyses were conducted in Spang Microanalytical Laboratory, Eagle Harbor, Michigan, and in the Analytical facility, Department of Chemistry and Chemical Engineering, Michigan Technological University. 2,3-*O*-Isopropylidene-D-ribofuranose[11] (**1**) and methyl D-ribofuranoside[14,15] (**16**) were prepared from D-ribose by the methods described in the references cited.

1,2,3-Tri-O-*acetyl-5*-O-p-*nitrobenzoyl-β-D-ribofuranose* (**4**). — A solution of 2,3-*O*-isopropylidene-1,5-di-*O*-*p*-nitrobenzoyl-β-D-ribofuranose[12] (**2**), (19.5 g, 0.04 mol), obtained by (*p*-nitrobenzoyl)ating 2,3-*O*-isopropylidene-D-ribofuranose[11] (**1**), in a cold mixture of acetic acid (400 mL), acetic anhydride (30 mL), and dichloromethane (200 mL) was stirred, and concentrated sulfuric acid (17 mL) was added dropwise while the temperature was kept below 10°. After being kept for 17 h at room temperature, the suspension was stirred with ice (600 mL) for 30 min, and filtered. The precipitate was dissolved in chloroform, and the filtrate was extracted with the same solvent (150 mL). The solution and the extract were combined, and washed successively with a saturated solution of sodium hydrogencarbonate (5 × 200 mL) and water (5 × 300 mL), dried (sodium sulfate), and evaporated to dryness, to give a syrup; yield, 20.7 g (28%); $[\alpha]_D^{23}$ +16.4° (*c* 1.9, chloroform); ^{1}H-n.m.r. (carbon tetrachloride): δ 8.32 (s, 4 H, arom.), 6.20 (d, *J*, 2 Hz, 1 H, H-1), 5.35 and 5.20 (broad, 2 H, H-2,3), 4.48 (broad, 3 H, H-4,5a,5b), and 2.12 (s, 9 H, 3 OAc).

Anal. Calc. for $C_{18}H_{19}NO_{11}$: C, 50.83; H, 4.50; N, 3.29. Found: C, 50.93; H, 4.41; N, 3.24.

5-O-p-*Nitrobenzoyl*-D-*ribofuranose* (**6**). — A solution of 2,3-*O*-isopropylidene-1,5-di-*O*-*p*-nitrobenzoyl-β-D-ribofuranose[12] (**2**) (9.8 g, 0.02 mol) in a mixture of trifluoroacetic acid (64 mL) and water (16 mL) was stirred for 4 h at room temperature. The precipitate was filtered off, the filtrate evaporated to dryness, the residue dissolved in acetone (250 mL), the solution made neutral with saturated sodium hydrogencarbonate solution (80 mL), the suspension filtered, the filtrate evaporated, the residue dissolved in ethyl acetate (100 mL), and the solution dried (sodium sulfate), and evaporated to dryness, to give a yellowish syrup which was used directly in the next reaction; yield 5.5 g (92%); $[\alpha]_D^{22}$ +7.7° (*c* 3.6, MeOH); ^{1}H-n.m.r. (acetone-d_6): δ 8.40 (s, 4 H, arom.), 5.30 (m, 1 H, H-1), and 4.65–3.90 (m, 8 H, 3 OH and H-2,3,4,5a,5b).

5-O-p-*Nitrobenzoyl-1,2,3-tri*-O-p-*toluyl-β*-D-*ribofuranose* (**8**). To a solution of compound **6** (5.2 g, 17 mmol) in dry pyridine (35 mL) was added dropwise *p*-toluyl chloride (10 g, 63 mmol) while the temperature was kept below 5°. When addition was complete, the mixture was kept overnight at room temperature, treated with cold water, the white precipitate dissolved in chloroform (100 mL), and the solution washed successively with saturated sodium hydrogencarbonate solution, water, cold 1.5M sulfuric acid, and water, dried (sodium sulfate), and evaporated to dryness; the residue crystallized from EtOH; yield, 6.5 g (58%); m.p. 183–189°, $[\alpha]_D^{24}$ +53.4° (*c* 1.6, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.35–7.15 (m, 16 H, arom.), 6.68 (s, 1 H, H-1), 6.05 (m, 2 H, H-2,3), 4.80 (m, 3 H, H-4,5a,5b), and 2.48 (d, 9 H, 3 Me).

Anal. Calc. for $C_{36}H_{31}NO_{11}$: C, 66.15; H, 4.78; N, 2.14. Found: C, 65.93; H, 4.67; N, 2.18.

1,2,3-Tri-O-*benzoyl-5*-O-p-*nitrobenzoyl-β*-D-*ribofuranose* (**9**). A solution of compound **6** (5.5 g, 18 mmol) in dry pyridine (30 mL) was treated with benzoyl chloride (8.4 g, 60 mmol) at 0°, and stirred overnight at room temperature. To the mixture was added ice (80 mL), the solid that separated was dissolved in chloroform (100 mL), and the solution washed successively with saturated sodium hydrogencarbonate solution, water, cold 1.5M sulfuric acid, and water, evaporated to dryness, and traces of solvents coevaporated with benzene, to give a syrup (yield, 10 g) which crystallized from absolute ethanol, to afford yellowish-white crystals, yield, 3.4 g (31%); m.p. 121–128°, $[\alpha]_D^{24}$ +37.3° (*c* 1.0, chloroform); ^{1}H-n.m.r. (carbon tetrachloride): δ 8.40–7.10 (m, 19 H, arom.), 6.65 (s, 1 H, H-1), 5.90 (m, 2 H, H-2,3), and 4.78 (m, 3 H, H 4,5a,5b).

Anal. Calc. for $C_{33}H_{25}NO_{11}$: C, 64.81; H, 4.12; N, 2.29. Found: C, 64.74; H, 3.95; N, 2.35.

1-O-*Acetyl-2,3,5-tri*-O-p-*nitrobenzoyl-α,β*-D-*ribofuranose* (**23**). – A solution of methyl 2,3,5-tri-*O*-*p*-nitrobenzoyl-β-D-ribofuranoside[9] (**18β**) (1.13 g; 18 mmol) in a mixture of dichloromethane (11 mL), acetic acid (25 mL), acetic anhydride (5 mL), and conc. sulfuric acid (0.2 mL) was kept overnight at 4°. The clear, yellowish solution was concentrated *in vacuo*, and the concentrate washed with cold water until the pH of the solution reached 5–6. The resulting, white solid (1.05 g; 89%) had m.p. 83–85°, $[\alpha]_D^{24}$ +40.8° (*c* 0.9, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.3 (m, 12 H, arom.), 6.78 and 6.53 (d, *J* 4 Hz, H-1α and s, H-1β; α:β = 2:3), 5.85 (m, 2 H, H-2,3), 4.75 (m, 3 H, H-4,5a,5b), and 2.14 (m, 3 H, Ac).

Anal. Calc. for $C_{28}H_{21}N_3O_{15}$: C, 52.29; H, 3.31; N, 6.57. Found: C, 52.49; H, 3.39; N, 6.49.

2,3-O-*Isopropylidene-1,5-di*-O-p-*toluyl-β*-D-*ribofuranose* (**3**). Compound **3** was synthesized from compound **1** as for the preparation of compound **2**, except that *p*-toluyl chloride was used instead of *p*-nitrobenzoyl chloride; yield: 76%; m.p. 96–97°, $[\alpha]_D^{22}$ +51.4° (*c* 1.4, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.20–7.10 (m, 8 H, arom.), 6.58 (s, 1 H, H-1), 4.97 (s, 2 H, H-2,3), 4.60 (m, 3 H, H-4,5a,5b), 2.40 (s, 6 H, 2 Me), and 1.45 (d, *J* 12 Hz, Me_2C).

Anal. Calc. for $C_{24}H_{26}O_7$: C, 67.59; H, 6.15. Found: C, 67.55; H, 6.14.

1,2,3-Tri-O-*acetyl-5*-O-p-*toluyl-β*-D-*ribofuranose* (**5**). — Compound **5** was synthesized from compound **3** as for the preparation of ester **4**, and isolated as a yellowish syrup in 36% yield; $[\alpha]_D^{23}$ +19.0° (*c* 2.1, chloroform); ^{1}H-n.m.r. (carbon tetrachloride): δ 8.13–7.14 (m, 4 H, arom.), 6.15 (m, 1 H, H-1), 5.52–5.10 (m, 2 H, H-2,3), 4.47 (s, 3 H, H-4,5a,5b), 2.40 (s, 3 H, Me), and 2.10 (m, 9 H, 3 OAc).

Anal. Calc. for $C_{19}H_{22}O_9$: C, 57.87; H, 5.62. Found: C, 57.79; H, 5.57.

5-O-p-*Toluyl*-D-*ribofuranose* (**7**). — Compound **7** was prepared from compound **3** as for the preparation of compound **6**, except that *p*-toluyl chloride was used instead of *p*-nitrobenzoyl chloride. The overall yield from D-ribose was 50%, which is considerably higher than the yield reported[10] for cyclization of the corresponding dithioacetal.

1,2,3-Tri-O-p-*nitrobenzoyl-5*-O-p-*toluyl-β*-D-*ribofuranose* (**10**). — Ester **7** was converted into the 1,2,3-tri-*O*-*p*-nitrobenzoyl derivative (**10**) in the usual way with *p*-nitrobenzoyl chloride in pyridine. It was obtained as white crystals in 16% yield; m.p. 178–180°, $[\alpha]_D^{23}$ +16.7° (*c* 1.6, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.40–7.08 (m, 16 H, arom.), 6.75 (s, 1 H, H-1), 6.10 (m, 2 H, H-2,3), 5.12–4.38 (m, 3 H, H-4,5a,5b), and 2.38 (s, 3 H, Me).

Anal. Calc. for $C_{34}H_{25}N_3O_{15}$: C, 57.07; H, 3.52; N, 5.87. Found: C, 57.02; H, 3.48; N, 5.96.

1,2,3-Tri-O-*benzoyl-5*-O-p-*toluyl-β*-D-*ribofuranose* (**11**). — Compound **11** was synthesized from 5-*O*-*p*-toluyl-D-ribofuranose (**7**) by benzoylation in the usual way. It was isolated as a syrup in 81% yield; $[\alpha]_D^{23}$ +26.8° (*c* 0.6, chloroform); ^{1}H-n.m.r. (carbon tetrachloride): δ 8.30–6.90 (m, 19 H, arom.), 6.68 (s, 1 H, H-1), 6.85 (m, 2 H, H-2,3), 5.70 (m, 3 H, H-4,5a,5b), and 2.33 (s, 3 H, Me).

Anal. Calc. for $C_{34}H_{28}O_9$: C, 70.34; H, 4.86. Found: C, 70.46; H, 4.89.

Methyl 2,3,5-tri-O-p-*toluyl*-D-*ribofuranoside* (**19**). — To a solution of methyl D-ribofuranoside[14,15] (**16**) (15.3 g) in dry pyridine (50 mL) was added *p*-toluyl chloride (25.8 g, 0.16 mol) during 30 min at 0°. After 3 h at room temperature, ice (250 mL) was added, and the mixture stirred for 3 h, and extracted with dichloromethane; the extract was washed successively with saturated sodium hydrogencarbonate solution, water, cold 1.5M sulfuric acid, and water, dried (sodium sulfate), and evaporated to a yellowish syrup which was used directly in the next reaction; yield: 27 g (100%); $[\alpha]_D^{23}$ +90.3° (*c* 2.2, chloroform); ^{1}H-n.m.r. (carbon tetrachloride): δ 8.15–6.95 (m, 12 H, arom.), 4.55 (s, 3 H, H-4,5a,5b), 3.45 (s, 3 H, OMe), and 2.40 (s, 9 H, 3 Me).

1-O-*Acetyl-2,3,5-tri*-O-p-*toluyl-β*-D-*ribofuranose* (**24**). — A solution of compound **19** (27 g, 0.05 mol) in a mixture of acetic acid (12 mL) and acetic anhydride (28 mL) was kept for 20 min at 0°, concentrated sulfuric acid (1.5–2.0 mL) was added dropwise with stirring, and the mixture was kept overnight at 4°. It was then washed with cold water until the pH of the solution became 5–6. The white precipitate formed was filtered off, and recrystallized from hot isopropyl alcohol, to give white crystals of **24**; yield 17 g (62%); $[\alpha]_D^{24}$ +62.2° (*c* 1.6, chloroform); ^{1}H-n.m.r.

($CDCl_3$): δ 8.20–7.10 (m, 12 H, arom.), 6.50 (s, 1 H, H-1), 5.84 (m, 2 H, H-2,3), 4.75 (m, 3 H, H-4,5a,5b), 2.40 (s, 9 H, 3 Me), and 2.02 (s, 3 H, OAc).

Anal. Calc. for $C_{31}H_{30}O_9$: C, 68.12; H, 5.53. Found: C, 68.30; H, 5.48.

2,3,5-Tri-O-p-*toluyl*-D-*ribofuranosyl bromide* (**28**). — HBr was bubbled into a solution of acetate **24** (55 g, 0.1 mol) in dry dichloromethane (150 mL), and the solution was kept for 20 min at 0°, and for 90 min at room temperature, evaporated to dryness *in vacuo* at 40°, and the traces of solvent coevaporated with benzene (70 mL) at 40°, to give a yellowish syrup (62 g): $[\alpha]_D^{24}$ +64.7° (*c* 1.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.30–6.95 (m, 12 H, arom.), 6.60 (s, 1 H, H-1), 4.85 (m, 3 H, H-4,5a,5b), and 3.40 (s, 9 H, 3 Me).

Anal. Calc. for $C_{29}H_{27}BrO_7$: C, 61.39; H, 4.80. Found: C, 61.52; H, 4.90.

2,5-Anhydro-3,4,6-tri-O-p-*toluyl*-D-*allononitrile* (**32**). — A solution of compound **28** (24 g, 42 mmol) in nitromethane (predried with 4A molecular sieves, 50 mL) was stirred for 22 h at room temperature with mercuric cyanide (predried under vacuum for 5–6 h at 90°, 18.5 g). The solid was filtered off, and the filtrate evaporated to dryness *in vacuo*. The residue was mixed with chloroform (70 mL), the suspension filtered, and the filtrate washed successively with 3% EDTA solution and water, dried (sodium sulfate), and evaporated to dryness; the resulting, light-brown syrup crystallized from ethyl ether; overall yield, 12.9 g (60%); m.p. 95–100°, $[\alpha]_D^{24}$ +30.0° (*c* 1.18, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.14–6.95 (m, 12 H, arom.), 5.85 (m, 2 H, H-3,4), 4.90 (d, *J* 4 Hz, H-2), 4.55 (broad, 3 H, H-5,6a,6b), and 2.36 (s, 9 H, 3 Me).

Anal. Calc. for $C_{30}H_{27}NO_7$: C, 70.17; H, 5.30; N, 2.73. Found: C, 70.25; H, 5.38; N, 2.59.

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