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THE SYNTHESIS OF MONO- AND OLIGOSACCHARIDE 1,2-ORTHOESTERS BY WAY OF A GLYCOSYL NITRATE INTERMEDIATE

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ABSTRACT

Sugar orthoesters with complex alcohols were obtained in high yield in the reaction of acylated 1,2-*cis*-glycosyl halides with partially protected sugar derivatives in the presence of silver nitrate and 2,4,6-trimethylpyridine in dry acetonitrile. The reaction has been shown to proceed by way of the acylated 1,2-*trans*-glycosyl nitrate intermediate.

INTRODUCTION

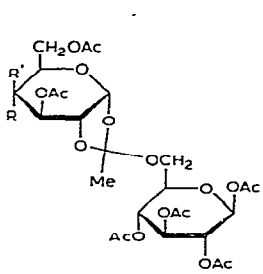
The well known[1–4] synthesis of O-acylated sugar 1,2-alkyl orthoesters from readily available 1,2-*cis*-glycopyranosyl halides involves either the initial anomerisation of the 1,2-*cis*-glycosyl halide to the 1,2-*trans* isomer[3] or the participation of solvent in this reaction[4]. Kochetkov *et al.*[5] have found *O*-acylated sugar 1,2-(D-glucopyranos-6-yl orthoacetates) to be convenient intermediates in a two-stage glycosylation by the orthoester method and to have some advantages over 1,2-(alkyl orthoacetates) in the synthesis of oligosaccharides. The synthesis of orthoesters of this type involves the transformation of glycosyl halides into 1,2-(alkyl orthoacetates) followed by re-esterification of the latter by partially protected monosaccharides.

The present paper describes a convenient synthesis of sugar 1,2-orthoesters with complex alcohols *via* glycosyl nitrates by the reaction of 1,2-*cis*-glycosyl halides with suitably blocked sugar derivatives containing free hydroxyl groups in the presence of silver nitrate and 2,4,6-trimethylpyridine. The mechanism of the reaction is discussed.

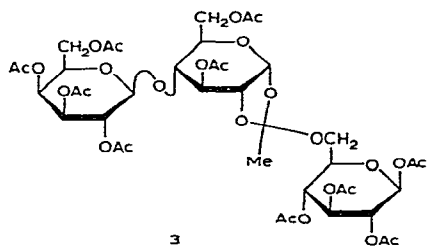
RESULTS AND DISCUSSION

The efficiency of the method described here was shown by the reaction of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**6**), 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**7**), or hepta-*O*-acetyl-α-lactosyl bromide (**8**) with 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose (**9**) or benzyl 2-acetamido-3,4-di-*O*-acetyl-2-deoxy-α-D-glucopyranoside (**10**). The interaction of the tetraacetate **9** with a slight excess of bromide **6** in the presence of silver nitrate in dry acetonitrile at room temperature led to 3,4,6-tri-*O*-acetyl-α-D-glucopyranose 1,2-(1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranos-

6-yl) orthoacetate (**1**) in 77% yield. Under the same conditions, bromides **6–8** and the partially protected sugars **9** and **10** gave the corresponding orthoesters **2–5** in good yield (42–86%). The orthoester **1** was formed also in the absence of silver nitrate (*cf.* Ref. 1) but under more drastic conditions (boiling acetonitrile).



1 R = OAc, R' = H
2 R = H, R' = OAc



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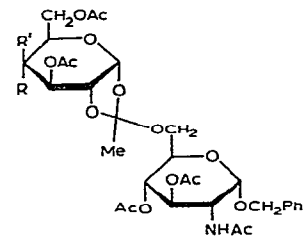


4 R = OAc, R' = H
5 R = H, R' = OAc

The structure of the orthoesters **1–5** is supported by the analytical data, by the results of the mild acid hydrolysis of the orthoester group, and by the n.m.r. spectra. The singlet at 1.65–1.68 p.p.m. is assigned[3,5,6] to the *endo*-methyl group at C-2 of the dioxolane ring and it indicates that the synthesized orthoacetates are *exo*-isomers. Furthermore, the structure of **1** was confirmed by its transformation into β-gentiobiose octaacetate[5].

The first stage of the formation of orthoester was assumed to involve an acylated glycosyl nitrate. To examine this hypothesis, the 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl (**11**) and -galactopyranosyl nitrates (**12**) were synthesized by treatment of the corresponding bromides **6** and **7** with silver nitrate in dry benzene. This solvent was shown to be suitable for the preparative synthesis of unstable 1,2-*trans*-glycosyl nitrates, but it was unsatisfactory in the orthoester synthesis from these nitrates apparently because of the low level of transformation of β-D-glycosyl nitrates into 1,2-acetoxonium intermediates.

In dry benzene and dry carbon tetrachloride, the nitrates **11** and **12** (as well as 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl chloride[7]) practically did not mutarotate during 5 days, but in dry acetonitrile at a concentration of 0.2M they slowly gave the anomeric tetra-*O*-acetyl-α-D-glucopyranosyl (**13**) and -galactopyranosyl nitrates (**14**) (about 40% after 7 days), determined by n.m.r. spectroscopy and t.l.c.; the dilution of the acetonitrile solution and the presence of nitrate ions accelerate the mutarotation and give the α-D nitrates in high yield.

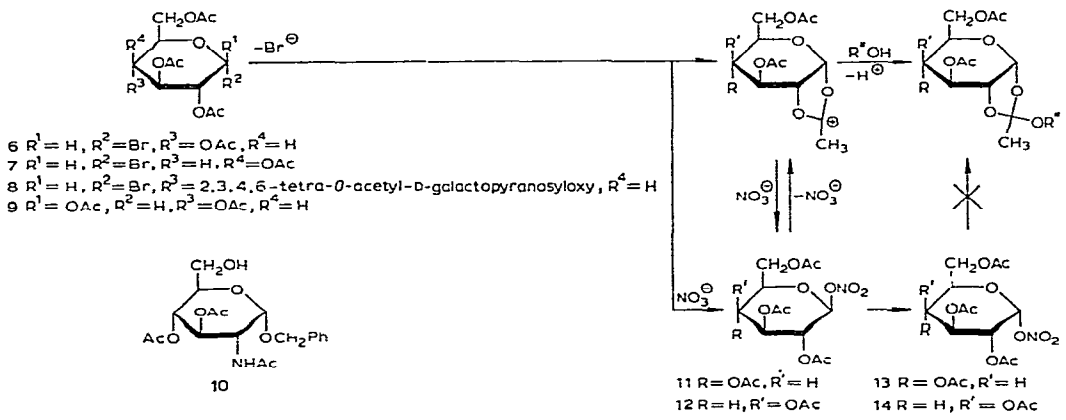
The reaction of bromide **6** with silver nitrate in acetonitrile in the absence of an alcohol led rapidly to the quantitative precipitation of silver bromide. N.m.r. spectroscopy showed the presence of a signal for the anomeric proton at 6.04 p.p.m. (spacing 8.8 Hz) 30 min after mixing the reagents. The gradual decrease of the intensity of this signal and the simultaneous appearance of a new signal at 6.38 p.p.m. (spacing 4.2 Hz) established the anomerisation of the β-D nitrate **11** into the α-D nitrate **13**. T.l.c. was the convenient method for monitoring this reaction since nitrates

11 and **13** (as well as **12** and **14**) had different mobilities on silica gel in 1:1 light petroleum–ether as the solvent and they showed $R_{compound\ 6}$ 0.71 and 0.86, respectively.

Though acylated glycosyl nitrates have been known for a long time[7–9], their structure had not been proven and *a priori* neither orthoester nor acetoxonium structures (the latter being suggested for sugar perchlorates[10,11]) could be excluded. The structures of the glycosyl nitrates were established as follows: In the n.m.r. spectra the signals for the anomeric protons of **13** and **14** appeared at 6.46 and 6.44 p.p.m. further downfield from the corresponding signals in the spectra of sugar 1,2-(alkyl orthoacetates) (5.65–5.72 p.p.m.[3]), approximately in the same region as those for 1,2-*cis*-glycosyl halides (6.62–6.67 p.p.m.[12]). The observed spacing $J_{1,2}$ 3.5 Hz for the nitrates **13** and **14** indicated an axial–equatorial relationship of the protons at C-1 and C-2 (*cf.* ref. 12). These values were essentially smaller than those for sugar 1,2-alkyl orthoesters (5.0 Hz[3]). The presence of four 3-proton singlets at the usual position for *O*-acetyl groups (1.95–2.10 p.p.m.)[13] proved the 1,2-*cis*-nitrate structure. The doublet for the anomeric proton at 5.82 p.p.m. (spacing 8.0 Hz) and four signals of acetyl groups confirmed the structure of nitrate **11**.

Use of Hudson's rule of isorotation[14], as modified by Korytnyk[15] for sugar derivatives containing highly polarisable aglycones, showed that the nitrates **11** and **13** were truly anomers, as the values A_{ONO_2}* (31,500) and B_{ONO_2} (28,500) and A_{Ac}/A_{ONO_2} (0.60) and B_{Ac}/B_{ONO_2} (0.73) were close to the previously reported A_{Ac}/A_{Cl} and B_{Ac}/B_{Cl} values (*cf.* ref. 15). All these data exclude orthoester or acetoxonium structures for the glycosyl nitrates.

Nitrate **11** and tetraacetate **9** in acetonitrile readily formed the orthoester **1** in the presence of 2,4,6-trimethylpyridine. Under the same conditions nitrate **12** reacted slowly with *tert*-butyl alcohol and so gave in a substantial degree the α-D anomer **14**. 3,4,6-Tri-*O*-acetyl-α-D-galactopyranose 1,2-(*tert*-butyl orthoacetate) (**15**) was obtained in high yield only in 2-methyl-2-propanol solution. The α-D nitrates **13** and **14** did not form orthoesters under the same conditions in the reaction with



*The subscripts show the substituent at C-1 in the acetylated sugar to which the A and B values refer.

tetraacetate **9** or with 2-methyl-2-propanol. Therefore, the following scheme of formation of the sugar orthoester has been proposed: The reaction proceeds *via* the intermediate 1,2-*trans*-glycosyl nitrates which readily yield sugar orthoacetates like 1,2-*trans*-glycosyl halides with alcohols in the presence of bases. The anomerisation of the β-D anomer into the α-D nitrate is the competetive process in these syntheses. Nevertheless, the rate of the mutarotation is low, even in polar, dry solvents, and allows the possible one-stage synthesis of orthoesters with complex alcohols.

A similar mechanism of the sugar orthoester formation probably takes place in the synthesis, by Wulff and Krüger[16], of orthoesters with complex alcohols from bromide **6** in the presence of silver salicylate after the byproduct of the reaction, 2,3,4,6-tetra-*O*-acetyl-1-*O*-salicyl-β-D-glucopyranose, is formed. The formation of 2-substituted glyco[2′,1′:4,5]-2-oxazolines from acylated 2-amino-2-deoxyglycosyl chlorides in the presence of silver nitrate and collidine[17], apparently proceeds with β-D nitrates as intermediates.

EXPERIMENTAL

General. — Acetonitrile was distilled five times in the presence of phosphorus pentaoxide and finally of anhyd. potassium carbonate and was stored over Linde molecular sieves 3A. Melting points were determined with a Boetius apparatus and correspond to corrected melting points. Optical rotations were determined, in semimicro tubes, with a Perkin–Elmer Model 141 polarimeter at 20–22°. N.m.r. spectra were recorded with a Varian XL-100 spectrometer and, if not otherwise specified, with chloroform-*d* as solvent and tetramethylsilane as internal standard. Chemical shift values are given on the δ scale. I.r. spectra were recorded for potassium bromide discs with a Perkin–Elmer Model 237 spectrophotometer. Column chromatography was performed on Silica Gel L 40–100 μ (Lachema, Czechoslovakia) or on alumina (neutral, Brockmann IV; Reanal, Hungary). Thin-layer chromatography (t.l.c.) was performed on Silica Gel LS 5–40 μ plates (Lachema, Czechoslovakia) with 1:1 light petroleum–ether (A) and 4:1 chloroform–butanone (B) or on alumina (Woelm, G.F.R.; both adsorbents with *ca.* 5% gypsum) with 4:1 light petroleum–acetone (C) and 1:7 benzene–chloroform (D). The spots were revealed by spraying with 1:10 (v/v) conc. sulfuric acid–methanol and heating at 100–120°. Evaporations were carried out *in vacuo* at a bath temperature below 35°.

N.m.r. spectra of all sugar orthoesters showed singlets at 1.65–1.68 p.p.m. All the sugar orthoesters are completely hydrolyzed by 5mM sulfuric acid in 90% aqueous acetone at 20° for 10–30 min. The hydrolysis was monitored by t.l.c. (disappearance of an orthoester spot and simultaneous appearance of a spot attributed to the products of hydrolysis).

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl nitrate (**11**). — A mixture of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**6**, 0.82 g), finely powdered silver nitrate (0.36 g), and 2,4,6-trimethylpyridine (0.02 ml) in dry benzene (10 ml) was stirred at

room temperature for *ca.* 4 h until **6** completely disappeared (t.l.c., solvent A). The silver salts were filtered off, washed with benzene, and the solution was evaporated. Crystallization of the residue from dry ether (twice) gave 0.48 g (61%) of fine prisms, m.p. 96–97°; $[\alpha]_D$ −4° (*c* 0.4, acetonitrile), −8° (*c* 1.0, carbon tetrachloride); n.m.r. data: δ 2.02, 2.04, 2.08, 2.10 (singlets, 4 OAc), 5.80 (doublet, spacing 8.0 Hz, H-1); i.r. data: ν_{max}^{KBr} 1672 s (asym. str. ONO_2), 1255 s (sym. str. ONO_2), 900 s cm^{-1} (β-D anomer); $R_{compound\ 6}$ 0.71 (solvent A); lit.[7]: m.p. 96°; $[\alpha]_D$ −8.4° (*c* 1, carbon tetrachloride).

*2,3,4,6-Tetra-*O*-acetyl-α-*D*-glucopyranosyl nitrate* (**13**). — A solution of **6** (4.11 g) in acetonitrile (20 ml) was added with stirring to a solution of silver nitrate (2.0 g) and 2,4,6-trimethylpyridine (0.1 ml) in acetonitrile (80 ml). The stirring was continued for *ca.* 7 days until complete transformation of **11** into **13** (t.l.c. monitoring in solvent A and n.m.r. analysis after 3 and 7 days) was observed. Silver bromide was filtered off, washed with benzene, and the solution was evaporated to dryness. The residue was treated with cold, abs. ethanol for a few min and the crystals were collected. Recrystallization from acetone–hexane gave 2.84 g (72%) of prisms, m.p. 153°; $[\alpha]_D$ +152° (*c* 1.0, chloroform), +147° (*c* 1.0, acetonitrile; no change after 24 h); n.m.r. data: δ 2.00–2.11 (4 OAc), 6.46 (doublet, spacing 3.2 Hz, H-1) [in acetonitrile: 6.38 (H-1, doublet, spacing 4.0 Hz)]; i.r. data: ν_{max}^{KBr} 1660 s (asym. str. ONO_2), 1250 s (sym. str. ONO_2), 858 m cm^{-1} (α-D anomer); $R_{compound\ 6}$ 0.86 (solvent A); lit.[9]: m.p. 150–151°; $[\alpha]_D$ +149° (chloroform).

*2,3,4,6-Tetra-*O*-acetyl-α-*D*-galactopyranosyl nitrate* (**14**). — Treatment of **7** (4.11 g), under the conditions described for the preparation of **13**, with silver nitrate (2.0 g) in acetonitrile (100 ml) gave the nitrate **14**, which was isolated by chromatography on a silica gel column. Elution with 3:2 light petroleum–ether gave 2.43 g (62%); m.p. 93–94° (recrystallized from carbon tetrachloride or from ether–hexane); $[\alpha]_D$ +159° (*c* 1.0, chloroform); n.m.r. data: δ 1.93, 1.97, 2.03, 2.10 (singlets, 4 OAc), 6.44 (doublet, spacing 3.5 Hz, H-1); i.r. data: ν_{max}^{KBr} 1650 s, 1254 s, 855 m cm^{-1} (α-D anomer); $R_{compound\ 6}$ 0.90 (solvent A); lit.[9]: m.p. 93–94°; $[\alpha]_D$ +153° (chloroform).

*3,4,6-Tri-*O*-acetyl-α-*D*-galactopyranose 1,2-(2-methyl-2-propyl orthoacetate)** (**15**). — Crude 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl nitrate (**12**) was obtained from **7** (4.11 g) and silver nitrate (1.75 g) in dry benzene (50 ml) as described for the preparation of **11**. It was dissolved in 2,4,6-trimethylpyridine (3 ml) and treated with anhyd. 2-methyl-2-propanol (20 ml) for 2 days. Collidine nitrate was filtered off and washed with benzene. The solution was evaporated and the product was isolated by chromatography on alumina. Elution with a gradient from hexane to 20:1 hexane–acetone yielded 3.0 g (74%) of **15** which was crystallized from dry ether in needles, m.p. 89–90°; $[\alpha]_D$ +80° (*c* 1.0, chloroform); n.m.r. data: δ 1.75 (singlet, *endo* C-CH_3), 5.76 (doublet, *J* 4.8 Hz, H-1); $R_{compound\ 7}$ 1.15 (solvent C).

Anal. Calc. for $C_{18}H_{28}O_{10}$: C, 53.46; H, 6.98. Found: C, 53.21; H, 6.98.

*This orthoester has been used for the synthesis of β-D-galactopyranosides, but its isolation and properties were not reported[18].

Equimolar amounts of **7**, silver nitrate, and collidine and an excess of 2-methyl-2-propanol in acetonitrile gave after 4 days about equal amounts of the orthoester **15** and of the nitrates **12** and **14**. Traces of D-galactose tetraacetate were also identified by t.l.c. (solvent C). T.l.c. monitoring (solvent C) of the treatment for 7 days of crude **12** with an excess of 2-methyl-2-propanol in benzene indicated only traces of **15** and unchanged **12** as a major component of the reaction mixture.

*3,4,6-Tri-*O*-acetyl-α-*D*-glucopyranose 1,2-(1,2,3,4-tetra-*O*-acetyl-β-*D*-glucopyranos-6-yl orthoacetate)* (**1**). — *A. From* **6**. Bromide **6** (3.50 g) was added to a solution of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose[19] (**9**, 2.44 g), silver nitrate (1.45 g), and collidine (1.15 ml) in acetonitrile (20 ml) and the mixture was stirred for 4 h at room temperature. The precipitate was filtered off and washed with benzene (50 ml). The combined filtrates were washed with water, dried ($MgSO_4$), and evaporated to a syrup. The latter crystallized from dry ether to give **1** (3.66 g, 77%), which was recrystallized from acetone–ether, m.p. 142°; $[\alpha]_D$ +29° (*c* 0.5, chloroform); $R_{compound\ 9}$ 1.55 (solvent B) or 4.1 (solvent D); lit.[5]: m.p. 137–138°; $[\alpha]_D$ +39° (*c* 1, chloroform).

Anal. Calc. for $C_{28}H_{38}O_{19}$: C, 49.55; H, 5.64. Found: C, 49.12, H, 5.54.

The orthoester **1** was converted[5] in 53% yield into β-gentiobiose octaacetate, m.p. 196–197°; $[\alpha]_D$ −4° (*c* 1.0, chloroform) (*cf.* Ref. 19).

B. From **6**. A solution of **9** (0.70 g), **6** (1.23 g), and collidine (0.40 ml) in acetonitrile (8 ml) was heated at reflux for 3 h. The collidine hydrobromide that precipitated on cooling was filtered off and washed with benzene (20 ml). The orthoester **1** (0.98 g, 72%) was isolated from the combined filtrates as just described.

C. From **11**. The t.l.c. monitoring (solvent B) of the reaction of **11** (39 mg) and **9** (35 mg) in acetonitrile (0.5 ml) in the presence of one drop of collidine showed the orthoester **1** to be the major product. Nitrate **13** did not react with **9** in acetonitrile, even after being heated at reflux for 2 h.

*3,4,6-Tri-*O*-acetyl-α-*D*-galactopyranose 1,2-(1,2,3,4-tetra-*O*-acetyl-β-*D*-glucopyranos-6-yl orthoacetate)* (**2**). — This compound was prepared from **7** (1.75 g), silver nitrate (0.72 g), and **9** (1.22 g) in acetonitrile (10 ml) in the presence of collidine (0.60 ml) in 76% yield as just described (method A). After crystallization from abs. ethanol or from benzene–ether **2** has m.p. 158–159°; $[\alpha]_D$ +62° (*c* 0.5, chloroform); $R_{compound\ 9}$ 1.55 (solvent B) or 4.3 (solvent D).

Anal. Calc. for $C_{28}H_{38}O_{19}$: C, 49.55; H, 5.64. Found: C, 49.64; H, 5.65.

*3,6-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-α-*D*-glucopyranose 1,2-(1,2,3,4-tetra-*O*-acetyl-β-*D*-glucopyranos-6-yl orthoacetate)* (**3**). — This orthoester was prepared as just described from hepta-*O*-acetyl-α-lactosyl bromide[20] (**8**, 1.82 g), silver nitrate (0.45 g), and **9** (0.70 g) in acetonitrile (10 ml) in the presence of collidine (0.40 ml). Chromatography on alumina (elution with 3:7 light petroleum–chloroform) gave **3** (0.81 g, 42%) which was crystallized from benzene–ether, m.p. 158–159°; $[\alpha]_D$ +15° (*c* 1.3, chloroform); $R_{compound\ 9}$ 1.0 (solvent B) or 3.4 (solvent D).

Anal. Calc. for $C_{40}H_{54}O_{27}$: C, 49.68; H, 5.62. Found: C, 50.12; H, 5.72.

3,4,6-Tri-O-acetyl-α-D-glucopyranose 1,2-(benzyl 2-acetamido-3,4-di-O-acetyl-2-deoxy-α-D-glucopyranosid-6-yl orthoacetate) (**4**). — Under the conditions described for the preparation of **1** (method A), a mixture of bromide **6** (1.23 g), benzyl 2-acetamido-3,4-di-*O*-acetyl-2-deoxy-α-D-glucopyranoside[21] (**5**, 0.79 g), and silver nitrate (0.51 g) was treated in acetonitrile (10 ml) with collidine (0.40 ml). The orthoester **4** was purified by chromatography on silica gel. Successive elution with chloroform, ether, and 50:1 ether–butanone yielded amorphous **4** (1.04 g, 72%), $[\alpha]_D$ +90° (*c* 1.0, chlcroform; after preceptitation from ether by light petroleum); $R_{compound\ 10}$ 1.95 (solvent D).

Anal. Calc. for $C_{33}H_{43}NO_{17}$: C, 54.63, H, 5.97; N, 1.93. Found: C, 54.77; H, 6.16; N, 2.22.

3,4,6-Tri-O-acetyl-α-D-galactopyranose 1,2-(benzyl 2-acetamido-3,4-di-O-acetyl-2-deoxy-α-D-glucopyranosid-6-yl orthoacetate) (**5**). — A mixture of bromide **7** (2.46 g), triacetate **10** (1.58 g), and silver nitrate (1.02 g) in acetonitrile (20 ml) was treated with collidine (0.80 ml) under the conditions described for the preparation of **4**. Chromatography on alumina (elution from benzene to 1:1 benzene–chloroform) and precipitation of the amorphous solid from ether with light petroleum gave 2.48 g, (86%); $[\alpha]_D$ +118° (*c* 0.8, chloroform); $R_{compound\ 10}$ 2.0 (solvent B).

Anal. Calc. for $C_{33}H_{43}NO_{17}$: C, 54.63; H, 5.97; N, 1.93. Found: C, 54.26; H, 5.90; N, 1.88.

REFERENCES

1 B. Helferich and K. Weiss, *Chem. Ber.*, 89 (1956) 314.
2 M. Schulz and H. Steinmaus, *Z. Naturforsch., B*, 19 (1954) 263.
3 R. U. Lemieux and R. Morgan, *Can. J. Chem.*, 43 (1965) 2199.
4 N. K. Kochetkov, A. Ya. Khorlin, and A. F. Bochkov, *Tetrahedron*, 23 (1967) 693.
5 A. F. Bochkov, V. I. Snyatkova, and N. K. Kochetkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1967) 2684; N. K. Kochetkov, A. F. Bochkov, T. A. Sokolovskaya, and V. J. Snyatkova, *Carbohyd. Res.*, 16 (1971) 17.
6 A. S. Perlin, *Can. J. Chem.*, 41 (1963) 399.
7 H. H. Schlubach, P. Stadler, and I. Wolf, *Ber.*, 61 (1928) 287.
8 A. Colley, *Compt. rend.*, 76 (1873) 436.
9 W. Koenigs and E. Knorr, *Ber.*, 34 (1901) 957.
10 H. Bredereck, W. Wagner, D. Geissel, W. Hutten, P. Gross, and H. Ott, *Chem. Ber.*, 95 (1962) 3056.
11 Yu. A. Zhdanov, G. A. Korol'chenko, G. N. Dorofeenko, and G. I. Zhungietu, *Dokl. Akad. Nauk SSSR*, 154 (1964) 861.
12 D. Horton and W. N. Turner, *J. Org. Chem.*, 30 (1965) 3387.
13 L. D. Hall, *Advan. Carbohyd. Chem.*, 19 (1964) 51.
14 C. S. Hudson, *J. Amer. Chem. Soc.*, 46 (1924) 1962.
15 W. Korytnyk, *J. Chem. Soc.*, (1959) 650.
16 G. Wulff and W. Krüger, *Carbohyd. Res.*, 19 (1971) 139.
17 A. Ya. Khorlin, M. L. Shul'man, S. E. Zurabyan, I. M. Privalova, and Yu. L. Kopaevich, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1968) 2094.
18 A. I. Bashkatova, G. V. Smirnova, V. N. Volynskaia, V. I. Shvets, and R. P. Evstigneeva, *Dokl. Akad. Nauk SSSR*, 201 (1971) 1231.
19 D. D. Reynolds and W. H. Evans, *J. Amer. Chem. Soc.*, 60 (1938) 2559.
20 P. A. Finan and C. D. Warren, *J. Chem. Soc.*, (1962) 2823.
21 M. L. Shul'man, G. V. Abramova, V. N. Piskaeva, and A. Ya. Khorlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1971) 630.