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Synthesis of some monodeoxy- and dideoxy-hexitols, and derivatives thereof, from D-glucono-1,5-lactone*†

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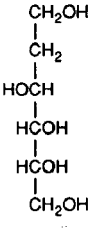
ABSTRACT

Syntheses of 2-deoxy-D-*arabino*-hexitol (**1**), D-rhamnitol (**2**), 1,2-dideoxy-D-*arabino*-hexitol (**3**), 2,3-dideoxy-D-*erythro*-hexitol (**4**), and some derivatives thereof are described. These compounds were obtained by reductive sequences on various compounds formed from methyl 3,4:5,6-di-*O*-isopropylidene-D-gluconate (**9**).

INTRODUCTION

In connection with studies of biologically active alditol derivatives, syntheses of the deoxyhexitols **1**–**4** were required which could be adapted for the incorporation of isotopic hydrogen into the deoxygenated positions. This requirement precluded the usual routes to **1** (ref. 1), **2** (ref. 2), and **4** (ref. 3). Compound **3** has not been characterised hitherto and was claimed[4] to be a product from the reaction between D-glucose or D-mannose with boiling anhydrous hydrazine.

Sterically defined vicinal diols and triols are useful building blocks in the synthesis of biologically active natural products[5]; hence, **3** and **4** may also be of interest in this respect as homologues.



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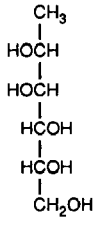

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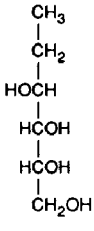

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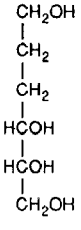

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We now describe alternative syntheses of **1**–**4**, their isopropylidene acetals **5**–**8**, and some derivatives thereof from methyl 3,4:5,6-di-*O*-isopropylidene-D-gluconate (**9**). This key intermediate can be obtained[6], in high yield, from D-glucono-1,5-lactone.

* Dedicated to Professor Leslie Hough in the year of his 65th birthday.
† The Chemistry of D-Gluconic Acid, Part V. For Part IV, see ref. 7.
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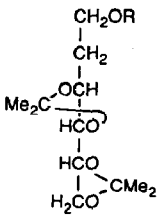
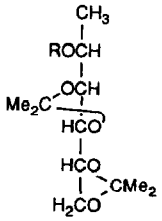
RESULTS AND DISCUSSION

A recent synthesis[7] of **5** involved reduction of the 2-deoxy-D-gluconate derivative **10** with lithium aluminium hydride. The ester **10** was obtained by chlorination (triphenylphosphine–carbon tetrachloride–imidazole) of **9**, followed by catalytic reduction of the resulting 2-chloro-2-deoxy-D-mannonate derivative **11**. The yield of **5** from this sequence was ~55%. However, treatment of **11** with lithium aluminium hydride in boiling 1,2-dimethoxyethane gave 98% of **5**. Reduction[7] of **11** with sodium borohydride in aqueous methanol did not yield **5** but only the 2-chloro-2-deoxymannitol derivative **12**. Compound **5**, which was the precursor for the dideoxyhexitol **3** *via* the diacetal **7** (see below), was characterised as the known[7] crystalline *p*-nitrobenzoate **13**. The isopropylidene groups of **5** were removed readily by treatment with dilute methanolic hydrogen chloride to give the required, crystalline 2-deoxy-D-*arabino*-hexitol (**1**). Compound **1** is also of interest, since it is oxidised[1] to 5-deoxy-D-*threo*-hexulose, a potentially useful sweetening agent, by immobilized cells of *Gluconobacter oxydans*.



5 R = H



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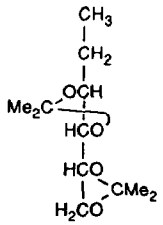

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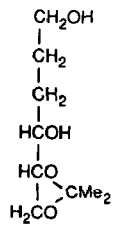

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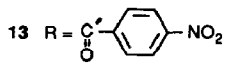
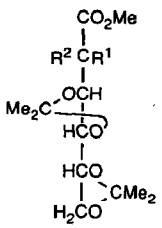


13 R = 4-nitrobenzoyl

15 R = Ts

20 R = Ts

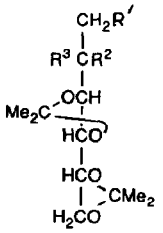


9 R^1 = OH, R^2 = H

10 R^1 = R^2 = H

11 R^1 = H, R^2 = Cl

14 R^1 = OTs, R^2 = H

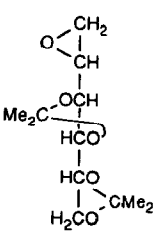


12 R^1 = OH, R^2 = H, R^3 = Cl

16 R^1 = R^2 = OH, R^3 = H

17 R^1 = R^2 = 4-nitrobenzoyloxy, R^3 = H

18 R^1 = OH, R^2 = OTs, R^3 = H



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The syrupy ester **9** has been characterised[6] as the crystalline 2-tosylate **14**. Both **5** and **6**, and thence **1** and **2**, were obtained from **14** by reduction with lithium aluminium hydride. Thus, on treatment of **14** with the reductant in boiling oxolane for 30 min, **5** (47%) and the D-rhamnitol derivative **6** (33%) were obtained after column chromatography. Compound **6** was characterised as the known[8] tosylate **15**, and hydrolysis with hot aqueous 10% acetic acid gave the required D-rhamnitol (**2**).

Reduction of **14** in boiling 1,2-dimethoxyethane gave **5** (52%), **6** (30%), and the diol **16** (9.5%), characterised[6] as the bis(1-*p*-nitrobenzoate) **17**. When the reduction of **14** was performed in boiling ether, no **6** was obtained and t.l.c. of the crude product revealed **5**, **16**, and the reduced 2-tosylate **18** (ref. 9). Column and flash-column chromatography of this mixture gave **5** (38%), **16** (20%, characterised as **17**), and **18** (1.2%). The remainder of the material was a mixture of **5** and **18**.

It is known that the course of reductions with lithium aluminium hydride can be affected by the choice of solvent, but the effect has not been examined systematically[10]. The initial step in the above reductions must be the conversion of the methyl ester **14** into the corresponding alcohol **18**. The free hydroxyl group of **18** can react with excess of the hydride to give a C-1-alkoxy aluminium hydride that imparts an intramolecular character on the subsequent reactions. Intramolecular nucleophilic displacement by the hydride ion accounts for the formation of **5**. The formation of **6** must involve the intermediate 1,2-anhydro-D-mannitol derivative **19**, formed from **14** by displacement of the tosyloxy group by the C-1 alkoxide ion generated in the initial reduction step. This inference was confirmed by treatment of **19** (ref. 9) with lithium aluminium hydride in boiling oxolane for 30 min, which gave 97% of crystalline **6**. Reduction of the tosylate **15** under similar conditions also yielded only **6**, and demonstrated the absence of direct, unassisted S_N2 displacement of the tosyloxy group by hydride ion.

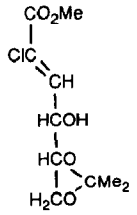
The yields of **5** obtained in the above reductions demonstrate that the intramolecular-assisted replacement of the tosyloxy group of **18** competes favourably with the epoxide formation–reduction sequence that leads to **6**. This situation was exemplified further by reaction of the D-glucitol 2-tosylate **18** (ref. 9) with lithium aluminium hydride in boiling 1,2-dimethoxyethane, which gave **5** (70%) and **6** (22%) as the only products. This result suggests that the epoxide **19** may be formed soon after the production of **18** or, more probably, in a process synchronous with the initial reduction step before complexation with the excess of hydride occurs.

The formation of deoxy sugar derivatives by the action of lithium aluminium hydride on "isolated" secondary tosyloxy groups in acyclic systems, although not widely studied, is not without precedent[11–13]. The above results accord in general with these earlier findings.

The desulfonoxylation of secondary *p*-toluenesulfonates of glycosides by lithium triethylborohydride[14] has been investigated[15], the results compared with those using lithium aluminium hydride, and the mechanistic differences discussed. Lithium triethylborohydride is a monovalent hydride, so that an internal transfer mechanism cannot operate during its reactions, and the reductions proceeded mainly *via* epoxide intermediates, often with high regio- and stereo-selectivity. The reagent does not appear to have

been applied to acyclic secondary sulfonates. When **14** was treated with the reductant in boiling oxolane for 30 min, 80% of crystalline **6** was obtained after chromatography, thereby providing a simple route to this acetal, the enantiomer of which is obtainable readily from L-rhamnose[8].

Evidence has also been presented[15] that lithium triethylborohydride can cause desulfonoxylation directly, especially when the formation of an intermediate epoxide is impossible. Nevertheless, in these examples, desulfonylation (O–S fission) was the favoured event. Thus, 1,2:5,6-di-*O*-isopropylidene-3-*O*-*p*-toluenesulfonyl-α-D-glucofuranose underwent exclusive desulfonylation, as it does[16] with lithium aluminium hydride. Compound **15** cannot yield an epoxide, and treatment with lithium triethylborohydride in boiling oxolane for 8 h and then for 20 h at room temperature gave **7** (31%) and **6** (10.5%), and 48% of **15** was recovered The yield of **7**, although good when based on the proportion of **15** consumed, was too low for our purposes. An improved yield (89%) was obtained by reduction of the tosylate (**20**) of **5** with lithium aluminium hydride in boiling oxolane. Treatment of **7** with aqueous 80% acetic acid then gave 63% of the required, crystalline 1,2-dideoxy-D-*arabino*-hexitol (**3**). It is also of potential significance for the interpretation of side reactions that can occur in the analysis of glycoproteins and glycopeptides by hydrazinolysis[4].



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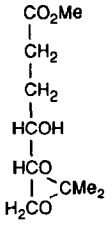

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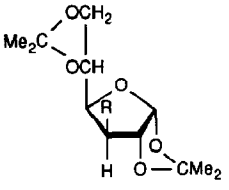

23 R = H

24 R = SCOSMe

The formation of the olefin **21** from the chloro ester **9** has been described[7]. Catalytic hydrogenation of **21** provided the dideoxy derivative **22**, reduction of which with lithium aluminium hydride in boiling oxolane gave the crystalline 2,3-dideoxy acetal **8** (60%) Compound **8** was claimed[3] as a by-product in the synthesis of the 3-deoxy-*ribo*-furanose derivative **23**, by reductive desulfuration of the dithiocarbonate **24** with Raney nickel. The independent synthesis described here confirms the assigned structure. Hydrolysis of **8** with aqueous 80% acetic acid yielded the required 2,3-dideoxy-D-*erythro*-hexitol (**4**).

EXPERIMENTAL

Optical rotations were determined with a Perkin–Elmer Model 241 automatic polarimeter on 1% solutions in chloroform at 20° unless stated otherwise. T.l.c. was performed on Kieselgel 60 (Merck) with light petroleum–ethyl acetate (1:1) and detec-

tion by charring with 0.1M $K_2Cr_2O_7$ in M sulfuric acid. Column chromatography and flash-column chromatography were performed on Silica Gel 60 and 60H, respectively (Merck), using the above solvent. Lithium triethylborohydride was purchased from Janssen Chimica as a M solution in oxolane. Oxolane, 1,2-dimethoxyethane, and ether were distilled from lithium aluminium hydride immediately before use. ^{1}H-N.m.r. spectra were recorded with a Varian EM 2940 (90 MHz) spectrometer on solutions in $CDCl_3$ (internal Me_4Si), and were used routinely to identify known products.

*2-Deoxy-3,4:5,6-*O*-isopropylidene-*D*-arabino-hexitol* (**5**). — A solution of **11** (0.85 g, 2.76 mmol) in 1,2-dimethoxyethane (10 mL) was added dropwise to a stirred suspension of lithium aluminium hydride (0.64 g, 6 mol. equiv.) in 1,2-dimethoxyethane (10 mL). The mixture was boiled under reflux for 5 h under nitrogen, then cooled (0°), treated dropwise with water (2.5 mL), followed by anhydrous magnesium sulfate (3 g), stirred for 30 min, filtered through a thin layer of anhydrous magnesium sulfate, and concentrated *in vacuo* to give **5** (665 mg, 98%); $[\alpha_D$ +10.6°; lit.[7] $[\alpha]_D$ +10.3.

The *p*-nitrobenzoate (**13**, 72%) of **5** had m.p. 73.5–75° (from aqueous 2-propanol), $[\alpha]_D$ +15.3°; lit.[7] m.p. 73.5–75.5°, $[\alpha]_D$ +14.6°.

*2-Deoxy-*D*-arabino-hexitol* (**1**). — A solution of **5** (642 mg) in methanol (10 mL), to which acetyl chloride (0.1 mL) had been added, was set aside for 20 h at room temperature and then concentrated *in vacuo*. Several portions (5 mL) of methanol were distilled from the residue to give a product which crystallised on storage. Recrystallisation from ethanol gave **1** (243 mg, 56%), m.p. 103.5–105°, $[\alpha]_D$ +17.5° (water); lit.[7] m.p. 104–106°, $[\alpha]$ +17.5° (water).

Reduction of tosylates with lithium aluminium hydride. (*a*) — A solution of **14** (ref. 6) (4.0 g, 9 mmol) in oxolane (40 mL) was added dropwise to a stirred suspension of reductant (2.51 g, 7.34 mol. equiv.) in oxolane (50 mL). The mixture was boiled under reflux for 30 min, then cooled (0°), treated dropwise with water (10 mL), followed by anhydrous magnesium sulfate (6.0 g), stirred for 30 min at room temperature, filtered through a thin layer of magnesium sulfate, and concentrated *in vacuo*. Flash-column chromatography of the residue gave 3,4:5,6-di-*O*-isopropylidene-D-rhamnitol (**6**; 0.72 g, 33%), m.p. 62–64°, $[\alpha]_D$ +16.2° (methanol); lit[17] m.p. 66.5–67; $[\alpha]_D$ +1° (methanol); lit.[18] m.p. 62–64°, $[\alpha]_D$ 0°; lit[8] (for the L enantiomer) m.p. 64–66°, $[\alpha]_D$ −16° (methanol).

Further elution gave **5** (1.045 g, 47%), $[\alpha]_D$ +10°.

The *p*-toluenesulfonate (**15**, 51%) of **6** had m.p. 84.5–85.5°; lit.[8] m.p. 83–84°.

(*b*) A solution of **14** (1.0 g, 2.25 mmol) in 1,2-dimethoxyethane (10 mL) was treated with reductant (0.6 g, 7.0 mol. equiv.) in 1,2-dimethoxyethane (20 mL) for 30 min at reflux temperature and then processed as in (*a*). Column chromatography of the crude product (552 mg, 99.5%) gave **6** (166 mg, 30%), m.p. 62–65° (from hexane); 2-deoxy-3,4:5,6-di-*O*-isopropylidene-D-*arabino*-hexitol (**5**; 287 mg, 52%), $[\alpha]_D$ +9.6°; and 3,4:5,6-di-*O*-isopropylidene-D-glucitol (**16**; 52.5 mg, 9.5%). The bis(*p*-nitrobenzoate) (**17**) of **16** had m.p. 108–111° (from ethanol), $[\alpha]_D$ −47.5°; lit.[16] m.p. 111–114°, $[\alpha]_D$ −49.5°.*

* Originally cited in error as a positive rotation (see ref. 6).

(*c*) A solution of **14** (ref. 6) (1.0 g, 2.25 mmol) in ether (10 mL) was added to a suspension of reductant (0.69 g, 7 mol. equiv.) in ether (20 mL), and the mixture was heated under reflux for 30 min and then processed as in (*a*). Column chromatography of the crude product (469 mg, 90%) gave a mixture (339 mg) that contained (t.l.c.) **2** and **18** ref. 9), then **16** (110 mg, 20%), characterised as **17**, m.p. 109–111°.

The mixture was rechromatographed to give **18** (11 mg, 1.2%), **5** (209 mg, 38%), and a mixture (103 mg) of **5** and **18**.

(*d*) A solution of **18** (ref. 9) (0.51 g, 1.22 mmol) in 1,2-dimethoxyethane (10 mL) was treated with reductant (0.2 g, 4.3 mol. equiv.) in 1,2-dimethoxyethane (10 mL), and the mixture was processed as in (*a*). Column chromatography of the crude product (302 mg, 100%) gave **6** (67 mg, 22%), m.p. 63–65° (from hexane), and **5** (210 mg, 70%).

(*e*) A solution of **19** (ref. 9) (0.5 g, 2.09 mmol) in oxolane (10 mL) was treated with reductant (0.332 g, 4.8 mol. equiv.) in oxolane (20 mL), and the mixture was processed as in (*a*). The crude product (469 mg, 97%) was recrystallised from light petroleum to afford **6** (378 mg, 73.5%), m.p. 61.5–64.5°.

(*f*) Treatment of **15** (361 mg) with reductant (0.137 g, 4 mol. equiv.) as in (*e*) gave **6** (0.24 g, 100%), m.p. 62–64° (from light petroleum).

Reductions with lithium triethylborohydride. — (*a*) A solution of **14** (0.5 g, 1.13 mmol) in oxolane (5 mL) was added dropwise to a M solution of reductant in oxolane (7.9 mL, 7 mol. equiv.). The mixture was heated for 30 min under reflux with stirring under nitrogen, then cooled to room temperature, treated with sodium sulfate decahydrate (1.0 g), and, after 10 min, with anhydrous sodium sulfate (1.0 g), then filtered through a mixture of silica gel (3.0 g) and anhydrous sodium sulfate (2.0 g). The inorganic material was washed with oxolane (2 × 10 mL), the combined filtrate and washings were concentrated *in vacuo*, and the crude product was chromatographed to give **6** (222 mg, 80%), m.p. 62–65° $[\alpha]_D$ +16° (methanol).

(*b*) A solution of **15** (0.5 g, 1.25 mmol) in oxolane (10 mL) was added dropwise to a M solution of reductant (6.5 mL, 5.2 mol. equiv.) in oxolane. The mixture was heated for 8 h under reflux with stirring under nitrogen, then stirred for 20 h at room temperature, and processed as in (*a*). Flash-column chromatography of the crude product gave 1,2-dideoxy-3,4:5,6-di-*O*-isopropylidene-D-*arabino*-hexitol (**7**; 89.5 mg, 31%) as an oil, $[\alpha]_D$ +12.6°. ^{1}H-N.m.r. data: δ 3.97 (m, 4 H), 3.55 (m, 1 H, H-3), 1.70 (m, 2 H, CH_2), 1.38 and 1.33 (2 s, each 6 H, $2CMe_2$), 1.00 (t, 3 H, CH_3).

Anal. Calc. for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.70; H, 9.80.

Further elution then gave **15** (239 mg, 48%), m.p. 80–83°, and **6** (32.5 mg, 10.5%), m.p. 62–65°.

2-Deoxy-3,4;5,6-di-O-*isopropylidene-1*-O-p-*toluenesulfonyl*-D-arabino-*hexitol* (**20**). — To a solution of **5** (3.0 g, 12 mmol) in dry pyridine (12 mL) at 0° was added tosyl chloride (2.78 g). The mixture was stored overnight at 5°, then treated with ice–water (1 mL), and, after 5 min, poured into ice–water (200 mL). The mixture was extracted with dichloromethane (2 × 75 mL), and the combined extracts were washed successively with 2M hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water, dried (Na_2SO_4), and concentrated *in vacuo*. Column chromatography of a portion of the

essentially pure (t.l.c.) residue (4.67 g, 96%) gave **20**, $[\alpha]_D$ +15°. ^{1}H-N.m.r. data: δ 7.8–7.3 (ABq, 4 H, aromatic H), 4.00 (m, 6 H), 3.43 (m, 1 H, H-3), 2.42 (s, 3 H, tosyl Me), 2.0 (m, 2 H, H-2,2') 1.35 (s, 3 H, CMe_2), 1.30 (s, 6 H, CMe_2), 1.27 (s, 3 H, CMe_2).

Anal. Calc. for $C_{19}H_{28}O_7S$: C, 56.98; H, 7.05; S, 8.01. Found: C, 56.32; H, 7.10; S, 7.56.

*1,2-Dideoxy-3,4:5,6-di-*O*-isopropylidene-*D-arabino-*hexitol* (**7**). — A solution of **20** (1.0 g, 2.52 mmol) in oxolane (10 mL) was added dropwise to a stirred suspension of lithium aluminium hydride (0.4 g, 4.2 mol. equiv.) in oxolane (10 mL). The mixture was heated for 1.5 h under reflux under nitrogen, then processed as in (*a*), and the essentially pure (t.l.c.) residue (577 mg) was distilled *in vacuo* to give **7** (516 mg, 89%), b.p. 75°/0.6 mbar, $[\alpha]_D$ +12.5°.

*1,2-Dideoxy-*D-arabino-*hexitol* (**3**). — A solution of **7** (475 mg) in aqueous 80% acetic acid (20 mL) was set aside at room temperature for 6 days, then concentrated *in vacuo*, and water (3 × 10 mL) and then ethanol (10 mL) were distilled *in vacuo* from the residue. Recrystallisation of the crude product from 2-propanol gave **3** (196 mg, 63%), m.p. 121–122°, $[\alpha]_D$ +4.3° (water). ^{1}H-N.m.r. data (D_2O): δ 3.73–3.47 (m, 5 H), 1.42 (m, 2 H, CH_2), 0.83 (t, 3 H, *J* 7 Hz, CH_3).

Anal. Calc. for $C_6H_{14}O_4$: C, 47.99; H, 9.40. Found: C, 48.38; H, 9.39.

*2,3-Dideoxy-5,6-*O*-isopropylidene-*D-erythro-*hexitol* (**8**). — A solution of **22** (ref. 7) (0.5 g, 2.29 mmol) in oxolane (10 mL) was added to a stirred suspension of lithium aluminium hydride (0.48 g, 5.5 mol. equiv.) in oxolane (10 mL). The mixture was heated for 8 h under reflux with stirring under nitrogen, then processed as in (*a*). Column chromatography of the residue (434 mg) yielded **8** (260 mg, 60%), m.p. 53–55°, $[\alpha]_D$ +13.6°; lit.[3] m.p. 52.5–53.5°, $[\alpha]_D$ +12.9°. ^{1}H-N.m.r. data: δ 3.97 (m, 3 H, H-5,6,6'), 3.67 (m, 3 H, H-1,1',4), 2.63 (bs, 1 H, OH), 1.70 (m, 4 H, H-2,2',3,3'), 1.33 and 1.41 (2 s, each 3 H, CMe_2).

A solution of a portion (242 mg) of the product in aqueous 80% acetic acid (10 mL) containing trifluoroacetic acid (25 mL) was set aside for 20 h at room temperature, then concentrated *in vacuo*. Water (3 × 2 mL) and ethanol (5 mL) were distilled *in vacuo* from the residue to leave 2,3-dideoxy-D-*erythro*-hexitol (**4**) as a colourless glass (191 mg, 99%), $[\alpha]_D$ −7.1° (water); lit.[3] $[\alpha]_D$ −4.9 ±1.2° (water).

D-*Rhamnitol* (**2**). — A solution of **6** (537 mg) in aquous 10% acetic acid (20 mL) was heated for 4 h at 100°, then concentrated *in vacuo*, and water (3 × 20 mL) and ethanol (20 mL) were distilled *in vacuo* from the residue, which crystallised on storage. Recrystallisation of the dried, crude product from ethanol–ether gave **2** (253 mg, 70%), m.p. 121–122°, $[\alpha]_D$ −12.6° (water); lit.[2] m.p. 122–123°, $[\alpha]_D$ −12° (water).

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