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Note

Synthesis of 3-hexuloses from 1,2:5,6-di-*O*-isopropylidenehexitols

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Abstract

A simple, but low-yielding method for the synthesis of 3-hexuloses has been elaborated. Oxidation of 1,2:5,6-di-*O*-isopropylidenehexitols with bromine in the presence of barium carbonate, followed by mild-acid hydrolysis of the oxidation products gave the free hexuloses. Oxidation occurred at only one of the carbon atoms bearing free hydroxyl groups. From the D-mannitol derivative, D-*arabino*-3-hexulose was obtained via the di-*O*-isopropylidene derivative, whereas the D-glucitol derivative gave a mixture of the 1,2:5,6-di-*O*-isoprpylidene derivatives of L-*xylo*- and D-*ribo*-3-hexulose, separable by column chromatography. Mild-acid hydrolysis of the oxidation products afforded the free hexuloses.

Keywords: 3-Hexuloses; Di-*O*-isopropylidenehexitols; Bromine oxidation; Mass spectrometry

3-Hexuloses constitute a group of monosaccharides having received relatively little attention. It is known that D-*arabino*-3-hexulose-6-phosphate is the primary product in formaldehyde fixation in some methylotrophic bacteria through aldol reaction with D-*erythro*-2-pentulose-5-phosphate (ribulose-5-phosphate).[1–3] The aldol reaction is catalysed by 3-hexulose-phosphate synthase (HPS), and this enzyme has been applied in synthesis of the 3-hexulose-6-phosphate, from which the free hexulose was obtained on dephosphorylation.[4] In connection with our interest in aldol reactions of small sugars, the preparation of D-*xylo*- and D-*lyxo*-3-hexuloses[5] as well as DL-*lyxo*-3-hexulose[6] and their isolation as di-*O*-isopropylidene derivatives was described in previous papers.

In continuation of this work, we needed to know the chromatographic behaviour and the mass spectra of the di-*O*-isopropylidene derivatives of the 3-hexuloses with arabino and ribo configurations, these 3-hexuloses are the expected products in the alkali-catalysed aldol reaction between *erythro*-2-pentulose and formaldehyde. The HPS-catalysed reaction mentioned above[4] requires the application of three different enzymes, and it is limited to the synthesis of the D-arabino-isomer. Preparation of 3-hexuloses by chromium trioxide oxidation in acetic acid of tetraacetates of ethylidene, methylene or benzylidene derivatives of hexitols has been described by Angyal et al.[7,8] Other, less general methods

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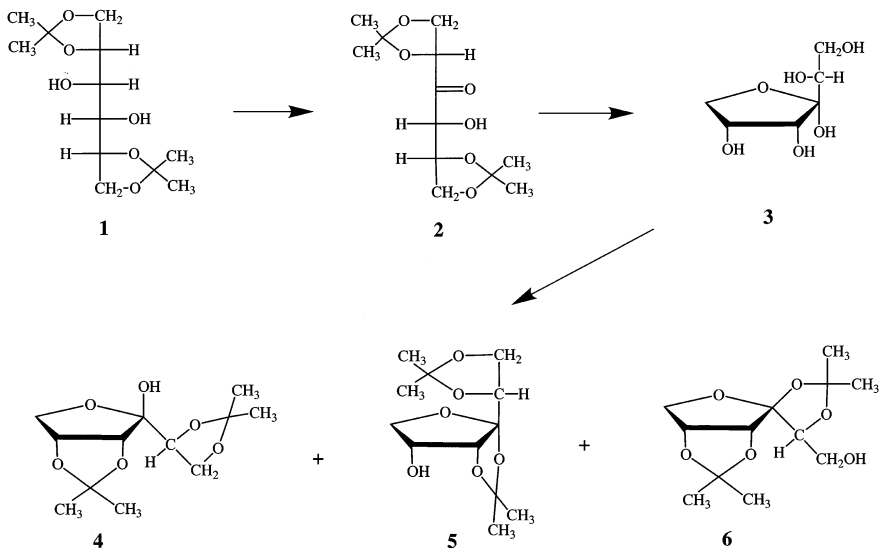
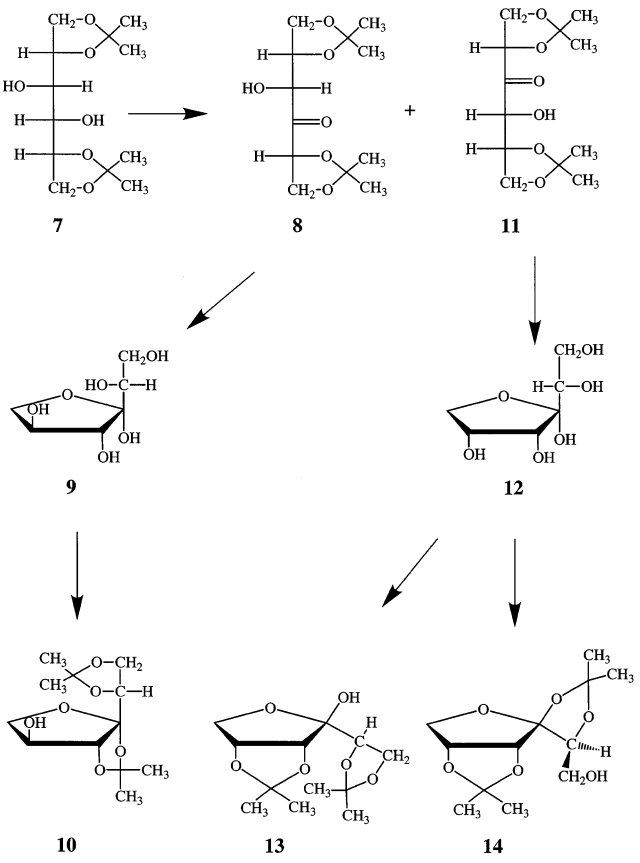
have also been reported for the preparation of such compounds.[9,10]The chromium trioxide route[7,8] seemed at first sight attractive, but for the preparation of the free 3-hexuloses from the hexitols, as many as six steps are needed. Even though some simplification is achieved by omitting isolation and purification of some of the intermediate products, we felt the need for a simpler method for the synthesis of the two required 3-hexuloses.

Oxidation of alditols by bromine is known to give several mono- and dicarbonyl compounds, but oxidation at neighbouring carbon atoms is usually not observed.[11] This fact and the availability of the 1,2:5,6-di-*O*-isopropylidene derivatives of D-mannitol and D-glucitol suggested bromine oxidation of these hexitol derivatives as a potential, rapid route to 3-hexuloses. The ease with which the terminal isopropylidene groups are removed by mild-acid hydrolysis[12] was expected to prevent degradation during the liberation of the 3-hexuloses from the primary oxidation products, a fact making this potential route particularly attractive. Due to its symmetry, the mannitol derivative should give only one product on oxidation at one carbon atom, the 1,2:5,6-di-*O*-isopropylidene derivative of D-*arabino*-3-hexulose, whereas the glucitol derivative is expected to give a mixture of the derivatives of D-*ribo*- and L-*xylo*-3-hexuloses. Treatment of 1,2:5,6-di-*O*-isopropylidene-D-mannitol (**1**) in water with bromine in the presence of barium carbonate gave 1,2:5,6-di-*O*-isopropylidene-D-*arabino*-3-hexulose (**2**) as single product, as shown by gas chromatography. More than half the original amount of **1** remained unchanged after 20 h, but the reaction was stopped in order to prevent the formation of secondary products. The product **2** was separated from **1** by column chromatography on Silica Gel. The infrared spectrum showed strong carbonyl absorption at 1710 cm^{-1}. In the mass spectrum, a peak was seen at m/z 245, representing the molecular ion after the loss of one methyl group, whereas the base peak appeared at m/z 101, due to a fragment which is the resonance stabilised 2,2-dimethyl-1,3-dioxolanylium ion characteristic of terminal *O*-isopropylidene groups.[13] The high abundance of this fragment is expected in the spectrum of compound **2**, which has two such groups. Compound **2** was easily hydrolysed under mild conditions to free D-*arabino*-3-hexulose (**3**). The ^{13}C NMR data of the α-furanose form, which dominates in aqueous solution, agree with those reported by Brockamp et al.[4] and Angyal et al.[14] The identity of the 3-hexulose was confirmed by treatment with acetone–sulphuric acid, which gave three different di-*O*-isopropylidene derivatives (**4**, **5** and **6**) in relative ratios approximately as reported by Angyal and Evans,[8] as seen by gas chromatography–mass spectrometry (Scheme 1). The anomeric configurations of compounds **4** and **6** have been assigned by Angyal



Scheme 1.



Scheme 2.

and Evans.[8] The mass spectrum of compound **4** showed the presence of a 1,2-*O*-isopropylidene group, fragments with *m*/*z* 101 and *m*/*z* 159 resulting from cleavage between C-2 and C-3. Furthermore, compound **4** has its hemiacetal hydroxyl group free, since it was reduced by sodium borohydride in contrast to compounds **5** and **6**, this is in accordance with the structure 1,2:4,5-di-*O*-isopropylidene-D-*arabino*-3-hexulofuranose. Compound **5**, which was present in only minute amounts, had a spectrum not very different from that of **4** and must be 1,2:3,4-di-*O*-isopropylidene-α-D-*arabino*-3-hexulofuranose. In the spectrum of compound **6**, the major isomer formed, no significant peaks were seen at *m*/*z* 101 or *m*/*z* 159, excluding the presence of a 1,2-*O*-isopropylidene group as expected for the reported[8] 2,3:4,5-di-*O*-isopropylidene-β-D-*arabino*-3-hexulofuranose.

When 1,2:5,6-di-*O*-isopropylidene-D-glucitol (**7**) was similarly treated with bromine and barium carbonate, two products were formed in a ratio of 2:1, as seen by GC. The mass spectra were almost identical with those of compound **2**. The compounds were separable on Silica gel. The major product is 1,2:5,6-di-*O*-isopropylidene-L-*xylo*-3-hexulose (**8**), giving L-*xylo*-3-hexulose (**9**) on mild-acid hydrolysis. Treatment of **9** with acetone–sulphuric acid gave 1,2:3,4-di-*O*-isopropylidene-β-L-*xylo*-3-hexulofuranose (**10**) as a single product, identified by comparison with the D-enantiomer.[5] The minor product from the oxidation of the glucitol derivative **7** was 1,2:5,6-di-*O*-isopropylidene-D-*ribo*-3-hexulose (**11**), from which D-*ribo*-3-hexulose (**12**) was liberated by hydrolysis. Treatment of **12** with acetone–sulphuric acid afforded a mixture of two di-*O*-isopropylidene derivatives in relative proportions about 5:1 as seen by GC. The mass spectrum of the major product was similar to that of compound **4**, and it must be 1,2:4,5-di-*O*-isopropylidene-D-*ribo*-3-hexulofuranose (**13**), whereas the minor isomer showed fragmentation like compound **6**, which is in accordance with the structure **14**: 2,3:4,5-di-*O*-isopropylidene-β-D-*ribo*-3-hexulofuranose (Scheme 2). These results are in agreement with those reported by Angyal and Evans.[8] Also for compounds **13** and **14** the anomeric configurations shown are those assigned by these authors, and for the free L-*xylo*-3-hexulose (**9**), the β-furanose form is known to be dominant in aqueous solution, and the ^{13}C NMR data are in accordance with those reported.[14] The optical rotation of D-*ribo*-3-hexulose (**12**) suggests the α-furanose form is preferred for this compound by comparison with D-*arabino*-3-hexulose, which is supported by the similarity of the ^{13}C NMR spectra of the two compounds.

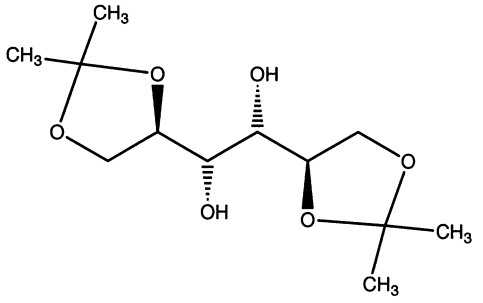
It is seen from the yields of the different 3-hexuloses that there is a somewhat higher reactivity at C-4 than at C-3 in the glucitol derivative **7**, and it is also higher than at C-3 and C-4 in the mannitol derivative **1**. A possible explanation for this fact may be that oxidation at C-4 in **7** removes an unfavourable 1,3-parallel interaction between OH-4 and O-2 in the extended, planar zigzag conformation of this compound (Fig. 1). No such interactions exist for the other free hydroxyl groups in the two hexitol derivatives. Support for this notion is found in MM2 calculations (energy

minimisation), giving a separation of 3.02 Å for the OH-4–O-2, and 3.85 Å for the OH-3–O-5 distances in compound **7**.

Despite the low yields in the bromine oxidation of the two di-*O*-isopropylidene hexitols, the simplicity of the method and the availability of the starting materials should make this route to 3-hexuloses an attractive alternative to existing methods.

1. Experimental

General methods.—Optical rotations were measured with a Carl Zeiss Kreispolarimeter 0.01°. GC was performed with a Shimadzu GC-14B gas chromatograph, equipped with an open tubular fused silica column, 25 m × 0.32 mm ID, wall coated with CP-SIL 43 CB, programmed at 6°/min from 90 to 225 °C. For mass spectrometry a JEOL JMX-DX 303 double focusing mass spectrometer with EB geometry was used, equipped with a 10 kV post acceleration conversion dynode detector and an electron ionisation–chemical ionisation (EI–CI) ion source, operated in EI mode at 70 eV and an ion source temperature at 180 °C. A Carlo–Erba high resolution gas chromatograph (HRGC) was applied for the GC–MS combination. High resolution mass spectrometry (HRMS) was performed with a ProSpecQ sector instrument (VG) operated in EI mode at 70 eV and an ion source temperature at 250 °C. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-300 instrument at 300 and 75 MHz, respectively. The isopropylidene acetals were all recorded in $CDCl_3$ with $CHCl_3$ as the internal standard, while the free carbohydrates were recorded in D_2O with DMSO as internal standard (^{13}C NMR δ_{ref} 40.40 ppm). Signal assignments are based on COSY, DEPT and HETCOR experiments where appropriate. IR spectra were recorded with a Perkin–Elmer Paragon 500 FT-IR spectrometer. Column chromatography was carried out on Silica Gel H (E. Merck, normally used for TLC) with A: 40:20:1 v/v $CHCl_3$–EtOAc–1-propanol under a slight external nitrogen pressure. Pre-coated Silica Gel G (E. Merck) plates were used for TLC with the same eluent. Paper chromatography was performed on Whatman No.1 paper with B: 6:4:3 v/v butanol–Py–water. Spots were detected with diphenylamine–aniline–phosphoric acid.[15]



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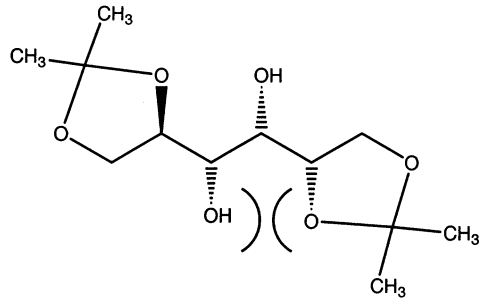

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Fig. 1. Planar zigzag conformation of compounds **1** and **7**, showing the 1,3-parallel interaction between OH-4 and O-2 in **7**.

Materials.—1,2:5,6-Di-*O*-isopropylidene-D-mannitol (**1**)[16] and 1,2:5,6-di-*O*-isopropylidene-D-glucitol (**7**)[17] were prepared according to the reported procedures.

1,2:5,6-Di-O-isopropylidene-D-arabino-3-hexulose (**2**).—To a solution of **1** (1.05 g) in water (30 mL) were added $BaCO_3$ (1.10 g) and Br_2 (0.26 mL), and the mixture was stirred at 30 °C in the dark for 20 h. Excess Br_2 was then removed in a stream of N_2 and the solution was saturated with Na_2SO_4. The solution was filtered and extracted with EtOAc (4 × 15 mL). TLC (solvent A) of the combined EtOAc solutions showed a single, red–brown spot, R_f 0.30, whereas unreacted **1** appeared as a white spot (R_f 0.12) on the pale blue plate on prolonged heating. GC showed the presence in a ratio of about 1:3 of **2** (R_t 14.7 min) and **1** (R_t 15.7 min). The solvent was evaporated under reduced pressure and the residue dissolved in hot dibutyl ether (6 mL),

from which much of compound **1** crystallised on cooling. The solution was filtered and concentrated under reduced pressure and the residue subjected to column chromatography, giving crystalline **2** (155 mg, 15%), mp 84–85 °C; $[\alpha]_D^{20}$ −41° (*c* 2, $CHCl_3$); IR: 1710 cm^{-1} (carbonyl); ^1H NMR δ: 1.35, 1.41, 1.46, 1.49 (4 × s, 4 × 3 H, 2 × $C(CH_3)_2$), 3.36 (d, 1 H, $J_{4,OH}$ 3.6 Hz, OH), 3.95–4.04 (m, 2 H, H-1a, H-6b), 4.05–4.18 (m, 2 H, H-5, H-6a), 4.23–4.32 (m, 2 H, H-1b, H-4), 5.04 (dd, 1 H, $J_{1a,2}$ 5.9, $J_{1b,2}$ 7.6 Hz, H-2); ^{13}C NMR δ: 25.2, 25.4, 26.0, 26.6 (CH_3 × 4), 66.2 (C-1), 66.6 (C-6), 75.3 (C-5), 75.5 (C-4), 79.0 (C-2), 110.3, 111.4 (O–C–O × 2), 207.5 (C=O). EIMS *m*/*z* (% rel. int.): 245 (61) $M^+ - CH_3$, 187 (40), 127 (24), 115 (18), 101 (100), 83 (20), 73 (72), 59 (68), 55 (60), 43 (93); HRMS: Calcd. for $C_{12}H_{20}O_6 - CH_3$: *m*/*z* 245.1025. Found: 245.1020.

D-arabino-*3-Hexulose* (**3**).—Compound **2** (130 mg) was dissolved in 0.005 M aq H_2SO_4 (4 mL) and the solution kept at 45 °C for 3 h. Neutralisation with Dowex 1 anion-exchange resin (HCO_3^-), filtration of the solution and concentration gave **3** as a syrup (79 mg, 88%), $[\alpha]_D^{20}$ −31° (*c* 1, water); lit. −32.8°;[18] PC: R_f 0.45 (solvent B); ^{13}C NMR (α-furanose) δ: 63.0 (C-1), 71.6 (C-5), 72.6 (C-4), 73.1 (C-6), 74.5 (C-2), 104.9 (C-3).

Di-O-*isopropylidene derivatives* (**4**, **5**, *and* **6**) *of* D-arabino-*3-hexulose*.—Compound **3** (10 mg) was stirred with acetone containing 1.5% H_2SO_4 (2 mL) for 2 h. The solution was neutralised with solid $NaHCO_3$, filtered and subjected to GC–MS. Three compounds, **4**, **5** and **6** were observed in relative proportions 30:5:65%, respectively:

1,2:4,5-Di-*O*-isopropylidene-D-*arabino*-3-hexulofuranose (**4**), R_t 10.7 min; EIMS *m*/*z* (% rel. int.): 245 (97), 185 (17), 159 (55) 127 (19), 101 (32), 85 (32), 59 (98), 43 (100).

1,2:3,4-Di-*O*-isopropylidene-α-D-*arabino*-3-hexulofuranose (**5**), R_t 11.3 min; EIMS: 245 (100), 185 (42), 159 (62), 127 (18), 101 (33), 59 (53), 43 (83).

2,3:4,5-Di-*O*-isopropylidene-β-D-*arabino*-3-hexulofuranose (**6**), R_t 11.9 min; EIMS: 245 (100), 227 (89), 147 (30), 127 (34), 85 (52), 59 (93), 43 (88).

The solvent was removed under reduced pressure from the solution containing **4**, **5** and **6**. The residue was dissolved in water (5 mL), and $NaBH_4$ (5 mg) was added. After 1 h, the solution was treated with Dowex 50 W (H^+) ion-exchange resin, filtered and evaporated to dryness. Methanol (2 × 4 mL) was distilled from the residue, which then was dissolved in $CHCl_3$ (5 mL). The solution was extracted with water (3 × 3 mL), after which GC showed the presence of compounds **5** and **6** only, in the $CHCl_3$ solution.

1,2:5,6-Di-O-*isopropylidene*-L-xylo- (**8**) *and* -D-ribo- (**11**)-*3-hexulose*.—Compound **7** (1.05 g) in water (30 mL) was treated with Br_2 in the presence of $BaCO_3$ as described above for compound **1**. TLC (solvent A) of the resulting EtOAc solution showed two red–brown spots with R_f 0.35 and 0.29 in addition to unreacted **7**, R_f 0.15. GC revealed the presence of **8** (R_t 13.9 min) and **11** (R_t 13.0 min) in a ratio of 2:1 in addition to compound **7** (R_t 14.7 min). The compounds were separated by column chromatography, compound **11** was eluted first, then **8**, and finally compound **7**.

Compound **8** was obtained as a syrup (177 mg, 17%), TLC: R_f 0.29 (solvent A); $[\alpha]_D^{20}$ +19° (*c* 1.5, $CHCl_3$); ^1H NMR δ: 1.33, 1.39, 1.40, 1.51 (4 × s, 4 × 3 H, 2 × $C(CH_3)_2$), 4.00–4.14 (m, 4 H, H-1a, H-6a, H-6b, OH), 4.28 (t, $J_{1a,1b} \approx J_{1b,2}$ 8.1 Hz, 1 H, H-1b), 4.46 (d, 1 H, $J_{4,5}$ 2.9 Hz, H-4), 4.60 (dt, 1 H, $J_{4,5}$ 2.9, $J_{5,6a} \approx J_{5,6b}$ 6.6 Hz), 4.81 (dd, 1 H, $J_{1a,2}$ 6.6, $J_{1b,2}$ 8.0 Hz); ^{13}C NMR δ: 24.7, 25.4, 26.0, 26.2 (CH_3 × 4), 65.8 (C-1), 66.4 (C-6), 74.5 (C-5), 74.8 (C-4), 79.0 (C-2), 109.9, 111.3 (O–C–O × 2), 207.5 (C=O). EIMS: 245 (24), 187 (11), 127 (12), 115 (8), 101 (100), 83 (13), 73 (17), 59 (27), 43 (63). HRMS: Calcd for $C_{12}H_{20}O_6$–CH_3: *m*/*z* 245.1025. Found: 245.1022.

Compound **11** was also obtained as a syrup (94 mg, 9%), TLC (solvent A): R_f 0.35; $[\alpha]_D^{20}$ −75° (*c* 0.5, $CHCl_3$); ^1H NMR δ: 1.35, 1.40, 1.44, 1.49 (4 × s, 4 × 3 H, 2 × $C(CH_3)_2$), 4.05–4.09 (m, 2 H, H-1a, H-6b), 4.11–4.20 (m, 2 H, H-5, H-6a), 4.20–4.23 (m, 2 H, H-1b, H-4), 4.64 (d, 1 H, $J_{4,OH}$ 6.6 Hz, OH), 4.76 (dd, 1 H, $J_{1a,2}$ 5.9, $J_{1b,2}$ 7.0 Hz, H-2); ^{13}C NMR δ: 25.2, 25.3, 26.1, 26.5 (CH_3 × 4), 66.1 (C-1), 66.4 (C-6), 74.8 (C-5), 77.0 (C-4), 79.1 (C-2), 110.4,

111.1 (O–C–O × 2), 209.8 (C=O). EIMS: 245 (13), 187 (7), 127 (6), 115 (6), 101 (100), 83 (9), 73 (15), 59 (21), 43 (62). HRMS: Calcd for $C_{12}H_{20}O_6$–CH_3: m/z 245.1025. Found 245.1029.

L-xylo-*3-Hexulose* (**9**) *and* D-ribo-*3-hexulose* (**12**).—Hydrolysis of compound **8** (150 mg) as described above for **2** gave **9** as a syrup (94 mg, 91%), PC (solvent B): R_f 0.49; $[\alpha]_D^{20}$ + 19° (*c* 0.8, water); lit. + 22°;[18] ^{13}C NMR (β-furanose) δ: 63.2 (C-1), 71.5 (C-6), 74.9 (C-2), 76.5 (C-5), 78.9 (C-4), 105.2 (C-3). Hydrolysis of **11** (80 mg) gave **12**, also as a syrup (49 mg, 88%); PC (solvent B): R_f 0.47, $[\alpha]_D^{20}$ − 29° (*c* 0.5, water); lit. − 32°;[18] ^{13}C NMR (α-furanose) δ: 63.3 (C-1), 71.7 (C-5), 72.0 (C-4), 73.2 (C-6), 75.6 (C-2), 104.5 (C-3).

1,2:3,4-Di-O-isopropylidene-β-L-xylo-3-hexulofuranose (**10**).—Compound **9** (130 mg) was stirred with acetone containing 1.5% H_2SO_4 (5 mL) for 90 min. After neutralisation with solid $NaHCO_3$, the solution was filtered and concentrated. Crystallisation of the residue from hexane gave **10** (141 mg, 75%); mp 102–104 °C; lit. 104–105 °C;[8] $[\alpha]_D^{20}$ − 14° (*c* 1, $CHCl_3$); lit. − 16.6°;[8] GC: R_t 10.6 min, indistinguishable from authentic D-enantiomer;[5] EIMS: 245 (100), 200 (59), 187 (17), 185 (25), 159 (75), 127 (36), 101 (65), 85 (16), 71 (18), 59 (78), 43 (90).

Di-O-isopropylidene derivatives (**13** *and* **14**) *of* D-ribo-*3-hexulose*.—Compound **12** (10 mg) was treated with acetone–H_2SO_4 as described for **3**, and the solution was subjected to GC–MS. Two compounds in relative proportions 5:1 were observed.

The major compound, 1,2:4,5-di-*O*-isopropylidene-D-*ribo*-3-hexulofuranose (**13**), had R_t 11.3 min and EIMS: 245 (40), 185 (8), 159 (70), 127 (17), 101 (29), 85 (15), 59 (100), 43 (62).

The minor compound, 2,3:4,5-di-*O*-isopropylidene-β-D-*ribo*-3-hexulofuranose (**14**), had R_t 10.7 min; EIMS: 245 (65), 227 (56), 171 (42), 147 (28), 127 (28), 85 (33), 59 (100), 43 (62).

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