

Preparation and Characterization of Some Sugar Nitriles

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Starting from suitably *O*-isopropylidenedated *D*-galactose, *D*-glucose, and *D*-mannose, several *O*-protected sugar nitriles useful as intermediates for further interesting carbohydrate derivatives were prepared by dehydration of corresponding oximes or by displacement reaction of corresponding triflate derivatives. The isolated compounds were characterized by the NMR and mass spectral data.

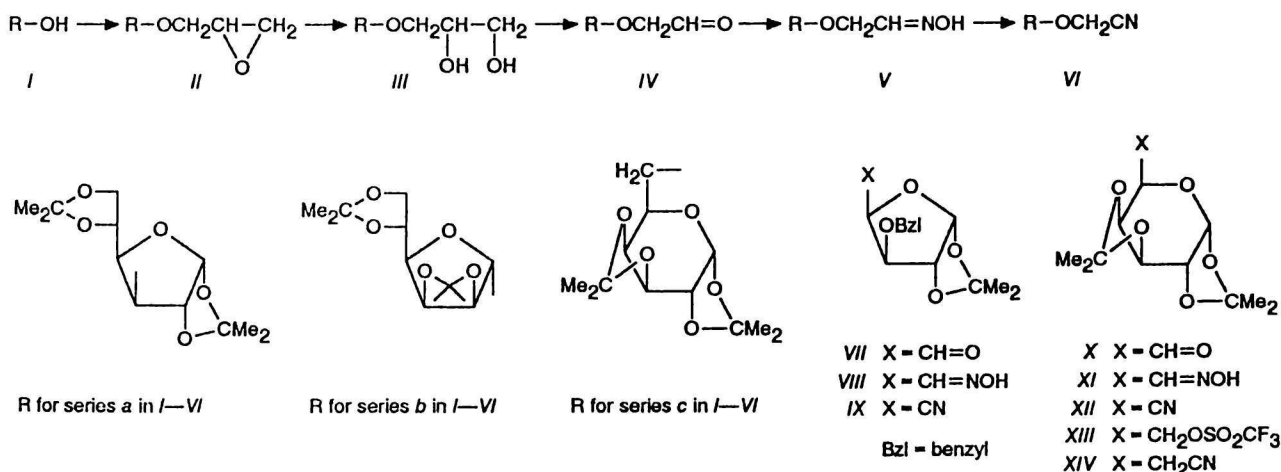
Nitriles represent an important group of intermediates in the chemistry of carbohydrates. The most frequently, they are further reduced to produce corresponding amines. In addition, they can be of use as a starting material for the preparation of carboxylic acids, esters or amides. Moreover, condensation reactions at α -position or Grignard reaction involving nitriles can afford further interesting saccharide derivatives.

The most general method for their preparation is dehydration of corresponding oximes (using acetic anhydride, benzoyl chloride, phosphorus pentachloride, phenyl isocyanate, thionyl chloride, triethyl orthoformate, *etc.*) or nucleophilic replacement reaction of tosylates, mesylates, halides, and triflates with sodium or potassium cyanide [1, 2].

Starting from suitably *O*-protected saccharides *I* (Scheme 1), *O*-epoxypropyl derivatives *II* were prepared according to the method described for *IIc* [3]. Likewise as in that case, compounds *IIa* and *IIb* represented mixtures ($x_r = 1:1$) of diastereomeric *O*-epoxypropyl derivatives. In contrast to *IIc* where (2*S*-

2,3-epoxypropyl diastereomer was obtained from the mixture by fractional crystallization [3], in the case of *IIa* and *IIb* such separation was unsuccessful. But with regard to subsequent reaction steps, separation of diastereomers was not necessary. Further reaction sequence involved hydrolysis of *II* to diols *III*, oxidative cleavage of these to aldehydes *IV* and preparation of oximes *V*. Subsequent dehydration of *V* with acetic anhydride afforded required nitriles *VI*. As expected, in the case of *D*-mannofuranose derivatives *IIb*—*VIb*, only α -anomers were isolated.

For the preparation of 3-*O*-benzyl-1,2-*O*-isopropylidene- α -*D*-xylofuranurononitrile (*IX*) and 1,2:3,4-di-*O*-isopropylidene- α -*D*-galactopyranurononitrile (*XII*), a similar reaction sequence (diol \rightarrow aldehyde \rightarrow oxime \rightarrow nitrile) was used. Compound *XII* had already been described [4] as a by-product formed in 25 % yield during the preparation of 6-*C*-azi-6-deoxy-1,2:3,4-di-*O*-isopropylidene- α -*D*-galacto-hexopyranose from aldehyde *X*. Although the same ^1H NMR spectra as reported in [4] confirming the structure of *X* were registered, significant differences were observed with



Scheme 1

Table 1. Characterization of the Prepared Compounds

| Compound | Formula | M_r | $w_i(\text{calc.})/\%$ | | | Yield % | M.p. °C | R_f^a |
|-------------|--------------------|--------|------------------------|------|------|------------|----------------------|---------|
| | | | C | H | N | | | |
| <i>Ib</i> | $C_{15}H_{24}O_7$ | 316.35 | 56.98 | 7.65 | – | 71 | <i>b</i> | 0.87 |
| | | | 57.03 | 7.69 | – | | | |
| <i>Va</i> | $C_{14}H_{23}NO_7$ | 317.35 | 52.99 | 7.31 | 4.41 | 88 | <i>b</i> | 0.62 |
| | | | 52.93 | 7.35 | 4.44 | | | |
| <i>Vb</i> | $C_{14}H_{23}NO_7$ | 317.35 | 52.99 | 7.31 | 4.41 | 87 | 86–87 | 0.63 |
| | | | 53.02 | 7.33 | 4.39 | | | |
| <i>Vc</i> | $C_{14}H_{23}NO_7$ | 317.35 | 52.99 | 7.31 | 4.41 | 84 | <i>b</i> | 0.66 |
| | | | 53.04 | 7.35 | 4.40 | | | |
| <i>VIa</i> | $C_{14}H_{21}NO_6$ | 299.33 | 56.18 | 7.07 | 4.68 | 93 | <i>b</i> | 0.80 |
| | | | 56.14 | 7.09 | 4.69 | | | |
| <i>VIb</i> | $C_{14}H_{21}NO_6$ | 299.33 | 56.18 | 7.07 | 4.68 | 88 | <i>b</i> | 0.79 |
| | | | 56.23 | 7.05 | 4.65 | | | |
| <i>VIc</i> | $C_{14}H_{21}NO_6$ | 299.33 | 56.18 | 7.07 | 4.68 | 90 | 102–103 | 0.79 |
| | | | 56.20 | 7.10 | 4.66 | | | |
| <i>VIII</i> | $C_{15}H_{19}NO_5$ | 293.32 | 61.42 | 6.53 | 4.78 | 86 | 148–149 | 0.80 |
| | | | 61.38 | 6.55 | 4.77 | | | |
| <i>IX</i> | $C_{15}H_{17}NO_4$ | 275.31 | 65.44 | 6.22 | 5.09 | 89 | <i>b</i> | 0.83 |
| | | | 65.39 | 6.25 | 5.06 | | | |
| <i>XII</i> | $C_{12}H_{17}NO_5$ | 255.27 | 56.46 | 6.71 | 5.49 | 85 | 126–127 ^c | 0.82 |
| | | | 56.50 | 6.74 | 5.48 | | | |
| <i>XIV</i> | $C_{13}H_{19}NO_5$ | 269.30 | 57.98 | 7.11 | 5.20 | 91 | <i>b</i> | 0.81 |
| | | | 57.93 | 7.13 | 5.22 | | | |

a) Eluent A; b) colourless oil; c) Ref. [4] gives for *XII* m.p. = 89°C.

regard to the values of melting points and optical rotations.

Our attempts to prepare 6-cyano-6-deoxy-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (*XIV*) from corresponding 6-*O*-mesyl, 6-*O*-tosyl or 6-deoxy-6-iodo derivatives and sodium or potassium cyanide were unsuccessful regardless of the solvent and reaction temperature used. Such difficulty in displacement at C-6 position in the *galacto* system is understandable in terms of the stereoelectronic effects [5, 6]. Considering two most heavily populated conformers arising from the rotation around the C-5, C-6 bond in the 6-*O*-tosylate, the nucleophile is repulsed either by the oxygen atom attached to C-4 or the nucleophile must follow a path which causes its interaction with the ring oxygen atom. Both stereoelectronic interactions in each case disable substitution. Starting from corresponding 6-triflate derivative *XIII*, displacement reaction with sodium cyanide afforded required nitrile *XIV* in high yields upon the conditions that dry *N,N*-dimethylformamide was used as a solvent. If acetone was used, no nitrile *XIV* was isolated. The use of well dried sodium cyanide is also crucial. It is to be noted that there is a mention in the literature [7] about preparation of compound *XIV* (in 57 % yield) by the reaction of corresponding 6-phosphite derivative with methyl thiocyanate. But regarding the characterization of *XIV*, only elemental analysis and R_f value was given.

Some characteristics of the prepared compounds are summarized in Table 1. The NMR spectral data

are shown in Tables 2 and 3. Mass spectral data of selected compounds are given in Experimental. Owing to an instability of aldehydes *IV*, *VII*, and *XI*, these were converted into corresponding oximes immediately after their isolation and these oximes were fully characterized.

EXPERIMENTAL

Starting 1,2:5,6-di-*O*-isopropylidene- α -D-glucopyranose (*Ia*), 2,3:5,6-di-*O*-isopropylidene-D-mannopyranose (*Ib*), and 1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (*Ic*) were prepared according to the known procedure [8]. *O*-Epoxypropyl derivatives *Iia* and *Iib* were obtained by the same method as described for *Iic* [3] although there is an alternative procedure for the preparation of *Iia* [9]. Preparation of following compounds has been described: 3-*O*-benzyl-1,2-*O*-isopropylidene- α -D-xylo-pentodialdo-1,4-furanose (*VII*) [10, 11]; 1,2:3,4-di-*O*-isopropylidene- α -D-*galacto*-hexodialdo-1,5-pyranose (*X*) [12–15] and its oxime *XI* [14, 15]; 1,2:3,4-di-*O*-isopropylidene-6-*O*-trifluoromethylsulfonyl- α -D-galactopyranose (*XIII*) [16, 17]. The other used chemicals were commercially available products (Merck, Aldrich, Fluka).

Melting points were determined with a Boetius PHMK 05 microscope. 1H and ^{13}C NMR spectra (in $CDCl_3$, internal standard Me_4Si) were measured with a Bruker AM-300 spectrometer operating at 300.13 MHz and 75.46 MHz working frequencies, respectively. For the assignment of signals in ^{13}C NMR spectra,

Table 2. ¹H NMR Spectral Data of the Prepared Compounds

| Compound | Chemical shifts, δ | | | | | | | | | | | |
|-------------------------|---------------------------|-----------|-----------|-----------|------------|------------|-------------|-------------------|-------------------|------------------|--------------------------------|------------------------------|
| | H-1 | H-2 | H-3 | H-4 | H-5 | H-6a | H-6b | H-7a ^a | H-7b ^a | H-8 ^a | CH ₃ | CH ₂ ^b |
| <i>IVc</i> | 5.54 d | 4.33 dd | 4.67 dd | 4.26 dd | 4.04 ddd | 3.82 dd | 3.68 dd | 3.60 dd | 3.48 dd | 9.74 dd | 1.55 s, 1.44 s, 1.34 s, 1.33 s | |
| <i>Vb</i> | 5.03 s | 4.62 d | 4.80 dd | 3.98 dd | 4.07 ddd | 4.19 dd | 4.11 dd | 4.42 d | 4.42 d | 7.45 t | 1.45 s, 1.38 s, 1.33 s, 1.32 s | |
| <i>Vb^c</i> | 5.01 s | 4.60 d | 4.78 dd | 3.98 dd | 4.07 ddd | 4.19 dd | 4.11 dd | 4.38 d | 4.38 d | 6.84 t | 1.45 s, 1.38 s, 1.33 s, 1.32 s | |
| <i>Vc</i> | 5.48 d | 4.27 dd | 4.56 dd | 4.20 dd | 3.92 ddd | 3.60 dd | 3.56 dd | 4.33 d | 4.33 d | 7.42 t | 1.50 s, 1.39 s, 1.30 s, 1.29 s | |
| <i>Vc^c</i> | 5.47 d | 4.26 dd | 4.53 dd | 4.17 dd | 3.89 ddd | 3.60 dd | 3.56 dd | 4.08 d | 4.08 d | 6.85 t | 1.50 s, 1.39 s, 1.30 s, 1.29 s | |
| <i>VIa</i> | 5.77 d | 4.56 d | 4.02 d | 4.05 dd | 4.12 dd | 3.99 dd | 3.91 dd | 4.36 s | 4.36 s | | 1.43 s, 1.35 s, 1.28 s, 1.25 s | |
| <i>VIb</i> | 5.04 s | 4.56 d | 4.73 dd | 3.92 dd | 4.02 ddd | 4.33 dd | 4.00 dd | 4.21 ABq | 4.21 ABq | | 1.39 s, 1.37 s, 1.30 s, 1.26 s | |
| <i>VIc</i> | 5.54 d | 4.33 dd | 4.62 dd | 4.22 dd | 3.99 ddd | 3.82 dd | 3.73 dd | 4.34 ABq | 4.34 ABq | | 1.54 s, 1.45 s, 1.34 s, 1.34 s | |
| <i>VIII</i> | 5.99 d | 4.65 d | 4.37 d | 4.75 dd | 7.73 d | | | | | | 1.49 s, 1.32 s | 4.58 ABq |
| <i>VIII^c</i> | 5.99 d | 4.61 d | 4.03 d | 5.23 dd | 6.97 d | | | | | | 1.49 s, 1.32 s | 4.60 ABq |
| <i>IX</i> | 5.90 d | 4.52 d | 4.08 d | 4.76 d | | | | | | | 1.37 s, 1.22 s | |
| <i>XIV</i> | 5.50 d | 4.34 dd | 4.66 dd | 4.23 dd | 4.05 dt | 2.67 d | 2.67 d | | | | 1.54 s, 1.45 s, 1.35 s, 1.34 s | |
| Coupling constants/Hz | | | | | | | | | | | | |
| | $J_{1,2}$ | $J_{2,3}$ | $J_{3,4}$ | $J_{4,5}$ | $J_{5,6a}$ | $J_{5,6b}$ | $J_{6a,6b}$ | $J_{7a,8}$ | $J_{7b,8}$ | $J_{7a,7b}$ | $J_{CH_2}^b$ | |
| <i>IVc</i> | 5.0 | 2.4 | 7.9 | 1.9 | 5.9 | 6.9 | 10.6 | 8.8 | 7.0 | 14.0 | | – |
| <i>Vb</i> | 0 | 5.9 | 3.6 | 7.4 | 5.9 | 8.7 | 12.1 | 5.5 | 5.5 | 0 | | – |
| <i>Vb^c</i> | 0 | 5.9 | 3.6 | 7.4 | 5.9 | 8.7 | 12.1 | 3.7 | 3.7 | 0 | | – |
| <i>Vc</i> | 5.0 | 2.6 | 7.9 | 1.9 | 5.4 | 7.0 | 10.2 | 5.6 | 5.6 | 0 | | – |
| <i>Vc^c</i> | 5.0 | 2.6 | 7.9 | 1.9 | 5.4 | 7.0 | 10.2 | 3.6 | 3.6 | 0 | | – |
| <i>VIa</i> | 3.7 | 0 | 3.2 | 5.6 | 6.0 | 4.8 | 8.7 | – | – | 0 | | – |
| <i>VIb</i> | 0 | 5.9 | 3.5 | 7.5 | 5.7 | 8.8 | 12.5 | – | – | 16.2 | | – |
| <i>VIc</i> | 5.0 | 2.5 | 7.9 | 2.0 | 4.3 | 7.5 | 10.3 | – | – | 16.1 | | – |
| <i>VIII</i> | 3.7 | 0 | 3.4 | 7.4 | – | – | – | – | – | – | | 12.0 |
| <i>VIII^c</i> | 3.7 | 0 | 3.4 | 3.9 | – | – | – | – | – | – | | 12.0 |
| <i>IX</i> | 3.5 | 0 | 3.3 | – | – | – | – | – | – | – | | 0 |
| <i>XIV</i> | 5.0 | 2.5 | 7.8 | 1.9 | 7.1 | 7.1 | 0 | – | – | – | | – |

a) Positions 7 and 8 represent CH₂ and CH in OCH₂CHO, OCH₂CHNOH, and OCH₂CN grouping; b) benzylic methylene; c) isomeric oxime.

Table 3. ^{13}C NMR Spectral Data of the Prepared Compounds

| Compound | Chemical shifts, δ | | | | | | | | | | |
|------------------------|---------------------------|------|------|------|------|------|------------------|-------|-------|------------------------|--------------------|
| | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 ^a | —CH= | CN | CH ₃ | Other ^b |
| <i>IVc</i> | 96.2 | 70.6 | 70.3 | 71.0 | 67.2 | 70.9 | 76.9 | 201.1 | — | 26.0, 25.9, 24.8, 24.4 | 109.3, 108.6 |
| <i>Vb</i> | 106.6 | 80.4 | 79.3 | 84.9 | 73.0 | 66.7 | 64.0 | 147.5 | — | 26.8, 25.8, 25.1, 24.5 | 112.7, 109.2 |
| <i>Vb^c</i> | 106.1 | 80.4 | 79.3 | 84.9 | 73.0 | 66.7 | 61.4 | 150.0 | — | 26.8, 25.8, 25.1, 24.5 | 112.7, 109.2 |
| <i>Vc</i> | 96.2 | 70.5 | 70.3 | 71.0 | 67.9 | 69.9 | 65.8 | 151.0 | — | 25.9, 25.8, 24.8, 24.4 | 109.3, 108.6 |
| <i>Vc^c</i> | 96.2 | 70.5 | 70.3 | 71.0 | 66.7 | 69.3 | 65.3 | 148.1 | — | 25.9, 25.8, 24.8, 24.4 | 109.3, 108.6 |
| <i>VIa</i> | 104.9 | 83.2 | 82.4 | 80.6 | 72.1 | 67.2 | 55.9 | — | 115.6 | 26.6, 26.5, 25.9, 25.0 | 111.9, 109.1 |
| <i>VIb</i> | 106.1 | 81.0 | 79.0 | 84.4 | 72.5 | 66.3 | 51.6 | — | 115.6 | 26.4, 25.5, 24.8, 24.2 | 112.6, 108.9 |
| <i>VIc</i> | 96.2 | 70.4 | 70.3 | 71.0 | 67.0 | 70.6 | 56.6 | — | 115.9 | 26.0, 25.9, 24.9, 24.4 | 109.5, 108.7 |
| <i>VIII</i> | 105.3 | 82.6 | 83.6 | 77.9 | — | — | — | 149.8 | — | 26.9, 26.3 | 112.1 |
| <i>VII^f</i> | 104.9 | 82.4 | 82.9 | 75.6 | — | — | — | 148.0 | — | 26.9, 26.3 | 112.1 |
| <i>IX</i> | 105.5 | 81.4 | 81.9 | 69.3 | — | — | — | — | 114.7 | 26.9, 26.0 | 113.0 |
| <i>XII</i> | 96.1 | 70.3 | 69.9 | 70.9 | 60.1 | — | — | — | 115.1 | 26.0, 25.9, 24.6, 24.5 | 111.0, 109.6 |
| <i>XIV</i> | 96.1 | 70.5 | 69.9 | 70.9 | 64.1 | 19.1 | — | — | 116.9 | 25.8, 25.6, 24.8, 24.2 | 109.5, 108.7 |

a) Position 7 represents OCH_2 in OCH_2CHO , OCH_2CHNOH , and OCH_2CN grouping; b) isopropylidene acetal carbon atom; benzylic methylene carbon atom was observed at $\delta = 72.6$; c) isomeric oxime.

DEPT and semiselective INEPT techniques [18] were used. The EI mass spectra (70 eV) were recorded on a Finigan MAT SSQ 710 spectrometer, applying the direct sample-introduction technique. Specific optical rotations were measured with a Perkin—Elmer 141 polarimeter (10 cm cell). Elemental analyses were performed on a Perkin—Elmer 240 analyzer. All reactions were monitored by TLC on silica gel 60 F₂₅₄ (Merck) plates using ethyl acetate—hexane ($\varphi_r = 3:2$ (A) or $\varphi_r = 1:1$ (B)) as an eluent. Visualization was effected with sulfuric acid, iodine vapour, or UV₂₅₄ light. Column chromatography was performed as flash chromatography on silica gel 60 (Merck, “230—400 mesh”) with the same eluents.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-hydroximinomethyl- α -D-glucofuranose (Va), Hydroximinomethyl 2,3:5,6-Di-*O*-isopropylidene- α -D-mannofuranoside (Vb), and 1,2:3,4-Di-*O*-isopropylidene-6-*O*-hydroximinomethyl- α -D-galactopyranose (Vc)

To oxirane *II* (5.4 g; 17.1 mmol) in dioxane (200 cm³), 0.5 M solution of NaOH in water (200 cm³) was added and the reaction mixture was stirred at 50 °C for 12 h. Then it was diluted with water (1 dm³) and neutralized with Amberlite IR-120 (H⁺). After filtration, the solvents were evaporated to dryness at diminished pressure. Resulting crude product was purified on a column of silica gel (eluent A) giving pure diol *III* (for *IIIa—IIIc*: colourless thick sirup; $R_f = 0.19$, A; ca. 82 % yield; satisfactory elemental analysis).

A cold solution of sodium periodate (4.28 g; 24 mmol) in water (50 cm³) was added dropwise in the course of 1 h to a well stirred solution of diol *III* (6.7 g; 20 mmol) in methanol (40 cm³) cooled to 0 °C. Reaction mixture was stirred for additional 1 h at room temperature and then methanol was evaporated under reduced pressure to give crude aldehyde *IV* (for *IVa—IVc*: colourless oil; $R_f = 0.55$, A; ca. 92 % yield).

For *IVc*: EI mass spectrum, $m/z(I_r/\%)$: 287 (70, [M - CH₃]⁺), 259 (38, [M - CH₃ - CO]⁺), 169 (22), 113 (37), 100 (58), 81 (100), 59 (44), 43 (93, [CH₃CO]⁺).

To a solution of aldehyde *IV* (4.0 g; 13.2 mmol) in methanol (40 cm³), a solution of hydroxylammonium chloride (1.12 g; 16.1 mmol) in water (8 cm³) and pyridine (8 cm³) was added and the mixture was stirred at 25 °C for 18 h. The solvents were evaporated under reduced pressure, resulting sirup was dissolved in benzene (250 cm³) and washed with water, 10 % H₂SO₄, 5 % NaHCO₃, and water. Organic layer was dried over Na₂SO₄, filtered and benzene evaporated under diminished pressure affording oxime *V* as a mixture of *E* and *Z* isomers.

For *Vb*: EI mass spectrum, $m/z(I_r/\%)$: 284 (79, [M - CH₃ - H₂O]⁺), 243 (30, [M - OCH₂CHNOH]⁺), 226 (17, [M - CH₃ - H₂O - Me₂CO]⁺), 101 (91,

[Me₂COOCH₂CH]⁺), 43 (100, [CH₃CO]⁺).

For *Vc*: EI mass spectrum, $m/z(I_r/\%)$: 284 (100, [M - CH₃ - H₂O]⁺), 226 (12, [M - CH₃ - H₂O - Me₂CO]⁺), 166 (32, [M - CH₃ - H₂O - Me₂CO - CH₃COOH]⁺), 138 (19), 100 (38), 81 (52), 59 (29), 43 (86, [CH₃CO]⁺).

3-*O*-Benzyl-1,2-*O*-isopropylidene- α -D-xylo-pentodialdo-1,4-furanose Oxime (VIII)

Starting from aldehyde *VII* and hydroxylammonium chloride, the same reaction procedure as reported for compounds *V* was used.

3-*O*-Cyanomethyl-1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose (VIa)

Into boiling acetic anhydride (40 cm³), oxime *Va* (5.8 g; 18.3 mmol) dissolved in acetic anhydride (20 cm³) was added and the reaction mixture was heated under reflux for 0.5 h. Evaporation of anhydride under reduced pressure afforded crude product which was purified on a column of silica gel using eluent B. $[\alpha](D, 20^\circ C, \rho = 10 \text{ g dm}^{-3}, \text{CH}_3\text{OH}) = -17^\circ C$. EI mass spectrum, $m/z(I_r/\%)$: 284 (9, [M - CH₃]⁺), 226 (14, [M - CH₃ - Me₂CO]⁺), 101 (100, [Me₂COOCH₂CH]⁺), 59 (23), 43 (100, [CH₃CO]⁺).

Cyanomethyl-2,3:5,6-di-*O*-isopropylidene- α -D-mannofuranoside (VIb), 6-*O*-Cyanomethyl-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (VIc), 3-*O*-Benzyl-1,2-*O*-isopropylidene- α -D-xylofuranurononitrile (IX), and 1,2:3,4-Di-*O*-isopropylidene- α -D-galactopyranurononitrile (XII)

Starting from corresponding oximes, these compounds were prepared by the same method as described for *VIa*.

For *VIb*: $[\alpha](D, 20^\circ C, \rho = 10 \text{ g dm}^{-3}, \text{CH}_3\text{OH}) = +68^\circ$.

For *VIc*: $[\alpha](D, 20^\circ C, \rho = 10 \text{ g dm}^{-3}, \text{CH}_3\text{OH}) = -68^\circ$.

For *IX*: $[\alpha](D, 20^\circ C, \rho = 10 \text{ g dm}^{-3}, \text{CH}_3\text{OH}) = -10^\circ$. EI mass spectrum, $m/z(I_r/\%)$: 275 (12, [M]⁺), 260 (11, [M - CH₃]⁺), 147 (25), 107 (24), 91 (100, [PhCH₂]⁺), 43 (48).

For *XII*: $[\alpha](D, 20^\circ C, \rho = 10 \text{ g dm}^{-3}, \text{CH}_3\text{OH}) = -104^\circ$. EI mass spectrum, $m/z(I_r/\%)$: 240 (100, [M - CH₃]⁺), 182 (64, [M - CH₃ - Me₂CO]⁺), 113 (47), 100 (17), 59 (25), 43 (94).

6-Cyano-6-deoxy-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (XIV)

Dry sodium cyanide (1.47 g; 0.03 mol) was added into a solution of triflate *XIII* (3.92 g; 0.01 mol) in dry *N,N*-dimethylformamide (30 cm³) and the mix-

ture was stirred at room temperature for 5 h. Then the solution was poured onto crushed ice (300 cm³) and the product was extracted with chloroform (4 × 40 cm³). Organic layer was dried (Na₂SO₄), filtered and solvents were evaporated under diminished pressure to give crude product. Decolourizing (with charcoal) in ether and evaporation of solvent afforded pure nitrile XIV as a colourless oil, [α]_D(20°C, ρ = 10 g dm⁻³, CH₃OH) = -53°. EI mass spectrum, *m/z*(*I_r*/%) : 254 (47, [M - CH₃]⁺), 196 (22, [M - CH₃ - Me₂CO]⁺), 136 (38, [M - CH₃ - Me₂CO - CH₃COOH]⁺), 108 (67, [M - CH₃ - Me₂CO - CH₃COOH - CO]⁺), 100 (40), 85 (35), 56 (50), 43 (100, [CH₃CO]⁺).

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