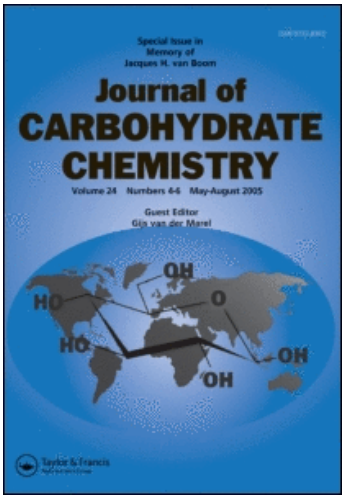

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SYNTHESIS OF PUSH-PULL BUTADIENES ON THE BASIS OF HEXOSE DERIVATIVES ☆

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ABSTRACT

3-*O*-Protected 6-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-uloses **2**, **4**, and **10** reacted with malononitrile to furnish the Knoevenagel compounds **5**, **6**, and **11**. Treatment of **5** and **6** with carbon disulphide and methyl iodide in the presence of sodium hydride afforded the sugar push-pull butadienes **7** and **8**.

INTRODUCTION

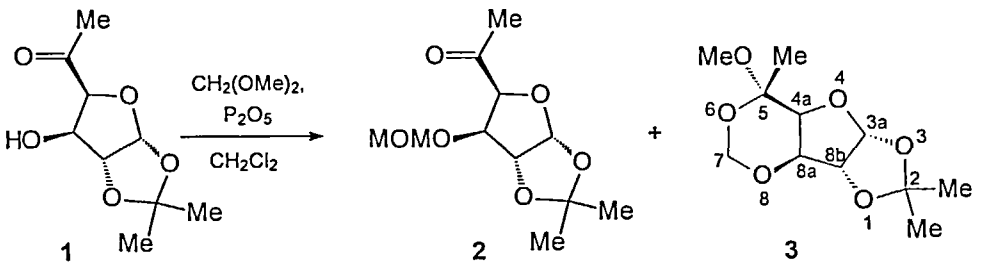
Carbohydrates with an integrated push-pull alkene have been obtained at first by chain elongation of deoxynitroaldoses with carbon disulphide, methyl iodide and sodium hydride.[1,2] On the other hand, the reaction of carbanions generated from sugar deoxyuloses with carbon disulphide afforded branched chain ulose derivatives with push-pull functionality.[2,3] We describe herein the first synthesis of furanosyl substituted push-pull butadiene starting from derivatives of 6-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose (**1**). Earlier studies have shown that aryl substituted 2-cyano-5,5-bis(methylthio)-2,4-pentadienenitriles can be converted into substituted nicotinonitriles.[5,6]

☆Dedicated to Professor Dr. Ing. *Vollrath Hopp* on the occasion of his 70th birthday.

This type of reaction transferred to furanosyl push-pull butadienes could offer a new way for the synthesis of unusual C-nucleoside analogues.

RESULTS AND DISCUSSION

6-Deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose (**1**) was synthesized by a procedure described by Ohle starting from D-glucose.[7-11] The introduction of the *O*-methoxymethyl group was performed under acid conditions using formaldehyde dimethyl acetal to give the completely protected ulose **2**.[12] We also isolated, besides **2**, compound **3** which was formed *via* reacetalization of **2** (Scheme 1). Although the molecular weights of **2** and **3** are the same and their NMR spectra looked similar, there is no carbonyl absorbance in the IR spectrum of **3**. Compound **3** was obtained only as the (5*S*) isomer, as proved by NOE measurement. To avoid the progress of reacetalization the reaction time should not be longer than 30 minutes.

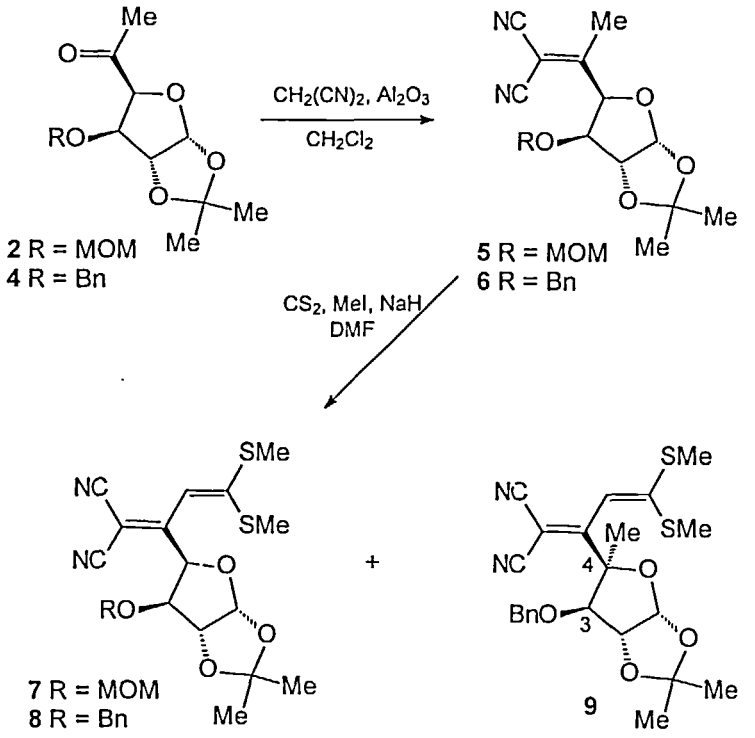


Scheme 1

The 3-*O*-benzylated ulose **4** was synthesized from D-glucose following described procedures.[13-17] Both uloses **2** and **4** were treated with malononitrile to give the Knoevenagel compounds **5** and **6**. These reactions were performed by using basic aluminium oxide[18] in dichloromethane at room temperature (Scheme 2).

In order to prepare furanosyl substituted push-pull butadienes, compounds **5** and **6** were reacted with carbon disulphide and methyl iodide in the presence of sodium

hydride in dimethylformamide to give 6-cyano-5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-methoxymethyl (benzyl)-5-[2,2-bis(methylthio)vinyl]-α-D-*xylo*-hept-5-enofuranuron-onitrile (7) and (8), respectively, as yellow crystals in 24% and 32% yield.

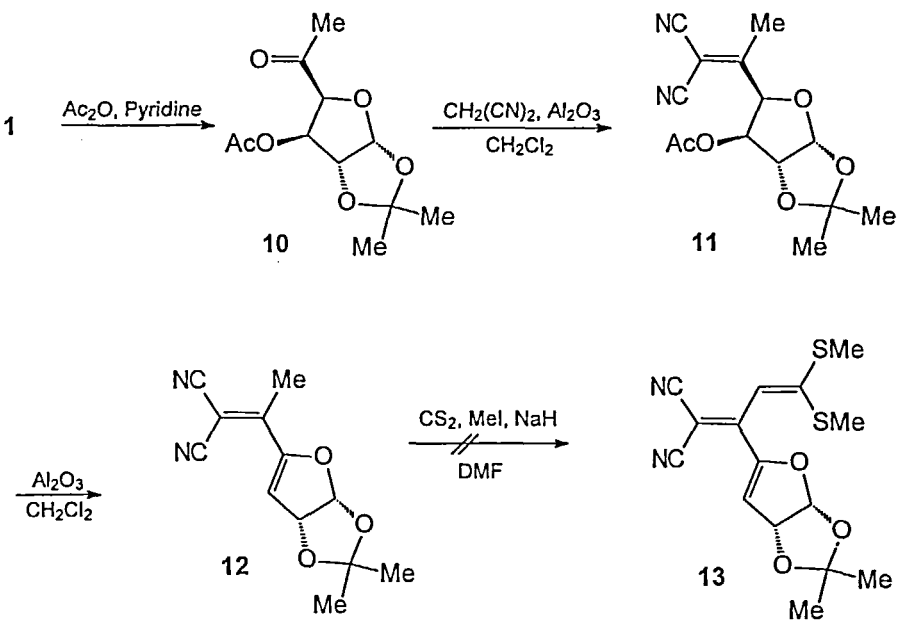


Scheme 2

The formation of different side products is the reason for these moderate yields. The first one results from further methylation of the furanoside moiety. In the reaction of Knoevenagel compound **6** to give the push-pull butadiene **8**, compound **9** was formed as well and could be isolated in a yield of 11%. NOE-measurements indicated the (4*S*) configuration for **9**, meaning that the 4-methyl group is placed on the same side as the 4-H in compound **8**.

The second side reaction is represented by the β-elimination of the substituent at position 3 to form a double bond between C-3 and C-4 of the furanose ring. It occurred

not only in the reaction to furnish the butadiene but also in the Knoevenagel reaction. Therefore, we investigated the synthesis of corresponding unsaturated derivatives to get the cross coupled butadiene derivative **13**. The best and easiest way to prepare the unsaturated compound **12** was to start with the acetylated ulose **10** which was obtained by acetylation of compound **1** using acetic anhydride in pyridine. The Knoevenagel reaction was performed under the same conditions as described for compounds **5** and **6** to yield the enofuranurononitrile **11**. The elimination of acetic acid could be realized by treatment of **11** with basic aluminium oxide to afford the compound **12** (Scheme 3). However, the acidity of this dienofuranurononitrile **12** in comparison with compounds **5** and **6** is lower. Therefore, treatment of **12** with carbon disulphide under the same conditions as described for the synthesis of the butadienes **7** and **8** to furnish the compound **13** failed.



Scheme 3

EXPERIMENTAL

General procedures. Melting points were determined with a Boëtius apparatus

and are corrected. Specific rotations were determined with a Polar LμP polarimeter. IR spectra were recorded with a Nicolet 205 FT-IR spectrometer. ^{1}H NMR (250.13 MHz) and ^{13}C NMR (75.47 and 62.90 MHz, respectively) spectra were recorded on Bruker instruments ARX 300 and AC 250, respectively, with $CDCl_3$ as solvent. The calibration of spectra was carried out by means of solvent peaks ($CDCl_3$: δ ^{1}H= 7.25; δ ^{13}C= 77.0). The ^{13}C NMR signals were assigned by DEPT and/or ^{1}H,^{13}C COSY experiments. The mass spectra were recorded on an AMD 402/3 spectrometer (AMD Intectra GmbH). For chromatography Merck silica gel 60 (230-400 mesh) was used. TLC was performed on silica gel 60 GF_{254} (Merck) with detection by using UV-light and charring with sulfuric acid. Elemental analyses were performed on a Leco CHNS-932 instrument.

6-Deoxy-1,2-*O*-isopropylidene-3-*O*-methoxymethyl-α-D-*xylo*-hexofuranos-5-ulose (2) and **3a*R*-(4aβ,5β,8aβ,8bα)-4a,5,8a,8b-tetrahydro-2,2,5-trimethyl-3a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-d][1,3]dioxin-5-ylmethyl ether (3)**. A solution of 6-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose (**1**, 1.0 g, 4.95 mmol) and formaldehyde dimethyl acetal (30 mL) in dichloromethane (30 mL) was cooled to 0 °C. Then tetraphosphorus decaoxide (3.6 g) was added, and the suspension was stirred vigorously at 0 °C for 30 min and then filtered. The filtrate was poured into cold saturated $NaHCO_3$ solution (250 mL) and extracted three times with dichloromethane (50 mL). The organic layers were combined and washed again with saturated $NaHCO_3$ solution and water, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (toluene/ethyl acetate 7:1) to yield a colourless oil of **2** (0.74 g, 61%); R_f = 0.23 (toluene/ethyl acetate 7:1); $[\alpha]_D^{24}$ -68.1° (*c* 1.0, chloroform); IR (capillary) 1720 (CO); ^{1}H NMR: δ = 6.04 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.61 (d, 1H, $J_{CH(a),CH(b)}$ = 6.7 Hz, CH_2(a)), 4.61 (d, 1H, $J_{3,4}$ = 3.7 Hz, H-4), 4.56 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 4.53 (d, 1H, CH_2(b)), 4.40 (d, 1H, H-3), 3.29 (s, 3H, OCH_3), 2.23 (s, 3H, CH_3), 1.45, 1.30 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR (62.9 MHz): δ = 206.6 (CO), 112.4 ($C(CH_3)_2$), 105.8 (C-1), 96.0 (CH_2), 85.2 (C-4), 82.6 (C-2), 81.5 (C-3), 55.9 (OCH_3), 28.2 (CH_3), 26.9, 26.3 ($C(CH_3)_2$). Mass spectrum, EI (*m/z*): 246 ([M]$^+$).

Anal. Calcd for $C_{11}H_{18}O_6$ (246.3): C, 53.65; H, 7.37. Found: C, 51.09; H, 7.25.

3 was isolated as colourless crystals (0.35 g, 29%): mp 44 °C; R_f = 0.41 (toluene/ethyl acetate 7:1); $[\alpha]_D^{22}$: +109.5 (*c* 1.0, chloroform); ^{1}H NMR: δ = 5.97 (d, 1H, $J_{3a,8b}$ = 3.7 Hz, H-3a), 4.85 (d, 1H, $J_{7a,7b}$ = 6.1 Hz, H-7a), 4.65 (d, 1H, H-7b), 4.48 (d, 1H, $J_{8a,8b}$ = 0

Hz, H-8b), 4.27 (d, 1H, $J_{4a,8a}$ = 2.0 Hz, H-8a), 3.76 (d, 1H, H-4a), 3.26 (s, 3H, OCH_3), 1.43 (s, 3H, CH_3), 1.46, 1.30 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR (62.9 MHz): δ = 111.6 (C-2), 105.2 (C-3a), 97.3 (C-5), 84.6 (C-7), 83.3 (C-8b), 76.5 (C-8a), 76.5 (C-4a), 47.8 (OCH_3), 26.6, 26.2 ($C(CH_3)_2$), 19.4 (CH_3); Mass spectrum, CI (*m/z*): 247 $[M+H]^+$.

Anal. Calcd for $C_{11}H_{18}O_6$ (246.3): C, 53.65; H, 7.37. Found: C, 53.43; H, 7.43.

***6*-Cyano-5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-methoxymethyl-5-methyl-α-D-*xylo*-hept-5-enofuranurononitrile (5).** Aluminium oxide (3 g, type T, Merck) was added to a mixture of **2** (0.3 g, 1.2 mmol) and malononitrile (0.18 g, 2.6 mmol) in dichloromethane (20 mL). The suspension was stirred for 1 h at room temperature and then filtered through Celite. The filtrate was concentrated and the residue was purified by column chromatography (toluene/ethyl acetate 7:1) to yield **2** as a colourless oil (0.11 g, 32%); R_f = 0.43 (toluene/ethyl acetate 6:1); $[\alpha]_D^{22}$: -130.3 (*c* 1.0, chloroform); IR (capillary) 2234 (CN); ^1H NMR: δ = 6.03 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.20 (d, 1H, $J_{3,4}$ = 3.7 Hz, H-4), 4.66 (d, 1H, $J_{CH(a),CH(b)}$ = 6.9 Hz, CH_2(a)), 4.63 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 4.49 (d, 1H, CH_2(b)), 4.49 (d, 1H, H-3), 3.33 (s, 3H, OCH_3), 2.23 (s, 3H, CH_3), 1.50, 1.33 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR (62.9 MHz): δ = 178.3 (C-5), 112.9 ($C(CH_3)_2$), 111.4, 110.6 (2 CN), 105.5 (C-1), 96.3 (CH_2), 85.4 (C-6), 82.8 (C-2), 82.3 (C-3), 81.2 (C-4), 56.1 (OCH_3), 26.9, 26.3 ($C(CH_3)_2$), 21.0 (CH_3). Mass spectrum, EI (*m/z*): 294 $[M]^+$.

Anal. Calcd for $C_{14}H_{18}N_2O_5$ (294.3): C, 57.14; H, 6.16; N, 9.25. Found: C, 56.99; H, 6.16; N, 9.35.

3-*O*-Benzyl-6-cyano-5,6-dideoxy-1,2-*O*-isopropylidene-5-methyl-α-D-*xylo*-hept-5-enofuranurononitrile (6). Aluminium oxide (3 g, type T, Merck) was added to a mixture of **4** (1.0 g, 3.4 mmol) and malononitrile (0.3 g, 4.4 mmol) in dichloromethane (75 mL). The suspension was stirred for 2 h at room temperature and then filtered through Celite. The filtrate was concentrated and the residue was purified by column chromatography (toluene/ethyl acetate 14:1) to yield **2** as a colourless syrup (0.71 g, 59%); R_f = 0.47 (toluene/ethyl acetate 7:1); $[\alpha]_D^{23}$: -144.3 (*c* 1.0, chloroform); IR (capillary) 2234 (CN); ^1H NMR: δ = 7.40-7.10 (m, 5H, Ph), 6.05 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.11 (d, 1H, $J_{3,4}$ = 4.0 Hz, H-4), 4.66 (d, 1H, $J_{CH(a),CH(b)}$ = 12.1 Hz, CH_2(a)), 4.63 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 4.37 (d, 1H, CH_2(b)), 4.29 (d, 1H, H-3), 2.26 (s, 3H, CH_3), 1.48, 1.33 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR (75.5 MHz): δ = 178.8 (C-5), 136.1 (i-

Ph), 128.9, 128.1 (o-, m-Ph), 128.7 (p-Ph), 112.9 ($C(CH_3)_2$), 111.4, 110.4 (2 CN), 105.6 (C-1), 85.1 (C-6), 83.2 (C-3), 82.2 (C-2), 81.3 (C-4), 72.6 (CH_2), 26.9, 26.3 ($C(CH_3)_2$), 21.0 (CH_3). Mass spectrum, EI (*m/z*): 340 $[M]^+$.

Anal. Calcd for $C_{19}H_{20}N_2O_4$ (340.4): C, 67.05; H, 5.92; N, 8.23. Found: C, 66.85; H, 5.86; N, 8.12.

6-Cyano-5,6-dideoxy-1,2-*O*-isopropylidene-3- *O*- methoxymethyl-5- [2,2-bis-(methylthio)vinyl]-α-D-*xylo*-hept-5-enofuranurononitrile (7). Sodium hydride (60%, 0.1 g, 2.2 mmol) was stirred 10 min in heptane (1 mL). The solvent was decanted after the sodium hydride had settled. Then toluene (1 mL) was added and stirring continued for another 5 min. A solution of **5** (0.3 g, 1.02 mmol), carbon disulphide (0.12 mL, 2.0 mmol) and methyl iodide (0.4 mL, 6.4 mmol) in dimethylformamide (6 mL) was added. The mixture was stirred for 40 min, then poured into ice water and extracted with chloroform. The combined organic layers were washed with water, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (toluene/ethyl acetate 10:1). Recrystallization from ethanol/water yielded **5** as yellow crystals (0.1 g, 24%): mp 73-75 °C; R_f = 0.29 (toluene/ethyl acetate 7:1); $[\alpha]_D^{23}$: -75.4 (*c* 1.0, chloroform); IR (KBr) 2217, 2211 (2 CN); ^{1}H NMR: δ= 6.30 (s, 1H, H-1'), 6.07 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 5.79 (d, 1H, $J_{3,4}$ = 3.7 Hz, H-4), 4.67 (d, 1H, $J_{CH(a),CH(b)}$ = 6.9 Hz, CH_2(a)), 4.67 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 4.57 (d, 1H, CH_2(b)), 4.56 (d, 1H, H-3), 3.34 (s, 3H, OCH_3), 2.57, 2.48 (2s, 6H, 2 SCH_3), 1.51, 1.35 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR (62.9 MHz): δ = 165.4 (C-2'), 157.9 (C-5), 116.6 (C-1'), 113.9, 112.9 (2 CN), 112.8 ($C(CH_3)_2$), 105.4 (C-1), 96.3 (CH_2), 83.5 (C-2), 82.2 (C-6), 81.7 (C-3), 80.1 (C-4), 56.0 (OCH_3), 27.1, 26.4 ($C(CH_3)_2$), 17.7, 17.2 (2 SCH_3). Mass spectrum, EI (*m/z*): 398 $[M]^+$.

Anal. Calcd for $C_{17}H_{22}N_2O_5S_2$ (398.5): C, 51.24; H, 5.56; N, 7.03; S, 16.06. Found: C, 51.30; H, 5.74; N, 7.05; S, 15.90.

3-*O*-Benzyl-6-cyano-5,6-dideoxy-1,2-*O*-isopropylidene-5- [2,2-bis(methylthio)vinyl]-α-D-*xylo*-hept-5-enofuranurononitrile (8) and 3-*O*-benzyl-6-cyano-5,6-dideoxy- 1,2-*O*- isopropylidene-4*C*- methyl-5- [2,2-bis(methylthio)vinyl]-α-D-*xylo*-hept-5-enofuranurononitrile (9). Sodium hydride (60%, 55 mg, 1.22 mmol) was stirred 10 min in heptane (2 mL). The solvent was decanted after the sodium hydride had settled. Then toluene (1 mL) was added and stirring continued for another 5 min. A solution of **6** (0.2 g, 0.61 mmol), carbon disulphide (0.08 mL, 1.3 mmol) and methyl

iodide (0.15 mL, 2.4 mmol) in dimethylformamide (12 mL) was added. The mixture was stirred for 40 min, then poured into ice water and extracted with chloroform. The combined organic layers were washed with water, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (toluene/ethyl acetate 20:1). Recrystallization from ethanol/water yielded **8** as yellow crystals (85 mg, 32%): mp 80-83 °C; R_f = 0.31 (toluene/ethyl acetate 7:1); $[\alpha]_D^{22}$: +30.6 (*c* 1.0, chloroform); IR (KBr) 2211 (CN); ^{1}H NMR: δ = 7.40-7.10 (m, 5H, Ph), 6.16 (s, 1H, H-1'), 6.05 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.67 (d, 1H, $J_{3,4}$ = 3.7 Hz, H-4), 4.66 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 4.66 (d, 1H, $J_{CH(a),CH(b)}$ = 12.0 Hz, CH_2(a)), 4.43 (d, 1H, CH_2(b)), 4.34 (d, 1H, H-3), 2.45, 2.37 (2s, 6H, 2 SCH_3), 1.49, 1.34 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR (75.5 MHz): δ = 166.0 (C-2'), 157.5 (C-5), 136.5 (*i*-Ph), 128.6, 128.0 (*o*-, *m*-Ph), 128.3 (*p*-Ph), 117.0 (C-1'), 113.8, 112.9 (2 CN), 112.8 ($C(CH_3)_2$), 105.5 (C-1), 83.1 (C-3), 82.8 (C-2), 82.0 (C-6), 80.4 (C-4), 72.6 (CH_2), 27.1, 26.5 ($C(CH_3)_2$), 17.7, 17.2 (2 SCH_3). Mass spectrum, EI (*m/z*): 444 $[M]^+$.

Anal. Calcd for $C_{22}H_{24}N_2O_4S_2$ (444.6): C, 59.44; H, 5.44; N, 6.30; S, 14.43. Found: C, 59.48; H, 5.21; N, 6.49; S, 14.34.

9 was isolated as a yellow syrup, (29 mg, 11%); R_f = 0.54 (toluene/ethyl acetate 7:1); ^{1}H NMR: δ = 7.40-7.30 (m, 5H, Ph), 6.27 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1), 5.93 (s, 1H, H-1'), 4.61 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 4.53 (m, 2H, CH_2), 4.47 (s, 1H, H-3), 2.38, 2.29 (2s, 6H, 2 SCH_3), 2.02 (s, 3H, CH_3), 1.53, 1.38 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR (62.5 MHz): δ = 155.7 (C-2'), 145.6 (C-5), 136.7 (*i*-Ph), 128.6, 127.9 (*o*-, *m*-Ph), 128.3 (*p*-Ph), 117.0 (C-1'), 115.6, 115.1 (2 CN), 115.1 ($C(CH_3)_2$), 108.3 (C-1), 102.7 (C-6), 82.0, 80.8 (C-2, C-3), 72.4 (CH_2), 33.2 (C-4), 27.9, 27.0 ($C(CH_3)_2$), 24.7 (CH_3), 16.8, 16.1 (2 SCH_3). Mass spectrum, CI (*m/z*): 459 $[M+H]^+$.

3-*O*-Acetyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose (10). To a solution of **1** (1.78 g, 8.8 mmol) in pyridine (20 mL) was added at 0 °C acetic anhydride (1.5 mL). The mixture was kept at room temperature for 24 h and then poured into ice water. After extraction with chloroform, the combined organic layers were washed with water, dilute hydrochloric acid, saturated $NaHCO_3$ solution and water again, dried (Na_2SO_4) and concentrated. Recrystallization from ether/pentane yielded **10** as colourless neeedles (1.86 g, 85%): mp 64-65 °C; R_f = 0.29 (toluene/ethyl acetate 4:1);

$[\alpha]_D^{22}$: -146.4 (*c* 1.0, chloroform); IR (KBr) 1733 (CO); ^{1}H NMR: δ= 6.02 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.43 (d, 1H, $J_{3,4}$ = 3.7 Hz, H-4), 4.71 (d, 1H, $J_{2,3}$ = 0 Hz, H-3), 4.52 (d, 1H, H-2), 2.23 (s, 3H, CH_3), 2.00 (s, 3H, CH_3COO), 1.49, 1.30 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR (62.9 MHz): δ = 204.2 (CO), 169.1 (CH_3COO), 112.6 ($C(CH_3)_2$), 105.3 (C-1), 83.7 (C-3), 82.8 (C-2), 77.3 (C-4), 27.7 (CH_3COO), 26.7, 26.1 ($C(CH_3)_2$), 20.5 (CH_3). Mass spectrum, EI (*m/z*): 229 $[M-CH_3]^+$.

Anal. Calcd for $C_{11}H_{16}O_6$ (244.2): C, 54.09; H, 6.60. Found: C, 53.95; H, 6.54.

3-*O*-Acetyl-6-cyano-5,6-dideoxy-1,2-*O*-isopropylidene-5-methyl- α-D-*xylo*-hept-5-enofuranurononitrile (11). Aluminium oxide (8 g, type T, Merck) was added to a mixture of **10** (3.0 g, 12.3 mmol) and malononitrile (0.9 g, 13.6 mmol) in dichloromethane (150 mL). The suspension was stirred for 1 h at room temperature and then filtered through Celite. The filtrate was concentrated. Recrystallization from ethanol yielded **11** as colourless crystals **11** (1.73 g, 48%): mp 113-115 °C; R_f = 0.36 (toluene/ethyl acetate 4:1); $[\alpha]_D^{22}$: -8.7 (*c* 1.0, chloroform); IR (KBr) 2237 (CN); ^{1}H NMR: δ= 6.06 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.48 (d, 1H, $J_{3,4}$ = 3.4 Hz, H-4), 5.17 (d, 1H, $J_{2,3}$ = 0 Hz, H-2), 4.60 (d, 1H, H-3), 2.29 (s, 3H, CH_3), 2.08 (s, 3H, CH_3COO), 1.52, 1.33 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR (62.9 MHz): δ = 174.4 (C-5), 168.9 (CH_3COO), 113.3 ($C(CH_3)_2$), 111.3, 110.4 (2 CN), 105.2 (C-1), 87.2 (C-6), 83.0 (C-2), 80.4 (C-4), 77.5 (C-3), 26.8, 26.2 ($C(CH_3)_2$), 20.8 (CH_3), 20.4 (CH_3COO). Mass spectrum, CI (*m/z*): 293 $[M+H]^+$.

Anal. Calcd for $C_{14}H_{16}NO_5$ (292.3): C, 57.33; H, 5.52; N, 9.58. Found: C, 57.58; H, 5.44; N, 9.53.

6-Cyano-3,5,6-trideoxy-1,2-*O*-isopropylidene-5-methyl- α-D-*glycero*-hepta-3,5-dienofuranurononitrile (12). Aluminium oxide (20 g, AI) was added to a mixture of **11** (1.14 g, 3.89 mmol) in dichloromethane (80 mL). The suspension was stirred for 30 min at room temperature, filtered through Celite and the filtrate was concentrated. Recrystallization from ether yielded **12** as colourless crystals (0.25 g, 28%): mp 111 °C; R_f = 0.44 (toluene/ethyl acetate 4:1); $[\alpha]_D^{23}$: -173.2 (*c* 1.0, chloroform); IR (KBr) 2232, 2220 (2 CN); ^{1}H NMR: δ= 6.18 (d, 1H, $J_{1,2}$ = 5.2 Hz, H-1), 6.08 (d, 1H, $J_{2,3}$ = 2.7 Hz, H-3), 5.38 (dd, 1H, H-2), 2.37 (s, 3H, CH_3), 1.45, 1.42 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR

(62.9 MHz): δ = 158.0, 154.3 (C-4, C-5), 113.4 ($C(CH_3)_2$), 112.3 (CN), 112.0 (C-3), 111.7 (CN), 106.4 (C-1), 86.0 (C-6), 82.5 (C-2), 28.1, 27.6 ($C(CH_3)_2$), 19.7 (CH_3). Mass spectrum, CI (*m/z*): 233 $[M+H]^+$.

Anal. Calcd for $C_{12}H_{12}N_2O_3$ (232.2): C, 62.06; H, 5.21; N, 12.06. Found: C, 62.22; H, 5.17; N, 11.97.

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REFERENCES

1. K. Peseke, H.-D. Ambrosi and M. Michalik, *Carbohydr. Res.*, **194**, 87 (1989).
2. P. Köll, S. Andreé, K. Peseke and J. Kopf, *Carbohydr. Res.*, **241**, 273 (1993).
3. K. Peseke, H. Feist and E. Cuny, *Carbohydr. Res.*, **230**, 319 (1992).
4. K. Peseke, G. Thiele and M. Michalik, *Liebigs Ann.*, 1633 (1995).
5. K. Peseke, M. Michalik and U. Schönhusen, *J. Prakt. Chem.*, **328**, 856 (1986).
6. M. Michalik, K. Peseke and R. Radeglia, *J. Prakt. Chem.*, **323**, 506 (1981).
7. E. Recondo and H. Rinderknecht, *Helv. Chim. Acta*, **43**, 1653 (1960).
8. R. L. Whistler and R. E. Gramera and A. Park, *J. Org. Chem.*, **28**, 3230 (1963).
9. H. Ohle and E. Dickhäuser, *Chem. Ber.*, **58**, 2593 (1925).
10. H. Ohle and L. von Vargha, *Chem. Ber.*, **61**,1208 (1928).
11. H. Ohle and R. Deplanque, *Chem. Ber.*, **66**, 12 (1933).
12. K. Fuji, *Synthesis*, 276 (1975).
13. K. M. Sun and B. Fraser-Reid, *Synthesis*, 28 (1982).
14. V. Salas-Reyes, *Z. Naturforsch.*, **50b**, 1537 (1995).
15. D. E. Kiely, H. Walls Jr. and R. L. Black, *Carbohydr. Res.*, **31**, 387 (1973).
16. M. L. Wolfrom and S. Hanessian, *J. Org. Chem.*, **27**, 2107 (1962).
17. M. L. Wolfrom and S. Hanessian, *J. Org. Chem.*, **27**, 1800 (1962).
18. F. Texier-Boullet and A. Foucaud, *Tetrahedron Lett.*, **23**, 4927 (1982).