Characterization and Identification of Cleavage Products of 3-Glycosyl-5-substituted-2-isoxazoline

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We report herein the synthesis of new synthons obtained by reductive opening of 3-glycosyl-5-substituted-2-isoxazolines. Different cleavage products have been obtained depending on the substituents (aliphatic or aromatic) in position five of the heterocycle ring. The new compounds are characterized physically and spectroscopically.

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Isoxazolinic rings are an interesting heterocyclic family, especially due to their diverse applications. Some isoxazolinic steroidal derivatives are used as antiinflammatory antedrugs [1] and other compounds containing this heterocyclic ring show inmunosuppressive activity [2]. However, the most important use of this kind of compounds is as a key intermediate for the construction of natural products [3]. The reductive cleavage of isoxazolinic rings generates attractive synthons, such as β-amino ketones or β-hydroxyketones.

In previous papers we described the synthesis of 2-isoxazolines from 2-deoxy-sugar oximes (D-*gluco* and D-*ribo* configuration), without the protection of the hydroxyl groups, with some dipolarophiles using 1,3-dipolar cycloaddition [4]. Afterwords, we extended this synthetic route to obtain protected carbohydrate derivatives [5].

We report herein the preferential cleavage products of 5-substituted isoxazolines (**1**, **2** and **8**) under different reductive procedures. The analysis of these compounds, allows us to understand the influence of the substituent (aromatic or aliphatic), in position five of the heterocycle ring, on the N-O or O-C bonds lability.

The reductive cleavage of compound **1**, using $Mo(CO)_6$ gave the expected β-hydroxyketone (**3**) and an unsaturated derivative (**4**), which was spectroscopically characterized as 6,7-dideoxy-7-cyclohexyl-1,2-*O*-isopropylidene-α-D-xylo-heptofuranos-6-en-5-ulose (Figure 1). The catalytic hydrogenation, for 6 hours, of compound **1** gave the same products but with much lower yields, as indicated by tlc.

However, the isoxazoline **2** under similar conditions ($Mo(CO)_6$ or catalytic hydrogenation) yield three compounds (**5** - **7**) (see Figure 2). Only one of them was identified as the corresponding β-hydroxyketone (**5**).

The ^{13}C nmr spectrum of the major product (compound **6**) shows duplication of the signals suggesting the presence of two structures. In the other hand, the signals at 158.3 and 159.1 ppm can be assigned to C=N bond, which is consistent with the observation of peaks at 1649.1 and 1603.9 cm^{-1} in the ir spectrum. Furthermore, signals corresponding to two methylene groups are observed in the DEPT-135 spectrum.

The mass spectrum of **6** shows a molecular ion with m/z 307 and fragment ions with m/z 91 and m/z 105, corresponding to β cleavage (tropillium ion) and the γ cleavage of the aromatic substituent respectively. Hence, the reductive treatment of compound **2** produces oximes (*syn* - *anti*), which result from C-O bond cleavage.

In a previous paper [6], we studied the gas-phase fragmentation of 3-glycosyl-5-aryl-2-isoxazolines under electron ionization conditions, using low-energy collision-induced dissociation (CID) (electron impact ms/ms) and electron ionization high-resolution mass spectrometry (electron impact hrms). These experiments show that the same C-O bond cleavage is a preferential fragmentation pathway.

A similar spectroscopic analysis, as described above for compound **6**, suggests a carbonyl structure for compound **7**. In order to determine the source of **7** we subjected **6** to hydrogenation under the same conditions, and obtained the carbonyl derivative **7** as the sole product. This shows that C-O bond cleavage leads to the formation of oxime **6**, which is then converted to the ketone **7** by further hydrogenolysis.

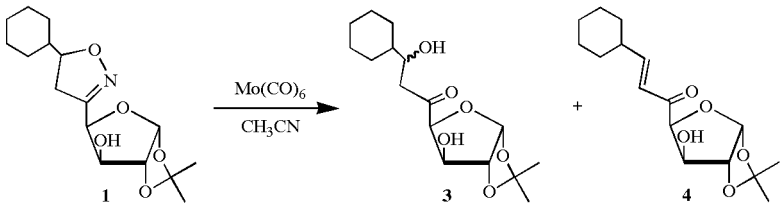

Figure 1

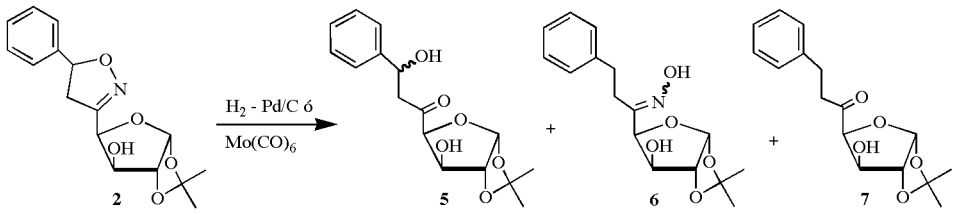

Figure 2

For the purpose of showing that this abnormal cleavage is due to the presence of an aromatic substituent at position five, we exposed compound **8** to the same reductive processes. In this case, only compounds **9** and **10** were obtained, which were assigned as oxime and ketone derivatives respectively (Figure 3). In this case, C-O bond cleavage occurs exclusively as no product was observed that results from the N-O bond cleavage.

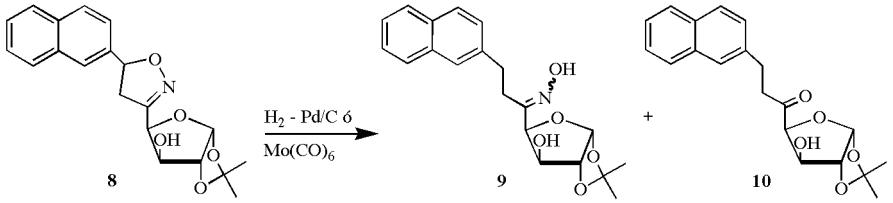

Figure 3

The differences between the reductive products obtained from compound **1**, **2** or **8**, suggests that the breaking of N-O versus C-O bonds depend on the nature of the substituents at position five. Auricchio *et al.* [7] reported that 2-isoxazolines, substituted with carbonyl or carboxyl groups in position three and an aromatic group in position five, gave oximes. However these results indicate that the only requirement for oxime formation is the presence of an aromatic substituent at position five. In those cases the C-O bond seems more labile than the N-O bond.

EXPERIMENTAL

General Methods.

Compounds **2** and **8** were synthesized as described in literature [5]. The melting points were measured on a Thomas Hoover melting point apparatus and are uncorrected. The $[\alpha]_D$ were determined using a Perkin Elmer 341 Polarimeter. The ^{1}H nmr spectra were recorded with a Bruker Spectrometer AC200 instrument at 200 MHz and the ^{13}C nmr spectra were recorded at 50 MHz and the solvent used is reported in each case, using tetramethylsilane as internal standard. The 2D-homonuclear spectra (COSY) were performed with a Bruker AC500 instrument. Thin layer chromatography (tlc) was carried out with Silica Gel G (Merck, Darmstadt) and uv light and H_2SO_4/ethanol/heat (1:10, v/v) for detection.

3-(1,2-*O*-Isopropylidene-α-D-xylofuranosyl)-5-cyclohexyl-2-isoxazoline (**1**).

To a 1,2-*O*-isopropylidene-α-D-xylo-pentadialdo-1,4-furanose-oxime [5] (2.82 g, 13.81 mmoles) and vinylcyclohexane (3.8 ml, 27.63 mmoles) in ethanol at 0 ºC solution, Chloramine-T (5.84 g, 20.70 mmoles) was slowly added. After the mixture reached room temperature it was heated at 60 °C for 3 hours. The reaction was monitored by tlc [toluene:ethylacetate (1:1) as eluent].

The product was purified by column chromatography, silica Gel G, using cyclohexane:acetone (80:20). An epimeric mixture of Compound **1** (2.40 g, 7.72 mmoles; 61.7 %) was obtained as an amorphous solid. ^{1}H nmr (deuteriochloroform): δ 0.98 – 1.89 (m, 22H, cyclohexyl hydrogens), 1.33 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 2.81 (dd, 1H, 4a-H, $J_{4a,5}$ = 9.1 Hz, $J_{4a,4b}$ = 17.9 Hz), 2.90 (dd, 1H, 4a-H, $J_{4a,5}$ = 9.3 Hz, $J_{4a,4b}$ = 18.4 Hz), 3.05 (dd, 1H, 4b-H, $J_{4b,5}$ = 10.7 Hz, $J_{4b,4a}$ = 18.0 Hz), 3.14 (dd, 1H, 4b-H, $J_{4b,5}$ = 10.4 Hz, $J_{4b,4a}$ = 17.9 Hz), 4.34 (dd, 1H, 5-H, $J_{5,4a}$ = 9.4 Hz, $J_{5,4b}$ = 10.2 Hz), 4.43 (d, 1H, 3'-H, $J_{3',4'}$ = 2.6 Hz), 4.59 (d, 1H, 2'-H, $J_{2',1'}$ = 3.7 Hz), 4.83 (br s, 1H, 4'-H), 5.99 ppm (d, 1H, 1'-H, $J_{1',2'}$ = 3.3 Hz); ^{13}C NMR (deuteriochloroform): δ 25.6, 25.7, 26.0, 26.2, 26.7, 28.3, 28.4 (CH_2 of cyclohexyl carbons), 38.6 (CH of cyclohexyl carbons), 38.8 (CH of cyclohexyl carbons), 42.1 (4-C), 42.2 (4-C), 75.9 (3'-C), 76.0 (3'-C), 76.6 (4'-C), 75.9 (4'-C), 84.6 (2'-C), 85.0 (5-C), 105.0 (1'-C), 111.9 [*C*$(CH_3)_2$], 156.3 (C=N), 156.4 ppm (C=N); ms: m/z 312 ($M^{+\bullet}$+H), 296 ($M^{+\bullet}$-$CH_3\bullet$), 252 ($M^{+\bullet}$ - CH_3COCH_3 - H•), 236 ($M^{+\bullet}$ - CH_3COOH - $CH_3\bullet$), 211 ($M^{+\bullet}$- $C_5H_8O_2$), 182 ($C_{10}H_{16}NO_2^{+\bullet}$), 152 ($C_9H_{14}NO^+$), 100 (base peak, $C_5H_8O_2^{+\bullet}$).

Anal. Calcd. for $C_{16}H_{25}NO_5$: C, 61.72; H, 8.09; N, 4.50. Found: C, 61.91; H, 8.01; N, 4.52.

General Method for Catalytic Hydrogenation using Pd/C 10% as Catalyst.

A small quantity of catalyst was added to a solution of isoxazolinic compound [methanol:acetic acid:water (10:2:1)]. The reaction mixture proceeded to react in the precense of H_2 for 6

hours at 2.8 atm. Then, the catalyst was filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography using cyclohexane:acetone (85:15) as eluent.

General Method for $Mo(CO)_6$ Reduction.

$Mo(CO)_6$ (0.75 equiv) was added to a solution of isoxazolinic compound in acetonitrile containing an equivalent amount of water. The reaction mixture was refluxed under a nitrogen atmosphere for 1.5 hours, and the solution was filtered through Celite. The filtrate was purified by column cromatography using cyclohexane:acetone (90:10).

Reduction of 3-(1,2-*O*-Isopropylidene-α-D-xylofuranosyl)-5-cyclohexyl-2-isoxazoline (**1**).

B) Reduction using $Mo(CO)_6$.

Following the method described above, from **1** (0.68 mmol, 0.21 g) we obtained compound **3** (0.22 mmol, 0.07 g; 32%) and compound **4** (0.22 mmol, 0.07 g; 33%)

6-Deoxy-7-cyclohexyl-1,2-*O*-isopropylidene-α-D-xylo-heptofuranos-5-ulose (**3**).

This compound has ^{1}H nmr (dueteriochloroform): δ 0.80 -1.90 (m, 22H, cyclohexyl protons), 1.32 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 2.68 (dd, 1H, 6a-H, $J_{6a,7}$ = 3.1 Hz, $J_{6a,6b}$ = 16.3 Hz), 2.69 (dd, 1H, 6a-H, $J_{6a,7}$ = 2.4 Hz, $J_{6a,6b}$ = 17.5 Hz), 2.74 (dd, 1H, 6b-H, $J_{6b,7}$ = 9.4 Hz, $J_{6b,6a}$ = 16.4 Hz), 2.91 (dd, 1H, 6b-H, $J_{6b,7}$ = 10.1 Hz, $J_{6b,6a}$ = 17.4 Hz), 3.93 (ddd, 1H, 7-H, $J_{7,6a}$ = 2.2 Hz, $J_{7,6b}$ = 10.1 Hz, $J_{7,1'}$ = 6.1 Hz), 3.97 (ddd, 1H, 7-H, $J_{7,6a}$ = 3.2 Hz, $J_{7,6b}$ = 9.3 Hz, $J_{7,1'}$ = 6.0 Hz), 4.52 - 4.56 (m, 3H, both 2-, and 3-H), 4.59 (d, 1H, 4-H, $J_{4,3}$ = 3.0 Hz), 4.61 (d, 1H, $J_{3,4}$ = 3.0 Hz), 4.72 (d, 1H, 4-H, $J_{4,3}$ = 3.0 Hz), 6.06 (d, 1H, 1-H, $J_{1,2}$ = 3.6 Hz), 6.08 ppm (d, 1H, 1-H, $J_{1,2}$ = 3.4 Hz); ^{13}C nmr (deuteriochloroform): δ 25.8 - 31.5 (cyclohexyl carbons), 26.2 (CH_3), 26.9 (CH_3), 43.3 (6-C), 44.2 (6-C), 72.0 (7-C), 70.2 (7-C), 75.8 (3-C), 76.6 (3-C), 84.4 (2-C), 84.5 (2-C), 86.3 (4-C), 87.0 (4-C), 105.5 (1-C), 105.7 (1-C), 112.2 [*C*$(CH_3)_2$], 112.3 [*C*$(CH_3)_2$], 208.3 ppm (C=O); ms: m/z 299 ($M^{+\bullet}$- $CH_3\bullet$), 187 ($M^{+\bullet}$ - $CH_2CHOHC_6H_{11}\bullet$), 159 ($M^{+\bullet}$ - $CH_2CHOHC_6H_{11}\bullet$ - CO), 155 ($M^{+\bullet}$ - $C_7H_{11}O_4\bullet$), 59 (base peak).

Anal. Calcd. for $C_{16}H_{26}O_6$: C, 61.13; H, 8.34. Found: C, 61.05; H, 8.37.

6,7-Dideoxy-7-cyclohexyl-1,2-*O*-isopropylidene-α-D-xylo-heptofuranos-6-en-5-ulose (**4**).

This compound has ^{1}H nmr (deuteriochloroform): δ 0.90 – 1.40 (m, 11H, cyclohexyl protons), 1.32 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 4.52 (d, 1H, 3-H, $J_{3,4}$ = 2.9 Hz), 4.55 (d, 1H, 2-H, $J_{2,1}$ = 3.6 Hz), 4.75 (d, 1H, 4-H, $J_{4,3}$ = 2.9 Hz), 6.05 (d, 1H, 1-H, $J_{1,2}$ = 3.6 Hz), 6.48 (dd, 1H, 6-H, $J_{6,7}$ = 15.9 Hz, $J_{6,1'}$ = 1.3 Hz), 7.01 ppm (dd, 1H, 7-H, $J_{7,6}$ = 15.9 Hz, $J_{7,1'}$ = 6.5 Hz); ^{13}C nmr (deuteriochloroform): δ 25.8 - 31.5 (cyclohexyl carbons), 26.2 (CH_3), 26.9 (CH_3), 76.1 (3-C), 84.4 and 84.5 (2-C and 4-C), 105.4 (1-C), 112.1 [*C*$(CH_3)_2$], 123.8 (7-C), 155.6 (6-C), 197.4 ppm (C=O).

Reduction of 3-(1,2-*O*-Isopropylidene-α-D-xylofuranosyl)-5-phenyl-2-isoxazoline (**2**).

A) Catalytic Hydrogenation using Pd/C 10% as Catalyst.

Following the general method described above, from **2** (0.66 mmol, 0.20 g) three different compounds, **5**, **6** and **7** were isolated. The main product (0.36 mmol, 0.11 g; 54.7%) was identified as 6,7-dideoxy-1,2-*O*-isopropylidene-7-phenyl-α-D-xylo-heptofuranos-5-ulose oxime (**6**). The other minor compounds **5** and **7** were identified as 6-deoxy-1,2-*O*-isopropylidene-7-phenyl-α-D-xylo-heptofuranos-5-ulose (0.23 mmol, 0.07 g; 35.1%) as an epimeric mixture and 6,7-dideoxy-1,2-*O*-isopropylidene-7-phenyl-α-D-xylo-heptofuranos-5-ulose (0.02 mmol, 6.2 mg; 3.1%) respectively. The spectroscopic data and physical constants are listed below.

B) Reduction using $Mo(CO)_6$.

Following the method described above, from **2** (0.33 mmol, 0.10 g) the same three compounds mentioned in the previous item could be isolated, but with different yields: compound **5** (0.10 mmol, 31.0 mg; 30.7%), compound **6** (0.08 mmol, 23.5 mg; 23.3%) and compound **7** (0.04 mmol, 12.6 mg; 13.2%).

6-Deoxy-1,2-*O*-isopropylidene-7-phenyl-α-D-xylo-heptofuranos-5-ulose (**5**).

This compound has ^{1}H nmr (deuteriochloroform): δ 1.31 (s, 6H, CH_3), 1.47 (s, 6H, CH_3), 2.83 (dd, 1H, 6a-H, $J_{6a,7}$ = 2.9 Hz, $J_{6a,6b}$ = 16.4 Hz), 2.87 (dd, 1H, 6a-H, $J_{6a,7}$ = 2.6 Hz, $J_{6a,6b}$ = 17.9 Hz), 3.06 (dd, 1H, 6b-H, $J_{6b,7}$ = 9.9 Hz, $J_{6b,6a}$ = 16.4 Hz), 3.25 (dd, 1H, 6b-H, $J_{6b,7}$ = 10.0 Hz, $J_{6b,6a}$ = 17.9, Hz), 4.52 (d, 1H, 2-H, $J_{2,1}$ = 3.7 Hz), 4.45 - 4.54 (m, 2H, 2-, and 3-H), 4.61 (d, 1H, 4-H, $J_{4,3}$ = 3.3 Hz), 4.65 (d, 1H, 3-H, $J_{3,4}$ = 2.9 Hz), 4.73 (d, 1H, 4-H, $J_{4,3}$ = 2.9 Hz), 5.24 (dd, 1H, 7-H, $J_{7,6a}$ = 2.9 Hz, $J_{7,6b}$ = 9.9 Hz), 5.28 (dd, 1H, 7-H, $J_{7,6a}$ = 2.5 Hz, $J_{7,6b}$ = 10.0 Hz), 6.03 (d, 1H, 1-H, $J_{1,2}$ = 2.6 Hz), 6.05 (d, 1H, 1-H, $J_{1,2}$ = 2.9 Hz), 7.10 – 7.40 ppm (m, 10H, phenyl protons); ^{13}C nmr (deuteriochloroform): δ 26.2 (CH_3), 26.9 (CH_3), 49.0 (6-C), 48.1 (6-C), 69.9 (7-C), 70.1 (7-C), 75.9 (3-C), 76.7 (3-C), 84.5 (2-C), 84.6 (2-C), 86.2 (4-C), 86.9 (4-C), 105.6 (1-C), 105.7 (1-C), 112.3 [*C*$(CH_3)_2$], 125.6 – 142.6 (phenyl carbons), 207.0 (C=O), 209.6 ppm (C=O); ms: m/z 308 ($M^{+\bullet}$), 293 ($M^{+\bullet}$- $CH_3\bullet$), 187 ($M^{+\bullet}$ - $CH_2CHOHC_6H_5\bullet$), 159 ($M^{+\bullet}$ - $CH_2CHOHC_6H_5\bullet$ - CO), 149 ($M^{+\bullet}$ - $C_7H_{11}O_4\bullet$), 43 (base peak, CH_3CO^+).

Anal. Calcd. for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.18; H, 6.73.

6,7-Dideoxy-1,2-*O*-isopropylidene-7-phenyl-α-D-xylo-heptofuranos-5-ulose Oxime (**6**).

This compound has mp 139-141°; $[\alpha]_D$ –86.0° (c 1.0, chloroform); ^{1}H nmr (deuteriochloroform): δ *Syn*, 1.30 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 2.64 – 2.97 (m, 2H, 6-, and 7-H), 4.26 (d, 1H, 3-H, $J_{3,4}$ = 2.2 Hz), 4.42 (d, 1H, 4-H, $J_{4,3}$ = 2.5 Hz), 4.52 (d, 1H, 2-H, $J_{1,2}$ = 3.7 Hz), 5.95 (d, 1H, 1-H, $J_{1,2}$ = 3.7 Hz), 7.14 – 7.27 (m, 5H, phenyl protons); *Anti*, 1.33 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 2.64 – 2.97 (m, 2H, 6-, and 7-H), 4.55 (d, 1H, 2-H, $J_{1,2}$ = 3.7 Hz), 4.79 (d, 1H, 3-H, $J_{3,4}$ = 3.3 Hz), 5.24 (d, 1H, 4-H, $J_{4,3}$ = 2.9 Hz), 6.01 (d, 1H, 1-H, $J_{1,2}$ = 3.7 Hz), 7.14 – 7.27 ppm (m, 5H, phenyl protons); ^{13}C nmr (deuteriochloroform): δ *Syn*, 26.1 (CH_3), 26.7 (CH_3), 28.9 (7-C), 31.3 (6-C), 75.3 (3-C), 79.7 (4-C), 84.4 (2-C), 104.7 (1-C), 111.7 [*C*$(CH_3)_2$], 125.9 – 140.9 (phenyl carbons), 158.3 (C=N), *Anti*, 26.3 (CH_3), 26.9 (CH_3), 32.6 and 33.1 (6-C, 7-C), 75.5 (3-C), 79.6 (4-C), 85.0 (2-C), 104.4 (1-C), 111.8 [*C*$(CH_3)_2$], 125.9 – 140.9 (phenyl carbons), 159.9 ppm (C=N); ms: m/z 307 ($M^{+\bullet}$), 292 ($M^{+\bullet}$- $CH_3\bullet$), 249 ($M^{+\bullet}$ - CH_3COCH_3), 232 ($M^{+\bullet}$ - CH_3COOH - $CH_3\bullet$), 149 ($PhCH_2CH_2CH{=}NOH^+$), 105 ($PhCH_2CH_2^+$), 91 ($C_7H_7^+$), 43 (base peak, CH_3CO^+).

Anal. Calcd. for $C_{16}H_{21}NO_5$: C, 62.53; H, 6.89; N, 4.56. Found: C, 62.39; H, 7.06; N, 4.46.

6,7-Dideoxy-1,2-*O*-isopropylidene-7-phenyl-α-D-xylo-heptofuranos-5-ulose (**7**).

This compound has mp 111-112º; ^{1}H nmr (deuteriochloroform): δ 1.32 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 2.91 (m, 1H, 7-H), 2.99 (m, 1H, 6-H), 4.51 (d, 1H, 3-H, $J_{3,4}$ = 3.0 Hz), 4.52 (d, 1H, 2-H, $J_{2,1}$ = 3.7 Hz), 4.61 (d, 1H, 4-H, $J_{4,3}$ = 3.2 Hz), 6.04 (d, 1H, 1-H, $J_{1,2}$ = 3.5 Hz), 7.11 – 7.25 ppm (m, 5H, phenyl protons); ^{13}C nmr (deuteriochloroform): δ 26.2 (CH_3), 26.9 (CH_3), 28.6 (7-C), 42.1 (6-C), 76.3 (3-C), 84.5 (2-C), 86.0 (4-C), 105.5 (1-C), 112.3 [*C*(CH_3)$_2$], 126.1 – 140.8 (phenyl carbons), 208.9 ppm (C=O); ms: m/z 293 ($M^{+\bullet}$+H), 277 ($M^{+\bullet}$- $CH_3\bullet$), 234 ($M^{+\bullet}$ - CH_3COCH_3), 217 ($M^{+\bullet}$ - CH_3COOH - $CH_3\bullet$), 159 ($M^{+\bullet}$- $PhCH_2CH_2CO^+$), 105 ($PhCH_2CH_2^+$), 91 ($C_7H_7^+$), 59 (base peak).

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.73; H, 6.89. Found: C, 65.49; H, 6.71.

Reduction of 3-(1,2-*O*-Isopropylidene-α-D-xylofuranosyl)-5-naphtyl-2-isoxazoline (**8**).

Catalytic Hydrogenation using Pd/C 10% as Catalyst.

Following the general procedure, from **8** (0.28 mmol, 0.10 g) we isolated compounds **9** and **10**, which were identified as 6,7-dideoxy-1,2-*O*-isopropylidene-7-naphtyl-α-D-xylo-heptofuranos-5-ulose oxime (0.18 mmol, 62.9 mg; 62.6%) and 6,7-dideoxy-1,2-*O*-isopropylidene-7-naphtyl-α-D-xylo-heptofuranos-5-ulose (0.09 mmol, 30.0 mg; 31.3%) respectively. Spectroscopic data and physical constants are listed below.

Reduction using $Mo(CO)_6$.

Following the general procedure, from **8** (0.28 mmol, 0.10 g) we are able to isolate the same two compounds **9** (0.09 mmol, 31.3 mg; 31.1%) and **10** (0.06 mmol, 20.1 mg; 20.0%).

6,7-Dideoxy-7-naphtyl-1,2-*O*-isopropylidene-α-D-xylo-heptafuranos-5-ulose Oxime (**9**).

This compound has mp 247-249º; $[\alpha]_D$ –70.4º (c 0.5, chloroform); ^{1}H nmr (deuteriochloroform): δ 1.31 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 2.74 – 3.14 (m, 2H, 6-, and 7-H), 4.31 (d, 1H, 3-H, $J_{3,4}$ = 1.8 Hz), 4.46 (d, 1H, 4-H, $J_{4,3}$ = 1.7 Hz), 4.56 (d, 1H, 2-H, $J_{1,2}$ = 3.4 Hz), 6.00 (d, 1H, 1-H, $J_{1,2}$ = 3.4 Hz), 7.40 – 7.82 ppm (m, 7H, naphtyl protons); ^{13}C nmr (methanol-d_4): δ 26.4 (CH_3), 26.9 (CH_3), 29.8 (7-C), 32.7 (6-C), 77.6 (3-C), 82.4 (4-C), 86.3 (2-C), 106.3 (1-C), 112.8 [*C*(CH_3)$_2$], 126.2 – 140.8 (naphtyl carbons), 158.4 ppm (C=N); ms: m/z 357 ($M^{+\bullet}$), 342 ($M^{+\bullet}$- $CH_3\bullet$), 282 ($M^{+\bullet}$ - CH_3COOH - $CH_3\bullet$), 202 ($M^{+\bullet}$ - $C_{10}H_7CH_2CH_2\bullet$), 198 ($C_{10}H_7CH_2CH_2CH{=}NOH^+$), 141 ($C_{11}H_9^+$), 59 (base peak).

Anal. Calcd. for $C_{20}H_{23}NO_5$: C, 67.23; H, 6.44. Found: C, 66.92; H, 6.62.

6,7-Dideoxy-7-naphtyl-1,2-*O*-isopropylidene-α-D-xylo-heptafuranos-5-ulose (**10**).

This compound has mp 127-129º ; $[\alpha]_D$ –69.2º (c 0.5, chloroform); ^{1}H nmr (benzene-d_6): δ 1.04 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 2.88 – 3.03 (m, 2H, 6-, and 7-H), 4.12 (d, 1H, 2-H, $J_{2,1}$ = 3.5 Hz), 4.28 (d, 1H, 3-H, $J_{3,4}$ = 2.7 Hz), 4.58 (d, 1H, 4-H, $J_{4,3}$ = 3.1 Hz), 5.89 (d, 1H, 1-H, $J_{1,2}$ = 3.5 Hz), 7.20 – 7.61 ppm (m, 7H, naphthyl protons); ^{13}C nmr (deuteriochloroform): δ 26.3 (CH_3), 26.9 (CH_3), 28.7 (7-C), 41.9 (6-C), 76.2 (3-C), 84.6 (2-C), 86.0 (4-C), 105.5 (1-C), 112.2 [*C*(CH_3)$_2$], 123.5 – 138.3 (naphtyl carbons), 208.9 ppm (C=O); ms: m/z 342 ($M^{+\bullet}$+H), 183 ($M^{+\bullet}$ -$C_7H_{11}O_4\bullet$), 159 ($M^{+\bullet}$ - $CH_2CH_2C_{10}H_7\bullet$ - CO), 141 ($C_{10}H_7CH_2^+$), 59 (base peak).

Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 69.97; H, 6.52.

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