Synthesis of some 6-*S*-Heterocyclic Derivatives of 1,2:3,4-Di-*O*-isopropylidene-α-*D*-galactopyranose

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We applied nucleophilic substitution to 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose using sulphur nucleophiles and obtained 6-*S*-derivatives of 1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose. We present the physical and spectroscopic characterization of these heterocyclic compounds as well as other related compounds obtained by substitution, using other substrates. The conformational studies of all products are presented and discussed.

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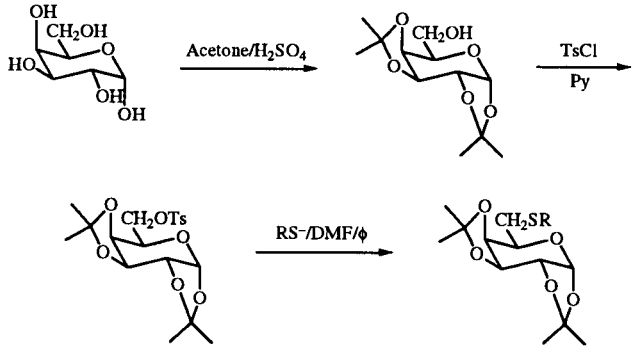
The heterocyclic carbohydrate derivatives have been widely studied due to their biological activities [1]. We have focused our interest on carbohydrate heterocyclic compounds containing sulfur in their composition, due to their possible activity [2].

In this work we synthesize some 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose derivatives, with a sulfur atom on C-6. We could obtain the corresponding thiol and thioethers by nucleophilic displacement using some charged sulfur nucleophiles and 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose [3]. The synthetic route is shown in Scheme 1, and in Figure 1 we present the new obtained compounds.

Scheme 1



For this synthesis, we made the displacement with the charged species. In the case of compounds **1-3**, and **5**, the anion was formed using sodium ethoxide in ethanol, or 5% sodium hydroxide solution for **6**, but in another case, compound **4**, we used the commercial reagent. In order to find the best conditions for the preparation of the heterocyclic derivatives, we also worked with other nucleophiles and obtained compounds **4-6** in good yields; in this reaction we used sulfide and aliphatic and aromatic sulfides. When we tried to synthesize the 2-thioglycolic acid ethyl ester derivative, we found that the principal isolable compound was product **4**. To synthesize compound **3**, the reactive species was obtained from 2-thiouracil, taking advantage of the displacement of thioketone-thiol equilibrium.

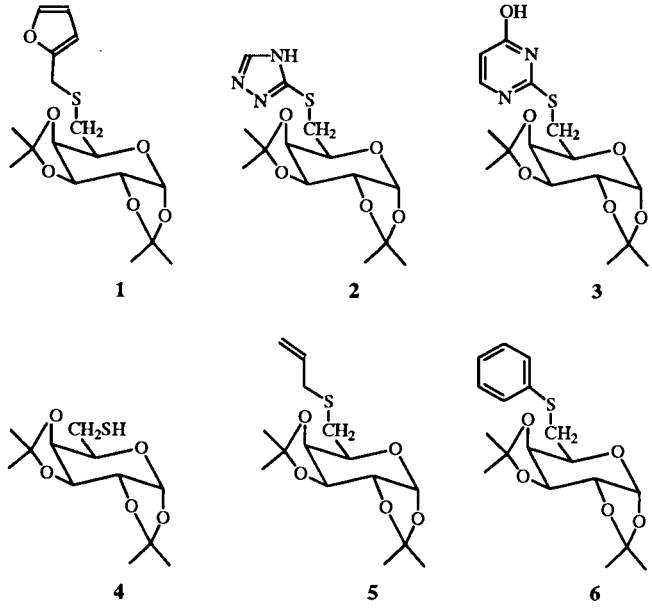


Figure 1. **1**, 6-*S*-[2'-Thiomethyl(furyl)]-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose; **2**, 6-*S*-[3'-(1',2',4'-Triazolyl)]-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose; **3**, 6-*S*-[2'-(4'-Hydroxypyrimidyl)]-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose; **4**, 6-*S*-1,2:3,4-Di-*O*-isopropylidene-α-*D*-galactopyranose; **5**, 6-*S*-Allyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose; **6**, 6-*S*-Phenyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose.

All ^{1}H nmr spectra were recorded at 200 MHz and permitted a complete assignation by first order analysis. Displacements of signals of the carbohydrate moiety for compounds **1** to **6** are summarized in Table 1, and coupling constants are listed in Table 2. The displacement of the characteristic protons of each structure are presented in the Experimental.

When we compare the spectroscopic analysis of all compounds, we observed an inversion in the measured coupling constants. In effect, if the conformation of the

Table 1

^{1}H NMR Chemical Shifts (δ) of Compounds **1-6**

Compound	1	2	3	4	5	6
H-1	5.43	5.57	5.47	5.52	5.43	5.50
H-2	4.22	4.33	4.25	4.29	4.19	4.26
H-3	4.54	4.63	4.57	4.63	4.52	4.58
H-4	4.22	4.38	4.31	4.35	4.22	4.36
H-5	3.82	4.09	4.08	4.06	3.78	3.84
H-6a	2.67	3.33	3.35	2.95	3.10	3.16
H-6b	2.67	3.33	3.28	2.95	3.09	3.16

products was a $^4C_1$ we must observe for $J_{2,3}$ and $J_{3,4}$ approximated values of 9.0-11.0 Hz and 1.0-3.0 Hz respectively, but the observed values for $J_{2,3}$ and $J_{3,4}$ were 2.2-2.6 and 7.8-10.2 respectively. The first order analysis was confirmed using computed simulation of data [4], and we found a good correlation between the simulated spectra and the experimental data.

Table 2

Vicinal Proton-Proton Coupling Constants (Hz) of Compounds **1-6**

Compound	1	2	3	4	5	6
$J_{1,2}$	5.0	5.0	4.9	5.0	4.9	5.0
$J_{2,3}$	2.2	2.5	2.4	2.5	2.6	2.3
$J_{3,4}$	7.9	7.9	7.9	10.2	7.8	7.9
$J_{4,5}$	1.5	1.7	1.7	1.7	1.5	1.6
$J_{5,6a}$	7.2	7.0	6.8	6.9	7.2	6.4
$J_{5,6b}$	6.9	7.0	5.8	7.0	7.2	7.3
$J_{6a,6b}$	12.6	12.4	12.6	12.4	12.6	12.4

The observed exchange in the coupling constant values can be attributed to a conformational change in the pyranose ring. These conformational changes for the 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose derivative in the solid state were reported in the literature using X ray analysis [5] . We supposed that this behavior was the same for the main structure present in the equilibrium in solution, because the molecules studied must be more rigid than other galactose derivatives due to the presence of two fused 1,3-dioxolane rings.

To confirm this supposition, we performed some conformational calculations [6] and found, for all compounds studied, that the lowest energetic conformation was a twisted boat ($^OT_2$) (Figure 2). As described for 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose [5], we found by calculation for compounds **1** to **6** that their valence angles in C-2 and C-3 have increased values (111 to 116 degrees). The fused 1,3-dioxolane rings make changes in the expected torsion angles for a chair conformation, especially at the C3-C4 linkage where the torsion angle is nearby zero. These distortions are responsible for the changes observed.

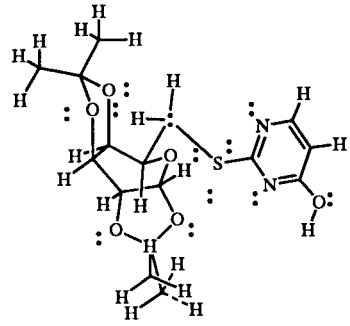


Figure 2.

The calculated coupling constants of the energy minimized structures were practically the same as those measured from the spectra. The simulated ^{1}H nmr spectra, using calculated values, were identical to those performed with experimental values.

We observed that all H-6a and H-6b signals appear like a doublet, instead of the traditional double-doublet with a great geminal coupling constant, however, this fact is due to the closeness of both displacements.

When spectra were simulated in basis of first order analysis data, we found that a geminal coupling constant existed and both double-doublets collapses into only one doublet.

For ^{13}C nmr assignments we used 1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose [7] as the model compound and found good correlation with all displacements. Values for the carbohydrate moiety and correlations with values of published data or model compounds for other carbons are listed in Table 3. For methyl groups, quaternary carbons from dioxolane rings and other characteristic displacements of each compound are given in the Experimental. In all cases we observed that the displacement of the signals of the pyranose ring show only small differences for C-1, C-2 and C-3. This fact could be attributed to the rigid conformation, together with the distance to the changed substituent at C-6. The displacement for C-5 remains unchanged, as it is involved in the pyranose ring formation and is less affected by changes on C-6. The differences observed on C-4 vary between 0.7 and 2.0 ppm, and can be attributed to steric and electronic effects

Table 3

^{13}C NMR Chemical Shifts (δ) of Compounds **1-6**

Compound	C-1	C-2	C-3	C-4	C-5	C-6
1	96.5	70.8	70.4	67.6	71.5	31.0
2	96.6	70.8	70.5	67.0	71.5	32.4
3	96.6	71.0	70.6	66.3	71.5	30.7
4	96.6	70.9	70.5	66.6	71.5	38.3
5	96.5	70.8	70.5	67.5	71.5	30.2
6	96.7	70.8	70.5	66.1	71.2	33.1
7 [a]	96.3	70.8	70.6	68.3	71.5	62.1

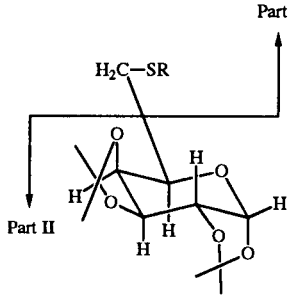
[a] **7**; 1,2:3,4-Di-*O*-isopropylydene-α-*D*-galactopyranose [7].

of the substituents on C-6 over the pseudo-axial position. The greatest differences were observed in C-6 due to the exchange of oxygen by sulfur.

The analysis of mass spectra of compounds **1-6** was made on the basis of the following procedure:

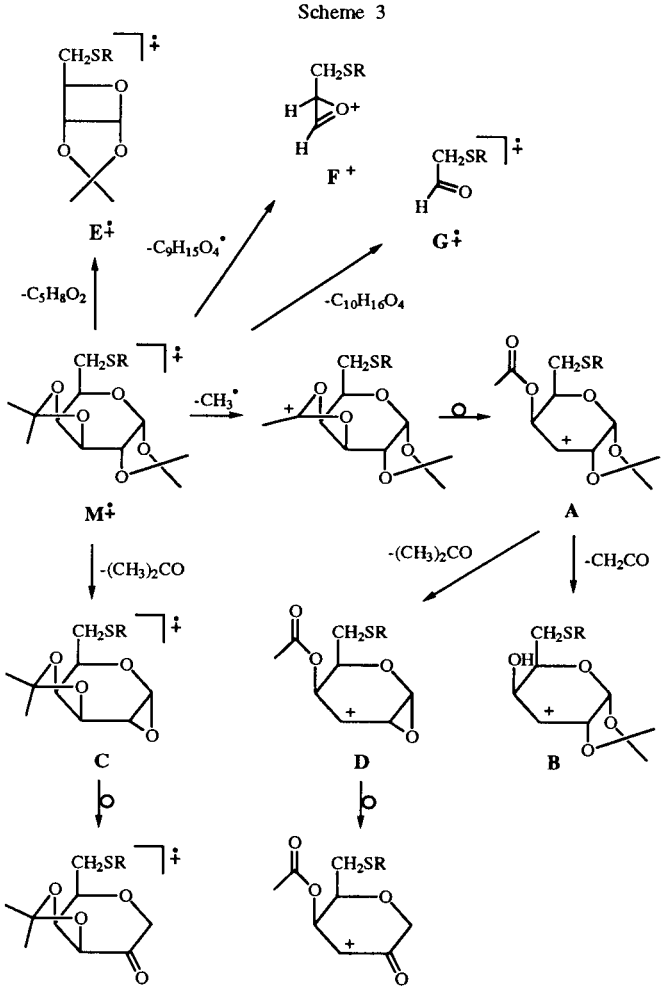
These *D*-galactopyranose derivatives can be divided in two parts (Scheme 2). In this way we can analyze three different types of ions.

Scheme 2



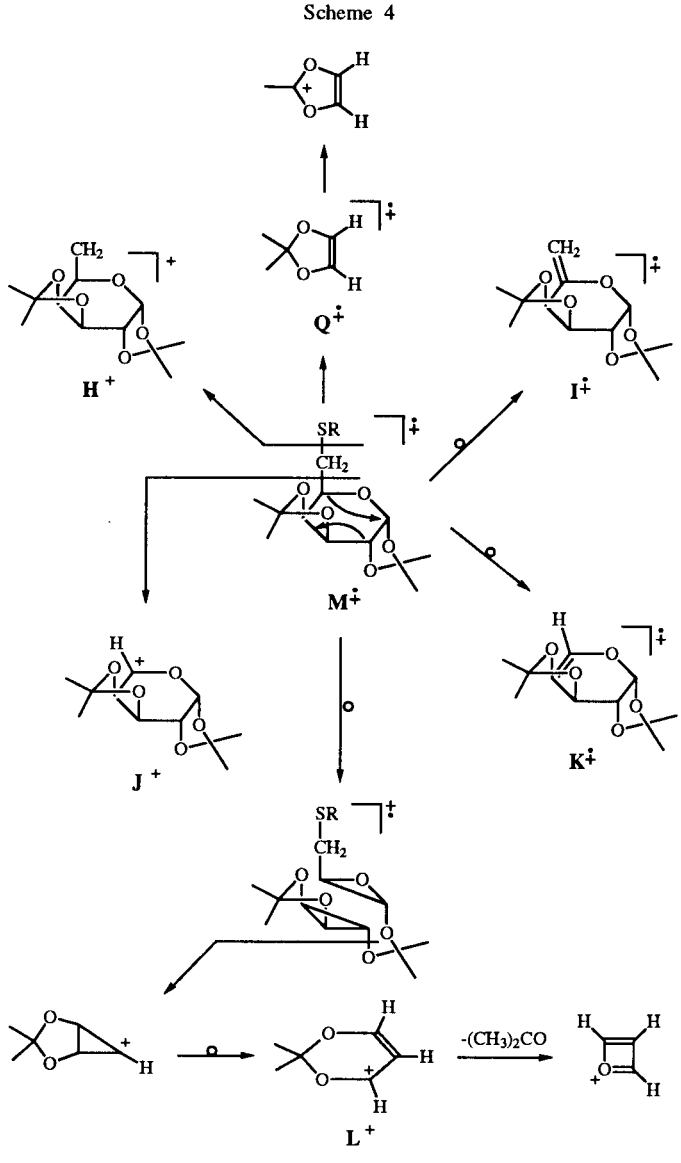
Type 1. Ions produced by the same fragmentations but with different m/z relationship due to the different mass of Part I (Scheme 3).

Scheme 3



Type 2. Ions produced by the same fragmentations with the same m/z relationship, originated by Part II (Scheme 4).

Scheme 4



Type 3. Ions produced by particular Part I fragmentations.

Based on this procedure we postulated a possible fragmentation pattern. In some cases, we can propose more than one route of fragmentation for the same m/z relationship, and these peaks can not be assigned to a specific fragmentation without a genetic study. For all of our compounds, we found that, as it is described in the literature for 1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose [8], the most important peaks are the m/z 43 [CH_3CO^+] (base peak for compounds **2**, **3**, **5** and **6**, 32% for compound **1** and 69% for compound **4**), 59 [$(CH_3)_2CO^+$], 85 [$Q^{+\bullet}$ -$CH_3^\bullet$], 100 [$Q^{+\bullet}$] and 113 [L^+]. In this type of structures with many ether oxygen moieties, it is common to observe an important $M^{+\bullet}+1$, which appears by ion-molecule collision, depending on the

sample pressure [9]. In our case we observed this peak for compounds **1**, **3**, **4** and **5**, as more important than $M^{+\bullet}$ for compound **3**.

Like it has been described for nucleotides [9], we also observed peaks attributable to [SR^+], [SR^+] + H and [SR^+] + 2H. For compounds described here, we found ions corresponding to [$CH_3SR^{+\bullet}$] (Part I + H) and [CH_2SR^+] (Part I) in all cases.

The main observed fragments for each compound are listed in the Experimental.

EXPERIMENTAL

General Methods.

The melting points were measured on a Thomas Hoover melting point apparatus and are uncorrected. The $[\alpha]_D$ were observed using a 141 Perkin Elmer Polarimeter. All ^1H nmr spectra were recorded with a Bruker Spectrometer at 200 MHz in deuteriochloroform, using TMS as the internal standard. The ^{13}C nmr were recorded at 50 MHz with the same apparatus. Mass spectra were recorded with a Shimadzu QP-5000 by electron impact ionization.

1,2:3,4-Di-*O*-isopropylidene-α-*D*-galactopyranose.

We used a modification of the method described for 2,3:5,6-di-*O*-isopropylidene-*D*-mannofuranose [10]. In a three neck round bottom flask equipped with a dropping funnel and a calcium chloride trap, acetone (370 ml), was stirred, cooling it in an ice-water bath. Concentrated sulphuric acid (11 ml) was carefully added, and then, 10 g of *D*-galactose with continuous stirring. The ice-water bath was removed and the mixture was kept at room temperature for 3 or 4 hours. It was neutralized with sodium carbonate, filtered, and evaporated under reduced pressure, obtaining the title compound as a syrup, 13.4 g, 93%, $[\alpha]_D$ = -54.5°, (lit = -54.7° [11]).

6-Tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose.

To a solution of 7.7 g of 1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose dissolved in pyridine (12 ml), 6.8 g of tosyl chloride was added with continuous stirring. The mixture was kept at room temperature during one night and then poured into crushed ice. The oil which formed was washed with fresh water and after a few hours it became a filterable solid (9.2 g, 75%). This product crystallizes from cyclohexane, mp 101-103°, (lit 102-103° [12]).

Nucleophilic Displacements. General Procedures.

The nucleophilic displacement was made by heating of 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose with the corresponding nucleophile in a 1:4 relationship, using DMF as the solvent. The nucleophile was generated as follows:

A solution of sodium ethoxide in ethanol was prepared adding metallic sodium (approximately 0.5 g) to ethanol (20 ml), cooled in an ice bath. The commercial reactant was suspended or dissolved in an equivalent quantity of sodium ethoxide solution, then gently heated on a water bath at 50° for a few minutes. The solvent was evaporated under reduced pressure, DMF and the corresponding quantity of 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose added and heated at reflux. The reaction was followed by tlc, until the starting material disappeared. The mixture was evaporated under reduced pressure, suspended in water and extracted with methylene chloride. The combined extracts were dried with sodium sulfate, filtered and concentrated. The syrupy residue was purified by column chromatography (silica gel) using benzene:ethyl acetate as the eluent.

6-*S*-[2'-thiomethyl(furyl)]-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose (**1**).

The title compound was prepared using the general procedure with 1.0 g of 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose and 2.2 ml of 2-thiomethylfurane. A yellow syrup was obtained, 0.6 g, yield 68%, $[\alpha]_D$ = -67.7° (chloroform); ^1H nmr: δ 3.71 (s, CH_2), δ 6.12 (dd, H-3', $J_{3'-4'}$ = 3.3 Hz, $J_{3'-5'}$ < 1 Hz), δ 6.22 (dd, H-4', $J_{3'-4'}$ = 3.3 Hz, $J_{4'-5'}$ = 1.9 Hz), δ 7.27 (dd, H-5', $J_{3'-5'}$ < 1 Hz, $J_{4'-5'}$ = 1.9 Hz), δ 1.26-1.46 (four signals, CH_3-groups) ppm; ^{13}C nmr (model compound, 2-methylfuran [13]) δ 28.5 (CH_2), δ 151.0 (C-2'), δ 107.5 (C-3'), δ 110.3 (C-4'), δ 142.0 (C-5'), δ 108.4 and δ 109.3 (quaternary carbons), δ 24.4-26.0 (four signals, CH_3-groups) ppm; ms: (type 1) m/z 356 ($M^{+\bullet}$), 341 (A^+), 155 ($G^{+\bullet}$-$H^\bullet$), 115 (SR^+ + 2H), 114 (SR^+ + H), 113 (SR^+ = $G^{+\bullet}$-CH_3CO^+), 112 ($G^{+\bullet}$-CH_2CO-H_2); (type 2) m/z 185 (H^+-$(CH_3)_2CO$), 100 ($Q^{+\bullet}$), 85 ($Q^{+\bullet}$- $CH_3^\bullet$), 81 (base peak, $I^{+\bullet}$-$(CH_3)_2CO$-CO-H_2O-CH_2CO- $CH_3^\bullet$); (type 3) m/z 289 ($M^{+\bullet}$-$C_4H_3O^+$), 201 ($M^{+\bullet}$-$C_4H_3O^\bullet$-$(CH_3)_2CO$-CO-H_2), 155 ($E^{+\bullet}$-$CH_3^\bullet$-CH_2CO-H_2O-C_2H_2), 139 ($E^{+\bullet}$-$CH_3^\bullet$-CH_2CO-H_2O-C_2H_2O), 87 (SR^+ - C_2H_2).

Anal. Calcd. for $C_{17}H_{24}O_6S$: C, 57.30; H, 6.74. Found: C, 57.11; H, 6.91.

6-*S*-[3'-(1',2',4'-triazolyl)]-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose (**2**).

The title compound was prepared by the general procedure using 1.0 g of 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose and 0.8 g of 1,2,4-triazole-3-thiol. The crude product was obtained in a quantitative yield. It was purified by flash chromatography. Compound **2** is a colorless syrup which crystallized from methanol, 0.58 g, yield 70%, mp, 96-97°, $[\alpha]_D$ = -39.2 (chloroform); ^1H nmr: δ 8.12 (s, H-5'), δ 1.32-1.47 (four signals, CH_3-groups) ppm, NH is not observed; ^{13}C nmr: (model compound, 1,2,4-triazole [14]) δ 148.2 (C-3' and C-4'), δ 108.9 and δ 109.5 (quaternary carbons), δ 24.3-25.9 (four signals, CH_3-groups) ppm; ms: (type 1) m/z 328 (A^+), 185 ($E^{+\bullet}$-$(CH_3)_2CO$), 155 ($G^{+\bullet}$- $H^\bullet$), 102 (SR^+ + 2H), 101 (SR^+ + H), 100 (SR^+); (type 2) m/z 243 (H^+), 127 ($I^{+\bullet}$-$(CH_3)_2CO$-$CH_3^\bullet$-CH_2CO), 100 ($Q^{+\bullet}$), 85 ($Q^{+\bullet}$-$CH_3^\bullet$), 81 ($I^{+\bullet}$-$(CH_3)_2CO$-CO-H_2O-CH_2CO-$CH_3^\bullet$), 43 (base peak, CH_3CO^+); (type 3) 129 ($F^{+\bullet}$-HCN), 84 ($F^{+\bullet}$-CH_2N_2-CH_2O).

Anal. Calcd. for $C_{14}H_{21}N_3O_5S{\bullet}CH_3OH$: C, 48.00; H, 6.66. Found: C, 48.17; H, 6.66.

6-*S*-[2'-(4'-Hydroxipyrimidyl)]-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose (**3**).

Compound **3** is obtained by the general procedure starting from 1.0 g of 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose and 1.2 g of thiouracil in quantitative yield. It gave a syrup which was purified by flash chromatography and recrystallized from cyclohexane. Product **3** was obtained as a solid, 0.65 g, 73% yield, mp 89-91°, $[\alpha]_D$ = -73.8° (chloroform); ^1H nmr: δ 6.15 (d, H-5', $J_{5'-6'}$ = 6.6 Hz), δ 7.76 (d, H-6', $J_{5'-6'}$ = 6.6 Hz), δ 12.85 (s, OH), δ 1.26-1.40 (four signals, CH_3- groups) ppm; ^{13}C nmr: (model compound, uracil [15]) δ 161.9 (C-2'), δ 164.4 (C-4'), δ 111.1 (C-5'), δ 154.7 (C-6'), δ 108.8 and δ 109.5 (quaternary carbons), δ 24.4-25.9

(three signals, CH_3- groups, one more intense) ppm; ms: (type 1) m/z 370 ($M^{+\bullet}$), 355 (A^+), 297 (D^+), 227 (D^+-CH_2CO-CO), 184 ($E^{+\bullet}$-CH_2CO-CO), 169 ($G^{+\bullet}$- $H^\bullet$), 129 (SR^+ + 2H), 128 (SR^+ + H = $G^{+\bullet}$-CH_2CO), 127 (SR^+ = $G^{+\bullet}$-$CH_3CO^\bullet$), (type 2) m/z 242 ($I^{+\bullet}$), 227 ($I^{+\bullet}$-$CH_3^\bullet$), 184 ($I^{+\bullet}$-$(CH_3)_2CO$), 169 ($I^{+\bullet}$-$(CH_3)_2CO$-$CH_3^\bullet$), 153 (H^+-$(CH_3)_2CO$-CO-$2H_2$), 113 (L^+), 100 ($Q^{+\bullet}$), 85 ($Q^{+\bullet}$- $CH_3^\bullet$), 81 ($I^{+\bullet}$-$(CH_3)_2CO$-CO-H_2O-CH_2CO-$CH_3^\bullet$), 43 (base peak, CH_3CO^+); (type 3) 244 (B^+-C_3H_3NO or $E^{+\bullet}$-C_2H_2), 242 ($E^{+\bullet}$-CO), 228 ($E^{+\bullet}$-C_2H_2O), 227 ($E^{+\bullet}$-CHNO), 201 ($E^{+\bullet}$-C_3H_3NO), 114($F^{+\bullet}$-C_3H_3NO), 86 (SR^+ -CHNO).

Anal. Calcd. for $2(C_{16}H_{22}N_2O_6S)\bullet C_6H_{12}$: C, 55.34; H, 6.80. Found: C, 55.06; H, 6.87.

6-*S*-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose (**4**).

Synthesis of compound **4** was performed by the general procedure with 1.0 g of 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose and 5.0 g of sodium sulphide nonahydrate. The nucleophilic species used was the commercial sodium sulfide. The crude yield was 71% as the product partially distills under reduced pressure. When the crude product was separated from the reaction mixture by extraction with methylene chloride and water, we obtained it in quantitative yield. Purified by flash chromatography it gave a colorless syrup which crystallizes from ethanol:water, 0.47 g yield, 70%, mp 119-121°, $[\alpha]_D$ = -88.7° (chloroform); ^1H nmr: δ 1.33-1.55 (four signals, CH_3-groups) ppm, δ 1.60 (5H); ^{13}C nmr: δ 108.7 and δ 109.2 (quaternary carbons), δ 24.3-26.0 (three signals, CH_3-groups) ppm; ms: (type 1) m/z 199 (A^+-CH_3COOH-H_2), 119 ($E^{+\bullet}$- CH_2CO-$CH_3^\bullet$), 117 ($E^{+\bullet}$-$CH_3^\bullet$-CH_2CO-H_2), 91 ($E^{+\bullet}$-$CH_3^\bullet$-CH_2CO-H_2-CO), 87 ($F^{+\bullet}$-H_2), 48 ($G^{+\bullet}$-CO), 47 ($G^{+\bullet}$-CO-$H^\bullet$); (type 2) m/z 243 (H^+), 185 (H^+-$(CH_3)_2CO$), 167 (H^+-$(CH_3)_2CO$-$CH_3^\bullet$), 127 ($I^{+\bullet}$-$(CH_3)_2CO$-CH_2CO-$CH_3^\bullet$), 113 (L^+), 100 ($Q^{+\bullet}$), 85 ($Q^{+\bullet}$-$CH_3^\bullet$), 83 (base peak, $I^{+\bullet}$-$(CH_3)_2CO$-$CH_3^\bullet$-CH_3COOH-C_2H_2), 81 ($I^{+\bullet}$-$(CH_3)_2CO$-CO-H_2O-CH_2CO-$CH_3^\bullet$).

Anal. Calcd. for $C_{12}H_{20}O_5S$: C, 52.16; H, 7.25. Found: C, 52.43; H, 7.17.

6-S-Allyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose (**5**).

The crude product, obtained by the general procedure on 1.2 g of 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose with 0.8 ml of allyl mercaptan, (92% crude yield), was purified using flash chromatography. It gave a slightly amber syrup, 0.55 g 60% yield, $[\alpha]_D$ = -72.9 (chloroform); ^1H nmr: δ 3.09 (dd, H-1'a, $J_{1'a\text{-}2'}$ = 7.4 Hz, $J_{1'a\text{-}1'b}$ = 12.4 Hz), δ 3.09 (dd, H-1'b, $J_{1'a\text{-}1'b}$ = 12.4 Hz, $J_{1'b\text{-}2'}$ = 7.4 Hz), δ 5.71 (m, H-2', $J_{2'\text{-}3'a}$ = 16.8 Hz, $J_{2'\text{-}3'b}$ = 9.8 Hz, $J_{2'\text{-}1'a}$ = $J_{2'\text{-}1'b}$ = 7.4 Hz), δ 5.02 (dd, H-3'a, $J_{2'\text{-}3'a}$ = 16.8 Hz, $J_{3'a\text{-}3'b}$ = 1.0 Hz), δ 5.00 (dd, H-3'b, $J_{2'\text{-}3'b}$ = 9.8 Hz, $J_{3'a\text{-}3'b}$ = 1.0 Hz), δ 1.24-1.45 (four signals, CH_3- groups) ppm; ^{13}C nmr: (lit [16]) δ 35.2 (C-1'), δ 134.2 (C-2'), δ 117.2 (C-3'), δ 108.4 and δ 109.1 (quaternary carbons), δ 24.4-26.0 (four signals, CH_3-groups) ppm; ms: (type 1) m/z 316 ($M^{+\bullet}$), 301 (A^+), 171 ($C^{+\bullet}$-$(CH_3)_2CO$-CO-$H^\bullet$), 159 ($E^{+\bullet}$-CH_2CO-$CH_3^\bullet$), 143 ($C^{+\bullet}$-$(CH_3)_2CO$-CO-$H^\bullet$), 141 ($E^{+\bullet}$-CH_2CO-H_2O-$CH_3^\bullet$), 129 ($F^{+\bullet}$), 116 ($G^{+\bullet}$), 87 ($G^{+\bullet}$-CO-$H^\bullet$), 101 ($M^{+\bullet}$-G-$(CH_3)_2CO$-H_2-$CH_3^\bullet$), 75 (SR^+ + 2H), 74 (SR^+ + H), 73 (SR^+), 72 ($C_3H_4S^{+\bullet}$); (type 2) m/z 243 (H^+), 185 (H^+-$(CH_3)_2CO$), 171 ($K^{+\bullet}$-CH_2CO- $CH_3^\bullet$), 127 ($I^{+\bullet}$-$(CH_3)_2CO$-CH_2CO-$CH_3^\bullet$), 113 (L^+), 100 ($Q^{+\bullet}$), 85 ($Q^{+\bullet}$- $CH_3^\bullet$), 81 ($I^{+\bullet}$-$(CH_3)_2CO$-CO-H_2O-CH_2CO-$CH_3^\bullet$), 71 ($I^{+\bullet}$-$(CH_3)_2CO$-2CO-CH_2CO-$CH_3^\bullet$), 43 (base peak, CH_3CO^+); (type 3) m/z 217 (D^+-C_2H_2), 189 ($E^{+\bullet}$-$C_2H_3^\bullet$), 131 ($E^{+\bullet}$-$CH_3^\bullet$-CH_2CO-C_2H_4), 103 ($F^{+\bullet}$-C_2H_2).

Anal. Calcd. for $C_{15}H_{24}O_5S$: C, 56.96; H, 7.59. Found: C, 56.72; H, 7.83.

6-*S*-Thiophenyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose (**6**).

The title compound was obtained by the general procedure, on 0.9 g of 6-*O*-tosyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose with 0.5 ml of thiophenol. It was purified by flash chromatography and gave an amber syrup, 0.62 g, 81% yield, $[\alpha]_D$ = -98.5° (chloroform), ^1H nmr: δ 7.09-7.40 (m, H-aromatics, 5H), δ 1.23-1.45 (four signals, CH_3-groups) ppm; ^{13}C nmr (model compound: thiophenol, lit [17]) δ 135.7 (C-1'), δ 129.4 (C-2' and C-6'), δ 128.8 (C-3' and C-5'), δ 126.0 (C-4'), 108.4 and δ 109.2 (quaternary carbons), δ 24.4-25.9 (four signals, CH_3-groups) ppm; ms: (type 1) m/z 352 ($M^{+\bullet}$), 337 (A^+), 219 (D^+-CH_2CO-H_2O), 152 ($G^{+\bullet}$), 123 ($G^{+\bullet}$-CO-$H^\bullet$) 111 (SR^+ + 2H), 110 (SR^+ + H), 109 (SR^+); (type 2) m/z 243 (H^+), 185 (H^+-$(CH_3)_2CO$), 171 ($K^{+\bullet}$-CH_2CO-$CH_3^\bullet$), 127 ($I^{+\bullet}$-$(CH_3)_2CO$-CH_2CO-CH_3), 113 (L^+), 100 ($Q^{+\bullet}$), 85 ($Q^{+\bullet}$-$CH_3^\bullet$), 81 ($I^{+\bullet}$-$(CH_3)_2CO$-CO-H_2O-CH_2CO-$CH_3^\bullet$), 71 ($I^{+\bullet}$-$(CH_3)_2CO$-2CO-CH_2CO-$CH_3^\bullet$), 43 (base peak, CH_3CO^+); (type 3) m/z 139 ($F^{+\bullet}$-C_2H_2), 77 ($C_6H_5^+$).

Anal. Calcd. for $C_{18}H_{24}O_5S$: C, 61.36; H, 6.82. Found: C, 61.65; H, 7.06.

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