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DERIVATIVES OF 6-AMINO-6-DEOXY-D-GALACTOSE*

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ABSTRACT

2-Cyano-3,3-bis(methylthio)acrylonitrile was treated with 6-amino-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, 6-amino-6-deoxy-D-galactose diethyl dithioacetal, and 6-amino-6-deoxy-2,3:4,5-di-*O*-isopropylidene-D-galactose diethyl dithioacetal to give the corresponding 6-deoxy-6-(2,2-dicyano-1-methylthiovinylamino)-D-galactose derivatives. 6-Deoxy-6-(2,2-dicyano-1-methylthiovinylamino)-D-galactose diethyl dithioacetal yielded 6-amino-6-deoxy-5-*O*,6-*N*-(2,2-dicyanovinylidene)-D-galactose diethyl dithioacetal. On heating with bases, 6-deoxy-6-(2,2-dicyano-1-methylthioacrylamido)-D-galactose afforded a mixture of two compounds.

INTRODUCTION

In a previous paper[1], we reported the reaction of 1-deoxy-1-methylamino-hexitols with 2-cyano-3,3-bis(methylthio)acrylonitrile (**1**). Elimination of both methylthio groups afforded 2,2-dicyanovinylidene derivatives, which were shown to be oxazolidines. The conversion of similar acyclic to cyclic nucleosides by intramolecular cyclisation has been reviewed[2,3]. Our program of incorporating parts of sugar molecules into heterocyclic ring systems by reaction with push–pull alkenes has led us to some 6-amino-6-deoxy-D-galactose derivatives. 6-Deoxy-1,2:3,4-di-*O*-isopropylidene-6-phthalimido-α-D-galactopyranose (**2**) and the corresponding 6-amino-6-deoxy compound **3** are readily available starting materials and were synthesized according to Coxon and Reynolds[4]. The reaction of push–pull alkenes, such as **1**, with amines and amino alcohols has been thoroughly investigated, but little work was done on their reaction with amino or hydrazino sugars. For example, 2-amino-2-deoxy-D-glucose was treated with ethyl 2-cyano-3-ethoxyacrylate[5], and D-ribosylhydrazine with another 3-ethoxyacrylic acid derivative[6].

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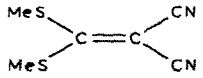

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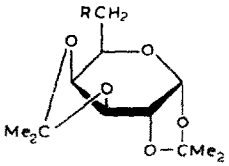
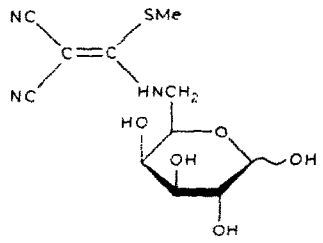


2 R = Phth
3 R = NH_2
4 R = NH—C(SMe)=C(CN)$_2$

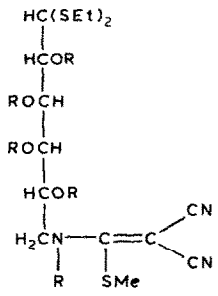


5

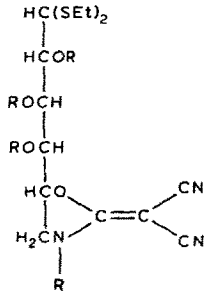
RESULTS AND DISCUSSION

In the present work 6-deoxy-6-(2,2-dicyano-1-methylthiovinylamino)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**4**) was synthesized from **1** by nucleophilic substitution of one of the methylthio groups by the amino group of 6-amino-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**3**). The n.m.r. spectra of **4** were consistent with the assigned *N,S*-ketene acetal structure. Selective deprotection failed, although free 6-deoxy-6-(2,2-dicyano-1-methylthiovinylamino)-D-galactose (**5**) was readily obtained. The pyranose structure of **5** seemed to be rather stable, and no cyclic ketene acetal involving 5-*O*,6-*N* was formed by elimination of the second methylthio group. Such cyclic, five-membered *N,O*-acetals were the only products obtained in our experiments with aminodeoxyhexitols[1]. It is well known that substitution of both methylthio groups on treatment of ketene dithioacetals with nucleophiles frequently requires basic catalysts, and heating of **5** in pyridine afforded a mixture of a furanose and pyranose compound as detected by ^{13}C-n.m.r. spectroscopy. The isolated mixture is still under investigation.

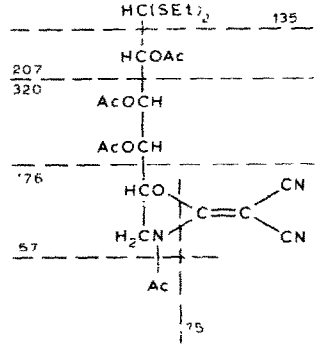
In order to obtain an open-chain derivative of **5**, 6-deoxy-6-(2,2-dicyano-1-methylthiovinylamino)-D-galactose diethyl dithioacetal (**6**) was synthesized by



6 R = H
7 R = Ac



8 R = H
9 R = Ac

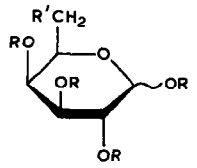


Scheme 1

treatment with ethane thiol in the usual manner. The open-chain *N,S*-acetal **6** seems to be less reactive than expected and could be isolated in 61% yield after recrystallization from ethanol. The presence of both nitrile groups was indicated by i.r. spectroscopy and that of the methylthio-group by ^{1}H-n.m.r. spectroscopy. The elimination of the second methylthio group required the presence of a base; triethylamine in boiling toluene afforded 6-amino-6-deoxy-5-*O*,6-*N*-(2,2-dicyano-1-vinylidene)-D-galactose diethyl dithioacetal (**8**). Both cyano groups were detected by i.r. spectroscopy and the absence of the methylthio group by ^{1}H-n.m.r. spectroscopy. Thus, ring closure had occurred in the expected way and not *via* addition of a hydroxyl to a cyano group. Acetylation of **6** and **8** in the usual way afforded a pentaacetate **7** and a tetraacetate **9**, respectively. The latter showed by m.s. analysis several oxazolidine-containing fragments (see Scheme 1). If compound **6** as well as **8** are regarded as push–pull alkenes, then the facility with which acetylation of the nitrogen atoms took place would be remarkable, because the electron density at these nitrogen atoms would be not very high.

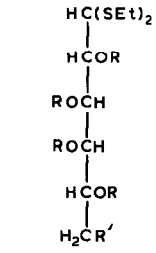
Coxon and Reynolds[4] did not describe the deblocking of the phthalimido derivative **2**. In order to obtain **6** by an alternative route, **2** was treated with trifluoroacetic acid to give 6-deoxy-6-phthalimido-D-galactose (**10**), characterized by the tetraacetyl derivative **11**. Dithioacetalation afforded crystalline 6-deoxy-6-phthalimido-D-galactose diethyl dithioacetal (**12**) which, on hydrazinolysis, yielded syrupy 6-amino-6-deoxy-D-galactose diethyl dithioacetal (**13**), characterized by the crystalline pentaacetyl derivative **14**. Condensation of crude **13** with **1** afforded **6**. However, this synthesis of **6** is less efficient than thioacetalation of **5** owing to the formation of by-products by the Gabriel synthesis.

Isopropylidenation of D-galactose dithioacetals has been investigated by Pacsu and Löb[7], and by Kochetkov and Usov[8]. The latter authors described the isolation of a mixture of 2,3:4,5- and 2,3:5,6-di-*O*-isopropylidene derivatives, in-



10 R = H, R′ = Phth

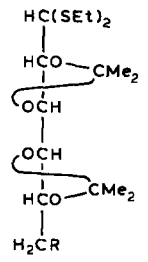
11 R = Ac, R′ = Phth



12 R = H, R′ = Phth

13 R = H, R′ = NH_2

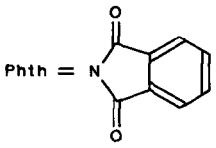
14 R = Ac, R′ = NH—Ac



15 R = Phth

16 R = NH_2

17 R = NH—C(SMe)=C(CN)$_2$



dicating the formation of 5-membered dioxolan rings in each case. As **12** has no OH-6, treatment with 2,2-dimethoxypropane in acetone yielded crystalline 6-deoxy-2,3:4,5-di-*O*-isopropylidene-6-phthalimido-D-galactose diethyl dithioacetal (**15**), the dioxolan rings being evidenced by ^{13}C-n.m.r. spectroscopy[9,10]. Hydrazinolysis of **15** yielded 6-amino-6-deoxy-2,3:4,5-di-*O*-isopropylidene-D-galactose diethyl dithioacetal (**16**), which was not isolated in pure form, but immediately condensed with **1** to give the 6-(2,2-dicyano-1-methylthio)vinylamino derivative **17**, further deblocked to afford **6**.

EXPERIMENTAL

General methods. — Melting points were determined with a Boetius micro apparatus BHMK 05 (VEB Rapido, Dresden) and are uncorrected. Optical rotations were measured on solutions in a 1-dm cell with an automatic polarimeter "Polamat A" (VEB C. Zeiss, Jena). I.r. spectra were recorded with a UR 20 instrument (VEB C. Zeiss, Jena). N.m.r. spectra were recorded with Tesla-spectrometers model BS 487 C at 80 MHz (^{1}H), and Bp 497 at 25.2 MHz (^{13}C). Chemical shifts are given relative to the signal of internal tetramethylsilane, ^{13}C-signal assignments were made by comparison with the spectra of related compounds[1,4,12,13]. Mass spectra were recorded with an LKB 9000 mass spectrometer. T.l.c. was performed on glass plates coated with Silica gel G (E. Merck AG, Darmstadt) and detection by spraying with a mixture consisting of methanol (45 mL), water (45 mL), conc. H_2SO_4 (10 mL), H_2MoO_4 (1 g), and $Ce(SO_4)_2$ (1 g). For column chromatography, Silica gel 60 (0.05–0.20 mm, E. Merck AG, Darmstadt) was used.

6-Deoxy-6-(2,2-dicyano-1-methylthiovinylamino)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**4**). — A solution of **3** (ref. 4) (2.43 g, 10 mmol) and **1** (ref. 11) (1.70 g, 10 mmol) in chloroform (40 mL) was refluxed for 30 min. The solvent was removed *in vacuo* and the resulting crude material crystallized from a small amount of ethanol to give pure **4**, yield 2.68 g (70%), colorless crystals, m.p. 156°, $[\alpha]_D^{20}$ −183° (*c* 1, methanol); ν_{max}^{Nujol} 2200 and 2220 cm^{-1} (CN); ^{1}H-n.m.r. ($CDCl_3$): δ 1.32 (s, 6 H, CMe_2), 1.50 (s, 6 H, CMe_2), 2.57 (s, 3 H, SMe), 3.73–4.07 (m, 3 H, H-5,6,6′), 4.20–4.42 (m, 2 H, H-2,4), 4.65 (dd, 1 H, H-3), 5.52 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), and 6.86 (s, 1 H, NH); ^{13}C-n.m.r.: δ 16.8 (SMe), 24.0, 24.8, 25.9, 26.1 (4 Me), 47.7 (C-6), 52.6 [=*C*$(CN)_2$], 65.1 (C-5), 70.5 (C-2), 70.8 (C-3), 71.9 (C-4), 96.3 (C-1), 109.0 (*C*Me_2), 115.0, 115.5 (2 CN), and 173.8 (≡*C*SMe).

Anal. Calc. for $C_{17}H_{23}N_3O_5S$ (381.4): C, 53.53; H, 6.08. Found: C, 53.25; H, 6.50.

6-Deoxy-6-(2,2-dicyano-1-methylthiovinylamino)-D-galactose (**5**). — A mixture of **4** (381 mg, 1 mmol) and 90% trifluoroacetic acid (5 mL) was stirred at ambient temperature and deblocking monitored by t.l.c. (10:1, dichloromethane–ethyl acetate). After 18 h, toluene (40 mL) was added and the solvents were evaporated *in vacuo*. The residue crystallized from ethanol to yield **5** (240 mg, 80%), m.p. 172°, $[\alpha]_D^{21}$ +112° (*c* 1, pyridine); ν_{max}^{Nujol} 2205 and 2225 cm^{-1} (CN); ^{1}H-n.m.r.

[($^2H_6$)Me_2SO]: δ 2.52 (s, 3 H, SMe), 3.12–3.30 (m, 2 H, H-6,6'), 3.47–3.72 (m, 4 H, H-2,3,4,5), 3.92–4.87 (m, 4 H, 4 OH), 6.52 (br.s, 1 H, H-1), and 8.60 (br.s, 1 H, NH).

Anal. Calc. for $C_{11}H_{15}N_3O_5S$ (301.3): C, 43.85; H, 5.02. Found: C, 43.59; H, 5.00.

A solution of **5** (900 mg, 3 mmol) in pyridine (10 mL) was heated to 90° for 1 h and then cooled to 0°. Acetic anhydride (5 mL) was added and the mixture stored at ambient temperature for 24 h. Chloroform (50 mL) was added and the solution extracted with 15% $KHSO_4$ solution, water, saturated $NaHCO_3$ solution, and again water (twice each). Drying with cotton and evaporation *in vacuo* yielded 1.0 g (79%) of, presumably, a mixture of 6-acetamido-1,2,3-tri-*O*-acetyl-6-deoxy-5-*O*,6-*N*-(2,2-dicyanovinylidene)-D-galactofuranose and 1,2,3-tri-*O*-acetyl-6-acetamido-6-deoxy-4-*O*,6-*N*-(2,2-dicyanovinylidene)-D-galactopyranose, soft. 35–45°; ν_{max}^{Nujol} 2225 sh, 2235 sh (CN), and 1750 sh cm^{-1} (CO); ^{1}H-n.m.r. ($CDCl_3$): δ 1.64–1.84 (m, OAc), 1.84–1.88 (2 s, NAc), and 4.91–5.30 (m, H-$1_{furanose}$ and H-$1_{pyranose}$); ^{13}C-n.m.r. (signals doubled), 99.0 (C-$1_{furanose}$), 92.5 (C-$1_{pyranose}$), 170.8–166.8 (2 × 4 CH_3CO), 49.5, and 49.8 (2 C-6).

Anal. Calc. for $C_{18}H_{19}N_3O_9$ (421.4): C, 51.30; H, 4.56; N, 9.97. Found: C, 51.03; H, 5.00; N, 9.83.

6-Deoxy-6-(2,2-dicyano-1-methylthiovinylamino)-D-galactose diethyl dithioacetal (**6**). — *From* **5**. To compound **5** (1.20 g, 4 mmol) in conc. HCl (5 mL) was added ethanethiol (2.48 g, 40 mmol) and the mixture shaken for 1 h. The crystalline crude product was filtered off, washed with benzene and ether, and recrystallized from ethanol to yield **6** (1.00 g, 61%), m.p. 117°, $[\alpha]_D^{21}$ +5.6° (*c* 1, pyridine); ν_{max}^{Nujol} 2200, 2215 (CN), 3290, 3350, 3425, and 3535 cm^{-1} (NH, OH); ^{1}H-n.m.r. [($^2H_6$)Me_2SO]: δ 1.16 (t, 6 H, 2 CH_2CH_3), 2.57 (s, 3 H, SMe), 2.61 (q, 4 H, 2 CH_2CH_3), 3.30–4.36 (complex m, 11 H, H-1,2,3,4,5,6,6', 4 OH), and 8.52 (2, 1 H, NH).

Anal. Calc. for $C_{15}H_{25}N_3O_4S_2$ (407.6): C, 44.20; H, 6.18; N, 10.31; S, 23.60. Found: C, 43.95; H, 6.40; N, 10.23; S, 23.60.

From **17**. Compound **17** (490 mg, 1 mmol) was stirred with 90% trifluoroacetic acid (5 mL) and the solution processed as described for **5** to yield a crude material from which **6** (160 mg, 36%) could be separated in crystalline form. From the mother liquors, compound **8** (100 mg, 28%), m.p. 77°, was separated by column chromatography (11:5:3 chloroform–ethyl acetate–methanol).

From **12**. To a solution of **12** (830 mg, 2 mmol) in ethanol (20 mL) was added 72% hydrazine hydrate (0.5 mL). The mixture was refluxed for 1.5 h, evaporated, and the residue codistillated with 5:1 toluene–ethanol (twice) and toluene (once) *in vacuo* to give mainly crude **13**. This was dissolved in ethanol (20 mL), **1** (380 mg, 2.2 mmol) was added, and the solution refluxed for 1 h. Evaporation *in vacuo* yielded a colorless solid which on crystallization from ethanol was fractionated to give *N,N*-phthaloylhydrazine and unchanged **1**. From the mother liquor, syrupy **6** was obtained, but crystallization was cumbersome owing to by-products. Chromatography, as described earlier, gave a yield not exceeding 30%.

2,3,4,5-Tetra-O-acetyl-6-[N-(2,2-dicyano-1-methylthiovinyl)acetamido]-6-deoxy-D-galactose diethyl dithioacetal (**7**). — To a solution of **6** (810 mg, 2 mmol) in pyridine (10 mL) was added acetic anhydride (4 mL) and the solution stored at 4° for 7 h. Chloroform (50 mL) was added and the solution extracted to remove pyridine as described for the treatment of **5**. The dried (cotton) organic layer was evaporated *in vacuo* and the residue dissolved in ethanol. Some **9** crystallized in some cases and was separated by filtration. The filtrate was chromatographed on silica gel (1:1, toluene–ethyl acetate) to give **7**, colorless crystals (750 mg, 60%), m.p. 170°, $[\alpha]_D^{23}$ +65.4° (*c* 1, acetone); ν_{max}^{Nujol} 2225, 2235 (CN), 1760, and 1770 cm^{-1} (CO); ^{1}H-n.m.r. ($CDCl_3$): δ 1.23 (t, 6 H, 2 CH_2CH_3), 2.10 and 2.23 (2 s, 15 H, 4 OAc and NAc), 2.53 (s, 3 H, SMe): 2.62 (q, 4 H, 2 CH_2CH_3), 3.74–5.32 (m, 6 H, H-2,3,4,5,6,6'), and 5.72 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1).

Anal. Calc. for $C_{25}H_{35}N_3O_9S_3$ (617.8): C, 48.60; H, 5.71. Found: C, 49.05; H, 6.00.

6-Amino-6-deoxy-5-O,6-N-(2,2-dicyanovinylidene)-D-galactose diethyl dithioacetal (**8**). — To a mixture of **6** (410 mg, 1 mmol) and toluene (10 mL) was added triethylamine (0.5 mL). The resulting solution was heated to 90° for 1 h with mechanical stirring. After evaporation *in vacuo*, the residue crystallized from ethanol to yield **8** (300 mg, 83%), colorless prisms, m.p. 77°, $[\alpha]_D^{23}$ −18.8° (*c* 1, acetone); ν_{max}^{KBr} 2205, 2225 (CN), 3200, 3260, and 3410 cm^{-1} (NH, OH); ^{1}H-n.m.r. [($^2H_6$)Me_2SO]: δ 1.14 (t, 6 H, 2 CH_2CH_3), 2.60 (q, 4 H, 2 CH_2CH_3), 3.34–4.84 (complex m, 9 H, H-2,3,4,5,6,6', 3 OH), and 5.34 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1).

Anal. Calc. for $C_{14}H_{21}N_3O_4S_2$: (359.5): C, 46.78; H, 5.89. Found: C, 46.80; H, 6.01.

6-Acetamido-2,3,4-tri-O-acetyl-6-deoxy-5-O,6-N-(2,2-dicyanovinylidene)-D-galactose diethyl dithioacetal (**9**). — To a solution of **8** (359 mg, 1 mmol) in pyridine (5 mL) was added acetic anhydride (2 mL). The mixture was stirred for 8 h at 60°. After cooling to ambient temperature, chloroform (30 mL) was added and pyridine removed by extraction (see treatment of **5**). The chloroform solution was dried (cotton) and evaporated *in vacuo*. Crystallization of the residue from ethanol afforded **8** (400 mg, 76%), m.p. 149°, $[\alpha]_D^{20}$ −15.8° (*c* 1, chloroform); ν_{max}^{Nujol} 2230, 2240, 1760, and 1770 cm^{-1} (CO); ^{1}H-n.m.r. ($CDCl_3$): δ 1.18 (t, 6 H, 2 CH_2CH_3), 2.02, 2.05, 2.13, and 2.28 (4 s, 12 H, 3 OAc and NAc), 2.61 (q, 4 H, 2 CH_2CH_3), 3.77–4.44 (m, 3 H, H-5,6,6'), 4.87–5.28 (m, 3 H, H-2,3,4), and 5.78 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1).

Anal. Calc. for $C_{22}H_{29}N_3O_8S_2$ (527.6): C, 50.08; H, 5.54; N, 7.96; S, 12.16. Found: C, 49.77; H, 5.61; N, 8.26; S, 12.31.

6-Deoxy-6-phthalimido-D-galactose (**10**). — To compound **2** (3.89 g, 10 mmol) was added 90% trifluoroacetic acid (40 mL) and the mixture stirred for 1 h at ambient temperature. The resulting solution was evaporated *in vacuo* and the acid removed by codistillation with toluene (twice). The residue crystallized from 1:1 ethanol–water to yield colorless **10** (3.07 g, 79%), m.p. 185°, $[\alpha]_D^{21}$ +125° (*c* 1.1, pyridine); ^{1}H-n.m.r. [($^2H_6$)Me_2SO]: δ 3.22–4.22 (complex m, 7 H, H-

2,3,4,5,6,6', and 1 OH, exchanged with D_2O), 5.0 (d, 1 H, $J_{1,2}$ 10 Hz, H-1), 5.02–5.24 (br.s, 3 H, exchanged with D_2O, 3 OH), and 7.80 (br.s, 4 H, C_6H_4).

Anal. Calc. for $C_{14}H_{15}NO_7$ (309.3): C, 54.37; H, 4.89. Found: C, 53.98; H, 4.80.

*1,2,3,4-Tetra-*O*-acetyl-6-deoxy-6-phthalimido-β-*D*-galactopyranose* (**11**). — To a solution of **10** (1.54 g, 5 mmol) in pyridine (15 mL) was added, with cooling to 0°, acetic anhydride (7 mL). The solution was stored at ambient temperature for 24 h and then poured into ice–water. The precipitate was filtered off and washed with cold water. Recrystallization from 1:1 methanol–water afforded **11**, yield 2.10 g (87%), m.p. 93°, $[\alpha]_D^{20}$ +36.5° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.82, 1.92, 1.97, 2.14 (4 s, 12 H, 4 OAc), 3.70–4.02 (m, 2 H, H-6,6'), 4.30 (q, 1 H, H-5), 5.04–5.42 (m, 3 H, H-2,3,4), 5.69 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), and 7.70 (m, 4 H, C_6H_4).

Anal. Calc. for $C_{22}H_{23}NO_{11}$: C, 55.35; H, 4.86. Found: C, 54.96; H, 5.00.

*6-Deoxy-6-phthalimido-*D*-galactose diethyl dithioacetal* (**12**). — To a suspension of **10** (1.17 g, 4 mmol) in conc. HCl (4 mL) was added ethanethiol (2.5 g, 40 mmol) and the mixture was processed as described for **6**, yield 1.50 g (65%), m.p. 198°, $[\alpha]_D^{21}$ +32° (*c* 1, pyridine); ^{1}H-n.m.r. [($^2H_6$)Me_2SO]: δ 1.14 (t, 6 H, 2 CH_2CH_3), 2.64 (q, 4 H, 2 CH_2CH_3), 3.37–4.44 (complex m, 11 H, H-1,2,3,4,5,6,6', and 4 OH), and 7.84 (br.s, 4 H, C_6H_4).

Anal. Calc. for $C_{18}H_{25}NO_6S_2$ (415.5): C, 52.03; H, 6.06; N, 3.37; S, 15.43. Found: C, 51.85; H, 6.10; N, 3.47; S, 15.72.

*6-Acetamido-2,3,4,5-tetra-*O*-acetyl-6-deoxy-*D*-galactose diethyl dithioacetal* (**14**). — Compound **12** (831 mg, 2 mmol) was hydrazinolyzed as described for **6** to give crude **13**. This was dissolved in pyridine (10 mL), and acetic anhydride (4 mL) was added. After storage for 3 d at ambient temperature, chloroform (50 mL) was added and the solution treated to remove pyridine as described for the treatment of **5**. The organic layer was dried (cotton) and evaporated to dryness *in vacuo*. Crystallization of the residue from ethanol gave **14** (450 mg, 45%), colorless crystals, m.p. 105°, $[\alpha]_D^{20}$ −17° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.19 (t, 6 H, 2 CH_2CH_3), 1.83–2.14 (m, 15 H, 4 OAc, NAc), 2.54 (q, 4 H, 2 CH_2CH_3), 3.02–3.89 (m, 3 H, H-5,6,6'), and 4.94–6.07 (m, 4 H, H-1,2,3,4).

Anal. Calc. for $C_{20}H_{33}NO_9S_2$ (495.6): C, 48.47; H, 6.71; N, 2.83; S, 12.94. Found: C, 49.00; H, 7.00; N, 2.94; S, 12.68.

*6-Deoxy-2,3:4,5-di-*O*-isopropylidene-6-phthalimido-*D*-galactose diethyl dithioacetal* (**15**). — To a suspension of **12** (415 mg, 1 mmol) in dry acetone (20 mL) were added *N,N*-dimethylformamide (1 mL), 2,2-dimethoxypropane (0.92 g, 10 mmol), and conc. H_2SO_4 (1 drop) and the mixture was refluxed for 2 h. The solution was cooled to room temperature, neutralized with $Pb(CO_3)_2 \cdot Pb(OH)_2$, centrifuged, and filtered by suction through silica gel. After evaporation *in vacuo*, the filtrate afforded a syrupy residue which crystallized after addition of 7:3 hexane–ethyl acetate, long needles (350 mg, 72%), m.p. 106°, $[\alpha]_D^{20}$ −46° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 0.94 (t, 6 H, 2 CH_2CH_3), 1.13, 1.15, 1.27, 1.33 (4 s, 12 H, 2

CMe_2), 2.62 (q, 4 H, 2 CH_2CH_3), 3.82–4.32 (m, 6 H, H-2,3,4,5,6,6'), 4.41 (d, 1 H, $J_{1,2}$ 6.5 Hz, H-1), and 7.74 (m, 4 H, C_6H_4); ^{13}C-n.m.r.: δ 168.2 (CO), 133.9, 132.4, 123.2 (C_6H_4), 109.9 (CMe_2), 77.5, 78.9, 81.1, 84.5 (C-2,3,4,5), 51.6 (C-1), 40.4 (C-6), 26.9, 26.4, 25.3, 25.1 [2 C(CH_3)$_2$], 26.9, 26.4 (CH_2CH_3), and 14.5 (CH_2CH_3).

Anal. Calc. for $C_{24}H_{33}NO_6S_2$ (495.7): C, 58.16; H, 6.71; N, 2.83; S, 12.94. Found: C, 57.95; H, 6.75; N, 2.88; S, 12.98.

*6-Deoxy-6-(2,2-dicyano-1-methylthiovinylamino)-2,3:4,5-di-O-isopropylidene-*D*-galactose diethyl dithioacetal* (**17**). — To a solution of **15** (1.98 g, 4 mmol) in ethanol (20 mL) was added 72% hydrazine (1 mL). After being refluxed for 1.5 h, the solution was evaporated to dryness, the residue extracted by dichloromethane, and the organic layer washed with 5% NaOH. The alkaline layer was reextracted with dichloromethane and the combined organic layers washed with water, dried (cotton), and evaporated *in vacuo* to give **16** (1.24 g, 85%), colorless syrup. A solution of this in chloroform (20 mL) was treated with **1** (0.75 g, 4.4 mmol) at reflux for 30 min. Evaporation *in vacuo* yielded a pale-yellow syrup which was purified by column chromatographie (2:1 toluene–ethyl acetate), yield 1.46 g (75%), $[\alpha]_D^{23}$ −24.2 (*c* 1, acetone); ν_{max}^{Nujol} 2205 and 2215 cm^{-1} (CN); ^{1}H-n.m.r. ($CDCl_3$): δ 1.24 (t, 6 H, 2 CH_2CH_3), 1.37 and 1.43 (2 s, 12 H, 2 CMe_2), 2.59 (s, 3 H, SMe), 2.68 (q, 4 H, 2 CH_2CH_3), 3.60–4.22 (m, 6 H, H-2,3,4,5,6,6'), 4.30 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), and 6.79 (br.s, 1 H, NH).

Anal. Calc. for $C_{21}H_{33}N_3O_4S_3$ (487.7): C, 51.72; H, 6.82; N, 8.62; S, 19.72. Found: C, 51.87; H, 7.00; N, 8.80; S, 19.90.

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