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C-Glycosyl Nucleosides. VI. Synthesis and Crystal Structure of Dithiane Glycoside Analog[1]

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In order to determine the absolute configuration of product from a reaction of sugar lactone and lithiated heterocycles, an X-ray crystal structural analysis of 1-(1,3-dithian-2-yl)-2,3: 5,6-di-*O*-isopropylidene-*β*-L-gulofuranose was carried out. This compound was prepared from 2,3: 5,6-di-*O*-isopropylidene-L-gulono-1,4-lactone and lithiated 1,3-dithiane. The crystals are monoclinic with space group $P2_1$ and unit cell dimensions of $a=18.566(7)$ Å, $b=9.544(2)$ Å, $c=6.462(1)$ Å, $\beta=91.68(3)°$, $z=2$. The X-ray analysis was carried out with the heavy-atom method and refined by the block-diagonal least-squares method including anisotropic thermal parameters, and the final R value was 0.071. In conclusion, the absolute configuration of the anomeric position was determined to be R chirality.

Keywords——modified nucleoside; 1-(1,3-dithian-2-yl)-2,3:5,6-di-*O*-isopropylidene-*β*-L-gulofuranose; lithiated 1,3-dithiane; mechanism of stereoselective reduction; circular dichroism; X-ray analysis; stereochemistry; H-bonding

The synthesis of 5-substituted pyrimidines by reaction of 2,4-dibenzyloxypyrimidine with sugar *γ*-lactones was first reported by Asbun and Binkley.[3] They obtained crystalline 5-*α*-D-mannityluracil [5-(D-*glycero*-D-*talo*-hexahydroxyhexyl)uracil] and 5-*β*-D-gulityluracil [5-(D-*glycero*-L-*talo*-hexahydroxyhexyl)uracil] in low yield(13 and 15% yield, respectively) by the reaction of the pyrimidine with 2,3: 5,6-di-*O*-isopropylidene-*γ*-D-mannolactone or -D-gulonolactone followed by removal of the protecting groups. The assignment of the C-1′ configuration was based on the optical rotatory dispersion (ORD) data. The assignment of 5-*β*-D-gulityluracil was further confirmed by ^{1}H nuclear magnetic resonance (NMR) studies of 5-D-gulopyranoyluracil ($J_{1',2'}=6$ Hz) prepared in several steps from the open-chain derivative.

Lerch *et al.*[4] described the reaction of 2,4: 3,5-di-*O*-benzylidene-D-ribose with 2,4-di-*tert*-butoxy-5-lithiopyrimidine. They[4] isolated 5-(2,4: 3,5-di-*O*-benzylidene-D-*allo*-pentahydroxypentyl)-2,4-di-*tert*-butoxypyrimidine and its *altro* isomer from the reaction mixture. The C-1′ configuration was assigned on the basis of ORD studies and careful chemical transformation of the open-chain derivatives (*allo*- and *altro*-compounds) into *α*- and *β*-pseudouridine, respectively, by acid treatment. They also prepared 1′-*O*-*p*-iodobenzoyl derivative of open-chain derivatives (*allo*- and *altro*-compounds) as tiny crystals which were not sufficiently large for X-ray studies.

Reaction of 2,3-*O*-isopropylidene-5-*O*-tetrahydropyranyl-D-ribonolactone with 2-lithio-2-methyl-1,3-dithiane gave C-(1,3-dithiane-2-methyl-2-yl)-2,3-*O*-isopropylidene-5-*O*-tetrahydropyranyl-D-ribofuranose which was isolated as a syrup by Sepulchre *et al.*[5] The C-1′ configuration of this compound was not determined.

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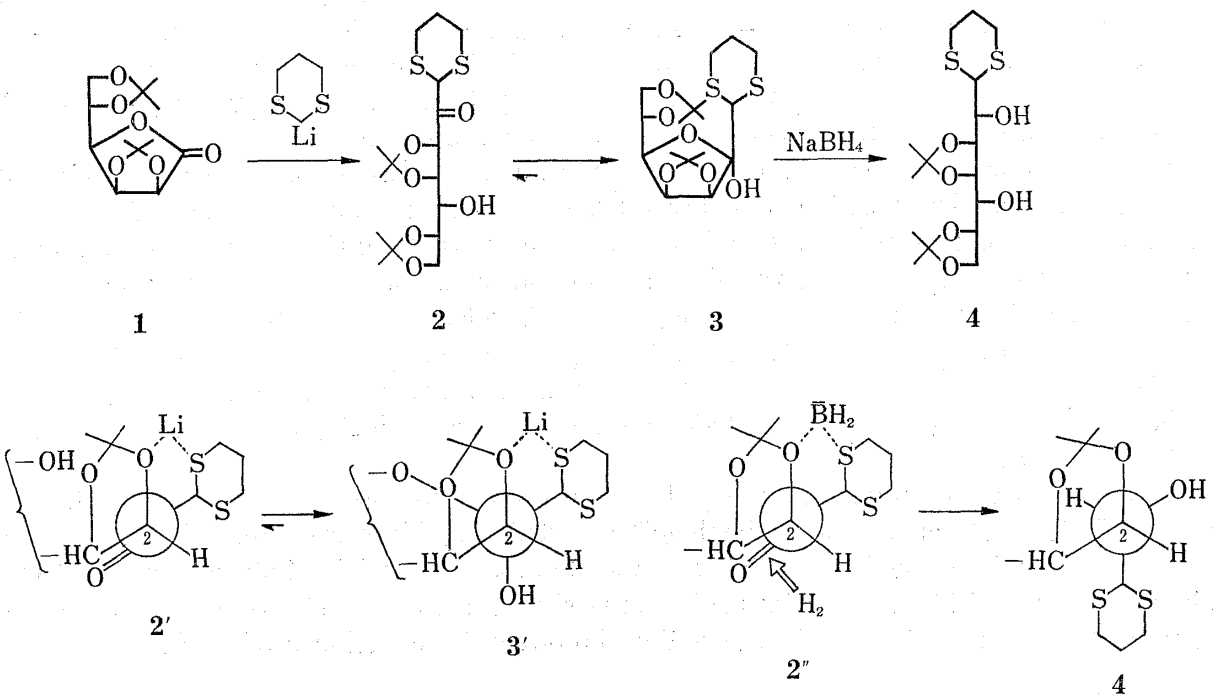

Fig. 1

Previously[6,7] we reported that reactions of lithiated ethynyl compounds or lithiated heterocycles with sugar lactones, *e. g.*, 2,3-*O*-isopropylidene-D-ribono-1,4-lactone and 2,3: 5,6-di-*O*-isopropylidene-L-gulono-γ-lactone, gave the corresponding adducts. Buchanan *et al.*[8] obtained ethynylketose and diethynyl ribitol by the reaction of 2,3-*O*-isopropylidene-D-ribonolactone with ethynyl magnesium bromide, which indicated the presence of keto-form. In our experiments the reaction of sugar lactone with lithiated heterocycles gave cyclic-form adducts in a fair yield, and the configuration of the adducts was assigned by comparing circular dichroism (CD) data of the adducts with those of the corresponding reduced products. The stereochemistry of the adducts was not expected from the Cram's rule.[9]

In this paper, we describe the configurational studies of 1-(1,3-dithian-2-yl)-2,3; 5,6-di-*O*-isopropylidene-β-L-gulofuranose based on X-ray analysis. The conclusions derived confirmed the stereochemistry of the adducts obtained from the reaction of lithiated compounds with sugar lactone.

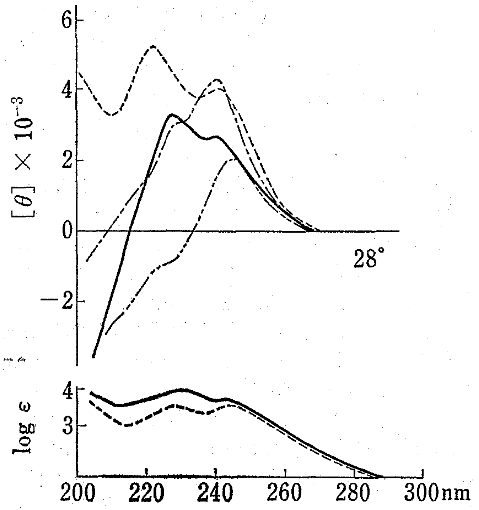

Fig. 2. CD and UV Curves of 1-(1,3-Dithian-2-yl)-2,3: 5,6-di-*O*-isopropylidene-β-L-gulofuranose

(MeOH ——; cyclohexane ----; MeCN —·—) and 1-(1,3-dithian-2-yl)-2,3: 5,6-di-*O*-isopropylidene-hexane-L-*glycero*-D-*galacto*-1,2,3,4,5,6-hexol (MeOH —···—)

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The reaction of 2,3: 5,6-di-*O*-isopropylidene-L-gulono-γ-lactone (**1**) with lithiated dithiane in hexane–tetrahydrofuran below $-75°$ gave 1-(1,3-dithian-2-yl)-2,3: 5,6-di-*O*-isopropylidene-β-L-gulofuranose (**3**) as colorless needles, mp 131—135°. Treatment of **3** with sodium borohydride afforded 1-(1,3-dithian-2-yl)-2,3: 5,6-di-*O*-isopropylidenehexane-L-*glycero*-D-*galacto*-1,2,3,4,5,6-hexol (**4**), mp 136—137°. The reaction of lithiated dithiane proceeded stereoselectively and the isomeric lactols were not detected by thin–layer chromatography (TLC) and gas chromatography. The reaction probably proceeds through an open-chain intermediate (**2**), because lithium is a strong electrophile and is bound with hetero atom in heterocycles and oxygen at position 2. The intermediate (**2'**) formation would fix the configuration of the adduct (**3**), which is not consistent with the Cram's rule. The equilibrium shifts from the open-chain intermediate (**2'**) to cyclized form (**3'**). Similarly, the reduction with sodium borohydride proceeds through the open-chain intermediate (**2**) in which the reagent is bound to hetero atoms to form an intermediate (**2''**) and a single product (**4**) was formed according to the Cram's rule.

The CD curves of polyhydroxyalkyl heterocycles was discussed by Snatzke,10) Chilton,11) and Moffatt.12) Hargreaves and Marshall13) reported the chiroptical properties of ethylene dithioacetals and diethyl dithioacetals of some aldoses. The positive Cotton effects of **3** was observed at 220—247 nm in various solvents as shown in Fig. 2. The same positive Cotton effect at 245 nm was observed in the sodium borohydride reduction product (**4**).

Experimental

1-(1,3-Dithian-2-yl)-2,3: 5,6-di-*O*-isopropylidene-β-L-gulofuranose (3)——To an ether solution (30 ml) of *n*-butyl lithium prepared from lithium (0.2 g, 0.03 mol) and *n*-butyl bromide (2.5 g, 0.02 mol), anhydrous hexane (200 ml) was added and cooled below $-75°$. Then, the solution of 1,3-dithiane (1.2 g, 0.01 mol) in tetrahydrofuran (30 ml) was added dropwise in 30—40 min to the above solution. After this reaction solution was stirred for 45 min below $-75°$, 2,3: 5,6-di-*O*-isopropylidene-L-gulonolactone (**1**, 2.5 g, 0.01 mol) in tetrahydrofuran (100 ml) was added to it and stirring was continued for 3—4 hr. The reaction mixture was treated with saturated ammonium chloride and extracted with ether. The organic layer was washed with water and dried ($MgSO_4$). The extracts were concentrated under reduced pressure to afford 1.2 g (32%) of **3** as colorless needles, mp 131—135°; CD (MeOH) $[\theta]^{28}_{227}$ +3213, $[\theta]_{243}$ +2608; ($CHCl_3$) $[\theta]^{28}_{240}$ +6662; (cyclohexane) $[\theta]^{28}_{220}$ +5485, $[\theta]_{247}$ +3698; UV λ^{MeOH}_{max} 230 (log ε 3.96), 245 (log ε 3.87) nm; IR ν (KBr) 3360 (OH), 1385, 1375 cm^{-1} (gem-CH_3); NMR δ (C_6D_6) 1.04, 1.32, 1.36, 1.42 (s, 12H, CH_3), 1.22—1.69 (m, 2H, $-CH_2-$), 2.20—2.80 (m, 4H, $-SCH_2-$), 3.65 (t, 1H, 5-H), 3.68 (bs, 1H, OH), 4.10—4.60 (m, 4H, 3,4,6-H), 4.62 (s, 1H, –SCHS–), 4.64 (d, $J=4$ Hz, 1H, 2-H); MS *m/e*: 378 (M^+). *Anal.* Calcd. for $C_{16}H_{26}O_6S_2$: C, 50.77; H, 6.92. Found: C, 50.64; H, 6.90.

1-(1,3-Dithian-2-yl)-2,3: 5,6-di-*O*-isopropylidene-hexane-L-*glycero*-D-*galacto*-1,2,3,4,5,6-hexol (4)——To a solution of **3** (378 mg, 1 mmol) in methanol (5 ml) sodium borohydride (20 mg) was added. After stirring for 24 hr at room temperature, excess reagent was decomposed with ethyl acetate and water. The reaction mixture was neutralized with 0.1 N HCl and extracted with ethyl acetate. The extract was washed with water and dried ($MgSO_4$) and evaporated under reduced pressure to leave crystalline residue. Recrystallization from chloroform–ether gave a 24% yield of **4** as colorless needles, mp 136—137°; CD (MeOH) $[\theta]^{28}_{245}$ +2058; IR ν (KBr) 3380—3360 (OH), 1385, 1375 cm^{-1} (gem-CH_3); NMR (C_6D_6) δ 1.40, 1.45, 1.55 (s, 12H, CH_3), 1.82—2.38 (m, 2H, $-CH_2-$), 2.68—3.14 (m, 4H, $-SCH_2-$), 3.60 (bs, 2H, OH), 3.72—4.55 (m, 7H, gulitol), 4.65 (d, $J=7$ Hz, 1H, –SCHS–); MS *m/e*: 380 (M^+). *Anal.* Calcd. for $C_{16}H_{28}O_6S_2$: C, 50.50; H, 7.42. Found: C, 50.38; H, 7.40.

X-Ray Analysis——Crystals of suitable quality for an X-ray analysis were obtained from an isopropanol solution as transparent prisms elongated along the *c* axis. The density was measured by the floatation method in an aqueous solution of potassium iodide. The intensity data were collected by means of a Rigaku four-circle diffractometer, using Cu Kα radiation from a graphite monochrometer. All intensities were obtained from a crystal with the dimension of $0.2 \times 0.2 \times 0.3$ mm^3. The accurate cell dimensions were determined by use of 2θ values of the 24 strong reflections in the range of $15° \leqq 2\theta \leqq 30°$.

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11) W.S. Chilton and R.C. Krahn, *J. Am. Chem. Soc.*, **89**, 4129 (1967); *idem, ibid.*, **90**, 1318 (1968).

12) W.A. Asbun and S.B. Binkley, *J. Org. Chem.*, **31**, 2215 (1966).

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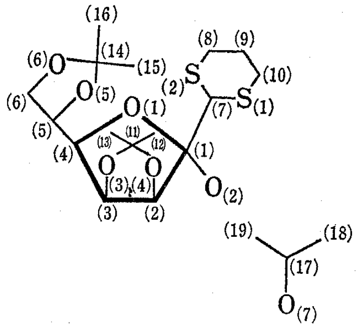
Crystal Data——$C_{16}H_{26}O_6S_2 \cdot C_3H_8O$ (438.60), mp 121—123°, monoclinic, $a=18.566(7)$ Å, $b=9.544(2)$ Å, $c=6.462(1)$ Å, $\beta=91.68(3)°$, $V=1141$ Å^3, $D_{obs.}=1.28$ g/cm^3, $D_{calc.}=1.279$ g/cm^3, $Z=2$, $F(000)=236$, absent reflection: *0k0* when *k* is odd. Space group: $P2_1$.

The three-dimensional intensity data were collected with $\omega-2\theta$ scanning technique at a scan rate of 2° per minute. The scan range of ω for each reflection was calculated by the formula $\omega=1.10°+0.5° \tan\theta$ and backgrounds were measured at both ends of the scan range for 10.0 second. Three standard reflection were measured after every 60 reflections. The maximum deviation of the standard reflections from their mean value was 0.6%.

The intensity data were corrected for the background count and for the usual Lorentz and polarization factors but not for absorption. A total of 1937 independent non-zero reflections had $|F_0|$ values greater than 3σ ($2\theta \leqq 140°$).

Determination of the Structure——The structure was solved by the heavy-atom method. From the three-dimensional Patterson map the position of the sulfur atom could easily be deduced. The position of the first sulfur atom was found the Harker section p(U, 1/2, W) to be $x=0.033$, $y=0.5$, and $z=0.155$.

Table I. Final Atomic Parameters and Their Standard Deviations ($\times 10^4$)



Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S (1)	332(1)	4940(4)	1547(5)	20(1)	83(3)	254(9)	0(1)	−14(2)	7(5)
S (2)	1011(2)	4264(4)	5717(5)	24(1)	104(3)	189(8)	−2(2)	7(2)	5(5)
O (1)	2326(4)	5737(8)	386(11)	17(2)	104(10)	185(21)	−12(4)	4(5)	4(12)
O (2)	1988(4)	3812(8)	1798(13)	26(2)	58(8)	310(27)	6(4)	15(7)	−11(12)
O (3)	1488(4)	7443(8)	784(12)	24(2)	63(8)	267(25)	5(4)	7(6)	19(12)
O (4)	2645(4)	8169(8)	576(13)	28(3)	76(9)	280(26)	−5(4)	−16(7)	41(13)
O (5)	3666(4)	6566(9)	5828(12)	21(2)	131(11)	227(24)	−2(4)	−5(6)	13(14)
O (6)	4654(4)	7252(11)	4151(13)	25(3)	172(15)	295(27)	−14(5)	−1(7)	−8(18)
O (7)	2562(6)	3458(14)	7986(15)	58(4)	283(23)	262(31)	83(9)	11(10)	−5(22)
C (1)	1811(5)	5231(11)	2353(16)	17(3)	71(13)	188(31)	3(5)	1(8)	−23(15)
C (2)	1900(5)	6185(11)	455(17)	21(3)	63(11)	198(11)	4(5)	3(8)	−12(15)
C (3)	2684(6)	6648(12)	576(19)	23(3)	83(13)	241(35)	−10(6)	−3(9)	−25(18)
C (4)	2958(5)	6116(12)	2757(19)	16(3)	87(13)	280(38)	−3(5)	11(9)	11(18)
C (5)	3378(6)	7196(13)	3976(18)	25(3)	108(15)	205(33)	−10(6)	−8(9)	−12(19)
C (6)	4069(6)	7684(18)	2831(21)	23(4)	218(25)	264(41)	32(8)	−8(10)	36(27)
C (7)	1075(5)	5274(11)	3351(17)	16(3)	82(13)	204(32)	1(5)	−2(8)	−1(16)
C (8)	885(7)	2469(13)	4806(22)	35(4)	82(14)	374(47)	−10(7)	−7(12)	17(22)
C (9)	207(7)	2353(16)	3371(22)	39(5)	116(17)	371(49)	−20(8)	1(13)	19(26)
C (10)	321(7)	3058(13)	1269(20)	38(5)	93(14)	285(41)	−22(7)	−24(11)	−8(21)
C (11)	1930(6)	8534(13)	70(20)	29(4)	80(13)	283(40)	−7(6)	4(10)	26(10)
C (12)	1849(7)	8654(18)	−2359(21)	35(5)	209(25)	242(41)	−16(9)	−11(12)	87(27)
C (13)	1736(8)	9881(16)	1284(24)	58(6)	79(15)	449(54)	18(9)	−2(15)	−52(26)
C (14)	4377(6)	7114(14)	6187(18)	17(3)	137(18)	238(37)	−3(6)	−1(9)	−3(22)
C (15)	4818(7)	6062(17)	7345(23)	32(5)	162(21)	363(49)	19(8)	−15(12)	26(27)
C (16)	4348(9)	8538(16)	7285(23)	63(7)	132(20)	295(48)	−27(10)	−2(15)	−36(26)
C (17)	3250(8)	3118(17)	7277(23)	39(5)	176(23)	308(47)	29(9)	11(13)	19(28)
C (18)	3195(9)	2214(21)	5443(24)	56(7)	221(30)	316(51)	34(13)	21(16)	−48(34)
C (19)	3677(9)	2481(26)	9134(25)	44(6)	391(47)	350(54)	66(15)	−40(15)	−3(43)

The anisotropic temperature factors are of the form;
$T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.
The estimated standard deviations are given in the parentheses.

The pseudo-mirror symmetry appeared in the first electron density distribution was destroyed by addition of the second sulfur (x=0.101, y=0.426, z=0.572), allowing to choose a set of atoms from enantiomers. Refinement of the positional and thermal parameters of the 28 atoms including two sulfur atoms and isopropanol molecule was carried out by the block-diagonal matrix least-squares method, in which the anisotropic thermal vibration for carbon atom was applied to the other non-hydrogen atoms. Six cycles of calculations gave an R-value of 0.14.

The oxygen atoms and carbon atoms were deduced from the chemical consideration, the bond lengths and the unusually low values of the thermal parameters due to taking oxygen atoms for carbon atoms. Four more cycles of block diagonal least-squares anisotropic approximation were computed and R index was reduced to 0.11. As the next step, five cycles of block diagonal anisotropic approximation were calculated giving R=0.071 for 1760 reflections.[14] The final atomic parameters and their standard deviations are shown in Table I. The computer programs used in these calculations were 3DFANDFR and HLSQ.[15]

TABLE II. Bond Lengths and Their Standard Deviations (Å)

S (1)-C (7)	1.800(10)	O (7)-C (17)	1.409(18)
S (1)-C (10)	1.853(13)	C (1)-C (2)	1.538(15)
S (2)-C (7)	1.810(11)	C (1)-C (7)	1.536(13)
S (2)-C (8)	1.831(13)	C (2)-C (3)	1.518(15)
O (1)-C (1)	1.437(12)	C (3)-C (4)	1.577(17)
O (1)-C (4)	1.437(13)	C (4)-C (5)	1.504(16)
O (2)-C (1)	1.443(12)	C (5)-C (6)	1.564(17)
O (3)-C (2)	1.442(13)	C (8)-C (9)	1.540(19)
O (3)-C (11)	1.412(14)	C (9)-C (11)	1.549(20)
O (4)-C (3)	1.453(14)	C (11)-C (12)	1.571(19)
O (4)-C (11)	1.403(14)	C (11)-C (13)	1.551(19)
O (5)-C (5)	1.423(14)	C (14)-C (15)	1.484(19)
O (5)-C (14)	1.432(14)	C (14)-C (16)	1.540(19)
O (6)-C (6)	1.429(15)	C (17)-C (18)	1.464(23)
O (6)-C (14)	1.422(14)	C (17)-C (19)	1.556(23)

TABLE III. Bond Angles and Their Standard Deviations

C (7)-S (1)-C (10)	102.9(5)°	O (5)-C (5)-C (4)	108.9(9)°
C (7)-S (2)-C (8)	104.1(5)	C (9)-C (8)-S (2)	110.2(9)
C (1)-O (1)-C (4)	106.0(8)	C (10)-C (9)-C (8)	112.0(11)
C (2)-O (3)-C (11)	104.5(8)	C (12)-C (11)-O (3)	109.7(10)
C (3)-O (4)-C (11)	107.0(8)	C (12)-C (11)-O (4)	108.3(10)
C (5)-O (5)-C (14)	107.5(8)	C (12)-C (11)-C (13)	115.2(11)
C (6)-O (6)-C (14)	106.6(9)	O (3)-C (11)-O (4)	107.1(9)
C (2)-C (1)-O (1)	105.5(8)	O (3)-C (11)-C (13)	107.4(10)
C (2)-C (1)-O (2)	109.0(8)	O (4)-C (11)-C (13)	108.8(10)
C (2)-C (1)-C (7)	116.2(8)	C (15)-C (14)-O (5)	108.9(10)
O (1)-C (1)-O (2)	109.6(8)	C (15)-C (14)-O (6)	108.5(10)
O (1)-C (1)-C (7)	106.3(8)	C (15)-C (14)-C (16)	113.0(11)
O (2)-C (1)-C (7)	109.9(8)	O (5)-C (14)-O (6)	104.0(9)
O (3)-C (2)-O (3)	105.1(8)	O (5)-C (14)-C (16)	110.7(10)
C (3)-C (2)-C (1)	104.8(8)	O (6)-C (14)-C (16)	111.3(10)
O (3)-C (2)-C (1)	107.7(8)	O (6)-C (6)-C (5)	104.5(10)
C (4)-C (3)-O (4)	109.5(9)	S (1)-C (7)-S (2)	113.6(6)
C (4)-C (3)-C (2)	193.7(9)	S (1)-C (7)-C (1)	113.1(7)
O (4)-C (3)-C (2)	104.2(9)	S (2)-C (7)-C (1)	115.2(7)
C (5)-C (4)-O (1)	109.3(9)	S (1)-C (10)-C (9)	110.1(9)
C (5)-C (4)-C (3)	113.6(9)	C (18)-C (17)-O (7)	111.6(13)
O (1)-C (4)-C (3)	106.5(9)	C (18)-C (17)-C (19)	115.2(14)
C (6)-C (5)-O (5)	103.3(9)	O (7)-C (17)-C (19)	106.1(13)
C (6)-C (5)-C (4)	111.9(10)		

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[14] The atomic scattering factors used in these calculations were taken from "International Tables for X-ray Crystallography," Vol. III, ed. by C.H. McGillavry and G.D. Rieck, Kynoch Press, Birmingham, 1968, p. 201.

[15] Y. Iitaka, 3DFANDFR and HLSQ, University of Tokyo, Tokyo.

Discussion of the Structure——The stereoscopic view of 1-(1,3-dithian-2-yl)-2,3 : 5,6-di-*O*-isopropylidene-β-L-gulofuranose (3) determined by the present analysis is shown in Fig. 3. Based on the known absolute configuration of the starting compound,[16] Fig. 3 illustrates the *c*-axis projection by a stereoscopic view (ORTEP) and the *z* direction points upward. The absolute configuration of the compound was established as shown in Fig. 3, and the configuration at C-1 is R chirality.

The bond lengths and angles of the molecule (Table II and III) calculated from the final atomic parameters. The crystal structure along *c*-axis is shown in Fig. 4, where the intramolecular Van der Waals contacts are indicated by the broken line with distance values in Å. The intermolecular hydrogen bond is formed between isopropanol and the molecule as shown in Fig. 5.

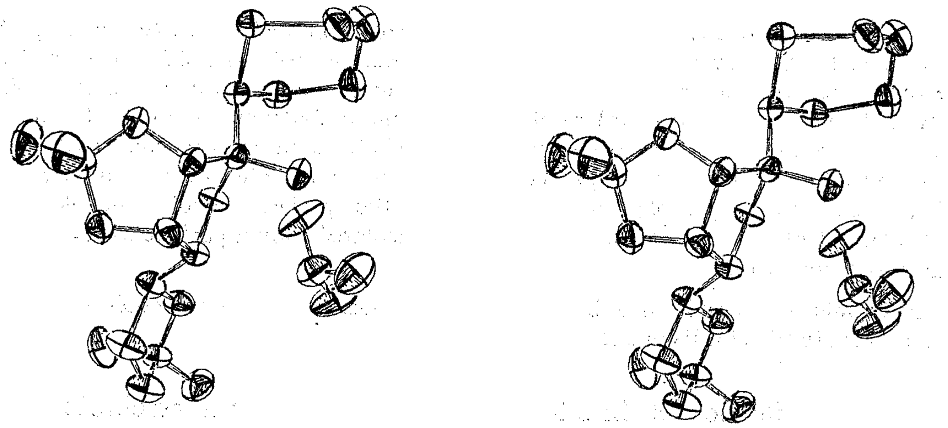

Fig. 3. Stereoscopic View (*c*-Axis Projection)

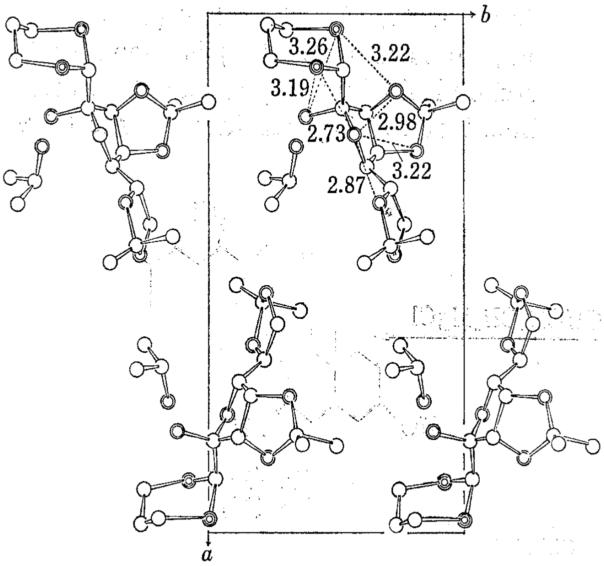

Fig. 4. Projection of the Crystal Structure along *c*-Axis

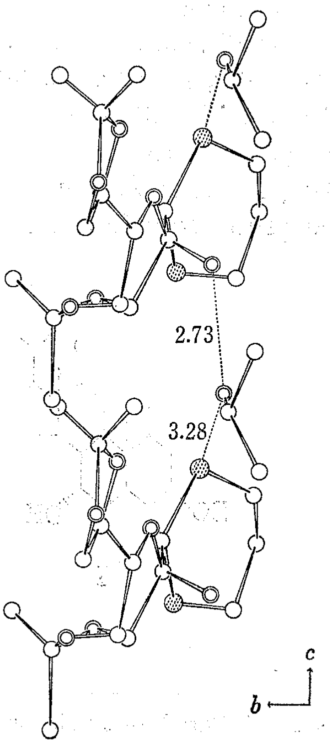

Fig. 5. The Intramolecular Hydrogen Bonds

In conclusion, the nucleophilic addition of sugar lactone with lithiated heterocycles gives 1-substituted β-L-gulofuranose stereoselectively, and the chirality of C-1 position is β.

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16) M. Matsui, M. Okada, and M. Ishidate, *Yakugaku Zasshi*, **86**, 110 (1966).