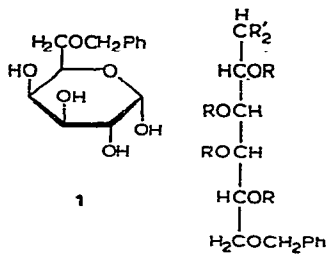
6-*O*-Benzyl-D-galactose and its dimethyl acetal

6-*O*-Benzyl-α-D-galactose (**1**) is a useful starting-material in synthetic work in which there is required a D-galactose derivative having the 6-hydroxyl group protected by a group that can subsequently be removed under mild conditions, such as hydrogenolysis. The dimethyl acetal (**5**) of the *aldehydo* form of **1** provides a convenient starting-point for the preparation of derivatives of D-galactoseptanose. The preparation of compounds **1** and **5** is now described.

The readily available 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[1] was easily hydrolyzed, and a crystalline product was isolated; this was formulated as 6-*O*-benzyl-α-D-galactopyranose (**1**), because of its slow, negative mutarotation. The free sugar **1** was converted, in four steps, into the dimethyl acetal (**5**) in 50% overall yield; the steps were mercaptalation of **1** to give **2**, acetylation of **2** to give **3**, demercaptalation of **3** to give **4**, and deacetylation of **4** to give **5**. The five new compounds **1** to **5** crystallized well, in contrast to the corresponding D-*gluco* compounds[2]. The excellent yield obtained in the demercaptalation of **3** to give **4** was unexpected.



1

	R	R'
2	H	SEt
3	Ac	SEt
4	Ac	OMe
5	H	OMe

EXPERIMENTAL

General. — The microanalyses were performed by the Australian Microanalytical Service, Melbourne. All evaporations and concentrations were conducted in a rotary evaporator under diminished pressure at ≯ 40° (bath temp.).

6-O-Benzyl-α-D-galactopyranose (**1**). — Hot M hydrochloric acid (100 ml) was added to a solution of 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (100 g) in *p*-dioxane (400 ml) at 100°, and the mixture was kept for 30 min at 100°, and cooled. The resulting crystals of compound **1** were filtered off, and the mother liquor was rendered acidic (pH 4), and evaporated to dryness. The residue, treated with *p*-dioxane, yielded more of **1**; total yield, over 90% (when pure starting material was used). The recrystallized compound had m.p. 96–98°, $[\alpha]_D^{25}$ +75.3° (5 min), +41.3° (2 days), and +32.7° (8 days) (*c* 1.0, methanol).

Anal. Calc. for $C_{13}H_{18}O_6$: C, 57.8; H, 6.7. Found: C, 57.7; H, 6.8.

6-O-Benzyl-D-galactose diethyl dithioacetal (**2**). — A mixture of finely powdered **1** (250 g), hydrochloric acid (d. 1.19, 750 ml) and ethanethiol (250 ml),

all precooled to 0°, was vigorously shaken for 5 min at 0°. The dithioacetal **2** crystallized, and was filtered off, washed with ice-cold water, and recrystallized from methanol as quickly as possible. The yield of pure **2** was 80–85%, m.p. 120°, $[\alpha]_D^{25}$ +3.4° (*c* 1.0, methanol).

Anal. Calc. for $C_{17}H_{28}O_5S_2$: C, 54.2; H, 7.5; S, 17.0. Found: C, 54.1; H, 7.5; S, 17.0.

*2,3,4,5-Tetra-*O*-acetyl-6-*O*-benzyl-*D*-galactose diethyl dithioacetal* (**3**). — The dithioacetal **2** (112 g), pyridine (360 ml), and acetic anhydride (720 ml) were mixed at 0°; the mixture was kept overnight at room temperature, and poured, with stirring, into ice–water (5 l). The acetate that crystallized was filtered off, and recrystallized from methanol (85% yield), m.p. 85°, $[\alpha]_D^{25}$ −12.6° (*c* 1.0, methanol).

Anal. Calc. for $C_{25}H_{36}O_9S_2$: C, 55.1; H, 6.7; S, 11.8. Found: C, 54.9; H, 6.8; S, 11.7.

*2,3,4,5-Tetra-*O*-acetyl-6-*O*-benzyl-*D*-galactose dimethyl acetal* (**4**). — The diethyl dithioacetal (**3**) (40 g) in dry methanol (400 ml) was vigorously stirred for 90 min with cadmium carbonate (48 g) and mercuric chloride (130 g) while being heated under reflux in an all-glass apparatus. The mixture was cooled, and filtered, and the filtrate was shaken with water (600 ml) and chloroform (600 ml). The chloroform layer was washed with water until free from chloride ions, (dried sodium sulfate,) and evaporated to a syrup which crystallized from ether at 0° (80% yield). Recrystallization gave **4** that had m.p. 58–60°, $[\alpha]_D^{25}$ −4.6° (*c* 1.0, methanol).

Anal. Calc. for $C_{23}H_{32}O_{11}$: C, 57.0; H, 6.7. Found: C, 56.9; H, 6.8.

*6-*O*-Benzyl-*aldehydo*-D-galactose dimethyl acetal* (**5**). — For the methanolysis, a solution of compound **4** (100 g) in 0.1% methanolic sodium methoxide (1 liter) was kept for 24 h at room temperature, and the solution was then concentrated. The product crystallized during the concentration, and was filtered off at intervals. Recrystallization from methanol gave **5** in 82% yield, m.p. 126–127°, $[\alpha]_D^{25}$ +13.2° (*c* 1.0, methanol).

Anal. Calc. for $C_{15}H_{24}O_7$: C, 56.9; H, 7.6. Found: C, 57.0; H, 7.6.

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