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DIISOPROPYLIDENE ACETALS OF D-ALLOSE† AND D-*ribo*-HEXULOSE (D-PSICOSE)

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ABSTRACT

Acetonation of D-allose in the presence of sulfuric acid gives 2,3 5,6-di-*O*-isopropylidene-β-D-allofuranose (**4**) in good yield Oxidation of **4** with methyl sulfoxide and acetic anhydride gave 2,3 5,6-di-*O*-isopropylidene-D-allono-1,4-lactone (**7**) Compound **4** was also obtained from 1,2 5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**) in one step by an acetal-migration reaction The acetonation of D-*ribo*-hexulose (D-psicose) in the presence of anhydrous copper sulfate and sulfuric acid has been re-examined, and the main product has been shown to be 1,2 3,4-di-*O*-isopropylidene-D-psicofuranose (**12**), by conversion of **12** into 6-deoxy-D-psicose (**16**) through 1,2 3,4-di-*O*-isopropylidene-6-*O*-*p*-tolylsulfonyl-D-psicofuranose (**14**)

INTRODUCTION AND DISCUSSION

Recent advances with oxidants such as ruthenium tetraoxide[1] and methyl sulfoxide with acid anhydrides[2,3] have greatly facilitated studies on rare sugars[4] For example, convenient preparations through oxidative procedures of D-allose from D-glucose[3,5], and D-*ribo*-hexulose (D-psicose) from D-fructose[6,7], have been reported in recent years Nevertheless, only a few derivatives of these two sugars are known These sugars have stimulated the attention of biochemists since, although D-allose is still unreported in Nature, D-psicose has been shown to exist in molasses[8], *Itea* plants[9], human urine[10], antibiotics[11], and metabolites of *Pseudomonas methanica*[12]. In this paper, the diisopropylidene acetals of D-allose and D-psicose are described

Crystalline D-allose was prepared[3,5] from 1,2 5,6-di-*O*-isopropylidene-α-D-glucofuranose, and a crystalline acetate (**2**) and benzoate (**3**) of the intermediate 1,2 5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**) were prepared.

Acetonation of D-allose in the presence of sulfuric acid yielded a crystalline diisopropylidene acetal (**4**) in good yield as the sole product (t l c). The diacetal **4** was apparently different from the known diacetal **1** and gave a crystalline monoacetate (**5**) and mono-benzoate (**6**) On the other hand, compound **4** was resistant

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to sulfonylation by *p*-toluenesulfonyl chloride in pyridine This fact implied that the anomeric hydroxyl group of **4** was free[14] Compound **4** did not reduce Fehling solution, but it is known that 2,3 5,6-di-*O*-isopropylidene-α-D-mannofuranose, which has a free hydroxyl group at the anomeric carbon atom, also resists the action of hot Fehling solution[15].

The structure of **4** was tentatively assigned as 2,3 5,6-di-*O*-isopropylidene-β-D-allofuranose because oxidation with methyl sulfoxide and acetic anhydride gave a lactone that was considered to be 2,3 5,6-di-*O*-isopropylidene-D-allono-1,4-lactone (**7**), since it had a characteristic i r absorption maximum at 1785 cm^{-1}, typical of a γ-lactone[16] The anomeric configuration of **4** was deduced by n m r spectroscopy (chloroform-*d*) The H-1 signal of **4** appeared at low field as a singlet at τ 4 65, and the small coupling ($J_{1,2}$ <0 5 Hz) signified a *trans*-arrangement[17] of the protons at C-1 and C-2

Further confirmation of the furanose structure was provided by mass spectroscopy As shown in Figs 1 and 2, a peak at *m/e* 101 was prominent in the mass spectra of **1** and **4**, indicating the well known fragmentation process of scission of the C-4–C-5 bond in the di-*O*-isopropylidenealdohexofuranose structure[18]. The mass spectra of **1** and **4** are closely similar Peaks at *m/e* 245 (M −15), 187, 159, 127, 73, 59, and 43 indicated that both **1** and **4** have a di-*O*-isopropylidenealdohexofuranose structure Compound **4** has an additional peak at *m/e* 243 (M −17), because of the location[18] of the hydroxyl group on the anomeric carbon atom rather than on C-3 These results are in good agreement with the data reported for the diacetal of D-talose[19] Treatment of 1,2 5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**) with sulfuric acid in acetone gave 2,3 5,6-di-*O*-isopropylidene-β-D-allofuranose (**4**) in high yield The

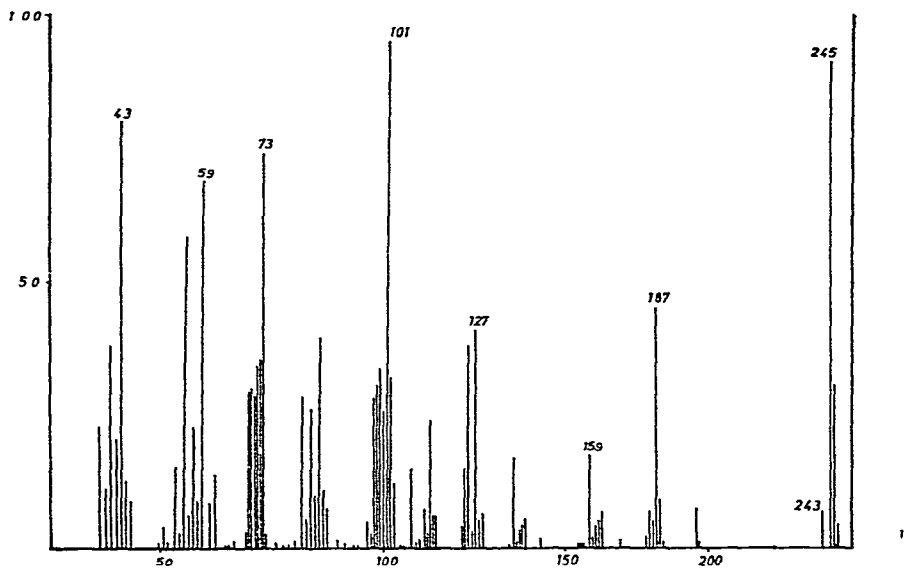


Fig 1 The mass spectrum of 2,3 5,6-di-*O*-isopropylidene-β-D-allofuranose (**4**)

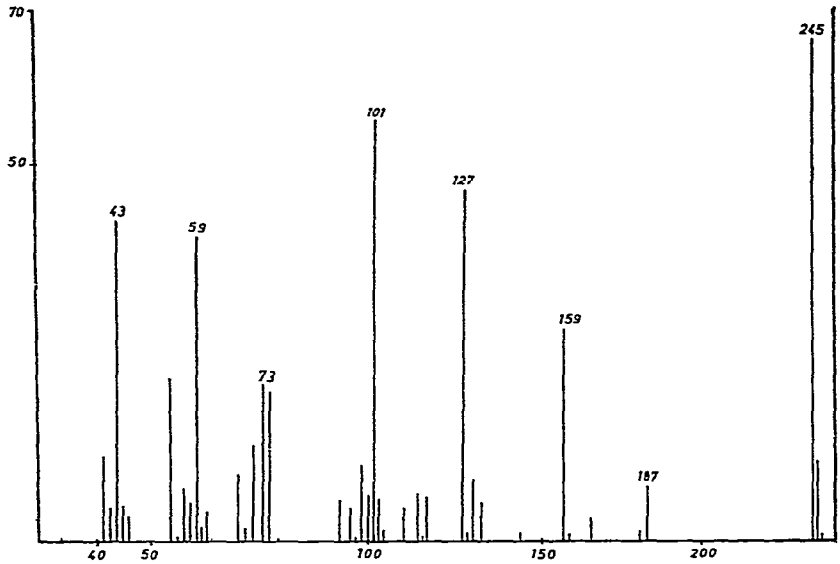
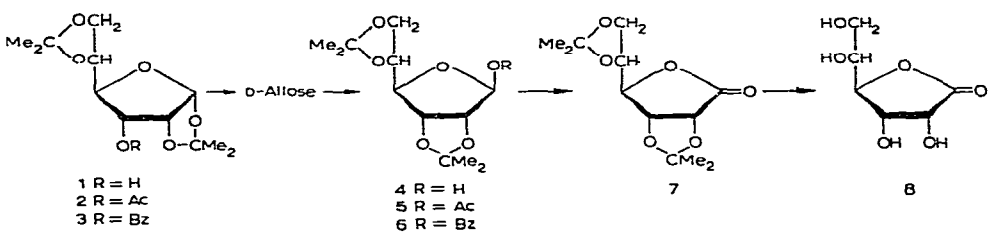
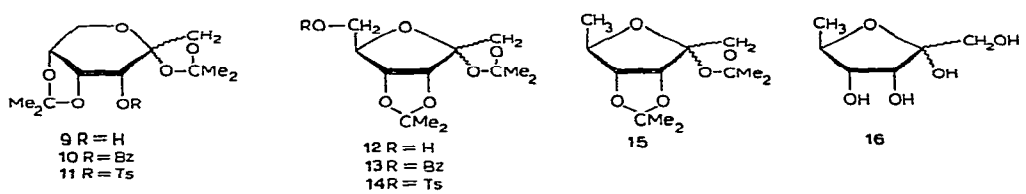


Fig 2 The mass spectrum of 1,2,5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**)

facile migration of the 1,2-acetal group is consistent with recent observations on the rates of hydrolysis of 1,2-*O*-isopropylidenealdoses[13]

In 1935, Steiger and Reichstein[20] reported that acetonation of L-psicose in the presence of anhydrous copper sulfate and sulfuric acid gave a crystalline diacetal as the main product The structure of 1,2 3,4-di-*O*-isopropylidene-L-psicofuranose was assigned since oxidation with potassium permanganate gave a carboxylic acid (indicating a primary hydroxyl group) which, after the removal of the isopropylidene groups, was not converted into the so-called ascorbic acid homolog (that is, it was not a 2-ketohexanoic acid) Later on, the diacetal of the D-sugar was also reported by the same authors[21] The ready availability of D-psicose[6 7] facilitated a re-examination of the diacetal[21]. The intermediate, known[6 7] diacetal 1,2 4,5-di-*O*-isopropylidene-D-





psicopyranose (**9**), was further characterized through the preparation of a crystalline 3-benzoate (**10**) and a crystalline 3-*p*-toluenesulfonate (**11**)

Acetonation of D-psicose according to the direction of Steiger and Reichstein[21] in the presence of anhydrous copper sulfate and sulfuric acid yielded a crystalline diacetal (**12**) having physical constants as stated. The acetal migration procedure[6] from **9** also gave the same diacetal **12** in high yield Benzoylation or *p*-toluenesulfonylation of **12** in the usual manner gave the crystalline 6-benzoate (**13**) and 6-*p*-toluenesulfonate (**14**), respectively, in good yield

Although 6-*p*-tolylsulfonyloxy groups in aldohexose derivatives undergo reduction with lithium aluminum hydride to give 6-deoxy derivatives, 1-*p*-tolylsulfonyloxy groups in ketohexoses, on the other hand, are usually only desulfonylated[14]. Accordingly, it was expected that the sulfonate **14** would be desulfonylated to the original diacetal **12** by lithium aluminum hydride if the tosyl group were to be at C-1

However, treatment of the sulfonate **14** with lithium aluminum hydride in tetrahydrofuran yielded a desulfonyloxylated product, 6-deoxy-1,2 3,4-di-*O*-isopropylidene-D-psicofuranose (**15**) as a mobile syrup, indicating that the sulfonyloxy group had been at C-6 Definitive structural proof for **15** was provided by n m r spectroscopy, since the newly formed methyl group in the sugar moiety resonated as a doublet (J = 6 Hz) centered at τ 8 75 The appearance of this signal as a doublet indicated that it arose from a methyl group at C-6, since a methyl group at C-1 of a ketose would have resonated as a singlet

Removal of the isopropylidene groups from **15** gave syrupy 6-deoxy-D-psicose (**16**), which was characterized as its known phenylosazone[22]. The anomeric configuration of the D-psicose derivatives is still unknown

Furanose derivatives such as **4** and **14** are of interest, since they provide potential intermediates for the preparation of nucleosides containing these sugars[23].

EXPERIMENTAL

General. — Melting points are uncorrected Evaporations of solvents were conducted under diminished pressure below 40° Reactions were followed by t l c on Silica Gel G (E Merck, Darmstadt, Germany), with solvent systems (*A*) 4 1(v/v) benzene–ether, (*B*) 3 1 ethyl acetate–light petroleum (b p 30–70°), and (*C*) 19 1 benzene–methanol Detections were effected with sulfuric acid or iodine vapor Descending paper chromatography was conducted on Whatman No 1 paper with the following solvent systems (*A*) 3 1 1(v/v) propyl alcohol–28% ammonia solution–water and (*B*) 14 3 3 ethyl acetate–acetic acid–water. Spots were detected by periodate–benzidine. I r spectra were obtained on Nujol mulls with a Shimazu spectrometer. N m r spectra were obtained at 60 MHz with a Hitachi H-60 spectrometer with tetramethylsilane as internal reference and chloroform-*d* as solvent Mass spectra were measured with a Hitachi IMU-6E spectrometer (ionizing potential 80 eV), by using an indirect insertion technique.

3-O-Acetyl-1,2 5,6-di-O-isopropylidene-α-D-allofuranose (**2**) — 1,2 5,6-Di-*O*-

isopropylidene-α-D-allofuranose[5] (**1**, 1 0 g), m p 74–75°, $[\alpha]_D^{20}$ +37°, was acetylated with acetic anhydride (5 ml) and pyridine (5 ml) overnight at room temperature The reaction mixture was poured into ice–water (200 ml) and extracted with dichloromethane (3 × 20 ml) The extract was washed successively with 5% sulfuric acid, saturated aqueous sodium hydrogen carbonate, and water The dried (sodium sulfate) solution was evaporated, and the residue was crystallized from light petroleum, yield 1 0 g (86%), m p 75 5–76 5°, $[\alpha]_D^{20}$ +107 6° (*c* 1 0, chloroform)

Anal Calc for $C_{14}H_{22}O_7$. C, 55 62, H, 7 34 Found C, 55 77, H, 7 37.

3-O-Benzoyl-1,2 5,6-di-O-isopropylidene-α-D-allofuranose (**3**) — The diacetal **1** (1 0 g) was benzoylated with benzoyl chloride (2 ml) and pyridine (5 ml) overnight at room temperature After decomposition of the excess reagent with ice, the mixture was poured into ice–water (200 ml) The precipitate was collected by filtration and recrystallized from cyclohexane, yield 760 mg (56%), m p. 73–74.5°, $[\alpha]_D^{20}$ +125 9° (*c* 1 0, chloroform)

Anal Calc for $C_{19}H_{24}O_7$ C, 62 62, H, 6 64 Found C, 62 54, H, 6 54

2,3 5,6-Di-O-isopropylidene-β-D-allofuranose (**4**) — *A* β-D-Allose was prepared from 1,2 5,6-di-*O*-isopropylidene-α-D-allofuranose **1** as follows: compound **1** (20 0 g) was suspended in water (300 ml) and stirred with the H^+ form of Amberlite IR-120 (50 ml) for 4 h at 80° The resin was removed by filtration and washed with water (3 × 50 ml) The combined filtrate and washings were concentrated to give a crystalline mass, which was recrystallized from ethanol–water, yield 11 6 g (85%), m p 127–128 5°, $[\alpha]_D^{20}$ +15° (equil , *c* 2 3, water) [lit [24], m p 128–128 5°, $[\alpha]_D$ +14° (equil , water)] D-Allose (10 0 g) was shaken with anhydrous acetone (300 ml) containing sulfuric acid (7 ml) for 6 h The reaction mixture was neutralized with anhydrous sodium carbonate (100 g), filtered, and the filter washed with acetone (3 × 50 ml) The filtrate and washings were concentrated to a syrup that was dissolved in ether (100 ml) The solution was washed with water, dried (sodium sulfate), and evaporated to dryness Crystallization and recrystallization were effected with light petroleum, yield 9 8 g (68%), m p 66–67°, $[\alpha]_D^{20}$ −27 4° (*c* 3 4, chloroform) and −1 5° (*c* 1 9, water), n m r data (after deuteration) τ 4 65 (1-proton singlet, H-1), τ 5 18 (1-proton doublet, *J* 10 Hz, H-2), τ 5 46 (1-proton doublet, *J* 10 Hz, H-3), τ 5 60–6 20 (4-proton multiplet, H-4,5,6,6′), τ 8 45 (6-proton singlet, 2Me), τ 8 68 (3-proton singlet, Me), and τ 8 70 (3-proton singlet, Me)

Anal. Calc for $C_{12}H_{20}O_6$ C, 55 37, H, 7 75 Found C, 55 18, H, 7 65

B. 1,2 5,6-Di-*O*-isopropylidene-α-D-allofuranose **1** (10 0 g) was dissolved in anhydrous acetone (200 ml) containing sulfuric acid (2 ml) and kept overnight at room temperature A spot having R_F 0 23 (solvent *B*), corresponding to the starting material **1**, had completely disappeared and a spot having R_F 0.40, corresponding to the rearranged product **4**, was detected by t l c The solution was neutralized with anhydrous sodium carbonate (50 g), filtered, and the filter was washed with acetone (3 × 50 ml) The combined filtrate and washings were evaporated to dryness and the residue was recrystallized from light petroleum, yield 8 9 g (89%), m p and mixed m p. 66–67°.

1-O-Acetyl-2,3-5,6-di-O-isopropylidene-β-D-allofuranose (**5**). — 2,3 5,6-Di-*O*-isopropylidene-β-D-allofuranose (**4**, 1 0 g) was acetylated with acetic anhydride (5 ml) and pyridine (5 ml) as described for **2** and the pure acetate **5** was obtained after recrystallization from ligroin, yield 870 mg (75%), m p. 51–51 5°, $[\alpha]_D^{20}$ −46 2° (*c* 1 1, chloroform)

Anal Calc for $C_{14}H_{22}O_7$ C, 55 62; H, 7 34 Found C, 55 76; H, 7 30

1-O-Benzoyl-2,3 5,6-di-O-isopropylidene-β-D-allofuranose (**6**) — Benzoylation of **4** (1 0 g) with benzoyl chloride (2 ml) and pyridine (5 ml) as described for **3**, with recrystallization of the product from ethanol, gave the pure benzoate **6**, yield 890 mg (64%), m.p 109–110°, $[\alpha]_D^{20}$ −38 5° (*c* 1 0, chloroform)

Anal Calc for $C_{19}H_{24}O_7$ C, 62 62, H, 6 64 Found C, 62 77, H, 6 72

2,3 5,6-Di-O-isopropylidene-D-allono-1,4-lactone (**7**) — The diacetal **4** (3 0 g) was dissolved in a mixture of dimethyl sulfoxide (50 ml) and acetic anhydride (30 ml) and kept overnight at room temperature Evaporation of the solvent below 70° gave a slightly colored syrup Crystallization and recrystallization were effected with light petroleum, yield 2 3 g (78%), m p 38–39°, $[\alpha]_D^{20}$ −78 7° (*c* 3 2, chloroform)

Anal Calc for $C_{12}H_{18}O_6$ C, 55 80, H, 7 03 Found C, 55 68, H, 6 95

D-Allono-1,4-lactone (**8**) — 2,3 5,6-Di-*O*-isopropylidene-D-allono-1,4-lactone (**7**, 1 0 g) was heated with Amberlite IR-120 (H^+) resin (2 ml) in water (10 ml) for 6 h on steam-bath The resin was removed by filtration and washed with water (2 × 5 ml) The combined filtrate and washings were concentrated to give crystalline mass, which was recrystallized from ethanol; yield 600 mg (87%), m p 119–120°, $[\alpha]_D^{20}$ −6.6° (*c* 4 2, water), λ_{max} 1770 cm^{-1} (γ-lactone) [Lit [25], m p 120°, $[\alpha]_D$ −6 8° in water]

Anal Calc for $C_6H_{10}O_6$ C, 40 45, H, 5 56 Found C, 40 32, H, 5 66

3-O-Benzoyl-1,2 4,5-di-O-isopropylidene-D-psicopyranose (**10**) — 1,2 4,5-Di-*O*-isopropylidene-D-psicopyranose (**9**, 1 0 g), m p 64–66°, $[\alpha]_D^{20}$ −125 5° in chloroform[6,7], was benzoylated with benzoyl chloride (2 ml) and pyridine (5 ml), and 730 mg (58%) of the benzoate **10** was obtained; m p 143–144°, $[\alpha]_D^{20}$ −141 7° (*c* 3 0, chloroform).

Anal Calc for $C_{19}H_{24}O_7$ C, 62 62, H, 6 67 Found C, 62 75; H, 6 76

1,2 4,5-Di-O-isopropylidene-3-O-p-tolysulfonyl-D-psicopyranose (**11**). — The diacetal **9** (1 0 g) was treated with *p*-toluenesulfonyl chloride (2 0 g) in pyridine (5 ml) overnight at room temperature After conventional processing, the sulfonate **11** was recrystallized from ethanol, yield 1 0 g (64%), m p 108–109°, $[\alpha]_D^{20}$ −103 2° (*c* 0 93, chloroform)

Anal Calc for $C_{19}H_{26}O_8S$ C, 55 18, H, 6 32, S, 7 73 Found C, 55 15, H, 6 44, S, 7.67.

1,2 3,4-Di-O-isopropylidene-D-psicofuranose (**12**) — *4* D-Psicose (10 0 g), $[\alpha]_D^{20}$ +3 3 in water[21], R_{Fru} 1 15 in solvent *A* and 1.41 in solvent *B*, was acetonated according to Steiger and Reichstein[21] with anhydrous copper sulfate (30 g) and sulfuric acid (1 ml) in anhydrous acetone (700 ml) for 48 h at room temperature. The title compound was obtained in 48% yield; m p. 56–58°, $[\alpha]_D^{20}$ −94 6° (*c* 2 6, chloro-

form), lit , m p 57–57 5°, $[\alpha]_D$ −89 6° in chloroform[6], m.p 57–58 5°, $[\alpha]_D$ −98 1° in chloroform[21]

Anal Calc for $C_{12}H_{20}O_6$ C, 55 37, H, 7 75 Found C, 55 38, H, 7 55

B The diacetal **9** (20 0 g) was dissolved in anhydrous acetone (300 ml) containing sulfuric acid (4 ml) and the solution was kept overnight at room temperature The diacetal **12** (12 8 g, 64%) was obtained after treatment as described for **4**, m p and mixed m p 56–58°.

6-O-Benzoyl-1,2 3,4-di-O-isopropylidene-D-psicofuranose (**13**) — The diacetal **12** (1 5 g) was benzoylated with benzoyl chloride (2 ml) and pyridine (5 ml) as described for **3**, and the pure benzoate was obtained after recrystallization from ethanol, yield 1 5 g (75%), m p 70–71°, $[\alpha]_D^{20}$ −59 6° (*c* 2 9, chloroform)

Anal Calc for $C_{19}H_{24}O_7$. C, 62 62, H, 6 67 Found C, 62 70, H, 6 62

1,2 3,4-Di-O-isopropylidene-6-O-p-tolylsulfonyl-D-psicofuranose (**14**) — The diacetal **12** (6 0 g) was treated with *p*-toluenesulfonyl chloride (6 0 g) in pyridine (50 ml) overnight at room temperature The reaction mixture was poured into ice–water (1 liter) The resultant precipitate was recrystallized from ligroin, yield 7 7 g (74%), m p 98–99°, $[\alpha]_D^{20}$ −42 4° (*c* 3 4, chloroform)

Anal Calc for $C_{19}H_{26}O_8S$ C, 55 18, H, 6 32; S, 7 73 Found C, 55 26, H, 6 36, S, 7 69

6-Deoxy-1,2 3,4-di-O-isopropylidene-D-psicofuranose (**15**) — 1,2 3,4-Di-*O*-isopropylidene-6-*O*-*p*-tolylsulfonyl-D-psicofuranose (**14**, 5 0 g) was dissolved in anhydrous tetrahydrofuran (100 ml) and lithium aluminum hydride (4 0 g) was added The reaction mixture was gently refluxed for 8 h under protection from moisture. The excess of hydride was then decomposed by the addition of water and the mixture was filtered The filtrate was evaporated to dryness, and the residue was dissolved in ether (100 ml), washed with water, dried (sodium sulfate), and evaporated to a syrup Distillation of the product under a high vacuum gave a mobile syrup, yield 2 5 g (85%), b p 85–90°/10^{-3} torr, $[\alpha]_D^{20}$ −97 3° (*c* 1 1, chloroform), n m r data τ 5 45 (2-proton quartet, H-1,1'), τ 5 60–6 20 (3-proton multiplet, H-3,4,5), τ 8 60 (6-proton singlet, 2Me), τ 8 65 (3-proton singlet, Me), τ 8 70 (3-proton singlet, Me), and τ 8 75 (3-proton doublet, H-6)

Anal Calc for $C_{12}H_{20}O_5$ C, 59 00, H, 8 25. Found C, 58 97, H, 8 17

6-Deoxy-D-psicose (**16**) — 6-Deoxy-1,2 3,4-di-*O*-isopropylidene-D-psicofuranose (**15**, 650 mg) was dissolved in water (10 ml) and treated with Amberlite IR-120 (H^+) (2 ml) for 4 h at 60° After removal of the resin, water was evaporated off to give a thick syrup, yield 370 mg (85%), optical rotation in water was not observed

Anal Calc for $C_6H_{12}O_5$ C, 43 90, H, 7 37 Found C, 43 75, H, 7 30

6-Deoxy-D-*ribo*-hexulose phenylosazone, m p 178–180°, $[\alpha]_D^{20}$ −67 2 (*c* 0 9, pyridine) was obtained by treatment of the sugar **16** with phenylhydrazine in aqueous acetic acid [lit [22], m p 179–180°, $[\alpha]_D$ −70 4° in pyridine–ethanol]

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