A SYNTHESIS OF METHYL α-MALTOSIDE*

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ABSTRACT

A mixture of methanol, bromine, and silver carbonate readily converted ethyl 1-thio-β-maltoside into a mixture containing methyl α,β-maltoside and traces of maltose. The α-anomer, which initially formed 85% of the maltoside fraction, was enriched by selective oxidation of the β-anomer with chromic acid. Chromatographic purification gave a 65% yield of methyl α-maltoside of 97% anomeric purity. N.m.r. spectral data for methyl α-maltoside heptaacetate were obtained.

INTRODUCTION

Lack of a practical synthesis of methyl α-maltoside (**3a**) has limited the use of this compound in enzyme-mechanistic studies and as a model for starch in solvolytic and substitution reactions. The reported enzymic and chemical syntheses seem poorly suited to large-scale preparation of **3a**.

When the glucosyl transferase activity of either potato D-enzyme[1] or *Bacillus macerans* amylase[2] was used to prepare a series of methyl α-maltooligosaccharides from methyl α-D-glucopyranoside, yields of **3a** were mediocre after chromatographic separations. Matsubara[3] found that Taka-amylase A forms **3a** in low yield during the hydrolysis of *p*-nitrophenyl α-maltoside in aqueous methanol and, additionally, claimed a direct synthesis of **3a** by the action of 0.1% methanolic hydrogen chloride on β-maltose. However, J. Lehrfeld, of this Laboratory, has shown, in work not published, that this method and several variations of it yield only complex mixtures of maltosides, glucopyranosides, and glucofuranosides, from which **3a** does not separate as claimed. Inouye and coworkers[4] obtained high yields of crude methyl α,β-maltoside heptaacetate (**3b**, **4b**) by anomerization of methyl β-maltoside heptaacetate (**4b**) with antimony pentachloride. The high specific rotation of their product mixture (+130° in chloroform) indicated that **3b** was the major component. However, this method and other anomerization procedures have not provided for selective removal of the admixed methyl β-maltoside.

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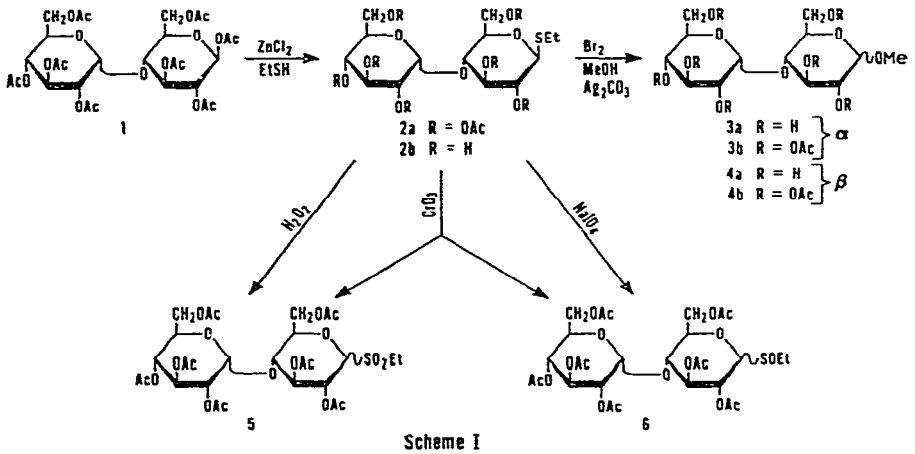
In 1969, Angyal and James[5] reported that methyl α-D-glucopyranoside tetraacetate (7) was oxidized much more slowly than the β-anomer (8) by chromium trioxide in acetic acid. The probability of an analogous selectivity for **4b** in the presence of **3b** prompted us to test the Angyal–James reagent on mixtures rich in **3b** to devise a practical, chemical synthesis of **3a**.

RESULTS AND DISCUSSION

The synthesis (Scheme I) is based on the reaction of Weygand *et al.*[6], who converted ethyl 1-thio-β-D-glucopyranoside into methyl α-D-glucopyranoside. A



Scheme I

mixture of methanol, bromine, and silver carbonate converted ethyl 1-thio-β-maltoside (**2b**) completely into a mixture of **3a**, **4a**, and a trace of maltose. G.l.c. analysis proved that conversion was complete and showed that **3a** constitutes 85% of the maltoside fraction.

Efforts were unsuccessful to decompose **4a** selectively with commercial β-glucosidase extracts. Incubation of the crude maltosides with emulsin (whose activity is known to be blocked by *O*-substitution at positions other than C-1 of the D-glucopyranose ring) was ineffective. Cellulase extracts, obtained from *Trichoderma viride*, *Aspergillus niger*, and *Rhizopus*, displayed both β-glucosidase and maltase activity; consequently, the maltoside mixture was completely hydrolyzed to methyl α-D-glucopyranoside and D-glucose.

The selective chromic acid oxidation of Angyal and James[5] successfully removed the methyl β-maltoside heptaacetate (**4b**) from methyl α-maltoside heptaacetate (**3b**). The oxidation of mixed methyl maltosides or glucosides under equivalent conditions established that the rate of reaction with chromic acid is nearly equal for each pair of homologs.

The similarities of the oxidations of the maltoside and glucoside suggested that the two systems would respond similarly to changes in reaction conditions, and that

conditions giving maximum conservation of the methyl α-form in the more easily analyzed oxidations of the glucoside would be directly applicable with the mixtures of maltosides. Therefore, a series of oxidations was planned for each glucoside anomer at each of three chromic acid–glucoside ratios (3:1, 2:1, or 1:1 w/w), and the apparent rate of each oxidation was determined.

The rate for the methyl α-form (**7**) was identical for each of the three ratios tested. For the methyl β-form (**8**), the rate of reaction depended on the amount of oxidant added, but it was judged that use of ratios higher than 3:1 (w/w) would not improve the selectivity of the reaction. The 3:1 (w/w) ratio utilized by Angyal and James[5] offered nearly optimal conditions. The findings are shown graphically in Fig. 1.

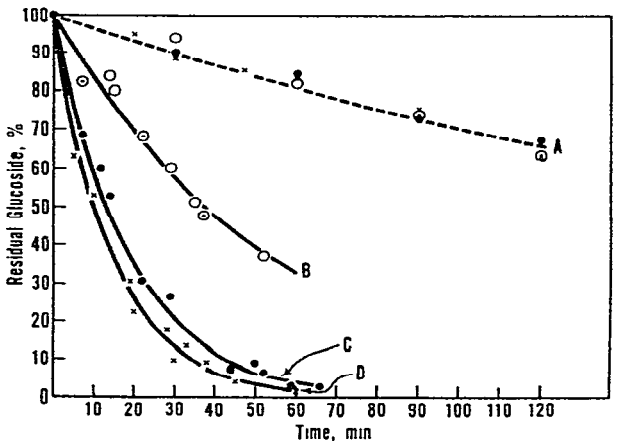


Fig 1. Oxidation of methyl α,β-D-glucopyranoside tetraacetates (**7** and **8**) by chromium trioxide–acetic acid. A. CrO_3–**7**, 1·1; 2·1; 3·1 (w/w) B CrO_3–**8**, 1·1 (w/w) C CrO_3–**8**, 2·1 (w/w). D CrO_3–**8**, 3·1 (w/w)

Oxidation of mixed **3b** and **4b** (85% as **3b**) on a preparative scale gave a final mixture of products that contained only 2–3% of **4b**. A portion of the mixture was separated by preparative t.l.c., to yield **3b** as a glass. N.m.r.-spectral data for **3b** are listed in Table I.

Attempts to separate **3b** from the oxidation byproducts by column chromatography on silica gel were unsuccessful. Deacetylation of the mixture did not improve the ease of separation until the mixture was treated with aqueous phenylhydrazine acetate[7]. Pure **3a** was then obtained by chromatography on a cellulose column in an overall yield of 65% (based on **1**).

It is essential that the methanolic bromine reagent reacts completely with **2b** before acetylation and oxidation of the crude mixture of maltosides. The oxidation of **2a**, regenerated from any residual **2b**, yields a mixture of previously unknown compounds, ethyl 1-thio-β-maltoside heptaacetate sulfone (**5**), and a component (**6**) presumed to be a mixture of diastereoisomeric sulfoxides. The identities of **5** and **6** were established by a comparison of their properties with those of materials derived from **2a** by use of specific oxidants reported to produce a sulfone (H_2O_2) or a mixture of

TABLE I

N.M.R. PARAMETERS FOR MALTOSIDE DERIVATIVES[a]

Compound	*Chemical shift, τ*								
	H-1	*H-1′*	*H-2*	*H-2′*	*H-3*	*H-3′*	*H-4*	*H-4′*	*H-5*
2a[b]	5.70d	4.51d	4.96t	4.99dd	4.64t	4.24dd	6.16t	4 68t	7.06m
3a[c]	5.47d	5.02d							
4a[c]	5.93d	4.99d							
3b[b]	5 25d	4 42d	5 15dd	4.96dd	4.22dd	4.25dd	5.99t	4.67t	6 29m
4b[b]	5.82d	4.50d	5.00dd	4.98dd	4.65t	4 23dd	6 09t	4.68t	6.92m

Compound	*Coupling constants, J (Hz)*							
	$J_{1,2}$	$J_{1',2'}$	$J_{2,3}$	$J_{2',3'}$	$J_{3,4}$	$J_{3',4'}$	$J_{4,5}$	$J_{4',5}$
2a[b]	9	4.5	9	9 8	9	9.8	9.5	9 8
3a[c]	3.5	3						
4a[c]	7.5	3						
3b[b]	3.6	4	9.5	10.5	9 5	9 5	9 5	9.5
4b[b]	7 8	4	9.3	9 5	9.3	10.5	9.5	9 7

[a]100 MHz; d = doublet, dd = doublet of doublets, t = triplet, m = mulitplet. [b]In benzene-d_6. [c]In methyl sulfoxide-d_6.

diastereoisomeric sulfoxides ($NaIO_4$) from methyl 1-thio-β-D-xylopyranoside triacetate[8]. Compounds **5** and **6**, if present in the oxidation products, cochromatograph with **3a** after deacetylation, and are not removed by the treatment with phenylhydrazine acetate.

EXPERIMENTAL

General. — N.m.r. spectra were measured at 100 MHz on a Varian* HA-100 spectrometer with tetramethylsilane ($\tau = 10.0$) as the internal standard. Chemical shifts and coupling constants are first-order, measured directly from spectral spacings. An F&M research chromatograph, Model 700, was employed for g.l.c. Hydroxyl derivatives were converted into trimethylsilyl ethers approximately 18 h before injection. Columns of 1/8-in. o.d. stainless-steel tubing were packed as follows: (A) 4 ft, 10% Apiezon L on Chromosorb W (80–100 mesh); (B) 4 ft, 1:1 w/w mixture[9] of 20% BDS and 20% Apiezon M separately coated on Chromosorb W (60–80 mesh); (C) 6 ft, 3% JXR on Gas Chrom Q (100–200 mesh); (D) 12 ft, 15% Carbowax 20M on Gas Chrom Q (80–100 mesh). Column programming was isothermal with helium as the carrier gas and with flame-ionization detection. Melting points were determined in capillary tubes and are corrected. Optical rotations were measured in a 1-dm tube. Pyridine was removed from organic phases by repeated washing with 5% aqueous cupric sulfate, and acetic acid was removed with aqueous

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sodium hydrogen carbonate. Solutions were evaporated below 40° under diminished pressure. Solvents were proportioned on a v/v basis. Microcrystalline cellulose (Avicel) was used for column chromatography. Precoated plates of Silica Gel F-254 (E. Merck, Darmstadt, Germany) were used for t.l.c. Layer thicknesses were 0 25 and 2.0 mm for analytical and preparative separations, respectively.

Ethyl **1-*thio*-β-*maltoside heptaacetate* (2a).** — A 35.5-g sample of β-maltose octaacetate (**1**) was dissolved in a cold solution containing 10 g of fused zinc chloride in 100 ml of ethanethiol. The temperature was maintained for 18 h below 5°, and then 50 ml of pyridine was added. The stirred mixture was treated dropwise with 140 ml of acetic anhydride with the internal temperature kept below 15° during the entire addition and reaction period. After 3 h, 10 ml of methanol was added, and then the mixture was kept for a final 0.5 h before it was poured into 1000 ml of ethyl acetate and washed with 1000 ml of water. The aqueous layer was separated and washed with a fresh 300 ml of ethyl acetate. The combined ethyl acetate extracts were freed of residual pyridine and acetic acid, dried, and evaporated. The crude product (36 g) was recrystallized from ethanol, and gave 29.5 g (83%) of **2a**: m.p. 135.5–136.5°, $([\alpha]_D^{20}$ +50.1° (*c* 1.1, chloroform); for n.m.r. data, see Table I.

Anal. Calc. for $C_{28}H_{40}O_{17}S$: C, 49.4; H, 5.9; S, 4.7. Found: C, 49.3; H, 6.0; S, 4.5.

Ethyl **1-*thio*-β-*maltoside* (2b)** — A 25-g portion of **2a** was added to 300 ml of cold methanol saturated with ammonia and the solution was kept for 24 h at −5°. Evaporation of the solution to a syrup and extraction with two 300-ml portions of hot ethyl acetate, yielded 8.6 g of **2b**. Evaporation of the extracts to approximately one-third of the original volume gave an additional 5.2 g of **2b**, for an overall yield of 97% After recrystallization from a mixture of methanol and ethyl acetate, **2b** had m p. 149–152°, $[\alpha]_D^{20}$ +55° (*c* 1.3, methanol).

Anal. Calc. for $C_{14}H_{26}O_{10}S$: C, 43.5; H, 6.8; S, 8.3. Found: C, 43.3; H, 6.9; S, 7.9.

Deacetylation of **2a** with 15 mM barium methoxide in methanol, followed by neutralization with acetic acid, gave a crude form of **2b** that could be carried directly through the remaining sequence of reactions without crystallization.

Reaction of **2b** *with bromine in methanol.* — A solution containing 6 g of **2b** in 300 ml of anhydrous methanol was protected from light and moisture. The solution was stirred and rapidly treated with 3 ml of bromine, 20 g of silver carbonate, and 20 g of anhydrous calcium sulfate (40 mesh). The yellow slurry was stirred for 18 h at room temperature before it was filtered through a talc pad. Residual silver salts in the filtrate were converted into the insoluble sulfide form by saturation with hydrogen sulfide in the presence of pyridine (5 ml). The mixture was filtered and evaporated. T.l.c. (7:2:1 butanol–pyridine–water, solvent A) showed that the syrup contained approximately 95% of methyl α,β-maltoside (**3a**, **4a**) and traces of maltose and other byproducts. G.l.c. analysis (column A, 225° or column C, 215°) showed that **3a** comprised approximately 85% of the total maltoside fraction.

The entire sample was dissolved in 20 ml of pyridine, treated with 40 ml of

acetic anhydride, and kept for 48 h at room temperature. Methanol (50 ml) was added, with cooling, and the solution was evaporated to a volume of approximately 50 ml. The product was dissolved in ethyl acetate, freed of residual pyridine and acetic acid, and evaporated. Multiple-ascent t.l.c. (7:3 methylcyclopentane–acetone, solvent B) showed that the oily mixture of **3b** and **4b** (10 g) was completely acetylated.

Action of β-glucosidases. — Four samples (100 mg) of a crude mixture of **3a** **4a** (85% as **3a**) were dissolved in 10 ml of an appropriate acetate buffer and treated with crude β-glucosidase extracts as follows: (*a*) pH 4.8 buffer with 35 mg of *T. viride* cellulase (Worthington CS II); (*b*) pH 4.8 buffer with 100 mg of *Rhizopus* cellulase (Sigma); (*c*) pH 4.45 buffer with 25 mg of *Aspergillus niger* cellulase (Worthington CS I); and (*d*) pH 4.65 buffer with 20 mg of crude emulsin After all solutions had been incubated for 36 h at 35°, they were treated with 200 mg of sodium hydrogen carbonate and evaporated. A portion of each was converted into its trimethylsilyl ether, and the remainder was acetylated with pyridine and acetic anhydride. Multiple-ascent t.l.c. (4:1 methyl cyclopentane–acetone, solvent C) of the acetylated portions showed that the methyl maltosides in (*a*), (*b*), and (*c*) had been converted into D-glucose and methyl D-glucoside. Sample (*d*) was unchanged. G.l.c. analysis (column B, 205°) of the acetylated fractions confirmed the t.l.c. findings in (*a*), (*b*), and (*c*) and additionally showed that the glucoside was in the methyl α-form. No change in the ratio of **3a** to **4a** could be detected for the trimethylsilylated sample of (*d*) (column C, 215°) from that of the initial composition.

Selective oxidation with chromic acid. — (*a*) Six 15 × 50 mm (i.d.) screw-cap bottles containing 167 mg of methyl α-D-glucopyranoside tetraacetate (**7**) and 100 mg of D-glucitol hexaacetate (**9**) in 5 ml of glacial acetic acid were prepared and serially treated with solid chromium trioxide. The first pair of samples was treated with 167 mg of CrO_3 each (CrO_3–glucoside 1:1 w/w, 3.6:1 moles/mole); the second pair, with 335 mg each (2:1 w/w, 7.3:1 moles/mole); and the third pair, with 500 mg each (3:1 w/w, 10.9:1 moles/mole). All samples were shaken vigorously at room temperature during oxidation. From 1 to 2 μl was removed periodically and analyzed by g.l.c. (column B, 210°). The peak areas of **7** and **9** were determined by triangulation, and the amount of residual **7** (in mg and as per cent of **7** at t_0) in each sample was calculated. Plots of $\log a_0/a_0-x$ versus t ($a_0 = 167$ mg of **7** at t_0, $a_0-x =$ residual mg of **7** at t) were linear for each oxidation, and colinear for the three series. The data were pooled and the best line was determined by least-squares analysis. An apparent rate-constant of $6 \times 10^{-5}.\text{sec}^{-1}$ was calculated (calculated from literature data[5], $k = 5.7 \times 10^{-5}.\text{sec}^{-1}$) and used to construct curve A in Fig. 1.

(*b*) *Oxidation of methyl-β-D-glucopyranoside tetraacetate* (**8**). The methodology described for **7** was used to oxidize six samples of **8**. Least-squares analysis of the data gave calculated rate-constants of 31×10^{-5}, 88×10^{-5}, and $113 \times 10^{-5}.\text{sec}^{-1}$ for the 1:1, 2:1, and 3:1 (w/w) ratios of CrO_3 to **9** (Fig. 1).

(*c*) *Oxidation of mixed* **7** *and* **8**. A solution containing 69 mg of **7** and 81 mg of **8** in 5 ml of glacial acetic acid was placed in a 15 × 50 mm (i.d.) screw-cap septum bottle and then was treated with 256 mg of CrO_3 (CrO_3–**9**, 11.5:1 moles/mole) and shaken

vigorously at room temperature. At intervals 0.2 ml was removed, quenched in 4 ml of 1.5M sodium methoxide in methanol, and kept overnight at −5°. The samples were neutralized with 0.2 ml of glacial acetic acid, evaporated to dryness, and converted into their trimethylsilyl ethers. The relative amount of residual **8** present in each sample was determined by g.l.c. (column D, 160°). Found: t_{min}, (% **8**); 0, (54); 5, (40); 12, (30); 20, (18.5); 30, (10.5).

(*d*) *Oxidation of mixed* **3b** *and* **4b**. A solution containing 69 mg of glassy **3b** and 81 mg of **4b** in 5 ml of acetic acid was placed in a 15 × 50 mm (i.d.) screw-cap septum bottle and then was treated with 142 mg of CrO_3 (CrO_3–**4b**, 11.5:1 moles/mole and shaken vigorously at room temperature. At intervals 0.2 ml was removed and handled as described for (*c*). The relative amount of residual **4b** in each sample was determined by g.l.c. analysis (column A, 230°). Found: t_{min}, (% **4b**); 0, (54); 7, (41); 15, (28); 22, (19); 30, (13).

(*e*) *Large-scale oxidation of mixed* **3b** *and* **4b**. A crude mixture of **3b** and **4b** (10 g) was dissolved in 100 ml of glacial acetic acid, poured into a 250-ml Erlenmeyer flask, and treated with 10 g of CrO_3. The mixture was stoppered, shaken vigorously for 45 min, and then poured into a stirred mixture of 1000 ml of ethyl acetate and 1000 ml of water. Sodium hydrogen carbonate (150 g) was added over a 2–3 min period, the layers were separated, and the aqueous phase was extracted with fresh ethyl acetate (750 ml). The combined ethyl acetate extracts were washed with fresh aqueous sodium hydrogen carbonate, dried, and evaporated. T.l.c. (solvent B) of the yellow syrup (9.5 g) showed that the bulk of the maltoside fraction has survived. G l.c. analysis (column A) of a deacetylated sample showed that the maltoside fraction contained less than 3% of **4b**.

Isolation of **3b**. — A 2-g sample of the oxidation mixture from (*e*) was streaked on four preparative t.l.c. plates and developed twice with solvent B. The bands containing **3b** were excised, extracted with chloroform, and evaporated. Pure **3b** (1.3 g) was a colorless glass after distillation at 250°/0.1 m torr, and had $[\alpha]_D^{20}$ +136° (*c* 0.7, chloroform). For n.m.r data, see Table I.

Anal. Calc for $C_{27}H_{38}O_{18}$: C, 49.9, H, 5.9; OMe, 4.8. Found: C, 50.2; H, 6.0; OMe, 4.8.

Isolation of **3a**. — The remainder of the crude **3b** from (*e*) was deacetylated in 200 ml of 15 mM barium methoxide in methanol, neutralized with 1 ml of glacial acetic acid, and evaporated. The residue was dissolved in 300 ml of water and treated with 40 ml of aqueous phenylhydrazine acetate[7]. The reaction mixture was heated for 0.5 h on a steam bath, chilled for 1 h in an ice bath, and filtered. The filtrate was serially extracted with chloroform (150 ml) and ethyl ether (150 ml), and the organic phases were discarded. The aqueous layer was evaporated to low volume, extracted with hot ethanol (250 ml), and filtered. The filtrate was evaporated and chromatographed on a column (60 × 750 mm) of microcrystalline cellulose with the upper phase of 2:5:5 pyridine–ethyl acetate–water[10] The final sample, after decolorization with charcoal, was a colorless syrup (2.7 g, 65%) that had $[\alpha]_D^{20}$ +174° (*c* 0.9, water). For n.m.r. data see Table I. Arndt has reported the spectrum of **3a** in D_2O[11].

Anal. Calc. for $C_{13}H_{24}O_{11} \cdot 0.7\ H_2O$: C, 42.3; H, 6.9; OMe, 8.4. Found: C, 42.3; H, 6.8; OMe, 8.5.

When taken up in absolute ethanol, **3a** formed a particulate, amorphous, hygroscopic solid that contained solvent. Two cycles of hydration in a chamber of 100% relative humidity and drying over phosphorus pentaoxide removed the ethanol.

Oxidations of **2a**. — (*a*) A 1.5-g portion of **2a** was dissolved in 15 ml of glacial acetic acid, treated with 6 ml of 30% aqueous hydrogen peroxide, and kept for 48 h at room temperature. The mixture was poured into 250 ml of ethyl acetate and freed of acetic acid. The ethyl acetate solution yielded 1.5 g of green syrup. T.l.c. examination (solvent B) showed almost complete conversion of **2a** into ethyl 1-thio-β-maltoside heptaacetate sulfone (**5**), with traces of a compound (**6**) having lower R_F described below. The entire sample was purified by preparative t.l.c. (solvent B). The extract yielded 1.3 g of crystals from methanol: m.p. 129–130° $[\alpha]_D^{20}$ +50° (*c* 1.0, chloroform).

Anal. Calc. for $C_{28}H_{40}O_{19}S$: C, 47.2; H, 5.7; S, 4.5. Found: C, 47.1; H, 5.8; S, 4.5.

(*b*) A solution containing 1 g of **2a** in 25 ml of 2-methoxyethanol was treated with 1 g of sodium periodate in 6 ml of water. The mixture was kept for 48 h at 45° and then evaporated The residue was extracted with 250 ml of ethyl acetate, washed twice with water, dried, and evaporated. The recovered solids weighed 0.9 g. T.l.c. (solvent B) examination indicated that approximately one-half of the **2a** originally present had been converted into the minor component (**6**) seen in (*a*). No effort was made to purify or separate the presumed diastereoisomeric sulfoxides (**6**).

(*c*) A solution of **2a** (1 g) in 10 ml of glacial acetic acid was mixed with 1 g of CrO_3 and shaken vigorously for 40 min at room temperature. The mixture was poured into 250 ml of ethyl acetate and worked up in the manner described for **3b**. T.l.c. examination (solvent B) showed complete conversion of **2a** into **5** and **6**, in an approximate ratio of 3:1. The mixture was purified by preparative t.l.c. (solvent B), and **5** was isolated as described earlier. Crystallization from methanol gave 0.5 g of product; m.p. 129–130°; m.p. with authentic **5**, undepressed; $[\alpha]_D^{20}$ +50.5° (*c* 1.2, chloroform).

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