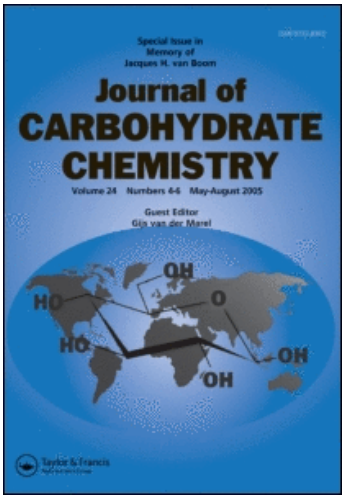

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SYNTHESIS OF A LIPODISACCHARIDIC REAGENT FOR THE CHEMICAL MODIFICATION OF ENZYMES

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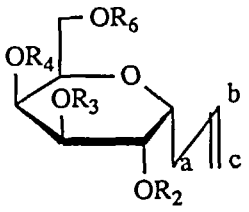
ABSTRACT

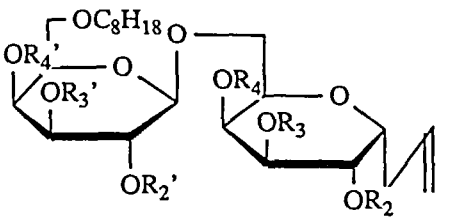
The preparation of an amphiphilic lipodigalactosyl hemiacetal is described. Use of benzoyl protecting groups and mild conditions for detritylation allow preparation of a 1-α-*C*-allyl galactosyl acceptor without intramolecular acyl transfer. Condensation with a lipogalactosyl donor and cleavage of the protecting groups gave a *C*-allyl disaccharide. Reductive ozonolysis of the double bond yielded an aldehyde which spontaneously formed a cyclic hemiacetal with the C-2 hydroxyl group. In the Lewis acid catalyzed allylation of the penta-*O*-acetyl galactose with allyltrimethylsilane, the reactivity of the β-anomer is much higher than that of the α-anomer.

INTRODUCTION

Lipoglycosylated enzymes may be useful as new biocatalysts for organic synthesis in polar, aprotic solvents.[1] Lipopolysaccharide derivatives are better able to maintain the essential layer of water around the enzyme in hydrophilic solvents than their monosaccharide analogs. The water stabilizes the protein in non-aqueous solvents and preserves their catalytic activity.

The reductive ozonolysis of substituted *C*-allyl, *O*-allyl, and *O*-butenyl galactosyl derivatives were reported[2] previously to give respectively 5-, 6-, and 7-membered fused hemiacetals. Reductive conjugation of these latent aldehydes with N^{α}-Z-L-lysine showed that the more strained five membered hemiacetal was the most reactive.[3] This





1α: R_2= R_3= R_4= R_6= $COCH_3$

2 : R_2= R_3= R_4= R_6= H

3 : R_2= R_3= R_4= H; R_6= $C(C_6H_5)_3$

4 : R_2= R_3= R_4= COC_6H_5; R_6= $C(C_6H_5)_3$

4': R_2= R_3= R_4= $CH_2C_6H_5$; R_6= $C(C_6H_5)_3$

5 : R_2= R_3= R_4= COC_6H_5; R_6= H

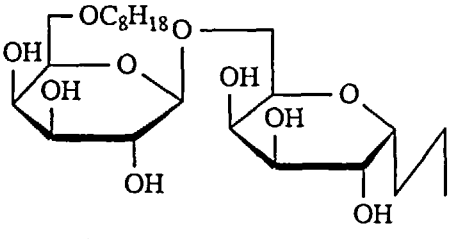
5': R_2= R_3= R_4= $CH_2C_6H_5$; R_6= H

7 : R_2= R_3= R_4= COC_6H_5
$R_{2'}$= $R_{3'}$= $R_{4'}$= $COCH_3$

7': R_2= R_3= R_4= $CH_2C_6H_5$
$R_{2'}$= $R_{3'}$= $R_{4'}$= $COCH_3$

7": R_2= R_3= R_4= $CH_2C_6H_5$
$R_{2'}$= $R_{3'}$= $R_{4'}$= H

8 : R_2= R_3= R_4= $R_{2'}$= $R_{3'}$= $R_{4'}$= H



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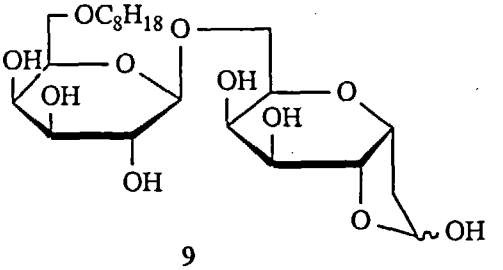

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Fig. 1. Structural formulas of compounds **1-10**

led us to undertake the synthesis of *O*-(6-*O*-octyl-β-D-*galacto*-pyranosyl)-(1→6)-1-allyl-1-deoxy-α-D-*galacto*-pyranose, **8**.

RESULTS AND DISCUSSION

Numerous methods have been proposed for the *C*-allylation of saccharides with allyltrimethylsilane[4-8] but few of them used fully acylated sugars as starting materials,[6-7] even though the latter compounds are easily available and removal of acyl protecting groups is a very facile process. For this reason we studied the condensation of the allytrimethylsilane with both the pure α- and β-anomers of galactose peracetate under different experimental conditions.

TABLE 1. Reaction of Penta-*O*-acetyl-α-D- and Penta-*O*-acetyl-β-D-*galacto*-pyranosides with Allyltrimethylsilane under Different Experimental Conditions.

Starting galactosyl acetate	Catalyst	Solvent	Temperature °C	Time h	*C*-allyl product 1 yield %	ratio α/β
α	$BF_3.Et_2O$	CH_3CN	4	48	0	-
α	$BF_3.Et_2O$	CH_3CN	50	8	60	9/1
β	$BF_3.Et_2O$	CH_3CN	4	48	70	9/1
α	$BF_3.Et_2O$	$(ClCH_2)_2$	40	48	0	-
α	$BF_3.Et_2O$	$(ClCH_2)_2$	80	48	10	7/3
β	$BF_3.Et_2O$	$(ClCH_2)_2$	40	24	50	6/4
α	$ZnBr_2$	CH_3CN	80	48	0	-
β	$ZnBr_2$	CH_3CN	80	48	0	-
β	$ZnBr_2$	$(ClCH_{2)2}$	80	24	70	6/4

The yield and α/β selectivity of the allylation reaction depends on the Lewis acid catalyst employed, the solvent, the temperature and the configuration of the 1-acetoxy group (Table 1). The variation in Lewis acid and solvent may lead to changes in mechanism from S_N2 via a complex to S_N1 via an oxocarbenium ion.[8] Under mild reaction conditions, the α-anomer does not react (Table 1). Due to the anomeric effect,[9-10] ionization to the electrophilic oxocarbenium ion is probably more difficult with the α-anomer. In the furanose series, the yield and the stereochemical outcome of the condensation with the allyltrimethylsilane are only slightly influenced by the stucture of the starting furanosyl acetate.[11]

The α- and β-*C*-allylated products were difficult to separate, the best experimental conditions for the allylation being the use of boron trifluoride etherate in acetonitrile, which gave a 9-1 mixture of the α- and β-anomers of the 1-allyl-1-deoxy-tetra-*O*-acetyl-D-*galacto*-pyranose **1**. In our hands, the direct *C*-allylation of disaccharides, such as 6'-*O*-octyl-β-D-*galacto*-pyranosyl-(1→6)-α-D-*galacto*-pyranose peracetate gives numerous products in poor yields; among them the α-

and β-1-*C*-allyl derivatives and *C*-allylated orthoesters were identified. Therefore, the *C*-allyl liposaccharide **8** was prepared by glycosidic synthesis.

Deacetylation of **1** and recrystallization gave pure starting material for the synthesis, the 1-allyl-1-deoxy-α-D-*galacto*-pyranose **2**. Tritylation of **2** yielded the 6-*O*-trityl derivative **3**, followed by benzoylation which yielded the tribenzoate **4**. Treatment of **4** with Me_3SiCl and NaI afforded the glycosyl acceptor **5**.

To avoid possible acetyl migration from C-4 to C-6 during the acidic cleavage of the 6-*O*-trityl group, more stable *O*-benzoyl protecting groups[12-14] and mild conditions for the removal of the trityl group[15] were used. To confirm that rearrangement did not occur, the synthesis of the hydrogenated derivative of **3**, the 1-*C*-propyl-(1→6)-α-D-galactobiose **10**, was also carried out by employing stable benzyl protecting groups during synthesis.

Condensation of **5** with the 6-*O*-octyl-tri-*O*-acetyl-*galacto*-pyranosyl bromide **6**,[16] in the presence of mercuric cyanide, gave the acylated *C*-allyl disaccharide **7** in 60% yield. Removal of both the acetyl and benzoyl protecting groups gave the *C*-allyl lipodisaccharide **8**, having six free hydroxyl functions.

A second route to the lipodisaccharide system was also followed. Perbenzylation of the tritylated galactopyranosyl derivative **3** gave **4'**, detritylation of which yielded the benzylated glycosyl acceptor **5'**. Condensation of **5'** with the glycosyl donor **6** led to the protected disaccharide **7'**, which after deacetylation yielded the disaccharide **7"**. Treatment of **7"** with Pd/C under hydrogen pressure resulted in both hydrogenolysis of the benzyl protecting groups and the reduction of the double bond to give **10**. The ^1H and ^{13}C NMR spectra of **10** were identical with those of the reduced derivative of **8**, unambiguously establishing the structure of the disaccharide **8**.

Reductive ozonolysis[2] of compound **8** led to the lipodisaccharide oxolanol **9**, the ^1H and ^{13}C NMR spectra of which lack the characteristic signals of an aldehyde group but show two hemiacetal carbon signals for C_b at 99.3 and 99.6 and two proton signals (each as doublets of doublets) for the hemiacetal H_b at 5.6 and 5.7 ppm, in agreement with the proposed structure. The model reductive alkylation of N^{α}-Z-L-lysine, as well as the chemical modification of enzymes, with this reagent, are under study.[3]

EXPERIMENTAL

General Procedures. Melting points were determined with a Mettler FP 61 apparatus and are uncorrected. Optical rotations were recorded at 22 °C with a Perkin-Elmer 241 polarimeter. ^1H NMR spectra were recorded at 200 or 300 MHz, ^{13}C

TABLE 2. ^{1}H NMR Chemical Shifts (ppm) and Coupling Constants (Hz) in $CDCl_3$ (A) or in CD_3OD (B)

Compound	1α	2	3	4	4'	5	5'	7
Solvent	A	B	A	A	A	A	A	A
Ha	2.2-2.5	2.5-2.7	2.3-2.6	2.4-2.8	2.3-2.4	2.5-2.7	2.2-2.4	2.4-2.8
Hb	5.75	6.06	5.92	5.87	5.80	5.80	5.70	5.80
Hc	5.1-5.2	5.2-5.3	5.0-5.2	5.1-5.2	5.0-5.1	5.1-5.2	5.0-5.2	5.1-5.2
H-1	4.31	4.18	3.93	4.46	3.97	4.62	4.07	4.56
H-2	5.28	4.08	3.84	5.61	3.67	5.93	3.70	5.79
H-3	5.21	3.86	3.62	5.81	*	5.83	3.76	5.81
H-4	5.42	4.14	3.86	5.96	*	5.85	3.98	5.86
H-5	4.08	*	3.45	4.35	*	4.18	3.91	4.32
H-6	4.1-4.2	*	3.2-3.3	3.1-3.5	3.1-3.9	3.5-3.8	3.6-4.1	3.8-4.0
J_{1-2}	4.8	5.2	5.1	5.0	4.2	5.8	3.8	4.9
J_{2-3}	9.3	8.7	8.8	9.1	7.1	9.8	6.3	7.6
J_{3-4}	3.0	3.4	3.1	3.2	*	3.2	2.8	2.5
J_{4-5}	2.4	1.7	0-1	2.5	*	0-1	4.6	4.5
J_{5-6}	5.5-7.3	*	4.0-7.6	6.5	*	7.0-6.2	4.0-7.2	3.9-7.4
J_{6A-6B}	11.6	*	9.9	9.3	10.2	11.6	11.6	10.9

* not determined.

NMR spectra at 20 MHz with TMS as an internal standard. Spectral data are reported in Tables 2 and 3. TLC was performed on silica gel 60F-254 (Merck) and visualized with UV light or by charring with sulfuric acid. Column chromatography was carried out on silica gel 60 (70-230 mesh). The eluents used in TLC were the same as those indicated in each case for column chromatography purification.

1-Allyl-1-deoxy-2,3,4,6-tetra-*O*-acetyl-D-galactopyranose (1). To a solution of penta-*O*-acetyl-β-D-galactose (3.9 g, 10 mmol) in dry acetonitrile (30 mL) was added allytrimethylsilane (3.57 mL, 20 mmol). The mixture was cooled to 4 °C under argon, then $BF_3.Et_2O$ (2.7 mL, 22 mmol) was slowly added and the reaction was continued for 24 h. The mixture was poured into water, extracted with dichloromethane, washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated to give a syrup. The residue was chromatographed (7:3 pentane-ethyl acetate) to give 1 (2.6 g, 70% yield) as a mixture (α:β = 9:1).

1-Allyl-1-deoxy-α-D-galactopyranose (2). Compound 1 (1.32 g, 5 mmol) in methanol (25 mL) was deacetylated by addition of sodium methoxide (50 mg). After 1 h

TABLE 3. ^{13}C NMR Chemical Shifts in $CDCl_3$ (A) or CD_3OD (B) at 20 Mhz

Compound	Solvent	Ca	Cb	Cc	C_1 to C_5	C_6	$C_{1'}$
1α	A	30.9	133.5	117.6	67.7-71.5	61.5	-
1β	A	36.9	133.2	117.9	67.6-75.7	62.8	-
2	B	30.4	136.1	116.9	69.7-75.6	61.9	-
3	A	30.8	136.7	117.0	69.9-75.7	64.0	-
4	A	31.0	*	117.6	68.7-71.9	60.9	-
4'	A	32.1	135.2	116.7	71.0-74.7	61.4	-
5	A	31.3	*	117.9	70.3-74.0	61.2	-
5'	A	32.8	134.9	117.2	70.3-74.0	60.8	-
7	A	31.9	*	117.9	67.6-73.0	-	101.1
7'	A	33.1	135.3	117.0	66.3-75.5	-	101.4
7"	B	32.9	134.8	117.4	66.8-75.2	-	103.8
8	B	33.0	136.8	117.2	69.0-75.7	-	105.2
9	B	39.3	99.3	-	68.9-82.7	-	105.2
		40.8	98.6	-	68.9-81.7	-	105.2
10	B	(14.4 to 33.0)			69.2-75.8	-	105.2

* Cb are hidden by C aromatics.

at room temperature, NaOMe was destroyed by addition of Amberlite CG-50, then methanol was evaporated and the residue purified by chromatography with 85:15 (V/V) dichloromethane-methanol as the eluent to give 2 (0.98 g, 95% yield) as a mixture (ratio α:β = 9:1). Crystallization from acetone gave the pure α isomer (78%): mp 134 °C; $[\alpha]_D$ + 104°, $[\alpha]_{546}$ + 123° (c = 1.5, $CHCl_3$).

Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found : C, 52.98; H, 7.95.

1-Allyl-1-deoxy-6-*O*-trityl-α-D-galactopyranose (3). To a solution of 2 (0.4 g, 2 mmol) in pyridine (10 mL) was added triphenylmethyl choride (1.12 g, 4 mmol). The reaction was maintained at room temperature under argon for 24 h. Evaporation of the solvent gave a syrup which was dissolved in diethyl ether and the solution was washed with water, dried (Na_2SO_4) and concentrated. The residue was chromatographed with 9:1 dichloromethane-methanol as the eluent to give 3 (0.5 g, 58% yield): R_f 0.48; mp 76 °C.

Anal. Calcd for $C_{28}H_{30}O_5$: C, 75.31; H, 6.77. Found : C, 75.04; H, 6.58.

1-Allyl-1-deoxy-6-*O*-trityl-2,3,4-tri-*O*-benzoyl-α-D-galactopyranose (4). Compound 4 was obtained by benzoylation of compound 3, or directly from compound 2. To a solution of 2 (0.39 g, 1.9 mmol) in dry pyridine at room temperature under argon was added triphenylmethyl chloride (1.07 g, 3.8 mmol). The reaction mixture was stirred

for 24 h, then benzoyl chloride (1.21 mL, 11.5 mmol) was slowly added. Stirring was continued for 5 h, then the pyridine was evaporated. The residue was dissolved in diethyl ether, washed with water and dried (Na_2SO_4). The obtained syrup was eluted from a silica gel column with 85:15 pentane-ethyl acetate to give **4** (1.01 g, 70% yield): R_f 0.60; mp 70 °C; $[\alpha]_D$ + 77.2°, $[\alpha]_{546}$ + 93.2° (*c* = 2, CH_2Cl_2).

Anal. Calcd for $C_{49}H_{42}O_8$: C, 77.55; H, 5.57. Found : C, 77.44; H, 5.23.

1-Allyl-1-deoxy-2,3,4-tri-*O*-benzoyl-α-D-galactopyranose (5). To a solution of **4** (0.76 g, 1 mmol) in dry acetonitrile (20 mL) was added NaI (0.3 g, 2 mmol). The suspension was stirred and cooled to 0 °C, then chlorotrimethylsilane (0.26 mL, 2 mmol) was added. After 1 h at 0 °C, the mixture was poured on water, extracted with diethyl ether, washed with aqueous sodium thiosulfate and dried (Na_2SO_4). Chromatography with 8:2 pentane-ethyl acetate as the eluent gave **5** (0.44 g, 85% yield): R_f 0.20; mp 68 °C; $[\alpha]_D$ +200°, $[\alpha]_{546}$ + 241° (*c* = 2, $CHCl_3$).

Anal. Calcd for $C_{30}H_{28}O_8$: C, 69.75; H, 5.46. Found : C, 69.35; H, 5.49.

1-Allyl-1-deoxy-6-*O*-trityl-2,3,4-tri-*O*-benzyl-α-D-galactopyranose (4'). The tritylated derivative **3** (0.23 g, 0.5 mmol) was dissolved in methyl sulfoxide and 1 g of crushed potassium hydroxide was added. The reaction mixture was maintained at room temperature during the dropwise addition of benzyl bromide (3.6 mL, 3 mmol). The mixture was stirred for 48 h, then diethyl ether was added, the ether solution was decanted, washed with water, dried (Na_2SO_4) and concentrated. The residue was chromatographed with dichloromethane as the eluent to give **4'** (0.24 g, 67% yield): R_f 0.85.

Anal.Calcd for $C_{49}H_{48}O_5$: C, 82.09; H, 6.75. Found : C, 82.25; H, 6.93.

1-Allyl-1-deoxy-2,3,4-tri-*O*-benzyl-α-D-galactopyranose (5'). Detritylation of compound **4'** was carried out as above for detritylation of compound **4**. Chromatography with 8:2 pentane-ethyl acetate as the eluent gave **5'** (54% yield): R_f 0.24; $[\alpha]_D$ + 28.4°, $[\alpha]_{546}$ + 23.6° (*c* = 1.6, $CHCl_3$).

***O*-(6-*O*-Octyl-2',3',4'-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→6)-1-allyl-1-deoxy-2,3,4-tri-*O*-benzoyl-α-D-galactopyranose (7).** To a solution of 6-*O*-octyl-2,3,4-tri-*O*-acetyl-α-D-galactopyranosyl bromide[16] (0.48 g, 1 mmol) in dichloromethane (20 mL) was added **5** (0.52 g, 1 mmol) and $Hg(CN)_2$ (0.2 g, 1.1 mmol). The reaction mixture was stirred for 48 h at room temperature and concentrated to dryness. The residue was chromatographed with 7:3 pentane-ethyl acetate as the eluent to give **7** (0.55 g, 60% yield): R_f 0.64; mp 71 °C; $[\alpha]_D$ + 79.8°, $[\alpha]_{546}$ + 96.2° (*c* = 2, $CHCl_3$).

Anal. Calcd for $C_{50}H_{60}O_{16}$: C, 65.49; H, 6.60. Found: C, 65.40; H, 6.63.

***O*-(6-*O*-Octyl-β-D-galactopyranosyl)-(1→6)-1-allyl-1-deoxy-α-D-galactopyranose (8).** Compound **7** (0.46 g, 0.5 mmol) was dissolved in methanol (10 mL) and

treated with sodium methoxide (27 mg, 0.5 mmol) for 2 h at room temperature. Chromatography with 8:2 dichloromethane-methanol as the eluent gave **8** (0.23 g, 96% yield): R_f 0.47; mp 166 °C; $[\alpha]_D$ + 26.8°, $[\alpha]_{546}$ + 31.3° (*c* = 1, CH_3OH); ^1H NMR (CD_3OD): δ 2.6 to 2.7 (Ha), 6.06 (Hb), 5.25 to 5.30 (Hc), 3.05 (H-1).

Anal. Calcd for $C_{23}H_{42}O_{10}$, 1/2 H_2O: C, 56.67; H, 8.89. Found : C, 56.64; H, 8.85.

***O*-(6-*O*-Octyl-2',3',4'-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→6)-1-allyl-1-deoxy-2,3,4-tri-*O*-benzyl-α-D-galactopyrano se (7').** The condensation was carried out as above for **7**. Chromatography with 3-1 pentane-ethyl acetate as the eluent gave **7'** (55% yield): R_f 0.80; $[\alpha]_D$ + 14.1°, $[\alpha]_{546}$ + 16.8° (*c* = 3, $CHCl_3$); ^1H NMR (CD_3OD): δ 2.2 to 2.4 (Ha), 5.75 (Hb), 4.95 to 5.00 (Hc), 3.95 (H-1).

***O*-(6-*O*-Octyl-β-D-galactopyranosyl)-(1→6)-1-allyl-1-deoxy-2,3,4-tri-*O*-benzyl-α-D-galactopyranose (7").** Deacetylation of **7'** by methanolic sodium methoxide for 1 h at room temperature gave **7"**, after chromatography with 9:1 dicloromethane-methanol as the eluent (98% yield): R_f 0.59; $[\alpha]_D$ + 23.4°, $[\alpha]_{546}$ + 26.7° (*c* = 1, $CHCl_3$); ^1H NMR (CD_3OD): δ 2.2 to 2.4 (Ha), 5.75 (Hb), 5.0 to 5.2 (Hc), 3.94 (H-1).

Anal. Calcd for $C_{44}H_{60}O_{10}$: C, 70.56; H, 8.07. Found : C, 70.26; H, 7.95.

***O*-(6-*O*-Octyl-β-D-galactopyranosyl)-(1→6)-1-propyl-1-deoxy-α-D-galacto-pyranose (10).** Product **10** was obtained by hydrogenation of either compound **8** or compound **7"** (1 mmol) in 50 mL of a 1:4 (V/V) tetrahydrofuran-methanol solvent mixture with 50 mg of 10 % Pd-C as a catalyst under a 40 psi hydrogen atmosphere in a Parr apparatus. After filtration and concentration, the residues were chromatographed with 8:2 dichloromethane-methanol as the eluent (90-92% yields): R_f 0.55; mp 166 °C; $[\alpha]_D$ + 26.9°, $[\alpha]_{546}$ + 31.2° (*c* = 1, CH_3OH); ^1H NMR (CD_3OD): δ 1.57 (Ha), 1.30 (Hb), 0.92 (Hc), 3.5 (H-1).

Anal. Calcd for $C_{23}H_{44}O_{10}$. H_2O : C, 56.44; H, 9.42. Found : C, 56.42; H, 9.26.

(*O*-(6-*O*-Octyl-β-D-galactopyranosyl)-(1→6)-α-D-galactopyrano)[2,1b] oxolan-5-ol (9). A solution of **8** (0.48 g, 1 mmol) in dry methanol (10 mL) was cooled to -78 °C and treated with ozone until the color of the solution became permanently grey-blue . The mixture was stirred for an additional 15 min, then an argon stream was passed through the solution to eliminate excess ozone. Triphenylphosphine (2 mmol) was slowly added and the solution was warmed to room temperature. The stirring was continued for 2 h at room temperature to reduce the ozonide. Triphenylphosphineoxide was filtered and the filtrate concentrated. The residue was chromatographed with 8:2 dichloromethane-methanol as the eluent to give **9** (0.36 g, 76% yield): R_f 0.40; mp 135

°C; $[\alpha]_D$ + 25.9°, $[\alpha]_{546}$ + 30° (*c* = 1, CH_3OH); ^1H NMR (CD_3OD): δ 2.1 to 2.4 (Ha), 5.6-5.73 (Hb), 3.5 (H-1).

Anal. Cald for $C_{22}H_{40}O_{11}$: C, 54.98; H, 8.39. Found : C, 55.05; H, 8.58.

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