Carbohydrate Research, 144 (1985) 317–324
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SELECTIVE ACYLATION OF 6-DEOXYGLYCALS*,†

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(Received February 12th, 1985; accepted for publication, April 17th, 1985)

ABSTRACT

L-Rhamnal was acylated under a variety of conditions with various acylating reagents. Substitution of the hydroxyl group in the allylic position was favored when acetyl chloride, *N*-acetylimidazole, benzoyl chloride, and *N*-benzoylimidazole were used (40–60% net yields), whereas the homoallylic group of L-rhamnal was selectively protected when acetic anhydride–pyridine was employed for the acylation. The monoacetates of L-fucal underwent O-3→O-4 migration of the acetyl group, and selective acylation of this glycal could not be achieved.

INTRODUCTION

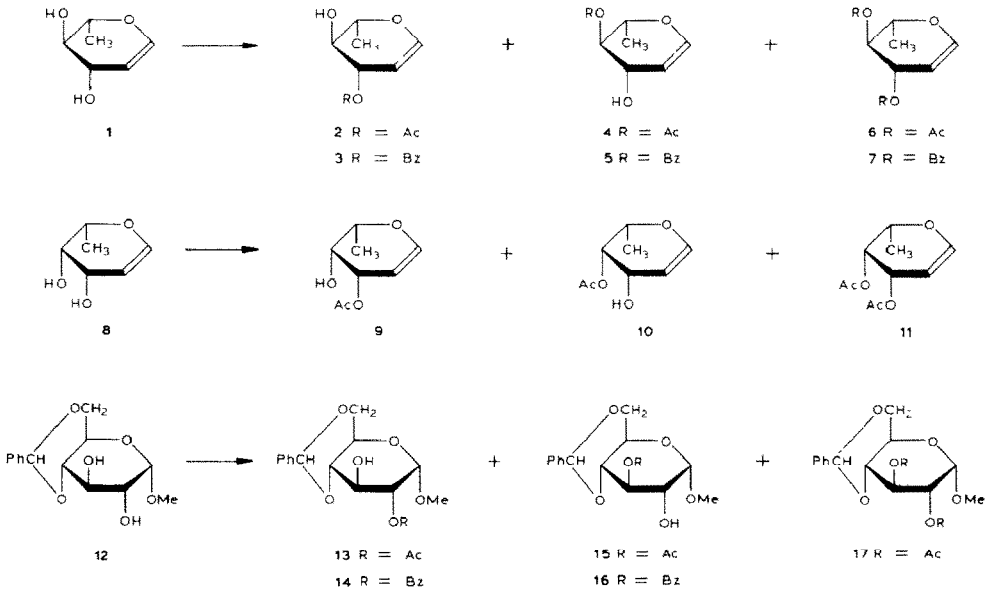
The glycals are cyclic vinyl ethers that have been widely used as synthetic intermediates because they readily undergo a variety of addition reactions and rearrangements[2]. In this laboratory, 6-deoxyglycals have been found especially useful in the synthesis of modified anthracycline antibiotics[3]. In connection with synthesis of anthracycline glycosides having a modified 6-deoxy-L-hexose or an oligosaccharide as the glycon, monosubstituted derivatives of L-rhamnal (**1**) and L-fucal (**8**) were required. These particular precursors give glycosides of favorable stereochemistry for high antitumor activity in the products.

The high cost of glycals **1** and **8** motivated a thorough investigation of their selective acylation with the goal of developing practical, high-yielding methods for their derivatization. Both glycals (**1** and **8**), in their favored $^5H_4$ (L) conformations[4], are diols having a quasiequatorially oriented hydroxyl group in the allylic position; the secondary homoallylic hydroxyl group is quasiequatorial in **1** and quasiaxial in **8**. Because of these stereochemical differences, it was anticipated that the hydroxyl groups of compounds **1** and **8** might exhibit different selectivity in their reactions.

The relative reactivity of hydroxyl groups in carbohydrate chemistry, although theoretically complex[5,6], is of high interest and has been intensively

*For a preliminary report, see ref. 1.
†Supported, in part, by Grant No. GM-11976 from the National Institute of General Medical Sciences, U.S. Public Health Service.

0008-6215/85/$ 03.30



studied[5]. In previous work from this laboratory, the substitution pattern of methyl α-D-glucopyranoside towards monoacetylation reactions with acetic anhydride–pyridine[7] and with *N*-acetylimidazole[8] was examined. We report herein acylation procedures that permit the selective derivatization of L-rhamnal (**1**) at either O-3 or O-4.

RESULTS AND DISCUSSION

Several reagents and various conditions were evaluated for selective monoacylation of the secondary allylic and homoallylic hydroxyl groups of L-rhamnal (**1**). The product mixtures were analyzed by g.l.c. (Table I). For preparative acylation of compounds **1** and **8**, the products were isolated by column chromatography and their structures established[4] by ^{1}H- and ^{13}C-n.m.r. spectroscopy. Comparison of the ^{13}C-n.m.r. spectra (Table II) of the 3-*O*-acylated (**2, 3**, and **9**) and 4-*O*-acylated (**4, 5**, and **10**) products with those of the unprotected glycals (**1** and **8**) showed that substitution at O-3 shifts the C-1 signals downfield by 1.3–2.0 p.p.m., and those of C-2 moved upfield (4.0–5.0 p.p.m.); these signals underwent only slight shifts when 4-*O*-substitution took place.

As shown in Table I, most of the acylating reagents, for instance, *N*-acetylimidazole, acetyl chloride, *N*-benzoylimidazole, and benzoyl chloride (but not acetic anhydride–pyridine) react selectively with the allylic hydroxyl group of L-rhamnal (**1**). Variations in solvent polarity, time of reaction, or of temperature did not significantly affect the stereoselectivity with *N*-acetylimidazole; the best results were obtained when the reaction was performed in toluene, for 3 h at 80°. Under these conditions, the ratio of 3-acetate (**2**), 4-acetate (**4**), and 3,4-diacetate

TABLE I

ACYLATION OF L-RHAMNAL UNDER VARIOUS CONDITIONS[a]

Reagent	*Base*	*Solvent*	*Time (h)*	*Temp. (degrees)*	*Ratio* **2**:**4**:**6** *(or* **3**:**5**:**7***)*	*Yield (%)* **2** + **4** *(or* **3** + **5***)*
Ac_2O	C_5H_5N	C_5H_5N	5	20	1.0:3.5:2.6	61
Ac_2O	C_5H_5N	C_5H_5N	20	20	1.0:3.5:2.8	61
Ac_2O	C_5H_5N	$HCONMe_2$	5	20	1.0:3.2:2.5	56
Ac_2O	C_5H_5N	PhMe	3	80	1.1:1.4:1.0	64
Ac_2O	$C_3H_4N_2$	$HCONMe_2$	20	20	6.0:3.5:1.0	61
AcCl	C_5H_5N	C_5H_5N	2	0	12.3:1.0:9.0	47
$C_3H_3N_2Ac$[b]		$HCONMe_2$	20	20	6.2:3.7:1.0	75
$C_3H_3N_2Ac$		$(CH_2Cl)_2$	10	reflux	2.5:1.1:1.0	68
$C_3H_3N_2Ac$[b]		$(CH_2Cl)_2$	3	80	5.4:3.1:1.0	60
$C_3H_3N_2Ac$[b]		PhMe	3	80	4.6:1.3:1.0	80
BzCl	C_5H_5N	C_5H_5N	1.5	0–20	11.5:1.0:1.3[c]	64
$C_3H_3N_2Bz$[b]		PhMe	3	80	8.9:1.3:1.0[c]	61

[a]See Experimental section. [b]$C_3H_3N_2Ac$–*N*-acetylimidazole; $C_3H_3N_2Bz$, *N*-benzoylimidazole. [c]Determined after isolation of the products through a silica gel column.

TABLE II

^{13}C-N M R CHEMICAL SHIFTS (δ) OF L-RHAMNAL (**1**), L-FUCAL (**8**), AND THEIR DERIVATIVES (**2–11**)

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Ac/Bz*
1	145.0	102.8	70.4	75.4	74.5	17.0	
2	146.7	98.9	73.7	72.5	74.6	16.8	172.8, 20.9
3	146.6	98.7	74.0	72.5	74.8	17.0	167.8, 133.3 129.7, 129.6, 128.3
4	144.5	102.9	67.5	76.6	72.4	16.6	171.4, 20.7
5	144.5	102.9	67.9	77.5	72.6	17.1	166.8, 133.6 133.5, 130.1 129.8, 128.5 128.4
6	146.1	98.8	68.2	71.8	72.4	16 3	170.6, 20.7 169.9, 20.5
7	146.1	98.8	68.8	72.1	72.7	16.7	166.0, 165.4 133.3, 133.1 129.8, 129.7 128.4, 128.3
8	144.8	102.9	64.9	68.3	73.3	16.8	
9	146.5	98.0	68.1	65.9	73.2	16.4	170.6, 21.1
10	144.8	102.1	63.4	69.3	71.5	16.8	171.4, 20.7
11	146.1	98.3	65.1	66.4	71 5	16.5	170.6, 170.3 20 8, 20.6

(**6**) was 4.6:1.3:1.0, and 3-*O*-acetyl-L-rhamnal (**2**) was obtained in 47% yield in the preparative-scale acetylation of L-rhamnal (**1**). Although acetyl chloride also appeared to be selective towards O-3, large proportions of diacetate **6** were formed, even at 0°, thus decreasing the net yield of **2** to 32%.

N-Acetylimidazole, *N*-benzoylimidazole, and benzoyl chloride have been evaluated as acylating reagents in the carbohydrate field[5,8,9]. *N*-Acetylimidazole showed no appreciable selectivity towards the primary hydroxyl group of common sugar derivatives[8]. The other two reagents have been successfully employed for selective protection of the secondary hydroxyl groups of hexopyranose derivatives of different configuration[5]. Acylation of L-rhamnal (**1**) with *N*-benzoylimidazole or benzoyl chloride took place primarily at O-3, giving the monobenzoate **3** in 55–60% yield. In both instances, the 4-monobenzoate **7** was formed in only low proportion (<8%).

The only observed instance in which preferential substitution of the homoallylic alcohol occurred was during the acetylation of **1** with acetic anhydride–pyridine, which gave the 4-acetate **4** in 40% yield. The polarity of the solvent had very little effect on the selectivity (Table 1). However, when imidazole was used instead of pyridine, the 3-acetate **2** was again the principal product. Differences in selectivity between acetic anhydride–pyridine and acyl chlorides has been observed in other systems[5]. For example, 1,4:3,6-dianhydro-D-glucitol reacts with one molar equivalent of acetic anhydride–pyridine to give primarily the 2-ester, whereas the 5-ester is the main product of acylation by acyl chlorides[10].

Esterification[11] of methyl 4,6-*O*-benzylidene-α-D-glucopyranosides (**12**) with benzoic anhydride–pyridine can be controlled to afford mainly the 3-benzoate **16**. Similar selectivity is observed when acetic anhydride is employed, whereas the 2-esters (**13** and **14**) are the main products in the reaction of **12** with acyl chlorides[11]. As the partial esterification of compound **12** has been studied with numerous acylating reagents[5,11], including *N*-benzoylimidazole[9] (which gave the 2-benzoate **14** in 78% yield), it was of interest to determine the selectivity of *N*-acetylimidazole in this system. As observed for L-rhamnal (**1**), *N*-acetylimidazole showed the same pattern of substitution as did acyl chlorides, and the 2-acetate **13** was the main product, isolated in 48% yield. Differences in the acylating species involved in these reactions may account for the different product distributions[12]. The (unstable) acetylpyridinium acetate is presumably the reactive intermediate in acylations with acetic anhydride–pyridine[13], whereas the resonance-stabilized acetylimidazolium ion[13] is the acylating species in reactions involving *N*-acetylimidazole.

Acetylation of L-fucal (**8**) with acetic anhydride–pyridine or *N*-acetylimidazole led to a mixture of all possible esters (**9**, **10**, and **11**), together with starting material **8**; the 3-acetate **9** was the principal product. Column-chromatographic separation of the mixture afforded fractions containing the monoacetates **9** and **10**. Rechromatography led only to partially enriched monoacetates and not to the pure isomers. Acetylation of **8** with either acetic anhydride–pyridine or *N*-acetylimidazole gave a similar ratio of the monoacetates **9** and **10** (3.2:1.0, as established by ^{1}H-n.m.r. spectroscopy). This result was unexpected, even though a different selectivity was anticipated[14] for the quasiaxial 4-hydroxyl group of compound **8** because that of glycal **1** is quasiequatorial [in the favored $^5H_4$(L) conformation[4]]. This observation, in conjunction with the difficulties in the separation of the

monoacetates by column chromatography (even though they were readily separated by t.l.c.), led to the conclusion that acetyl migration was taking place between the vicinal, *cis*-hydroxy groups. Such migration has been proposed for acylated *cis*-2,3-diols in compounds having the *manno* configuration[15].

The O-3→O-4 migration of acetyl groups in the L-fucal derivatives was confirmed experimentally. Monitoring by t.l.c. of a solution of the 3-acetate **9** in pyridine showed proportions of monoacetate **10** increasing with time. Similar migration of the *tert*-butyldimethylsilyl group has also been observed in L-fucal derivatives[16]. The facile migration of substituents probably depends on a favorable orientation of *cis*-vicinal, quasiequatorial and quasiaxial hydroxyl groups.

The different reactivities of hydroxyl groups during acylation reactions was explained by various authors in terms of steric factors[5,14], hydrogen bonding[5], or polar interactions[17], but none of these appear to provide a completely satisfactory explanation of the present experimental results. Possible changes in the reactivity of hydroxyl groups caused by partial substitution of the molecule must be considered[6], and detailed kinetic studies would be required to furnish a better understanding of the factors that influence selectivity in acylation reactions of polyols. For the purposes of the present work, a preparatively useful discrimination of the hydroxyl groups to afford either the 3-esters of 4-esters of L-rhamnal was achieved.

EXPERIMENTAL

General methods. — Melting points were determined in open glass capillaries in a Thomas–Hoover apparatus, and are uncorrected. Optical rotations were recorded, with a Perkin–Elmer Model 141 polarimeter. I.r. spectra were recorded with a Perkin–Elmer 457 grating spectrophotometer. ^{1}H- and ^{13}C-N.m.r. spectra were determined at 200 and 50 MHz, respectively, with a Bruker WP-200 spectrometer by Drs. O. Mols and P. Bhaté; chemical shifts refer to an internal standard of tetramethylsilane (δ = 0.00 p.p.m.). G.l.c. was performed isothermally at 120° with a Hewlett–Packard 5720A chromatograph, equipped with a 3% OV-101 glass column (2 m). T.l.c. was performed on precoated plastic sheets of Silica Gel 60F 254 (E. Merck, Darmstadt, G.F.R.) with the following proportions of hexane–ethyl acetate as eluant: (*A*) 1:1, (*B*) 2:1, and (*C*) 1:3. Detection was effected by spraying the plates with 5% H_2SO_4 with subsequent heating. Column chromatography was performed with Silica Gel 60 (230–400 mesh; E. Merck). Elemental analyses were performed by Atlantic Microlab, Atlanta, Georgia.

Quantitative determination of the product distributions (Table I). — To a solution of L-rhamnal (**1**; 26 mg, 0.2 mmol) in pyridine (0.5 mL) was added the acylating agent (0.22 mmol). When other, non-basic solvents (0.5 mL) were employed, 0.5 mmol of base was added. The times and temperatures for each reaction are presented in Table I. The mixtures were analyzed by g.l.c. and the ratio of products

was determined from relative peak areas. The retention times for the products were: **1**, 1.0 min; **2**, 2.3 min; **4**, 3.4 min; and **6**, 6.5 min.

The mixtures resulting from acetylation of L-fucal (**8**) were examined by g.l.c. with different columns (OV-17, OV-101, OV-225, and SE 30) and under various conditions, but in all instances the monoacetates gave a single broad peak, and they could not be separated.

Acetylation of L-*rhamnal* (**1**) *to give 3-*O*-acetyl-*L*-rhamnal* (**2**), *4-*O*-acetyl-*L*-rhamnal* (**4**), *and 3,4-di-*O*-acetyl-*L*-rhamnal* (**6**). — (*a*) *With acetic anhydride–pyridine.* L-Rhamnal (**1**, 6.5 g, 50 mmol) was dissolved in pyridine (150 mL) and acetic anhydride (6.05 mL, 64 mmol) was added dropwise. The mixture was stirred for 20 h at 25°. Pyridine was evaporated off <50° under diminished pressure with addition of toluene. A solution of the residue in dichloromethane was washed with 5% HCl, water, 10% aqueous $NaHCO_3$, and water. The organic solution was dried ($MgSO_4$), and evaporated. Products were separated by column chromatography with 5:1 hexane–ethyl acetate as eluant. The fastest-migrating component was 3,4-di-*O*-acetyl-L-rhamnal (**6**; 2.7 g, 25%). The next fraction was 3-*O*-acetyl-L-rhamnal (**2**; 0.72 g, 8.5%), isolated as a colorless syrup; $[\alpha]_D^{25}$ +21° (*c* 2.0, chloroform), R_F 0.50 (solvent *A*).

Anal. Calc. for $C_8H_{12}O_4$: C, 55.81; H, 7.03. Found: C, 55.74; H, 7.03.

Later fractions afforded syrupy 4-*O*-acetyl-L-rhamnal (**4**; 3.45 g, 40%); $[\alpha]_D^{25}$ −41° (*c* 1.5, chloroform), R_F 0.42 (solvent *A*).

Anal. Calc. for $C_8H_{12}O_4$: C, 55.81; H, 7.03. Found: C, 55.58; H, 7.09.

(*b*) *With acetic anhydride–imidazole.* To a solution of L-rhamnal (**1**, 3.9 g, 30 mmol) in *N,N*-dimethylformamide (8 mL) was added imidazole (5.1 g, 75 mmol) and acetic anhydride (3.4 mL, 36 mmol). The solution was stirred for 20 h at 25°, diluted with dichloromethane, and extracted and purified as in part (*a*). Chromatography of the mixture afforded compounds **6** (1.4 g, 22%), **2** (1.4 g, 27%), and **4** (0.76 g, 15%).

(*c*) *With* N-*acetylimidazole*[18]. A solution of L-rhamnal (**1**, 2.6 g, 20 mmol) and *N*-acetylimidazole (2.2 g, 20 mmol) in toluene (50 mL) was stirred for 2.5 h at 80°. Toluene was removed by evaporation and the resultant mixture was readily separated by column chromatography, affording compounds **6** (0.36 g, 8%), **2** (1.6 g, 47%), and **4** (0.5 g, 14%).

(*d*) *With acetyl chloride–pyridine.* A solution of L-rhamnal (**1**; 2.6 g, 20 mmol) in pyridine (50 mL) was cooled in an ice–water bath and acetyl chloride (1.57 mL, 22 mmol) was added dropwise. The ice–water bath was removed after 0.5 h and stirring was continued for 1.5 h. The same isolation as in part (*a*) gave compounds **6** (0.9 g, 21%), **2** (1.1 g, 32%), and **4** (0.1 g, 3%).

Benzoylation of L-*rhamnal* (**1**) *to give 3-*O*-benzoyl-*L*-rhamnal* (**3**), *4-*O*-benzoyl-*L*-rhamnal* (**5**), *and 3,4-di-*O*-benzoyl-*L*-rhamnal* (**7**). — (*a*) *With* N-*benzoylimidazole*[18]. A solution of L-rhamnal (**1**; 1.3 g, 10 mmol) and *N*-benzoylimidazole (1.72 g, 10 mmol) in toluene (30 mL) was stirred for 3 h at 80°. Toluene was evaporated off and a solution of the residue in dichloromethane was

processed as before. The mixture was separated by column chromatography by using 7:1 (2 vol.) and then 5:1 hexane–ethyl acetate as eluants. The first product isolated from the column was syrupy 3,4-di-*O*-benzoyl-L-rhamnal (**7**; 0.14 g, 4%), $[\alpha]_D^{23}$ +229° (*c* 1.2, chloroform); R_F 0.64 (solvent *B*).

Anal. Calc. for $C_{20}H_{18}O_5$: C, 71.00; H, 5.36. Found: C, 70.73; H, 5.46.

From the next fractions, crystalline 3-*O*-benzoyl-L-rhamnal (**3**) was obtained; yield 1.24 g (53%). Recrystallization from benzene–cyclohexane gave colorless needles, m.p. 64–65°, $[\alpha]_D^{25}$ +120° (*c* 1.0, chloroform), R_F 0.48 (solvent *B*).

Anal. Calc. for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.79; H, 6.06.

Later fractions from the column afforded crystalline 4-*O*-benzoyl-L-rhamnal (**5**; 0.18 g, 8%). Recrystallized from ether–hexane, it had m.p. 76°, $[\alpha]_D^{25}$ −79° (*c* 1.0, chloroform), R_F 0.38 (solvent *B*).

Anal. Calc. for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.55; H, 6.04.

(*b*) *With benzoyl chloride.* L-Rhamnal (**1**; 1.3 g, 10 mmol) dissolved in pyridine (30 mL) was cooled in an ice–water bath and benzoyl chloride was added dropwise. The mixture was stirred for 1.5 h at ~5° and then 1 h at room temperature. Evaporation with toluene and the same isolation as in part (*a*) afforded compounds **7** (0.16 g, 5%), **3** (1.4 g, 60%), and **5** (0.12 g, 5%).

Acetylation of L-*fucal*[19] (**8**) *to give 3-*O*-acetyl-*L*-fucal* (**9**) *4-*O*-acetyl-*L*-fucal* (**10**), *and 3,4-di-*O*-acetyl-*L*-fucal* (**11**). — (*a*) *With acetic anhydride–pyridine.* A solution of L-fucal (**8**; 0.26 g, 2 mmol) in pyridine (30 mL) was acylated with acetic anhydride (0.25 g, 2.4 mmol) under the conditions described for compound **1**. Chromatographic purification with 5:1 hexane–ethyl acetate afforded the 3,4-diacetate **11** (70 mg, 16%) and a mixture (0.21 g, 68%) of monoacetates **9** and **10** [R_F 0.43 and 0.32 (solvent *A*), respectively], uncontaminated by **11**. ^{1}H-N.m.r. examination of the mixture showed the 3-acetate (**9**) and 4-acetate (**10**) in 3.2:1.0 ratio. Rechromatography with 8:1 hexane–ethyl acetate gave the 3-acetate **9** (25 mg) slightly contaminated with **10**. This sample had $[\alpha]_D^{25}$ −5° (*c* 0.6, chloroform).

Anal. Calc. for $C_8H_{12}O_4$: C, 55.81; H, 7.03. Found: C, 55.86; H, 7.07.

(*b*) *With* N-*acetylimidazole.* A mixture of L-fucal (**8**, 0.52 g, 4 mmol) and *N*-acetylimidazole (0.44 g, 4 mmol) in toluene (20 mL) was stirred for 3 h at 80°. Toluene was evaporated off and the residue purified by column chromatography in 5:1 hexane–ethyl acetate to afford a mixture (0.45 g, 65%) of the monoesters **9** and **10** in 3.2:1 ratio, as evaluated by ^{1}H-n.m.r. spectroscopy.

*Acetyl-group migration in 3-*O*-acetyl-*L*-fucal* (**9**) *to give* **9** *and* **10**. — A solution of compound **9** (12 mg, 0.05 mmol, R_F 0.43; contaminated with ~15% of compound **10**, R_F 0.32) in pyridine (0.5 mL) was stirred at 25°. T.l.c. monitoring showed progressive intensification of the component having R_F 0.32. After ~66 h, pyridine was evaporated off under diminished pressure. The ^{1}H-n.m.r. spectrum of the resultant syrup indicated it to be a mixture of the monoacetates **9** and **10**, in 2.4:1.0 ratio.

*Acetylation of methyl 4,6-*O*-benzylidene-α-*D*-glucopyranoside* (**12**) *to give the 2-*O*-acetyl* (**13**), *3-*O*-acetyl* (**15**), *and 2,3-di-*O*-acetyl derivative* (**17**). — A solution

of compound[20] **12** (0.56 g, 2 mmol) in 1,2-dichloroethane (10 mL) was boiled under reflux for 10 h with *N*-acetylimidazole (0.22 g, 2 mmol). The solvent was evaporated off, and a solution of the residue in dichloromethane was treated as described for the preceding acylation reactions. Column chromatography with 1:1 hexane–ethyl acetate gave the 2,3-diacetate **17** (0.10 g, 14%), m.p. 110°, $[\alpha]_D^{25}$ +73° (*c* 1.0, chloroform), R_F 0.73 (solvent *C*); the 2-acetate **13** (0.31 g, 48%), m.p. 134–136°, $[\alpha]_D^{25}$ +108° (*c* 1.2, chloroform), R_F 0.61 (solvent *C*); and the 3-acetate **15** (0.14 g, 20%), m.p. 176–177°, $[\alpha]_D^{25}$ +114° (*c* 0.8, chloroform), R_F 0.44 (solvent *C*). The m.p., $[\alpha]_D$ values, and i.r. and ^{1}H-n.m.r. spectra of compounds **13**, **15**, and **17** were in good agreement with those reported in the literature[7,11,21].

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