Carbohydrate Research, 162 (1987) 159–165
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

Partial tosylation of methyl α- and β-L-arabinopyranoside

YÔTARO KONDO
Department of Agricultural Chemistry, Tottori University, Tottori 680 (Japan)
(Received June 30th, 1986; accepted for publication in revised form, October 7th, 1986)

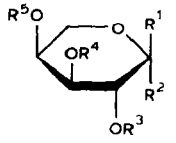
Previous studies on selective sulfonylation of methyl α- and β-D-xylopyranoside[1], 1,5-anhydro-L-arabinitol[2], and 1,5-anhydroxylitol[3] with *p*-toluenesulfonyl chloride indicated influences of steric and electronic factors on the relative reactivity of the hydroxyl groups. In connection with these studies, partial tosylation of methyl α- and β-L-arabinopyranoside is now described.

Tosylation of methyl β-L-arabinopyranoside (**1**) with 2 molar equivalents of *p*-toluenesulfonyl chloride in pyridine at 0° gave (quantitative t.l.c.) the 2,3,4-trisulfonate **2** (9%), the 2,4-disulfonate **3** (11%), the 2,3-disulfonate **4** (68%), the 2-sulfonate **5** (10%), and the 4-sulfonate **6** (2%) (total yield from column chromatography, 95%). Monomolar tosylation of **1** with *p*-toluenesulfonyl chloride gave **3** (1%), **4** (24%), **5** (73%), and **6** (2%) (total yield from column chromatography, 62%).

The structure of **3** and **4** was deduced from comparison of their ^{1}H-n.m.r. spectra with those of their corresponding benzoates **7** and **8**, which clearly showed the downfield position of the signal for the proton in the HCOBz group. The location of the benzoyl and tosyl groups in related compounds was determined in a similar way. The structure of **5** was ascertained from comparison of its physical and spectral properties with those of an authentic sample[4]. The benzoylated ditosylates **7** and **8** were distinguishable from the ditosylate **9**, prepared from the known methyl 2-*O*-benzoyl-β-L-arabinopyranoside[5] by tosylation. The structure of **6** was confirmed by comparing its physical constants with those of an authentic sample prepared from the known methyl 2,3-di-*O*-benzoyl-β-L-arabinopyranoside[6] by tosylation followed by *O*-debenzoylation.

Tosylation of methyl α-L-arabinopyranoside (**12**) with 2 molar equivalents of *p*-toluenesulfonyl chloride in pyridine at 0° yielded (quantitative t.l.c.) the 3,4-disulfonate **13** (85%), the 3-tosylate **14** (12%), and the 4-tosylate **16** (3%), together with a trace of **15** (total yield from column chromatography, 67%). Treatment of **12** with 1 molar equivalent of *p*-toluenesulfonyl chloride gave **13** (6%), a mixture of **14** and **15** (69%), and **16** (25%) (total yield from column chromatography, 21%).

0008-6215/87/$ 03.50



	R^1	R^2	R^3	R^4	R^5
1	H	OCH_3	H	H	H
2	H	OCH_3	Ts	Ts	Ts
3	H	OCH_3	Ts	H	Ts
4	H	OCH_3	Ts	Ts	H
5	H	OCH_3	Ts	H	H
6	H	OCH_3	H	H	Ts
7	H	OCH_3	Ts	Bz	Ts
8	H	OCH_3	Ts	Ts	Bz
9	H	OCH_3	Bz	Ts	Ts
10	H	OCH_3	Ts	Bz	Bz
11	H	OCH_3	Bz	Bz	Ts
12	OCH_3	H	H	H	H
13	OCH_3	H	H	Ts	Ts
14	OCH_3	H	H	Ts	H
15	OCH_3	H	Ts	H	H
16	OCH_3	H	H	H	Ts
17	OCH_3	H	Bz	Ts	Ts
18	OCH_3	H	Bz	Ts	Ts
19	OCH_3	H	Ts	Bz	Bz
20	OCH_3	H	Bz	Bz	Ts

Compounds **14** and **15** could not be separated by quantitative t.l.c., but were fractionated by column chromatography on silica gel, and obtained in yields of 60 and 9 mol%, respectively. The structure of compounds in this series was established by ^{1}H-n.m.r. spectroscopy. In addition, to confirm the structures assigned, compounds **15** and **19** were prepared (see Experimental section).

The preponderance of **4** over **3** in the crude product of dimolar tosylation of **1** shows the relative reactivity of the hydroxyl groups in **1** to be HO-2 > HO-3 > HO-4, which is consistent with the results of Buchanan and Fletcher[7]. In monomolar tosylation of **1**, the high yield of **5** and the low yield of **6** in the crude monotosylated products indicate that the reactivity of the hydroxyl groups of **1** is in the order: HO-2 > HO-4 > HO-3. On the other hand, the highest yield of **13** and the preponderance of **14** over **15** and **16** in the crude product of ditosylation of **12** shows that the order of the reactivity of the hydroxyl groups in **12** is HO-3 > HO-4 > HO-2. In monomolar tosylation of **12**, the highest yield of **14** and the preponderance of **16** over **15** shows that the order of the reactivity of the hydroxyl groups in **12** is HO-3 > HO-4 > HO-2.

The finding that HO-2 in **1** show the highest reactivity towards tosylation compares well with the result of selective sulfonylation of methyl α-D-xylopyranoside[1], and can be rationalized in terms of intramolecular hydrogen-bonding between the HO-2 group and the axial methoxyl group on C-1. It appears that the reactivity of HO-2 is more affected by the *cis*-OH–OR intramolecular hydrogen-bonding than by the *cis*-OH–OH intramolecular hydrogen-bonding. For the purpose of confirming the difference in reactivity in the second stage of dimolar tosylation of **1**, the 2-tosylate **5** was further tosylated with 1 molar equivalent of *p*-toluenesulfonyl chloride. Selective tosylation of **5**, followed by benzoylation, gave **7** and **8** in the molar ratio of 1:3. This result indicates that the OH-3 group is more reactive than the OH-4 group, which is contrary to the result obtained[2] for selective tosylation with tosyl chloride of 1,5-anhydro-L-arabinitol and its 2-tosylate, where the axial OH-4 group was shown to be more reactive than the other equatorial hydroxyl groups. This finding suggests that the retarding effect of the tosyloxy group at C-2 on the reactivity of the neighboring hydroxyl group at C-3 is negligible, and it is therefore improbable that the reactivity of OH-3 is decreased by steric hindrance (*gauche* interactions) of the neighboring tosyloxy group at C-2, as proposed previously for selective tosylation of methyl α-D-xylopyranoside[1] and 1,5 anhydro-L-arabinitol[2]. Interestingly, in the selective tosylation of **12**, OH-3 is the most reactive, and the axial OH-4 is more reactive than the equatorial OH-2, due to the lack of the *cis*-OH–OR intramolecular hydrogen-bonding. On the other hand, HO-4 in 1,5-anhydro-L-arabinitol and its 2-tosylate[2] is the most reactive. It is surprising that methyl α-L-arabinopyranoside differs from 1,5-anhydro-L-arabinitol in relative reactivity, because the two compounds have the same configuration, except at C-1, but their conformations are very different. In addition, HO-3 in methyl α- and β-D-xylopyranoside are the least reactive towards selective tosylation, and an accelerating effect of a methoxyl group at C-1 on the reactivity of HO-3 could not be observed[1]. Therefore, it seems likely that a methoxyl group at C-1 in **1** and **12** has a lessening effect on the reactivity of the axial HO-4, rather than an enhancing effect on that of HO-3. Thus, the reactivity of the axial HO-4 in both anomers (**1** and **12**) is inactivated by an inductive effect caused by the methoxyl group at C-1, in spite of the existence of such activating effects as intramolecular hydrogen-bonding between HO-3 and HO-4 and the least steric hindrance at C-5. It seems that this type of inductive effect exerted upon the equatorial HO-4 group is very weak (*c.f.*, selective tosylation of methyl α- and β-D-xylopyranoside[1], where the reactivity of HO groups is in the order: HO-4 > HO-3).

EXPERIMENTAL

General methods. — ^{1}H-N.m.r. spectra (60 MHz) were recorded for solutions in $CDCl_3$ with a Hitachi R-24 spectrometer (internal Me_4Si). Quantitative analysis of the products of partial tosylation was performed by thin-layer chromatography

on a quartz rod as described previously[1]. T.l.c. was conducted on Silica G 60 (Merck) with benzene–acetone, and column chromatography on silica gel 60 (70–230 mesh, Merck).

Partial tosylation of methyl β-L-arabinopyranoside (**1**). — *p*-Toluenesulfonyl chloride (1.275 g, 1.1 mol. equiv.; or 2.55 g, 2.2 mol. equiv.) was added portionwise at 0° to a stirred solution of **1** (1 g) in dry pyridine (20 mL). The mixture was kept for 24 h at 0°, stirred for 48 h at 5°, and then extracted with dichloromethane. The extract was successively washed with dilute hydrochloric acid, saturated sodium hydrogencarbonate, and water, dried (sodium sulfate), and directly used for quantitative t.l.c. analysis of the components in the mixture.

Evaporation of the solvent and column chromatography of the resultant residue gave four products.

Methyl 2,3,4-tri-*O*-*p*-tolylsulfonyl-β-L-arabinopyranoside (**2**) was obtained as a syrup; $[\alpha]_D^{16}$ +101° (*c* 0.9, chloroform); R_F 0.60 (4:1); lit.[7] m.p. 110–111°, $[\alpha]_D$ +100° (*c* 0.44, chloroform).

Methyl 2,4-di-*O*-*p*-tolylsulfonyl-β-L-arabinopyranoside (**3**) was obtained as a syrup; $[\alpha]_D^{21}$ +107.8° (*c* 0.6, chloroform); R_F 0.68; ^{1}H-n.m.r.: δ 4.75 (m, 1 H, H-4), 4.68 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.57 (broad q, 1 H, $J_{3,4}$ 4 Hz, H-3, sharpened by the addition of D_2O), 3.70 (d, 2 H, H-5,5′), 3.22 (s, 3 H, OCH_3), and 2.08 (s, 3 H, $C_6H_5CH_3$).

Methyl 2,3-di-*O*-*p*-tolylsulfonyl-β-L-arabinopyranoside (**4**) was obtained as a syrup; $[\alpha]_D^{18}$ +79.1° (*c* 1.7, chloroform); R_F 0.63 (2:1); ^{1}H-n.m.r.: δ 4.72 (s, 3 H, H-1,2,3), 4.15 (m, 1 H, H-4), 3.65 (s, 2 H, H-5,5′), 3.21 (s, 3 H, OCH_3), and 2.40 (s, 6 H, 2 $C_6H_5CH_3$).

Methyl 2-*O*-*p*-tolylsulfonyl-β-L-arabinopyranoside (**5**) was obtained as a syrup; $[\alpha]_D^{20}$ +107.2° (*c* 2.6, chloroform); R_F 0.40; lit.[4] $[\alpha]_D^{18}$ +110.9° (chloroform).

Methyl 4-*O*-*p*-tolylsulfonyl-β-L-arabinopyranoside (**6**) crystallized from chloroform in long needles; m.p. 150–151°, $[\alpha]_D^{20}$ +129.9° (*c* 0.9, chloroform); R_F (2:1); ^{1}H-n.m.r. (in acetone-d_6): δ 4.72 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 4.65 (m, 1 H, H-4), 3.33 (s, 3 H, OCH_3), and 2.42 (s, 3 H, $C_6H_4CH_3$). The ^{1}H-n.m.r. spectrum and other physical constants were identical with those of an authentic sample prepared from the known methyl 2,3-di-*O*-benzoyl β-L-arabinopyranoside[8] by tosylation followed by *O*-debenzoylation.

Anal. Calc. for $C_{13}H_{18}O_7S \cdot H_2O$: C, 46.41; H, 6.00; S, 9.53. Found: C, 46.65; H, 5.87; S, 9.56.

Methyl 3-O-benzoyl-2,4-di-O-p-tolylsulfonyl-β-L-arabinopyranoside (**7**). — Benzoyl chloride (0.1 mL) was added to a solution of **3** (23 mg) in pyridine (2 mL) at 0°, and the mixture was stirred overnight at room temperature. Water was added, and the mixture was extracted with dichloromethane. The extract was evaporated to a syrup which crystallized from ethanol to give **7** (23 mg, 82%); m.p. 186–187°, $[\alpha]_D^{16}$ +125.6° (*c* 1.0, chloroform); ^{1}H-n.m.r.: δ 5.30 (broad q, 1 H, H-3), 4.98 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.93–4.70 (m, 2 H, H-2,4), 3.80 (s, 2 H, H-5,5′), 3.30 (s, 3 H, OCH_3), and 2.35 and 2.13 (2 s, 6 H, 2 $C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{28}O_{10}S_2$: C, 56.24; H, 4.89; S, 11.12. Found: C, 56.11; H, 4.85; S, 11.26.

Methyl 4-O-benzoyl-2,3-di-O-p-tolylsulfonyl-β-L-arabinopyranoside (**8**). — Benzoylation of **4** (443 mg) with benzoyl chloride–pyridine gave a foamy product which crystallized from ethanol to afford **8** (421 mg, 78%); m.p. 153–154°, $[\alpha]_D^{16}$ +176.2° (*c* 1.7, chloroform); ^{1}H-n.m.r.: δ 5.37 (m, 1 H, H-4), 5.10 (q, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 3 Hz, H-3), 5.03 (d, 1 H, H-4), 5.10 (q, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.72 (q, 1 H, H-2), 3.83 and 3.82 (2 s, 2 H, H-5,5′), 3.38 (s, 3 H, OCH_3), and 2.42 and 2.32 (2 s, 6 H, 2 $C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{28}O_{10}S_2$: C, 56.24; H, 4.89; S, 11.12. Found: C, 55.95; H, 4.89; S, 11.31.

Methyl 2-O-benzoyl-3,4-di-O-p-tolylsulfonyl-β-L-arabinopyranoside (**9**). — Methyl 2-*O*-benzoyl-β-L-arabinopyranoside[5] (74 mg) was treated with *p*-toluenesulfonyl chloride (200 mg) in pyridine (1 mL) for 3 days at room temperature. The mixture was evaporated to a crystalline residue. Recrystallization from chloroform–petroleum ether gave **9** (82 mg, 52%); m.p. 166–167°, $[\alpha]_D^{16}$ +200.0° (*c* 0.5, chloroform); ^{1}H-n.m.r.: δ 5.43–4.87 (m, 4 H, H-1,2,3,4), 3.85 (s, 2 H, H-5,5′), 3.30 (s, 3 H, OCH_3), and 2.40 and 2.28 (2 s, 6 H, 2 $C_6H_4CH_3$); lit.[6] m.p. 162–163°, $[\alpha]_D^{21}$ +207° (*c* 0.997, chloroform).

Methyl 3,4-di-O-benzoyl-2-O-p-tolylsulfonyl-β-L-arabinopyranoside (**10**). — The sulfonate **5** (70 mg) was benzoylated with benzoyl chloride, to afford **10** (84 mg, 72%); m.p. 135–136°, $[\alpha]_D^{18}$ +301.2° (*c* 1.3, chloroform).

Anal. Calc. for $C_{27}H_{27}O_9S$: C, 61.58; H, 4.98; S, 6.09. Found: C, 61.32; H, 4.98; S, 6.06.

Partial tosylation of methyl α-L-arabinopyranoside (**12**). — A solution of **12** (500 mg) in pyridine (10 mL) was treated with *p*-toluenesulfonyl chloride (638 mg, 1.1 mol. equiv.; or 1.275 g, 2.2 mol. equiv.) as described for the β anomer. Chromatographic fractionation of the products on silica gel gave four products.

Methyl 3,4-di-*O*-*p*-tolylsulfonyl-α-L-arabinopyranoside (**13**) was obtained as a foam; $[\alpha]_D^{10}$ +27.9° (*c* 0.9, chloroform); R_F 0.50 (4:1); ^{1}H-n.m.r.: δ 4.87 (m, 1 H, H-4), 4.45 (q, 1 H, $J_{2,3}$ 9, $J_{3,4}$ 3 Hz, H-3), 4.08 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 4.07 (q, 1 H, $J_{4,5a}$ 3, $J_{5a,5e}$ 13 Hz, H-5*a*), 3.60 (q, 1 H, H-2), 3.47 (q, 1 H, $J_{4,5e}$ 1 Hz, H-5*e*), 3.40 (s, 3 H, OCH_3), and 2.42 (s, 6 H, 2 $C_6H_4CH_3$).

Methyl 3-*O*-*p*-tolylsulfonyl-α-L-arabinopyranoside (**14**); m.p. 128° (from CH_2Cl_2), $[\alpha]_D^{20}$ +59.9° (*c* 1.1, chloroform); R_F 0.45 (2:1); ^{1}H-n.m.r. (in acetone-d_6): δ 4.43 (q, 1 H, $J_{2,3}$ 8, $J_{3,4}$ 4 Hz, H-3), 4.13 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), 3.77 (s, 3 H, OCH_3), and 2.40 (s, 3 H, $C_6H_4CH_3$).

Anal. Calc. for $C_{13}H_{18}O_7S \cdot 0.5\ H_2O$: C, 47.69; H, 5.86; S, 9.79. Found: C, 47.45; H, 5.79; S, 9.87.

Methyl 2-*O*-*p*-tolylsulfonyl-α-L-arabinopyranoside (**15**); m.p. 128° (from CH_2Cl_2–petroleum ether), $[\alpha]_D^{16}$ +0.4° (*c* 1.8, acetone); R_F 0.33 (2:1); ^{1}H-n.m.r. δ 4.52 (t, 1 H, $J_{1,2} = J_{2,3}$ 6 Hz, H-2), 4.28 (d, 1 H, H-1), 3.26 (s, 3 H, OCH_3), and 2.43 (s, 3 H, $C_6H_4CH_3$).

Anal. Calc. for $C_{13}H_{18}O_7S$: C, 49.05; H, 5.07; S, 10.07. Found: C, 48.45; H, 5.74; S, 9.85.

Methyl 4-*O*-*p*-tolylsulfonyl-α-L-arabinopyranoside (**16**); $[\alpha]_D^{18}$ −10.0° (*c* 1.7, chloroform); R_F 0.30 (2:1); ^{1}H-n.m.r. δ 4.77 (m, 1 H, H-4), 4.17 (d, 1 H, $J_{1,2}$ 6 Hz, H-1), and 3.45 (s, 3 H, OCH_3).

Anal. Calc. for $C_{13}H_{18}O_7S \cdot 0.25\ H_2O$: C, 48.36; H, 5.79; S, 9.92. Found: C, 48.45; H, 5.74; S, 9.85.

Methyl 2-O-benzoyl-3,4-di-O-p-tolylsulfonyl-α-L-arabinopyranoside (**17**). — Benzoylation of **13** (142 mg) with benzyl chloride followed by recrystallization from dichloromethane–petroleum ether afforded **17** (101 mg, 58%); m.p. 175–176°, $[\alpha]_D^{16}$ +57.2° (*c* 1.2, chloroform); ^{1}H-n.m.r.: δ 5.30 (q, 1 H, $J_{1,2}$ 6, $J_{2,3}$ 8 Hz, H-2), 4.98 (m, 1 H, H-4), 4.65 (q, 1 H, $J_{3,4}$ 4 Hz, H-3), 4.42 (d, 1 H, H-1), 4.23 (q, 1 H, $J_{4,5a}$ 12 Hz, H-5*a*), 3.61 (q, 1 H, $J_{4,5e}$ 2 Hz, H-5*e*), 3.37 (s, 3 H, OCH_3), and 2.40 and 2.25 (2 s, 6 H, 2 $C_6H_4CH_3$).

Anal. Calc. for $C_{22}H_{22}O_{10}S_2$: C, 56.24; H, 4.89; S, 11.12. Found: C, 56.17; H, 4.82; S, 11.13.

Methyl 2,4-di-O-benzoyl-3-O-p-tolylsulfonyl-α-L-arabinopyranoside (**18**). — Treatment of **14** (48 mg) with benzoyl chloride yielded **18** (73 mg, 92%); $[\alpha]_D^{14}$ +110.2° (*c* 0.2, chloroform); ^{1}H-n.m.r.: δ 5.45 (m, 2 H, H-2,4), 4.97 (q, 1 H, $J_{2,3}$ 9, $J_{3,4}$ 4 Hz, H-3), 4.53 (q, 1 H, $J_{1,2}$ 6 Hz, H-1), 4.27 (q, 1 H, $J_{4a,5a}$ 5, $J_{5a,5e}$ 12 Hz, H-5*a*), 3.70 (q, 1 H, $J_{4,5e}$ 2 Hz, H-5*e*), 3.45 (s, 3 H, OCH_3), and 2.18 (s, 3 H, $C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{26}O_9S$: C, 61.58; H, 4.98; S, 6.09. Found: C, 61.85; H, 5.13; S, 6.11.

Methyl 3,4-di-O-benzoyl-2-O-p-tolylsulfonyl-α-L-arabinopyranoside (**19**). — (*a*) Compound **5** (40 mg) was benzoylated with benzoyl chloride–pyridine to yield **19** (54 mg, 82%); m.p. 141°, $[\alpha]_D^{14}$ +136.4° (*c* 0.5, chloroform); ^{1}H-n.m.r.: δ 5.55 (m, 1 H, H-4), 5.42 (q, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 4 Hz, H-3), 5.00 (q, 1 H, $J_{1,2}$ 7 Hz, H-2), 4.40 (d, 1 H, H-1), 4.17 (q, 1 H, $J_{4,5a}$ 3, $J_{5a,5e}$ 13 Hz, H-5*a*), 3.70 (q, 1 H, $J_{4,5e}$ 2 Hz, H-5*e*), 3.35 (s, 3 H, OCH_3), and 2.23 (s, 3 H, $C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{26}O_9S$: C, 61.58; H, 4.98; S, 6.09. Found: C, 61.88; H, 4.91; S, 6.30.

(*b*) A solution of **12** (470 mg) in *N,N*-dimethylformamide (5 mL) containing *p*-toluenesulfonic acid monohydrate (20 mg) was heated for 2 h at 70° with 2,2-dimethoxypropane (5 mL). After neutralization of the acid with triethylamine, the mixture was evaporated to a syrup which was extracted with dichloromethane, the extract chromatographed on silica gel. Treatment of a portion (91 mg) of the syrup obtained (201 mg, 25%) with *p*-toluenesulfonyl chloride (260 mg), followed by *O*-deisopropylidenation in 70% acetic acid, afforded a crude solid (104 mg). Recrystallization from dichloromethane–petroleum ether gave **15** (77 mg, 95%), identical with the 2-tosylate isolated from partial tosylation of **12**. Benzoylation of the 2-tosylate gave the title compound **19**. The spectral and physical properties were identical with those of the compound prepared in (*a*).

Methyl 2,3-di-O-benzoyl-4-O-p-tolylsulfonyl-α-L-arabinopyranoside (**20**). — Benzoylation of **6** (81 mg) followed by recrystallization from ethanol gave **20** (106 mg, 79%); m.p. 190–191°, $[\alpha]_D^{18}$ +75.7° (*c* 2.2, chloroform); ^{1}H-n.m.r.: δ 5.58 (q, 1 H, $J_{1,2}$ 7, $J_{2,3}$ 8 Hz, H-2), 5.18 (q, 1 H, $J_{3,4}$ 3 Hz, H-3), 5.03 (m, 1 H, H-4), 4.55 (d, 1 H, H-1), 4.30 (q, 1 H, $J_{4,5a}$ 3, $J_{5a,5e}$ 13 Hz, H-5*a*), 3.73 (q, 1 H, $J_{4,5e}$ 2 Hz, H-5*e*), 3.45 (s, 3 H, OCH_3), and 2.17 (s, 3 H, $C_6H_4CH_3$).

Anal. Calc. for $C_{27}H_{26}O_9S$: C, 61.58; H, 4.98; S, 6.09. Found: C, 61.32; H, 4.96; S, 6.19.

ACKNOWLEDGMENT

The author thanks Mr. O. Kato, Iatron Laboratories, Inc., for performing the quantitative t.l.c.

REFERENCES

1 Y. KONDO, *Carbohydr. Res.*, 110 (1982) 339–344.
2 Y. KONDO, *Carbohydr. Res.*, 128 (1984) 175–181.
3 Y. KONDO, *Carbohydr. Res.*, 103 (1982) 154–157.
4 J. HONEYMAN, *J. Chem. Soc.*, (1946) 990–993.
5 M. A. OLDHAM AND J. HONEYMAN, *J. Chem. Soc.*, (1946) 986–989.
6 E. J. REIST, L. V. FISHER, AND D. E. GUEFFROY, *J. Org. Chem.*, 31 (1966) 226–229.
7 J. G. BUCHANAN AND R. FLETCHER, *J. Chem. Soc., C*, (1966) 1926–1931.
8 E. J. REIST, L. V. FISHER, AND L. GOODMAN, *J. Org. Chem.*, 32 (1967) 2541–2544.