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REINVESTIGATION OF THE ACETALATION OF D-GLUCITOL WITH ACETONE–ZINC CHLORIDE

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ABSTRACT

The acetonation of D-glucitol in the presence of zinc chloride has been studied in detail by gas–liquid chromatographic techniques. From among the 12 different peaks, those belonging to the 1,2:3,4:5,6-tri-, 1,2:3,5:4,6-tri-, 3,4:5,6-di-, 2,3:5,6-di-, 1,2:3,4-di-, 1,2:5,6-di-, 1,2:4,6-di-, 1,2-mono-, 2,3-mono-, 3,4-mono-, and 5,6-mono-acetals could be identified. The course of the reaction was also studied by g.l.c. From the time-dependent ratio of the different acetals, it could be concluded that the reaction is kinetically controlled at the beginning, when terminal acetals are mainly formed. In the thermodynamically controlled equilibrium, reached after 5 days, the 1,2:3,4:5,6-tri- and the 2,3:5,6-di-acetal are present in almost equal proportions. The structure of the (new) 1,2:3,5:4,6-triacetal was established by mass-spectrometric and ^{13}C-n.m.r. investigation.

INTRODUCTION

In a previous paper[1], it was mentioned that g.l.c. investigation of the acetalation reaction of D-glucitol with acetone–zinc chloride revealed the presence of 13 well-differentiated peaks (see Fig. 1). That means that, besides the unreacted starting-material, at least 12 different acetals* are formed in the reaction, instead of the 6 isomers detected by Bonner *et al.*[2], who used a similar technique, but a g.l.c. column of lower performance. The inaccurate data obtained with this column led to erroneous identification of the different components, and, consequently, to misinterpretation of the whole reaction.

In the chromatogram obtained from an acetylated, crude reaction-mixture (see Fig. 1), three sets of peaks can be detected besides the starting material. The first set contains two triacetals, namely, **A** and **B**; the second, five diacetals, **C–G**; and the third, five monoacetals, **H–L**.

*The crude reaction-mixture actually contains more than 12 different acetals, as, even in our g.l.c. system, two different compounds, the 1,2:3,4- and 1,2:5,6-diacetals, were eluted with the same retention-time (peak **F**).

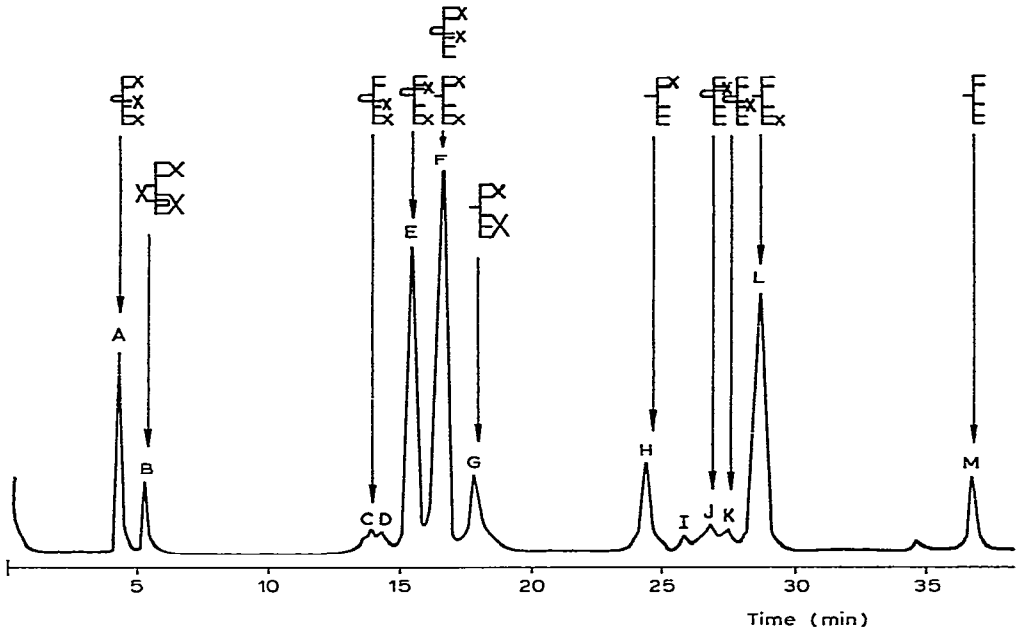


Fig. 1. G.l.c. of the acetylated, crude reaction-mixture obtained from D-glucitol and acetone in the presence of anhydrous zinc chloride after 2 h. (**A**, 1,2:3,4:5,6-tri-; **B**, 1,2:3,5:4,6-tri-; **C**, 3,4:5,6-di-; **E**, 2,3:5,6-di-; **F**, 1,2:3,4-di- and 1,2:5,6-di-; **G**, 1,2:4,6-di-; **H**, 1,2-mono-; **J**, 2,3-mono-; **K**, 3,4-mono-; **L**, 5,6-mono-*O*-isopropylidene-D-glucitol; and **M**, D-glucitol.)

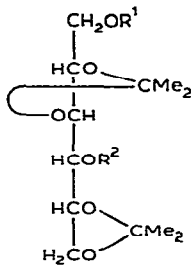
RESULTS AND DISCUSSION

Identification of the peaks. — The following peaks were identified by comparison with authentic samples of acetals having known structures*: **A**, 1,2:3,4:5,6-tri-*O*-isopropylidene-D-glucitol[3]; **C**, 3,4:5,6-di-*O*-isopropylidene-D-glucitol[3]; **F**, 1,2:5,6-di-*O*-isopropylidene-D-glucitol[4]; **H**, 1,2-*O*-isopropylidene-D-glucitol[4]; **K**, 3,4-*O*-isopropylidene-D-glucitol[3]; and **M**, D-glucitol.

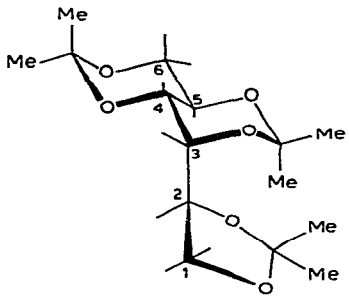
Peak **E** corresponded to 2,3:5,6-di-*O*-isopropylidene-D-glucitol[1] (**1**), but the compound, obtained by column chromatography of the crude reaction-mixture, always contained 1–2% of other isomers; therefore a pure sample was synthesized as follows. The primary tosyloxy group of the crystalline 1,4-ditosylate[1] **2** was exchanged with benzoate to give **3** which, on debenzoylation, afforded the 4-ester **4**; detosylation of **4** with sodium amalgam then gave the desired diacetal **1**.

Peak **B** corresponded to a new tri-*O*-isopropylidene isomer[1], the ^{1}H-n.m.r. spectrum of which is very similar to that of the 1,2:3,4:5,6-triacetal **A** (*e.g.*, for both compounds, the CMe_2 groups give two singlets, at 1.35 and 1.45 p.p.m.**, having 18-H

*All compounds containing free OH groups were acetylated before examination by g.l.c.
For **A, Bonner *et al.*[2] gave chemical shifts of 1.27 and 1.30 p.p.m., using dimethyl sulfoxide-d_6 as the solvent.



1 $R^1 = R^2 = H$
2 $R^1 = R^2 = Ts$
3 $R^1 = Bz, R^2 = Ts$
4 $R^1 = H, R^2 = Ts$
13 $R^1 = R^2 = Ac$



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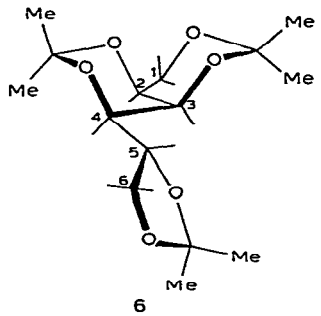

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intensity). The presence of the abundant *m/e* 101 ion (base peak) and ion *m/e* (M — 101) in the mass spectrum of compound **B** (M^+ 302) indicates a triacetal containing a terminal dioxolane ring. This is in accordance with the ^{13}C-n.m.r. spectrum, in which the quaternary carbon atom of one isopropylidene group appeared at 108.9 p.p.m., whereas the other two gave signals at 98.4 and 98.6 p.p.m., proving the presence of one dioxolane and two dioxane rings[5]. In the ^{13}C-n.m.r. spectrum of **A**, the corresponding signals appear at 109.5 and 109.8 p.p.m. (the latter originates from two carbon atoms, giving overlapped lines). According to these facts only, the 1,2:3,5:4,6- (**5**) or the 1,3:2,4:5,6-triacetal structure (**6**) had to be taken into consideration for peak **B**. In isomer **5**, the two dioxane rings are *trans*-fused, representing a system more stable than **6**, where these rings are *cis*-fused. On the other hand, the quite bulky, terminal dioxolane ring is *axially* oriented in **5** and *equatorially* in **6**, in the favored chair–chair conformation; consequently, the difference in energy of the two compounds might be small.

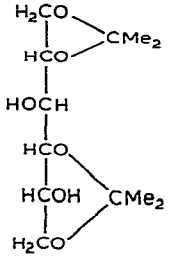
The ^{13}C-n.m.r. chemical-shifts of compound **B**, compared to those of the triacetal **A**, unambiguously confirmed the postulated structure **5**. For isomer **A**, the six lines of the isopropylidene methyl groups appear in a very narrow range (25.3, 25.8, 26.4, 26.7, 27.0, and 27.3 p.p.m.), whereas, in the case of isomer **B**, two methyl signals appeared at considerably smaller chemical-shifts (19.0 and 19.4 p.p.m.) compared to the other four (25.4, 27.0, 29.1, and 29.6 p.p.m.). This upfield shift (steric compression shift[6]) is a consequence of the steric hindrance existing between the *endo*-methyl groups of the 1,2- and 3,5-isopropylidene rings in compound **5**.

In isomer **6**, there would be no methyl group similarly sterically hindered; consequently, no upfield shift could be expected. The influence of the field effect mentioned may also be observed for the carbon atoms of the hexitol skeleton, as the line of the more hindered methylene group (C-1) is shifted upfield (61.8 p.p.m.) compared to the terminal-methylene carbon signals of isomer **A** (66.2 and 68.0 p.p.m.), and a similar, upfield shift can be detected at two methine lines (63.4 and 63.7 p.p.m. for C-2 and C-3, respectively) while the other two methine carbon atoms (C-4 and C-5) appeared at 72.1 and 73.1 p.p.m. respectively.

Besides the spectroscopic evidence, structure **5** is also supported by the fact that the two triacetal isomers **A** and **D** are formed simultaneously when 1,2-*O*-isopropylidene-D-glucitol is treated with acetone–zinc chloride (see later), suggesting the presence of a 1,2-linked dioxolane ring in both compounds.

For identifying the diacetal peaks **D** and **G**, the 1,2:3,4:5,6-triacetal was submitted to partial hydrolysis with ethanol–5M HCl. A sample was analyzed after 1 h, and, after 2 h, the reaction was processed as described in the literature[2]. The 1-h sample already contained, besides the starting material (**A**), the 3,4:5,6-diacetal (**C**), 1,2:3,4-diacetal (**F**), 3,4-monoacetal (**K**), and completely hydrolyzed material, D-glucitol (**M**), in the ratios of 50:12.5:5:4:5. That means that the terminal dioxolane ring on positions 1 and 2 (**C**) is hydrolyzed 2.5 times as fast as its counterpart at positions 5 and 6 (**F**). The peaks of the 1,2:3,4-diacetal and the 1,2:5,6-diacetal (**F**) coincide, but the mass spectra of these two isomers differ significantly* (*e.g.*, the 1,2:3,4-isomer gives a base peak at *m/e* 85, whereas that of the 1,2:5,6-isomer is at *m/e* 101; for details, see the Experimental part.)

The relatively large proportion of compound **G**, as well as the fact that it is also formed rapidly in the acetalation reaction of the 1,2-acetal (see Fig. 3), suggests that it has the 1,2:4,6-diacetal structure **7**, which should be the precursor in the synthesis of the new triacetal **5**.



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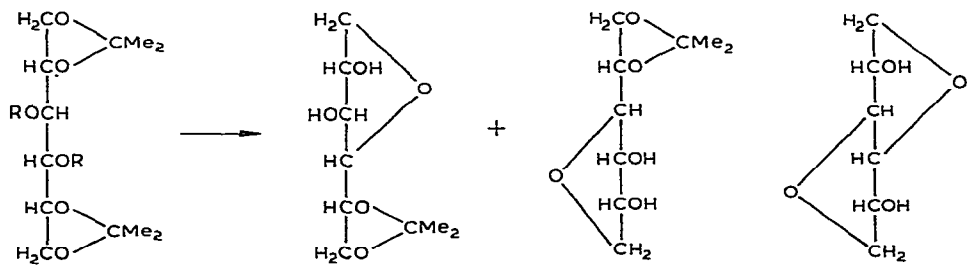
For studying the unidentified, monoacetal peaks for **I**, **J**, and **K**, the 1,2:5,6-diacetal **8** (**F**) was submitted to graded, acid hydrolysis[2]. This reaction is much

*The mass spectrum of the 1,2:3,4-diacetal was obtained by using g.l.c.–m.s. equipment.

faster than for the triacetal **A**, as the peak of the starting material had disappeared completely after 15 min, and only two components could be detected, each of which had a shorter retention time in g.l.c. than the starting material (**F**). The only plausible explanation of these facts would appear to be the formation of anhydro rings, which is a favored process under acidic conditions. That means that the protonated, dioxolane rings are attacked by the OH-3 and OH-4 groups, respectively, affording the 1,4-anhydro (**9**) and 3,6-anhydro (**10**) derivatives. Both can undergo hydrolysis, yielding the acetal-free products, or a second intramolecular attack can take place leading to the dianhydro compound **11**. G.l.c. investigation of the prolonged hydrolysis showed a very complex mixture. When the hydrolysis was quenched after 5 min, the peaks of the 1,2- (**H**) and 5,6-monoacetal (**L**) could be detected, but the aforementioned peaks of the anhydro compounds appeared with the same intensity. To avoid this side reaction, the 3,4-diacetate[4] **12** was submitted to hydrolysis under



8 R = H
12 R = Ac

9 10 11

identical conditions. As acid-catalyzed deacetylation is a much slower process than the hydrolysis of the acetal groups, no side reaction took place, proving the aforementioned hypothesis of anhydro-ring formation. Besides the two monoacetals, **H** and **L**, expected, only the completely hydrolyzed material, hexitol **M**, could be detected, Interestingly, in this case, the hydrolysis was even slower than that of the triacetals and, after 3 h at room temperature, the proportions of the components were 1,2:5,6-diacetal (48%), 1,2-acetal (18%), 5,6-acetal (20%), and D-glucitol (14%). According to these facts, the stability of the two terminal acetal groups is almost identical, whereas, for the triacetal, the 5,6-acetal group is 2.5 times as resistant to hydrolysis as the 1,2-acetal group. On the other hand, the very fast hydrolysis of the "unprotected" diacetal **8** is obviously the consequence of the anhydro ring-formation, the driving force of which speeds up the normal deacetalation reaction.

For identifying the remaining two monoacetal peaks of **I** and **J**, the 2,3:5,6-diacetal **1** (**E**) was hydrolyzed. To avoid any possible anhydro ring-formation, the diacetate **13** was prepared, and treated with hydrochloric acid in ethanol. The reaction was even slower than that of the di-*O*-acetyl-1,2:5,6-diacetal **12**, and ~6 h was needed for a similar degree of hydrolysis of the starting material. Besides **E** (47%), only the peak of the 2,3-acetal (**K**, 50%) and that of D-glucitol (**M**, 3%) could be detected.

TABLE I

RELATIVE INTENSITIES (%) OF G.L.C. PEAKS OBTAINED AFTER ACETYLATION OF THE REACTION MIXTURE OF D-GLUCITOL WITH ACETONE IN THE PRESENCE OF ZINC CHLORIDE

Reaction time (h)	*Peaks*[a]												
	A	B	C	D	E	F	G	H	I	J	K	L	M
t^b	1	1.3	3.8	3.9	4.1	4.5	5	7.2	7.8	8.1	8.2	8.7	11.6
0.5	1	1	1	1	6	19	3	13	2	2	4	33	14
1	3	1	1	1	13	22	5	10	2	3	3	29	8
2	6	3	1	1	23	26	6	7	1	2	2	20	3
4	10	4	1	1	31	26	6	4	1	3	0.4	14	1
6	12	5	1	1	33	23	6	3	0.6	2	0.3	13	—
24	22	5	1	—	37	14	8	2	0.3	4	—	7	—
120	34	3	3	—	35	11	6	0.4	0.3	3	—	4	—

[a]Compounds lettered as in Fig. 1. [b]Retention times relative to that of A.

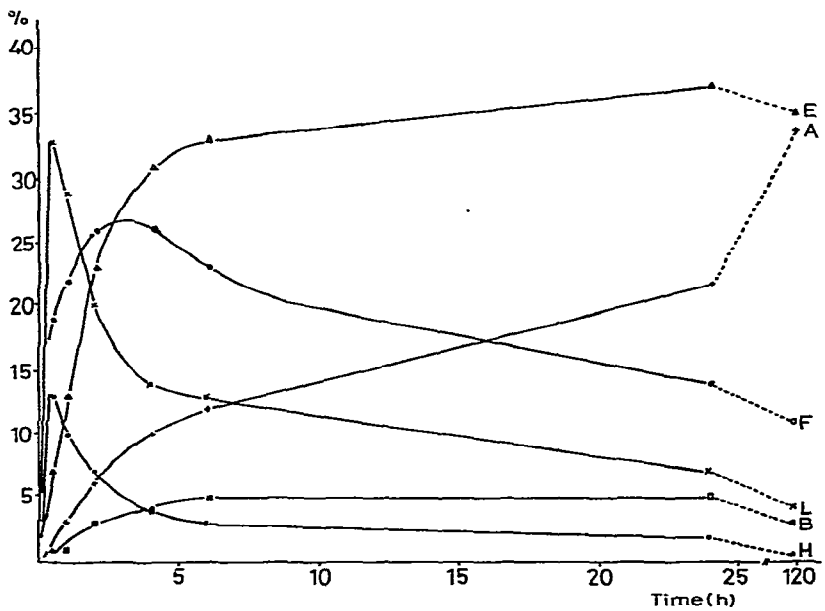


Fig. 2. Progress of the acetalation of D-glucitol with acetone in the presence of zinc chloride. (Compounds lettered as in Fig. 1.)

Investigation of the acetalation reaction. — After having established the structure of the acetals corresponding to the main peaks in g.l.c., the course of the reaction was studied in detail. Aliquots of the reaction mixture were quenched at 0.5, 1, 2, 4, 6, 24, and 120 h, and, after acetylation, analyzed by g.l.c. The exact data for all components are given in Table I, but, for analyzing the acetalation process, it is

sufficient to monitor the change in the proportions of the main components during the reaction, as shown in Fig. 2. From Fig. 2, it is evident that the ratios of the different components are kinetically controlled at the beginning of the reaction, but that, after a few hours, thermodynamic control becomes dominant. It is known[2] that the terminal hydroxyl groups of the hexitol react first; consequently, the 1,2- and 5,6-monoisopropylidene acetals **H** and **L** are present after 30 min in relatively high proportions. Primary attack of the secondary hydroxyl group is kinetically disfavored; therefore, the nonterminal dioxolane derivatives (*i.e.*, **J** and **K**) are formed in only very low yields. The attachment of a second isopropylidene group on the remaining free terminal of both **H** and **L** leads to the 1,2:5,6-diacetal **F**; therefore, its proportion also rises rapidly. After 2 h, however, when the starting material (**M**) is almost consumed (3%), the proportion of the monoacetals **H** and **L** decreases rapidly, due to their transformation into the diacetals **E** and **F***. From these, the former can be formed either directly, by the acetalation of the 5,6-acetal **L**, or by a rearrangement of **F** into **E**, which is not a kinetically, but a thermodynamically, controlled process, as the *trans*-substituted dioxolane ring, involving two secondary hydroxyl groups, is more stable than the terminal one, protecting a primary hydroxyl group[7]. To check this hypothesis, the crystalline 1,2-monoisopropylidene derivative **H** was

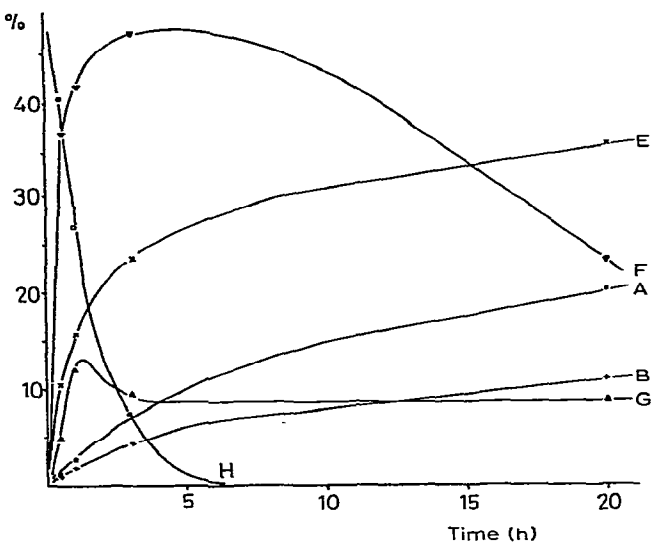


Fig. 3. Progress of the acetalation of 1,2-*O*-isopropylidene-D-glucitol with acetone in the presence of zinc chloride. (Compounds lettered as in Fig. 1.)

* The amount of the 1,2:5,6-diacetal cannot be calculated exactly from peak **F**, as the peak of the 1,2:3,4-diacetal appears at the same place. Nevertheless, as the formation of "vicinal" diacetals is very improbable as long as a free terminal position is available for the formation of the second dioxolane ring, the amount of the 1,2:3,4-diacetal might be in the same range as that of the 3,4:5,6-diacetal **A**, which is essentially negligible (~ 1%) during the reaction. Accordingly, peak **F** corresponds fairly well to the amount of the 1,2:5,6-diacetal.

treated with acetone–zinc chloride under similar conditions. Samples were quenched at 0.5, 1, 3, and 20 h, and analyzed by g.l.c. From the results, depicted in Fig. 3, it may be seen that the starting material **H** is rapidly converted into the 1,2:5,6-diacetal **F** in a kinetically controlled reaction. After 5 h, however, when the starting material has been consumed, the amount of the 1,2:5,6-diacetal **F** decreases faster than could be accounted for by its conversion into the triacetal **A**, indicating its simultaneous conversion into the more stable 2,3:5,6-diacetal **E**. Nevertheless, from Fig. 2, it may be seen that, in complete equilibrium, which is reached in 5 days, the triacetal **A** is present to about the same extent as the 2,3:5,6-diacetal **E**; consequently, their relative stability (*i.e.*, their free energy) must be very similar. For investigating whether the migration of the acetal group from O-1,2 to O-2,3 is an exception, or whether any other acetal group can migrate as well, the behavior of the 3,4-mono acetal (**K**) under similar conditions was checked. G.l.c. investigation of the reaction mixture, quenched after 0.5, 1, 3, and 24 h, showed that the 3,4-acetal group does *not* migrate, as only the expected 1,2:3,4- (**F**) and 3,4:5,6-diacetal (**C**) and the triacetal **A** were formed. The reaction itself is a much faster process than the direct acetalation of D-glucitol as, for example, after 1 h, the triacetal **A** is present in a yield of 32%, compared to the yield of 3% in the direct reaction (see Table I). This difference is due to the fact that, in the kinetically controlled reaction, the terminal positions of D-glucitol are acetalated first, and the subsequent acetalation of the OH-3,4 groups is a sterically hindered process, whereas, in the case of the 3,4-isopropylidene derivative, only the terminal positions have to be acetalated.

Another conclusion, important from the preparative point of view, may be drawn from Fig. 2. For obtaining the maximum yield of the 1,2:5,6-diacetal **F**, it is advisable to stop the reaction after 2 h, whereas a maximum yield of the 2,3:5,6-diacetal **E** is reached after 24 h.

EXPERIMENTAL

General methods. — All evaporations were conducted in a rotary evaporator under diminished pressure, after the organic solution had been dried with sodium sulfate. Light petroleum used had b.p. 60–80°. Optical rotations were determined in chloroform (*c* 1), if not stated otherwise. T.l.c. was effected on Kieselgel G with ethyl acetate–carbon tetrachloride, 1:1 (*A*) and 1:5 (*B*). For detection, 1:1 0.1M potassium permanganate–M sulfuric acid was used at 105°. Column chromatography was performed on Kieselgel 40 (63–200 μm). ^{13}C-N.m.r. spectra (25.16 MHz) and ^{1}H-n.m.r. spectra (60 MHz) were recorded at room temperature with a Varian XL-100 Ft-spectrometer for solutions in chloroform-*d*, with tetramethylsilane as the internal standard. G.l.c. was conducted with a Hewlett–Packard 5720A gas chromatograph, using a glass column (1.6 m × 4 mm) packed with 5% of QF-1 on Gas-Chrom Q (100–120 mesh); temperature, 2°.min^{-1} from 150 to 220°; carrier, nitrogen gas at the rate of 45 mL.min^{-1}. Mass spectra were recorded with a Varian MAT

SM-1 and a Hewlett–Packard 5990A gas chromatograph–mass spectrometer, using the same column, at 70 eV electron energy and 2.600 keV multiplier voltage.

1,4-Di-O-acetyl-2,3:5,6-di-O-isopropylidene-D-glucitol (**13**). — To a solution of ditosylate[1] **2** (5.7 g) in *N,N*-dimethylformamide (60 mL) were added sodium benzoate (3.8 g) and water (12 mL). The mixture was boiled for 5 h, to give, after cooling, evaporation, and the usual processing, a syrup (5.2 g) which, according to t.l.c. (*A*), contained, besides the 1-*O*-benzoyl derivative **3** (R_F 0.50), ~10% of the starting material **2** (R_F 0.40). This crude benzoate was dissolved in a mixture of chloroform (30 mL) and methanol (10 mL), and the solution was treated in the presence of phenolphthalein with 4M methanolic sodium methoxide (0.5 mL). The mixture was boiled on a steam bath until the material having R_F 0.50 was completely converted into the debenzoylated compound having R_F 0.15 (30 min). The chilled solution was made neutral with carbon dioxide, to give, after evaporation and column chromatography, pure 4-tosyl compound **4** (3.9 g, 72%) as a semisolid material, $[\alpha]_D^{20}$ +7.6°; R_F 0.75 (*B*).

A solution of this tosylate (2.2 g) in a mixture of methanol (20 mL) and water (5 mL) was stirred overnight in the presence of sodium amalgam (4%, 2.2 g). The clear solution was decanted from the mercury, made neutral with carbon dioxide, and evaporated. The residue was filtered with the aid of ethanol, the filtrate was evaporated, and the residue was freed of salts by column chromatography (*B*). The fractions having R_F 0.15 gave, on evaporation, pure 2,3:5,6-diacetal **1** in quantitative yield (1.3 g), $[\alpha]_D^{20}$ −16°; lit.[1] $[\alpha]_D^{20}$ −15.5°.

Acetylation of the aforementioned syrup (1.1 g) in pyridine (3 mL) with acetic anhydride (2 mL) gave, after the usual processing, pure diacetate **13**, $[\alpha]_D^{20}$ −1.3°, which, in g.l.c., showed only peak **E**; ^{1}H-n.m.r. data: δ 1.35 and 1.40 (s, 3 H and 9 H, 2 CMe_2), 2.10 and 2.15 (s, 2 acetyl-Me), and 5.10 (dd, J 6 and 4 Hz, H-4).

G.l.c. investigations of the acetalation reaction starting from D-glucitol. — D-Glucitol (36.4 g) was added to a stirred solution of anhydrous zinc chloride (70 g) in acetone (350 mL) at room temperature. At intervals of 0.5, 1, 2, 4, 6, 24, and 120 h, samples (40 mL) were removed and poured into a vigorously stirred, ice-cooled solution of potassium carbonate (9 g) in water (9 mL). The precipitate was filtered off, and washed with acetone (3 × 50 mL). Conc. ammonium hydroxide solution (0.5 mL) was added to the combined filtrates, and then they were evaporated. The residue was dissolved in pyridine (30 mL), acetic anhydride (20 mL) was added, and the mixture was kept overnight at room temperature, and then processed in the usual way. The resulting residue was analyzed by g.l.c.; the relative intensities of the different components are given in Table I.

G.l.c. investigation of the acetalation reaction starting from 1,2-O-isopropylidene-D-glucitol. — To a solution of zinc chloride (0.8 g) in acetone (4 mL) was added 1,2-monoacetal **H** (0.22 g). Samples (1 mL) were taken from the reaction mixture at 0.5, 1, 3, and 20 h, and were treated with 50% aqueous potassium carbonate solution (0.4 mL). The precipitate was filtered off and washed with acetone, and the filtrate

was processed as described for the reaction with D-glucitol. The g.l.c. results obtained are depicted in Fig. 2.

G.l.c. investigation of the acetalation reaction starting from 3,4-O-isopropylidene-D-glucitol. — A sample of the 3,4-monoacetal **K** (0.22 g) was treated with acetone–zinc chloride as described for the 1,2-monoacetal. G.l.c. investigation of the samples withdrawn after 0.5, 1, 3, and 24 h gave the following results: 1,2:3,4:5,6-triacetal (**A**): 12, 32, 60, and 84%; 3,4:5,6-diacetal (**C**): 18, 20, 17, and 10%; 1,2:3,4-diacetal (**F**): 24, 25, 17, and 5%; and 3,4-monoacetal (**K**): 46, 23, 6, and <1%.

Graded hydrolysis of 1,2:3,4:5,6-tri-O-isopropylidene-D-glucitol. — A solution of triacetal **A** (32.3 g) in a mixture of ethanol (800 mL) and 5M hydrochloric acid (16 mL) was kept at room temperature. After 1 h, a sample (50 mL) was quenched with M sodium hydroxide, and evaporated. The residue was acetylated with acetic anhydride (10 mL) in pyridine (20 mL), and processed in the usual way. G.l.c. investigation of the mixture obtained gave 1,2:3,4:5,6-triacetal (**A**), 65%; 3,4:5,6-diacetal (**C**), 16.3%; 1,2:3,4-diacetal (**F**), 6.5%; 3,4-monoacetal (**K**), 5.2%; and D-glucitol (**M**), 6.5%.

The original reaction-mixture was processed after 2 h according to the literature[3], yielding, after column chromatography (*B*), evaporation, and recrystallization of the residue from ether–light petroleum, pure 3,4:5,6-diacetal (2.2 g), m.p. 58–60°, $[\alpha]_D^{20}$ +27° (*c* 1.4, ethanol); R_F 0.30 (ethyl acetate); lit.[3] m.p. 55–56°, $[\alpha]_D^{20}$ +25.2° (*c* 1.4, ethanol).

G.l.c. investigation of the acetylated compound showed a single peak (**C**).

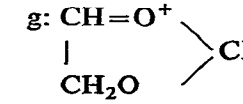
Graded hydrolysis of 1,2:5,6-di-O-isopropylidene-D-glucitol. — A solution of the diacetal **8** (2.6 g) in a mixture of ethanol (80 mL) and 5M hydrochloric acid was kept at room temperature. Samples (10 mL) were withdrawn at 5, 15, 30, and 60 min, and quenched with M sodium hydroxide. G.l.c. analysis of the acetylated, crude reaction-mixture after 5 min showed, besides the starting material (**F**), the peaks of the 1,2- (**M**) and 5,6-monoacetal (**L**), as well as two peaks having retention times of 3.1 and 4.0 relative to that of triacetal **A**. The relative retention-time of **F** is 4.5. After 15 min, no starting material, but only the two (new) faster-running components could be detected, with a relative intensity of 5:1.

Graded hydrolysis of 3,4-di-O-acetyl-1,2:5,6-di-O-isopropylidene-D-glucitol. — A solution of the diacetyl compound **12** (0.36 g) in a mixture of ethanol (8 mL) and 5M hydrochloric acid (0.16 mL) was kept at room temperature. Samples (2 mL) were withdrawn at intervals of 10, 30, 60, and 180 min, and analyzed as just described. Besides the starting material (**F**), only the peaks of the 1,2- (**H**) and 5,6-monoacetal (**L**), as well as that of D-glucitol (**M**), could be detected. After 3 h, the proportions of these components were 49, 18, 20, and 14%, respectively.

Graded hydrolysis of 1,4-di-O-acetyl-2,3:5,6-di-O-isopropylidene-D-glucitol. — A solution of diacetate **13** (0.36 g) was hydrolyzed as described for the 1,2:5,6-diacetal. Samples were withdrawn and analyzed after 1, 3, 6, and 20 h, to give the following g.l.c. results: 2,3:5,6-diacetal (**E**): 88.4, 70.5, 46.6, and 19.5%; 2,3-monoacetal (**J**): 19.6, 26.8, and 60%; and D-glucitol (**M**): 0, 1.4, 3.4, and 20%.

Mass-spectral data. — Masses and relative intensities of some fragments formed from 3,4-di-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-D-glucitol: 331[a] (11), 273[b] (19), 153[c] (46), 143[d] (5), 127[e] (5), 111[f] (56), 101[g] (100), and 85[h] (19).

Masses and relative intensities of some fragments formed from 5,6-di-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-D-glucitol: 331[a] (15), 273[b] (9), 153[c] (45), 143[d] (14), 127[e] (22), 111[f] (75), 85[h] (100), 245[i] (9), 201[j] (5), and 187[k] (15).

Fragments a: $M^+ - \cdot CH_3$; b: $M^+ - \cdot CH_3 - C_3H_6O$; c: $M^+ - \cdot CH_3 - C_3H_6O$ — 2 AcOH; d: $M^+ - \cdot CH(OAc)CH_2OAc - C_3H_6O$; e: $M^+ - 101 - C_3H_6O$ — AcOH; f: $M^+ - \cdot CH_3 - C_3H_6O$ — 2 AcOH — CH_2CO; g:  h: $M^+ - \cdot CH(OAc)CH_2OAc - 2\ C_3H_6O$; i: $M^+ - 101$; j: $M^+ - \cdot CH(OAc)CH_2OAc$; and k: $M^+ - 101 - C_3H_6O$.

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