PREPARATION, THIN LAYER CHROMATOGRAPHY, AND ULTRAVIOLET SPECTRA OF SOME O-BENZYL DERIVATIVES OF D-GLUCOSE[1]

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ABSTRACT

A new method for benzylation of carbohydrates has been developed which facilitated complete substitution of hydroxyl groups in one of the compounds prepared. Thin layer chromatography provides a good criterion of purity and is also a preparative method for separation of identifiable amounts of *O*-benzyl derivatives of carbohydrates. The number of benzyl groups in a compound can be determined by ultraviolet absorption spectroscopy. The following compounds were prepared, some of which have not been reported previously: benzyl-2,3,4,6-tetra-*O*-benzyl-α-D-glucoside; benzyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucoside; methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside; 2,3,4,6-tetra-*O*-benzyl-α-D-glucose; 1-*O*-(*p*-nitrobenzoyl)-2,3,4,6-tetra-*O*-benzyl-α-D-glucose; octa-*O*-benzyl sucrose; 3,5-di-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-xylose.

The value of the benzyl group in syntheses of carbohydrate derivatives has been recognized by chemists for many years and the subject has been reviewed by McCloskey (1). More extensive use of poly-*O*-benzyl derivatives of carbohydrates has been somewhat limited undoubtedly because many of them are not crystalline at room temperature and therefore of uncertain purity. Nevertheless, a number of important compounds have been prepared from these amorphous products (2, 3, 4). The success of thin layer chromatography in separating carbohydrate acetates (5) prompted the present study to see if the same method would be useful as a criterion of homogeneity for poly-*O*-benzyl derivatives of carbohydrates. The ultraviolet absorption properties of these *O*-benzyl derivatives were also examined and found to provide a method of analysis for *O*-benzyl groups.

The compounds used in this investigation may be considered as derivatives of 2,3,4,6-tetra-*O*-benzyl-D-glucose in which substituents at the anomeric carbon were α-*O*-benzyl; β-*O*-benzyl; α-*O*-methyl; α-hydroxyl; α-*O*-(*p*-nitrobenzoyl); and α-*O*-(1,3,4,6-tetra-*O*-benzyl-β-D-fructofuranosyl), i.e. octa-*O*-benzyl sucrose.

Separations were obtained on thin layers of silica gel G by development with light petroleum containing 3–5% of methanol. As with the benzene–methanol solvent system used for carbohydrate acetates (5) the mobilities of the various components were strongly dependent upon the concentration of methanol. These two solvent systems are complementary in that they give a wide range of solvent polarity.

Figure 1 shows the separation of the fully benzylated glucoses and the resolution that can be obtained in this series with various substituents at the anomeric carbon atom. The large differences in mobilities between fully substituted derivatives and those containing a free hydroxyl group clearly indicate that thin layer chromatography is an ideal method for following reactions which involve formation of ether, ester, or acetal groups. This feature was emphasized in the attempted benzylation of benzyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucoside by the usual benzyl chloride – powdered potassium hydroxide procedure (1). Thin layer chromatography of the crude reaction mixture showed a yield of only 33% of the expected benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside and some 60% of a product corresponding to a tetra-*O*-benzyl glucose derivative. All attempts to force the benzylation

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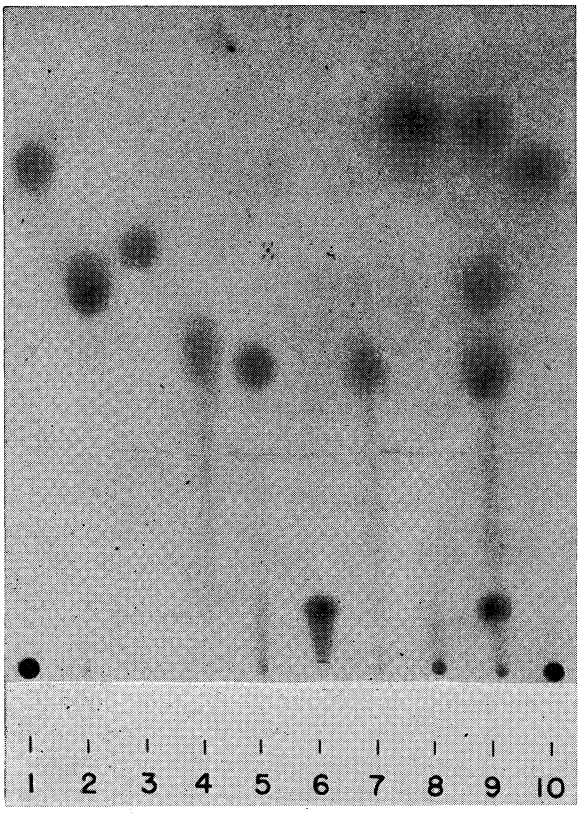

FIG. 1. Thin layer chromatogram of some D-glucose benzyl ethers.
Adsorbent, silica gel G; solvent, light petroleum (b.p. 65–110° C) containing 5% (v/v) of methanol; single ascending development to 14.7 cm.
Components in decreasing order of mobility:

1, 10. (Marker dyes) Sudan III, methyl orange
2. I
3. II
4. V
5. III
6. IV
7. VI
8. Dibenzyl ether, impurity
9. Compounds 8, 2, 4, 5, and 6

to completion by raising the temperature or extending the time of reaction were unsuccessful and led to excessive formation of dibenzyl ether. However, the tetra-*O*-benzyl glucose derivative was smoothly benzylated by benzyl chloride and sodium hydride at 130° C to give a 90% yield of crystalline benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside. This method of benzylation, which does not appear to have been applied to carbohydrates before, was based upon an observation by Cristol, Ragsdale, and Meek (6) that benzyl chloride does not react with sodium hydride at temperatures up to 170° C. The use of sodium hydride also prevents the formation of dibenzyl ether, which is a major by-product in other methods of benzylation. The new method forms a useful adjunct to the older procedures (1) and is especially valuable for the benzylation of hindered hydroxyl groups. The preparation of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside as described in the experimental section is an example of benzylation by the benzyl chloride – sodium hydride procedure.

The key compound 2,3,4,6-tetra-*O*-benzyl-α-D-glucose was prepared by hydrolysis of

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its methyl glycoside (3) but in much better yield by hydrolysis of the corresponding benzyl glycoside. The acetate of 2,3,4,6-tetra-*O*-benzyl-α-D-glucose was not crystalline; however, a crystalline *p*-nitrobenzoate was obtained. Octa-*O*-benzyl sucrose was prepared by benzylation of sucrose with benzyl bromide, silver oxide, and barium oxide (7), the product being isolated by a procedure previously described (2) and purified for analysis by preparative thin layer chromatography. Benzylation of 1,2-*O*-cyclohexylidene-α-D-xylofuranose to the 3,5-di-*O*-benzyl derivative provided another compound to test the spectrophotometric estimation of *O*-benzyl groups as described below.

It was apparent in this work that some method for determining the number of *O*-benzyl groups in a compound would be very valuable, just as the methoxyl determination has been so useful in the chemistry of methylated carbohydrates. The early work on benzylated carbohydrates utilized the hydriodic acid fission of ethers, as used for methoxyl estimation, for determining benzyl groups (8). However, that method involves isolation of the lachrymatory benzyl iodide and is rendered invalid by the presence of a methoxyl group in the compound being analyzed. The ultraviolet absorption spectrum of the benzyl group has been used as the basis of a spectrophotometric method for the estimation of benzyl penicillin (9). Accordingly, the ultraviolet spectra of a number of crystalline *O*-benzyl derivatives of carbohydrates were examined to see if the method could be used for quantitative estimation of *O*-benzyl broups in these compounds.

With one exception, all the *O*-benzyl derivatives examined so far have shown an $\epsilon_{258.5}$ value per benzyl group of 186±2. The single exception was benzyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucoside, which, in ethanol, gives a spectrum with no clear maximum at 258.5 mμ. In cyclohexane this maximum is revealed but the $\epsilon_{258.5}$ value (245) per benzyl group is much greater than those for the other compounds. Those benzyl derivatives which gave the $\epsilon_{258.5}$ value per benzyl group of 186±2 all exhibited a pronounced minimum in the vicinity of 230–240 mμ; unless this minimum is present estimates of benzyl groups from $\epsilon_{258.5}$ are likely to be in error. The spectra obtained are in agreement with that recorded (10) for benzyl alcohol, which also gives an $\epsilon_{258.5}$ value of 185. The validity of Beer's law was established for benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside over the concentration range 0.02–0.12% and the constancy of the $\epsilon_{258.5}$ value per benzyl group in other compounds with varying degrees of *O*-benzyl substitution indicated its validity for them as well, over the range of concentration used.

The successful application of ultraviolet spectroscopy for estimating *O*-benzyl groups in amorphous compounds is largely dependent on the purity of those compounds. Thin layer chromatography is the method of choice for purification because the samples isolated from a single plate are more than sufficient for spectroscopic analysis. In turn, the ultraviolet spectra provide useful information about the degree of substitution in the compounds isolated and the methods therefore mutually enhance the value of each other.

EXPERIMENTAL

Thin Layer Chromatography

Glass plates (20×20×0.3 cm) were coated with silica gel G* or with silica gel G containing 1% (w/w) of fluorescent zinc silicate.† The plates were prepared and samples were applied to them as previously described (5). The dyes Sudan III and methyl orange were used as markers and plates were developed with light petroleum (b.p. 65–110° C) – methanol mixtures containing 3–5% (v/v) of methanol. As with the carbohydrate acetates (5) the methanol content of the solvent was varied, within the above limits, depending on the compounds being separated. The separation shown in Fig. 1 was obtained with a single

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ascending development (solvent front 14.7 cm) in 40 minutes using light petroleum (b.p. 65–110° C) containing 5% (v/v) of methanol. Fresh solvent was made up each day because of gradual depletion of the methanol content by adsorption onto the silicic acid.

Detection

Reaction of the components on the plates with iodine vapor was the most convenient and sensitive method of detection for routine work. A saturated atmosphere of iodine vapor was obtained by keeping 3–5 g of iodine crystals in the bottom of a covered glass jar. The thin layer chromatograms were dried in a current of air from a fan and were then placed in the tank containing the iodine. The compounds on the chromatograms became visible in a few minutes and the spots reached their maximum intensity after 30 minutes. This method will clearly detect 0.4 μg of benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside. The chromatograms can be covered with clean glass plates for ease of handling or tracing. For non-destructive detection the plates were prepared from the fluorescent silica gel G described above; the chromatograms, developed and dried, were then examined under a suitable shortwave source of ultraviolet light (Mineralight S. L. 2537). Factors involved in the selection of fluorescent materials and light sources have been examined by Sease (11); the technique has been applied to thin layer chromatography by Kirchner *et al.* (12). The sensitivity of this method of detection for benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside was 4 μg but obviously the level of detection will vary with the molar extinction coefficient (ϵ) of the compound being detected. In general, the iodine vapor technique was used for analytical work and the ultraviolet method for semimicro preparative plates.

Semimicro Preparative Separation

Plates were prepared as described for the analytical separations and the *O*-benzyl derivatives were applied as contiguous spots to give 30–100 mg per 20-cm plate. Fluorescent silica gel G was used and the plates were developed with light petroleum (b.p. 65–110° C) containing 5% (v/v) of methanol. The developed plates were dried in air and the zones were detected in ultraviolet light as dark areas on a fluorescent yellow background. The zones were outlined with a scalpel and scraped from the plate for elution of the separate components. This technique was described in detail for thin layer chromatography of carbohydrate acetates (5). In the majority of separations elution of the zone scrapings with chloroform yielded analytically pure samples. Products recovered for analysis were dried at 60° C in a high vacuum (0.01 mm of mercury) for 18 hours.

Preparation of O-Benzyl Derivatives

I. Benzyl 2,3,4,6-Tetra-O-benzyl-α-D-glucoside

Benzyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucoside (1.0 g (13, 14); $E^{1\%}_{1\,cm}$ = 4.2 at 258.5 mμ, $\epsilon_{max/benzyl\,group}$ = 184) was benzylated by benzyl chloride (8.0 ml) and powdered potassium hydroxide (3.0 g) (1). The product was a colorless sirup (1.5 g), $[\alpha]_D^{25}$ +66.4 (*c*, 3% in chloroform). Thin layer chromatography of this sirup showed the presence of dibenzyl ether and two other products: A (R_f 0.33) and B (R_f 0.09); Sudan III had R_f 0.51. Pure samples of products A (32.2 mg) and B (48.0 mg) were obtained by preparative thin layer chromatography of a portion of the sirup.

Product A crystallized when triturated with methanol (1 ml). The crystals were filtered and washed with methanol (2×0.5 ml) to give benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside I (17.8 mg) as colorless needles with a melting point of 93.5–94.5° C unchanged on recrystallization from the same solvent. Anal.: Calc. for $C_{41}H_{42}O_6$: C, 78.07%; H, 6.71%. Found: C, 77.84%; H, 6.92%. $[\alpha]_D^{28}$ +55.8° (*c*, 1.63% in chloroform). $E^{1\%}_{1\,cm}$ = 14.8 at 258.5 mμ; $\epsilon_{max/benzyl\,group}$ = 187.

Product B could not be induced to crystallize but analysis showed that it was a tetra-*O*-benzyl derivative of glucose. Anal.: Calc. for $C_{34}H_{36}O_6$: C, 75.53%; H, 6.71%. Found: C, 75.63%; H, 6.81%. $[\alpha]_D^{24}$ +90.8° (*c*, 1.42% in chloroform). Benzylation of this sirupy tetra-*O*-benzyl derivative (50 mg) by sodium hydride and benzyl chloride, as described below for methyl α-D-glucopyranoside, yielded crude benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside, m.p. 91–93° C (53 mg, 91%); one recrystallization from methanol provided a pure product, m.p. 93.5–94.5° C (41 mg, 70%).

Overall yields in the benzylation were 33% of benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside and 60% of the tetra-*O*-benzyl derivative. The unresolved mixture in methanol solution gave a further 270 mg of benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside when seeded with crystals of the pure product obtained by thin layer chromatography.

II. Benzyl 2,3,4,6-Tetra-O-benzyl-β-D-glucoside

Benzyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucoside (0.44 g (13); $E^{1\%}_{1\,cm}$ = 5.6 at 258.5 mμ, $\epsilon_{max/benzyl\,group}$ = 245) was benzylated with powdered potassium hydroxide (1.5 g) and benzyl chloride (5 ml) as described above. The oily product (0.6 g) crystallized partially when triturated with methanol at 0° C. The crystals were washed with methanol (2×0.5 ml) and dried; m.p. 79–81° C, 209 mg, 33%. Thin layer chromatography revealed trace quantities of a slower-moving component. Recrystallization from methanol (5 ml) provided pure benzyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucoside, m.p. 83–84° C, $[\alpha]_D^{25}$ −14.9° (*c*, 1.48% in chloroform); reported (8), m.p. 83.5° C. Anal.: Calc. for $C_{41}H_{42}O_6$: C, 78.07%; H, 6.71%. Found: C, 77.90%; H, 6.50%. $E^{1\%}_{1\,cm}$ at 258.5 mμ = 14.8; $\epsilon_{max/benzyl\,group}$ = 187.

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III. Methyl 2,3,4,6-Tetra-O-benzyl-α-D-glucoside

This compound has been reported by Schmidt *et al.* (3), who prepared it by benzylation of methyl α-D-glucopyranoside with powdered potassium hydroxide and benzyl chloride. However, the specific rotation reported is not in agreement with that found in the present work and the only analytical value cited was methoxyl content. In the present study methoxyl analysis of these compounds was found to be unreliable and gave consistently high values, probably due to interference by the *O*-benzyl groups.

A mixture of methyl α-D-glucopyranoside (5 g, finely powdered), benzyl chloride (125 ml), and sodium hydride (11 g) was stirred magnetically under anhydrous conditions for 3 hours at 125–130° C. During the strongly exothermic reaction the mixture became thick and gelatinous and then changed to a thin slurry as the reaction reached completion. The progress of the reaction was followed by thin layer chromatography, which showed that benzylation was virtually complete after 3 hours. The reaction mixture was centrifuged, the supernatant liquor was decanted, and the residue was washed with benzene (4×50 ml) by centrifugation and decantation. The excess of sodium hydride was destroyed by adding the solid residue to a large volume of ethanol. The combined benzene supernatant liquors were steam-distilled until the distillate was clear and the oily residue was extracted with chloroform (4×50 ml). The extract was dried by passage through a wad of cotton and evaporated to give a yellow sirup (22.0 g). This product was sufficiently pure for the preparation of 2,3,4,6-tetra-*O*-benzyl-D-glucose as described below. A small aliquot was purified by preparative thin layer chromatography to give methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside as a colorless sirup, $[\alpha]_D^{25}$ +18.7° (*c*, 1.5% in chloroform); reported (3), $[\alpha]_D^{25}$ +32.2 (*c*, 5% in chloroform). Anal.: Calc. for $C_{35}H_{38}O_6$: C, 75.79%; H, 6.91%. Found: C, 75.67%; H, 7.00%. λ_{max} 258.5 mμ; calc. $E^{1\%}_{1\,cm}$ = 13.4, found $E^{1\%}_{1\,cm}$ = 13.4; $\epsilon_{max/benzyl\,group}$ = 186.

IV. 2,3,4,6-Tetra-O-benzyl-α-D-glucose

(a) Hydrolysis of methyl 2,3,4,6-tetra-O-benzyl-α-D-glucoside.—The method of Schmidt *et al.* (3) was modified to give an improved overall yield. Crude methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside (21.7 g) was dissolved in glacial acetic acid (400 ml) and the solution was heated to 90° C on a steam bath. Sulphuric acid (108 ml, 2 *N*) was added and the heating was continued for 2 hours. Thin layer chromatography showed that considerable amounts of starting product were still present. A further portion (84 ml) of 2 *N* sulphuric acid was added and the solution was heated for 18 hours, after which thin layer chromatography showed that none of the initial product remained. The hydrolyzate was poured into water (3.5 l.) whereupon a yellow oil was precipitated which gradually solidified. The solid was isolated by filtration and washed with cold methanol to give colorless crystals of 2,3,4,6-tetra-*O*-benzyl-α-D-glucose (5.0 g, 35%), m.p. 146–149° C. Recrystallization of this product from methanol (160 ml) yielded needles having a melting point of 150–151° C and $[\alpha]_D^{24}$ +20.7 (*c*, 2.47% in chloroform); reported (3), m.p. 148° C, $[\alpha]_D^{20}$ +21.2° (*c*, 3.5% in chloroform). Total yield of pure product recovered from the recrystallization was 4.2 g, 30%.

(b) Hydrolysis of benzyl 2,3,4,6-tetra-O-benzyl-α-D-glucoside.—Compound I (2.0 g) was dissolved in hot, 90% acetic acid (60 ml) and to the solution was added 2 *N* sulphuric acid (16 ml). The solution was heated on a steam bath for 3 hours and then a second portion (12 ml) of 2 *N* sulphuric acid was added. The reaction was heated for a further 3 hours, after which hydrolysis was shown to be complete by thin layer chromatography. The hydrolyzate was poured into boiling water (900 ml) whereupon the product crystallized. The crystals were isolated by filtration and washed with cold methanol (2×4 ml) to give colorless needles (1.0 g), m.p. 142–145° C. Recrystallization from methanol yielded 2,3,4,6-tetra-*O*-benzyl-α-D-glucose (0.81 g, 47%), m.p. 150–151° C, $[\alpha]_D^{24}$ +20.7° (*c*, 2.5% in chloroform). $E^{1\%}_{1\,cm}$ = 13.8 at 258.5 mμ, $\epsilon_{max/benzyl\,group}$ = 186. The 1-*O*-(*p*-nitrobenzoyl)-2,3,4,6-tetra-*O*-benzyl-α-D-glucose (V) was prepared by heating IV with *p*-nitrobenzoyl chloride in anhydrous pyridine and after recrystallization from ethanol had m.p. 126–127° C and $[\alpha]_D^{26}$ +72.3° (*c*, 2.13% in chloroform). Anal.: Calc. for $C_{41}H_{39}O_9N$: C, 71.39%; H, 5.70%. Found: C, 71.43%; H, 5.40%. The high positive rotation of this derivative suggests assignment of the α-D-configuration. Catalytic de-*O*-acylation of V gave a 74% yield of Compound IV, m.p. 147–149° C raised to 150–151° C by two recrystallizations from methanol.

V. 1,3,4,6-Tetra-O-benzyl-β-D-fructosyl-2,3,4,6-tetra-O-benzyl-α-D-glucoside (Octa-O-benzyl Sucrose)

Sucrose (0.5 g) was benzylated in dimethylformamide (5 ml) by benzyl bromide (5 ml), silver oxide (5 g), and barium oxide (2.5 g) (7). Examination of the product (1.2 g) by thin layer chromatography showed the presence of two components, one of which was dibenzyl ether. Preparative thin layer chromatography of a small portion of the crude sirup yielded the second constituent, octa-*O*-benzyl sucrose, as a colorless sirup, $[\alpha]_D^{26}$ +31.6° (*c*, 1.65% in chloroform). Anal.: Calc. for $C_{68}H_{70}O_{11}$: C, 76.81%; H, 6.64%. Found: C, 76.30%; H, 6.67%. λ_{max} 258.5 mμ; calc. $E^{1\%}_{1\,cm}$ = 14.0, found $E^{1\%}_{1\,cm}$ = 14.2; $\epsilon_{max/benzyl\,group}$ = 188. The crude product could be purified on a larger scale by dissolution of the sirup in hot absolute ethanol (25 ml), which was then allowed to cool to room temperature (2). The oily product, precipitated from the cooled solution, was washed by decantation and was then dried to a yellow sirup (0.45 g, 29%).

VI. 3,5-Di-O-benzyl-1,2-O-cyclohexylidene-α-D-xylose

1,2-*O*-Cyclohexylidene-α-D-xylofuranose (6.9 g), m.p. 86–87° C, $[\alpha]_D^{25}$ −6.2° (*c*, 2.0% in methanol) (15), was benzylated by benzyl chloride (75 ml) and powdered potassium hydroxide (22.0 g) (1). The product crystallized when nucleated with seed crystals obtained by trituration of a small portion of the oil with *n*-hexane. Recrystallization from *n*-hexane (30 ml) yielded 3,5-di-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-xylose

as colorless needles (10.7 g, 87%); m.p. 91–92° C, $[\alpha]_D^{27}$ −31.3° (*c*, 1.64% in chloroform). Anal.: Calc. for $C_{25}H_{30}O_5$: C, 73.14%; H, 7.37%. Found: C, 73.13%; H, 7.37%. $E^{1\%}_{1\,cm}$ = 9.1 at 258.5 mμ, $\epsilon_{max/benzyl\,group}$ = 186.

Ultraviolet Spectroscopy

The spectra reported in this work were measured with a Cary recording spectrophotometer Model 11M using 1-cm quartz cells. The solvent used was 95% ethanol except for benzyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucoside, which gave a satisfactory spectrum only in cyclohexane. A spectrum of benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside in cyclohexane showed no significant difference in $\epsilon_{258.5}$ to that obtained in 95% ethanol. The $E^{1\%}_{1\,cm}$ at 258.5 mμ for benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucoside in 95% ethanol varied from 15.0–14.8 over the concentration range 0.02–0.12%, indicating the validity of Beer's law within the reproducibility (2–3%) of the method. The $E^{1\%}_{1\,cm}$ values, cited for the compounds prepared, are of importance as a method of characterization (16). The values may be calculated for any benzylated compound from:

$$E^{1\%}_{1\,cm} = \frac{\epsilon \times 10}{\text{Mol. Wt.}}.$$

As shown here $\epsilon_{258.5} = n \times 186 \pm 2$ where n is the number of benzyl groups in the molecule; hence $E^{1\%}_{1\,cm} = 1860n/\text{Mol. Wt.}$ This value for all benzylated compounds should lie between 0 and 18.8 (the value of $E^{1\%}_{1\,cm}$ for dibenzyl ether) if there is no interference from other chromophores.

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