

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Structure of Dibenzylidene Dulcitol (1,3:4,6-Dibenzylidene-dulcitol)¹

BY W. T. HASKINS, RAYMOND M. HANN AND C. S. HUDSON

Emil Fischer,² in 1894, described a dibenzylidene-dulcitol which melted with decomposition at 215–220° (uncor.). Nothing has been known in the past regarding the structure of this compound. In the present communication we supply proof that it has the structure of 1,3:4,6-dibenzylidene-dulcitol.

The dibenzylidene-dulcitol, which was prepared by a modification of Fischer's procedure, agreed with his compound in melting point and other physical properties. Evidence for the presence or absence of contiguous hydroxyl groups in it was first sought. It was concluded that they are absent, because dibenzylidene-dulcitol was attacked by lead tetraacetate in glacial acetic acid solution so slowly (0.07 of a mole of oxidant consumed in nineteen hours) that hydrolysis of the benzylidene groups appears to be necessary before oxidation can occur.

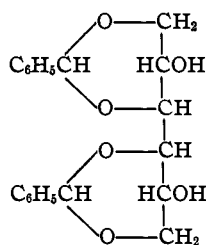
This dibenzylidene-dulcitol readily forms a series of diacyl derivatives. The dibenzoate is of particular importance in the determination of its structure because it yields, upon treatment with an acid acetylating mixture, a dibenzoyl-tetraacetyl-dulcitol which is different from either the 1,4-dibenzoyl-2,3,5,6-tetraacetyl-D,L-galactitol³ or the 1,6-dibenzoyl-2,3,4,5-tetraacetyl-dulcitol previously described. The fact that these three dibenzoyl-tetraacetyl-hexitols are different substances excludes positions 1–4 and 1–6 for the benzoyl groups in the new dibenzoyl-tetraacetyl-dulcitol. From the conclusion that dibenzylidene-dulcitol does not contain a glycol grouping it follows that the pair of benzoyl groups in its dibenzoate cannot occupy any one of the positions 1–2, 2–3 or 3–4. These exclusions limit the possible positions of the two benzoyl groups to carbons 1–3, 1–5, 2–4 or 2–5 of the molecule. Two of these four possible structures, namely, 1–3 and 1–5, require the presence of a primary hydroxyl group in the diacetal; it seems unlikely that such a group is present in view of the following experimental findings. Firstly, the failure to obtain

either a mono- or ditrityl compound from dibenzylidene-dulcitol by employing the customary reaction conditions with triphenylchloromethane. Secondly, the observation that the ditosyl derivative of dibenzylidene-dulcitol was recovered unchanged from reactions which generally bring about the substitution of iodine for the tosyl group if it be attached to a primary hydroxyl group. There is thus strong evidence that dibenzylidene-dulcitol contains no primary hydroxy group; it is thus concluded that the benzoyl groups in its dibenzoate occupy positions 2,4 or 2,5. It seems highly probable, therefore, that dibenzylidene-dulcitol is either 1,3:4,6-dibenzylidene-dulcitol (I) or 1,3:5,6-dibenzylidene-D,L-galactitol (II). A decision between these two structures was sought first through periodate oxidation of the dibenzoate (2,5-dibenzoyl-dulcitol or 2,4-dibenzoyl-D,L-galactitol) which should result upon removal of the benzylidene groups from dibenzoyl-dibenzylidene-dulcitol. Unfortunately, as described in the experimental part, acyl migration of the benzoyl groups occurred during the selective hydrolysis of the diacetal-dibenzoate, resulting in the formation of a complex mixture of dibenzoylated-dulcitol and D,L-galactitols. On the other hand, it was possible to obtain a crystalline dibenzyl ether of the dibenzylidene-dulcitol (III), and this substance yielded a stable crystalline dibenzyl-hexitol upon acid hydrolysis. The previous inferences would limit its structure to that of 2,5-dibenzyl-dulcitol (V) or 2,4-dibenzyl-D,L-galactitol (VI). It was found that the oxidation with sodium metaperiodate of the dibenzyl ether consumed only one molecular equivalent of oxidant without the production of formaldehyde. This experimental fact proves that *the ether contains a single glycol grouping* and limits the position of the benzyl groups to carbons two and five; the absence of formaldehyde as an oxidation product proves that *both primary hydroxyl groups are attended by substituted hydroxyl groups* (carbons two and five) and *the glycol group must then be on carbons three and four*. Dibenzyl-dulcitol is thus shown to be 2,5-dibenzyl-dulcitol (V) and Fischer's dibenzylidene-dulcitol is 1,3:4,6-dibenzylidene-dulcitol (I).

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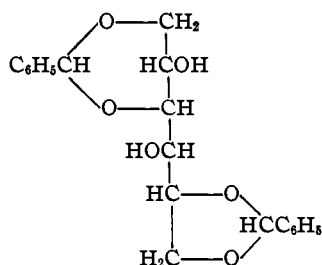
(2) Fischer, *Ber.*, **27**, 1524 (1894).

(3) Hann, Maclay and Hudson, *THIS JOURNAL*, **61**, 2432 (1939). The conventions which we use regarding the names dulcitol and galactitol have been explained in that article.

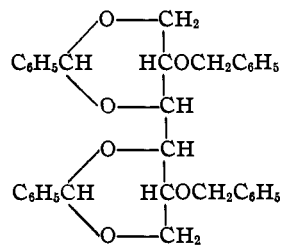


(I)

1,3:4,6-Dibenzylidene-dulcitol

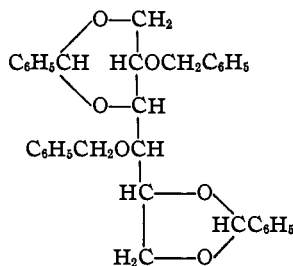


(II)

1,3:5,6-Dibenzylidene-D,L-galactitol⁴

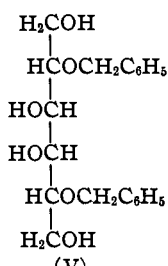
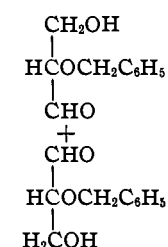
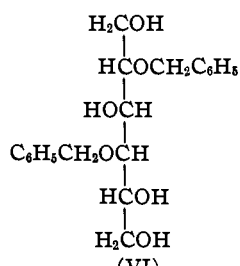
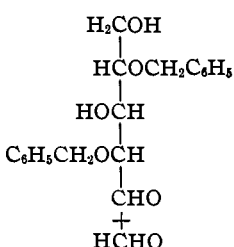
(III)

2,5-Dibenzyl-1,3:4,6-dibenzylidene-dulcitol



(IV)

2,4-Dibenzyl-1,3:5,6-dibenzylidene-D,L-galactitol

(V)
2,5-Dibenzyl-dulcitol(VII)
2-Benzyl-D,L-glyceraldehyde(VI)
2,4-Dibenzyl-D,L-galactitol(VIII)
2,4-Dibenzyl-D,L-lyxose

The results of this oxidation also constitute a definitive proof of the prior deduction that *dibenzylidene-dulcitol* does not contain a free primary hydroxyl group since any dibenzyl-dulcitol in which a benzyl group was attached through a primary

(4) Those formulas which refer to racemic structures are written here for only the D-form, to save space, but formula VII comprises both enantiomorphs. The benzylidene groups contain an asymmetric carbon atom; it is therefore possible that structures such as (I) may indeed be racemic ones. Present evidence does not permit a decision.

hydroxyl group would reduce more than one equivalent of periodate.

An independent conclusive proof of the structure of dibenzylidene-dulcitol may be deduced from the experimental results obtained in a study of the lead tetraacetate oxidation products of dibenzyl-dulcitol. The dibenzyl ether, upon oxidation, yields a benzyl-D,L-glyceraldehyde (isolated as the crystalline semicarbazone); since the benzyl group in this aldehyde cannot be attached through a primary hydroxyl group, the aldehyde must be 2-benzyl-D,L-glyceraldehyde (VII); hence one of the benzyl groups in dibenzylidene-dulcitol (III) must be attached through the hydroxyl group on carbon two. In order that 2-benzyl-D,L-glyceraldehyde (VII) may result from the oxidation of dibenzyl-dulcitol by lead tetraacetate the second benzyl group cannot be attached through the hydroxyl groups of either carbons three or four, and since the possibility of its attachment through the hydroxyl group on carbon six has been previously excluded, it must be attached to the hydroxyl group on carbon five; therefore the ether is 2,5-dibenzyl-dulcitol (V) and the diacetal is 1,3:4,6-dibenzylidenedulcitol (I). Further confirmation for the correctness of the indicated structure of 2,5-dibenzyl-dulcitol was obtained from the fact that it was possible to isolate 2-benzyl-D,L-glyceraldehyde semicarbazone in a yield of more than 50% (actually, 59%), a result which is compatible only with the 2,5-structure. As indicated in formulas II, IV, VI and VIII the isomeric 1,3:5,6-dibenzylidene-dulcitol structure would yield a 2,4-dibenzyl-D,L-galactitol, which upon periodate or lead tetraacetate oxidation, should consume one molecular equivalent of oxidant and produce formaldehyde and 2,4-dibenzyl-D,L-lyxose as oxidation products. The experimental results thus definitely exclude the 2,4 positions for the benzyl groups.

We express our appreciation to Dr. A. T. Ness for performing the microchemical analyses in connection with this work, and to the Atlas Powder Company for furnishing a supply of dulcitol.

Experimental

1,3:4,6-Dibenzylidene-dulcitol (I).—A rapid stream of dry hydrochloric acid gas was passed for ten minutes through a suspension of 32 g. of dulcitol in 40 g. (2.15 molecular equivalents) of redistilled benzaldehyde. The reaction mixture was allowed to stand at room temperature for two hours and the viscid solution scratched to induce

crystallization. After standing overnight at room temperature the nearly solid mass was broken up and transferred to a flat dish, which was placed in an evacuated desiccator containing sodium hydroxide and sulfuric acid for a period of twenty-four hours. The mass of crystals was ground under ether in a mortar to remove excess benzaldehyde, then refluxed a few minutes with 100 cc. of water to remove unchanged dulcitol, and finally washed with water until the washings gave no reaction for chloride ion. The yield was 58.4 g. (93%). Recrystallized from five parts of dioxane, the diacetal was obtained in quadrilateral plates which decompose at 215–220°⁵ as reported by Fischer.²

Anal. Calcd. for C₂₀H₂₂O₆: C, 67.02; H, 6.19. Found: C, 67.20; H, 6.14.

Action of Lead Tetraacetate on 1,3:4,6-Dibenzylidene-dulcitol.—A sample of 0.1114 g. of the diacetal was dissolved in 80 cc. of glacial acetic acid, 10 cc. of 0.0971 *N* lead tetraacetate-acetic acid solution (1.56 molecular equivalents) was added, and the solution adjusted to a volume of 100 cc. with acetic acid. Subsamples of 10 cc. were analyzed at the expiration of fifteen and forty-five minutes, two and nineteen hours, at which times 0.00, 0.04, 0.05 and 0.07 molecular equivalents of lead tetraacetate were found to have been consumed. It is evident that the diacetal is only very slightly attacked by the tetraacetate; the slight consumption of this reagent appears to be due to a very slow hydrolysis of the diacetal with consequent production of an α -glycol group.

Diacyl Derivatives of 1,3:4,6-Dibenzylidene-dulcitol.—

(a) A solution of 1.0 g. of the diacetal in a mixture of 10 cc. of pyridine and 2 cc. of acetic anhydride was allowed to stand at room temperature. After five hours the diacetate began to crystallize. After twenty-four hours the reaction mixture was poured into ice and water and the crystalline *2,5-diacetyl-1,3:4,6-dibenzylidene-dulcitol* was isolated in a yield of 1.25 g. (quantitative). The substance was recrystallized from 75 parts of glacial acetic acid, forming clusters of elongated prisms which decomposed at 265°.

Anal. Calcd. for C₂₄H₂₆O₈: C, 65.15; H, 5.92. Found: C, 65.21; H, 5.83.

(b) A solution of 8.0 g. of dibenzylidene-dulcitol in 75 cc. of pyridine was cooled to –10° and a solution of 10 g. of dichloroacetyl chloride in 40 cc. of carbon tetrachloride was added dropwise with constant stirring. After standing at 0° for two hours, the reaction mixture was treated with 100 cc. of ice water, and the carbon tetrachloride layer separated and concentrated to obtain the diacyl derivative; yield 10 g. (77%). The *2,5-bis-dichloroacetyl-1,3:4,6-dibenzylidene-dulcitol* was recrystallized from 50 parts of glacial acetic acid, in the form of fine needles which decomposed at 228–229°.

Anal. Calcd. for C₂₄H₂₂O₈Cl₄: C, 49.67; H, 3.82. Found: C, 49.74; H, 3.98.

(c) The action of benzoyl chloride on a pyridine solution of the diacetal gave a quantitative yield of *2,5-dibenzoyl-1,3:4,6-dibenzylidene-dulcitol*. It was recrystallized from 50 parts of pyridine or 40 parts of dioxane, from which it separated in minute rhombs which decomposed at 285°.

(5) The melting points of the compounds described in the experimental part are all corrected melting points. None of the compounds exhibits optical activity.

Anal. Calcd. for C₃₄H₃₀O₈: C, 72.07; H, 5.34. Found: C, 72.18; H, 5.47.

(d) A solution of 1 g. of dibenzylidene-dulcitol in 10 cc. of pyridine was cooled in ice and 1.3 g. (2.2 molecular equivalents) of tosyl chloride added gradually. After standing overnight at room temperature the reaction mixture was poured into crushed ice and the ditosyl derivative crystallized readily. The yield was 1.7 g. (89%). The *2,5-ditosyl-1,3:4,6-dibenzylidene-dulcitol* was recrystallized from 70 parts of pyridine; the crystals formed microcrystalline elongated plates which melted with decomposition at 215°.

Anal. Calcd. for C₃₄H₃₄O₁₀S₂: C, 61.24; H, 5.14. Found: C, 61.42; H, 5.17.

2,5-Dibenzoyl-1,3:4,6-tetraacetyl-dulcitol.—A solution of 2.0 g. of *2,5-dibenzoyl-1,3:4,6-dibenzylidene-dulcitol* in 50 cc. of a rearranging solution (prepared by adding 1 cc. of concentrated sulfuric acid dropwise to an ice-cold mixture of 35 cc. of acetic anhydride and 15 cc. of acetic acid) was allowed to stand overnight at room temperature. The reaction mixture was poured into 300 g. of crushed ice and the precipitated *2,5-dibenzoyl-1,3,4,6-tetraacetyl-dulcitol* (1.9 g.; 96%) was recrystallized from 15 parts of alcohol, forming elongated plates which melted at 157–158°. The isomeric *1,6-dibenzoyl-2,3,4,5-tetraacetyl-dulcitol* and *1,4-dibenzoyl-2,3,5,6-tetraacetyl-D,L-galactitol* previously described³ melted at 225–226° and 113°, respectively.

Anal. Calcd. for C₂₈H₃₀O₁₂: C, 60.21; H, 5.41. Found: C, 60.40; H, 5.52.

Comparison of the Reactions of 2,5-Ditosyl-1,3:4,6-dibenzylidene-dulcitol and 1,6-Ditosyl-2,3,4,5-diisopropylidene-dulcitol toward Certain Reagents.—(1a) A solution of 0.5 g. of *2,5-ditosyl-1,3:4,6-dibenzylidene-dulcitol* in 35 cc. of pyridine was refluxed for one and one-half hours. Upon cooling, the ditosyl derivative was recovered unchanged and in nearly quantitative yield. (1b) A solution of 1.0 g. of *1,6-ditosyl-2,3,4,5-diisopropylidene-dulcitol* in 10 cc. of pyridine was refluxed for one and one-half hours, then cooled and treated with 25 cc. of ether, when 1.0 g. (78%) of dipyridinium-*1,6-ditosyl-2,3,4,5-diisopropylidene-dulcitol*⁶ crystallized. The substance was recrystallized from four parts of alcohol by the cautious addition of 20 parts of ether, and formed minute plates which melted at 199–200°.

Anal. Calcd. for C₃₆H₄₄O₁₀S₂N₂: C, 59.32; H, 6.09. Found: C, 59.31; H, 6.11.

(2a) A solution of 0.1 g. of *2,5-ditosyl-1,3:4,6-dibenzylidene-dulcitol* and 0.1 g. of sodium iodide in 25 cc. of acetic anhydride was refluxed for one hour. Upon cooling, 0.09 g. of unchanged ditosylated diacetal separated. (2b) Under similar experimental conditions *1,6-ditosyl-2,3,4,5-diisopropylidene-dulcitol* gave a nearly quantitative yield of *1,6-di-iodo-2,3,4,5-diisopropylidene-dulcitol*.³ The inertness of the tosyl groups in the *2,5-ditosyl-dibenzylidene-dulcitol* as compared to the reaction of those in the *1,6-ditosyl-diisopropylidene-dulcitol* makes it seem highly probable that in the former compound they are both at-

(6) Other compounds of this nature have been described by Ohle and Spencker, *Ber.*, **59**, 1836 (1926), Helferich and Goetz, *ibid.*, **62**, 2790 (1929), and Hess and Neumann, *ibid.*, **68**, 1368 (1935).

tached to secondary hydroxyl groups and that therefore 1,3:4,6-dibenzylidene-dulcitol contains in its structure no free primary hydroxyl group.

Acyl Migration of Benzoyl Groups during the Acid Hydrolysis of 2,5-Dibenzoyl-1,3:4,6-dibenzylidene-dulcitol.—A suspension of 10.0 g. of the dibenzoylated diacetal in a mixture of 400 cc. of dioxane and 100 cc. of *N* hydrochloric acid was refluxed for one hour, solution being complete in forty minutes. After removal of the hydrochloric acid as silver chloride, the solution was concentrated *in vacuo* to dryness and the dry residue extracted with 50 cc. of hot alcohol. The insoluble portion (0.7 g., m. p. 199–201°), after recrystallization from 10 parts of glacial acetic acid, melted at 208° and showed no depression in melting point upon admixture with authentic 1,6-dibenzoyl-dulcitol.³ On cooling, the alcoholic filtrate deposited a crop of crystals (2.0 g., the product melted at 173–175°, then solidified and remelted at 195°) which upon recrystallization from 15 parts of alcohol was separated into 0.3 g. of 1,6-dibenzoyl-dulcitol and 1.4 g. of 1,4-dibenzoyl-D,L-galactitol⁸ (the product melted at 171–172°, then solidified and remelted at 188–190°). The 1,4 and 1,6-dibenzoyl derivatives were further characterized by conversion to their known crystalline acetates.³ The alcoholic mother liquors of the original hydrolysis, upon further fractionation, yielded an additional 0.3 g. of 1,4-dibenzoyl-D,L-galactitol and a sirupy residue, probably a mixture of benzoylated dulcitol and D,L-galactitol, which could neither be crystallized directly, nor converted into a crystalline acetate. In summary, the acid hydrolysis of 2,5-dibenzoyl-1,3:4,6-dibenzylidenedulcitol yielded 15% of 1,6-dibenzoyl-dulcitol, 29% of 1,4-dibenzoyl-D,L-galactitol and 56% of a non-crystallizable sirup.

2,5-Dibenzyl-1,3:4,6-dibenzylidene-dulcitol (III).—To a solution of 10.0 g. of dibenzylidene-dulcitol in 250 cc. of purified dioxane, 1.3 g. of finely divided sodium was added and the suspension refluxed for nine hours. The sodium dissolved slowly and a flocculent precipitate of sodium derivatives of dibenzylidene-dulcitol was formed. The solution was cooled, 10 cc. of benzyl chloride added, and refluxing renewed for a further nine hours, the flocculent precipitate being replaced by a fine granular precipitate of sodium chloride. The warm reaction mixture was filtered, and the dibenzyl ether crystallized in the filtrate as it cooled. The substance was recrystallized from 50 parts of dioxane, in the form of fine needles which decomposed at 246–250°. The yield was 6.9 g. (46%).

Anal. Calcd. for $C_{34}H_{34}O_6$: C, 75.81; H, 6.36. Found: C, 75.87; H, 6.23.

2,5-Dibenzyl-dulcitol (V).—A suspension of 1 g. of 2,5-dibenzyl-1,3:4,6-dibenzylidene-dulcitol in a mixture of 40 cc. of dioxane and 10 cc. of *N* hydrochloric acid was heated under a reflux condenser for one hour. After removal of the hydrochloric acid as silver chloride, the solution was concentrated to dryness *in vacuo* and the dry residue extracted with 5 cc. of hot alcohol. The alcoholic extract on cooling deposited 0.6 g. (90%) of fine needles which were purified readily by recrystallization from 25 parts of alcohol and then melted at 168–169°.

Anal. Calcd. for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C, 66.24; H, 7.37.

Sodium Metaperiodate Oxidation of 2,5-Dibenzyl-dulcitol.—To a sample of 0.1000 g. of 2,5-dibenzyl-dulcitol

dissolved in 50 cc. of 50% alcohol 3.60 cc. of 0.0722 *M* sodium metaperiodate solution (0.98 molecular equivalent) was added and the volume was adjusted to 100 cc. with water. Subsamples of 10 cc. were analyzed after the expiration of one, twenty-three and twenty-seven hours; they showed consumptions of 0.15, 0.85 and 0.95 molecular equivalents of oxidant, respectively. Titration of a further subsample indicated that no acid was produced in the oxidation and no dimedone formaldehyde compound was formed when the oxidized solution was treated with dimedone reagent. The oxidized solution from a 0.1000 g. sample of 1,4-dibenzoyl-D,L-galactitol was treated with the dimedone reagent under the same experimental conditions and it gave an abundant precipitate of the dimedone formaldehyde derivative. The consumption of one equivalent of sodium metaperiodate proves that a single glycol group is present in 2,5-dibenzyl-dulcitol. The absence of formaldehyde as an oxidation product proves that neither primary hydroxyl group is adjacent to an unsubstituted secondary hydroxyl group; hence the positions of the two benzyl groups are limited to 2 and 5 and the position of the glycol group is limited to positions 3 and 4 of the dibenzyl-dulcitol molecule.

Lead Tetraacetate Oxidation of 2,5-Dibenzyl-dulcitol.—A sample of 0.1020 g. of 2,5-dibenzyl-dulcitol was dissolved in 20 cc. of 0.0250 *M* lead tetraacetate glacial acetic acid solution (1.70 molecular equivalents) and the volume adjusted to 25 cc. with glacial acetic acid. Subsamples of 5 cc. were analyzed at the expiration of one, twenty-one, twenty-eight and forty-five hours, at which times 0.14, 0.80, 0.96 and 1.06 molecular equivalents of lead tetraacetate were found to have been consumed.

2-Benzyl-D,L-glyceric Aldehyde Semicarbazone.—A solution of 0.2463 g. of 2,5-dibenzyl-dulcitol in 15 cc. of 0.0649 *M* lead tetraacetate-glacial acetic acid solution (1.4 molecular equivalents) was allowed to stand at 20° for forty-eight hours. To the clear solution was added 5 cc. of water, and a solution of 1 g. of semicarbazide hydrochloride and 1 g. of sodium acetate in 10 cc. of water, and the reaction mixture was allowed to stand at 20° for forty-eight hours. The lead was precipitated as sulfide and the lead-free solution concentrated *in vacuo* (bath, 40°) to dryness. The dry residue was dissolved in 6 cc. of boiling water and on cooling immediately to room temperature the glyceric aldehyde semicarbazone crystallized in a yield of 0.19 g. (59%). The substance was recrystallized from hot water as shining plates which melted at 132–134°. The parent aldehyde could not be isolated since it polymerized very readily to form an oily material which did not reduce Fehling solution.

Anal. Calcd. for $C_{11}H_{16}O_3N_2$: C, 55.68; H, 6.37; N, 17.71. Found: C, 55.90; H, 6.41; N, 17.70.

2-Benzyl-1,3:4,6-dibenzylidene-dulcitol.—The dioxane mother liquor from the preparation of 2,5-dibenzyl-1,3:4,6-dibenzylidene-dulcitol upon concentration *in vacuo* to dryness gave a crystalline residue; upon recrystallization from 40 parts of alcohol the mono-benzyl ether separated in the form of fine matted needles which melted at 164–165°. The compound was converted to the dibenzyl ether of the diacetal by treatment with sodium and benzyl chloride.

Anal. Calcd. for $C_{27}H_{34}O_4$: C, 72.30; H, 6.29. Found: C, 72.44; H, 6.35.

2-Benzyl-5-acetyl-1,3:4,6-dibenzylidene-D,L-galactitol.
—A mixture of 3.8 g. of mono-benzyl dibenzylidene-D,L-galactitol, 0.6 g. of fused sodium acetate and 25 cc. of acetic anhydride was refluxed for one hour. As the solution cooled, the acetylated benzyl-dibenzylidene-dulcitol crystallized spontaneously. The reaction mixture was poured upon crushed ice and the precipitated material was separated by filtration and recrystallized from 13 parts of methyl ethyl ketone or 4 parts of dioxane. The yield was 3.8 g. (91%). The substance crystallized in clusters of elongated prisms which melted at 204–206°.

Anal. Calcd. for $C_{26}H_{30}O_7$: C, 70.99; H, 6.17. Found: C, 70.88; H, 6.27.

Summary

Evidence has been obtained from lead tetraacetate oxidation that Fischer's dibenzylidene-dulcitol does not contain a glycol grouping. The dibenzoyl-tetraacetyl-dulcitol derived from dibenzoyl-dibenzylidene-dulcitol by acid acetylation is different from 1,6-dibenzoyl-2,3,4,5-tetra-

acetyl-dulcitol or 1,4-dibenzoyl-2,3,5,6-tetraacetyl-D,L-galactitol, excluding positions 1,4 and 1,6 as possible positions for the pair of free hydroxyls in benzylidene-dulcitol. The results of a study of ditosyl-dibenzylidene-dulcitol indicate that neither of these hydroxyl groups is primary and limit their probable position in the dibenzylidene-dulcitol structure to carbons 2,4 or 2,5. It is then shown that the dibenzyl ether of dulcitol derived from dibenzylidene-dulcitol consumes one molecular equivalent of lead tetraacetate upon oxidation and produces more than one molecular equivalent of 2-benzyl-D,L-glyceric aldehyde, but no formaldehyde or formic acid. These results constitute a definite proof that Fischer's dibenzylidene-dulcitol is 1,3:4,6-dibenzylidene-dulcitol.

BETHESDA, MARYLAND

RECEIVED AUGUST 22, 1941

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A New Dibenzylidene Dulcitol (2,3,4,5-Dibenzylidene-dulcitol)¹

BY W. T. HASKINS, RAYMOND M. HANN AND C. S. HUDSON

In 1894 Emil Fischer² prepared a dibenzylidene-dulcitol, which melted with decomposition at 215–220° (uncor.), by the condensing action of gaseous hydrochloric acid on a mixture of dulcitol and benzaldehyde. In the accompanying paper we offer definitive proof that its structure is that of 1,3:4,6-dibenzylidene-dulcitol. In the present communication we describe a new isomeric dibenzylidene-dulcitol and show that it is 2,3,4,5-dibenzylidene-dulcitol.

The dibenzoate of the new diacetal was prepared by passing dry hydrochloric acid gas through a mixture of benzaldehyde and 1,6-dibenzoyl-dulcitol, the structure of which has been previously established.³ The method of synthesis limits the structure of the dibenzoyl diacetal to that of 1,6-dibenzoyl-2,3,4,5-dibenzylidene-dulcitol, provided that no acyl migration occurs during the condensation with benzaldehyde. This possibility has been excluded through the observation that the treatment of the 1,6-dibenzoyl-2,3,4,5-dibenzylidene-dulcitol with an acid acetylating mixture produces the known 1,6-dibenzoyl-2,3,4,5-tetraacetyl-dulcitol.³ The new 2,3,4,5-

dibenzylidene-dulcitol [m. p. 149–150° (cor.)] results from the debenzoylation of 1,6-dibenzoyl-2,3,4,5-dibenzylidene-dulcitol in chloroform solution with sodium methylate. The acetylation of the new dibenzylidene-dulcitol yields crystalline 1,6-diacetyl-2,3,4,5-dibenzylidene-dulcitol which is identical with the compound that has been obtained from the condensation of 1,6-diacetyl-dulcitol with benzaldehyde by the action of gaseous hydrochloric acid. The series of reactions leaves no doubt that the new diacetal is 2,3,4,5-dibenzylidene-dulcitol.

We express our appreciation to Dr. A. T. Ness for performing the microchemical analyses in connection with this work, and to the Atlas Powder Company for furnishing a supply of dulcitol.

Experimental

1,6-Dibenzoyl-2,3,4,5-dibenzylidene-dulcitol from 1,6-Dibenzoyl-dulcitol.—A rapid stream of dry hydrochloric acid gas was passed through a suspension of 1.5 g. of 1,6-dibenzoyl-dulcitol³ in 1 cc. of benzaldehyde for a few minutes and the reaction mixture, which had set to a solid mass, was allowed to stand for twelve hours in an evacuated desiccator containing small beakers of solid potassium hydroxide and concentrated sulfuric acid. The solid was then triturated with ether to remove excess benzaldehyde and acid, and after recrystallization from 45 parts of alco-

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(2) Fischer, *Ber.*, **27**, 1524 (1894).

(3) Hann, Maclay and Hudson, *THIS JOURNAL*, **61**, 2432 (1939).