

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.

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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).

hol it was obtained in colorless elongated six-sided plates which melted at 119–120° (cor.); yield 1.9 g. (86%).

Anal. Calcd. for $C_{24}H_{26}O_8$: C, 72.07; H, 5.34; C_6H_5CO , 37.1. Found: C, 72.21; H, 5.28; C_6H_5CO , 37.0.

1,6-Dibenzoyl-2,3,4,5-tetraacetyl-dulcitol from 1,6-Dibenzoyl-2,3,4,5-dibenzylidene-dulcitol.—The solution of 0.7 g. of 1,6-dibenzoyl-2,3,4,5-dibenzylidene-dulcitol in 25 cc. of a rearranging solution (prepared by adding 2 cc. of concentrated sulfuric acid dropwise to an ice-cold mixture of 70 cc. of acetic anhydride and 30 cc. of acetic acid) was complete in fifteen minutes at 20°. Shortly thereafter spontaneous crystallization of characteristic quadrilateral plates of 1,6-dibenzoyl-2,3,4,5-tetraacetyl-dulcitol occurred. After standing overnight at 20° the reaction mixture was filtered and the separated tetraacetate (0.6 g.; 86%) recrystallized from 10 parts of glacial acetic acid. The substance melted at 224–225° (cor.) and a mixed melting point with authentic 1,6-dibenzoyl-2,3,4,5-tetraacetyl-dulcitol⁸ gave the same value.

2,3,4,5-Dibenzylidene-dulcitol from 1,6-Dibenzoyl-2,3,4,5-dibenzylidene-dulcitol.—A solution of 20 g. of 1,6-dibenzoyl-2,3,4,5-dibenzylidene-dulcitol in 25 cc. of chloroform was cooled in an ice-bath and 5 cc. of 0.1 *N* sodium methylate solution added. The mixture was allowed to stand at 5° for twenty hours, and after addition of 5 cc. of 0.1 *N* sulfuric acid, the solvent was removed by concentration *in vacuo*, and the dry residue extracted with 20 cc. of warm alcohol. The dibenzylidene-dulcitol, which separated from the extract as it cooled, was recrystallized from 7 parts of 95% alcohol or 25 parts of 50% alcohol and obtained in approximately rectangular plates which melted at 149–150° (cor.); yield 1.1 g. or 85%.

Anal. Calcd. for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19. Found: C, 67.08; H, 6.29.

1,6-Diacetyl-2,3,4,5-dibenzylidene-dulcitol.—(1) A solution of 0.2 g. of 2,3,4,5-dibenzylidene-dulcitol in a mixture of 2 cc. of pyridine and 2 cc. of acetic anhydride was allowed to stand at room temperature. After two hours,

spontaneous crystallization of clusters of prisms occurred from the solution and after twenty hours they were filtered off and recrystallized from 50 parts of alcohol by addition of 8 parts of dioxane; yield 0.25 g. (quantitative). The substance melts at 168–169° (cor.). A mixed melting point determination with 1,6-diacetyl-dulcitol,³ which melts at almost the same temperature, 167–168° (cor.), gave a melting point range of 161–165° (cor.). (2) A rapid stream of dry hydrochloric acid gas was passed through a suspension of 1.8 g. of 1,6-diacetyl-dulcitol³ in 3 cc. of benzaldehyde for three minutes. Complete solution occurred during the first minute and was followed by an immediate separation of crystalline material. After standing overnight, the pasty mass was triturated with 5 cc. of ether, and the solid reaction product separated by filtration. Recrystallized from a mixture of alcohol and dioxane, the pure compound melted at 168–169° (cor.) and a mixed melting point determination with 1,6-diacetyl-2,3,4,5-dibenzylidene-dulcitol prepared by acetylation of 2,3,4,5-dibenzylidene-dulcitol, as described in the preceding paragraph, showed a melting point of 168–170° (cor.); yield 2.5 g. (83%).

Anal. Calcd. for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92; CH_3CO , 19.5. Found: C, 65.18; H, 5.99; CH_3CO , 19.4.

Summary

The dibenzoate of a new dibenzylidene-dulcitol has been prepared from 1,6-dibenzoyl-dulcitol and benzaldehyde. The dibenzoate is converted to the known 1,6-dibenzoyl-2,3,4,5-tetraacetyl-dulcitol by an acid acetylating mixture. The diacetate of the diacetal is identical with 1,6-diacetyl-dibenzylidene-dulcitol prepared from 1,6-diacetyl-dulcitol and benzaldehyde. These facts establish the structure of the diacetal as 2,3,4,5-dibenzylidene-dulcitol.

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A Second 2,3,4,5-Dibenzylidene-dulcitol

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

In a recent communication¹ we described a 1,6-dibenzoyl-2,3,4,5-dibenzylidene-dulcitol [m. p. 119–120° (cor.)] which was obtained from 1,6-dibenzoyl-dulcitol and benzaldehyde by the condensing action of gaseous hydrochloric acid. It has now been observed that the substitution of fused zinc chloride as a condensing agent in the reaction yields not only this derivative of melting point 119–120°, but in addition an isomer which melts at 147–148° (cor.). It will be shown that both of the isomers are 1,6-dibenzoyl-2,3,4,5-

dibenzylidene-dulcitol. For purposes of clarity, the previously described isomer (m. p. 119–120°) will be designated provisionally as the stable isomer (or I) and the newly discovered isomer (m. p. 147–148°), which can be converted into the stable isomer (I), will be designated the unstable isomer (or II). The yield of the unstable isomer (II) was markedly affected by the character of the zinc chloride employed and by the temperature at which the condensation was conducted. As described in the experimental part, a commercial fused zinc chloride of reagent quality was su-

(1) Haskins, Hann and Hudson, *This Journal*, **64**, 136 (1942).