

Neither during the synthesis from sorbitol and benzaldehyde, nor during hydrolysis experiments, did we encounter another isomer of dibenzylidene-D-sorbitol, such as the one described by Meunier,⁴ m. p. 162°. This substance was probably a mixture of di- and tri-benzylidene-D-sorbitols.

In the experimental part we give improved physical constants of mono- and tri-benzylidene-D-sorbitol and of 5,6-diacetyl-1,3:2,4-dibenzylidene-D-sorbitol.

Experimental⁵

2,4-Monobenzylidene-D-sorbitol.—Vargha² gives m. p. 172–73°, $[\alpha]_D^{20}$ 5.3°. His sample was obviously contaminated with dibenzylidene-D-sorbitol, because he recrystallized from alcohol, in which the latter substance is fairly soluble. We prepared the mono-compound according to his directions, but recrystallized it from 6 parts of water which left the diacetal undissolved. The substance so prepared had m. p. 176–77°, $[\alpha]_D^{17}$ –1.1° (c, 1.0) in water.

*Anal.*⁶ Calcd. for C₁₃H₁₈O₆: C₆H₅CH, 33.33. Found: C₆H₅CH, 33.1

2,4-Monobenzylidene-D-sorbitol from 1,3:2,4-dibenzylidene-D-sorbitol.—Three grams of the diacetal¹ was refluxed on the steam-bath with a mixture of 120 ml. 80% alcohol and 67 ml. glacial acetic acid for one hour. The solution was evaporated to dryness under reduced pressure. Thirteen ml. of water was added to the residue, the solution made carefully alkaline with sodium carbonate and boiled for a short time; 0.9 g. of unchanged dibenzylidene-D-sorbitol remained undissolved. The solution was filtered and on standing in the refrigerator deposited 0.27 g. of crystals (m. p. 173–74°, 17% yield on dibenzylidene-sorbitol not regained). After recrystallization from 1.5 ml. water the m. p. was 174–75°; mixed m. p. with the previous substance, 174–75°.

1,3:2,4:5,6-Tribenzylidene-D-sorbitol.—Prepared as directed by Karrer and Büchi.³ Their method of purification is applicable to very small quantities only. We dissolved the crude triacetal (10 g.) in 100 ml. of chloroform, filtered from undissolved dibenzylidene-D-sorbitol and precipitated with 300 ml. alcohol (7–8 g.). The melting point of this substance shows a peculiar behavior. Pure samples recrystallized from chloroform-alcohol (1:3) or pyridine-water (3:1) have m. p.'s between 195 and 199°. Occasional pure samples had m. p.'s as low as 190°. When dissolved in pyridine and evaporated to dryness at 80° all these samples melted at 203°. Apparently the substance is dimorphous, one form melting at 203°, but we were unable to isolate the other in pure form. All pure samples have $[\alpha]_D^{15}$ +26.9° (c, 2.0) in chloroform. Karrer and Büchi³ give m. p. 191°, Simada and Matukawa⁷ m. p. 201–204°, no rotation.

Anal. Calcd. for C₂₇H₃₆O₆: C₆H₅CH, 60.54. Found: C₆H₅CH, 60.4.

1,3:2,4-Dibenzylidene-D-sorbitol from Tribenzylidene-D-sorbitol.—Four grams of tribenzylidene-D-sorbitol (m. p. 203°) was dissolved in 40 ml. of hot chloroform, a mixture of 300 ml. 90% alcohol and 60 ml. of glacial acetic acid added, and refluxed on the steam-bath for two hours. The solution was evaporated to dryness under reduced pressure, the residue powdered and extracted, first with 50 ml. of

chloroform, then with 30 ml. of boiling water. The residue weighs 2.1 g. (76% yield), and has m. p. 220–21°. On acetylation with pyridine (10 ml.) and acetic anhydride (6 ml.) it gives a substance similar in all properties to 5,6-diacetyl-1,3:2,4-dibenzylidene-D-sorbitol.

5,6-Diacetyl-1,3:2,4-dibenzylidene-D-sorbitol.—This substance shows the same peculiar behavior of its melting point as tribenzylidene-D-sorbitol. Samples from benzene or acetone have m. p.'s between 202 and 206°. On evaporation from pyridine at 80° it melts at 208–209°. Wolfe, Hann and Hudson¹ report 201–204°.

Anal. Calcd. for C₂₄H₂₆O₈: C₆H₅CH, 40.73. Found: C₆H₅CH, 40.8.

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An Orange-colored Pigment of Cottonseed

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We have isolated an orange-colored pigment from cottonseed by the following procedure. An ethereal extract of cottonseed was re-extracted with a dilute aqueous solution of sodium hydroxide containing sodium dithionite (Na₂S₂O₄). The yellow-colored ethereal layer which separated from the aqueous extract when it was exactly neutralized with concentrated hydrochloric acid was withdrawn. Addition of an equal volume of glacial acetic acid to the ethereal solution caused the precipitation of gossypol "acetate" within a few minutes. When the filtrate was allowed to stand for about a week, an orange-colored solid slowly precipitated. This solid was extracted with hot acetone from which orange-colored crystals precipitated on cooling. The product was recrystallized first from hot acetone and finally from a mixture of hot chloroform and ether.

The orange-colored pigment differs markedly from gossypol. It is less soluble than gossypol in most organic solvents. It melts at 212° (cor.) to form a more deeply colored solid, which melts with decomposition at 238–239° (cor.). It is insoluble in alkali. It does not form a precipitate with aniline, reduce Fehling solution, or give a positive fuchsin-aldehyde test. The orange-colored pigment reacts with hydroxylamine and with dinitrophenylhydrazine, but the products differ in melting point from the corresponding products obtained with gossypol.

The orange-colored pigment forms a brilliant yellow solution in concentrated sulfuric acid which slowly changes to the scarlet color characteristic of gossypol in sulfuric acid.

The absorption spectrum of a chloroform solution of the orange-colored pigment exhibits a well defined maximum at 435 m μ , whereas that of gossypol occurs at 365 m μ .¹ The unstable reaction product of the orange-colored pigment with antimony trichloride has an absorption maximum at 450–460 m μ ; whereas that of gossypol exhibits two maxima, one at 380 m μ and the other at 510–

(4) Meunier, *Ann. chim. phys.*, [6] **22**, 412 (1891).

(5) All melting points are corrected.

(6) For the benzylidene determination ca. 100 mg. of the substance was dissolved in 5 ml. of hot glacial acetic acid in an atmosphere of nitrogen. Forty ml. of a 0.5% solution of 2,4-dinitrophenylhydrazine in *N* sulfuric acid was added, and the solution heated on a steam-bath under reflux for one hour. After cooling in ice the precipitate was collected in a Gooch crucible and dried *in vacuo* at 70°: wt. of precipitate \times 0.3147 = benzylidene.

(7) Simada and Matukawa, *C. A.*, **33**, 533^s (1939).

(1) Boatner, *Oil & Soap*, **21**, 10–15 (1944).

520 $m\mu$.¹ When a chloroform solution of the orange-colored pigment is treated with concentrated hydrochloric acid and then with antimony trichloride, the solution exhibits the absorption spectrum characteristic of the gossypol-antimony trichloride reaction product. This observation indicates that the final reaction products of both pigments are the same and that concentrated hydrochloric acid converts the orange-colored pigment into gossypol.

The absorption spectra curves of chloroform extracts of some raw cottonseeds and cottonseed meals, as well as those of their reaction products with antimony trichloride, have maxima which indicate the presence of the orange-colored pigment.² The production of a characteristic gossypol reaction when such extracts are treated with concentrated hydrochloric acid prior to their reaction with antimony trichloride² confirms the presence of the orange-colored pigment in the seeds and meals. The occurrence of this pigment in high concentration in certain cottonseed meals may account, at least in part, for the frequently observed lack of correlation³ of gossypol content with toxicity of these meals when the gossypol is determined as the dianilino compound.

(2) Boatner, Caravella and Kyame, in press.

(3) Gallup, *Ind. Eng. Chem.*, **20**, 59-63 (1928).

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The Preparation of Ethyl ϵ -Bromocaproate

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Ethyl ϵ -bromocaproate may be prepared conveniently and inexpensively from cyclohexanone. The crude mixed lactones of ϵ -hydroxycaproic acid, obtained by the procedure of Robinson and Smith,¹ may be treated directly with hydrobromic and sulfuric acids, thus obviating the losses involved in the use² of ethyl ϵ -hydroxycaproate as an intermediate.

The oxidation of 174 g. of cyclohexanone was carried out between 10 and 15° as described¹ in the preparation under the heading of ethyl 6-hydroxyhexoate using an oxidizing mixture prepared from 919 g. of potassium persulfate.

The 200 g. of crude lactones was then treated with a cooled mixture of 1 liter of 48% hydrobromic acid and 240 cc. of concentrated sulfuric acid. After standing for two hours at room temperature, this was heated for four hours on the steam cone, was cooled and poured into 2 liters of water. The organic layer was separated and the water solution was saturated with ammonium sulfate and was extracted four times with ether.

(1) R. Robinson and L. H. Smith, *J. Chem. Soc.*, 371 (1937).

(2) G. Barger, R. Robinson and L. H. Smith, *ibid.*, 718 (1937).

The combined organic layer and extract were washed three times with saturated ammonium sulfate, and were dried and concentrated.

The 250 g. of crude bromo acid was esterified by refluxing for eight hours with 600 cc. of absolute alcohol and 15 cc. of sulfuric acid. After concentrating *in vacuo*, the residue was taken up in ether and was washed with water and with 5% sodium carbonate. The ether solution was dried over sodium sulfate and was distilled yielding 178 to 218 g. of the product distilling at 120-125° at 14 mm., n_D^{25} 1.4566, d_{25}^{25} 1.241, $M_R D$ 48.92 (calcd. 48.57). This represents an over-all yield from cyclohexanone of 45-55%. No evidence of the inhomogeneity noted once by Barger, Robinson and Smith² has been observed. The product has been used satisfactorily in the preparation of η -ketopelargonic acid.²

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Polymerization of Undecylenic Acid in the Presence of Boron Fluoride

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It has been found that when undecylenic acid is treated with gaseous boron fluoride at room temperature much heat is evolved and the acid polymerizes to a dark heavy oily material. This polymer, after having been freed of catalyst, exhibits the characteristic properties of an acid and also those of an ester. Thus it shows some tendency to dissolve in dilute aqueous caustic and regenerates carboxyl groups on refluxing in alkaline solutions.

The loss in carboxyl function has been found to be directly related to the fall in iodine value which indicates that one of the processes of polymerization is the esterification of the carboxyl group by means of the unsaturated linkage. (It had been previously demonstrated that the same treatment of stearic acid did not cause decarboxylation.) Since the fall in iodine value was stoichiometrically greater than the loss of carboxyl function it appeared that some double bond polymerization also took place. The analytical data show that this is a reaction of secondary importance with esterification assuming the major role.

The oil resulting from saponification of the polymer gave a positive iodoform test which indicates the hydroxy acid produced had the methyl-carbinol structure. This proves the orientation of at least part of the polymerization process.

This type of polymerization² of undecylenic

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(2) Unpublished results obtained in this Laboratory by Cann and by H. R. Nace indicate that this behavior is also shown by the fatty acids from drying oils and also by crotonic acid. The latter requires somewhat more strenuous conditions, however, due to its conjugated structure.