ultraviolet absorption spectra and optical rotation data.

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An Unexpected Reaction of 3,5-Di-*O*-benzoyl-2-deoxy-D-ribose

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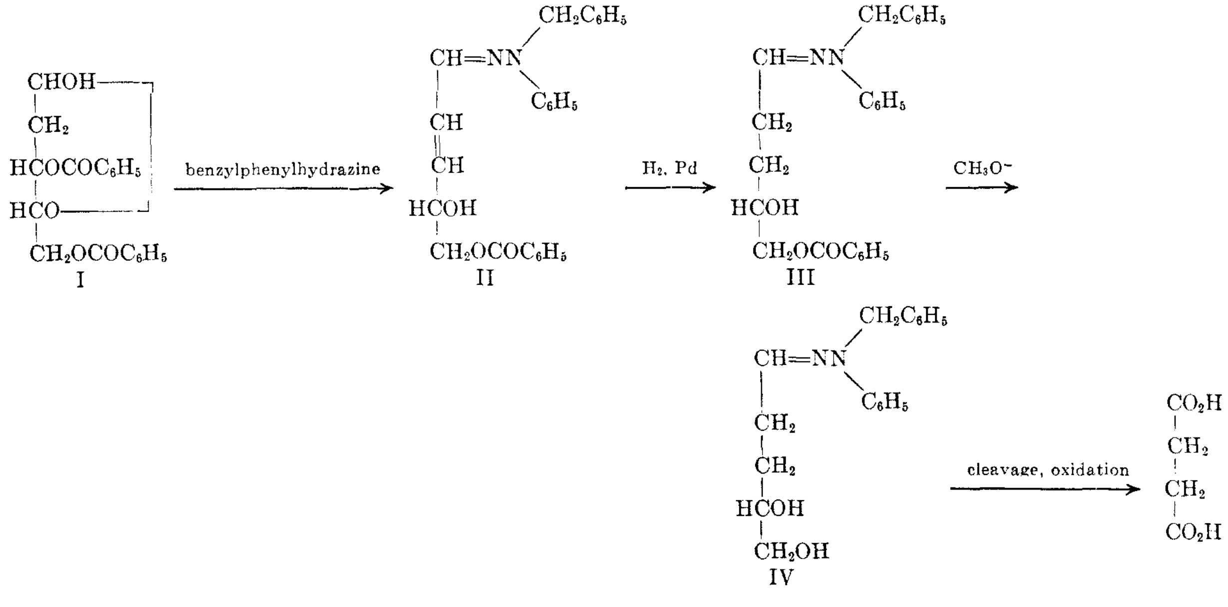
Relative to a synthetic program in the 2-deoxy-D-ribose series, we have prepared crude, amorphous 3,5-di-*O*-benzoyl-2-deoxy-D-ribose. An attempt was made to characterize this substance by converting it in the usual manner to a benzylphenylhydrazone. A crystalline hydrazone was indeed obtained, but its analysis revealed that loss of benzoic acid had accompanied the reaction. The product was shown to be 5-*O*-benzoyl-D-*glycero*-4,5-dihydroxy-2-pentenal benzylphenylhydrazone by reduction of the double bond, cleavage of substituents, and oxidation to succinic acid.



The unsaturated hydrazone was obtained readily in the presence of 1-benzyl-1-phenylhydrazine in aqueous ethanol, and somewhat more slowly with the hydrazine and acetic acid in aqueous ethanol. This unexpected, facile β-elimination of an ester group may be related to certain difficulties we have encountered in attempting to apply routine reaction conditions for syntheses based on 2-deoxy-D-ribose.

Acetylation of 3,5-di-*O*-benzoyl-2-deoxy-D-ribose in pyridine proceeded normally to give a crystalline monoacetate. This product conceivably could be either 4-*O*-acetyl-3,5-di-*O*-benzoyl-*aldehydo*-2-deoxy-D-ribose or the isomeric 1-*O*-acetyl-3,5-di-*O*-benzoyl-2-deoxy-D-ribose. Since the substance shows no mutarotation in USP chloroform, which contains ethanol, it has been assigned the latter structure.

EXPERIMENTAL

Methyl 3,5-di-O-benzoyl-2-deoxy-α,β-D-ribofuranosides. Three grams of 2-deoxy-D-ribose[1] in 60 ml. of absolute methanol was treated with 4.5 ml. of 0.14*N* hydrogen chloride in methanol and the resulting glycosidation was followed polarimetrically.[2] After 15 min., when a maximum positive specific rotation of +39.6° based on starting sugar had been reached, the solution was passed through a column containing 10 ml. of Duolite A-4 resin (wet with methanol) onto 2 ml. of pyridine. The solution was concentrated to dryness at reduced pressure and the resulting sirup was dried in high vacuum over phosphorus pentoxide. The dried sirup was dissolved in 33 ml. of dry pyridine and treated at 0° with 10.5 ml. of benzoyl chloride. After 1 day at room temperature, several drops of water were added and the solution was concentrated to a thin sirup in a stream of dry air. The residue was taken up in chloroform and washed successively with cold 3% sulfuric acid, water, saturated sodium bicarbonate solution, and water. After drying over sodium sulfate, the solution was concentrated at reduced pressure to a sirup (8.4 g.).

Fractional distillation of products prepared similarly gave about 70% of distillate, b.p. 135–138° (vapor temp.) at 10^{-4} mm., n_D^{25} 1.5456 to 1.5459, $[\alpha]_D^{33}$ +41° to +43° (*c* 1.5 in chloroform) and methoxyl content 8.47% to 8.65% (theory 8.71%). Qualitative paper chromatography, and the hydrolysis experiment described below, indicated such

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(1) J. C. Sowden, *J. Am. Chem. Soc.*, **76**, 3541 (1954).

(2) R. E. Deriaz, W. G. Overend, M. Stacey, and L. F. Wiggins, *J. Chem. Soc.*, 2836 (1949).

products to be mixtures consisting of about 80% furanosides and 20% pyranosides.

Crude 3,5-di-O-benzoyl-2-deoxy-D-ribose, (I). The sirupy product described above (8.4 g.) was dissolved in 200 ml. of acetone, and 60 ml. of water followed by 45 ml. of 6*N* hydrochloric acid was added. After 2 days at room temperature, when the mutarotation had become essentially constant, the solution was deionized over Duolite A-4 (wet with 75% acetone) and concentrated at reduced pressure to a sirup. This was dissolved in chloroform, dried over sodium sulfate, and again concentrated to a sirup (7.2 g.). The methoxyl content of the sirupy product was about 1.8%, presumably due to unhydrolyzed methyl pyranosides.

5-O-Benzoyl-D-glycero-4,5-dihydroxy-2-pentenal benzylphenylhydrazone (II). The crude 3,5-di-*O*-benzoyl-2-deoxy-D-ribose (7.2 g.) was diluted with a small volume of ethanol and 4.7 g. of 1-benzyl-1-phenylhydrazine was mixed in to give a homogeneous solution. After 1 day, the mixture was extracted by trituration with petroleum ether (b.p. 33–58°) and the residue was diluted with ethanol followed by water to give 3.4 g. of crystals in two crops. After recrystallization from benzene-ether, the 5-*O*-benzoyl-D-*glycero*-4,5-dihydroxy-2-pentenal benzylphenylhydrazone melted at 138–139°, $[\alpha]^{26}_{D}$ $-14°$ in benzene, *c* 2.

Anal. Calcd. for $C_{25}H_{24}O_3N_2$: C, 75.0; H, 6.04; N, 7.00. Found: C, 74.7; H, 5.80; N, 6.97.

The same unsaturated benzylphenylhydrazone was formed, but somewhat more slowly, when an equivalent amount of acetic acid was added with the 1-benzyl-1-phenylhydrazine in the above reaction.

5-O-Benzoyl-D-glycero-4,5-dihydroxypentanal benzylphenylhydrazone, (III). The unsaturated benzylphenylhydrazone (3.4 g.) was hydrogenated at room temperature and atmospheric pressure in ethyl acetate solution in the presence of 0.5 g. of 10% palladium-on-carbon catalyst. The hydrogenation was complete in 2 hr. with the absorption of approximately one molecular equivalent of hydrogen. Filtration and evaporation gave a crystalline residue. Recrystallization from ether yielded 2.66 g. of 5-*O*-benzoyl-D-*glycero*-4,5-dihydroxypentanal benzylphenylhydrazone, m.p. 98–99°, $[\alpha]^{25}_{D}$ $+3.7°$ in benzene, *c* 3.6.

Anal. Calcd. for $C_{25}H_{26}O_3N_2$: C, 74.6; H, 6.51; N, 6.96. Found: C, 74.6; H, 6.43; N, 7.15.

D-Glycero-4,5-dihydroxypentanal benzylphenylhydrazone, (IV). A solution of 1.5 g. of III in 300 ml. of methanol containing 0.3 g. of sodium was refluxed for 5 hr. The solution was then cooled, deionized, and concentrated, finally with water to remove methyl benzoate. The resulting crystals (1.05 g.) were recrystallized from ethanol-ether–petroleum ether (b.p. 32–37°) to give pure IV, m.p. 77–78°, $[\alpha]^{25}_{D}$ $-14°$ in absolute ethanol, *c* 3.4.

Anal. Calcd. for $C_{18}H_{22}O_2N_2$: C, 72.5; H, 7.43; N, 9.39. Found: C, 72.5; H, 7.49; N, 9.31.

Degradation of IV *to succinic acid.* An amount of 570 mg. of III was shaken for 1 day with 1 ml. of benzaldehyde, 0.3 g. of benzoic acid, and 15 ml. of water. The mixture was then extracted three times with ether and the remaining aqueous phase was further treated with 5.3 ml. of 0.4*M* sodium metaperiodate solution for 7 hr. at room temperature. A few drops of ethylene glycol then were added, the solution was deionized, and the effluent and washings were treated with 1 g. of potassium permanganate. After 6 hr., excess permanganate was destroyed with acetaldehyde, manganese dioxide was removed by filtration and potassium ion by ion exchange, and the solution was concentrated to a semicrystalline residue. This was dissolved in dilute sodium hydroxide, extracted thoroughly with ethyl acetate, decolorized with carbon, again freed of sodium ion by ion exchange, and concentrated. The resulting crude succinic acid (m.p. 178–180°) was converted to the *p*-bromobenzyl pseudothiuronium salt,[3] m.p. 167°; yield, 100 mg. The melting point of this product was undepressed by admixture with the *p*-bromobenzyl pseudothiuronium salt (m.p. 167°) prepared from authentic succinic acid, and the x-ray diffraction patterns given by the two preparations were identical.

1-O-Acetyl-3,5-di-O-benzoyl-2-deoxy-D-ribose. Thoroughly dried, crude 3,5-di-*O*-benzoyl-2-deoxy-D-ribose (840 mg.) was acetylated at 0° with acetic anhydride and pyridine in the usual manner. Addition of the reaction mixture to ice-water yielded a semicrystalline precipitate. This was separated by decantation, triturated with fresh ice-water, and recrystallized from ethanol to yield 205 mg. of crystalline product. Further recrystallization from ether–petroleum ether (b.p. 63–69°) yielded pure 1-*O*-acetyl-3,5-di-*O*-benzoyl-2-deoxy-D-ribose, m.p. 88–89°, $[\alpha]^{27}_{D}$ $-23.7°$, constant in USP chloroform, *c* 2.

Anal. Calcd. for $C_{21}H_{20}O_7$: C, 65.6; H, 5.25. Found: C, 65.7; H, 5.42.

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[3] B. T. Dewey and H. G. Shasky, *J. Am. Chem. Soc.*, **63**, 3526 (1941).

The Structure and Synthesis of Rhetsinine (Hydroxyevodiamine)

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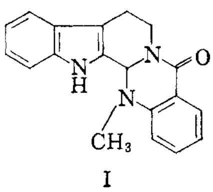
The chemistry of the alkaloid evodiamine (I), derived from the Chinese drug plant *Evodia rutecarpa* Benth. and Hook., was studied many years ago by Asahina and his co-workers. During the course of their investigations, a yellow base, $C_{19}H_{17}N_3O_2$, was derived upon potassium permanganate oxidation of the alkaloid.[1] The product was named hydroxyevodiamine and was assigned structure II. Later Ohta[2] observed that hydroxyevodiamine may react with acids with loss of water and suggested formula III for the salts. Upon addition



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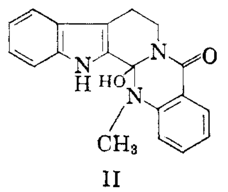
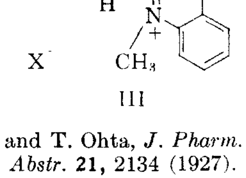


II



III

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[1] Y. Asahina and T. Ohta, *J. Pharm. Soc. Japan*, **530**, 293 (1926); *Chem. Abstr.* **21**, 2134 (1927).

[2] T. Ohta, *J. Pharm. Soc. Japan* **65B**, 89 (1945).