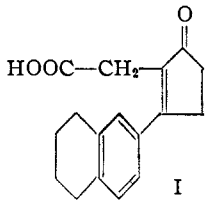
ones.[1,2] A similar reaction has now been observed with a γ-keto-ester. The crude Stobbe half-ester mixture from methyl β-(5,6,7,8-tetrahydro-2-naphthoyl)-propionate could not be purified because there was decomposition in an attempted vacuum distillation. It was hydrolyzed with alcoholic potash to give the cyclized product, 3-(5,6,7,8-tetrahydro-2-naphthyl)-2-cyclopenten-1-one-2-acetic acid (I), in 40% yield.

The structure of this cyclopentenone was easily demonstrated by preparing the same product from 2-acetyl-5,6,7,8-tetrahydronaphthalene by an established method.[3,4] The initial product of the Stobbe condensation was probably a 2-carbomethoxycyclopenten-1-one which lost its carbomethoxy group on hydrolysis.

The Stobbe condensation is the better of the two methods of preparation described.



I

Experimental

Furfurylidene-2-acetyl-5,6,7,8-tetrahydronaphthalene.—To 260 g. of 2-acetyltetrahydronaphthalene[5] in 600 ml. of ethanol and 124 ml. of furfural, was added 10 ml. of 45% aqueous potassium hydroxide solution. After standing overnight, the product was filtered; yield 350 g., m.p. 65–68°. A sample was recrystallized from ethanol, m.p. 65–66°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.87; H, 6.30.

ε-(5,6,7,8-Tetrahydro-2-naphthoyl)-homolevulinic Acid.—Treatment of 600 g. of the preceding with 7200 ml. of ethanol and 1800 ml. of concentrated hydrochloric acid followed by repeated extraction with a mixture of 3600 ml. of concentrated hydrochloric acid, 3600 ml. of acetic acid and 7200 ml. of water in the usual manner[3,4] gave 187 g. of the diketo acid (25%). A sample was recrystallized from ether–pentane, m.p. 114.5–115°.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.95; H, 6.99.

3-(5,6,7,8-Tetrahydro-2-naphthyl)-2-cyclopenten-1-one-2-acetic Acid.—(a) This was prepared in the usual manner[3,4] from the preceding in 95% yield. The product was recrystallized from chloroform and then from ether, m.p. 129–130°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.32; H, 6.65.

The oxime of this keto-acid was prepared in pyridine–ethanol and recrystallized from ethyl acetate, m.p. 160–161° (dec.).

Anal. Calcd. for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71. Found: C, 71.55; H, 6.70.

The methyl ester made with diazomethane in ether was crystallized from ethanol, m.p. 88–89°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.72; H, 7.00.

(b) Methyl β-(5,6,7,8-tetrahydro-2-naphthoyl)-propionate was prepared by the esterification of the acid[6] using the method of Clinton and Laskowski.[7] The ester has been described by Newman and Zahm.[5] The ester (246 g.) dissolved in 292 g. of dimethyl succinate was added to a refluxing solution of 52 g. of potassium in 900 ml. of dry *t*-butyl alcohol in an atmosphere of nitrogen. A solid potassium salt separated immediately. The mixture was kept in an oil-bath at 110–130° for 30 minutes, cooled, and worked up by the usual method.[8] The acidic fraction weighed 325 g. (90%).

A 14-g. sample was dissolved in 100 ml. of ethanol containing 15 ml. of 45% aqueous potassium hydroxide. The solution was heated on the steam-bath. Water was added (50 ml.) to dissolve the precipitated salt and heating was continued for 30 minutes. The solution was cooled, acidified with dilute hydrochloric acid and extracted with ether. The ethereal solution was treated in the usual manner and the ether was removed. The residue was crystallized from chloroform–pentane giving 4.7 g. (45%), m.p. 129–130° undepressed on admixture with the preparation of (a) above. A repetition of the hydrolysis on a larger scale (116 g.) gave 36 g. of crude product and 25 g. of recrystallized material (m.p. 129–130°). An additional 14 g. (m.p. 128–130°) was recovered by treatment of the mother liquor with Girard Reagent T, followed by recrystallization of the ketonic fraction from chloroform.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.51, 75.44; H, 6.63, 6.65.

The oxime, made as in (a) and crystallized from ethyl acetate had m.p. 161–162° (dec.) undepressed on admixture with the oxime of (a).

Anal. Calcd. for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71. Found: C, 71.63; H, 6.81.

The methyl ester was made with diazomethane and crystallized from ethanol, m.p. 87–89° undepressed on admixture with the ester of (a).

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.02; H, 7.05.

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Methylpentaerythrityl Ether

BY S. WAWZONEK AND J. P. HENRY[1]

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In the formation of the methyl and dimethyl ethers of pentaerythritol by the Tollens condensation of acetaldehyde and formaldehyde in 50% methanol, β-methoxypropionaldehyde has been postulated as an intermediate.[2] This assumption has now been verified by the preparation of the methyl ether of pentaerythritol using β-methoxypropionaldehyde in the Tollens condensation in place of the acetaldehyde. The similar yield of this ether (13.4%) to that (11.4%) obtained from the condensation using acetaldehyde indicates that β-methoxypropionaldehyde is partly dissociated into acrolein and methanol in the Tollens condensation. This behavior is consistent with the mechanism proposed.[2]

Experimental[3]

β-Methoxypropionaldehyde[4] was prepared by adding acrolein (56.0 g.) to a solution of sodium methoxide (from 0.4 g. of sodium) in absolute methanol (150 ml.) at 0° in the course of three hours and allowing the resulting solution to

(1) Abstracted in part from the M.S. thesis of J. P. Henry, June, 1948.
(2) S. Wawzonek and D. A. Rees, THIS JOURNAL, **70**, 2433 (1948).
(3) Melting points and boiling points are not corrected.
(4) M. Heyse, German Patent 554,946; *C. A.*, **26**, 5964 (1932).

stir further for three hours at −5°. The product was not isolated but was added to a suspension of paraformaldehyde (180 g.) in methanol (100 ml.) and water (250 ml.). This mixture was treated with calcium oxide and the products isolated in a manner similar to that reported previously.[2] Fractionation of the propionates gave the tripropionate of methylpentaerythrityl ether (42.5 g.), b.p. 170–178° at 7 mm., $n^{25}D$ 1.4423. Wawzonek and Rees[2] reported a boiling point of 170–172° (6 mm.), $n^{25}D$ 1.4410.

Saponification of this ester (42.5 g.) in ethanol (25 ml.) with 6 *N* sodium hydroxide (250 ml.) by refluxing for four hours, followed by evaporation of the resulting solution, gave a solid which was extracted three times with 200-ml. portions of hot chloroform. Concentration and cooling of the chloroform gave methylpentaerythrityl ether (10.6 g.) (53%) melting at 70°. A mixture with an authentic sample[5] melted at the same point.

The ester fraction (15.3 g.) boiling below 170° (7 mm.) and that (18.7 g.) boiling at 178–200° (7 mm.), which no doubt contained the propionates of dimethylpentaerythrityl ether and pentaerythritol, respectively, were not investigated further.

(5) L. Orthner and Freyss, *Ann.*, **484**, 131 (1930).

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α-Maltosyl β-D-Fructofuranoside, a Trisaccharide Enzymically Synthesized from Sucrose[1]

BY JONATHAN W. WHITE, JR., AND JEANNE MAHER

RECEIVED OCTOBER 23, 1952

In the course of an investigation of the action of honey invertase upon sucrose with the objective of comparing such oligosaccharides as may be formed with those occurring in honey, six saccharides other than glucose, fructose and sucrose were demonstrated by paper chromatography.[2]

The synthesis of oligosaccharides during the action of yeast invertase upon sucrose has been described.[3] The most extensive data[4] describe five such compounds, two of which are non-reducing trisaccharides composed of two fructose and one glucose molecules. No data other than R_f values are given. deWhalley[5] has reported further data for one of the trisaccharides, confirming its monosaccharide composition and giving $[\alpha]^{22}D$ +26.61°. He named it kestose.

Since honey invertase differs from yeast invertase in its action on sucrose and other sugars[2,6] it might be expected that the intermediates formed in the action of these enzymes upon sucrose differ.

The principal trisaccharides formed by yeast invertase from sucrose contain two fructose and one glucose molecules[4,5]; the principal trisaccharide formed by honey invertase from sucrose contains two glucose and one fructose molecules.

This sugar has been isolated from a honey invertase digest of sucrose in a yield of 11% of the original weight of sucrose. The structure 4-(α-D-glucopyranosyl)-α-D-glucopyranosyl β-D-fructofuranoside is proposed for this compound. A more convenient name is α-maltosyl β-D-fructofuranoside. The proposed structure is based on the following reactions.

The trisaccharide is non-reducing to Fehling solution and gives glucose and fructose on hydrolysis. Yeast invertase splits the molecule only at the glucose–fructose linkage to give fructose and maltose, toward which the enzyme is inactive. This fixes the glucose–glucose linkage as α-1,4. Honey invertase, which synthesizes the sugar, also can degrade it completely to constituent monosaccharides. However, its mode of action is such that the terminal glucose is first split off, leaving sucrose. There is an accumulation of sucrose during the reaction, which eventually is hydrolyzed completely. This fixes the glucose–fructose linkage as that in sucrose, or β-D-fructofuranosyl α-D-glucopyranoside. Thus, linkages and stereochemical forms of the constituent monosaccharides in the trisaccharide are fixed by identification of maltose and sucrose as degradation products.

Experimental

Preparation of α-Maltosyl β-D-Fructoside.—A honey invertase concentrate was prepared from unheated 1948 fall flower honey by the procedure of Nelson and Cohn.[7] One ml. of the preparation (equivalent to the enzyme content of 32 g. of honey) inverted 0.86 g. of sucrose in 125 minutes at 26°, *p*H 5.8 in 10 ml. of 15% sucrose solution.

A solution of 8.35 g. of sucrose, 2 ml. of 2 *M* acetate buffer at *p*H 5.7 and 5.55 ml. of honey invertase was made to 50 ml. and allowed to stand 128 minutes at 26°. At this time 24% of the original sucrose remained. The solution was heated and subjected to chromatography on a 36 × 160 mm. carbon–diatomaceous earth column as described by Whistler and Durso.[8] Details of the separation are given elsewhere.[2] The fraction eluted with 50% ethanol (0.944 g.) contained all compounds higher than disaccharides, since it followed the 5% ethanol (disaccharide) fraction directly.

Paper chromatography of this fraction showed it to contain principally a non-reducing, ketose-containing material of R_S[9] 0.57 (solvent, butanol 3, pyridine 1, water 1.5)[10]. Small amounts of other materials were present whose migration on the papergram corresponded to that of disaccharides (R_S 1.00) and tetrasaccharides (R_S 0.26).

In a typical purification, 160 mg. of the crude material was freed of these contaminants by chromatography on a powdered cellulose column essentially as described by Hough, *et al.*[11] The solvent used was butanol 41.6, ethanol 47.6, water, 22.5 parts by volume, a single-phase solvent which gives relatively rapid movement of trisaccharides. Samples from the 1-ml. eluate fractions were chromatographed on paper to locate the constituents. The eluate fractions containing only the trisaccharide were combined to yield 123 mg. of material. Since the product has not been crystallized, material from several runs was evaporated and dried for analysis at a pressure of 1.6 mm. at 105° to constant weight. It had $[\alpha]^{25}D$ +121.8° (2.3% in water). No definite melting point was obtained for the amorphous material.

α-Maltosyl β-D-Fructoside Hendecaacetate.—The trisaccharide (100 mg.) was treated with acetic anhydride in pyridine at room temperature by the procedure of Barker and Bourne.[12] The product was dried at pressure of 2 mm. at 60° to constant weight. It was not crystallized. It had $[\alpha]^{25}D$ +86.0° (1.2%, $CHCl_3$).

(1) Report of work carried out under the provisions of the Research and Marketing Act of 1946. Presented at the 122nd Meeting of the American Chemical Society, Division of Sugar Chemistry, Atlantic City, N. J., Sept. 16, 1952.

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(9) R_S is ratio of travel of spot to travel of sucrose on same paper.

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