gave a Δ of 0.25° corresponding to a molecular weight of 180.5. Calcd. 170.1).

The amino acids glycine, *d,l*-leucine, *d,l*-alanine and *d,l*-phenylalanine do not dissolve in β-naphthol and remain unchanged.

The Treatment of Proteins with β-Naphthol.—Edestin and ovalbumin mixed with respectively 5 and 10 times their weight of β-naphthol were treated in the same manner as were the peptides. The products obtained after washing with ether were seen under the microscope, to consist of crystals. On repeated boiling with absolute alcohol, over 80% of the substance remains undissolved. On evaporation of the first alcoholic extract, a brown mass which in part dissolved in ether but was not investigated further, was obtained. The part insoluble in absolute alcohol, on reëxamination under the microscope, proved beautifully crystalline as was the mother material.

Summary

On heating with β-naphthol at a temperature of 135–150°, dipeptides enter into solution and yield diketopiperazines; this circumstance gives an easy method for the preparation of the latter.

Tripeptides treated in a corresponding manner with β-naphthol are decomposed so that they yield the terminal amino acid in a free form and a diketopiperazine consisting of the first amino acid which carries the free amino group and the second adjacent amino acid. This property provides a method for the identification of the amino acid bearing the free carboxyl group in tripeptides.

A tetrapeptide treated under the same conditions yielded a diketopiperazine corresponding to the two amino acid pairs.

Benzoylated dipeptides and a benzoylated tripeptide, though soluble in β-naphthol, underwent no change. Free amino acids and glycylglycine do not dissolve in β-naphthol and remain unchanged.

Edestine and ovalbumin dissolve in hot β-naphthol and yield beautifully crystalline products which are largely insoluble in hot alcohol and therefore are not simple diketopiperazines.

The significance of the above findings for our knowledge of protein structure is discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

α-Ethyl-*l*-sorbopyranoside and its Tetraacetate

BY ROY L. WHISTLER AND R. M. HIXON

During a study of Fischer's method[1] for glycoside formation with relation to *l*-sorbose it was observed that a solution of this sugar in ethanol underwent an optical rotatory change analogous to the change occurring during the formation of α-methyl-*l*-sorboside in methanol (Fig. 1). The close similarity in the optical changes indicated a reaction between sorbose and the ethanol solution with formation of an ethyl sorboside, which like the methyl sorboside would be expected to be of the *alpha* configuration. The reaction is essentially complete in four hours at room temperature.

A small quantity of *l*-sorbose was subjected to the action of a 1% solution of hydrogen chloride in dry ethanol with recovery, at the end of four hours, of fine colorless needles having a melting point of 116° and an optical rotation[2] of −73.9°. The strong negative rotation as compared to *l*-sorbose (−43.4°) indicates an α-glycoside. On solution in dilute hydrochloric acid the hydrolysis curve followed closely that found for α-methyl-*l*-sorboside, taking ten days for complete hydrolysis in 0.1 *N* acid and approximately thirty days in 0.015 *N* acid (Fig 1). The true end-point in the latter solution was indefinite due to mold growth which became noticeable after twenty-eight days.

Acetylation of the α-ethyl-*l*-sorboside produced an α-ethyl-*l*-sorboside tetraacetate which was identical with that obtained through the ethylation of sorbose tetraacetate. Thus, the ring structure of α-ethyl-*l*-sorboside must be the same as that in sorbose tetraacetate. The structure of sorbose tetraacetate-[3,4] as 1,3,4,5-tetraacetylsorbose can be established through the fact that acetylation of α-methyl-*l*-sorbopyranoside whose configuration has been proved[5] yields an α-methyl-*l*-sorboside tetraacetate[6] identical with the compound obtained through the methylation[5] of sor-

(1) Fischer, *Ber.*, **28**, 1145 (1895).

(2) All rotations are specific rotations taken with the D-line of sodium at 26°.

(3) Arragon, *Compt. rend.*, **196**, 1133 (1933).

(4) Arragon, *ibid.*, **198**, 1508 (1937).

(5) Whistler and Hixon, THIS JOURNAL, **59**, 2047 (1937).

(6) Arragon, *Bull. soc. chim. biol.*, **17**, 831 (1935).

bose tetraacetate. This series of reactions, then, indicates a normal pyranoid ring structure for α-ethyl-*l*-sorboside and its tetraacetate.

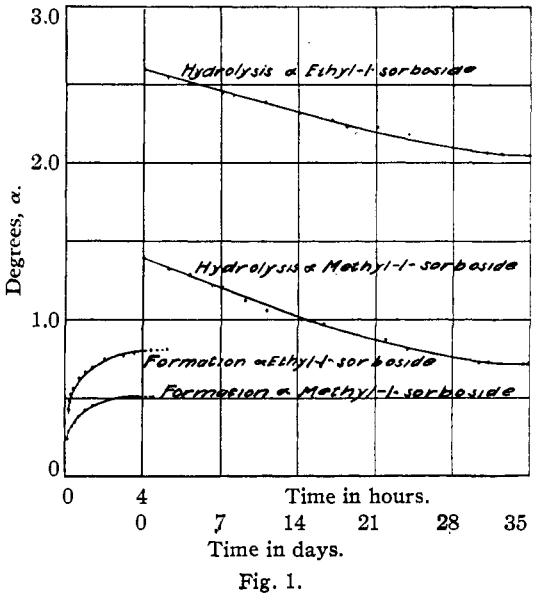

Fig. 1.

Experimental

α-Ethyl-*l*-sorbopyranoside.—Twenty grams of finely powdered dry sorbose was dissolved with shaking in 1500 cc. of ethanol which previously had been dried with sodium and distilled. To this solution was added 250 cc. of dry ethanol containing 20 g. of dry hydrogen chloride. The mixture at once became a light pink in color. After standing for four hours the solution was light amber in shade. A solution of 13 g. of sodium dissolved in dry ethanol was added and this mixture shaken for five minutes. Then carbon dioxide was passed through the solution for one hour. The solution was distilled under reduced pressure at a temperature no higher than 50°. The residue was extracted repeatedly with boiling ethyl acetate and ethanol. The solvents were removed from the combined extracts by distilling under reduced pressure at 50°. The red sirupy residue was extracted with boiling ethyl acetate until only a brittle red gum remained. From the ethyl acetate extracts there separated on cooling a flocculent white precipitate which did not reduce Fehling's solution; yield 10 g. This material was dissolved in hot acetone and filtered from norite. On cooling, long needles separated of m. p. 114–115°. One recrystallization from ethyl acetate raised the melting point to 115–116°; optical rotation −73.9° in water (*c*, 2.3). This solution showed no mutarotation after standing for twenty-four hours.

Anal. Calcd. for $C_6H_{11}O_5(OC_2H_5)$: C, 46.15; H, 7.69; OC_2H_5, 21.63. Found: C, 45.98; H, 7.79; OC_2H_5, 21.77.

α-Ethyl-*l*-sorbopyranoside Tetraacetate. First Method.—To 4 g. of α-ethyl-*l*-sorbopyranoside dissolved in 25 cc. of dry pyridine was added 13 cc. of acetic anhydride. After standing overnight the mixture was poured into 500 cc. of ice water and extracted twice with 75-cc. portions of chloroform. The combined extract was washed successively with sodium bisulfate solution, sodium bicarbonate solution and water. The chloroform extract was dried over anhydrous sodium sulfate and the chloroform removed under diminished pressure. The sirup crystallized from 45% alcohol: yield 3 g., m. p. 74–75°, rotation −54.6° in chloroform (*c*, 2.8).

Anal. Calcd. for $C_{14}H_{19}O_9(OC_2H_5)$: C, 51.06; H, 6.38; OC_2H_5, 11.96. Found: C, 50.94; H, 6.37; OC_2H_5, 11.95.

Second Method.—Twenty grams of powdered sorbose tetraacetate, 75 g. of freshly prepared silver oxide and 128 g. of ethyl iodide were heated under reflux until reaction began, enough heat being generated after the reaction started to maintain the solution at the boiling point. When the reaction had subsided the solution was boiled for two and one-half hours longer under reflux. At this time the ethyl iodide was distilled off and the residue extracted with ether. On removal of the ether the residue was taken up in petroleum ether (b. p. 30–40°) from which long needles crystallized; yield, 14 g. On recrystallization from 45% alcohol fine, soft needles were obtained, m. p. 74°, rotation −54.6° in chloroform (*c*, 2.8).

Summary

α-Ethyl-*l*-sorbopyranoside and its tetraacetate have been prepared and characterized for the first time. By means of a series of well established reactions through which the ring system remains unimpaired these compounds can be linked definitely to α-methyl-*l*-sorbopyranoside whose structure has been definitely established.

Sorbose tetraacetate has been shown to be 1,3,4,5-tetraacetylsorbose.

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