Whether the hexachlorobenzene is formed by the explosion or by a pyrolysis, the $\rightarrow CCl$ radical seems an obvious intermediate between it and chloroform.

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The Fluorescence of Double Salts of Calcium Phosphate

BY JULIAN GLASSER AND GORTON R. FONDA

Ox teeth are known to consist of 1% of organic matter combined with calcium phosphate in an apatite structure. Their fluorescence under ultraviolet radiation is destroyed by burning out their organic content at 600° or higher, but is increased by firing at an optimum temperature of 400°. After solution in acid and precipitation in alkali, the fluorescence is fully restored by refiring at 400°.

A similar product can be made synthetically by coprecipitating a calcium salt with a mixture of sodium phosphate and tartrate and firing at 400°. An optimum fluorescence bluish-white in color is obtained when the solution of sodium phosphate contains 11 molar per cent. of sodium tartrate. The 400° treatment is effective only when carried out in the presence of oxygen. It burns off most of the tartrate but leaves an oxidized residue at a concentration of about 2% by weight combined with the phosphate. The fluorescence under 3650 Å. is double that of teeth and is about 4% of the theoretical, on the basis of complete quantum conversion. The product again has the apatite structure but with an apparently slight contraction of the lattice. Its fluorescence is retained after solution in acid and reprecipitation with alkali. It is destroyed by firing at temperatures above 400°.

A fluorescent product also results by firing at 400° the coprecipitate of calcium phosphate contaminated with some other organic radical, such as succinate or lactate. In fact it appears that the contaminant may even be the calcium salt of an inorganic acid radical, such as borate or chromate. The fluorescence of solids is generally associated with the presence of a small amount of metallic impurity as activator. In this case, however, it appears that the activator may be a foreign acid radical. The possibility of such a type of fluoreseence is being studied further.

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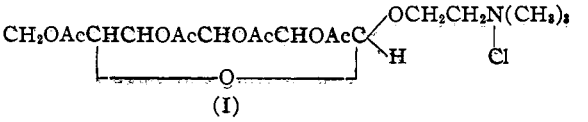
beta-Tetraacetylcholine-*d*-glucoside[1,2]

BY ERNEST L. JACKSON

Schroeter and Strassberger[3] prepared 2-chloroethyl-*d*-glucoside by the reaction of glucose with ethylene chlorohydrin containing hydrogen chloride, condensed their impure 2-chloroethylglucoside with trimethylamine, and from the products prepared a phosphomolybdate of cholineglucoside. The chloride of cholineglucoside, showing $[\alpha]^{15}D + 49.5°$ in water, was obtained in crystalline condition from the phosphomolybdate.

By the reaction of trimethylamine with pure crystalline beta-tetraacetyl-2-chloroethyl-*d*-glucoside[4] in benzene solution the writer has prepared the crystalline chloride of tetraacetylcholine-*d*-glucoside (I) which has a melting point of 230° and a specific rotation[5] of −25.6° in water and −13.5° in chloroform.



(I)

This compound must be a beta-pyranoside, since the parent tetraacetyl-2-chloroethylglucoside was prepared from ethylene chlorohydrin, acetobromoglucose and silver carbonate, a reaction which in the case of other alcohols is known generally to produce beta-pyranosides. Although the chloride of beta-cholineglucoside has not been prepared in crystalline condition, its rotation as determined by an indirect method is near −27° in water. The dextrorotation of Schroeter and Strassberger's product indicates it to be an alpha form which was separated from the mixture of glycosides expected to result from their method of preparation.

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) The pharmacological properties of this compound are under investigation by Dr. M. I. Smith of this Institute.

(3) G. Schroeter and L. Strassberger, *Biochem. Z.*, **232**, 454 (1931).

(4) Walter Schoelier and Hans-Georg Allardt, German Patent 527,036 (1926); *Chem. Zentr.*, **102**, II, 1452 (1931).

(5) Except where otherwise stated, all rotations in this article are specific rotations at 20° for sodium light.

Experimental

beta-Tetraacetyl-2-chloroethyl-*d*-glucoside.—A solution of 91 g. of acetobromoglucose (0.22 mole) and 268 g. of pure ethylene chlorohydrin (3.33 moles) in 625 cc. of dry benzene was shaken at 8–10° with 92 g. of dry silver carbonate until the test for bromine was negative. After filtration and thorough extraction with water, the solution was dried over anhydrous sodium sulfate and then concentrated *in vacuo* to dryness. The product was recrystallized as long, prismatic needles from absolute ethanol, a second crop being obtained from ether–petroleum ether; yield, 63 g. or 69% on the acetobromoglucose. The pure compound melts at 118.5–119.5° (uncorr.) and rotates −13.7° in chloroform (*c*, 3.9).

Anal. Calcd. for $C_{16}H_{23}O_{10}Cl$: C, 46.76; H, 5.64; Cl, 8.64; CH_3CO, 41.91. Found: C, 46.72; H, 5.74; Cl, 8.64; CH_3CO, 41.94.

beta-Tetraacetyl-*d*-glucosido-ethyltrimethylammonium Chloride (beta-Tetraacetyl-(choline Chloride)-*d*-glucoside).—A solution of the trimethylamine from 7 g. of trimethylamine hydrochloride, and 10 g. of pure beta-tetraacetyl-2-chloroethylglucoside in 110 cc. of dry benzene was sealed at 0°, and kept at 62–64° for eighty-seven hours; then, due to excessive coloration, the temperature was changed to 50–52° for fifteen days. After the flask had been opened at 10°, the crystals were filtered off, washed with 15 cc. of benzene and dried at 25° *in vacuo* over calcium chloride; yield, 6.8 g. or 60%. The reaction was incomplete, as shown by the separation of 2.9 g. of crystals (total yield, 85%) from the filtrate kept sealed at room temperature for several months. When the reaction was carried out at 50–52° for fifteen days, although there was less coloration, the yield was only 4.7 g. or 41%. After the solution of the product in two parts of absolute ethanol had been decolorized with activated carbon, the tetraacetate crystallized readily as white prismatic needles upon the addition of dry ether. The pure compound melted at 230° (uncorr.) and rotated −25.6° in water (*c*, 1.1) and −13.5° in chloroform (*c*, 1.1). It is hygroscopic, is readily soluble in cold water, chloroform and ethanol, and slightly soluble in benzene and ether. From its solution in cold water the chlorine is removed quantitatively by silver nitrate.

Anal. Calcd. for $C_{19}H_{32}O_{10}NCl$: C, 48.54; H, 6.87; N, 2.98; Cl, 7.55; CH_3CO, 36.63. Found (dried at 25° *in vacuo* over phosphorus pentoxide): C, 48.41, 48.30; H, 7.01, 6.85; N, 2.95, 3.00; Cl, 7.46, 7.46; CH_3CO, 36.66, 36.56.

For the chloride of beta-cholineglucoside a specific rotation of −26.5° in water was calculated from the rotation of the solution obtained by the deacetylation of the tetraacetate. To a solution of 0.2641 g. of pure tetraacetate in 8 cc. of water at 0–5° was added 6 cc. of *N* sodium hydroxide solution. After twenty hours at 0–5° the solution, neutralized to phenolphthalein with hydrochloric acid (calcd. 2.25 cc. of *N* sodium hydroxide; found 2.25 cc.) and diluted with water to 25 cc. at 20°, rotated 0.36° to the left in a 2-dm. tube.

NATIONAL INSTITUTE OF HEALTH
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Changes That Occur in the Proteins of Soybean Meal as a Result of Storage

BY D. BREESE JONES AND CHAS. E. F. GERSDORFF

It has been observed from time to time when extracting proteins from ground seeds that the amount of nitrogen which can be extracted with neutral salt solutions decreases with the aging of the meal. These observations suggested that other changes may occur which could well affect not only the chemical properties of the proteins but also their nutritional value. If so, it is obvious that this presents a problem of far-reaching importance. Large quantities of grains and other seeds, both whole and ground, undergo periods of storage and shelf aging before they reach the consumer.

Studies have been started to investigate the nature and extent of changes which occur in the proteins of seeds (both whole and ground) when stored under different conditions. Results thus far obtained show that marked changes in the chemical properties of the proteins of ground soybeans occur very soon after grinding. Some of these changes suggest a decrease in the biological value of the proteins.

Two portions of freshly ground soybeans were solvent-extracted. One portion was made practically fat-free, and the other to contain about 11% fat. Samples of both lots of the meal were stored in sealed jars and in bags, in constant temperature rooms at 76 and 30F°. The samples were analyzed at intervals of one, three, and six months, and the results compared with those obtained at the start on the freshly ground meal.

Table I shows percentage decreases in the amount of nitrogen extracted by 10% sodium chloride solution, in true protein content, as determined by the Stutzer method, and in digestibility of the protein *in vitro*. Analyses were made at the end of one, three, and six months' storage periods. At the end of one month significant decreases in values had occurred in all the samples. On further storage the values continued to decrease. By the end of six months the digestibility of the protein of the low-fat meal stored in bags at 76° had dropped nearly 19% below that of the meal when freshly ground. The greatest changes occurred at 76°, although at 30° the changes were surprisingly high. Greater changes occurred in the meals stored in bags than in those stored in sealed jars. Of