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
WASHINGTON, D. C. RECEIVED JANUARY 29, 1938

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

TABLE I

PERCENTAGE DECREASES IN VALUES FOR TRUE PROTEIN, SOLUBILITY AND DIGESTIBILITY OF PROTEIN, AFTER STORAGE OF SOYBEAN MEAL UNDER DIFFERENT CONDITIONS FOR ONE, THREE, AND SIX MONTHS

Storage conditions		True Protein, % 1 mo.	3 mos.	6 mos.	Extractability, % 1 mo.	3 mos.	6 mos.	Digestibility, % 1 mo.	3 mos.	6 mos.
STORED IN JARS										
High-fat meal	30°F.	0.31	2.88	4.35	1.18	3.08	4.53	0.92	5.61	7.26
High-fat meal	76°F.	2.15	4.83	7.16	2.92	5.91	8.71	4.53	9.49	12.05
Low-fat meal	30°F.	3.01	4.21	5.44	1.51	5.04	7.53	3.80	10.41	12.97
Low-fat meal	76°F.	3.95	6.36	8.71	3.82	8.47	10.72	5.57	15.30	17.25
STORED IN BAGS[a]										
High-fat meal	30°F.	..	..	5.85	..	..	8.92	..	...	10.43
High-fat meal	76°F.	..	..	8.75	..	..	13.11	..	...	14.48
Low-fat meal	30°F.	..	..	6.76	..	..	8.94	..	...	15.13
Low-fat meal	76°F.	..	..	9.97	..	..	12.39	..	...	18.94

[a] Analyses of meals stored in bags were made only after six months' storage.

interest is the consistently greater changes that occurred in the low-fat samples than in the high-fat samples. The total nitrogen and free ammonia content of all the samples remained constant throughout the storage periods. The high-fat samples showed a slight increase in free fatty acids, particularly in the samples stored at 76°.

Storage of soybean meal apparently results in partial denaturation of the proteins as indicated by their decreased solubility in salt solution. A proteolysis is also indicated by the drop in true protein values. The nature of the marked decrease in digestibility *in vitro* is being studied.

The chemical studies outlined above are being supplemented by feeding experiments to determine the effects of storage on the biological value of the proteins. Storage studies on the samples will be continued for two years or more. Final results and details of the work will be published later. Similar studies on the proteins of other seeds of importance as foodstuffs will be made both on the meals and on the whole grains.

PROTEIN AND NUTRITION RESEARCH DIVISION
BUREAU OF CHEMISTRY AND SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C. RECEIVED FEBRUARY 7, 1938

The Standard Electromotive Force of the Lead Electrode

BY JAMES J. LINGANE

There is considerable uncertainty in the literature regarding the standard e. m. f. of the lead electrode. The value 0.122 v., given in the "International Critical Tables,"[1] was calculated by Lewis and Randall,[2] from Gerke's measurements[3] of the cell $Pb/PbCl_2$, AgCl(s)/Ag, and an activity coefficient of saturated lead chloride computed from the data of Brönsted.[4]

Carmody[5] later studied this cell more carefully, extending the measurements to very small concentrations of lead chloride, and he obtained the value 0.1263 v. for E^0_{Pb} at 25°. Using the accurate activity coefficients of lead chloride obtained from his measurements, Carmody recalculated E^0_{Pb} from Gerke's data and obtained the value 0.1264 v., which agrees very well with his own value.

However, Randall and Cann,[6] in an apparently equally careful study, later obtained the value 0.1203 v. for E^0_{Pb}, from their measurements of the cell $Pb/Pb(NO_3)_2/KNO_3/KCl$, AgCl(s)/Ag with *flowing* liquid junctions. Carmody recently[7] has attributed this lower value of Randall and Cann to the fact that they flowed the cell solutions *directly* over the silver–silver chloride electrodes. He has shown[8] that flowing the electrolyte directly over silver–silver chloride electrodes causes their potential to become about 6 mv. positive to the same electrodes in equilibrium with the cell solution. When this correction of 6 mv. is applied to the data of Randall and Cann, the corrected value becomes 0.1263 v., in exact agreement with Carmody's value.

Since this correction is somewhat uncertain, and may depend on the method of preparing the silver–silver chloride electrodes, it is very desirable to obtain further evidence before it is accepted.

The standard e. m. f. of the lead electrode can

(1) "International Critical Tables," Vol. VI, 1929, p. 332.
(2) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 424.
(3) R. H. Gerke, THIS JOURNAL, **44**, 1684 (1922).
(4) J. N. Brönsted, *Z. physik. Chem.*, **56**, 645 (1906).
(5) W. R. Carmody, THIS JOURNAL, **51**, 2905 (1929).
(6) M. Randall and J. Y. Cann, *ibid.*, **52**, 589 (1930).
(7) W. R. Carmody, *ibid.*, **54**, 210 (1932).
(8) W. R. Carmody, *ibid.*, **54**, 188 (1932).