125° F. This characteristic of this portland cement is also noticeable on Figure 2, where there is a more decided increase in the slope of the curves from 100° to 120° F. (each after reaching bath temperature) than there is from 120° to 140°. Since the slope of the curves after they reach the temperature of the bath is dependent mainly on the heat of hydration, it seems that there is a somewhat greater rate increase between 100° and 120° F. than there is between 120° and 140° F. Likewise the slopes of the succeeding curves at higher temperatures increase only slightly. These observations tend to indicate that definite compound formation was taking place at the initial set, and that this compound formation was accompanied by an amount of heat which characterizes the reaction. This is in accord with the observations of Woods, Steinour, and Starke (*16*) who established the fact that there is a relation between the heat of hydration and chemical composition of the cement. Also, the rate of this reaction, as evidenced by the heat evolution, is rather constant, and is not influenced appreciably by temperatures between 125° and 150° F.

On Figure 6 is plotted the heat evolution from cement when allowed to set under adiabatic conditions. It is immediately discernible that the total amount of heat evolved under these conditions is three to four times that evolved at 150° F. in the same length of time. This behavior would be expected, since no heat leaves the cement mass. This fact, in conjunction with the data given in Figure 7, well accounts for the low heat flow from cements which set at temperatures of 150° to 200° F.—i. e., under oil well conditions.

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Inactive Inositol and Its Derivatives

PREPARATION AND PROPERTIES

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BARTOW and Walker (*1*) prepared inositol from the steep water obtained in the manufacture of starch from corn without the use of acids. This work was continued for the purpose of obtaining larger quantities of inositol, of improving the process of preparing inositol, of finding other sources of inositol, and of studying the preparation and properties of its derivatives.

Preparation of Inositol

Inositol was prepared by the simple method of Bartow and Walker (*1*). The raw material (obtained from Penick & Ford, Ltd.) was the precipitate made by adding lime to steep water. It had the consistency of thin paste and contained about 20 per cent of solids. A 225-kg. batch of this wet material, equivalent to 45 kg. of dry substance, was heated in a large autoclave for 10 hours under 5.6 kg. per sq. cm. steam pressure. After being heated, the material was neutralized with milk of lime (to phenolphthalein alkalinity), diluted with water to about 680 liters, then agitated, and boiled for 5 minutes by passing in steam. After the sludge settled, the supernatant liquid was removed by decantation. The sludge was diluted with water, heated with steam, and allowed to settle, and the supernatant liquid was again decanted. This process was repeated and the combined liquids from the three decantations were evaporated to a small volume in large open evaporators; they were filtered while hot to remove precipitated impurities. The inositol which crystallized out on cooling was removed by filtration, the mother liquor was further concentrated, and the residual inositol was precipitated by adding glacial acetic acid and alcohol. The average yield for the first nine experiments was 12.00 per cent of the dry matter in the material used.

A lower yield of inositol was obtained when an attempt was made to remove the liquid from the sludge by filtration. Only 10.00 per cent of inositol was obtained when the liquid was separated from the sludge by filtration on an Oliver filter. More washing on the filter should increase the yield.

EFFECT OF pH ON YIELD FROM PRECIPITATES. Precipitates were carefully prepared by the Clinton Company by adding milk of lime to steep water until the desired pH values were reached. Five samples precipitated at pH values ranging from 5.5 to 7.5, inclusive, gave a yield of inositol decreasing regularly as the pH increased (Table I). About 3 kg. of the precipitate (dry) were used in each of these tests. The amount of precipitate obtained from given quantities of steep water at the lower pH values is small; hence it is less practical to use material precipitated below a pH of 6.5. The precipitate obtained at the higher pH values probably contains such impurities as $CaCO_3$ or $CaHPO_4$. The crude inositol obtained at a pH of 7 or higher was very dark and impure, but a recrystallization gave good quality.

TABLE I. YIELD OF INOSITOL WHEN PRECIPITATE WAS FORMED AT DIFFERENT pH VALUES

Sample No.	pH	Yield of Inositol, %
11	5.5	11.94
12	6.0	10.80
13	6.5	10.14
14	7.0	8.85
15	7.5	6.25

INOSITOL FROM WHEAT BRAN. Wheat bran was steeped for 24 hours at 50° C. in a solution containing 0.4 per cent of hydrochloric acid. The steep water, which contained the acid-soluble portion of the bran and some starch and gluten, was drained from the bran; and after settling for several hours, the supernatant liquid was siphoned from the starch-gluten mixture. Neutralization with milk of lime to phenolphthalein alkalinity brought down an insoluble precipitate from which inositol was obtained by hydrolysis. The same procedure was used as with the precipitate from steep water obtained in the manufacture of cornstarch.

The yield of inositol from wheat bran in five experiments was relatively small—only 0.52 per cent. Bran is less satisfactory than steep water as a source of inositol. Since bran is valuable as a stock food, its use as a source of inositol can be practical only if the treated bran can still be used as feed.

Organic Esters of Inositol

Müller (*3*) prepared the hexacetyl derivative by heating inositol with an excess of acetic anhydride in the presence of zinc chloride. Griffin and Nelson (*2*) prepared inositol hexabenzoate by heating benzoyl chloride and inositol to 120° C. in the presence of quinoline.

INOSITOL HEXACETATE, $\mathrm{C_6H_6(OCOCH_3)_6}$, was prepared according to the method of Müller (*3*) by heating inositol with an excess of acetic anhydride in the presence of zinc chloride. The reaction proceeded without difficulty, and a pure product was obtained. The melting point was 212° C., and the yield was almost quantitative.

Inositol hexacetate was also prepared by refluxing inositol (1 gram) and an excess (5 grams) of acetyl chloride in the presence of a little zinc chloride. Without zinc chloride little or no reaction took place, but when this reagent was added, the reaction proceeded briskly without further application of heat. After recrystallization from alcohol, the white crystalline compound melted at 212° C., which is the same as that recorded by Müller (*3*).

INOSITOL HEXAPROPIONATE, $\mathrm{C_6H_6(OCOC_2H_5)_6}$, was prepared by refluxing inositol with an excess of propionyl chloride for one hour in the presence of zinc chloride. When the mixture was poured into ice water, the derivative precipitated immediately. The precipitate was washed repeatedly with portions of water and finally recrystallized with alcohol. The white crystalline substance melted at 100° C. and had a molecular weight of 532.

INOSITOL HEXABUTYRATE, $\mathrm{C_6H_6(OCOC_3H_7)_6}$, was prepared by refluxing inositol with an excess of *n*-butyryl chloride in presence of zinc chloride. After being heated for one hour, the dark colored sirupy liquid was poured into a beaker of ice water. The solid ester precipitated immediately and was separated by filtration, thoroughly washed with water, dried, and recrystallized from alcohol. It was necessary to recrystallize twice from alcohol to obtain a pure product, which melted at 81° C. and had a molecular weight of 587.

INOSITOL HEXAISOBUTYRATE, $\mathrm{C_6H_6[OCOCH(CH_3)_2]_6}$, was prepared by refluxing inositol and *sec*-butyryl chloride in the presence of zinc chloride in the manner previously described. The white crystalline product melted at 181° C. and had a molecular weight of 624.

INOSITOL HEXAVALERATE, $\mathrm{C_6H_6(OCOC_4H_9)_6}$, AND INOSITOL HEXAISOVALERATE, $\mathrm{C_6H_6[OCOCH_2CH(CH_3)_2]_6}$, were prepared by refluxing inositol with an excess of valeryl chlorides in the presence of zinc chloride for 45 minutes on an oil bath at 120° C. In each case a brisk reaction began when a temperature of about 90° C. was reached, and much hydrochloric acid gas was evolved. After refluxing, the dark colored sirupy liquid was poured into ice water. At first no solid precipitate was formed, but instead an oily layer appeared in the bottom of the beaker which would not harden. After prolonged stirring, the dark colored oil began to crystallize. The precipitate in each case was pulverized, washed repeatedly with water, and finally filtered. Recrystallization from alcohol gave a white crystalline product in each case. Inositol hexavalerate melted at 63° C. and had a molecular weight of 668. Inositol hexaisovalerate melted at 147° C. and had a molecular weight of 697.

TABLE II. MELTING POINTS AND MOLECULAR WEIGHTS OF THE ORGANIC ESTERS

Derivative	Formula	M. P., ° C.	Mol. Weight Detd.	Mol. Weight Theoretical
Acetyl	$\mathrm{C_6H_6(OCOCH_3)_6}$	212	...	432
Propionyl	$\mathrm{C_6H_6(OCOC_2H_5)_6}$	100	532	516
n-Butyryl	$\mathrm{C_6H_6(OCOC_3H_7)_6}$	81	587	600
sec-Butyryl	$\mathrm{C_6H_6[OCOCH(CH_3)_2]_6}$	181	624	600
n-Valeryl[a]	$\mathrm{C_6H_6(OCOC_4H_9)_6}$	63	668	684
Isovaleryl[a]	$\mathrm{C_6H_6[OCOCH_2CH(CH_3)_2]_6}$	147	697	684
3,5-Dinitrobenzoyl	$\mathrm{C_6H_6[OCOC_6H_3(NO_2)_2]_6}$	86	1252	1380

[a] Reaction was carried out by heating on an oil bath at 110° to 120° C. for 45 minutes.

The melting points of derivatives of the normal acids decrease as the molecular weights of the fatty acids used increase. The branched-chain acid derivatives have a higher melting point than the corresponding straight-chain acid derivatives.

Attempts to prepare derivatives of *n*-caproic, isocaproic, and *n*-capric acids have thus far been unsuccessful. In each case inositol was heated with an excess of the corresponding acid chloride in presence of a little zinc chloride. A brisk reaction took place and much hydrochloric acid gas was given off. In each case an oily substance was obtained which would not crystallize.

INOSITOL HEXA-3,5-DINITROBENZOATE, $\mathrm{C_6H_6[OCOC_6H_3(NO_2)_2]_6}$, was prepared by heating inositol with an excess of 3,5-dinitrobenzoyl chloride for 3 to 5 minutes over a free flame. When the mixture was poured into ice water, a solid precipitated and was recrystallized from alcohol. The molecular weight was found to be 1252 (theoretical, 1380); the melting point was 86° C.

ACTION OF CERTAIN CHLORIDES AND ANHYDRIDES. Unsuccessful attempts were made to prepare derivatives of succinic acid, phthalic acid, and the chloroacetic acids. In each case a mixture of inositol with the chlorides or anhydrides was heated with or without zinc chloride as catalyst and with or without pyridine as a solvent. Unchanged inositol was recovered except when decomposition took place.

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