2. Methods are described for the preparation of tetraphenylgermanium and triphenylgermanium bromide.

3. Triphenylgermanium fluoride, triphenylgermanium iodide, sodium triphenyl germanide, sodium triphenyl germanolate, triphenyl germanol, triphenylgermane and trimethylstannyl-triphenylgermane have been prepared and some of their properties and reactions have been studied.

4. Germanium compounds are much more stable toward oxidizing agents than are the corresponding tin compounds, but toward strong reducing agents their behavior is very similar to that of the latter. The triphenylgermanium halides hydrolyze and ammonolyze much more readily than do the corresponding halides of tin.

Providence, Rhode Island

[Contribution from the Russell-Miller Milling Company]

RELATION OF THE MAGNESIUM IN THE ASH AND THE LIPOID-PROTEIN RATIO TO THE QUALITY OF WHEATS

By Betty Sullivan and Cleo Near

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Introduction

Recognizing the importance of the effect of small amounts of salts and electrolytes on the behavior of cereals, it was thought that possibly there might be some difference in the amounts of the inorganic elements present in various wheats and that this difference might offer an explanation for "strong" and "weak" wheats. The purpose of this investigation, therefore, was to determine whether there were any marked differences between the inorganic constituents present in wheats coming from such areas as North Dakota, Montana and Canada, known to produce quality-strong wheats, and those coming from the Pacific Coast States where the wheats are extremely soft and starchy, and regarded as less suitable for bread making.

Experimental Part

Twenty wheats from different localities, and of widely varying quality and protein content, were chosen for the analyses. The wheats were ashed by a special method which, it is believed, gives results more closely approaching a pure ash basis than the present methods. Merck's c. p. superoxyl (30%) was diluted to 5% with distilled water, and a quantity sufficient to moisten it thoroughly was added to the sample of flour or ground wheat or bran. In order to accomplish this satisfactorily, the mixture was stirred with a small glass rod, after which any flour adhering to the rod was taken off with a small piece of ashless filter paper and added to the sample. When the effervescence due to the action of the hydrogen peroxide on enzymes had ceased, the sample was dried in the muffle at a low temperature and the temperature then raised to 610–620°, until a white ash free from carbon was obtained. A fairly large, flat-bottomed dish should be employed for ashing to prevent loss after hydrogen peroxide is added. No correction for a blank is necessary as in the glycerol-alcohol method since there is practically no residue left on evaporation of even large volumes of diluted superoxyl. In this connection, it is well to caution against the use of the 3% hydrogen peroxide sold for pharmaceutical purposes because of the residue from impurities in the acetanilide used for its preservation. This method of ashing gives, in a shorter time, a cleaner, whiter ash on all flours, wheat or bran. The percentage of phosphorus in wheat ash obtained by the use of hydrogen peroxide and ignition at 620° for 12–16 hours was the same as that obtained by the following method. Three g. of wheat together with 10 cc. of concd. sulfuric acid, 20 cc. of concd. nitric acid and 20 cc. of 5% hydrogen peroxide were heated in a Pyrex flask until destruction of the organic matter was complete. Phosphorus was then determined in the clear liquid.

In making an analysis, 0.3 g. of ash obtained by the peroxide method was taken up with a few cubic centimeters of concd. hydrochloric acid and evaporated to dryness. After the silica was filtered off, phosphorus was determined by the gravimetric pyrophosphate method. Calcium was determined in the filtrate from the yellow precipitate by the volumetric permanganate method and magnesium was determined in the filtrate from calcium by the method of B. Schmitz. A 0.2g. sample was taken for the potassium determination by the perchloric acid method. Lipoids were determined by a method described in a recent publication by the authors.[1]

In Table I, the wheats from each separate area are arranged as nearly as possible in order of their quality as regards protein content and physical characteristics of their glutens.

Discussion

In the ash of the wheats examined, the percentage of phosphorus, calcium and potassium showed no direct relationship to wheat quality. In general, the softer wheats showed a higher percentage of potassium oxide, though a high percentage of potassium oxide was likewise found in stronger wheats where the phosphorus pentoxide was below average.

There is, however, a definite relationship between the percentage of magnesium oxide and the quality of the wheats, the magnesium oxide content being 3–4% higher in the strong wheats grown in Canada and the Northwest than in the softest wheats analyzed, which were grown in California. Samples 5, 6 and 7, of Kota, Marquis and Quality (Table I) were all grown on the same soil at the University of North Dakota Agricultural Experimental Station. Samples 17, 18, 19 and 20 were grown at

[1] Accepted for publication by *Ind. Eng. Chem.*

TABLE I

ANALYSIS OF WHEATS[a]

No.	Variety	Location	Wt. per bushel, lbs.	Protein, % (N × 5.7)	Gluten, %	Gluten quality	Analysis of ash: Ash, %	MgO, %	CaO, %	P_2O_5, %	K_2O, %	SiO_2 + C %	Total, %
1	Marquis	Outlook, Montana	58½	19.65	16.28	Very good	1.90	16.30	3.14	46.05	33.35	1.06	99.90
2	Marquis	Alberta, Canada		18.95	15.09	Good	1.827	16.10	3.50	51.01	28.83	2.33	101.77
3	Garnet	Indian Head, Saskatchewan, Canada W. H. Gibson Experimental Farm	59	18.13	15.01	Good	1.700	16.00	3.15	44.24	33.00	1.90	99.29
4	Marquis	Western North Dakota		15.09	14.97	Good	2.005	15.69	2.83	50.67	28.48	1.67	99.34
5	Kota	Agricultural Experiment Station, Grand Forks, North Dakota (Nos. 5–7)		15.64	14.20	Elastic but soft	2.184	15.68	2.58	54.42	25.45	1.14	99.27
6	Marquis			14.08	13.08	Good	2.231	15.35	2.06	54.09	26.01	1.43	98.94
7	Quality			14.06	12.09	Soft, weak	1.883	15.56	2.94	49.73	28.14	1.50	97.87
8	Amber Durum (Mixed with small amt. of spring)	Stain, South Dakota	60½	14.06	13.86	Fair	1.870	15.00	3.38	50.57	31.00	1.09	101.04
9	Turkey Red	Dupree, South Dakota	59½	13.64	12.00	Poor	2.075	14.25	3.38	50.74	28.75	1.10	98.22
10	Red Durum (Slight amt. of spring)	Langford, South Dakota	60	13.67	13.42	Poor	2.140	13.76	2.55	50.77	31.45	1.50	100.03
11	Kansas A	Kansas		16.02	13.41	Good	2.209	13.50	3.75	51.06	29.50	1.63	99.44
12	Kharkof	Manhattan, Kansas	59	15.76	13.04	Good	1.724	15.30	4.47	46.53	31.79	1.26	99.35
13	Kansas B	Kansas		12.24	10.95	Poor	2.146	14.78	3.00	50.53	28.80	2.10	99.21
14	Missouri A	Central and Western Missouri		13.78	12.08	Fair	1.991	14.54	2.68	53.29	27.75	1.27	99.53
15	Missouri B	Valley Land near St. Louis, Missouri		11.19	10.27	Very poor	2.117	13.10	3.15	53.63	27.83	1.66	99.37
16	Dicklow	Oregon		13.03	10.45	Very poor	1.952	13.37	3.33	51.10	29.92	1.46	99.18
17	White Australian	Agricultural Experimental Station, Davis, California (Nos. 17–20)		12.02	9.03	Very poor	1.994	13.30	2.09	52.88	30.76	0.80	99.83
18	Early Baart			11.58	10.11	Very poor	2.098	12.72	2.44	52.10	31.37	1.10	99.73
19	Little Club			11.30	9.68	Very poor	2.104	12.47	2.85	49.50	33.01	1.43	99.26
20	Sonora			10.43	9.10	Very poor	1.954	11.47	3.26	51.45	30.89	1.37	98.44

[a] All results calculated to dry basis.

the California Experimental Station at Davis. The wheats within these two groups of samples are, therefore, the most comparable and interesting. It will be noted that the Montana and the two Canadian wheats, Marquis 1 and 2 and Garnet 3, have a protein content of 18% upwards, while the magnesium oxide in the ash is extremely high (16% and up), the magnesium oxide increasing progressively with the protein. Marquis 4 grown in North Dakota comes next with a protein content of 15.09% and a magnesium oxide content in the ash of 15.69%. Kota, Marquis and Quality from the experiment station at Grand Forks show protein contents ranging from 14.06 to 15.64%, with magnesium oxide 15.35 to 15.68%, all close together. Of these three samples, Kota had the highest protein, 1.5% above either Marquis or Quality, but its gluten was soft and it made a poorer loaf of bread than Marquis. From South Dakota are listed two Durum wheats and Turkey Red. Amber Durum is decidedly the best of these three samples, showing the highest protein (14.06%), the highest and best gluten, and the highest magnesium oxide of the group. In the series from Kansas was found the one real exception of the table—Kansas A. This wheat, equal to Kharkof and of excellent quality, was distinctly better in every way than the wheat Kansas B, yet Kansas B had a magnesium oxide content 1.2% higher. Kansas A and B were not grown on the same soil. Kansas B was partly germinated at the time of analysis, which might explain the difference to some extent. From Missouri the wheats employed are labeled Missouri A and B. A was superior to B (which was soft and starchy) in every test and showed a higher magnesium oxide content. In the remaining soft wheats, Dicklow from Oregon and the California varieties (all grown at Davis, California) show a direct relation of protein to magnesium oxide in the ash. None of the softer wheats from Missouri, Oregon or California showed as high a magnesium oxide content as the harder wheats. In these experiments magnesium oxide followed the protein content still more closely in wheats grown on the same soil.

It would be unwise to generalize on results of comparatively few samples when so many species and varieties of wheats are grown on soils whose composition varies widely. Too many factors influence the composition of wheats—climate, irrigation, soil, etc.—to make inflexible statements which admit of no exception. Nevertheless, the direct relation of magnesium oxide to protein in the wheat would merit further study, particularly of the way in which magnesium is held in the organic complex with reference to nitrogen.

The role of magnesium in the nutrition of cereals has been studied but little and our knowledge is most fragmentary. That magnesium is an important plant food is evident from its constant and abundant occurrence in the seeds of grain. Magnesium is present in chlorophyll. It is also known that this mineral takes some part in the transfer of phosphoric acid through the plant tissues.

Lipoid-Protein Ratio of Wheats and its Importance

In a recent article by the authors it was shown that the percentage of lipoids in glutens from straight and clear flours milled from a hard wheat was greater than that contained in the gluten from the patent flour of the same wheat. The conclusion was that lipoids must also be a most important factor in determining wheat quality. In Table II the lipoid contents of a number of the wheats are given. The lipoid content of all

Table II

Lipoid Content, Lipoid-Gluten and Lipoid-Protein Ratio of Wheats[a,b]

		Lipoid, %	Lipoid/gluten	Lipoid/protein
1	Marquis	2.76	0.1695	0.1405
3	Garnet	3.25	.2165	.1793
4	Marquis	3.40	.2270	.2253
5	Kota	3.20	.2254	.2046
6	Marquis	2.30	.1758	.1633
7	Quality	2.94	.2432	.2091
8	Amber Durum	3.84	.2771	.2731
10	Red Durum	3.70	.2758	.2707
11	Kansas A	2.77	.2066	.1729
13	Kansas B	2.85	.2603	.2328
14	Missouri A	2.53	.2094	.1836
15	Missouri B	3.47	.3378	.3101
17	White Australian	2.62	.2901	.2180
18	Early Baart	2.99	.2958	.2582
19	Little Club	3.25	.3357	.2876
20	Sonora	3.11	.3417	.2982

[a] For gluten and other analyses on these wheats see Table I.

[b] All results calculated to dry basis.

samples varied within a very narrow limit, 2.53–3.84%. It might be expected from preceding work, relative to the injurious effect of an excess of phosphatides on the physical characteristics of gluten, that the better wheats would naturally contain less lipoids than the poorer varieties. In some cases, the softer wheats show the same or slightly lower percentage than the better samples. If, however, the ratio of parts of lipoid per parts of gluten or protein is calculated, it will be found that this figure will give a valuable index as to the gluten and value of wheats—the higher numerical values being given by the softer wheats. In the case of Sonora, the poorest sample examined, the ratio of lipoid to protein was 0.2982, while in the case of the strongest wheat, Marquis from Outlook, Montana, the lipoid-protein ratio was only 0.1405. Likewise, the lipoid-protein or lipoid-gluten ratios seem to give an index as to what is commonly referred to as the "softness" of a gluten. In Samples 5, 6 and 7, all grown at Grand

Forks, North Dakota, the Marquis having a protein content of 14.08% had the best and most elastic gluten and made the best bread. The ratio of its lipoid to protein was very low. Kota, although it has a larger amount of protein and gluten than either Marquis or Quality, had a fairly elastic gluten which was much softer than the Marquis sample. Quality, containing as much protein as Marquis, had a soft, rather weak gluten and its ratio is higher than either Marquis or Kota. It is interesting to note the relatively high percentage of lipoids in the two Durum wheats, suggesting, perhaps, a relation between the color and the lipoid content.

In the three wheats, Garnet, Marquis 4 and Australian, the ratio of phosphorus pentoxide in the ash to the phosphorus pentoxide in the lipoids was calculated. Garnet, a hard wheat having a phosphorus pentoxide content of only 44.07%, Marquis, hard, and Australian, a soft wheat with a relatively high percentage of phosphorus pentoxide in the ash, all showed a fairly constant relation of phosphorus pentoxide in the ash to phosphorus pentoxide in the lipoids. This ratio varied from 23.85–26.04%.

Table III

	P_2O_5 in ash, %	P_2O_5 in lipoid, %	Ratio, P_2O_5 in ash/lipoid
Garnet	44.07	1.743	25.28
Marquis	52.99	2.222	23.85
Australian	52.68	2.023	26.04

The authors wish to thank Professor Harry Snyder of the Russell-Miller Milling Company and Professor Maurice Javillier of the University of Paris for their interest in this work.

Summary

In analyses of twenty wheats of widely different character and origin it was found that:

1. The magnesium content bore a direct ratio to the strength of wheats as determined by protein percentage and gluten quality.

2. The percentage of calcium, potassium and phosphorus in the ash showed no distinct relation to the quality of the wheats.

3. The lipoid contents of the wheats examined varied within very narrow limits, 2.53–3.84%. The ratio of lipoid to gluten or protein gives valuable information as to the character of the gluten and quality of wheat. The higher ratios are shown by the softer wheats.

Minneapolis, Minnesota