THE RELATION OF PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION TO MEALINESS IN THE POTATO. II. CHEMICAL COMPOSITION[1]

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INTRODUCTION AND LITERATURE REVIEW

In a previous paper (30), some experimentally determined relationships between mealiness and certain physical properties of the potato were described. This paper is a report of studies on the chemical composition of potatoes and its relationship to mealiness.

Many investigations (3, 6, 13) have dealt with the chemical composition of potato tubers. Likewise, many experiments have been conducted to determine the relationships between various chemical components and quality characteristics of potatoes. Only papers of the latter type related to this report are reviewed.

Several characteristics which may be attributed to physiological changes occurring in the raw tuber have a definite effect on the cooking quality of potato tubers. For instance, high sugar content imparts a sweet taste to boiled potatoes which is generally considered to be undesirable. Appleman (2) showed that increases in sugar content during storage of tubers at approximately 32° F. was at the expense of starch. Sweetman (29) states that tubers will become sweet when stored at any temperature below 40° F. and that sugar accumulation is detrimental to flavor, mealiness and other culinary qualities. The sugar content of tubers which have been stored at low temperatures can be reduced by conditioning at 68-72° F. for 10-14 days which in effect removes accumulated sugars by increasing respiration rates and/or partially reconverting sugar to starch. It is of considerable value to be able to predict general quality of tubers and from results of relatively recent experiments, Heinze *et al* (15) concluded that dry matter, alcohol insoluble solids, starch content and specific gravity all gave reliable quality predictions.

Several studies on the relationships between nitrogen compounds and quality of potatoes have been reported. As early as 1897, Coudon and Bussard (10) reported that the ratios of nitrogen and protein nitrogen to starch were highest for non-mealy potatoes and lowest for mealy tubers. Rathsack (27) reported that high nitrogen content appeared to have a deleterious effect on palatability. Harcourt (14) and East (12), however, found no relation of nitrogen or protein nitrogen to quality of potatoes. Of considerable interest are also the physical and chemical nature of the proteins and other nitrogenous components of the potato. The early fractionation of potato proteins by Osborne and Campbell (26) and a series of more recent investigations, notably by Neuberger and Sanger (24), Chick and Slack (7), Slack (28), Levitt and Todd (21) and Levitt (18, 19, 20) describe potato proteins in some detail.

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The relation of starch content to mealiness in the potato has been recognized for some time. The positive correlation of starch content with mealiness has been shown by a number of investigators (5,8,9). However, simple starch determinations yield no information concerning the two components of starch and their relative concentrations. By a spectrophotometric assay for amylose, McCready and Hassid (22) determined the amylose/amylopectin ratios for various starches and found that potato starch contained about 25 per cent of the straight chained polymer amylose, the rest being the branched chain polymer, amylopectin. Because of the different physical properties of these two starch components (16), variations in the relative concentrations of each could well alter the gelling properties of starch granules and thus affect mealiness of boiled potatoes. Some evidence that the gelling properties of different tuber groups vary has been presented by the authors in a previous paper (30).

MATERIALS AND METHODS

Conditions and cultural practices under which the potatoes that were used in these experiments were grown are described elsewhere in this journal (30). Wherever possible, the same tubers which had been used for organoleptic tests were used for subsequent chemical analysis. Where separate tubers were used, these were drawn from tuber lots that had received the same post-storage conditioning treatments as those used for organoleptic tests.

1. *Dry Matter*:

Dry matter was determined by treating raw, ground tubers with a constant volume of 0.5 per cent sodium bisulphite to prevent excessive air oxidation and then drying the samples of tissue first at 67° C. and then to constant weight at 85-90° C.

2. *Ash Determinations*:

Portions of raw, ground tissue (no bisulphite added) were dried to constant weight and this material was used for ash determinations. A constant volume of magnesium acetate was added to the samples of pulverized dry tissue and these mixtures were then ignited in an electric muffle furnace at 750-800° C.

3. *Nitrogen Content*:

Nitrogen determinations were carried out on dried tissue (bisulphite added during drying) as follows. The tissue samples were partially digested with concentrated sulphuric acid until a translucent, brown liquid was obtained. This solution was then adjusted to a desired volume with distilled water and the nitrogen in small volumes of the diluted solutions determined using the method of Lanni, Dillon and Beard (17). The solubility of the nitrogenous components was determined by extracting weighed quantities of finely ground, raw tissue with distilled water, dilute salt solution, or 85 per cent ethanol (aqueous) and then determining the nitrogen content of these solutions.

4. *Analyses for Soluble Sugars*:

Soluble sugars were determined by the Lane-Eynon method (25) and by paper chromatographical analysis. Simple sugars were extracted with hot 85 per cent ethanol. Aqueous solutions of the sugars were used in the Lane-Eynon method. Alcoholic solutions were used in the quantitative chromatographical analysis as follows: microliter quantities of solution were transferred to paper chromatograms which were developed for 36-40 hours using n-butanol ethanol: water as the irrigant. The sugar bands were located by spraying narrow marginal strips with Tollens reagent. The sugars were eluded from the paper with water and then determined quantitatively by the phenol-sulphuric acid spectrophotometric method of Smith *et al.* (11).

5. *Determination of Non-Starch Polysaccharide*:

Pulverized lyophilized tissue was soaked in water, filtered through asbestos Gooch filters, and the soluble proteins removed by precipitation with trichloroacetic acid. The solutions did not give a color with iodine — KI reagent. The sugar content was determined directly on the aqueous extract. The amount of polysaccharide was calculated by subtracting from the obtained values the total soluble sugar values previously determined by chromatographic analysis.

6. *Determination of Starch Content*:

Starch content was determined by acid hydrolysis and by the polarimetric method of Balch (4). In the acid hydrolysis, samples of dried, ground tissue were hydrolysed in sealed tubes using 0.5 N sulphuric acid. After neutralization of the hydrolysates with barium carbonate, the material was filtered while hot, the precipitate washed several times with hot water, the final volume of filtrate evaporated under reduced pressure, and the residue dissolved in 95 per cent ethanol. The amount of glucose was determined chromatographically.

7. *Fractionation of Pure Starch*:

In order to conduct some of the experiments described in succeeding paragraphs. it was necessary to obtain pure starch from the different specific gravity tuber lots of each of the three varieties. Raw tubers were thoroughly macerated in a Waring blender using 0.5 per cent sodium bisulphite solution as the initial extractant. The starch granules were separated from the lighter non-starch material by a series of centrifugations and re-suspensions until a white, granular product was obtained. The starch was dried by extraction with absolute ethanol, acetone, and ether in that order and then ground in a Wiley mill to pass a 60 mesh screen, and finally passed through a 120 mesh bolting silk screen. The purity of the final product was determined by hydrolysis of small quantities of the starches in the usual manner followed by chromatographic and polarimetric determinations of glucose. The starch samples were further analyzed with respect to purity by the method of Balch (4) and comparing the experimental figures with the reported specific rotation of starch (+193°).

8. *Fractionation of Amylose*:

Starch, from one of the prepared samples, was fractionated into amylose and amylopectin using the method of Montgomery, Hellman and Senti (23). The amylose obtained by this method was further purified by fractional precipitation with alcohol. An amylose fraction was obtained which gave $E^{1\%}_{1\,cm.}$ value similar to that obtained for a reference sample of amylose prepared by another method. The amylose sample obtained was used as a standard in the determination of amylose-amylopectin ratios of the various starch samples.

9. *Determination of Amylose — Amylopectin*:

The various starch samples were analyzed for amylose content by the method of McCready and Hassid (22). Instead of using 100 milligram quantities suggested in this method. 500 milligram quantities were used to ensure better sampling. A number of determinations were made for each starch sample.

10. *Periodate Oxidation Studies*:

Small amounts of amylose and amylopectin were subjected to periodate oxidation following essentially, the method of Abdel-Akher and Smith (1). Similarly, periodate oxidations were carried out on various potato starches. Using the combined data from these experiments, the previously determined amylose-amylopectin ratios, and the amount of formic acid produced in the oxidation of amylose, the incidence of branching of the amylopectins of the various starch samples was estimated.

RESULTS AND DISCUSSION

The dry matter, ash and protein contents of tubers from the 1954 crop are given in table 1. Although there is a fairly close correlation between mealiness and dry matter content, this association does not hold for varietal comparisons. Whereas differences between the dry matter contents of high specific gravity Red Pontiac, Cobbler and Waseca are small, the mealiness score of the Red Pontiac sample is significantly lower than those of the other two varieties. Similarly, in the comparison of lower specific gravity tuber lots, only small differences in dry matter exist but Waseca was scored significantly higher in mealiness than the other two varieties. Within varieties, mealiness is directly proportional to dry matter content (and specific gravity) in Cobbler and Waseca, but not in Red Pontiac.

The ash content of raw tubers of Red Pontiac appears to be somewhat higher than in comparable lots of the other two varieties. This difference is not evident in the boiled tubers. As indicated by the correlation coefficients, there is little, if any, association between mealiness and ash content.

Total crude protein in both raw and boiled tubers appears to be inversely related to specific gravity. However, little association between protein content and mealiness is apparent. Solubility studies show that more than ⅔ of the total extractable nitrogenous material was dialyzable. This indicates that most of the nitrogen is present as small polypeptides, free amino acids or nitrogen bases. The data in table 1 indicate that mealiness is negatively correlated with the content of nitrogenous material solution in 85 per cent ethanol. This association would be of real significance if, for instance, the simple nitrogenous compounds in some manner acted as "mortar agents" between gelatinized starch granules or as anti-swelling agents by forming a protective layer around the partially gelatinized starch granules.

Sugar, polysaccharide and starch contents are presented in table 2. The rather high concentrations of total sugars in Red Pontiac tubers

TABLE 1.—*Dry matter, ash, and protein content of potatoes differing in variety and/or specific gravity and the mealiness scores of each tuber lot.*

Variety and Spec. Gravity	Mealiness Score	Dry Matter	Ash in Dried Tissue of		Crude Protein in:		"Protein" Soluble in 85 per cent Ethanol
			Raw Tubers	Boiled Tubers	Raw Tubers	Boiled Tubers	
		Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Red Pontiac							
1.065	3.0	17.9	......	......	......	......	......
1.080	5.2	23.8	4.29	3.47	8.39	7.20	1.58
1.100	4.9	26.2	3.70	2.90	7.50	6.51	1.68
Cobbler							
1.080	5.4	24.0	3.64	3.31	9.45	7.73	1.64
1.100	7.9	27.3	3.24	2.88	7.37	7.02	1.15
Waseca							
1.080	6.2	24.9	3.60	3.35	8.97	8.18	1.15
1.100	8.0	27.7	3.64	2.87	7.27	7.12	1.17
"*r*"—With mealiness		.88*	—.61	—.57	—.66	—.01	—.87*

*Correlation coefficient significant at the 1 per cent level.

and in low specific gravity Cobbler and Waseca may, to some extent, account for the lower degree of mealiness of these tuber lots. The high concentrations of sugars, and soluble polysaccharides may act in the same manner as previously suggested for the small molecular weight nitrogenous compounds.

Although mealiness is apparently negatively correlated with polysaccharide content, low specific gravity Waseca tubers contained approximately the same amount of polysaccharide as did Red Pontiac tubers, yet were scored significantly higher for mealiness. This points out that mealiness cannot be related to a single factor but is most probably affected in varying degree by a combination of factors.

The data for starch content are also shown in table 2. Since the values obtained by different methods were in reasonably close agreement, only those obtained by acid hydrolysis are shown. In general, starch content was directly proportional to specific gravity. However, it should be noted that tubers of identical specific gravity but differing in variety do not necessarily have the same starch content. Low specific gravity Red Pontiac had a lower starch content than comparable samples of Cobbler and Waseca. Although a positive relationship between mealiness and starch content is evident, the low mealiness score of high specific gravity Red Pontiac cannot be explained on the basis of starch content alone.

The results from a number of tests suggested that the prepared starch samples (which were later used for amylose determinations) were reasonably pure. In a series of acid hydrolyses of the different starch samples, the specific optical rotations of the solutions after 5 hours hydrolysis ranged from 51.1° to 53.9°. The glucose recovered chromatographically ranged from 95.7 to 97.9 per cent of the theoretically expected amount of glucose. These values are within a reasonably narrow error

TABLE 2.—*Glucose, fructose, sucrose, total sugar, polysaccharide and starch contents of potatoes differing in variety and/or specific gravity.*

Variety and Spec. Gravity	Mealiness Score	Percentages (On a dry wt. basis) of: Glucose	Fructose	Sucrose	Total Sugar	Polysacc. as Glucose	Starch
Red Pontiac							
1.065	3.0	......	......	......	......	5.91	63.0
1.080	5.2	1.93	1.42	2.08	5.43	4.06	66.5
1.100	4.9	1.31	1.06	1.61	3.98	2.27	78.6
Cobbler							
1.080	5.4	0.86	0.43	1.19	2.48	2.55	73.6
1.100	7.9	0.38	0.21	0.55	1.14	1.41	79.6
Waseca							
1.080	6.2	0.41	0.58	1.22	2.21	2.39	70.6
1.100	8.0	0.59	0.25	0.57	1.41	1.39	77.3
"*r*" with mealiness					—.82*	—.88**	.94**

range. Further tests for purity included the measurement of optical rotation of starch solutions according to the method of Balch (4) and then relating the specific rotations to samples of starch of known purity. The results obtained are shown in table 3. The data show that the samples were of a high degree of purity and it appears that the rotation values reported for pure starch should be revised upward.

Using the method of McCready and Hassid(22), the amylose that was fractionated from one of the starch samples was compared to reference samples of amylose and was found to compare favorably. Using the prepared amylose sample as a reference standard in the preparation of a standard curve, the amylose contents of the various starch samples were determined by the method mentioned above. The results are presented in table 4. In general, starch from the low specific gravity tubers contained less amylose. Cobbler and Waseca tubers contained more amylose than did Red Pontiac tubers of the same specific gravity. Mealiness and amylose content are positively correlated. It should be noted that the low specific gravity Waseca tubers scored higher in mealiness than the low specific gravity Cobbler, and also contained more amylose.

The relative amounts of the two components of starch, amylose and amylopectin, may be important in influencing mealiness of potatoes because of differences in the chemical and physical properties of these components. Amylose exists as long alpha — 1,4 — linked polyglucosan chains. This chain is spacially arranged in the form of a spiral or helix, and upon treatment of a solution of amylose with iodine — KI reagent, the typical blue to purple iodine--amylose complex results.

Because of the straight, unbranched chain arrangement of amylose, parallel alignment of the individual chains and strong hydrogen bonding occurs and leads to a rigid crystalline complex. This tendency toward chain alignment causes amylose to retrograde rapidly after it has been dissolved in hot water and allowed to cool.

TABLE 3.—*The purity of the starch samples as determined by the optical rotation of starch solutions, concentration 1 per cent.*

Variety	Specific Gravity	Observed *L*	$[L]^{22}_{D}$	Purity Per cent*
Red Pontiac	1.065	1.86	204	105.8
	1.080	1.90	209	108.1
	1.100	1.90	209	108.1
Cobbler	1.080	1.87	205	106.5
	1.100	1.87	205	106.5
Waseca	1.080	1.89	207	107.6
	1.100	1.85	203	105.2
Corn Starch		1.83	201	104.1

*Values based on the reported specific rotation of starch of 163°.

TABLE 4.—*Amylose contents of starch from the different tuber lots.*

Variety	Specific Gravity	Mealiness Score	Per cent Amylose: In Pure Starch	In Lyophilized Tissue	On Fresh Wt. Basis
Red Pontiac	1.065	3.0	26.9	16.9	3.13
	1.080	5.2	31.6	21.7	5.17
	1.100	4.9	33.6	26.3	6.66
Cobbler	1.080	5.4	32.8	24.5	5.88
	1.100	7.9	36.0	29.7	8.10
Waseca	1.080	6.2	36.7	27.2	6.79
	1.100	8.0	35.2	28.7	7.81
"r" with mealiness			0.86*	0.90**	0.93**

Amylopectin is also an alpha -1, 4- linked polyglucosan but an additional linkage exists in that periodically a branch point occurs in which a 1,4,6 linkage is involved, the C_6 of a glucose molecule of one chain linked to a C_1 glucose of the other chain. This type of branching gives amylopectin an arborescent structure more easily hydrated and consequently more water soluble. Amylopectin shows very little, if any, tendency toward retrogradation.

Because of these differences in physical properties, high concentrations of amylose in potato starch may confer greater mealiness while high amylopectin content may cause pastiness in boiled and mashed potato tissue. The relationship apparent between amylose content and mealiness, as shown in table 4, agrees with this supposition.

The solution tendency of amylopectin could conceivably vary somewhat depending on the degree of branching or the length of the repeating unit. Thus, short chain lengths of the repeating unit result in a denser "tree-like" molecule, whereas longer chain lengths would give a more open structure. The chain lengths of the repeating units of amylopectin in the different starch samples as determined by periodate oxidation studies are presented in table 5. Short chain lengths indicate a greater branching frequency. The less mealy samples apparently contain amylopectin with a greater degree of branching than do the more mealy samples. Since, as indicated previously, the hydration of the more highly branched chains would be greater, this factor could conceivably contribute to pastiness or stickiness of boiled potato tissue. This observation warrants further study.

TABLE 5.—*The chain lengths (moles anhydro-glucose per repeating unit) of amylopectin in starch of the different tuber lots.*

Variety and Spec. Gravity	Mealiness Score	Moles Anhyd. Glucose/ Repeating Unit*
Red Pontiac		
1.065	3.0	16.6
1.080	5.2	15.5
1.100	4.9	14.8
Cobbler		
1.080	5.4	16.4
1.100	7.9	18.2
Waseca		
1.080	6.2	18.1
1.100	8.0	18.4
"r" with mealiness		.69

*Calculated on basis of amylopectin content of the starch sample.

SUMMARY AND CONCLUSIONS

1. Chemical characteristics which were found to be associated with mealiness are:
   (a) dry matter content, (b) starch content, (c) sugar and polysaccharide content, (d) content of small molecular weight nitrogen compounds, and (e) amylose content.
2. Mealiness is apparently not associated with (a) crude protein content and (b) ash content.
3. Characteristics which need further investigation to determine more precisely their relation to mealiness in potatoes are: (a) the nature of the polysaccharides that are apparently present in potatoes, (b) the physical effects of high concentrations of soluble sugars, polysaccharide and nitrogen-containing compounds on gelling of starch granules in potato tubers, and (c) the molecular structure of the two components of potato starch — amylose and amylopectin.

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