Fatty Acid Composition of Buckwheat Seed[1]

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Abstract

The embryo, endosperm, testa and pericarp from seeds of three buckwheat species were analyzed for total lipid content and fatty acid composition. The average lipid content of these tissues was 8.2%, 0.4%, 2.0% and 0.5%, respectively. Eighteen fatty acids were tentatively identified in buckwheat oil. The following eight constituted an average of more than 93% of the total acids: palmitic, stearic, oleic, linoleic, linolenic, arachidic, behenic and lignoceric acids. The embryo tissue of cultivated and Tartary buckwheats contained the fewest minor acids with an average of 95% of the acids containing either 16 or 18 carbons. The pericarp, or hull, had a unique composition with higher levels of saturated acids, odd carbon acids and acids of 20 or more carbons than any other tissues. The compositions of the testa and endorsperm were intermediate.

Introduction

Lipids represent a very small portion of the chemical constituents in cereals but have been implicated in the deterioration of stored seed and flour (1, 2). In recent years some cargos of buckwheat subjected to prolonged storage and transit to the Orient have produced inferior flour when milled and used in the production of noodles. Little information is available on the total lipids of buckwheat or how milling affects the levels of fatty acids in the flour. Belova et al. (3) reported that palmitic, oleic, linoleic, linolenic and gondoic acids account for about 95% of the fatty acids. They detected a total of 11 fatty acids in the whole seeds of cultivated buckwheat. Similar findings were reported in wild buckwheat (4). Although no information is available on the distribution of fatty acids within buckwheat seed, reports on cereals, specifically wheat, indicate that fatty acids are not distributed uniformly; therefore the type of tissues included in the flour directly affect its composition (5).

This study was conducted to identify the fatty acids present in the oil of buckwheat seed, to examine the distribution of fatty acids in the seed tissue, and to determine if the fatty acid composition or distribution patterns characterized different species or cultivars of buckwheat.

Experimental Procedures

Seed of three morphologically distinct species, cultivated, *Fagopyrum sagittatum* (Gilib.), Tartary, *F. tataricum* (Gaertn.) and wild buckwheat, *Polygonum convolvulus* L., were analyzed. Two cultivars, Silverhull and Tokyo of *F. sagittatum* were examined.

The seed was obtained from samples grown at the same location in the same year and represented commonly available buckwheat. Seeds of good quality were selected and soaked for a short period to facilitate dissection into pericarp, testa, endosperm and embryo fractions (Fig. 1). The fractions were dried, ground and extracted with petroleum ether (30–60 C) for 8 hr. The solvent was removed under vacuum and the oil dried, weighed and stored under nitrogen. Aliquots of oil were saponified and the fatty acids converted to methyl esters with 5% BF_3 in methanol (6). A portion of the esterified oil was subsequently hydrogenated to aid in identification. Approximately 30 mg of ester, 1 ml of methanol and 5 mg of 10% palladium on carbon were added to a screw cap vial. Hydrogen was bubbled in for 8 min, the vial sealed and then heated for 45 min with frequent shaking. After cooling, the esters were transferred to hexane, dried, then taken up and injected into the GC in carbon-disulfide. All gas liquid chromatography (GLC) determinations were conducted on a Model 5750 F and M gas chromatograph equipped with a flame ionization detector and operated under the conditions specified in Table I.

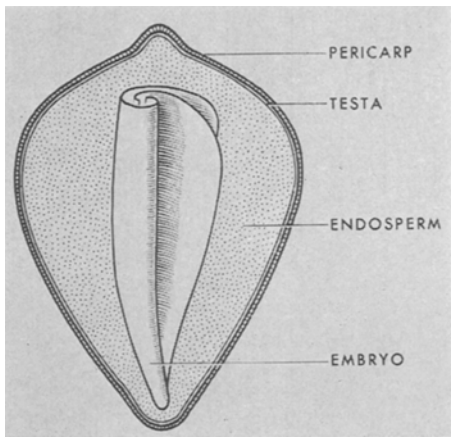

FIG. 1. Diagram of a buckwheat seed showing position of tissues analyzed.

Component fatty acids were tentatively identified by comparing the equivalent chain lengths (ECL) (7) of the unknown acids with those of pure reference fatty acids (Applied Science) and reported values (8). Some fatty acids were also cochromatographed. Retention times and per cent composition of the various fatty acids were determined by electronic integration.

Results and Discussion

Distribution of Oil in Buckwheat Seed

The lipids were concentrated in the embryo tissue (Table II). In cultivated and Tartary buckwheats, this tissue contained an average of 6.5% oil, whereas in wild buckwheat, the content was 13.6%. However, because the embryo of wild buckwheat was propor-

TABLE I

Column Specifications

	Column liquid phase		
	DEGS	DEGA	SE-30
Liquid phase content, %	17	17	20
Solid support	Chromsorb W(AW-S)	Chromsorb W(AW-S)	Diatoport (S)
Column size, cm	4.8 × 152	4.8× 152	4.8 × 183
Carries flow, ml/min	65	65	75
Oven temperature, C	190	200	230

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TABLE II

Distribution of Dry Matter and Oil Among Components of Buckwheat Seeds[a]

Tissue	Buckwheat types	Proportion of seed, %	Oil content, %	Proportion of total oil, %
Pericarp	Silverhull	23.2	0.4	5.1
	Tokyo	20.1	0.9	8.8
	Tartary	24.6	0.3	4.0
	Wild	42.2	0.3	7.7
Testa	Silverhull	13.7	2.3	18.2
	Tokyo	12.0	2.5	18.3
	Tartary	14.0	1.6	13.1
	Wild	15.0	1.8	19.3
Endosperm	Silverhull	44.4	0.3	6.9
	Tokyo	52.2	0.3	10.1
	Tartary	40.2	0.2	4.4
	Wild	36.1	0.6	15.7
Embryo	Silverhull	18.7	6.5	69.8
	Tokyo	15.7	6.5	62.8
	Tartary	21.2	6.4	78.4
	Wild	6.1	13.6	57.3

[a] Moisture-free basis corrected for loss of tissue during dissection of seed.

tionately smaller, it actually contributed less to the total oil content than embryos of the other buckwheat types.

The endosperm and the pericarp, or hull, each contained about 0.5% oil. The testa, or true seed coat, on the other hand, contained 1.6–2.5% oil (13–19% of the total seed oil) depending upon the type of buckwheat analyzed.

Since buckwheat milling normally involves removing the pericarp and grinding all remaining tissues into flour, it is perhaps more meaningful to report the lipid content of the groats. The appropriate values for Silverhull, Tokyo, Tartary and wild buckwheats were 2.1%, 1.9%, 2.2% and 3.2%, respectively.

The oil content and distribution in buckwheats did not vary greatly from values previously reported for most cereals (5) and indicated that the fat content of the milled product would vary directly with the amount and type of tissue removed.

Fatty Acid Composition of Buckwheat Types

A detailed analysis of four buckwheat types and their individual seed components revealed the presence of 23 fatty acids, 18 of which were tentatively identified.

Methyl heptadecanoate appears as a shoulder of 16:1, therefore, the values given may be inaccurate. On DEGS the ECL of 16:1 and 17:0 were 16.55 and 16.97, respectively. Values are not reported for 20:1 as it is completely hidden by 18:3 on the DEGS column. However, on DEGA, these two acids are separated. Two of the unknown acids, ECL of 15.4 and 23.5 (DEGS), are not modified by hydrogenation and have retention times very similar to iso 16 and iso 24 branched-chain fatty acids. However, no further proof of their existence is presented.

Fourteen of the known acids were present in all types and all tissues. The eight main acids which represented an average of more than 93% of the total acids are as follows in order of ascending concentration: arachidic, behenic, stearic, lignoceric, linolenic, palmitic, linoleic and oleic acids. Of these acids, the five 16 or 18 carbon acids are commonly found in all cereals. The long chain acids, arachidic, behenic and lignoceric, which represented an average of 8% of the total acids in buckwheat, are only minor components or are not present at all in cereals. However, such cereals as wheat and rye do contain numerous minor acids with 14 to 18 carbons many of which are monoenes (2,9–11). Branched-chain or odd car-

TABLE III

Total Fatty Acid Composition of Lipids From Seed Tissues and Calculated Values for Whole Seeds of Various Buckwheats

Fatty acid	Per cent composition																			
	Pericarp				Testa				Endosperm				Embryo				Whole seed[a]			
	Silverhull	Tokyo	Tartary	Wild	Silverhull	Tokyo	Tartary	Wild	Silverhull	Tokyo	Tartary	Wild	Silverhull	Tokyo	Tartary	Wild	Silverhull	Tokyo	Tartary	Wild
Unid.[b]	Trace[c]	1.0	0.2	0.8	0.1	0.2	0.1				0.1	Trace					Trace	0.1	Trace	Trace
12:0	1.6	1.7	0.8	1.8	0.3	0.4	0.2	0.6	0.6	0.6	0.2	1.0	0.2	0.3	0.2	0.2	0.3	0.5	0.2	0.5
13:0	1.2	1.0	0.4	1.0	0.3	0.2	0.5	0.2	0.5	0.4	1.0	0.5	0.1	0.2	Trace	0.2	0.2	0.3	0.2	0.3
Unid.		0.5	0.5	0.7	Trace	0.1	0.1	0.2			Trace	0.4		0.1		0.1		0.1	Trace	0.2
14:0	3.2	2.7	1.8	2.6	0.6	0.7	0.5	1.1	1.1	1.0	0.6	2.5	0.3	0.4	0.4	0.4	0.6	0.7	0.5	1.0
15:0	2.3	1.1	1.3	2.6	0.4	0.6	0.5	1.0	0.9	0.5	0.3	1.4	0.2	0.4	0.1	0.3	0.4	0.5	0.2	0.8
Unid.	1.0	1.6	1.0	1.8	0.1	Trace	0.3	0.4	Trace	Trace	Trace	1.0	Trace		Trace	0.2	0.1	0.1	0.1	0.5
16:0	11.6	11.8	11.3	11.4	16.8	16.4	13.2	10.4	19.0	20.0	14.9	16.8	17.4	16.1	14.2	10.8	16.6	16.2	13.9	11.7
16:1	3.4	3.4	2.7	2.3	0.8	0.4	0.7	2.2	1.4	Trace	0.9	4.8			Trace	1.6	0.4	0.4	0.3	2.3
16:2	0.8	0.8	1.3	1.7	0.2	0.3	0.6	0.9	0.6	0.4	0.6	3.3	0.2	0.2	0.1	0.8	0.2	0.3	0.2	1.3
17:0			1.3	1.8		0.4	0.3											0.1	0.1	0.1
18:0	4.2	2.5	5.0	4.9	2.2	2.2	2.8	2.2	3.0	2.2	3.6	3.7	2.2	1.9	1.6	1.6	2.4	2.0	2.2	2.3
18:1	14.6	15.8	19.6	18.4	28.7	28.8	33.9	33.2	31.0	32.5	34.7	35.5	36.6	35.9	40.5	33.2	33.6	32.5	38.5	32.4
18:2	20.9	13.0	25.5	25.7	32.7	31.4	27.6	29.5	31.0	33.0	28.0	16.3	32.4	32.9	36.8	35.9	31.8	30.9	34.7	30.8
18:3	3.4	3.8	2.9	4.2	6.1	6.4	4.4	6.2	5.4	5.7	3.5	2.6	6.0	6.5	3.0	2.4	5.8	6.2	3.2	3.3
20:0	5.0	5.3	3.8	3.3	2.4	3.3	2.8	1.0	1.8	1.6	3.1	1.8	1.6	1.6	1.1	1.4	1.9	2.2	1.5	1.5
20:1	4.9	6.6	3.8	2.6	0.5	0.5	0.6	1.2	0.7	0.6	0.9	2.4	0.2	0.4	0.2	1.4	0.5	1.0	0.4	1.6
20:2	6.2	5.8	4.2	0.1	2.8	2.9	4.0	1.2	1.8	0.9	2.4	1.3	1.5	1.7	0.8	1.1	2.0	2.2	1.4	1.1
22:0			1.6		0.4	0.3	1.2				1.2		0.1		0.3	1.1	0.1	Trace	0.5	0.6
22:1	8.6	12.0	4.2	3.1	0.5	0.6	0.6	2.0			0.7	1.2	Trace	0.1	Trace	1.0	0.5	1.2	0.3	1.4
23:0					1.1	1.2	0.4				Trace						0.2	0.2	0.1	.....
Unid.	7.0	9.7	6.8	5.6	2.1	2.4	2.7	5.5	1.1	0.6	3.2	3.4	0.9	1.3	0.6	4.6	1.4	2.2	1.2	4.7
24:0				3.8	0.8	0.3	2.0	1.0				Trace				1.7	0.1	Trace	0.2	1.5
Unid.																				

[a] Weighted average based on oil content and fatty acid composition of specific tissues.
[b] Unidentified fatty acids.
[c] Trace, <0.05%.

bon acids are not common or characteristic of wheat or other cereals.

The buckwheat analyzed represented three distinct species including the cultivated types and a weed. Although the analysis was replicated to avoid sampling errors, no attempt was made to study the range in fatty acid composition within a species or cultivar. It can be assumed that the composition would vary with the source of seed because of the inherent heterozygosity of buckwheat, and with the environment in which the seed was grown. However, in the material examined, all but three acids, heptadecanoic and two unidentified peaks were found in all types. The cultivated types, Tokyo and Silverhull, contained higher than average levels of palmitic and linolenic acids but were not unusual otherwise. Tartary buckwheat was characterized by the lack of minor acids; in fact, 93% of all acids contained either 16 or 18 carbon atoms. Less than 1% of the acids contained an odd number of carbon atoms. In contrast, more than 15% of the wild buckwheat seed oil was composed of acids that contained other than 16 or 18 carbons.

Distribution of Fatty Acids Among Seed Components

The four tissues examined had unique fatty acid compositions. However, when the compositions of individual tissues in the three species were compared, they were sufficiently consistent to permit certain generalizations to be made.

The embryo consistently had the largest proportion of unsaturated acids and the fewest minor acids, particularly those of 15 or less carbons. Considering only cultivated and Tartary buckwheats, 95% of the acids in the embryo contained either 16 or 18 carbons. In addition, the eight major acids accounted for all but 1.8% of the acids. The embryo tissue in these types was unique in that it was completely devoid of 16:1 and four of the five unknown peaks. The embryo of wild buckwheat, on the other hand, was distinctive since it not only contained these acids but also 20 of the 22 acids found in whole wild buckwheat seed. In addition, it contained almost double the amount of acids with 20 or more carbons when compared with other tissues. Most of this increase was due to lignoceric acid. With the noted exception of wild buckwheat, the embryo tissue contained fewer acids than any of the other tissues and greatly diluted the effect of the extreme composition of the pericarp. Because it contained an average of two thirds of the total seed oil, this tissue actually controlled the fatty acid composition of the whole seed.

The fatty acid compositions of the testa and endosperm did not differ greatly from the overall seed average and represented a compromise between the embryo and the pericarp. With a few exceptions, the fatty acid distribution pattern in the testa and endosperm of cultivated and Tartary buckwheat were quite similar. However, since these tissues are of different origin and development, they will be discussed separately.

The testa contained less oleic acid but considerably more of the long chain acids, especially linolenic and the unidentified acids, than the endosperm or the overall seed average. As was found with all tissues, wild buckwheat had a completely different distribution pattern. The short chain acids (less than 16 carbons) were present at higher levels while the concentrations of palmitic, arachidic and behenic acids were considerably lower than in the other types.

The endosperm of the buckwheat types studied contained less than 0.4% oil and therefore had a minimal effect on total composition. However, there were certain patterns worth mentioning. The most notable deviations were the high level of palmitic acid found in all types and the absence of the four unidentified acids in the cultivated types. In general, there was a small percentage of acids with 20 or more carbons. The fatty acid composition of oil from the endosperm of wild buckwheat followed the same trend as that of the testa.

Since the pericarp, which contained only 6% of the total oil, is removed during milling, the quality of the oil was only of academic interest. However, the fatty acid composition of the pericarp was radically different from all other tissues and the levels of individual and groups of acids were unique to this tissue. The pericarp perhaps can be best characterized by the unusually high level of saturation and the high proportion of acids with other than 16 to 18 carbon atoms. Most of this deviation can be attributed to the abnormal levels of odd carbon acids and to those acids of 20 or more carbon atoms. There was, however, a low level of the unidentified acids. As has been noted in the three tissues discussed, wild and, sometimes, Tartary buckwheat contained a proportionately larger amount of the minor acids than did the cultivated buckwheats. The reverse was true in the pericarp. The cultivated types contained almost twice the amount of odd carbon acids and a considerably higher level of saturated acids than either Tartary or wild buckwheat.

In many species the "fruit-coat fats," which are the combined fats from the pericarp and testa, contain an appreciably narrower range of component fatty acids than the remainder of the seed (12). This was not the case with buckwheats as both the pericarp and test contained a wider range of acids than the other tissues. Since the pericarp has a distinctive composition and is removed in milling, the composition of the groats were calculated to estimate the quality of the milled product.

As expected, the composition of the groats differed from the whole seed. The level of unsaturation increased, due primarily to an increase in oleic acid. The odd carbon chain acids in cultivated and Tartary seed decreased to an average of 0.6%, half the previous level. Further, there was a reduction in those acids with 20 or more carbons, particularly 23:0, but an increase in the level of the combined 16 and 18 carbon acids from an average of 90.8% to 93.0% of the total. In contrast, removing the hull had little effect on the composition of wild buckwheat.

Although the fatty acid distribution pattern in buckwheat deviated from most of the oilseed crops (13), there were a few exceptions. For example, the ratio of saturated to unsaturated acids was found to be the lowest in the embryo axis, intermediate in the test, and highest in the pericarp. The same trend was reported by Worthington (14) for peanuts.

It is hardly surprising that the four tissues analyzed had different fatty acid patterns since each is under different genetic and microenvironmental pressures. Although both the pericarp and testa are female tissues, the pericarp develops from the ovary wall while the testa develops from the ovule. The endosperm and embryo on the other hand are the result of gamete fusion and thus differ genetically from the

maternal tissue in which their development and lipid synthesis occurs.

Total lipids or high levels of specific fatty acids could play a role in the storage deterioration of buckwheat seed or flour. However, the lipid content of the buckwheats examined was no higher than that reported for most cereals (5) and the levels of linolenic acid or other acids capable of rapid autoxidation were relatively low.

This study has tentatively established the identity of 18 fatty acids in the oil from buckwheat seed. Four of these were found to be odd carbon fatty acids. Each of the buckwheat species examined had distinctive compositions and, as in most seeds, each of the seed components had a unique fatty acid composition.

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