A Comparison of the Amino Acid Composition of Two Commercial Oat Groats[1]

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Cereal Chem. 59(5):323-327

ABSTRACT

The crude protein content of commercially available dehulled oats averaged 14.97% for cv. Oxford, grown in eastern Canada and 13.30% for cv. Sentinel, grown in western Canada. Although the total lipid content (6.57%) and metabolizable energy (17.74 MJ/kg db) of western oat groats differs considerably from eastern grown oat groats (3.7%, 16.91 MJ/kg db), their crude fiber contents did not differ significantly and ranged from 3.4 to 3.7% of the elemental composition. Both commercial oat groats contained good quality protein, with an amino acid profile superior to that of other cereals and an excellent balance of essential amino acids limited only in lysine. The values obtained for methionine and cystine far exceeded those previously reported for other oat varieties, and the present analyses yielded values 10–15% higher for the sum of lysine, threonine, and methionine. Excellent recovery of tryptophan in oat groat proteins was achieved for the first time. 4-Hydroxyproline, previously thought to be confined almost exclusively to the collagens and elastin of vertebrates and invertebrates, was also found in both commercial sources of oat groats at 0.22 and 0.14 g/kg, respectively.

Oats is the third largest cereal crop in Canada and the fifth largest in the world. However, until recently, oats have served primarily as a feed grain for livestock in the temperate regions of the world. The main reasons for this are the high crude fiber content and the low metabolizable energy of the hulls, which make them unsuitable for human consumption. The dehulled seed (groat) resembles that of other cereals in that it consists of a starchy endosperm and an oily embryo. According to Cluskey et al (1979) and Pomeranz (1973), oats contain good quality protein and have the highest lysine content of the common cereals. Recently, new methods for production of mechanically dehulled oat groats and preparation of protein concentrates and isolates from oats were developed (Cluskey et al 1973, 1976, 1978; Wu and Stringfellow 1973; Youngs 1974). Although these new commercial oat products are very promising, their protein quality and nutritive value as food and feed have yet to be determined.

Feeding experiments with chickens (Sibbald 1979, Sraon et al 1975) and growing-finishing pigs (Anderson et al 1978, Wahlstrom and Libal 1979) have shown that high-protein oats are 82% digestible, produce an overall metabolizable energy of 72%, and may be a good replacement for more expensive protein concentrates in chicken and pig diets. According to Hischke et al (1968), oat proteins have protein efficiency ratios (PER) between 2.25 and 2.38, although no standard protein is used for comparison. Lower PER values of 1.9 for high-protein oats and 1.8 for concentrates were recently reported by Cluskey et al (1979). The PER value for casein is 2.5. Kim et al (1979) showed that oat protein is comprised of glutelins (66%), albumins (7.5%), globulins (12.9%), and prolamines (13.9%). Oats, therefore, represent a major untapped protein resource of great economic potential that could be used much more extensively in both human and animal diets.

The amino acid composition of oat groats (OG) has been reported by several investigators. Robbins et al (1971) determined 17 amino acids in 289 samples of OG proteins covering a wide range of genetic material varying in protein content from 12.4 to 24.4% (average 17.1%). Genetically distinct oat varieties differ considerably (Reeves 1974), both in protein and in their amino acid profiles (Hischke et al 1968, Robbins et al 1971). Soil fertility may also affect the protein and amino acid composition of oats (Eppendorfer 1978). Information on the composition of commercially milled OG products is limited and often contradictory (Robbins et al 1971), particularly concerning levels of lysine, sulfur-containing amino acids, and especially threonine (Bressani and Elias 1968). Moreover, data on the tryptophan content of OG proteins are not available (Tkachuk and Irvine 1969).

One purpose of this investigation was to ascertain the detailed amino acid composition of commercially available OG products typical of oats grown in eastern and western Canada. A second objective was to relate OG amino acid composition to nutritive value assessed in experimental broiler chicken diets (Hulan et al 1981).

MATERIALS AND METHODS

Sampling of Oat Groats

A representative sample of each of two varieties of OG, cv. Oxford, grown in eastern Canada, and cv. Sentinel, grown in western Canada, was obtained from Coop Atlantic, Moncton, New Brunswick, in 1-t quantities and kept in a cool, dry place until needed. Large batches of these oats were dehulled in a commercial oat groater (Roscamp Manufacturing Inc., Cedar Falls, IA). Separation of the OG from the hulls by air classification and final milling of the dehulled products were done at the feed processing plant. For analysis, samples of these materials were pulverized in an electric end-runner mill and passed through a 152-μm mesh sieve.

Chemicals and Resins

Type W-2 11.0 ± 1.0 μm and type W-3 9.0 ± 0.5 μm spherical resins, and a type I standard amino acid calibration mixture were obtained from Beckman Instruments Inc., Palo Alto, CA. L-Tryptophan, D-glucosamine·HCl, and DL-ornithine (5-aminonorvaline) were from Schwarz/Mann, Orangeburg, NY. The diastereoisomer mixture of 5-hydroxy-DL-lysine and *allo*-5-hydroxy-DL-lysine, D-galactosamine·HCl, *O*-phospho-L-serine, taurine, and ethanolamine were from Calbiochem, La Jolla, CA. All other chemicals and reagents were of the highest purity commercially available and were used without further purification.

Proximate and Elemental Composition

Standard methods for moisture (7.003, 14.002), total ash (14.006), crude fiber (7.069), phosphorus (7.118), and crude protein (2.057; N × 5.83, Kjeldahl method) were followed (AOAC 1980). Ether-extractable lipids were determined as described by Crampton (1956). Chlorine was determined separately by a modification of the Volhard method (Caldwell and Moyer 1955), using an automatic chloride titrator (Amino-Cotlove American Instrument Co., Silver Spring, MD) equipped with a silver generator electrode and a silver anode. Similarly, calcium, zinc, iron, potassium, sodium, and magnesium were determined separately by atomic absorption spectrophotometry (2.109) using the official lanthanum oxide method (AOAC 1980).

True metabolizable energy (TME) was determined by the method of Sibbald (1976).

[1]Contributions 458, Food Research Institute, and 1728, Kentville Research Station.

0009-0352/82/05032305/$03.00/0

Amino Acid Analyses

Amino acid analyses were performed with a conventional (Beckman Spinco model 120C) or a fully automated amino acid analyzer (Beckman Spinco model 121MB), both equipped with a Module control (Autolab Spectra-Physics Gmbh, 61 Darmstadt, West Germany) and a companion Autolab system AA (Beckman methodology bulletins AA-TB-001 to AA-TB-014) for computing peak concentrations. Data processing and actual statistical computations of results were done by standard computer programming techniques.

Triplicate OG samples (0.5 g) were hydrolyzed in thick-walled ignition tubes (18 × 150 mm) under vacuum (below 10 μm of mercury) with 20–40 times their own weight of glass-distilled constant-boiling HCl (6.0*M*) at 110°C for 24, 48, 72, and 96 hr (Zarkadas 1975, 1978). The small amounts of insoluble humin formed during acid hydrolysis and the fat plug were removed by filtration (0.22-μm Millipore microfilter). Standard amino acid analyses of individual filtrates were performed in duplicate by methods previously described (Moore and Stein 1963, Zarkadas 1978, 1979). 4-Hydroxyproline was determined separately by the modified procedure of Piez and Morris (1960) as described previously (Hulan et al 1979). Similarly, methionine and cysteine were determined in separate samples (0.1 g) as their oxidation products by the performic acid procedure of Moore (1963) as described previously (Hidiroglou and Zarkadas 1976).

Tryptophan in OG samples (0.1 g) was determined separately after alkaline hydrolysis (Hugli and Moore 1972) by an improved chromatographic procedure (Zarkadas 1978).[2] Samples were eluted from a 25 × 0.9-cm column of type W-2 resin amino acid analyzer (Beckman model 120C) with 0.21*M* sodium citrate buffer (pH 5.40) at 51°C at a flow rate of 50 ml/hr, and 827 kN/m^2. Elution time for tryptophan was 88.4 min.

RESULTS AND DISCUSSION

The means and standard deviations of the proximate and elemental composition of the two representative commercial OG samples used in this study are given in Table I. Data for wheat and corn are also included for comparison. Total crude protein (moisture-free basis) for both eastern- and western-grown OG averaged 14.97 and 13.30%, respectively. These values are much lower than the average value (17.1%) reported for 289 different cultivars of OG by Robbins et al (1971). The total lipid content of western OG (6.57%) differs considerably from oats produced in eastern Canada (3.7%). The higher TME values of the western OG (17.74 MJ/kg, dry matter, compared to 16.91 MJ/kg, dry matter, for the eastern OG) can most likely be attributed to the higher lipid content of this commercial product because their carbohydrate content appears to be very similar. The difference in the crude fiber content of the two products was not statistically significant. Although the fiber components of OG were not determined in this study, oat bran reportedly contains 8% water-insoluble hemicellulose, 3% cellulose, and 3% lignin (Jeltema and Zabik 1979), whereas oat hulls consist of 35% cellulose and 6.7% lignin (Rasper 1979). The values for total ash and for each of the elements analyzed are comparable for both oat products, with only minor differences in the levels of total ash, calcium, phosphorus, sodium, and chlorine.

The amino acid composition of the two commercial OG samples is summarized in Table II. The data reported for serine, threonine, and tyrosine represent the average of values extrapolated to zero time of hydrolysis, because their rate of decomposition in 6.0*M* HCl at 110°C is progressive and linear with time (Rees 1946, Sanger and Thompson 1963). The values for valine, isoleucine, and phenylalanine are averages of data from 48, 72, and 96 hr of hydrolysis (Blackburn 1978). The recovery of cystine plus cysteine as cysteic acid and methionine as the sulfone (Moore 1963) was calculated in proportion to the yields obtained by the performic-acid treatment of standard solutions of these amino acids (Hidiroglou and Zarkadas 1976). All others are reported as the average values from 24, 48, 72, and 96 hr of hydrolysis.

With three exceptions (leucine, threonine, and tryptophan), eastern OG contained a significantly higher level of each individual amino acid than western OG. The total amino acid recovery from both samples was excellent, considering their high carbohydrate content. The extrapolated values for ammonia shown in Table II represent the amide groups mainly from asparagine and glutamine in the oat proteins. Although the amide nitrogen in these samples was not determined in this study, Robbins et al (1971) reported that 69% of glutamic and aspartic acids in oats were in the form of their amides.

Oat groat proteins contain significant amounts of tryptophan and very small amounts of 4-hydroxyproline (Table II). Tkachuck and Irvine (1969) estimated the tryptophan in oats, but the barium hydrolysis procedure used may have caused serious losses of tryptophan. Because tryptophan is an important amino acid in human and animal nutrition, analysis of the tryptophan content of the two commercial OG products after alkaline hydrolysis (Hugli and Moore 1972) was performed by a very sensitive and precise

[2]C. G. Zarkadas. Unpublished results.

TABLE I
Proximate Composition[a] of Eastern and Western Oat Groats, Corn, and Wheat

	Oat Groats[b]			
	Eastern (cv. Oxford)	Western (cv. Sentinel)	Corn[c]	Wheat[c]
Moisture	106.9 ± 3.6	123.9 ± 2.2	142.7	140.0
Total nitrogen	23.95 ± 0.01	21.24 ± 0.01	16.46	15.81
Crude protein (N × 5.83)	139.6 ± 0.06	123.8 ± 0.06	96.0	92.2
Crude fiber	34.4 ± 0.33	37.0 ± 0.57	37.9	27.9
Total lipid	43.8 ± 0.11	65.7 ± 0.06	25.9	17.4
Total ash	22.8 ± 0.6	22.4 ± 0.33	17.50	19.76
Calcium	1.37 ± 0.02	0.96 ± 0.02	0.12	0.58
Phosphorus	4.39 ± 0.00	4.03 ± 0.00	2.92	4.73
Magnesium	1.18 ± 0.01	1.13 ± 0.02	1.28	1.16
Potassium	4.60 ± 0.00	4.24 ± 0.00	3.85	5.23
Iron	0.067 ± 0.00	0.074 ± 0.00	0.020	0.058
Manganese	0.052 ± 0.006	0.040 ± 0.005	0.01	0.069
Zinc	0.040 ± 0.003	0.035 ± 0.000	0.01	0.011
Sodium	0.094 ± 0.00	0.076 ± 0.005	0.10	0.023
Chlorine	1.045 ± 0.07	0.161 ± 0.06	...	...
True metabolizable energy (MJ/kg)[d]	16.91 ± 0.12	17.71 ± 0.18	17.27	16.20

[a]G/kg, db.
[b]Mean values of three determinations ± standard deviation.
[c]From Hubbel (1981).
[d]Mean of four determinations ± standard deviation.

TABLE II
Amino Acid Composition[a] of Eastern and Western Oat Groats, Corn, and Wheat

Amino Acid	Oat Groats: Eastern (cv. Oxford)	Oat Groats: Western (cv. Sentinel)	t[b]	Corn[c]	Wheat[c]
Phenylalanine[d]	7.13 ± 0.58	6.36 ± 0.54	**	4.32 ± 0.23	6.0
Tyrosine	2.78 ± 0.16	3.77 ± 0.04	**	2.39 ± 0.08	4.4
Histidine[d]	3.67 ± 0.31	3.29 ± 0.28	**	2.78 ± 0.14	2.7
Isoleucine[d]	5.97 ± 0.56	5.37 ± 0.46	**	4.43 ± 0.21	5.0
Leucine[d]	11.09 ± 0.93	10.57 ± 1.16	ns	11.50 ± 0.70	9.0
Methionine[d]	5.28 ± 0.04	4.54 ± 0.05	**	2.09 ± 0.11	2.5
Cystine	2.31 ± 0.03	2.25 ± 0.01	**	1.86 ± 0.06	3.0
Valine[d]	8.03 ± 0.63	7.19 ± 0.64	**	4.43 ± 0.27	6.0
Arginine[d]	8.45 ± 0.91	7.67 ± 0.64	*	3.77 ± 0.28	6.0
Lysine[d]	6.44 ± 0.65	4.84 ± 0.47	**	2.76 ± 0.29	3.6
Threonine[d]	4.97 ± 0.51	4.81 ± 0.18	ns	3.48 ± 0.04	3.8
Tryptophan[d]	1.67 ± 0.01	1.70 ± 0.07	ns	0.52 ± 0.01	1.8
Total essential amino acids	67.79	62.36		44.24	53.8
Total essential amino acids (mg/gN)[e]	2324.4	2419.8		2678	
Aspartic acid	13.02 ± 1.39	11.63 ± 1.30	*	n.a.[f]	n.a.[f]
Glutamic acid	30.88 ± 1.98	25.45 ± 1.84	**	16.90 ± 0.99	n.a.[f]
Serine	5.12 ± 0.42	6.07 ± 0.28	**	4.31 ± 0.23	5.0
Glycine	7.33 ± 0.56	6.65 ± 0.57	**	3.64 ± 0.15	5.0
Alanine	6.81 ± 0.55	6.34 ± 0.56	*	6.92 ± 0.33	n.a.[f]
Proline	9.38 ± 0.74	7.26 ± 0.56	**	8.07 ± 0.56	n.a.[f]
4-Hydroxyproline	0.22 ± 0.02	0.14 ± 0.01	**	0.34 ± 0.02	n.a.[f]
Total amino acid	140.55	125.90			
Ammonia	4.56 ± 0.49	3.19 ± 0.51	**		
Recovery by wt (%)	93.89	94.85			
Essential amino acid index[g]	75.01	76.45		70.11	
Protein score[e]	83.04	75.18		45.02	

[a] G/kg, db.
[b] *T*-test (Eastern vs Western). Significance denoted by: * = $P<0.05$; ** = $P<0.01$; ns = not significant.
[c] From Hubbell (1981).
[d] Considered essential for the chicken (Scott et al 1969).
[e] Calculated as recommended by FAO/WHO (1965).
[f] Not available.
[g] Calculated as described by Oser (1951).

ion-exchange chromatographic method developed recently (Zarkadas 1978)[3] that completely separates tryptophan from other compounds, especially from lysinoalanine [N^6-(DL-2-amino-2-carboxyethyl)-L-lysine]. Thus, excellent recovery of tryptophan in oat proteins was achieved. The recovery of tryptophan in oat groats was calculated in proportion to the yields from the alkaline hydrolysis of standard solutions of this amino acid as recommended by Hugli and Moore (1972). Both sources of OG contain good quality protein with an amino acid profile that is superior to that of other cereals such as corn and wheat (Table II).

The present results differ from those of Robbins et al (1971) in several ways: the present analyses yielded lower values for glutamic acid, phenylalanine, tyrosine, and arginine and higher values for lysine (not for western OG), valine, aspartic acid, glycine, proline, isoleucine, and threonine. Some of these differences may arise from the fact that Robbins et al (1971) used only one time (22 hr) of hydrolysis, whereas the present data represent averages of duplicate determinations from triplicate 24-, 48-, 72-, and 96-hr hydrolysates. This is especially apparent with the results from threonine, valine, isoleucine, and lysine, however, the largest discrepancy is in the determination of total methionine. Robbins et al (1971) concluded that the high variability in the sulfur-containing amino acids may be partly attributed to their low levels in the OG and to analytical error resulting from the fact that those amino acids each yield two products after hydrolysis. The values for total methionine and cystine obtained in the present study exceed those previously reported. The present analyses yielded values 10–15% higher for the sum of lysine, threonine, and methionine.

The small amounts of 4-hydroxyproline in the acid hydrolysates

[3] C. G. Zarkadas. Unpublished results.

TABLE III
Comparison of the Amino Acid Composition[a] of Eastern and Western Canadian Oat Groats

Amino Acid	Oat Groats: Eastern[b] (cv. Oxford)	Oat Groats: Western[b] (cv. Sentinel)	Means[c]
Phenylalanine	5.07	5.05	5.3
Tyrosine	2.98	2.98[b]	3.1
Histidine	2.61	2.61	2.2
Isoleucine	4.25	4.27	3.9
Leucine	7.89	8.39	7.4
Methionine	3.76	3.23	2.5
Cystine	1.64	1.78	1.6
Valine	5.71	5.71	5.3
Arginine	6.01	6.09	6.9
Lysine	4.58	3.84	4.2
Threonine	3.54	3.82	3.3
Tryptophan	1.19	1.35	···
Total essential amino acids	49.23	49.53	···
Aspartic acid	9.26	9.24	8.9
Glutamic acid	21.97	20.21	23.9
Serine	3.64	4.82	4.2
Glycine	5.22	5.28	4.9
Alanine	4.85	5.04	5.0
Proline	6.67	5.77	4.73
4-Hydroxyproline	0.16	0.11	···
Ammonia	3.20	2.53	2.55
Sum of Lysine + Threonine + Methionine	10.89	10.0	8.72

[a] Percent of total amino acids.
[b] Means calculated from Table II.
[c] Obtained for 289 cultivars by Robbins et al (1971).

of the OG proteins and corn are particularly interesting (Tables II and III). The separation for 4-hydroxyproline by the modified system of Piez and Morris (1960) as described in this study and by Hulan et al (1979) is illustrated in Fig. 1. The 300 × 2.8-mm microcolumn packed (21 mm) with Beckman W-3 resin was operated at 30°C using 0.140*M*-sodium citrate thiodiglycol (10 ml/L), ethanol (10 ml/L), octanoic acid (0.1 ml/L), and phenol (1.0 g/L, pH 2.85 ± 0.01) at a rate of 8.8 ml per hr and (3,096 kN/m^2) on a Beckman model 121 MB fully automated amino acid analyzer. Each of the four acidic components and 4-hydroxyproline of a synthetic mixture emerged as discrete peaks (Fig. 1a). A typical chromatographic analysis of an acid hydrolysate of OG proteins (Fib. 1b) clearly demonstrates the complete separation of 4-hydroxyproline from aspartic acid and four minor peaks. The resolving power of the chromatographic method is illustrated by the separation of all these unknown components in the various OG samples analyzed, in addition to phosphoserine, taurine, phosphoethanolamine, and 4-hydroxyproline from aspartic acid (Fig. 1). This chromatographic procedure has an advantage over other methods (Kivirikko 1963, Laurent et al 1978, Woessner 1961) in that complete separation of all these compounds is possible in a single analysis in less than 20 min.

4-Hydroxyproline was once thought to be confined almost exclusively to the connective tissue fibrous proteins collagen and elastin (Adams and Frank 1980, Bentley and Hanson 1969, Eastoe 1967), and was used as the basis for determining the connective tissue content of various animal protein supplements and foods such as muscle and composite meat products (Pearson 1975). The discovery of small amounts of 4-hydroxyproline in both OG (0.22 g/kg db) and corn (0.11 g/kg db) supports recent evidence of its presence in algae (Lamport 1977), lectins (Allen and Neuberger 1973), corn pericarp (Boundy et al 1967), and mung bean, broadbean, and soybean seedlings (Chao and Dashek 1973, Clarke and Ellinger 1967). The hydroxylated amino acid has also been found in animal proteins other than connective tissues, including acetyl cholinesterase (Anglister et al 1976) and Clq complement protein (Adams and Frank 1980, Porter and Reid 1978). The use of 4-hydroxyproline as an index for determining connective tissue content of either animal protein supplements or foods should be discontinued.

These results indicate that OG proteins are a very good source of dietary protein and could be important in the diets of both humans and animals. Chemical analyses of commercially prepared OG indicated that their amino acid profile is superior to that of other cereals, and that OG proteins have an excellent balance of essential amino acids limited only in lysine. The nutritive value of commercial OG grown in eastern and western Canada and assessed in experimental broiler chicken diets by Hulan et al (1981) can be related to their protein and amino acid composition.

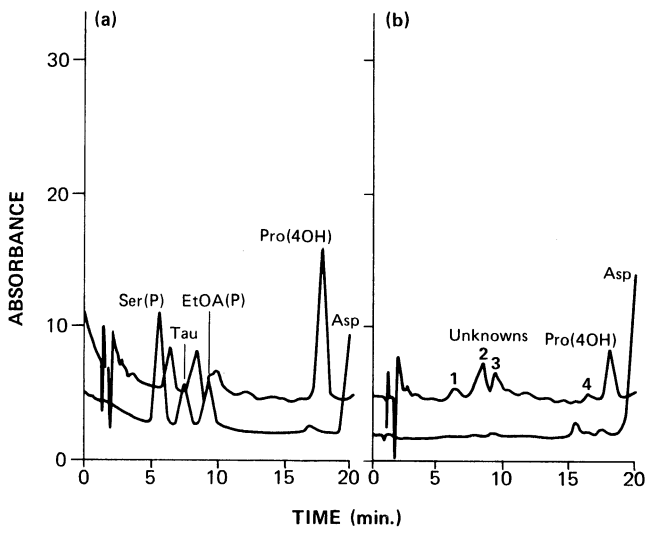

Fig. 1. Typical separation of 4-hydroxyproline from other amino acids in eastern oat groat hydrolysates. **a,** Separation of a synthetic physiological amino acid calibration mixture. Lower curve shows absorbance at 570 nm and upper curve at 440 nm; **b,** Separation of a 72-hr hydrolysate of an eastern oat groat sample. Upper curve shows absorbance at 440 nm and lower curve at 570 nm. 1–4 = unidentified ninhydrin-positive peaks. Ser(P) = phosphoserine; Tau = taurine; EtOA(P) = phosphoethanolamine; Pro(4OH) = 4-hydroxyproline; Asp = aspartic acid.

ACKNOWLEDGMENTS

The authors acknowledge Dennis Nash for his excellent technical assistance; Pat J. Roy, a University of Waterloo Cooperative student, and John Emery of the Chemistry and Biology Research Institute, for their excellent assistance in amino acid analyses; R. M. G. Hamilton, Animal Research Institute, for true metabolizable energy determinations; Analytical Chemistry Services of CBRI, Agriculture Canada, for proximate and elemental analyses and for the use of amino acid analyzers; and Coop Atlantic, Moncton, NB, for providing the oat groats.

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[Received July 2, 1981. Accepted January 20, 1982]