Comparison of Yield and Composition of Oil Extracted from Corn Fiber and Corn Bran

006667

Robert A. Moreau,[1,2] Vijay Singh,[3] Steven R. Eckhoff,[3] Michael J. Powell,[1] Kevin B. Hicks,[1] and Robert A. Norton[4]

ABSTRACT

Cereal Chem. 76(3):449–451

We recently reported that corn fiber oil contains high levels of three potential cholesterol-lowering phytosterol components: ferulate-phytosterol esters (FPE) (3–6 wt%), free phytosterols (1–2 wt%), and phytosterol-fatty acyl esters (7–9 wt%). A previous study also indicated that corn bran oil contained less phytosterol components than corn fiber oil. The current study was undertaken to attempt to confirm this preliminary observation using more defined conditions. Accordingly, oil was extracted from corn fiber and corn bran prepared under controlled laboratory conditions, using the same sample of corn hybrid kernels for each, and using recognized bench-scale wet-milling, and dry-milling procedures, respectively. After extraction, the chemical composition of the phytosterol components in the oil were measured. This study confirmed our previous observation—that FPE levels were higher in corn fiber oil than in corn bran oil. During industrial wet-milling, almost all of the FPE are recovered in the fiber fraction (which contains both fine and coarse fiber). During laboratory-scale wet-milling, ≈60–70% of the FPE are recovered in the coarse fiber (pericarp) and 30–40% are recovered in the fine fiber. During laboratory-scale dry-milling, <20% of the FPE are recovered in the bran (pericarp), and the rest in the grits. The recoveries of the other two phytosterol components (free phytosterols and phytosterol-fatty acyl esters) revealed a more complex distribution, with significant levels found in several of the dry- and wet-milled products.

Previously, we reported that the levels of ferulate-phytosterol esters (FPE) were higher in corn fiber oil (3–6 wt%) than in corn bran oil (1.50 wt%) (Moreau et al 1996). Corn fiber is a pericarp-enriched fraction obtained by the wet-milling of corn, whereas corn bran is a pericarp-enriched fraction obtained by the dry-milling of corn. The samples of corn fiber and corn bran used in our previous study were from commercial wet and dry mills, respectively, and were most likely obtained from bulk corn shipments representing mixtures of hybrids. This study was conducted to prepare corn fiber and corn bran from the same corn hybrids under controlled laboratory conditions, to extract them, and to compare the FPE levels and other lipid components (especially other phytosterols) in these oils. Preliminary feeding studies at the University of Massachusetts indicated that corn fiber oil lowers the levels of total serum cholesterol and LDL cholesterol in hamsters (R. Nicolosi, *personal communication*). It is thought that the high levels of FPE and other phytosterols in corn fiber oil impart valuable cholesterol-lowering properties. Norton (1995) reported that sitostanol-ferulate is the most abundant molecular species of FPE in corn bran oil. Other clinical studies have demonstrated the cholesterol-lowering properties of free and esterified sitostanol (Miettenin et al 1995).

MATERIALS AND METHODS

Corn kernels, commercial yellow dent hybrids of three different endosperm hardnesses (Pioneer 3317 [soft]; Pioneer 3394 [medium]; and Pioneer 338R7CD4 [hard]) were obtained from the University of Illinois. Bench-scale wet-milling was performed according to the method of Eckhoff et al (1996). Bench-scale dry-milling was performed according to the method of Brekke et al (1972). All milling fractions were dried to <5% moisture by either lyophilization or air-drying. All samples were ground to 20 mesh in a Wiley mill, extracted by mixing 4 g of sample/40 mL of hexane in a 55-mL screw-top vial, shaking horizontally for 1 hr in a wrist-action shaker, filtering the sample through a Whatman GF/A glass fiber filter, removal of part of the sample for HPLC analysis as previously described (Moreau et al 1996), and evaporation and measurement of the mass of the rest of the sample. Each experiment was performed two times and each analytical data point represents the mean of duplicate analyses ± standard error.

RESULTS

Three different corn hybrids (representing soft, medium, and hard kernels) were subjected to bench-scale dry- and wet-milling and the bran and fiber fractions were weighed and extracted (Table I). In the dry-milled samples, the mass in the bran fraction was 4.51–5.95%, based on the mass of the starting kernels (Table I). After wet-milling, the masses of fine fiber were 8.575–9.555%, and the masses of coarse fiber were 4.570–5.475%, based on the mass of the starting kernels. The wt% of oil (hexane-extractable material) in kernels, bran, and fibers was 1.84–3.14 wt%. The FPE levels were 0.351–0.411 wt% in the oils from the three kernels: 0.82–1.40 wt% in the corn bran oils, 1.68–2.58 wt% for the fine fiber oils, and 4.82–5.71 wt% in the coarse fiber oils. These FPE levels are comparable to those reported in corn fiber oil and corn bran oil obtained from commercial samples of fiber and bran (Moreau et al 1996). These results, using laboratory-scale wet- and dry-milling, confirmed our previous observation (Moreau et al 1996) that the FPE levels are much higher in corn fiber oil than in corn bran oil. Commercial industrial corn fiber is a mixture of coarse and fine fibers, so the data observed for the coarse and fine fibers in this study need to be combined to compare it with the data on commercial corn fiber oil in our previous study (Moreau et al 1996).

Examination of the recovery levels for FPE in corn bran oil revealed that only 9.7–15.6% of the original FPE level measured in the kernel were recovered in the bran fraction (Table I). In contrast, in the fiber fractions, essentially all of the FPE was recovered, with the distribution of 59–74% recovered in the coarse fiber and 35–41% recovered in the fine fiber.

Comparing the effect of kernel hardness with the values in Table I revealed similar results but some interesting trends were found. Corn bran obtained from hybrids with softer kernels appears to have more oil and more total FPE. In contrast, slightly higher proportions of FPE were found in the coarse fiber than in the fine fiber as kernel hardness increased.

[1] Eastern Regional Research Center, ARS, USDA, 600 East Mermaid Lane, Wyndmoor, PA 19038. Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

[2] Corresponding author. E-mail: rmoreau@arserrc.gov Phone: 215/233-6428. Fax: 215/233-6406.

[3] Department of Agricultural Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61802.

[4] National Center for Agricultural Utilization Research, ARS, USDA, 1815 N. University, Peoria, IL, 61604.

Publication no. C-1999-0418-02R.

Thus, it is clear that essentially all of the FPE from the kernel is recovered in corn fiber oil but only a small amount is recovered in the corn bran oil (<16%). The main question that arises is: what happens to the rest of the FPE during dry-milling?

Milled corn kernels of medium hardness (Pioneer hybrid 3394) yielded three dry-milling fractions and six wet-milling fractions which were each then weighed, ground to 20 mesh, and extracted with hexane (Table II). Because only minor differences in the oil from kernels with different hardnesses were observed earlier (Table I), only the medium endosperm hardness hybrid was used in this part of the study. The mass of each of these fractions is consistent with those previously reported using other laboratory-scale wet- and dry-milling operations (Singh and Eckhoff, 1996, Brekke et al 1972). In both wet- and dry-milling streams, most of the oil was recovered in the germ, as expected. For both the dry- and wet-milling product streams, the fraction with the next highest level of oil was the fiber or bran. Very little oil was found in the starch and steepwater.

The lipid class composition of the oils from each of the three dry-milling fractions and each of the six wet-milling fractions was then compared (Table III). In all fractions, triacylglycerols (TAG) occurred in the highest concentration, and as expected, the TAG levels in the germ oils from both milling processes were >96 wt%. The levels of phytosterol fatty acyl esters (St:E), free phytosterols (St), and ferulate phytosterol esters (FPE) were highest in the oils from coarse fiber and fine fiber, and were only slightly lower than those reported in the oil from commercial (a mixture of coarse and fine fibers) corn fiber (Moreau et al 1996). In the dry-milling fractions, the FPE level in oil from the grits was actually higher than in the oil from the bran, giving us a clue about the whereabouts of the FPE that were unaccounted for in Table I.

To resolve the FPE recovery question, the recoveries of each lipid component in each fraction were examined (Table IV). The results revealed that during wet-milling, almost all of the FPE (25 + 67 = 94 relative%) were localized in the coarse and fine fiber fractions, whereas during dry-milling only 17% of the FPE were localized in the bran fraction, and almost all of the rest was in the grits (75%) (Table IV). Examination of the localization of the other two phytosterol components (St:E and St) revealed a more complex distribution, with significant levels in several milled fractions. The St and St:E are nearly evenly divided in the grits and germ fractions of dry-milling. In wet-milling, the highest levels of St:E and St are recovered in the germ, but significant quantities are also distributed in the gluten, coarse fiber, and fine fiber. The germ fractions from both processes had the highest recoveries of γ-tocopherol, but significant recoveries of γ-tocopherol in the coarse fiber, fine fiber, and grits fractions were also observed. Although the total levels of each of the seven lipid classes theoretically should have been identical in the sum of the dry- and wet-milled fractions, there was some variability. The total amounts of TAG, FFA, St:E, St, and FPE were higher in the dry-milled fractions and the total amounts of DAG and γ-tocopherol were higher in the wet-milled fractions. This variability could be attributed to degradation (oxidation) during milling, incomplete recovery of products, or variable degrees of extraction efficiency.

DISCUSSION

This study confirmed our previous observation that the levels of FPE are *much* higher in corn fiber oil than in corn bran oil. Although both corn fiber and corn bran are pericarp-enriched fractions, it appears that only in wet-milling (perhaps due to heat or SO_2 and lactic acid used in steeping) are most of the FPE (94%) recovered in the fiber. In contrast, during dry-milling only 18% of the FPE are localized in the bran and 81% are in the grits. It is interesting that high levels of FPE are associated with both the coarse fiber and fine fiber fractions of wet-milling, and it is convenient that both of these fractions are combined in the corn fiber produced by essentially all modern corn wet mills (Singh and Eckhoff 1996). Significant recoveries (≥ 9 wt%) of the other two phytosterol components (St:E and St) were found in all three dry-milled fractions and in four out of six of the wet-milling fractions.

Tamura et al (1958) were the first to identify and isolate sitostanol ferulate as a minor component in corn germ oil. Seitz, later (1989) identified a variety of sitostanyl, campestanyl, sitosteryl, and campesteryl ferulates in ground corn. Norton (1994) examined corn bran as a pericarp-enriched fraction for FPE isolation and identified a total of 16 different ferulate and *p*-coumarate phytosterol esters (CPE), of which sitostanol ferulate was the major species. Norton later (1995) examined nine different raw and processed corn bran fractions from dry-milling to find the most suitable sources for the

TABLE II
Mass of Product Streams from Dry- and Wet-Milling of Hybrid 3394 and Yield of Oil in Each Fraction

Fraction	g of Fraction/ 100 g of Kernel	g of Oil/ 100 g of Kernel	Wt% Oil in Fraction
Dry-milling fractions			
Grits	82.63	0.521 ± 0.025	0.63 ± 0.03
Germ	11.24	1.686 ± 0.042	15.00 ± 0.37
Bran	6.13	0.129 ± 0.002	2.11 ± 0.03
Wet-milling fractions			
Starch	68.48	0.014 ± 0.007	0.02 ± 0.01
Gluten	8.34	0.074 ± 0.000	0.89 ± 0.00
Fine fiber	8.58	0.117 ± 0.004	1.36 ± 0.05
Coarse fiber	5.48	0.122 ± 0.003	2.19 ± 0.05
Germ	4.90	1.74 ± 0.020	35.56 ± 0.41
Steepwater	3.33	0.002 ± 0.003	0.06 ± 0.08

TABLE I
Oil and Ferulate Phytosterol Esters (FPE) in Kernels, Bran, and Fiber from Three Corn Hybrids

Sample	g/100 g of Kernels	Wt% Oil in Sample	Wt% FPE in Oil	Wt% FPE in Sample	mg of FPE/ 100 g of kernels	% FPE Recovered/ 100 g of kernels
Kernels						
3317 (soft)	100	2.78 ± 0.03	0.351 ± 0.005	0.0098	9.8	100
3394 (med)	100	2.82 ± 0.04	0.400 ± 0.004	0.0113	11.3	100
33R87CD4 (hard)	100	2.64 ± 0.10	0.411 ± 0.012	0.0108	10.8	100
Bran						
3317	5.95	3.14 ± 0.12	0.82 ± 0.09	0.025	1.53	15.6
3394	4.51	1.98 ± 0.01	1.28 ± 0.05	0.026	1.15	11.1
33R87CD4	5.04	1.47 ± 0.02	1.40 ± 0.04	0.020	1.04	9.7
Fiber						
3317 (fine)	9.175	2.58 ± 0.08	1.68 ± 0.01	0.044	4.0	41
3317 (coarse)	4.570	2.69 ± 0.49	4.82 ± 0.62	0.128	5.8	59
3394 (fine)	8.575	1.84 ± 0.06	2.38 ± 0.17	0.044	3.8	35
3394 (coarse)	5.475	2.67 ± 0.06	5.71 ± 0.23	0.121	6.6	61
33R87CD4 (fine)	9.555	1.60 ± 0.11	2.71 ± 0.01	0.044	4.2	37
33R87CD4 (coarse)	5.460	2.23 ± 0.04	5.42 ± 0.17	0.153	8.4	74

TABLE III
Composition of Lipids in the Oil from Each Milling Fraction of Hybrid 3394[a]

Sample	Wt% of Oil						
	TAG	DAG	FFA	γ-Tocopherol	St:E	St	FPE
Dry-milling fractions							
Grits	92.07 ± 1.31	0.44 ± 0.03	1.35 ± 0.11	0.12 ± 0.00	3.00 ± 0.08	1.67 ± 0.07	1.35 ± 0.00
Germ	97.00 ± 0.95	0.88 ± 0.02	0.51 ± 0.04	0.09 ± 0.01	0.87 ± 0.02	0.61 ± 0.02	0.04 ± 0.00
Bran	88.55 ± 0.31	1.79 ± 0.04	4.01 ± 0.02	0.08 ± 0.00	3.00 ± 0.01	1.36 ± 0.01	1.21 ± 0.03
Wet-milling fractions							
Starch	91.77 ± 15.99	0	0	3.90 ± 2.14	0	3.73 ± 1.46	0.60 ± 0.84
Gluten	90.54 ± 2.46	0.94 ± 0.00	2.06 ± 0.00	0	2.62 ± 0.54	3.46 ± 0.14	0.38 ± 0.01
Fine fiber	88.76 ± 1.35	2.09 ± 0.04	2.74 ± 0.09	1.14 ± 0.04	2.47 ± 0.02	1.15 ± 0.02	1.65 ± 0.04
Coarse fiber	84.53 ± 2.23	1.71 ± 0.01	2.11 ± 0.06	0.76 ± 0.06	5.61 ± 0.27	1.17 ± 0.01	4.11 ± 0.26
Germ	96.79 ± 0.16	1.77 ± 0.03	0.31 ± 0.00	0.17 ± 0.01	0.47 ± 0.00	0.48 ± 0.01	0.01 ± 0.00
Steepwater	99.40 ± 6.73	0	0	0	0.60 ± 0.84	0	0

[a] TAG = triacylglycerols; DAG = diacylglycerols; FFA = free fatty acids; St:E = phytosterol fatty acyl esters; St = free phytosterols; and FPE = ferulate phytosterol esters.

TABLE IV
Recovery of Lipids in Milling Fractions of Hybrid 3394[a]

Sample	mg of Lipid/100 g of Kernels (relative %)						
	TAG	DAG	FFA	γ-Tocopherol	St:E	St	FPE
Dry-milling fractions							
Grits	479.7 (22)	2.3 (12)	7.0 (34)	0.63 (28)	15.6 (46)	8.7 (42)	7.0 (75)
Germ	1,635.4 (73)	14.8 (76)	8.6 (41)	1.52 (68)	14.7 (43)	10.3 (50)	0.7 (8)
Bran	1,14.2 (5)	2.3 (12)	5.2 (25)	0.10 (4)	3.9 (11)	1.8 (9)	1.6 (17)
Total	2,229.3 (100)	19.4 (100)	20.8 (100)	2.25 (100)	34.2 (100)	20.8 (101)	9.3 (100)
Wet-milling fractions							
Starch	12.8 (1)	0	0	0.5 (9)	0	0.5 (4)	0.1 (1)
Gluten	67.0 (3)	0.7 (2)	1.5 (12)	0	1.9 (10)	2.6 (18)	0.3 (4)
Fine fiber	103.8 (5)	2.4 (7)	3.2 (25)	1.3 (23)	2.9 (15)	1.3 (9)	1.9 (25)
Coarse fiber	103.1 (5)	2.1 (6)	2.6 (20)	0.9 (16)	6.8 (34)	1.4 (10)	5.0 (67)
Germ	1,686.1 (85)	30.8 (86)	5.4 (43)	3.0 (53)	8.2 (41)	8.4 (59)	0.2 (3)
Steepwater	2.0 (0)	0	0	0	0	0	0
Total	1,974.8 (99)	36.0 (101)	12.7 (100)	5.7 (101)	19.8 (100)	14.2 (100)	7.5 (100)

[a] TAG = triacylglycerols; DAG = diacylglycerols; FFA = free fatty acids; St:E = phytosterol fatty acyl esters; St = free phytosterols; and FPE = ferulate phytosterol esters.

isolation of steryl cinnamic acid derivatives. The highest-yielding bran fractions contained ≈0.77% oil, of which ≈2.6% were FPE and CPE. Other bran fractions in that study contained 0.3–1.5% total FPE and CPE, these data are consistent with our studies on raw, unprocessed bran. Interestingly, Norton's (1995) richest bran fractions contained FPE levels higher than our unprocessed bran and even higher than our fine fiber fractions. However, Norton's FPE levels were significantly lower than the FPE levels in our coarse fiber fraction.

Through dissection studies, Seitz (1989) showed that FPE were associated primarily with the inner pericarp. If this is the case, then perhaps the inner pericarp (or the thin aleurone layer immediately interior to the pericarp) adheres to the pericarp during wet-milling but not during dry-milling. These results also raise the question of whether other potential coproducts may be differentially fractionated during dry- and wet-milling. It is clear that the processes of dry- and wet-milling need to be examined more carefully, especially by those attempting to obtain value-added natural products from the streams generated by each.

CONCLUSIONS

The FPE levels are *much* higher in corn fiber oil than in corn bran oil. Although both corn fiber and corn bran are pericarp-enriched fractions, it appears that only in the wet-milling fraction (corn fiber) are most of the FPE enriched. Commercial corn fiber thus appears to be the best industrial starting material to produce an oil rich in FPE. Corn fiber also appears to contain the highest levels of natural sitostanol of any other plant material yet reported.

LITERATURE CITED

Brekke, O. L., Peplinski, A. J., Griffin, E. L., and Ellis, J. J. 1972. Dry milling of corn attacked by Southern Leaf Blight. Cereal Chem. 49:466.

Eckhoff, S. R., Singh S. K., Zehr, B. E., Rausch, K. D., Fox, E. J., Mistry, A. K., Haken, A. E., Niu, Y. X., Zou, S. H., Buriak, P., Tumbleson, M. E., and Keeling, P. L. 1996. A 100-g laboratory corn wet-milling procedure. Cereal Chem. 73:54-57.

Miettinen, T. A., Puska, P., Gylling, H., VanHanen, H., and Vartianen, E. 1995. Reduction of serum cholesterol with sitostanol-ester margarine in a mildly hypercholesterolemic population. N. Engl. J. Med. 333:1308-1312.

Moreau, R. A., Powell, M. J., and Hicks, K. B. 1996. The extraction and quantitative analysis of oil from commercial corn fiber. J. Agric. Food Chem. 44:2149-2154.

Norton, R. A. 1994. Isolation and identification of steryl cinnamic acid derivatives from corn bran. Cereal Chem. 71:111-117.

Norton, R. A. 1995. Quantitation of steryl ferulate and *p*-coumarate esters from corn and rice. Lipids 30:269-274.

Seitz, L. M. 1989. Stanol and sterol esters of ferulic acid and *p*-coumaric acids in wheat, corn, rye, and triticale. J. Agric. Food Chem. 37:662-667.

Singh, N., and Eckhoff, S. R. 1996. Wet milling of corn—A review of laboratory-scale and pilot-scale procedures. Cereal Chem. 73:659-667.

Tamura, T., Sakaedmani, N., and Matsumoto, T. 1958. Isolation of dihydro-β-sitosteryl ferulate from corn germ oil. Nippon Kagaku Zasshi 79:1011-1014.

[Received October 23, 1998. Accepted February 17, 1999.]