Progress Report on the Chemical and Nutritional Characteristics of Berry Seed Oils

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by

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Summary

The present report updates our progress since June of 2002 when our first progress report was submitted. This research is a collaboration between Dr. Terry Isbell and Mr. Bliss Phillips (USDA-ARS) and Dr. Boxin Ou (Brunswick Laboratories). The work in my laboratory has been performed by Mr. Jimmie M. Crane. Dr. Shaun Bushman, a postdoctoral research associate who began working in my laboratory in July of 2002, has expertise in secondary chemistry in plants and is working on the genetics of nutritionally important traits in oilseeds. I selected Shaun to lead the analysis of the data and write the manuscript describing the chemical and nutritional characteristics of caneberry seed oils and meals. We are attaching a cover page for the manuscript. Besides the manuscript, we may present the results at the American Oil Chemists Society meeting or a similar meeting next year.

We met with Terry at the Association for the Advancement of Industrial Crops Meeting in Saskatoon, Saskatchewan on 27 August 2002 to review the results of the chemical analyses completed thus far and prepare this report. The USDA has completed protein, amino acid, and fatty acid analyses and are in the process of completing oxidative stability index (OSI) measurements. They did not complete tocopherol (Vitamen E) analyses as originally planned; hence, Shaun Bushman is setting up a protocol on our HPLC and will complete the tocopherol measurements within two weeks. Dr. Boxin Ou (Brunswick Laboratories) indicated that tocopherols were probably not the primary determinants of oxidative stability in caneberry oils. The most probably protectants are lipophilic phenols. We are using OSI and oxygen radical absorbance capacity (ORAC) to measure the oxidative stability of caneberry oils in relation to other oils. OSI tests are being performed by the USDA, while ORAC tests are being performed by Boxin Ou. The ORAC measurements ranged from 150.7 for black raspberry to 539.7 for red raspberry. The ORAC of red raspberry oil, which was outstanding, was significantly greater than that of the other four caneberry oils and double that of grapeseed oil (Table 1).

OSU performed fatty acid analyses (using gas chromatography) which were presented in the June 2002 report. We had the USDA-ARS repeat the analyses to confirm our results. This was important because we could not separate oleic and vaccinic acid. Terry and Bliss repeated the analyses using gas chromatography and found vaccinic, γ-linoleic, and steariodonic acid, in addition to the common fatty acids found in the initial analyses. Terry reported that they are planning to analyze the oil using gas chromatography-mass spectroscopy (GC-MS) to positively identify all of the fatty acids produced in caneberry seeds. We will update the fatty acid data once

we receive the GC-MS results. Of the more unusual fatty acids found in the oil, the most intriguing from a nutritional standpoint is γ-linoleic, although the caneberries do not produce high concentrations of γ-linoleic and thus are not outstanding primary sources of this fatty acid.

Seed Processing

Seed processing and cleaning should not present a problem for the berry industry. We obtained frozen 0.5 kg samples of marionberry, blackberry, red raspberry, black raspberry, and boysenberry seed from the ORBC for analysis. The samples, which were a mixture of seed and pulp, were thawed and oven dried at 50^{o}C for 18 hours, threshed using a standard laboratory seed thresher, and cleaned using a standard forced air seed cleaner. Once dried, the samples were readily processed using standard seed threshing and cleaning equipment and yielded exceptionally clean seed samples. Based on our limited laboratory scale experience, the berry industry should have no difficulty scaling up the process of cleaning dried berry seeds. Dried samples can processed on a commercial scale using using standard seed cleaning equipment commonly found in the Willamette Valley. The primary technical problem to be addressed is seed drying.

Seed Oil and Protein and Seed Meal Amino Acids

The oil concentrations of the caneberry seeds ranged from 11.4 to 18.7% (Table 1); thus, roughly 72,400 kg of oil can be extracted from 500,000 kg of berry seed. This is an extraordinarily small quantity of oil by commercial oilseed standards, especially if the seeds of the various berries are individually processed and maintained in separate ‘identity preserved’ streams. Because most oilseed processing facilities have daily capacties many-fold greater than this, e.g., 150 to 250 tons per day, the most promising path for commercializing berry oils might be to work with small scale processors producing cold-pressed oils for nutraceutical markets. Depending on post-press processing, cold-pressed oils could contain natural colors (e.g. anthocyanin pigments) and nutraceuticals (e.g., phenols, tocopherols, and ellagic acid) naturally present in the pulp residue and seed, thereby creating red and purple tinted oils laden with antioxidants and nutraceuticals.

The protein concentrations of the caneberry seeds ranged from 6.3 to 7.1% (Table 1). The meal is fibrous and similar in nature to many other generic seed meals, e.g., cottonseed and flaxseed meals. The amino acid compositions of the meal proteins were not unusual or extraordinary (Table 4).

Seed Oil Fatty Acids

We originally reported that caneberry seed oils contain fatty acids commonly found in other seed oils (Table 2). This is correct; however, follow-up analyses by the USDA identified a few unusual fatty acids, in addition to the common fatty acids. The former were vaccinic, γ-linoleic, and steariodonic acid. The USDA is confirming the identity of the unusual fatty acids using GC-MS as noted earlier. We will update the fatty acid data once the GC-MS data are produced. Our original assessment of the nutritional characteristics of the oils will not fundamentally change, although the presence of γ-linoleic acid, albeit in low concentrations, does increase the marketability of the oil from a nutraceutical standpoint. The presence of vaccinic and steariodonic acid has no effect either way on the marketability of the oil.

The fatty acid profiles of berry seed oils are nutritionally outstanding, with a very high concentrations of polyunsaturated fatty acids (PUFAs) and low concentrations of saturated fatty acids. Berry seed oils should appeal to health conscious consumers. The saturated fatty acid concentrations were exceptionally low in four of the five berry seed oils (evergreen blackberry was the exception), and well below the concentrations found in widely consumed vegetable oils, e.g., soybean and cottonseed oil. The saturated fat contents of the berry seed oils rival those of high-oleic sunflower oil and Canola oil.

The fatty acid profiles of caneberry seed oils are similar to hemp (*Cannabis sativa* L.) oil (Table 2). Hemp oil has been promoted in Canada and Europe as an 'omega-3' oil to compete against other omega-3 oils, e.g., flax (*Linum usitatissimum* L.). Hemp production has not reached the US because of the narcotic stigma attached to the crop. Moreover, hemp production seems to be declining in Canada where the crop has been grown for fiber (seed oil was a co-product). The ratio of linoleic to linolenic acid in hemp oil is 3 : 1. The ratios of linoleic to linolenic acid in caneberry seed oils range from 1.7 : 1 to 4.1 : 1 (Table 2). Because linoleic and linolenic acid are essential fatty acids and are required in a ~3 to 1 ratio in the human diet, hemp oil has been promoted as the perfect oil for human nutrition. There is no scientific data to support this. The fact that the caneberry oils are rich in PUFAs is nutritionally positive, regardless of the ratio.

The form of linolenic acid found in berry seed oil was primarily α-linolenic (Table 2). Evening primrose (*Oenothera biennis* L.) and borage (*Borago officinalis* L.) oil are rich sources of γ-linolenic acid, while hemp oil contains ~3% γ-linolenic acid. While γ-linolenic acid has special medicinal and nutritional properties and applications, the nutritional merits of γ- relative to α-linolenic acid are uncertain. The fact that berry oils are rich sources of PUFAs is probably more important than the form of linolenic acid.

Tocopherols and Ellagic Acid

Because ellagic acid is an important nutraceutical found in high concentrations in caneberry fruits (Wada and Ou, 2002), we had Boxin Ou perform ellagic acid analyses of the caneberry oils. Predictably, ellagic acid concentrations were significantly less in oils than fruits. Ellagic acid concentrations ranged from 47 to 90 mg/g in fruits and from 0.06 to 0.32 mg/g in oils. The presence of ellagic acid in the oil is a nutritional positive, but the fruits per se are much richer and more important sources of ellagic acid. Tocopherol measurements will be completed within two weeks.

Table 1. Caneberry seed oil and protein concentrations, 1000-seed weights, and seed oil oxygen radical absorbance capacities (ORACs).

Source	Oil	Protein	1000-Seed Weight	ORAC
	------------ %	-------------	----- g -----	
Marionberry	14.0	6.7	2.40	146.0 ± 14.7
Evergreen Blackberry	13.3	6.9	3.61	199.7 ± 8.4
Red Raspberry	18.7	6.5	1.45	539.7 ± 22.9
Black Raspberry	15.0	7.1	1.76	150.7 ± 7.5
Boysenberry	11.4	6.3	3.65	255.0 ± 25.2

Table 2. Palmitic (16:0), stearic (18:0), vaccinic and oleic (18:1), α-linoleic and γ-linoleic (18:2), and linolenic (18:3) acid concentrations in five caneberry seed oils.

Fatty Acid	Marionberry	Evergreen Blackberry	Red Raspberry	Black Raspberry	Boysenberry
	--- g/kg ---				
Palmitic	3.41	4.47	2.43	1.98	3.72
Stearic	2.20	3.65	1.00	0.89	1.70
Oleic	16.04	19.39	11.51	11.99	13.61
Linoleic	63.13	52.30	53.73	54.05	58.55
Linolenic	15.22	20.18	31.14	31.09	22.43

Table 3. α-, β-, δ-, and γ-tocopherol (vitamen E) and ellagic acid concentrations of caneberry seed oils.

Caneberry	Tocopherol α	Tocopherol β	Tocopherol δ	Tocopherol γ	Ellagic Acid
	------------------------ μg/mg ------------------------				mg/g
Marionberry					0.32
Evergreen Blackberry					0.21
Red Raspberry					0.08
Black Raspberry					0.06
Boysenberry					0.30

Table 4. Caneberry seed meal amino acid concentrations (W/W% = g per 100 g).

Amino Acid	Red Raspberry	Black Raspberry	Evergreen Blackberry	Marionberry	Boysenberry
Taurine	0.01	0.06	0.05	0.06	0.05
Hydroxyproline	0.04	0.04	0.06	0.03	0.04
Aspartic Acid	0.68	0.76	0.72	0.69	0.64
Threonine	0.23	0.24	0.23	0.22	0.22
Serine	0.27	0.27	0.25	0.25	0.23
Glutamic Acid	1.40	1.60	1.48	1.56	1.33
Proline	0.27	0.31	0.32	0.27	0.26
Lanthionine	0.00	0.00	0.00	0.00	0.00
Glycine	0.40	0.40	0.48	0.44	0.40
Alanine	0.33	0.34	0.31	0.30	0.36
Cysteine	0.17	0.19	0.16	0.18	0.14
Valine	0.33	0.34	0.35	0.32	0.31
Methionine	0.14	0.14	0.13	0.14	0.12
Isoleucine	0.32	0.34	0.35	0.32	0.3
Leucine	0.47	0.49	0.49	0.46	0.44
Tyrosine	0.14	0.15	0.15	0.14	0.13
Phenylalanine	0.28	0.29	0.30	0.27	0.26
Hydroxylysine	0.00	0.00	0.00	0.00	0.00
Histidine	0.18	0.19	0.20	0.20	0.19
Ornithine	0.01	0.01	0.01	0.01	0.01
Lysine	0.30	0.32	0.30	0.29	0.29
Arginine	0.54	0.58	0.59	0.58	0.54
Tryptophan	0.04	0.04	0.04	0.04	0.04
Total Protein	6.51	7.06	6.93	6.73	6.26