

Physical Properties and Fatty Acid Profiles of Oils from Black, Kidney, Great Northern, and Pinto Beans

Nongnuch Sutivisedsak · Bryan R. Moser · Brajendra K. Sharma ·
Roque L. Evangelista · Huai N. Cheng · William C. Lesch ·
Robert R. Tangsrud · Atanu Biswas

Received: 22 February 2010/Revised: 2 August 2010/Accepted: 16 August 2010/Published online: 2 September 2010
© US Government 2010

Abstract Four common beans (black, kidney, great northern, and pinto) were extracted with hexane and found to contain about 2% triacylglycerols. The fatty acids in these bean oils were mainly linolenic (41.7–46 wt%), linoleic (24.1–33.4 wt%), palmitic (10.7–12.7 wt%) and oleic (5.2–9.5 wt%). Because of the high levels of polyunsaturated fatty acids, the bean oils had iodine values between 174 and 177 g/100 g (compared to 130 g/100 g for soybean oil). Yet, the bean oils exhibited high oxidative stability due to the presence of high amounts of tocopherols (2,670–2,970 ppm). The bean oils had lower pour points (−18 to −11 °C) compared to −9 °C for soybean oil. Among the four bean oils, kidney bean oil had the highest

acid value (15.4 mg KOH/g) and kinematic viscosities over a wide range of temperatures.

Keywords Fatty acid · Oxidation stability · Tocopherol · Iodine value · Induction period · Common bean · Kinematic viscosity · Acid value · Antioxidant

Introduction

Common beans (*Phaseolus vulgaris* L.) are well known as a good source of nutrients and bioactive compounds [1–8]. Some of the bioactive compounds such as flavonoids, polyphenols and phenolics exhibit natural antioxidant properties. There have been a number of studies on the common edible bean's antioxidant and oxidative stability properties. For instance, the thermal processing (boiling and steaming at atmospheric and high pressure) on pinto and black bean was investigated as the significant factors toward the antioxidant properties of beans [9]. In another study [10], the phenolic compounds in the oils obtained from the hull and dehulled black soybeans were found to be effective in promoting good health. The oil extracted from the navy bean hull was found to be a potential natural antioxidant for use in vegetable oils such as soy and sunflower oils [11]. Many of the bioactive compounds occurring in common beans partition into different oil fractions upon solvent-assisted extraction. Although a lot of studies have recently focused on oils from seeds, e.g., sunflower, soybean, corn, cottonseed, and field pennycress [12–19], the study of oils in common beans and their nutritional benefits have usually been overlooked due to the much lower oil contents in these beans. The goal of this study was to evaluate the chemical composition, including fatty acid (FA) profile, tocopherol content, oxidative stability,

N. Sutivisedsak · B. R. Moser · B. K. Sharma ·
R. L. Evangelista · A. Biswas (✉)
National Center for Agricultural Utilization Research,
United States Department of Agriculture,
Agricultural Research Service, 1815 N. University St,
Peoria, IL 61604, USA
e-mail: Atanu_biswas@ars.usda.gov

N. Sutivisedsak
e-mail: nuch.sutivisedsak@ars.usda.gov

B. K. Sharma
Illinois Sustainable Technology Center,
University of Illinois, Urbana-Champaign,
1 Hazelwood Dr., Champaign, IL 61820, USA

H. N. Cheng
Southern Regional Research Center,
United States Department of Agriculture,
Agricultural Research Service, 1100 Robert E. Lee Blvd,
New Orleans, LA 70124, USA

W. C. Lesch · R. R. Tangsrud
Department of Marketing, University of North Dakota,
P.O. Box 8366, Grand Forks, ND 58202-8366, USA

and other physical properties of oils from four common edible beans (black, dark red kidney, great northern and pinto beans).

Experimental Procedures

Four common beans (*P. vulgaris* L.) including black, dark red kidney, great northern, and pinto beans were provided by the Northarvest Bean Growers Association (Frazee, MN, USA) as whole dry raw seeds. Fatty acid methyl ester (FAME) standards were purchased from Nu-Chek Prep, Inc. (Elysian, MN, USA). Crude soybean oil (SBO) was obtained from Archer Daniels Midland Company (Decatur, IL, USA). All other chemicals and reagents were obtained from Sigma-Aldrich, Inc. (St. Louis, MO, USA) and used as received.

Preparation of Samples

Whole raw seeds were soaked in distilled water overnight and then dried in an oven overnight at 60 °C. Whole seeds were ground with a Retsch® mill to pass a 0.6 mm (USA # 30) screen and kept in a refrigerator at 4 °C until needed. Soxhlet extraction of the ground seeds (thimble size 60 mm × 180 mm, single thickness) was accomplished with hexane for 6 h. Hexane was removed from the oil extracts in vacuo to provide the crude oils, which were collected in amber jar bottles, purged with nitrogen, and kept frozen until use. Prior to analysis, residual hexane was removed from the crude oil samples by rotary evaporation under reduced pressure (10 mbar, 30 °C) followed by the application of high vacuum (10⁻³ torr) utilizing a vacuum manifold which was connected to a Fisher Scientific (Pittsburgh, PA, USA) Maxima C Plus vacuum pump. The solids that were visible at room temperature in the oil were removed by vacuum filtration.

Physical Properties

Pour point (PP, °C) was determined following ASTM D5949 [20] using a model PSA-70S Phase Technology Analyzer (Richmond, BC, Canada). Pour point was rounded to the nearest whole degree (°C). For better accuracy, the measurements were done with a resolution of 1 °C instead of the specified 3 °C increment. Experiments were run in triplicate with mean values reported in Table 1.

The kinematic viscosity (mm²/s) was measured with Cannon-Fenske viscometers (Cannon Instrument Co., State College, PA, USA) at 25, 40 and 100 °C in accordance to ASTM D445 [21]. The viscosity index (VI) was calculated from kinematic viscosity data (40 and 100 °C) according to ASTM D2270 [22]. All experiments were run in triplicate with the mean values reported in Table 1.

Acid value (AV, mg KOH/g) titrations were performed as described in AOCS official method Cd 3d-63 [23] using a Metrohm 836 Titrando autotitrator equipped with a model 801 stirrer, a Metrohm Solvotrode electrode, and Tiamo 1.1 Light software. However, the official method was modified to use 2 g of the sample and 0.02 M KOH. The titration endpoint was determined by the instrument and visually verified using a phenolphthalein indicator. Samples were run in duplicate with the mean values reported in Table 1.

The iodine value (IV, g I₂/100 g; Table 1) was calculated from the FA profiles depicted in Table 2 according to AOCS official method 1c-85 [24].

The Gardner color (single determination; Table 1) was measured on a Lovibond 3-Field Comparator from Tintometer, Ltd. (Salisbury, England) following AOCS official method Td 1a-64 [25].

The average calculated molecular weight (MW_{calc}, g/mol; Table 1) was determined by a weighted average method utilizing the FA profiles depicted in Table 2.

Table 1 Physical properties of crude black bean, kidney bean, great northern, and pinto bean oils, with crude soybean oil shown for comparison

	Black Bean	Kidney Bean	Great Northern	Pinto Bean	Soybean
MW _{calc} , g/mol	872.94	871.57	871.75	869.65	873.33
PP, °C	-11 (0.6)	-18 (0.6)	-13 (0.6)	-15 (0)	-9 (0.6)
IP, 110 °C, h	41.7 (1.0)	15.5 (0)	60.4 (3.1)	13.1 (0.6)	6.2 (0.2)
Kinematic viscosity, mm ² /s					
25 °C	57.07 (0.07)	117.91 (0.20)	57.26 (0.07)	62.33 (0.04)	50.93 (0.10)
40 °C	32.68 (0.02)	60.54 (0.03)	33.33 (0.11)	35.92 (0.09)	30.19 (0.14)
100 °C	7.96 (0)	12.00 (0.02)	8.11 (0.03)	8.58 (0.02)	7.45 (0.01)
VI	230	199	231	230	230
AV, mg KOH/g	5.16 (0.16)	15.37 (0.03)	7.18 (0.12)	7.93 (0.22)	1.13 (0.09)
IV, g I ₂ /100 g	174	174	177	176	130
Gardner color	12	14	12	13	10

Values in parentheses are the standard deviations from the reported mean

Table 2 Fatty acid compositions (area %) of crude oils from black bean, kidney bean, great northern, and pinto beans, with crude soybean oil shown for comparison

Fatty acid ^a	Black Bean	Kidney Bean	Great Northern	Pinto Bean	Soybean
C14:0	0.1	0.1	0.1	0.1	0.1
C16:0	10.7 (0.4)	12.3 (0.9)	11.5 (0.5)	12.7 (0.8)	11.4 (0.5)
C16:1 Δ9	0.3	0.3	0.2	0.2	0.1
C18:0	1.8	1.4 (0.1)	2.0 (0.1)	1.7 (0.1)	3.9
C18:1 Δ9	9.3	9.5 (0.1)	5.2 (0.1)	5.9 (0.2)	22.1 (0.3)
C18:1 Δ11	1.9	2.6 (0.1)	1.8	1.7 (0.1)	1.6 (0.1)
C18:2 Δ9, 12	31.1	24.1	33.4 (0.1)	32.1 (0.1)	52.4 (0.6)
C18:3 Δ9, 12, 15	41.7 (0.2)	46.0 (0.9)	42.8 (0.5)	43.3 (0.6)	7.4 (0.2)
C20:0	0.5	0.5 (0.1)	0.5 (0.2)	0.3	0.2
C20:1 Δ11	0.2	0.2	0.1	0.1	0.2
C22:0	0.5	0.7	0.5 (0.2)	0.4 (0.1)	0.3
C22:2 Δ13, 16	0.1	0.4	0.2	0.1 (0.1)	
C22:3 Δ13, 16, 19	0.7	0.5 (0.1)	0.7 (0.2)	0.3 (0.1)	
Unknown (sum)	0.9	1.4	1.0	1.1	0.3
Σ Sat ^b	13.8	15.0	14.6	15.2	15.9
Σ Monounsats ^c	11.7	12.6	7.3	7.9	24.0
Σ Polyunsats ^d	73.6	71.0	77.1	75.8	59.8

^a The first number indicates the length of the fatty acid chain and the second the number of double bonds (all *cis*) with Δ signifying the location of the double bond(s). Numbers in parentheses are the standard deviations from the reported mean. Where not indicated, the standard deviation was less than 0.1

^b Σ Sat = C14:0 + C16:0 + C18:0 + C20:0 + C22:0

^c Σ Monounsats = C16:1 + C18:1 + C20:1

^d Σ Polyunsats = C18:2 + C18:3 + C22:2 + C22:3

Specifically, the molecular weight of each FA found in the vegetable oil was multiplied by its corresponding weight percentage as determined by GC. The sum of these values (minus the acidic proton) was multiplied by three and the glycerol fragment (minus the hydroxyl groups, as they were accounted for in the FA fragments) was added, resulting in an average calculated MW_{calc} of vegetable oil. For the sake of providing calculated MW_{calc} values that were not artificially low, unknown constituents were assumed to be oleic acid.

Fatty Acid Profile by GC

Fatty acid methyl esters were prepared from methanolic KOH as described previously [26] and separated using a Varian (Walnut Creek, CA, USA) 8400 GC equipped with an FID detector and SP2380 (Supelco, Bellefonte, PA, USA) column (30 m × 0.25 mm i.d., 0.20 μm film thickness). Carrier gas was He at 1 mL/min. The oven temperature was initially held at 150 °C for 15 min, then increased to 210 °C at 2 °C/min, followed by an increase to 220 °C at 50 °C/min, and held at 220 °C for 10 min. The injector and detector temperatures were set at 240 and 270 °C, respectively. FAME peaks were identified by

comparison to the retention times of reference standards. FAME determinations were run in triplicate with mean values reported in Table 2.

Oxidative Stability

The induction period (IP, h) was measured following the European Committee for Standardization (CEN) official method EN 14112 [27] at 110 °C utilizing a Metrohm USA, Inc. (Riverview, FL, USA) model 743 Rancimat instrument. The flow rate of air through 3 ± 0.01 g of sample was 10 L/h. The block temperature was 110 °C with a correction factor (Δ*T*) of 1.5 °C. The vessel that measured conductivity contained 50 ± 0.1 mL of deionized water. Samples were run in duplicate with the mean values reported in Table 1. IP was mathematically determined as the inflection point of a computer-generated plot of conductivity (μS/cm) of deionized water versus time (h).

The oxidative onset temperature (OT, °C) and signal maximum (SM, °C) temperatures were measured using PDSC (DSC Q10 thermal analyzer, TA Instruments, New Castle, DE, USA). A 2 μL sample in a pinhole hermetically sealed aluminum pan was oxidized in the presence of air

Table 3 Oxidation stability of crude black bean, kidney bean, great northern, and pinto bean oils as determined by PDSC, with crude soybean oil shown for comparison

Method	Black Bean	Kidney Bean	Great Northern	Pinto Bean	Soybean
OT, °C	195.4 (1.1)	190.0 (0.5)	197.4 (0.2)	184.5 (0.3)	181.1 (0.3)
SM, °C	201.2 (1.6)	197.3 (0.5)	203.0 (0.8)	190.4 (0.1)	200.2 (0.8)

Values in parentheses are the standard deviations from the reported mean

OT Onset temperature, SM signal maximum temperature

(1378.95 kPa, 200 psi) by heating at a ramp rate of 10 °C min⁻¹. The OT and SM values were calculated from the exotherm in each case. The OT was obtained from extrapolating the tangent drawn on the steepest slope of reaction exotherm. High OT would suggest a high oxidative stability of the vegetable oil. All oil samples were run in triplicate with the mean values and standard deviations reported in Table 3.

Tocopherol Content by HPLC

Tocopherols were quantified by HPLC according to AOCS official method Ce 8-89 [28]. Samples were diluted in hexane to a concentration of 50–100 mg/mL, filtered through 0.45 µm centrifugal filters and analyzed by a Varian HPLC, Pro-Star model 230 pump, model 410 autosampler, and model 363 fluorescence detector using excitation and emission wavelengths of 290 and 330 nm, respectively. The mobile phase consisted of hexane: 2-propanol (99.5:0.5 v/v, made fresh daily) pumped at a rate of 1 mL/min. Samples were injected by autosampler using the full loop option (100 µL), and tocopherols were separated using an Inertsil (Varian) silica column (5 µm, 150 Å, 250 mm × 4.6 mm i.d.). Tocopherols were identified by comparison to the retention times of known reference standards. A mixture of α-, β-, γ-, and δ-tocopherols standards was injected before analysis to verify HPLC response. Samples were quantified using external standards curves. All experiments were run in triplicate with the mean values reported in Table 4.

Table 4 Tocopherol (ppm) contents of crude black bean, kidney bean, great northern, and pinto bean oils, with crude soybean oil shown for comparison

	Black Bean	Kidney Bean	Great Northern	Pinto Bean	Soybean
α-Tocopherol	110 (4)	151 (4)	25 (2)	29 (1)	123 (9)
β-Tocopherol	— ^a	— ^a	— ^a	— ^a	17 (2)
γ-Tocopherol	2,692 (21)	2,380 (19)	2,828 (24)	2,737 (32)	817 (14)
Δ-Tocopherol	157 (6)	137 (3)	116 (3)	88 (3)	344 (11)
Total Tocopherols	2,959	2,668	2,969	2,854	1,301

Values in parentheses are the standard deviations from the reported mean

^a Not quantified

Results and Discussion

The total weights of ground beans used for oil extraction were 4.59, 4.80, 2.52 and 3.04 kg, for pinto, dark red kidney, black, and great northern beans, respectively. The oil yields were 73.41, 63.37, 55.27 and 55.68 g, which represented 1.6, 1.3, 2.2 and 1.8 mass% of the original bean weight, respectively.

The crude oils obtained from black bean, kidney, great northern, and pinto beans were dark in appearance. All oils had Gardner color values (Table 1) of 12 or greater (1 being the lightest and 18 the darkest). For comparison, crude SBO exhibited a Gardner color of 10.

The AVs of the crude kidney bean oils were substantially higher than was observed in the case of crude SBO (Table 1). In particular, kidney bean oil displayed a value (15.37 mg KOH/g) that was roughly two to three times higher than the other bean oils and fourteen times higher than SBO. AV correlates directly to free fatty acid (FFA) content (FFA = AV × 0.5).

The primary FA found in black bean, kidney bean, great northern, and pinto bean oils were linolenic (C18:3, 41.7–46 area %) and linoleic (C18:2, 24.1–33.4 area %), with palmitic (C16:0, 10.7–12.7 area %) and oleic (C18:1, 5.2–9.5 area %) acids also detected in significant quantities (Table 2). The high content of polyunsaturated FAs in these oils (>70 area %;) resulted in high IVs (>170 g I₂/100 g; Table 1).

The iodine value is often purported to be a predictor of oxidative stability, as these parameters are frequently

inversely related [29]. However, other important factors besides IV may influence IP, such as the concentrations of native antioxidants (e.g., tocopherols, tocotrienols, and polyphenolics), different sample histories (e.g., prior exposure to elevated temperatures, UV irradiation and oxygen, or extended storage), and differences in FFA content (a pro-oxidant) [28]. The current study is a good example of the tenuous relationship between IV and IP. As seen in Table 1, crude SBO had the lowest IV among the oils but also exhibited the lowest IP. Furthermore, the bean oils had similar IV, but widely varying IP. Therefore, the IP results obtained for black bean, kidney bean, great northern, and pinto bean oils cannot be explained by examination of the FA profile alone. It is therefore presumed that these oils contained a favorable mixture of synergistic antioxidants, with great northern and black bean oils containing greater or more favorable amounts than kidney bean and pinto bean oils. This presumption is consistent with an earlier report on the analysis of antioxidants in these beans, which showed higher overall levels of antioxidants in great northern and black beans [30, 31].

Because the oils from black, kidney, great northern, and pinto beans contained higher percentages of polyunsaturated and lower percentages of saturated FAs than SBO, these oils exhibited lower PP values than SBO (Table 1). In the case of FAME, the melting point (mp) decreases with an increasing level of unsaturation in compounds of similar chain length, as evidenced by the mp of methyl esters of stearic (mp 39 °C), oleic (mp -20 °C), linoleic (mp -35 °C), and linolenic (mp -52 °C) acids [32]. Other low temperature properties such as cloud point (CP) were not determined in this study as a result of the opaqueness of the samples. The propensity of chemical species with greater amounts of polyunsaturation to exhibit lower melting points explains why these oils displayed superior low temperature properties in comparison to SBO.

The kinematic viscosities of the oils from black bean, great northern, and pinto bean were approximately similar, and slightly higher than the corresponding values obtained for crude SBO (Table 1). Ordinarily, based on the FA profiles of these oils, lower viscosities would be expected versus SBO, since kinematic viscosity decreases with increasing level of unsaturation [33]. SBO, as explained previously, contains fewer polyunsaturated FA than the other oils. Consequently, a higher viscosity would be expected.

Ordinarily, such a high content of polyunsaturated FAs would result in abysmal oxidative stability, but these oils exhibited unusually long IPs (Table 1). In fact, all four oils had IP values longer than crude SBO, which paradoxically contained significantly fewer polyunsaturated FAs (Tables 1, 2). In particular, the IPs of black bean oil (41.7 h) and great northern oil (60.4 h) were exceptionally

long. Trienoic FAs are particularly susceptible to oxidative degradation, as evidenced by relative rates of oxidation of 0.04, 1.63, and 3.90 mole O₂/acid equiv/100 h for ethyl esters of oleic, linoleic, and linolenic acids, respectively [34]. As seen in Table 1, all four oils contained >40% (area) of linolenic acid. For comparison, SBO, which is less stable to oxidation, contained 7.4 wt% of linolenic acid. Additionally, a previous study determined that the IPs (at 110 °C) of methyl esters of oleic, linoleic, and linolenic acids were 2.5, 1.0, and 0.2 h, respectively [35]. The comparatively higher content of FFAs in black bean, great northern, and pinto bean oils versus SBO may in part explain their unexpectedly higher kinematic viscosities. The viscosity of the bean oils increases with increasing AV (Fig. 1). Kidney bean oil was especially viscous, exhibiting kinematic viscosities and AVs significantly higher than the other oils. It is likely that a non-vegetable oil component of high kinematic viscosity was present in this sample. The VIs of the oils were very similar (228–231, Table 1), with the exception of kidney bean oil, which had a lower value (199).

The oxidative stability of lubricating oils and the oxidation inhibition capacity of antioxidant additives can be evaluated using methods such as pressurized differential scanning calorimetry (PDSC), rotary bomb oxidation test (RBOT), thin film micro oxidation test (TFMO), turbine oil stability test (TOST), and hydroperoxide titration test [36–38]. In this study, PDSC which is an effective way to evaluate the antioxidant efficiency and oxidation stability of base oils [39–41] was employed. This allows the use of lower test temperatures or shorter test times at the same temperatures. The PDSC is also a rapid and accurate technique for measuring parameters that correlate with oxidation reactions of oils [39, 42, 43]. PDSC experiments run in a programmed temperature mode were used to measure OT [40, 41, 43–45] of vegetable oil oxidation. The OT was at least 3 °C higher for pinto bean oil and 16 °C higher for great northern bean oil compared to crude SBO.

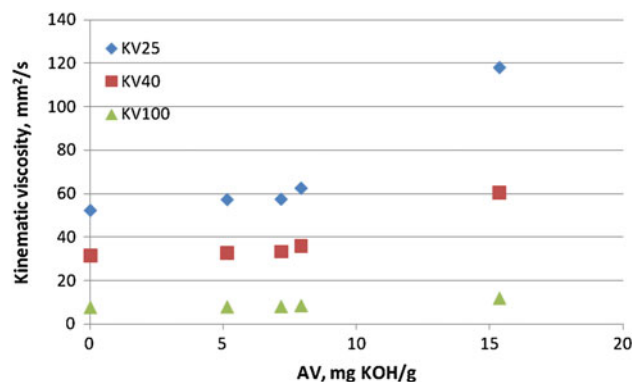


Fig. 1 Variation of kinematic viscosity (KV) with increasing acid values (AV)

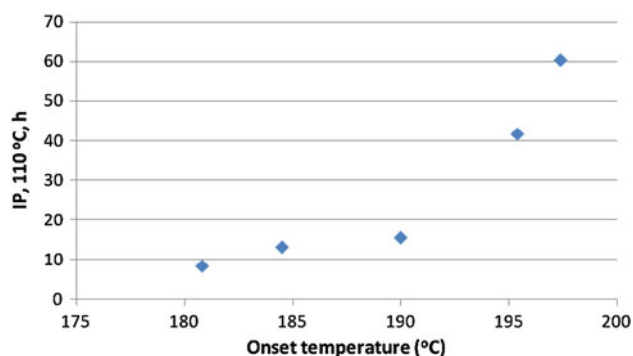


Fig. 2 Variation of induction period (IP, h) with increasing OT (°C)

Similar results were obtained from the IP values measured using Rancimat method EN 14112 as discussed above. A big advantage of the PDSC technique is that it uses microgram amount of sample, while the Rancimat test uses 3 g of sample. Also, we have shown earlier that oxidative stability data generated using PDSC is more reproducible than IP [45]. In addition, another study demonstrated that higher stability oils show poor repeatability in the Rancimat test [46], while the PDSC method can be used for low as well as very high oxidative stability oils. A higher stability oil, like great northern bean oil, has a much higher standard deviation (3.1) for IP compared to a low-stability oil like crude SBO (0.2). Figure 2 shows that IP values increase slowly initially with OT and then rise sharply after 190 °C. We found good correlation between PDSC and IP. The OT showed R-square value of 0.98 on polynomial regression, 0.94 on power and exponential regression, and 0.84 on linear regression with IP. Similarly, SM showed R^2 value of 1.00 on polynomial regression, 0.77 on power, logarithmic, and exponential regression, and 0.78 on linear regression with IP. As discussed earlier, the higher oxidative stability shown by black bean oil and great northern bean oil was hard to explain with the FA composition data, IV and AV. Despite having much higher IVs and AVs compared to crude SBO, all of the bean oils still demonstrated a high oxidative stability, again pointing to the presence of synergistic combinations of naturally occurring antioxidants.

The concentration of β -tocopherol was not quantified (Table 4). The total tocopherols in the bean oils ranged from 2,670 to 2,970 ppm (Table 4). The values obtained for γ -tocopherol in all cases were above the range of the standard curve, which is calibrated up to 1,200 ppm. The extremely high content of γ -tocopherol (09–96%) in these oils are noteworthy and may be in part responsible for the high oxidative stability of the oils. Oxidation stability, as measured by Rancimat and PDSC, increases slowly with an increasing amount of γ -tocopherol in oil samples up to 2,400 ppm, and increases sharply thereafter with a further increase in γ -tocopherol content.

Table 5 summarizes and shows a comparison of bean oil properties with soybean oil. The oxidation stability of black and great northern bean oils are excellent, while the other two bean oils have good stability compared to soybean oil based on IP and PDSC results. The low temperature properties (LTP) show an opposite trend with kidney and pinto bean oil which had good LTP (lowest PP) and black and great northern bean with average LTP (lower PP than soybean oil) compared to soybean oil. The viscosity index for bean oils except kidney bean oil is at par with soybean oil. Although polyunsaturation (PU) and in turn IV are higher compared to soybean oil, it is generally accepted that Rancimat-IP [47] or PDSC-OT qualifies for oil storage stability rather than IV. The IP and OT values depend on the double bond positions, i.e. allylic and bis-allylic positions and on the content of natural antioxidants in the oil. Even with higher PU and IV of all bean oils, the IP and OT values demonstrate that the higher stability is due to the presence of natural antioxidants.

Conclusion

Although the properties of bean oils are promising, their market potential is largely dependent on bean production, their current utilization, and oil content. The presence of a small amount of oils in these beans will most likely direct their use to nutritional supplement as a source of natural antioxidants. Identifying the synergistic combination of antioxidants may open up a new source of natural

Table 5 Comparison of crude bean oil properties with crude soybean oil

Oil	PU	IV	AV	VI	PP	Oxidation stability
Black bean	High	High	Poor	At par	Good	Excellent
Kidney bean	High	High	Poor	Low	Excellent	Good
Great northern bean	High	High	Poor	At par	Good	Excellent
Pinto bean	High	High	Poor	At par	Excellent	Good
Soybean	Baseline	Baseline	Baseline	Baseline	Baseline	Baseline

PU polyunsaturation, IV iodine value, AV acid value, VI viscosity index, PP pour point

antioxidants to be used for providing stability to edible oils, biodiesel, and biolubricants.

Acknowledgement The authors thank Benetria N. Banks and Erin L. Walter for excellent technical assistance.

References

- Geil PB, Anderson JW (1994) Nutrition and health implications of dry beans: a review. *J Am Coll Nutr* 13:549–558
- Azevedo L, Gomes JC, Stringheta PC, Gontijo AMMC, Padovani CR, Ribeiro LR, Salvadori DMF (2003) Black bean as protective agent against damage in mice. *Food Chem Toxicol* 41:1671–1676
- Venkateswaran S, Pari L, Saravanan G (2002) Effect of *Phaseolus vulgaris* on circulatory antioxidants and lipids in rats with streptozotocin-induced diabetes. *J Med Food* 5:97–103
- Anderson JW, Story L, Sieling B, Chen WJL, Petro MS, Story J (1984) Hypocholesterolemic effects of oat-bran or bean intake for hypercholesterolemic men. *Am J Clin Nutr* 48:749–753
- Bazzano LA, He J, Ogden LG, Loria C, Vupputuri S, Myers L, Whelton PK (2001) Legume consumption and risk of coronary heart disease in US men and women. *Arch Intern Med* 161:2573–2578
- Hangen L, Bennink MR (2002) Consumption of black beans and navy beans (*Phaseolus vulgaris*) reduced azoxymethane induced colon cancer in rats. *Nutr Cancer* 44:60–65
- Simard RE, Barampama Z (1993) Nutrient composition, protein quality and antinutritional factors of some varieties of dry beans (*Phaseolus vulgaris*) grown in Burundi. *Food Chem* 47:159–167
- Hughes JS, Ganthavorn C, Wilson-Sanders S (1997) Dry beans inhibit azoxymethane-induced colon carcinogenesis in F344 rats. *J Nutr* 127:2328–2333
- Xu B, Chang SKZ (2009) Total phenolic, phenolic acid, anthocyanin, flavan-3-ol, and flavonol profiles and antioxidant properties of pinto and black beans (*Phaseolus vulgaris* L.) as affected by thermal processing. *J Agric Food Chem* 57(11):4754–4764
- Xu B, Chang SKZ (2008) Antioxidant capacity of seed coat, dehulled bean, and whole black soybeans in relation to their distribution of total phenolics, phenolic acids, anthocyanins, and isoflavones. *J Agric Food Chem* 56(18):8365–8373
- Onyeneho SN, Hettiarachchy NS (1991) Effect of navy bean hull extract on the oxidative stability of soy and sunflower oils. *J Agric Food Chem* 39(10):1701–1704
- Biswas A, Shogren RL, Willet JL, Erhan SZ, Cheng HN (2008) Enzymatic products from modified soybean oil containing hydrazinoester. *Polymer biocatalysis and biomaterials II*, Chapter 5, ACS Symposium Series, vol 999, pp 76–85
- Teng G, Gao L, Xiao G, Liu H (2009) Transesterification of soybean oil to biodiesel over heterogeneous solid base catalyst. *Energy Fuels* 23(9):4630–4634
- Pasias SA, Barakos NK, Papayannakos NG (2009) Catalytic effect of free fatty acids on cotton seed oil thermal transesterification. *Ind Eng Chem Res* 48:4266–4273
- Rashid U, Anwar F, Moser BR, Ashraf S (2008) Production of sunflower oil methyl esters by optimized alkali-catalyzed methanolysis. *Biomass Bioenergy* 32:1202–1205
- Wang H, Wang T, Johnson LA (2009) Effect of low-shear extrusion on corn fermentation and oil partition. *J Agric Food Chem* 57:2302–2307
- Wang H, Wang T, Johnson LA, Pometto AL (2008) Effect of the corn breaking method on oil distribution between stillage phases of dry-grind corn ethanol production. *J Agric Food Chem* 56:9975–9980
- Moser BR, Shah SH, Winkler-Moser JK, Vaughn SF, Evangelista RL (2009) Composition and physical properties of cress (*Lepidium sativum* L.) and field pennycress (*Thlaspi arvense* L.). *Oils Ind Crops Prod* 30:199–205
- Moser BR, Knothe G, Vaughn SF, Isbell TA (2009) Production and evaluation of biodiesel from field pennycress (*Thlaspi arvense* L.). *Oil Energy Fuels* 23:4149–4155
- ASTM (2001) Standard test method for pour point of petroleum products (automatic pressure pulsing method) ASTM (D5949-01). In: ASTM Annual Book of Standards, ASTM International, West Conshohocken
- ASTM (2006) Standard test method for kinematic viscosity of transparent and opaque liquids (and calculation of dynamic viscosity) ASTM (D445-06). In: ASTM Annual Book of Standards, ASTM International, West Conshohocken
- ASTM (2004) Standard practice for calculating viscosity index from kinematic viscosity at 40 and 100 °C. In: ASTM Annual Book of Standards, ASTM International, West Conshohocken
- CEN (2003) Fat and oil derivatives. Fatty acid methyl esters (FAME). Determination of oxidative stability (accelerated oxidation test) EN (14112:2003). CEN, Brussels
- AOCS (1999) Acid value. In: Official methods and recommended practices of the American Oil Chemists Society, 5th edn. AOCS, Champaign, pp Cd 3d-63
- AOCS (1999) Calculated iodine value. In: Official methods and recommended practices of the American Oil Chemists Society, 5th edn. AOCS, Champaign, pp Cd 1c-85
- Ichihara K, Shibahara A, Yamamoto K, Nakayama T (1996) An improved method for rapid analysis of the fatty acids of glycerolipids. *Lipids* 31:535–539
- AOCS (1999) Gardner color 1963 (glass standards). In: Official methods and recommended practices of the American Oil Chemists Society, 5th edn. AOCS, Champaign, pp Td 1a-64
- AOCS (1999) Determination of tocopherols and tocotrienols in vegetable oils and fats by HPLC. In: Official methods and recommended practices of the American Oil Chemists Society, 5th edn. AOCS, Champaign, pp Ce 8-89
- Moser BR (2008) Influence of blending canola, palm, soybean, and sunflower oil methyl esters on fuel properties of biodiesel. *Energy Fuels* 22:4301–4306
- Biswas A, Sutivisedsak N, Cheng HN, Willett JL, Rose D, Lesch WC, Tangsrud RR (2009) Extraction and analysis of antioxidant capacity in eight edible beans. *J Food Agric Env* (abstract submitted)
- Sutivisedsak N, Cheng HN, Willett JL, Lesch WC, Tangsrud RR, Biswas A (2010) Microwave-assisted extraction of phenolics from bean (*Phaseolus vulgaris* L.). *Food Res Int* 43:516–519
- Anonymous (2007) Dictionary section. In: Gunstone FD, Harwood JL, Dijkstra AJ (eds) *The lipid handbook*, 3rd edn. CRC Press, Boca Raton, pp 428–445
- Knothe G, Steidley KR (2005) Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel standards. *Fuel* 84:1059–1065
- Holman RT, Elmer OC (1947) The rates of oxidation of unsaturated fatty acids and esters. *J Am Oil Chem Soc* 24:127–129
- Moser BR (2009) Comparative oxidative stability of fatty acid alkyl esters by accelerated methods. *J Am Oil Chem Soc* 86:699–706
- Cermak SC, Isbell TA (2003) Improved oxidative stability of estolide esters. *Ind Crops Prod* 18(3):223–230
- Gatto VJ, Grina MA, Tat TL, Ryan HT (2002) The influence of chemical structure on the physical properties and antioxidant response of hydrocracked base stocks and polyalphaolefins. *J Synth Lubr* 19(1):1–18
- Qiu C, Han S, Cheng X, Ren T (2006) Determining the antioxidant activities of organic sulfides by rotary bomb oxidation test

- and pressurized differential scanning calorimetry. *Thermochim Acta* 447:36–40
39. Sharma BK, Stipanovic AJ (2003) Development of a new oxidation stability test method for lubricating oils using high-pressure differential scanning calorimetry. *Thermochim Acta* 402(1–2):1–18
 40. Sharma BK, Adhvaryu A, Sahoo SK, Stipanovic AJ, Erhan SZ (2004) Influence of chemical structures on low temperature rheology, oxidative stability, and physical properties of group II and III base oils. *Energy Fuels* 18(4):952–959
 41. Adhvaryu A, Sharma BK, Hwang HS, Erhan SZ, Perez JM (2006) Development of biobased synthetic fluids: application of molecular modeling to structure-physical property relationship. *Ind Eng Chem Res* 45:928–933
 42. Kowlaski B, Gruczynska E, Maciaszek K (2000) Kinetics of rapeseed oil oxidation by pressure differential scanning calorimetry measurements. *Eur J Lipid Sci Technol* 102(5):337–341
 43. Adhvaryu A, Erhan SZ, Liu ZS, Perez JM (2000) Oxidation kinetic studies of oils derived from unmodified and genetically modified vegetables using pressurized differential scanning calorimetry and nuclear magnetic resonance spectroscopy. *Thermochim Acta* 364:87–97
 44. Dunn RO (2000) Analysis of oxidative stability of methyl soyate by pressurized-differential scanning calorimetry (P-DSC). *Trans ASAE* 43(5):1203–1208
 45. Sharma BK, Rashid U, Anwar F, Erhan SZ (2009) Lubricant properties of moringa oil using thermal and tribological techniques. *J Therm Anal Calorim* 96:999–1008
 46. Kodali DR (2005) Oxidative stability measurement of high-stability oils by pressure differential scanning calorimeter (PDSC). *J Agric Food Chem* 53:7649–7653
 47. Knothe G (2002) Structure indices in FA chemistry. How relevant is the iodine value? *J Am Oil Chem Soc* 79:847–854