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Oil Goldenberry (*Physalis peruviana* L.)

MOHAMED F. RAMADAN* AND JÖRG-T. MÖRSEL

Institute of Food Chemistry, Technical University of Berlin, TIB 4/3-1, Gustav-Meyer-Allee 25, D-13355 Berlin, Germany

Whole berries, seeds, and pulp/peel of goldenberry (*Physalis peruviana* L.) were compared in terms of fatty acids, lipid classes, triacylglyerols, phytosterols, fat-soluble vitamins, and β-carotene. The total lipid contents in the whole berries, seeds, and seedless parts were 2.0, 1.8, and 0.2% (on a fresh weight basis), respectively. Linoleic acid was the dominating fatty acid followed by oleic acid as the second major fatty acid. Palmitic and stearic acids were the major saturates. In pulp/peel oil, the fatty acid profile was characterized by higher amounts of saturates, monoenes, and trienes than in whole berry and seed oils. Neutral lipids comprised >95% of total lipids in whole berry oil and seed oil, while neutral lipids separated in lower level in pulp/peel oil. Triacylglycerols were the predominant neutral lipid subclass and constituted ca. 81.6, 86.6, and 65.1% of total neutral lipids in whole berry, seed, and pulp/peel oils, respectively. Nine triacylglycerol molecular species were detected, wherein three species, C54:3, C52:2, and C54:6, were presented to the extent of ~91% or above. The highest level of phytosterols was estimated in pulp/peel oil that contained the highest level of unsaponifiables. In both whole berry and seed oils, campesterol and β-sitosterol were the sterol markers, whereas Δ5-avenasterol and campesterol were the main 4-desmethylsterols in pulp/peel oil. The tocopherols level was much higher in pulp/peel oil than in whole berry and seed oils. β- and γ-tocopherols were the major components in whole berry and seed oils, whereas γ- and α-tocopherols were the main constituents in pulp/peel oil. β-Carotene and vitamin K_1 were also measured in markedly high levels in pulp/peel oil followed by whole berry oil and seed oil, respectively. Information provided by the present work is of importance for further chemical investigation of goldenberry oil and industrial utilization of the berries as a raw material of oils and functional foods.

KEYWORDS: ***Physalis peruviana* L.; goldenberry; fatty acids; seed oil; pulp/peel oil; triacylglycerols; phytosterols; tocopherols; β-carotene; vitamin K_1**

INTRODUCTION

Goldenberry or cape gooseberry (*Physalis peruviana* L.) has long been a minor fruit of the Andes and has also been grown in California, South Africa, East Africa, India, New Zealand, Australia, and Great Britain (*1*−*3*). So far, however, it has nowhere become a major crop. Nonetheless, this interesting and unusual botanical relative of potatoes and tomatoes has commercial promise for many regions. Goldenberries are succulent golden spheres the size of marbles with a pleasing taste. They are protected by papery husks resembling Chinese lanterns (**Figure 1**). It is somewhat tomato-like in flavor and appearance, although the taste (sweet and sour) is much richer with a hint of tropical luxuriance. The plant is fairly adaptable to a wide variety of well-drained soils, and very good crops are obtained on rather poor sandy ground (*1*, *4*). A single plant may yield 300 fruits and carefully tended plants can provide 20−33 tons per hectare. Fruits are long-lasting when stored in a sealed container and kept in a dry atmosphere for several months, and they also freeze well. In most places where they are grown, goldenberries are now considered fruits only for backyard gardens or for children to pluck and eat; however, they do carry prestige in some international markets. Europeans, for example, often pay premium prices for the fruits, which are dipped in chocolate or used to decorate cakes and tortes. In addition to having a future as fresh fruits, the exotic fruit can be enjoyed in many ways as an interesting ingredient in salads, cooked dishes, desserts, jams, natural snacks, and preserves. Moreover, many medicinal properties have been attributed to the goldenberry, including antiasthmatic, diuretic, and antiseptic properties, strengthening of the optic nerve, treatment for throat afflictions, and elimination of intestinal parasites and amoebas as well as albumin from kidneys (*1*−*4*).

Previous work on goldenberry has focused on the isolation and characterization of several bioactive withanolides from the whole plant (*5*, *6*), leaves (*7*), roots (*8*), and berries with the surrounding calyx (*9*). The fruit has been widely used as an excellent source of vitamins A and C as well as minerals. The general proximate composition of goldenberry was reported (*1*, *3*, *4*), wherein the lipid content was estimated to range from

* Author to whom correspondence should be addressed [telephone +49 (0)30 31472813; fax +49 (0)30 31472823; e-mail hassanienmohamed@hotmail.com].

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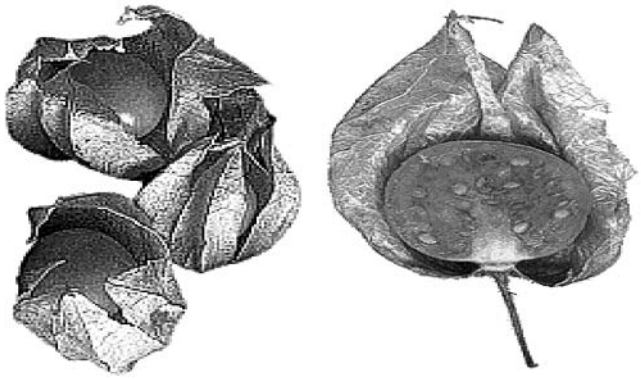

Figure 1. Goldenberry (*P. peruviana* L.) in opened calyx. The fruit is a berry, 0.5–0.75 in. (1.25–2 cm) wide, with a smooth, waxy, orange-yellow skin and a juicy pulp containing numerous small yellowish kernels. The part of the goldenberry that can be used is composed of the husk (5%) and the berry (95%). The berries can be further subdivided into seeds (~17%) and a pulp/peel fraction (~83%), the latter being the basis for fruit and juice products.

0.16 to 1.30% (on a fresh weight basis) without enough information on extraction conditions and the degree of ripeness of the berries. No detailed data, however, about goldenberry oil are yet available. In the present study, we analyzed the seeds, soft parts, and whole berries to obtain an informative profile of lipids in goldenberries, which will serve as a basis for further detailed chemical investigation and nutritional evaluation of the berries. In addition, it was the purpose of this paper to present a comprehensive assessment of the lipid composition of goldenberry and to address stability issues and the potential for their delivery in functional foods.

EXPERIMENTAL PROCEDURES

Berries and Chemicals. Two kilograms (~300 berries per kilogram) of goldenberries, product of Colombia, was purchased from a local supermarket in Berlin, Germany, in 2001. Intact fruits were carefully selected according to the degree of ripeness measured by fruit color (brilliant orange) and the pH value of the pulp (pH 3.6) as well as the total titratable acidity (0.71%). The following highly purified simple triacylglycerols (TAG) were obtained from Serva (Heidelberg, Germany): trilaurin (36:0), trimyristin (42:0), tripalmitin (48:0), tripalmitolein (48:3), trimargrin (51:0), tristearin (54:0), triolein (54:3), and trilinolein (54:6). 1,2-Dioleoyl-3-palmitoyl-*rac*-glycerol (52:2) was purchased from Sigma Chemical Co. (St. Louis, MO). Standards used for phytosterols (ST) characterization, β-sitosterol, stigmasterol, lanosterol, ergosterol, campesterol, Δ5-avenasterol, and Δ7-avenasterol, were purchased from Supelco (Bellefonte, PA). Standards used for vitamin E (α-, β-, γ-, and δ-tocopherols), β-carotene, and vitamin K_1 (2-methyl-3-phytyl-1,4-naphthochinon) characterization were purchased from Merck (Darmstadt, Germany). All reagents and chemicals used were of the highest purity available.

Extraction of Total Lipids (TL). Seeds were isolated from berries by pressing the juice and rinsing the residue with distilled water. Separated seeds, pulp/peel, and the whole pressed berries were separately lyophilized (Alpha 1−5, Martin Christ, Osterode am Harz, Germany) to 10−25% of the original weight, depending on the berry fraction and composition. Samples (5 g) of lyophilized seeds, pulp/peel (seedless parts of the berries), and whole berries were ground (Analysenmühle A10, Janke & Kunkel GmbH, Staufen Br., Germany), and then the lipids were isolated using a chloroform/methanol extraction procedure (*10*, *11*). The sample was homogenized in methanol (50 mL) for 1 min in a blender, chloroform (100 mL) was added, and homogenization was continued for a further 2 min. The mixture was filtered and the solid residue resuspended in chloroform/methanol (2:1, v/v, 150 mL) and homogenized for 3 min. The mixture was filtered again and washed with fresh solvent (2:1, v/v, 150 mL). The combined filtrates were cleaned with a repeat addition of 0.2 volume of 0.75% aqueous sodium chloride solution. The whole was thoroughly mixed without shaking, the layers were allowed to separate, and the chloroform layer was recovered. The purified lipids were collected in a flask and subsequently treated with sodium sulfate to remove traces of water; after filtration, the extract was taken to dryness on a rotary evaporator at 40 °C. TL recovered were weighed and stored under chloroform at −20 °C until analyzed.

Gas Chromatography (GC) Analysis of Fatty Acids. Fatty acids were transesterified into methyl esters (FAME) by heating in boron trifluoride (10% solution in methanol, Merck, Darmstadt, Germany) according to the procedure reported by Metcalfe et al. (*12*). FAME were identified on a Shimadzu GC-14A equipped with a flame ionization detector (FID) and a C-R4AX Chromatopac integrator (Kyoto, Japan). The flow rate of the carrier gas (helium) was 0.6 mL/min, and the split valve, with a ratio of 1:40, was opened after 1 min. A sample of 1 μL was injected on a 30 m × 0.25 mm × 0.2 μm film thickness Supelco SP-2380 (Bellefonte, PA) capillary column. The injector and FID temperature was set at 250 °C. The initial column temperature was 100 °C programmed at 5 °C/min to 175 °C and kept for 10 min at 175 °C, then programmed at 8 °C/min to 220 °C and kept for 10 min at 220 °C. A comparison between the retention times of the samples with those of authentic standard mixture (Sigma, St. Louis, MO; 99% purity specific for GLC), run on the same column under the same conditions, was made to facilitate identification. The quantification of each fatty acid was carried out by comparing the peak of its methyl ester with that of methyl nonadecanoate without application of any correction factor.

Thin-Layer Chromatography (TLC) of Lipid Classes. Analytical and preparative TLC separation of the main lipid classes was conducted on silica gel F_{254} plates (thickness = 0.25 mm; Merck), which were activated at 120 °C for 2 h immediately before use. Development with chloroform separated total lipids into neutral lipids (NL) and polar lipids (PL). NL were further separated into their subclasses using *n*-hexane/diethyl ether/acetic acid (60:40:1, v/v/v). Plates were air-dried and stained by rhodamine in ethanol (0.5 g L^{-1}). Identification of the bands was made with the aid of the references (Sigma Chemical Co.) by comparing the bands on one and the same chromatogram: TAG [retention factor (R_f) = 0.79]; free fatty acids (FFA, R_f = 0.56); monoacylglycerols (MAG, R_f = 0.14); diacylglycerols (DAG, R_f = 0.39); ST (R_f = 0.37); and sterol esters (STE, R_f = 0.95). Individual bands were visualized under UV light after being sprayed with rhodamine, scraped from the plates, and recovered by extraction with 10% methanol in diethyl ether, followed by diethyl ether. Data presented are the average of three gravimetric estimations.

Gas Chromatography Analysis of Triaclyglycerols (TAG). After purification of TAG using the TLC procedure described above, TAG were analyzed on a Mega series high-resolution GC (HRGC 4160, Carlo Erba Strumentazione, Milan, Italy) equipped with an FID. A 30 m × 0.25 mm i.d. RTX-65TG column (65% diphenyl−35% dimethylpolysiloxan; Restek GmbH, Sulzbach, Germany) was used. The initial column temperature was kept at 260 °C for 5 min and then programmed at 5 °C/min to 360 °C and maintained at 360 °C for 25 min. Detector and injector were maintained at 360 and 340 °C, respectively. The carrier gas (H_2) had a flow rate of 10 mL/min (split−splitless injection was used). The identification of individual peaks was carried out by co-injection with standard compounds. TAG were solubilized in dichloromethane at 10 mg mL^{-1} for each TAG, and 2 μL was injected. TAG levels were estimated on the basis of peak areas of known concentrations of the standards.

Gas Chromatography Analysis of Phytosterols (ST). Separation of ST was performed after saponification of the oil samples without derivatization. After the addition of cholesterol acetate (1.5 mg; Sigma) as an internal standard, lipids (250 mg) were refluxed with 5 mL of ethanolic KOH solution (6%, w/v) and a few antibumping granules for 60 min. The unsaponifiables were first extracted three times with 10 mL of petroleum ether; the extracts were combined and washed three times with 10 mL of neutral ethanol/water (1:1, v/v) and then dried overnight with anhydrous sodium sulfate. The extract was evaporated in a rotary evaporator at 25 °C under reduced pressure, and then ether was completely evaporated under nitrogen. GC-FID

analyses of unsaponifiable residues were carried out using a Mega series (HRGC 5160, Carlo Erba Strumentazione) equipped with an FID. The following parameters were tested and found to be useful: GC column, ID phase DB 5, packed with 5% phenylmethylpolysiloxan (J&W Scientific, Folsom, CA), 30 m length, 0.25 mm i.d., 1.0 μm film thickness; carrier gas (helium) flow 38 mL/min (split−splitless injection). Detector and injector were set at 280 °C. The oven temperature was kept constant at 310 °C, and the injected volume was 2 μL. All ST homologues eluted within 45 min, and total analysis was set at 60 min to ensure the elution of all ST. The quantification of sterol compounds was carried out with a cholesterol internal standard and calculated by applying the detector response of sitosterol. The content of ST in seeds, pulp/peel, and whole berry oils was calculated according to the oil contents in these fractions and the contents of sterols in the oils (isolated by TLC). The repeatability of the analytical procedure was tested, and the relative standard deviation of three repeated analyses of a single sample was <5%. Quantitative analyses were performed with a Shimadzu (C-R6A Chromatopac, Kyoto, Japan) integrator.

Normal Phase High-Performance Liquid Chromatography (NP-HPLC) Separation, Identification, and Quantification of Fat-Soluble Vitamins (FSV) and β-Carotene. *Procedure.* NP-HPLC was selected to avoid extra sample treatment (e.g., saponification). Analysis was performed with a solvent delivery LC-9A HPLC (Shimadzu, Kyoto, Japan). The chromatographic system included a model 87.00 variable-wavelength detector and a 250 × 4 mm i.d. LiChrospher-Si 60, 5 μm, column (Knauer, Berlin, Germany). Separation of all vitamins was based on isocratic elution when the solvent flow rate was maintained at 1 mL/min at a column back-pressure of ∼65−70 bar. The solvent system selected for tocopherol elution was isooctane/ethyl acetate (96:4, v/v) with detection at 295 nm. An isooctane/2-propanol (99:1, v/v) mixture was used to elute β-carotene (detection at 453 nm) and vitamin K_1 (detection at 244 nm). Twenty microliters of the diluted solution of TL in the selected mobile phase was directly injected into the HPLC column. FSV and provitamin A were identified by comparing their retention times with those of authentic standards.

Preparation of Standard Curves. Standard solutions of vitamins were prepared by serial dilution to concentrations of approximately 5 mg mL^{-1} of vitamin E, 0.7 mg mL^{-1} of β-carotene, and 1.4 mg mL^{-1} of vitamin K_1. Standard solutions were prepared daily from a stock solution, which was stored in the dark at −20 °C. Twenty microliters was injected, and peak areas were determined to generate standard curve data.

Quantification. All quantitation was by peak area using the Shimadzu C-R6A Chromatopac integrator. Standard curves (concentration versus peak area) were calculated from six concentration levels by linear regression. On the basis of the established chromatographic conditions, repeated injections of different concentrations of the standard FSV and β-carotene were made three times onto the HPLC system. Injections in triplicte were made at each concentration for both standards and samples. All work was carried out under subdued light conditions.

All of the experiments were repeated three times when the variation on any one was routinely <5%. Small differences between values of the whole berry oil spectra and calculated values of seed oil plus pulp/peel oil spectra may result from sample semihomogeneity or analysis errors.

RESULTS AND DISCUSSION

Recovered Lipids and Fatty Acid Profile of Total Lipids. In the present investigation whole berries were found to contain ∼2.0% oil (on a fresh weight basis), in which seed oil comprised ∼90% (1.8% oil of the whole berry fresh weight) and pulp/peel oil constituted ∼10% (0.2% oil of the whole berry fresh weight). Analysis of FAME in the whole berry oil (WBO), seed oil (SO), and pulp/peel oil (PO) of *P. peruviana* L. gave the proportion of linoleic, oleic, palmitic, stearic, and γ-linolenic (GLA) esters as the major FAME. According to the results shown in **Table 1** 15 fatty acids were detected. In the different studied oils linoleic acid was the dominating fatty acid followed by oleic acid as the second major fatty acid, wherein the ratio of linoleic acid to oleic acid was more than 2:1 in PO and around 5:1 in WBO and SO. It is well-known that dietary lipids, rich in linoleic acid, prevent cardiovascular disorders such as coronary heart diseases, atherosclerosis, and high blood pressure. Also, linoleic acid derivatives serve as structural components of the plasma membrane and as precursors of some metabolic regulatory compounds (*13*). These oils also contain appreciable amounts of saturated normal-chain fatty acids. Palmitic acid (∼9%) and stearic acid (∼2.5%) were the major saturated fatty acids in all examined oils. PO, however, was characterized by a relatively high amount of saturated fatty acids, which comprised >16% of total FAME. The four fatty acids (linoleic, oleic, palmitic, and stearic) constituted ∼95% of total FAME in WBO and SO, and accounted for ∼77% in PO. Five minor fatty acids, namely, gadoleic, dihomo-γ-linolenic (DHGLA), erucic, lignoceric, and nervonic acids, were identified in higher levels in PO and in lower amounts in WBO, whereas they were not detected in SO. Unlike SO, which contains a very low level of trienes (GLA, α-linolenic acid, and DHGLA), PO could be a good source of this type of polyunsaturated fatty acids. The total content of trienes in PO was ∼11.7%, and the oil was characterized by a relatively high level of GLA (8.66% of total FAME), whereas ω−3 fatty acid (α-linolenic acid) and DHGLA were estimated at lower levels. Interest in the polyunsaturated fatty acids as health-promoting nutritents has expanded dramatically in recent years, and a rapidly growing literature illustrates their benefits (*14*−*16*). The fatty acid composition and high amounts of polyunsaturated fatty acids make the goldenberry a special fruit for nutritional applications.

Table 1. Fatty Acid Compositions (As a Percentage of Total FAME) of Goldenberry Oils[a]

fatty acid	WBO	SO	PO
C12:0	0.49 ± 0.03	0.35 ± 0.01	0.91 ± 0.04
C14:0	1.00 ± 0.06	1.00 ± 0.05	0.50 ± 0.02
C16:0	8.62 ± 0.25	7.29 ± 0.19	9.58 ± 0.33
C16:1*n*–7	0.63 ± 0.02	0.52 ± 0.02	1.06 ± 0.04
C18:0	2.57 ± 0.09	2.51 ± 0.07	2.92 ± 0.10
C18:1*n*–9	13.0 ± 0.43	11.7 ± 0.39	20.1 ± 0.55
C18:2*n*–6	70.5 ± 3.05	76.1 ± 3.11	44.4 ± 1.28
C18:3*n*–6	1.79 ± 0.04	0.31 ± 0.03	8.66 ± 0.12
C20:0	0.28 ± 0.01	0.20 ± 0.01	0.40 ± 0.05
C18:3*n*–3	0.11 ± 0.01	0.02 ± 0.004	1.09 ± 0.04
C20:1*n*–9	0.01 ± 0.001	nd[b]	0.22 ± 0.01
C20:3*n*–6	0.22 ± 0.01	nd	1.95 ± 0.18
C22:1*n*–9	0.26 ± 0.02	nd	2.70 ± 0.07
C24:0	0.22 ± 0.01	nd	1.85 ± 0.06
C24:1*n*–9	0.30 ± 0.02	nd	3.66 ± 0.29
total saturates	13.1 ± 0.32	11.3 ± 0.26	16.1 ± 0.78
total monoenes	14.2 ± 0.45	12.2 ± 0.21	27.7 ± 2.02
total dienes	70.5 ± 4.55	76.1 ± 4.84	44.4 ± 3.22
total trienes	2.12 ± 0.16	0.33 ± 0.08	11.7 ± 0.29
S/U ratio[c] (%)	15.1	12.8	19.2

[a] Values given are the mean of three replicates ± standard deviation. [b] nd, not detected. [c] Ratio of saturated fatty acids to unsaturated fatty acids.

Lipid Classes and Their Fatty Acid Composition. The levels of lipid classes presented in the goldenberry (*P. peruviana* L.) oils and the fatty acid profile of these classes are shown in **Tables 2**−**4**. The results showed that WBO and SO contained more NL (∼95% of TL) than PO, which was characterized by a high amount of PL (7.34% of TL). TAG were the predominant NL subclass in all oils under investigation and constituted ca. 81.6, 86.6, and 65.1% of total NL in WBO, SO, and PO, respectively. MAG, DAG, and FFA, moreover, were found in relatively higher levels in the PO compared with the SO and WBO. The results of our investigation revealed that the fatty

Table 2. Levels and Fatty Acid Compositions (As a Percentage of Total FAME) of Lipid Classes in the Whole Berry Oil[a]

fatty acid	MAG	DAG	TAG	FFA	STE	PL
	1.23 ± 0.06[b]	1.65 ± 0.08	78.2 ± 4.86	3.13 ± 0.24	0.49 ± 0.05	4.15 ± 0.62
C12:0	0.23 ± 0.02	0.16 ± 0.01	0.56 ± 0.04	0.63 ± 0.04	0.16 ± 0.01	2.64 ± 0.10
C14:0	0.56 ± 0.03	0.40 ± 0.02	0.82 ± 0.04	1.44 ± 0.06	0.40 ± 0.02	0.47 ± 0.02
C16:0	36.0 ± 3.13	18.0 ± 1.56	7.04 ± 0.82	16.1 ± 1.33	8.61 ± 0.85	12.9 ± 1.02
C16:1*n*–7	7.20 ± 0.63	2.21 ± 0.12	0.44 ± 0.02	1.20 ± 0.21	0.13 ± 0.01	1.73 ± 0.32
C18:0	14.0 ± 1.06	9.83 ± 0.92	2.64 ± 0.14	6.77 ± 0.52	4.32 ± 0.31	6.14 ± 0.62
C18:1*n*–9	11.6 ± 1.26	19.2 ± 2.38	13.5 ± 1.96	13.8 ± 2.02	11.9 ± 1.74	11.8 ± 1.36
C18:2*n*–6	28.5 ± 2.82	49.0 ± 3.55	72.2 ± 4.82	55.3 ± 3.06	70.0 ± 4.68	61.3 ± 3.89
C18:3*n*–6	1.11 ± 0.10	0.10 ± 0.01	1.67 ± 0.22	2.64 ± 0.42	0.25 ± 0.02	1.69 ± 0.36
C20:0	0.02 ± 0.006	0.07 ± 0.009	0.21 ± 0.01	0.02 ± 0.005	0.01 ± 0.001	0.20 ± 0.01
C18:3*n*–3	0.09 ± 0.006	0.03 ± 0.006	0.09 ± 0.007	0.10 ± 0.01	0.18 ± 0.01	0.12 ± 0.01
C20:1*n*–9	0.53 ± 0.03	0.20 ± 0.01	0.02 ± 0.002	0.21 ± 0.01	0.20 ± 0.01	0.01 ± 0.001
C20:3*n*–6	0.04 ± 0.007	0.03 ± 0.004	0.18 ± 0.01	0.30 ± 0.01	0.02 ± 0.001	0.02 ± 0.002
C22:1*n*–9	0.06 ± 0.003	0.22 ± 0.01	0.23 ± 0.03	0.07 ± 0.006	0.30 ± 0.02	0.28 ± 0.03
C24:0	0.01 ± 0.001	0.43 ± 0.04	0.17 ± 0.01	0.73 ± 0.03	0.02 ± 0.002	0.18 ± 0.003
C24:1*n*–9	0.05 ± 0.002	0.12 ± 0.01	0.23 ± 0.01	0.69 ± 0.04	3.50 ± 0.11	0.52 ± 0.12

[a] Values given are the mean of three replicates ± standard deviation. [b] This row of data is given in grams per 100 g of total lipids.

Table 3. Levels and Fatty Acid Compositions (As a Percentage of Total FAME) of Lipid Classes in Goldenberry Seed Oil[a]

fatty acid	MAG	DAG	TAG	FFA	STE	PL
	1.04 ± 0.06[b]	1.36 ± 0.09	84.0 ± 4.82	2.12 ± 0.36	0.34 ± 0.07	2.99 ± 0.62
C12:0	0.02 ± 0.003	0.10 ± 0.01	0.43 ± 0.03	0.47 ± 0.02	0.05 ± 0.008	2.42 ± 0.36
C14:0	0.53 ± 0.12	0.36 ± 0.05	0.75 ± 0.09	0.85 ± 0.08	0.28 ± 0.04	0.42 ± 0.07
C16:0	37.9 ± 4.22	17.9 ± 1.85	6.23 ± 0.92	15.5 ± 1.26	8.88 ± 0.96	12.6 ± 1.02
C16:1*n*–7	6.36 ± 0.76	2.18 ± 0.26	0.50 ± 0.13	1.16 ± 0.32	0.19 ± 0.02	1.84 ± 0.36
C18:0	14.8 ± 1.53	11.9 ± 1.16	2.48 ± 0.33	6.52 ± 0.69	4.25 ± 0.38	5.32 ± 0.42
C18:1*n*–9	11.2 ± 0.92	18.9 ± 1.33	11.9 ± 0.87	13.2 ± 1.08	11.5 ± 1.02	10.4 ± 0.95
C18:2*n*–6	28.7 ± 2.56	48.5 ± 3.59	77.2 ± 4.88	59.8 ± 3.81	74.6 ± 4.66	66.1 ± 4.31
C18:3*n*–6	0.34 ± 0.02	0.03 ± 0.008	0.32 ± 0.04	2.35 ± 0.16	0.11 ± 0.02	0.68 ± 0.05
C20:0	0.10 ± 0.01	0.11 ± 0.01	0.18 ± 0.02	0.08 ± 0.007	0.02 ± 0.002	0.16 ± 0.03
C18:3*n*–3	0.05 ± 0.002	0.02 ± 0.002	0.01 ± 0.003	0.07 ± 0.008	0.12 ± 0.02	0.06 ± 0.009
C20:1*n*–9	nd[c]	nd	nd	nd	nd	nd
C20:3*n*–6	nd	nd	nd	nd	nd	nd
C22:1*n*–9	nd	nd	nd	nd	nd	nd
C24:0	nd	nd	nd	nd	nd	nd
C24:1*n*–9	nd	nd	nd	nd	nd	nd

[a] Values given are the mean of three replicates ± standard deviation. [b] This row of data is given in grams per 100 g of total lipids. [c] nd, not detected.

Table 4. Levels and Fatty Acid Compositions (As a Percentage of Total FAME) of Lipid Classes in Goldenberry Pulp/Peel Oil[a]

fatty acid	MAG	DAG	TAG	FFA	STE	PL
	2.76 ± 0.15[b]	2.46 ± 0.12	60.3 ± 4.92	5.16 ± 0.61	0.65 ± 0.09	7.34 ± 0.89
C12:0	2.11 ± 0.24	0.45 ± 0.07	0.95 ± 0.11	0.92 ± 0.09	0.26 ± 0.03	4.94 ± 0.45
C14:0	2.26 ± 0.32	0.81± 0.07	0.37 ± 0.05	1.84 ± 0.23	0.49 ± 0.09	0.74 ± 0.15
C16:0	25.6 ± 2.06	18.7 ± 1.72	7.71± 0.63	20.5 ± 1.88	7.81 ± 0.84	13.9 ± 1.69
C16:1*n*–7	3.02 ± 0.58	2.08 ± 0.41	1.10 ± 0.22	3.06 ± 0.55	nd[c]	1.56 ± 0.32
C18:0	8.61 ± 1.15	6.97 ± 0.84	2.93 ± 0.39	7.57 ± 0.83	2.58 ± 0.34	5.98 ± 0.76
C18:1*n*–9	21.1 ± 1.98	25.1 ± 1.85	22.3 ± 1.77	23.8 ± 1.96	12.8 ± 1.18	16.9 ± 1.52
C18:2*n*–6	23.9 ± 1.93	31.1 ± 2.22	46.1 ± 2.76	26.9 ± 2.00	38.9 ± 2.44	39.4 ± 2.36
C18:3*n*–6	8.30 ± 0.96	4.68 ± 0.79	9.26 ± 1.00	6.91 ± 0.83	3.37 ± 0.32	12.2 ± 1.11
C20:0	0.09 ± 0.005	0.06 ± 0.003	0.33 ± 0.08	nd	nd	0.37 ± 0.09
C18:3*n*–3	0.12 ± 0.04	0.08 ± 0.009	1.06 ± 0.13	0.15 ± 0.01	0.55 ± 0.06	0.43 ± 0.06
C20:1*n*–9	3.51 ± 0.32	2.35 ± 0.25	0.24 ± 0.05	1.21 ± 0.12	1.86 ± 0.34	0.02 ± 0.004
C20:3*n*–6	0.51 ± 0.06	1.59 ± 0.29	1.83 ± 0.61	1.79 ± 0.46	0.16 ± 0.03	0.09 ± 0.006
C22:1*n*–9	0.68 ± 0.07	3.48 ± 0.72	1.63 ± 0.63	1.14 ± 0.11	3.87 ± 0.82	1.24 ± 0.44
C24:0	0.02 ± 0.002	1.43 ± 0.35	1.22 ± 0.45	1.80 ± 0.62	0.25 ± 0.03	0.38 ± 0.06
C24:1*n*–9	0.17 ± 0.08	1.12 ± 0.32	2.97 ± 0.85	2.41 ± 0.82	27.1 ± 3.03	1.85 ± 0.71

[a] Values given are the mean of three replicates ± standard deviation. [b] This row of data is given as grams per 100 g of total lipids. [c] nd, not detected.

acid compositions of the lipid classes resemble each other in the examined samples. Linoleic acid and oleic acid were the major unsaturated fatty acids detected in most of the lipid classes. Saturated fatty acids, namely, plamitic and stearic, were detected in higher amounts in all lipid classes, especially MAG, which was characterized by extremely high levels of palmitic acid (>25%). STE in both WBO and PO were also characterized by exceptionally high levels of nervonic acid, whereas GLA was detected in higher level in the PL fraction of PO.

Triacylglycerols Composition. The increasingly efficient separation of individual TAG present in fats and oils that can now be carried out is gradually increasing the understanding of

Table 5. Levels of Triacylglycerols, Sterols, Fat-Soluble Vitamins, and β-Carotene in Goldenberry Oils[a]

compound	WBO	SO	PO
Triacylglycerols Composition[b]			
36:0[c]	0.65 ± 0.08	0.59 ± 0.05	0.96 ± 0.12
42:0	0.09 ± 0.007	0.07 ± 0.005	0.04 ± 0.006
48:0	0.69 ± 0.04	0.58 ± 0.05	0.92 ± 0.07
48:3	0.08 ± 0.006	0.06 ± 0.007	0.17 ± 0.02
50:1	2.38 ± 0.32	2.33 ± 0.036	3.85 ± 0.52
52:2	27.8 ± 2.77	27.6 ± 2.69	33.6 ± 3.21
54:0	0.15 ± 0.04	0.14 ± 0.04	0.26 ± 0.08
54:3	8.80 ± 0.87	8.53 ± 0.91	16.3 ± 1.27
54:6	58.1 ± 4.00	59.0 ± 3.83	41.1 ± 3.62
unknown	1.26 ± 0.12	1.10 ± 0.07	2.80 ± 0.19
Sterols Composition[d]			
ergosterol	1.16 ± 0.12	1.04 ± 0.09	8.62 ± 1.03
campesterol	6.70 ± 0.88	6.48 ± 0.95	11.5 ± 1.09
stigmasterol	1.69 ± 0.23	1.32 ± 0.36	6.17 ± 0.76
lanosterol	2.51 ± 0.46	2.27 ± 0.29	7.44 ± 0.96
β-sitosterol	5.73 ± 0.86	5.71± 0.82	4.99 ± 0.75
Δ5-avenasterol	4.70 ± 0.66	4.57 ± 0.59	11.8 ± 1.03
Δ7-avenasterol	1.21 ± 0.23	1.11 ± 0.15	2.68 ± 0.36
total sterols	23.7 ± 3.43	22.5 ± 3.25	53.2 ± 4.53
Fat-Soluble Vitamins and β-Carotene Composition[d]			
α-tocopherol	2.38 ± 0.32	0.88 ± 0.09	22.5 ± 1.76
β-tocopherol	11.7 ± 1.29	11.3 ± 1.24	13.1 ± 1.36
γ-tocopherol	10.4 ± 1.02	9.08 ± 0.86	50.4 ± 4.28
δ-tocopherol	8.22 ± 0.84	8.44 ± 0.73	0.30 ± 0.07
total vitamin E	32.7 ± 2.21	29.7 ± 2.13	86.3 ± 4.87
β-carotene	2.22 ± 0.36	1.30 ± 0.21	3.26 ± 0.49
vitamin K_1	0.19 ± 0.08	0.12 ± 0.03	2.12 ± 0.34

[a] Values given are the mean of three replicates ± standard deviation. [b] Grams per 100 g of triacylglycerols. [c] Carbon number:double bonds. [d] Grams per kilogram of total lipids.

their structural composition. The availability of such data would facilitate the understanding of TAG biosynthesis and deposition on plant cells. With high-temperature GC-FID and H_2 carrier gas, the actual TAG molecular species of goldenberry oils were separated. The method, however, enables the determination of TAG homologues, which differ in fatty acid composition without giving information about positional and optical isomers of TAG. The pattern of TAG elution sequence with each TAG category with the same carbon number starts with the TAG with the lowest number of double bonds and terminates with those with the highest number of double bonds. In these oils, containing ≤16.1% of saturated fatty acids, almost all TAG contain two or three unsaturated acyl groups and a high proportion of them contain two or three polyethanoid acyl groups. According to our results (**Table 5**) these oils contain nine TAG molecular species, but three species, C54:3, C52:2, and C54:6, were presented to the extent of ∼91% or above. It could be said that in goldenberry oils the probable dominant TAG present are trilinolein, triolein, dioleoyl palmitoyl glycerol, and/or palmitoyl stearoyl linoleoyl glycerol. Chromatographic analysis of the 0 double-bond fraction indicated that its composition resembles that of total lipids except that the C48:0 peak was reduced in size. This would, of course, have been expected if the oleic and linoleic acids were presented as dipalmitoyl oleoyl glycerol (C50:1) or dioleoyl palmitoyl glycerol and/or palmitoyl stearoyl linoleoyl glycerol (C52:2).

Phytosterols Composition. Phytosterols are of interest due to their antioxidant activity and impact on health. The content and composition of free phytosterols determined in goldenberry (*P. peruviana* L.) oils are shown in **Table 5**. Phytosterols were estimated in high levels, and data showed no remarkable differences between WBO (∼6.14% unsaponifiables) and SO (∼5.76% unsaponifiables) in terms of ST content and composition. By contrast, PO (∼15.3% unsaponifiables) was characterized by extremely higher level of phytosterols. In both WBO and SO, campesterol and β-sitosterol were the 4-desmethylsterol markers and detected at approximately equal amounts (∼25−28% of total ST). The next major components were Δ5-avenasterol (∼20%) and lanosterol (∼10%). These four major components comprised >85% of total ST. In the PO, the major phytosterols were, in order of decreasing prevalence, Δ5-avenasterol > campesterol > ergosterol > lanosterol > stigmasterol > β-sitosterol > Δ7-avenasterol. Δ5-Avenasterol and campesterol were detected at equal levels and comprised together about a half of the ST content. Ergosterol, in PO, was present in relatively higher amount (∼16% of total ST) than in WBO (∼4.9%) and SO (4.6%). Recently, a new frontier in food science and nutrition has quickly developed, which is now called "functional food". One example of a successful functional food is the incorporation of phytosterols into vegetable oil spreads (*17*). This type of product is now available in the market and has been scientifically proven to lower blood LDL cholesterol by ∼10−15% as part of a healthy diet (*18*−*20*).

Fat-Soluble Vitamins and β-Carotene Composition. The nutritionally important components such as carotenes (provitamin A) and tocopherols (vitamin E) improve stability of the oil. The effectiveness of tocopherols as lipid antioxidants has been attributed mainly to their ability to break chain reactions by reacting with fatty acid peroxy radicals. In addition, epidemiologic evidence suggests a physiologic role for intact β-carotene in cancer prevention (*21*). Data on the qualitative and quantitative compositions of vitamins E and K_1 and β-carotene are summarized in **Table 5**. The vitamin E level was extremely high in PO (∼8.6% of TL), whereas it was estimated in low amounts in WBO (∼3.2%) and SO (∼2.9%). Although there are certain differences in the levels of the separated individual tocopherols, β- and γ-tocopherols seem to be the major components in WBO and SO, whereas γ- and α-tocopherols were the main constituents in PO. β-Tocopherol comprised ca. 35.7 and 38.0% of total vitamin E content in WBO and SO, respectively. On the other hand, γ-tocopherol constituted ∼58.4% of total vitamin E content in PO followed by α-tocopherol (∼26.0%). α-Tocopherol is the most efficient antioxidant of these compounds. β-Tocopherol has 25−50% of the antioxidative activity of α-tocopherol and γ-tocopherol, 10−35% (*22*). With regard to the stability issue, high amounts of vitamin E detected in the examined oils may contribute to great stability toward oxidation of these oils. Carotenoids, as singlet oxygen quenchers, protect oils from photo-oxidation, whereas their role in autoxidation is associated with the presence of tocopherols. In this study, evaluation of carotenoid levels is restricted to β-carotene. The most common and most effective provitamin A is β-carotene. None of the other provitamin A carotenoids has more than half the activity of β-carotene, and they are less widespread in nature, so that vitamin A from carotenoids is provided overwhelmingly by β-carotene (*23*). Carotenoids are responsible for the orange hues of goldenberry PO. The level of pigments, however, depends on the stage of fruit ripeness, the extraction process, and the storage conditions. High amounts of β-carotene were detected in the studied oils. β-Carotene was measured in the highest level in PO (0.32% of TL) followed by WBO (0.22%) and then SO (0.13%), the latter being characterized by light yellow hues. Furthermore, oils under investigation were characterized by a high level of vitamin K_1 (phylloquinone), which comprised >0.2% of TL in PO, whereas it was detected in lesser amounts (∼0.01% of TL) in WBO and SO. The phylloquinone requirement of the adult human is

extremely low. However, relatively few values for dietary items are available (*24*). Addition of phylloquinone-rich oils in the processing of foods that are otherwise poor sources of vitamins (for example, peanut and corn oils) makes them potentially important dietary sources of the vitamin.

The results of our investigation provide useful information for the industrial application of goldenberry seeds and berries. The data obtained will be important as an indication of the potentially nutraceutical and economical utility of goldenberry as a new source of fruit oils. For a plant to be suitable for oil production on the scale required today, the lipid content must reach the minimum for commercially viable exploitation and the plant must be suitable for high acreage cultivation (*25*). Unlike other fruits that must be processed close to the place of harvest, goldenberry is characterized by unique storage properties: the fruits are long-lasting and can be stored in a dry atmosphere for several months. Thus, goldenberry could be a suitable plant for oil production. It could be said that the yield of pulp/peel oil is low, but the oil is a rich source of essential fatty acids, phytosterols, carotenes, and fat-soluble vitamins. Utilization of the whole berries makes commercialization of oil more economic and reduces waste from seeds to procure hitherto neglected substances for technological and nutritional purposes such as fatty oil as a valuable contribution to the human diet. Goldenberry could become a commercial fruit of particular interest to the world's upscale restaurants and bakeries. This is the strategy that established markets for kiwifruits in the 1960s and led to a multimillion dollar annual crop.

ABBREVIATIONS USED

TAG, triacylglycerols**;** ST, phytosterols; FAME, fatty acid methyl esters; NL, neutral lipids; PL, polar lipids; FFA, free fatty acids; MAG, monoacylglycerols; DAG, diacylglycerols; STE, sterol esters; WBO, whole berry oil; SO, seed oil; PO, pulp/peel oil; GLA, γ-linolenic.

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