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Value-Added Processing of Peanut Skins: Antioxidant Capacity, Total Phenolics, and Procyanidin Content of Spray-Dried Extracts

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ABSTRACT: To explore a potential use for peanut skins as a functional food ingredient, milled skins were extracted with 70% ethanol and filtered to remove insoluble material; the soluble extract was spray-dried with or without the addition of maltodextrin. Peanut skin extracts had high levels of procyanidin oligomers (DP2−DP4) but low levels of monomeric flavan-3-ols and polymers. The addition of maltodextrin during spray-drying resulted in the formation of unknown polymeric compounds. Spray-drying also increased the proportion of flavan-3-ols and DP2 procyanidins in the extracts while decreasing larger procyanidins. Spray-dried powders had higher antioxidant capacity and total phenolics and increased solubility compared to milled skins. These data suggest that spray-dried peanut skin extracts may be a good source of natural antioxidants. Additionally, the insoluble material produced during the process may have increased value for use in animal feed due to enrichment of protein and removal of phenolic compounds during extraction.

KEYWORDS: *Arachis hypogaea, peanut skins, antioxidants, phenolic compounds, procyanidins, spray-drying*

INTRODUCTION

The most economically important part of the peanut plant, the seed, represents only 40% of the entire plant, and the remaining biomass presently has very limited uses.[1] Byproducts of peanut processing, including leaves, skins, hulls, and stems, have been established as sources of phenolic compounds.[1−5] Peanut skins are particularly rich in procyanidins (tannins), which consist of two or more flavan-3-ols (catechin and epicatechin) linked together to form oligomeric and polymeric compounds.[6,7] Two flavan-3-ol units are most commonly linked by a C4−C8 or C4−C6 linkage, known as a B-type linkage. Peanut skins, however, primarily contain doubly linked A-type procyanidins, which have a C4−C8 as well as a C2−O7 linkage.[6] Recently, researchers have identified procyanidins in peanut skins with degrees of polymerization (DP) of 1−9 primarily containing A-type linkages as well as some novel compounds.[8]

Peanut skins, which are typically removed from the seed during blanching, or after dry roasting, currently have only very limited use as an animal feed ingredient.[9] Due to their high content of procyanidins, which interfere with protein digestion/absorption and hence adversely affect animal performance, peanut skins are usually restricted to approximately 5−8% of the feed.[9,10] Historically, procyanidins were known only for these negative effects on protein digestion; however, in recent years, along with other polyphenolic compounds, numerous studies have highlighted their antioxidant and other health-promoting properties, including defense against inflammation, cardiovascular disease, and cancer.[11−13] Specifically, phenolic compounds in peanut skins, including procyanidins have been shown to improve lipid homeostasis, reduce markers of inflammation, and act as natural antioxidants and antimicrobial agents.[8,14−16] The multitude of health benefits associated with antioxidants has been well established in animal and human trials.[5,17] Additionally, antioxidants can be used in foods to prevent oxidation and extend shelf life.[18] Currently, natural sources of antioxidants for foods are increasing in popularity over synthetic antioxidants, which have been previously linked to carcinogenic activity in animal models.[14,19]

Given that peanut skins are a rich source of polyphenolic compounds and are a significant waste product of the peanut industry, recent research efforts have focused on utilization. The feasibility of incorporating peanut skins (blanched and roasted) into peanut butter has been evaluated.[20] Researchers found that blanched peanut skins could be incorporated at higher levels (3.75%) than roasted peanut skins without noticeably altering the physical properties of the peanut butter compared to controls. Furthermore, addition of peanut skins increased the total phenolics content of the peanut butters. Incorporation of whole peanut skins in food products is limited by the fact that they are largely insoluble. To combat this, researchers have prepared hot-water infusions of peanut skins for potential use as a food ingredient or an antioxidant-rich beverage.[21] A process involving extraction, concentration, and spray-drying represents another potential means by which to convert peanut skins into a value-added food ingredient. Several plant extract powders including those from green tea, pomegranate, and grape pomace have been produced using such a process.[22−24] Spray-drying is a well established and relatively inexpensive process in the food industry.[25] Benefits of spray-dried products include a longer shelf life and lower overall volume compared to the original product.[26] In micro-encapsulation by spray-drying, the presence of a carrier agent helps to protect the core material from light, oxygen, and other

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environmental factors that could cause degradation of sensitive materials.[27] Microencapsulation can also increase solubility, decrease hygroscopicity, and improve the handling and flow properties of the core material.[28,29] Frequently, carbohydrate-based carrier agents such as maltodextrins are used in the food industry due to their low costs and bland flavor.[29] Maltodextrins have been investigated in the microencapsulation of polyphenolic compounds with resulting protective effects against degradation.[23,27]

The goal of this research was to produce spray-dried powders from peanut skin extracts with high antioxidant activity and procyanidin content that could be used as value-added food ingredients. Through utilization of a waste product of the peanut industry, there is potential to increase the value of peanut skins while identifying an additional source of natural antioxidants for use by the food industry. Additionally, the insoluble material remaining after extraction of polyphenolic compounds could be explored as an improved animal feed ingredient.

MATERIALS AND METHODS

Plant Material. Blanched peanut skins (Virginia/runner-type blend) were obtained from Universal Blanching (Sylvester, GA, USA). Peanuts were blanched at 120−200 °F in multiple drying zones. Upon receipt, the skins were stored at 4 °C and protected from oxygen and light exposure prior to use.

Extraction Procedure. Peanut skins were milled into a fine powder using a Wiley model 4 laboratory mill (Thomas Scientific, Swedesboro, NJ, USA) fitted with a 0.5 mm screen. The milled skins (600 g) were extracted with 70% (v/v) ethanol in water (2603 g) on the basis of a previous study that optimized the conditions for extraction of polyphenolic compounds from peanut skins [14] to give a 1:5 milled skins to solvent ratio. Dispersions were stirred using a Wheaton overhead stirrer (Wheaton Industries, Inc., Millville, NJ, USA) for 20 min at speed setting 2.8. This extraction procedure was performed under low actinic lighting to minimize light exposure of the extracted materials. Following extraction, the slurry was vacuum-filtered twice using Whatman no. 50 filter paper (Whatman International Ltd., Maidstone, UK) to separate the soluble extract from the insoluble material. Ethanol was then evaporated from the soluble extract using a TurboVapII (Caliper Life Sciences, Hopkinton, MA, USA) within a nitrogen stream between 5 and 10 psi and a water bath setting of 40 °C. After removal of the ethanol, 30 mL of the soluble extract was removed to serve as a pre-spray-drying control. The resulting soluble extracts were stored in separate glass containers wrapped in foil at 4 °C until spray-dried.

Spray-Drying. Prior to each spray-drying run, the soluble extracts were divided into two fractions. Half of the soluble extract was spray-dried with Maltrin M150 maltodextrin (Grain Processing Corp., Muscatine, IA, USA) as a carrier agent in a 1:4 solids to maltodextrin ratio. The remaining half was spray-dried without the addition of maltodextrin. The soluble extracts, with and without maltodextrin, were individually fed into a Büchi B-290 mini spray-dryer (Büchi Labortechink AG, Flawil, Switzerland) with a constant inlet temperature of 160 °C and an outlet temperature of 90 ± 5 °C. The solution feed pump rate was set at 30% (~10 mL/min), the nitrogen flow rate was set at 40, and the aspirator was set at 100% for each of the runs. Each spray-drying run produced two fractions: (1) spray-dried soluble extract; (2) spray-dried soluble extract with the addition of maltodextrin. Resulting spray-dried powders, designated as spray-dried (SD) and spray-dried with maltodextrin (SDM), were stored protected from light in glass containers at 4 °C until further analysis.

Total Solids. Total solids contents of soluble extracts and insoluble materials were determined through a modified oven-drying method.[26] Samples were weighed, heated for 14 h, cooled for 1 h, and weighed again. Measurements were performed in triplicate for each spray-drying run for both the soluble extract and insoluble material.

Total Phenolics. Total phenolics for the soluble extract, SD, and SDM were determined using the Folin−Ciocalteu assay with gallic acid (Sigma-Aldrich, St. Louis, MO, USA) as a standard at concentrations ranging from 0 to 750 mg gallic acid/L.[30] Samples were diluted in deionized water (1:25 for soluble extract and SDM; 1:100 for SD), and 0.5 mL of Folin−Ciocalteu reagent (diluted 1:10) and 1.5 mL of sodium carbonate (60 g/L) were added to 100 μL of diluted sample or standards. Samples and standards were incubated at room temperature for 2 h, and absorbance was read at 765 nm and 27 °C using a Tecan Safire[2] microplate reader (Tecan Group Ltd., Männedorf, Switzerland); total phenolics for each sample were determined by comparison to the gallic acid standard curve and expressed as milligram gallic acid equivalents (GAE) per gram of sample.

Hydrophilic Oxygen Radical Absorption Capacity (H-ORAC). The antioxidant capacity for the soluble extract, SDM, and SD was determined by H-ORAC using Trolox as a standard (50−3.12 μM) as previously described by Prior et al.[31] with slight modifications as described by Davis et al.[18] Briefly, samples were diluted in 75 mM phosphate buffer (1:10000 for soluble extract and SDM; 1:100000 for SD). Fluorescein (Sigma-Aldrich, St. Louis, MO, USA) (70 nM in 75 mM phosphate buffer) was used as the fluorophore in the reaction, and 153 mM 2,2′-azobis(2-amidinopropane) dihydrochloride (AAPH) (Wako Chemicals, Richmond, VA, USA) was used as the peroxyl radical generator. Diluted samples (130 μL) were added to the wells of a flat-bottom black 96-well microplate. Fluorescein (60 μL) was added rapidly using a multichannel pipet, and the plate was incubated at 37 °C for 15 min. Following incubation, 60 μL of AAPH was added to each well, and fluorescence was read using an excitation wavelength of 483 nm and an emission wavelength of 525 nm over 90 min at 37 °C using a Tecan Safire.[2] Antioxidant capacity was expressed as micromole Trolox equivalents (TE) per gram of sample.

HPLC Analysis of Procyanidins. HPLC analysis of flavan-3-ols and procyanidins was performed on the soluble extract, SD, and SDM. For the soluble extract, 10 mL of extract (<10 mg total procyanidins) was purified by solid phase extraction using Sephadex LH-20 as previously described.[32] Resulting extracts were evaporated to dryness using a SpeedVac concentrator (ThermoSavant, Holbrook, NY, USA) and resuspended in 1 mL of acetone/water/acetic acid (AWA, 70:29.5:0.5). For analysis of powders, SD (10 mg) and SDM (50 mg) were dissolved in 10 mL of AWA, and acetone was evaporated using a SpeedVac concentrator prior to purification by solid phase extraction as described above. The resulting extracts were evaporated to dryness and resuspended in 1 mL of AWA, as above. All samples were filtered through a 0.45 μm PVDF filter prior to HPLC analysis. Analysis was performed using a Dionex Summit HPLC system (Sunnyvale, CA, USA) consisting of a model P680 quaternary pump, an ASI-100 autosampler, a TCC-100 column oven, an RF2000 fluorescence detector with a model UVD340U photodiode array detector in tandem according to the method of Hammerstone et al.[33] with modifications as described by White et al.[32] Samples (10 μL) were injected onto and separated using a 5 μm, 250 × 4.6 mm, Luna silica column (Phenomenex, Torrance, CA, USA) with an oven temperature of 37 °C and a flow rate of 1 mL/min. Peaks were monitored by fluorescence with excitation of 276 nm and emission of 316 nm. Monomers (DP1) through tetramers (DP4) were quantified using external calibration curves of commercial standards. Procyanidins with DP ≥ 5 including polymers were expressed as DP4 equivalents. Catechin and epicatechin were obtained from Sigma-Aldrich (St. Louis, MO, USA), procyanidin A2 was obtained from ChromaDex (Irvine, CA, USA), and a procyanidin trimer [Epi-4β6′, 2β-O-7′)-Epi-(4′β-8″, 2β-O-7′)-Cat] and tetramer [Epi-(4β-8′, 2β-O-7′)-Epi-(4′α-6)-Epi-(4′β-8‴, 2′β-O-7″)-Cat] were obtained from Planta Analytica (Danbury, CT, USA).

HPLC-ESI-MS Analysis of Procyanidins. Procyanidins were identified using an Agilent 1200 HPLC system equipped with an autosampler, a binary pump, a column compartment, and a fluorescence detector (Agilent Technologies, Palo Alto, CA, USA). HPLC separation of procyanidins was as described in the previous section. The HPLC was connected to a high-capacity (HCT) ion trap

mass spectrometer (Bruker Daltonics, Billerica, MA, USA). Conditions of the mass spectrometer were as previously described.[34]

Conversion of Data to Skin Weight Basis. To demonstrate the effects of spray-drying and maltodextrin addition, total phenolics, H-ORAC, and procyanidins were converted to a skin weight basis using the formula

$$C_{skins} = C_{product} \times R$$

where C_{skins} = concentration based on skin weight, $C_{product}$ = concentration in the product, and R = ratio of the mass of the product to the mass of the skins used to produce that product. This allowed for all concentration and dilution effects to be accounted for so that skins, soluble extracts, and spray-dried powders could be compared on an equivalent basis.

Proximate Analysis, Protein, and Amino Acids. Proximate analysis including moisture, fat, total protein, fiber, and ash of milled skins and insoluble material was performed by Barrow-Agee Laboratories, LLC (Memphis, TN, USA). Protein content of spray-dried powders was determined by measuring the amount of nitrogen using a CHN Elemental Analyzer (Perkin-Elmer, Waltham, MA, USA) and multiplying by the conversion factor 5.43. Amino acid content was determined using a Hitachi L-8900 amino acid analyzer (Hitachi High-Technologies Corp., Schaumburg, IL, USA) for milled peanut skins, SD, and the insoluble material. Samples of SD (0.2g), insoluble material (0.2g), and milled skins (0.1g) were hydrolyzed for amino acid analysis in triplicate.

Powder Solubility. Percent solubility was determined for 5% solutions of milled peanut skins, SDM, SD, and Maltrin M150 using a modified weight difference method.[26]

Statistical Analysis. Extraction and spray-drying were performed in triplicate, and results are expressed as the mean ± standard deviation. Analysis of variance was performed using JMP 10.0 (SAS, Cary, NC, USA), and when significant, means were separated using Student's t test ($p = 0.05$).

RESULTS AND DISCUSSION

Extraction and Spray-Drying Process Recoveries. An outline of the extraction and spray-drying process along with a mass balance is illustrated in Figure 1. The extraction of 600 g of peanut skins with 2603 g of 70% ethanol produced an average of 1262 ± 112 mL of soluble extract and 1144 ± 23 g of insoluble material on a wet weight basis. The majority of the solids entering the process were in the insoluble fraction (88 ± 1.0%). The soluble extract after ethanol evaporation contained an average of 5.4% solids. In the absence of maltodextrin addition, spray-drying of approximately 631 g of soluble extract produced 13.4 g of spray-dried powder. Percent recovery, calculated from the amount of solids present in the soluble extract before spray-drying and the amount of spray-dried powder produced, averaged 40.0%. Losses during spray-drying are attributed to material retained in the drying chamber and cyclone, as well as the loss of very small particles through the exhaust air.[35]

Total Phenolics and Antioxidant Capacity. Total phenolics and antioxidant capacity of the soluble extract, SD, and SDM are given in Table 1. Results are presented on an "as-is" basis, that is, per gram of soluble extract or spray-dried material, to demonstrate the concentration effects. Results were also converted to a skin weight basis to demonstrate the effects of spray-drying and maltodextrin addition. On an "as-is" basis, SD has the greatest amount of total phenolics (712.9 mg GAE/g). SDM has fewer total phenolics (106.7 mg GAE/g), followed by the soluble extract (25.8 mg GAE/g). This demonstrates the concentration effect of the spray-drying process because the total phenolics of the spray-dried powder are much greater than the soluble extract fed into the spray-dryer. Additionally, SD

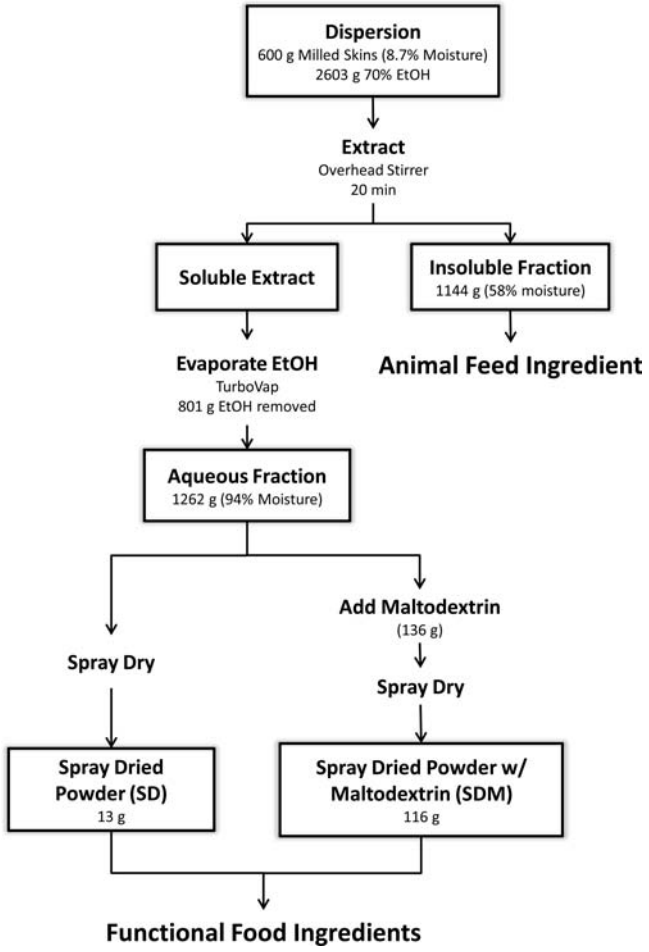

Figure 1. Flow diagram and mass balance of process to produce spray-dried powders from ethanol extracts of peanut skins. The entire process was performed in triplicate, and mass values represent averages of the three replications.

contains a greater amount of total phenolics than SDM due to a dilution effect when maltodextrin is present in the powder. Spray-drying resulted in a >4-fold increase in total phenolics when maltodextrin was included and a >27-fold increase without the use of maltodextrin. When these data are converted to a skin weight basis, the soluble extract has the highest total phenolics (55.6 mg GAE/g) followed by SD (40.7 mg GAE/g) and SDM (30.5 mg GAE/g). This indicates that the spray-drying process resulted in a 26.8% destruction of phenolics likely due to heat. Furthermore, the addition of maltodextrin did not appear to protect the phenolics from destruction, but rather resulted in greater degradation (45.1%). This is in contrast to other research that found that the addition of maltodextrin protected polyphenols and anthocyanins in spray-dried pomegranate extracts.[23] This is likely due to differences in the polyphenolic composition of pomegranates, which contain primarily anthocyanins, and peanut skins, which contain primarily procyanidins. Additional research is needed to explore ways to minimize losses of total phenolics during spray-drying.

Similar trends were observed in antioxidant capacity (Table 1). On an "as-is" basis, SD has the greatest antioxidant capacity (3823.2 μmol TE/g) followed by SDM (701.4 μmol TE/g) and the soluble extract (131.3 μmol TE/g). Again, the increase in antioxidant capacity of spray-dried powders supports a concentration effect through the spray-drying process as there

Table 1. Total Phenolics and Antioxidant Capacity of Soluble Extract and Spray-Dried Powders Presented on "As-Is[a]" and "Skins[b]" Bases[c]

	"as-is" basis		"skins" basis	
sample	total phenolics (mg GAE/g)	H-ORAC (μmol TE/g)	total phenolics (mg GAE/g skins)	H-ORAC (μmol TE/g skins)
soluble extract	25.8 ± 0.82c	131.3 ± 1.9c	55.6 ± 4.3a	283.0 ± 35.1a
SD	712.9 ± 13.2a	3823.2 ± 44.2a	40.7 ± 3.5b	218.6 ± 24.5b
SDM	106.7 ± 5.2b	701.4 ± 39.3b	30.5 ± 2.9c	199.6 ± 11.1b

[a]Values given are on a wet weight basis of each material. [b]Values given are normalized per gram of skin required to produce each material. [c]Values within each column followed by different letters are significantly different ($p < 0.05$).

was a >5-fold increase in antioxidant capacity for SDM and a >29-fold increase for SD.

Comparatively, SD and SDM contain much greater antioxidant capacity on an "as-is" basis than many other foods due to the concentration of phenolics during spray-drying. Commonly recognized food sources of natural antioxidants, such as blueberries (62 μmol TE/g) and cranberries (93 μmol TE/g), contain considerably less antioxidant capacity than both SD and SDM. Most spices recognized for their antioxidant capacities typically fall between SDM and SD. Ground cinnamon (2641 μmol TE/g) and dried oregano (1831 μmol TE/g) contained greater antioxidant capacity than SDM but less than SD.[36] It should be noted, however, that dietary polyphenols have a variety of functions other than antioxidant capacity, and ORAC values do not necessarily imply health benefits. Due to the high concentration of polyphenolic compounds and high antioxidant capacity of SD and SDM, both should be evaluated for potential food ingredient applications. Potentially, spray-dried peanut skin extracts could be used as a natural source of dietary polyphenols as well as to prevent oxidation in food without the use of synthetic antioxidants.

HPLC and HPLC-ESI-MS Analysis of Procyanidins. Peanut skins have been established in the literature as a particularly rich source of flavan-3-ols and A-type procyanidins.[5−7] Flavan-3-ols and procyanidins in the 70% ethanol extract of peanut skins, SD, and SDM were identified by HPLC-ESI-MS and quantified using authentic standards of flavan-3-ols and DP2−DP4 procyanidins containing A-type linkages (Figure 2). Procyanidins of DP1−DP6 were identified in the peanut skin extracts and spray-dried powders, although the levels of monomeric flavan-3-ols (DP1) were quite low. Some procyanidins identified contained exclusively B-type linkages, whereas others also contained one or more A-type linkage within their structure. The profiles observed were similar to those previously observed using a similar HPLC method.[6] An unresolved peak corresponding to polymeric procyanidins was also observed. The concentrations of flavan-3-ols and procyanidins (DP2−DP4) observed in the peanut skin extracts were very similar to those observed by Yu et al.,[7] which suggests the use of authentic standards for quantification of procyanidins is appropriate. Both SD and SDM contained significantly higher levels of total procyanidins than peanut skin extracts on an "as-is" basis. Excluding polymers, SDM contained approximately 5 times less procyanidins than SD, which reflects a dilution effect by the addition of maltodextrin. The profiles of peanut skin extract and SDM revealed a split peak corresponding to both an A-type and a B-type DP2 procyanidin, whereas in the SD profile this eluted as a single peak. This suggests that the DP2 procyanidins in SDM may be more structurally similar to those in the skin extract due to protection afforded by the maltodextrin; however, more advanced analytical techniques would be required to understand this effect. A polymeric procyanidin peak was observed in all samples, but was particularly prominent in SDM. This peak had a UV trace characteristic of procyanidins and is likely the result of reactions between maltodextrin and procyanidins. Given that the ORAC values and total phenolics of SDM were not significantly higher than those of SD, it is likely that these polymeric compounds are an artifact of spray-drying with maltodextrin and do not significantly contribute to antioxidant capacity or any purported health benefits. Further research is needed to characterize the compounds responsible for this peak.

The concentration of procyanidins per 100 g of skins or spray-dried powder ("as-is" basis) is shown in Figure 3. It is evident procyanidins were concentrated by extraction and spray-drying as there were 16.3- and 7.7-fold increases in procyanidins in SD and SDM, respectively, compared to the milled skins. To observe the effects of spray-drying and maltodextrin addition, procyanidin concentrations were converted to a skin weight basis (Table 2). This revealed that spray-drying with or without maltodextrin resulted in approximately a 2-fold increase in monomeric flavan-3-ols and 1.5-fold increase in DP2 procyanidins. This was coupled with a decrease in procyanidins of DP3 and DP > 4, but no change in DP4 procyanidins was observed. This suggests that spray-drying was capable of depolymerizing higher molecular weight procyanidins to release low molecular weight compounds. To our knowledge, this phenomenon has never been reported for spray-drying of procyanidin-containing materials. When procyanidins from grape seeds were spray-dried with maltodextrin, no changes in procyanidin profiles were observed.[37] However, extrusion processing has been shown to similarly affect procyanidin distribution in extruded cranberry, blueberry, and sorghum products.[38−40] Excluding polymers, there were no differences in total procyanidin concentrations among skins and spray-dried powders. This suggests that spray-drying resulted in a redistribution of procyanidin molecular weight, but overall quantities were retained. Such redistribution is likely beneficial because in vivo absorption of procyanidins is primarily dependent on the size of the molecule. Monomeric flavan-3-ols and dimers can be absorbed, whereas trimers are absorbed to a much lesser extent.[41,42] Procyanidins with DP > 3 are not absorbed and pass into the colon, where they are fermented by gut microflora.[43] Therefore, spray-drying of peanut skin extracts has the potential to enhance procyanidin bioavailability in vivo.

Analysis of Insoluble Material. In addition to producing spray-dried powders rich in polyphenolic compounds with high antioxidant capacity, the insoluble material remaining from this material could be further processed into a value-added feed ingredient. The current extraction process was designed to maximize the extraction of phenolic antioxidants from peanut

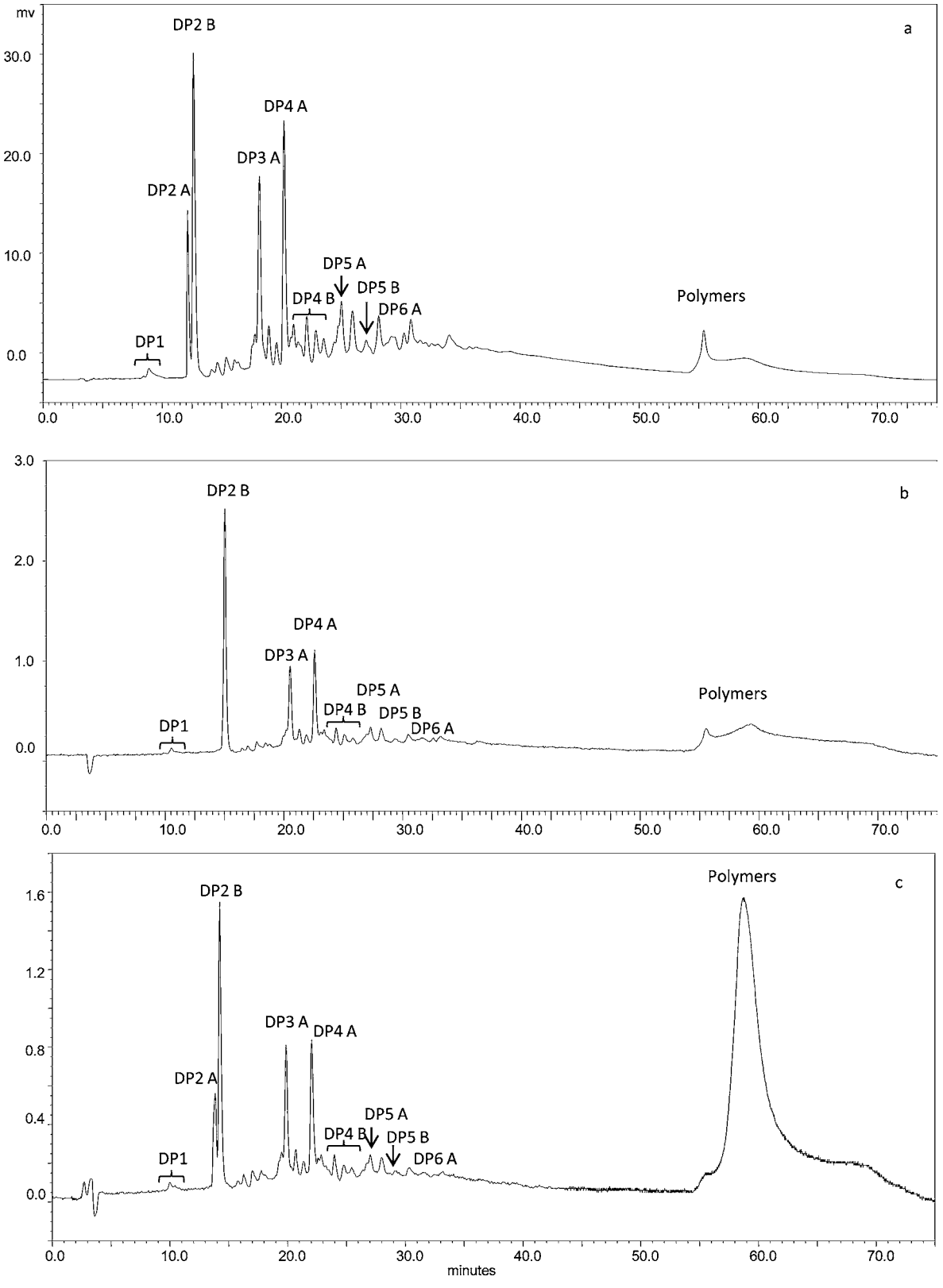

Figure 2. HPLC chromatogram of procyanidins in peanut skin (a) soluble extract, (b) SD, and (c) SDM detected by fluorescence with ex 276 and em 216. Procyanidins were identified by HPLC-ESI-MS as described in the text. DP1, *m/z* 289; DP2 A, *m/z* 575; DP2 B, *m/z* 577; DP3 A, *m/z* 863 and 859; DP4 A, *m/z* 1149; DP4 B, *m/z* 1151; DP5A, *m/z* 1437 and 1439; DP5 B, *m/z* 1441; DP6 A, *m/z* 1727.

skins,[14] meaning the remaining insoluble material could be an improved animal feed ingredient as decreased polyphenolic content could improve protein availability.

Proximate analyses of the milled peanut skins and insoluble material are provided in Table 3. On a dry weight basis, percent fat, protein, and fiber were higher in the insoluble fraction than in the milled skins, whereas percent ash was higher in milled

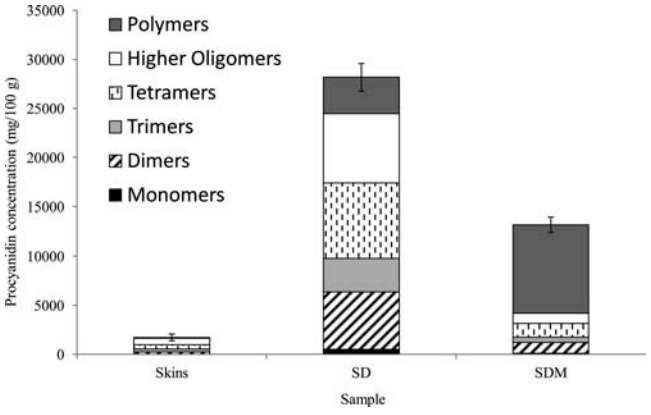

Figure 3. Procyanidin concentration (mg/100 g) of peanut skins, SD, and SDM presented on an "as-is" basis. Error bars represent the mean ± standard deviation (n = 3) of total procyanidins. All values are statistically different ($p < 0.05$).

skins. Therefore, in addition to the removal of polyphenolic compounds, the insoluble material is slightly enriched in fat, protein, and fiber compared to peanut skins, which could allow it to be used in greater quantities in animal feed. Ash, which represents minerals, including salts, are soluble in the aqueous fraction of the extraction solvent, which leads to the decrease in percent ash from the milled skins to the insoluble material.

Protein and Amino Acids. The protein contents of the milled skins, SD, and SDM were measured and determined to be 18.64 ± 0.06, 1.83 ± 0.03, and 0.53 ± 0.08, respectively. Peanut skins had a relatively high protein content, although literature on the proteins present in skins is lacking. This presents a potential problem for the use of whole peanut skins as food ingredients because peanut allergenicity is known to be an adverse reaction to peanut proteins.[44] Extraction and subsequent spray-drying greatly reduced the amount of proteins present in SD and SDM, as a majority of the protein remained in the insoluble fraction. A small amount of protein remained in the soluble extract as indicated by low protein contents of the spray-dried powders, and this might suggest reduced allergenicity of the powders compared to the skins due to reduction in the amount of potentially allergenic proteins. Additionally, procyanidins from peanut skins have been investigated for antiallergic properties, which are attributed to their ability to inhibit degranulation of RBL-2H3 cells upon antigen stimulation.[45] However, further research is required to investigate this potential in the spray-dried powders.

The amino acid composition of peanut seed (provided as a reference), milled skins, insoluble material, and SD is presented in Table 4. The major differences in amino acid composition between the seed and skins were observed in glutamic acid, arginine, lysine, and glycine. The seed contained 20.8% glutamic acid and 11.9% arginine, whereas the skins contained 12.0% glutamic acid and 6.7% arginine. In contrast, the skins contained higher levels of both glycine (22.3%) and lysine (5.6%) compared to the seeds, which contained 6.4 and 1.4%, respectively. This suggests that although many of the same proteins may be present in the peanut skins as in the peanut seed, some differences are likely. Overall, the amino acid profile of the insoluble material reflected that of the milled skins, as minimal differences were observed.

The most unique amino acid composition among materials tested was observed for SD (Table 4). Both aspartic acid and glycine were present below detectable levels in this material, whereas these amino acids accounted for at least 10.7 and 6.4%, respectively, in the other tested materials. Additionally, SD contained much higher percentages of alanine (11.5%), phenylalanine (10.9%), and proline (36.5%) than the other samples. SD had relatively low protein content (1.8%), and the

Table 3. Proximate Composition of Insoluble Material and Milled Skins[a]

sample	% fat	% protein	% fiber	% ash
insoluble material	22.09	21.18	21.16	2.09
milled skins	19.67	18.64	18.12	2.15

[a]Values are reported on a dry weight basis.

Table 4. Amino Acid Composition[a] (%) of Peanut Seeds, Skins, Insoluble Material, and Spray-Dried Powder (SD)

amino acid	peanut seed	milled skins	insoluble material	SD
Asp	13.7 ± 0.5 a	11.7 ± 0.2 b	10.7 ± 0.3 c	BDL
Thr	2.7 ± 0.3 a	2.7 ± 0.1 a	2.6 ± 0.1 a	1.6 ± 0.2 b
Ser	4.6 ± 0.0 d	8.9 ± 0.3 b	8.5 ± 0.1 c	9.2 ± 0.0 a
Glu	20.8 ± 0.0 a	12.0 ± 0.0 b	12.0 ± 0.0 b	6.1 ± 0.1 c
Gly	6.4 ± 0.1 b	22.3 ± 0.8 a	22.1 ± 0.1 a	BDL
Ala	4.1 ± 0.0 b	2.1 ± 0.2 c	1.9 ± 0.0 c	11.5 ± 0.6 a
Val	4.6 ± 0.0 a	3.1 ± 0.3 c	3.6 ± 0.1 b	3.2 ± 0.1 c
Met	1.0 ± 0.0 a	1.0 ± 0.0 a	0.6 ± 0.0 b	0.2 ± 0.2 c
Ile	3.4 ± 0.0 a	2.3 ± 0.3 c	2.8 ± 0.0 b	2.0 ± 0.2 c
Leu	7.9 ± 0.1 a	6.0 ± 0.1 c	6.3 ± 0.0 b	2.4 ± 0.2 d
Tyr	4.6 ± 0.0 a	4.3 ± 0.3 a	4.4 ± 0.1 a	4.3 ± 0.1 a
Phe	5.5 ± 0.1 b	3.3 ± 0.2 c	3.4 ± 0.1 c	10.9 ± 0.1 a
Lys	1.4 ± 0.3 d	5.6 ± 0.1 b	5.9 ± 0.0 a	1.8 ± 0.0c
His	2.5 ± 0.0 b	3.4 ± 0.1 a	3.4 ± 0.0 a	1.0 ± 0.2 c
Arg	11.9 ± 0.0 a	6.7 ± 0.2 d	6.9 ± 0.0 c	9.3 ± 0.2 b
Pro	4.8 ± 0.2 b	4.7 ± 0.3 b	5.0 ± 0.1 b	36.5 ± 0.8 a

[a]Values for each amino acid represent a percent of the total amino acids identified. Values within each row followed by different letters are significantly different ($p < 0.05$). Abbreviations: SD, spray-dried powder; Asp, aspartic acid; Thr, threonine; Ser, serine; Glu, glutamic acid; Gly, glycine; Ala, alanine; Val, valine; Met, methionine; Ile, Iisoleucine; Leu, leucine; Tyr, tyrosine; Phe, phenylalanine; Lys, lysine; His, histidine; Arg, arginine; Pro, proline; BDL, below detection level.

Table 2. Procyanidin Content of Peanut Skins and Spray-Dried Powders on a "Skins" Basis

	procyanidin content[a] (mg/100g skins)					
sample	DP1	DP2	DP3	DP4	DP > 4	polymers
peanut skins	13.7 ± 1.4 b	207.4 ± 2.7 b	252.9 ± 6.3 a	373.2 ± 8.4 a	597.4 ± 26.5 a	83.9 ± 9.5 b
SD	29.7 ± 1.7 a	332.3 ± 14.9 a	193.8 ± 11.9 b	432.2 ± 14.9 a	405.9 ± 77.8 b	210.6 ± 15.8 b
SDM	28.8 ± 8.6 a	317.6 ± 49.4 a	155.8 ± 14.0 c	394.4 ± 40.1 a	304.8 ± 54.0 b	2585.4 ± 434.5 a

[a]Values represent the mean ± standard deviation (n = 3). Values within each column followed by different letters are significantly different ($p < 0.05$).

amino acid composition strongly suggests this protein is not representative of all peanut skin proteins, but is selectively retained by ethanol extraction. Proteins are well established to tightly bind polyphenolic compounds, particularly procyanidins.[46] These protein−phenolic complexes are stabilized primarily by hydrogen bonding between the hydroxyl groups of the phenolics and carbonyl groups on the proteins.[47] Hydrogen bonding is enhanced in proline-rich proteins because proline is a particularly good hydrogen bond acceptor,[47] which likely explains the extremely high relative concentration of proline in SD.

Solubility of Spray-Dried Powders. The solubility of 5% solutions of milled skins, SD, SDM, and maltodextrin was evaluated to determine the effect of spray-drying and maltodextrin on powder solubility (Table 5). There was a 6-fold increase in solubility from the milled skins (13.0%) compared to SD (78.6%), indicating that spray-dried extracts are much more soluble than milled peanut skins. When maltodextrin was included, the solubility of the resulting powders was enhanced (87.7%) and not significantly different from that of maltodextrin alone ($p < 0.05$). The improved solubility of SD and SDM could enhance food ingredient applications of these materials. The addition of maltodextrin as a spray-drying aid further enhances their solubility. Extraction with 70% ethanol and subsequent spray-drying represents a feasible process to generate a potential antioxidant food ingredient that is soluble and contains high levels of antioxidant polyphenols from peanut skins.

Table 5. Water Solubility[a] (%) of Milled Skins, Spray-Dried Powders, and Maltodextrin

sample	solubility (%)
milled skins	13.0 ± 0.5 c
SD	78.6 ± 8.6 b
SDM	86.7 ± 2.6 a
maltodextrin	94.2 ± 4.9 a

[a]Solubility was determined for 5% solutions of each matrix in water.

In conclusion, spray-drying of peanut skin extracts produces powders rich in polyphenolics with high antioxidant capacity. Among the polyphenolic compounds extracted and concentrated by spray-drying, procyanidins are the most abundant. SD and SDM were much more soluble than milled skins, which potentiates their likelihood as suitable food ingredients. The resulting spray-dried powders could be used as a natural source of dietary polyphenols and/or as a natural antioxidant in food to enhance shelf life. To ensure the safety of the spray-dried powders as food ingredients, proper regulatory hurdles would need to be addressed. Future work should focus on incorporating the spray-dried powders in food products along with sensory analysis to determine to what extent such incorporation contributes any adverse flavors. Additionally, it will be necessary to evaluate the insoluble materials produced alongside the powders for use as an animal feed ingredient.

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Notes

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