Data Article

Analytical dataset of Ecuadorian cocoa shells and beans

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Article info
Article history:
Received 22 August 2018
Received in revised form
25 November 2018
Accepted 26 November 2018
Available online 29 November 2018

Abstract
Full analytical data of Ecuadorian cocoa wastes (raw shells) and beans (as benchmark), are herein reported. A detailed characterization of production residues may pave the road to a zero-waste strategy for the cocoa industry. Multiple analytical techniques have been exploited to define the composition of the matrices, among them: elemental analyses, FTIR, Py-GC/MS/FID and UHPLC-ESI-MS/MS.

Quali-quantitative data of carbohydrates, lipids, lignin, poly-phenols, alkaloids and proteins have been obtained by Py-GC/MS/FID and UHPLC-ESI-MS/MS. Assignations are fully supported by literature references. The FAMEs composition of lipophilic UAE extract is also reported for sake of comparison with cocoa butter. This data collection completes a wider valorization work, “Cocoa bean shell waste valorisation; extraction from lab to pilot-scale cavitational reactors” (Grillo et al., 2018).

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**Specifications table**

| Subject area       | Chemistry |
|--------------------|-----------|
| More specific subject area | Extraction and Valorization |
| Type of data       | Tables and figures (chromatograms, spectra and instruments) |
| How data was acquired | FTIR spectra: FTIR spectrometer (Spectrum One, PerkinElmer); CHN contents: according to EN 15104:2011 standard, elemental analyser (Vario MACRO, ELEMENTAR Analysensysteme); Carbohydrate composition: Alditol acetate procedure, GC-FID quantification (Agilent 6850 Series GC system); Py-GC/MS/FID: Frontier Lab Micro Double-shot Pyrolyser (Py-3030D), coupled to a Shimadzu 2D FID/MS gas chromatography system (MS-GC/GC–MS-2010); FAMEs composition: GC–MS qualitative analysis (Agilent Technologies 6850, Network GC System using a 5973 Network Mass Selective Detector) and GC-FID quantitative analysis (Agilent Technologies 7820A, Network GC System equipped with a FID detector); UHPLC-ESI-MS/MS: UPLC system (Acquity, Waters Corp., Singapore), coupled with a quadrupole-time of flight (Q-TOF) MS instrument (UPLC/Synapt Q-TOF MS, Waters, Milford, MA, USA) with an electrospray ionisation (ESI) source. |
| Data format        | Raw, analysed and formatted. |
| Experimental factors | Analysed samples are composed by cocoa shells, raw or extracted by UAE. Cocoa beans were used as a benchmark. |
| Experimental features | Multiple analysis were performed for the sake of comparison between cocoa beans and residual biomass (shells) or its extract. |
| Data source location | All matrices originate from Ecuador. The Cocoa bean shells were kindly provided by Gobino S.r.l. (Turin, Italy). |
| Data accessibility | Data are reported in this article. |
| Related research article | G. Grillo, L. Boffa, A. Binello, S. Mantegna, G. Cravotto, F. Chemat, T. Dizhbite, L. Lauberte, G. Telysheva. Cocoa bean shell waste valorisation; extraction from lab to pilot-scale cavitation reactors, FOODRES-D-18–01707R1 (2018) (In Press) [1]. |

**Value of the data**

- Full chemical characterization of raw waste material from cocoa industry (shells).
- Spectra and chromatograms can be used as fingerprints for quick matching.
- The comparison with cocoa beans composition shed light on the potential use and exploitability of the recovered fractions.
- Reported data could pave the way to new valorization processes, providing a useful benchmark.

1. Data

A fingerprint of the matrices is obtained by FTIR spectra and elemental analysis. Carbohydrates composition was defined by alditol acetate protocol and by Py-GC/MS/FID. This technique was also used to quantify lipids, lignin, alkaloids, proteins and polyphenols by means of precursor identification. Definition of polyphenols was achieved by UHPLC-ESI-MS/MS analysis. Furthermore, FAMEs identification and quantification of shells lipophilic extract is reported. All data can be used for a full comparison with extracts reported by Grillo et al. [1].

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2. Experimental design, materials and methods

2.1. Materials

Cocoa beans and shells from Ecuador were kindly provided by Gobino S.r.l. (Turin, Italy). Shells extracts are provided according the procedure reported by Grillo et al. (see Ref. [1], Paragraph 2.3.1 US-assisted extraction).

2.2. Methods

2.2.1. FTIR analysis

FTIR spectra of the cocoa beans and shells (raw material) samples were recorded in KBr pellets on a Spectrum One FTIR spectrometer (PerkinElmer) in the 4000–450 cm\(^{-1}\) range (resolution 4 cm\(^{-1}\), number of scans 64). The resulting spectra (Fig. 1) were normalised to the highest absorption intensity in each spectrum (in the ca. 3400 cm\(^{-1}\) range). Bands assignments are reported in Table 1, according to wave numbers.

![Normalized FTIR spectra of the cocoa beans (black) and shells (red).](image)

**Table 1**

| Wave number (cm\(^{-1}\)) | Assignment |
|---------------------------|------------|
| 3367                      | -OH stretching vibration |
| 2918, 2851                | C-H stretch in CH\(_2\) and CH\(_3\) groups, mainly in lipids |
| 1735                      | C=O stretch in unconjugated esters, carboxylic acids, aldehydes and ketones |
| 1660                      | C=C valence deformation in fatty acid plus C=O stretch in conjugated aryl ketones |
| 1630                      | amide I in proteins (C=O stretch in amide) |
| 1549                      | amide II in proteins (NH\(_2\) deformation vibration) |
| 1510                      | aromatic skeletal vibrations, mainly phenolics |
| 1444                      | deformation vibration of C-H in CH\(_2\) and CH\(_3\) groups of carbohydrates |
| 1285                      | C-H stretch (various) |
| 1250                      | C-O valent deformation in acetyl groups |
| 1152                      | C-O-C asymmetric vibration in carbohydrates and glucosides |
| 1107 - 1028               | C-C, C-OH, C-H various vibrations in carbohydrates |
| 890 - 763                 | out-of-plane aromatic C-H vibrations |
| 717                       | long chain C-C skeletal vibration in fatty acid |
2.2.2. CHN content
C, H, N, contents in cocoa beans and shells (raw material) were measured according to the EN 15104:2011 standard using a Vario MACRO elemental analyser (ELEMENTAR Analysensysteme). Direct comparisons of H/C and N/C for the two matrices are reported in Fig. 2.

2.2.3. Carbohydrate composition
Carbohydrate composition of cocoa beans and shells (raw material) was determined using an alditol acetate procedure by Blakeney, Harris, Henry and Stone, 1983 [2] after cocoa sample hydrolysis with 72% sulphuric acid. The alditol acetates were quantified by GC-FID (Agilent 6850 Series GC system) using a DB1701 column (60 m x 0.25 mm, film thickness 0.25 μm), and methyl α-D-glucopyranoside as the internal standard.

Results were expressed as mannose (Man), galactose (Gal), glucose (Glc), rhamnose (Rha), arabinose (Ara) and xylose (Xyl) contents (Table 2).

2.2.4. Pyrolyser(Py)-GC/MS/FID analysis
Py-GC/MS/FID analysis of cocoa beans and shells (raw material) were performed using a Frontier Lab Micro Double-shot Pyrolyser Py-3030D (pyrolysis temperature 500 °C, heating rate 600 °C/s) that was directly coupled to a Shimadzu 2D FID/MS gas chromatography system MS-GC/GC–MS-2010 with a RTX-1701 capillary column (Restek, 60 m x 0.25 mm x 0.25 μm film). The injector temperature was 250 °C, the ion source 250 °C (EI 70 eV), the MS scan range m/z was 15 to 350, the carrier gas was helium (flow rate 1 mL min⁻¹) and the split ratio was 1:30. The amount of sample analysed was 1.00 ± 2.00 mg. The oven temperature was kept at 60 °C for 1 min, increased at 6 °C/min to 270 °C and finally held at 270 °C for 10 min.

The identification of the individual compounds was performed using GC/MS chromatograms from the Library MS NIST 14, whereas the relative peak area of individual compounds was calculated using Shimadzu software on the basis of GC/FID data. The summed molar areas of the relevant peaks were normalised to 100% and the data for 5 repetitive pyrolysis experiments, at least, were averaged. Relative peak areas, calculated as percentages, for pyrolysis products of different origin were used to

![Fig. 2. H/C (A) and N/C (B) atomic ratios for cocoa beans and shells.](image)

| Table 2 |
| Carbohydrates contents in cocoa samples, determined using an alditol acetate procedure. |
|---|---|---|---|---|---|---|---|---|---|---|
| **Cocoa Sample** | **Carbohydrates % (w/w on o.d. ash free biomass)** | **Rha** | **Ara** | **Xyl** | **Man** | **Gal** | **Glc** | **Total as MS** | **Total as PS** |
| **Beans** | | 0.01 ± 0.01 | 1.9 ± 0.03 | 0.1 ± 0.01 | 0.7 ± 0.01 | 2.0 ± 0.1 | 18.8 ± 0.5 | 18.5 ± 0.5 | 23.5 ± 0.5 | 21.1 ± 0.5 |
| **Shells** | | 0.8 ± 0.1 | 1.7 ± 0.1 | 1.2 ± 0.2 | 2.6 ± 0.2 | 3.1 ± 0.2 | 16.5 ± 0.5 | 15.1 ± 0.5 | 25.9 ± 0.5 | 23.2 ± 0.5 |

MS = monosaccharides, PS = polysaccharides
Table 3
Summary of cocoa samples Py-GC/MS/FID analysis, including GC diagnostic peaks assignments and relative contents (%) of carbohydrates (CH), lipids (Lip), fatty acids (FA), lignin (Lg) and other polyphenols (Pph), alkaloids (Alk) and proteins (Pr) derived products detected in volatiles.

| Compound/Group of compounds | Compounds precursors | Compound proportion in volatiles from analytical pyrolysis, % |
|-----------------------------|----------------------|-----------------------------------------------------------|
| **Acids, Esters, Aldehydes, Ketones, Cyclopentane deriv., Furan deriv., Sugars, including:** | **Carbohydrates** | **Beans** | **Shells** |
| acetic acid                  | CH                   | 10.53     | 18.27     |
| 2-oxo-propanoic acid         | CH                   | 0.06      | 0.12      |
| propanoic acid               | CH                   | 0.58      | 1.49      |
| 2-propenoic acid, methyl ester | CH                | 0.19      | 0.20      |
| 2-oxo- propanoic acid, methyl ester | CH           | 0.67      | 0.51      |
| 3-methyl- butanoic acid      | CH                   | 0.20      | 0.16      |
| propanoic acid, 2-methylpropyl ester | CH   | 0.15      | n.d.      |
| pentanoic acid               | CH                   | n.d.      | n.d.      |
| 2-methyl-propanal            | CH                   | 1.19      | 0.53      |
| 2,3-butanedione              | CH                   | 1.95      | 2.86      |
| 3-methyl- butanal            | CH                   | 1.19      | 0.59      |
| 2-methylbutanal              | CH                   | 0.95      | 0.69      |
| 3-methyl-3-buten-2-one       | CH                   | 0.06      | n.d.      |
| 2-butenal                    | CH                   | 0.06      | 0.00      |
| 1-hydroxy- 2-propanone       | CH                   | 7.59      | 7.15      |
| 2-propanone                  | CH                   | 2.51      | 1.33      |
| 1-((acetyloxy)-2-butanone    | CH                   | 0.13      | 0.10      |
| pentanal                     | CH                   | 1.67      | 0.86      |
| 2-cyclopenten-1-one          | CH                   | 0.78      | 0.80      |
| 2-methyl- 2-cyclopenten-1-one | CH              | 0.33      | 0.55      |
| 1,2-cyclopentanediene        | CH                   | 1.43      | 1.31      |
| 2,3-dimethyl- 2-cyclopenten-1-one | CH     | n.d.      | 0.14      |
| 3-methyl-2-cyclopenten-1-one | CH                   | 0.20      | 0.37      |
| 2-cyclopenten-1-one, 2,3-dimethyl-, isomer | CH | 0.22   | 0.39 |
| 3-methyl-1,2-cyclopentanediene | CH   | 1.25      | 1.47      |
| 3-ethyl-2-hydroxy-2-cyclopenten-1-one | CH | 0.47      | 0.53      |
| 2(3H)-furanone               | CH                   | 0.28      | 0.24      |
| 3(2H)-furanone               | CH                   | 0.48      | 0.33      |
| furfural                     | CH                   | 0.33      | 0.53      |
| acetylfuran                  | CH                   | 0.41      | 0.59      |
| 5-methyl-2-furancarboxaldehyde | CH          | 0.07      | 0.20      |
| 2(3H)- dihydro-furanone      | CH                   | 0.52      | 0.92      |
| 2(5H)-furanone               | CH                   | 0.76      | 0.61      |
| isosorbide (1,4;3,6-dianhydro-D-glucitol) | CH | n.d.      | 0.43      |
| **Phenyl and benzyl derivatives, including:** | **Lignin + Polyphenols** | 7.70 | 7.76 |
| methyl-benzene               | Pph                  | 0.93      | 0.61      |
| ethyl-benzene,               | Pph                  | 0.33      | 0.45      |
| ethynyl-benzene,             | Pph                  | 0.28      | 0.24      |
| phenol                       | Pph, Lg              | 2.42      | 2.25      |
| 2-methyl-phenol, (o-cresol)   | Pph, Lg              | 0.58      | 0.59      |
| 4-methyl- and 3-methyl-phenol, (p- & m-cresols) | Pph, Lg | 2.05 | 1.82 |
| 3,4-dimethyl-phenol          | Pph                  | 0.26      | 0.24      |
| 4-ethyl-phenol               | Pph                  | 0.33      | 0.41      |
| **1,2-benzenediol (tannins derivative)** | Pph | 0.15 | 0.16 |
| guaiacol                     | Lg                   | 0.07      | 0.35      |
| 4-vinylguaiacol              | Lg                   | n.d.      | 0.08      |
| syringol                     | Lg                   | 0.11      | 0.31      |
| 2,3-dihydro-benzofuran       | Lg                   | 0.19      | 0.24      |
| **aliphatic compounds, including:** | **Lipids + Fatty acids** | 16.83 | 4.63 |
Table 3 (continued)

| Compound/Group of compounds | Compounds precursors | Compound proportion in volatiles from analytical pyrolysis, % |
|-----------------------------|----------------------|------------------------------------------------------------|
| Acids, Esters, Aldehydes, Ketones, Cyclopentane deriv., Furan deriv., Sugars, including: | Carbohydrates | Beans 37.21 | Shells 44.28 |
| 1-nonene | Lip | 0.24 | n.d. |
| undecane | Lip | 0.11 | n.d. |
| 1-undecene | Lip | 0.32 | n.d. |
| (Z)-5-undecene | Lip | 0.15 | 0.06 |
| (Z)-3-octen-2-ol | Lip | 0.33 | 0.24 |
| Dodecane | Lip | 0.22 | 0.16 |
| 1-dodecene | Lip | 0.35 | 0.12 |
| 1-dodecyne | Lip | 0.11 | n.d. |
| tridecane | Lip | 0.22 | 0.12 |
| (Z)-6-tridecene | Lip | 0.35 | 0.12 |
| tetradecane | Lip | 0.30 | 0.10 |
| 1-tetradecene | Lip | 0.56 | 0.10 |
| 3,4-dimethylcyclopentanone | Lip | 0.54 | 0.41 |
| pentadecane | Lip | 1.49 | 0.59 |
| 1-pentadecene | Lip | 0.26 | 0.06 |
| 1-hexadecene | Lip | 0.69 | 0.18 |
| 8-heptadecene | Lip | 1.10 | 0.16 |
| heptadecane | Lip | 1.43 | 0.31 |
| (Z)-3-hexadecene | Lip | 0.15 | n.d. |
| 2-hexadecanone | Lip | 0.30 | 0.20 |
| pentadecaonic acid, ethyl ester | FA | n.d. | 0.16 |
| octadecaonic acid, 2-propenyl ester | FA | 1.95 | 0.16 |
| n-hexadecaonic acid | FA | 0.87 | 1.06 |
| 2-nonadecaconone | Lip | 0.19 | n.d. |
| cyclohexancanemethanol | Lip | 1.28 | n.d. |
| octadecaonic acid, 2-propenyl ester, isomer | FA | 2.86 | 0.20 |
| hexadecaonic acid, ethenyl ester | FA | 0.45 | 0.08 |
| alkaloids derived volatiles, including: | Alkaloids | 34.15 | 38.75 |
| 1H-pyrrole, 1-methyl- | Alk | 0.56 | 0.39 |
| pyridine or picolinic acid | Alk | 0.49 | 0.99 |
| 1H-pyrrole, 1-ethyl- | Alk | 0.25 | 0.49 |
| pyrrole | Alk | 2.85 | 3.75 |
| 1H-pyrrole, 2-methyl- | Alk | 0.47 | 0.24 |
| 1H-pyrrole, 2-ethyl- | Alk | 0.93 | 0.63 |
| 1H-pyrrole, 3-ethyl- | Alk | 0.06 | 0.03 |
| 2,5-pyrrolidinedione | Alk | 0.91 | 0.93 |
| 1H-purine-2,6-dione, 3,7-dihydro-1,3,7-trimethyl- (Caffeine) | Alk | 3.44 | 4.53 |
| 1H-purine-2,6-dione, 3,7-dihydro-3,7-dimethyl- (Theobromine) | Alk | 20.76 | 25.30 |
| indole | Alk | 2.56 | 0.78 |
| 1H-indole, 3-methyl- | Alk | 0.88 | 0.69 |
| amides and nitriles, including: | Lipids + Proteins | 3.57 | 1.87 |
| propanenitrile | Lip, Pr | 0.17 | 0.64 |
| 3-methyl-butanenitrile | Lip, Pr | 0.27 | 0.28 |
| 4,4-dimethyl-3-oxopentanenitrile | Lip, Pr | n.d. | 0.35 |
| 4-methyl-pentanenitrile | Lip, Pr | n.d. | 0.35 |
| tetradecanenitrile | Lip, Pr | 0.46 | 0.25 |
| hexadecanenitrile | Lip, Pr | 0.40 | n.d. |
| tetradecanamide | Lip, Pr | 0.72 | n.d. |
| (Z)-9-octadecenamide | Lip, Pr | 0.62 | n.d. |
| octadecanamide | Lip, Pr | 0.93 | n.d. |

n.d.- not detected
assess biomass sample composition (Table 3). Measurement error did not exceed 5% of the mean area value.

2.2.5. UHPLC-ESI-MS/MS analysis of polyphenols

Analytical samples of raw cocoa shells were obtained from: 70% v/v aqueous acetone extract (A) and 80% v/v aqueous ethanol extract (B). All samples were dissolved in a 1:1 acetonitrile/water mixture, filtered over a nylon filter (0.45 μm pore size) and analysed by UHPLC-ESI-MS/MS (Fig. 3). An Acquity UPLC system (Waters Corp., Singapore) that was coupled with a quadrupole-time of flight (Q-TOF) MS instrument (UPLC/Synapt Q-TOF MS, Waters, Milford, MA, USA) with an electrospray ionisation (ESI) source was used. A U-HPLC column (2.1 mm x 50 mm i.d., 1.7 μm, BEHC18, Waters Acquity) was used at a flow rate of 0.30 mL min\(^{-1}\). The mobile phases were water with 0.1% formic acid (A) and acetonitrile (B). The gradient program was: 0–0.5 min, 5%–5% (B); 0.5–10 min, 5%–95% (B); 10–15 min, 95%–95% (B). The injection volume was 2 μL. The major operating parameters for Q-TOF MS were set as follows: capillary voltage, 2 kV (–); cone voltage, 40 V; cone gas flow, 50 L/h; collision energy, 4 eV; source temperature, 120 °C; desolvation temperature, 350 °C; collision gas, argon; desolvation gas, nitrogen; flow rate, 600 L/h; data acquisition range, m/z 50–1,200 Da; ionisation mode, negative.

Peaks assignments has been performed by mass fragmentations (Table 4), available literature reference are shown. A composition comparison is possible, referring to UHPLC-ESI-MS/MS analysis of

![Fig. 3. Total ion chromatogram (negative ionisation) resulting from the UHPLC-ESI-MS/MS analysis of the conventional extracts obtained from Ecuador cocoa shells: (A) 70% v/v aqueous acetone extract; (B) 80% v/v aqueous ethanol extract.](image)

Table 4

| Compound                              | Peak Nr. | [M-H], Main fragments | Ref. |
|---------------------------------------|----------|-----------------------|------|
| Gglucionic acid sodium salt/glucose acid | 1        | 195, 177, 129, 85, 75 | [3]  |
| citric acid                           | 2        | 191, 11, 87           | [3]  |
| protocatechuic acid                   | 3        | 153, 109, 65          | [3]  |
| procyanidin tetramer                  | 4        | 1153, 577, 289        | [4]  |
| N-caffeoyl-L-aspartate derivative     | 5        | 276, 179, 131         | [5]  |
| catechin or epicatechin with a cinnamic acid side-group | 6        | 633, 329, 305, 289, 267, 225 | [6]  |
| procyanidin dimer                     | 7        | 730, 577, 289, 165    | –    |
| catechin/epicatechin derivative       | 8        | 289, 245,205,179      | –    |
| flavone/luteolin                      | 9        | 329, 311, 229, 211, 171, 139, 127 | [3]  |
| hydroxybenzoic acid sugar derivative  | 10       | 299, 137              | –    |
| linoleic acid                         | 11       | 279                   | [3]  |
| oleic acid                            | 12       | 281                   | –    |
| citric acid derivative                | 13       | 191, 111, 87          | [3]  |
| coumaric acid derivative              | 14       | 163, 145              | [7]  |
| procyanidin trimer                    | 15       | 865, 860, 577, 305, 289, 245 | [4]  |
cocoa shells extract, reported by Grillo et al. (see Fig. 3 and Table 9 in Ref. [1], Paragraph. 3.3.2 Extraction screening).

2.2.6. GC analysis of fatty acid methyl esters (FAMEs)

The fatty acid composition of the lipophilic (hexane) phase derived from a ternary mixture extracts.

(see Ref. [1], Paragraph 2.3.1 US-assisted extraction) of raw shells, was determined according to the procedure described by Bermúdez Menéndez et al. in 2014 [8]. GC–MS qualitative analysis were performed in an Agilent Technologies 6850 Network GC System using a 5973 Network Mass Selective Detector, a 7683B Automatic Sampler (Santa Clara, California, USA), and a capillary column (HP-5MS 5% Phenyl Methyl Siloxane, length 30 m, i.d. 0.25 mm, film thickness 0.25 μm). GC-FID quantitative analysis were performed in an Agilent Technologies 7820 A Network GC System equipped with a FID detector, using a capillary column (Mega WAX, length 30 m, i.d. 0.25 mm, film thickness 0.25 μm, Mega S.r.l., Legnano, MI, Italy) and according to the internal standard amount (methyl heptadecanoate, Me C17). All the lipophilic extracts (~10 mg) were derivatised before analysis [8].

FAMEs identification was performed by checking correspondence with C8–C24 saturated and unsaturated external standards (Sigma-Aldrich), which were prepared in solution with GC grade cyclohexane, and with Wiley7n and NIST11 GC libraries (for GC–MS analysis). All identification and quantification results are reported in Table 5, showing an overall matching with cocoa butter content profile, according to literature [9].

Acknowledgements

This work was supported by the University of Turin (Fondi Ricerca Locale 2016). The authors warmly acknowledge EPIC srl for their kind assistance with the Rotocav® tests.

Transparency document. Supporting information

Transparency data associated with this article can be found in the online version at https://doi.org/10.1016/j.dib.2018.11.129.
References

[1] G. Grillo, L. Boffa, A. Binello, S. Mantegna, G. Cravotto, F. Chemat, T. Dizhbite, L. Lauberte, G. Telysheva, Cocoa bean shell waste valorisation; extraction from lab to pilot-scale cavitation reactors, Food Res. Int. (2018). https://doi.org/10.1016/j.foodres.2018.08.057.

[2] A.B. Blakeney, P.J. Harris, R.J. Henry, B.A. Stone, A simple and rapid preparation of alditol acetates for monosaccharide analysis, Carbohydr. Res. 113 (1983) 291–299.

[3] A.A. Karim, A. Azlan, W.A. Ismail, P. Hashim, S.S. Abd Gani, B.H. Zainudin, N.A. Abdullah, Phenolic composition, antioxidant, anti-wrinkles and tyrosinase inhibitory activities of cocoa pod extract. BMC Complement. Altern. Med. 14 (2014) 381–393.

[4] J.F. Hammerstone, S.A. Lazarus, A.E. Mitchell, R. Rucker, H.H. Schmitz, Identification of procyanidins in Cocoa (Theobroma cacao) and chocolate using high-performance liquid chromatography/mass spectrometry, J. Agric. Food Chem. 47 (1999) 490–496.

[5] G. Pereira-Caro, G. Borges, C. Nagai, M.C. Jackson, T. Yokota, A. Crozier, H. Ashihara, Profiles of phenolic compounds and purine alkaloids during the development of seeds of Theobroma cacao cv. Trinitario, J. Agric. Food Chem. 61 (2013) 427–434.

[6] K.A. Reed, Identification of Phenolic Compounds from Peanut Skin using HPLC-MS (Ph.D. Dissertation), Food Science and Technology, Polytechnic Institute and State University, Blacksburg, Virginia, 2009.

[7] F. Sánchez-Rabaneda, O. Jáuregui, I. Casals, C. Andrés-Lacueva, M. Izquierdo-Pulido, R.M. Lamuela-Raventós, Liquid chromatographic/electrospray ionization tandem mass spectrometric study of the phenolic composition of cocoa (Theobroma cacao), J. Mass Spectrom. 38 (1) (2003) 35–42.

[8] J.M. Bermúdez Menéndez, A. Arenillas, J.A. Menéndez Díaz, L. Boffa, S. Mantegna, A. Binello, G. Cravotto, Optimization of microalgae oil extraction under ultrasound and microwave irradiation, J. Chem. Technol. Biotechnol. 89 (2014) 1779–1784.

[9] M. Lipp, E. Adam, Review of cocoa butter and alternative fats for use in chocolate-Part A. Compositional data, Food Chem. 62 (1) (1998) 73–97.