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Analytical dataset of Ecuadorian cocoa shells and beans

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**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 exploi- ted 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 collec- tion 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* ﬁ*gures (chromatograms, spectra and instruments)*

How data was acquired *FTIR spectra: FTIR spectrometer (Spectrum One, PerkinElmer);*

*CHN contents: according to EN 15104:2011 standard, elemental ana- lyser (Vario MACRO, ELEMENTAR Analysensysteme);*

*Carbohydrate composition: Alditol acetate procedure, GC-FID quanti-*

ﬁ*cation (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* ﬂ*ight (Q-TOF) MS instrument (UPLC/Synapt Q-TOF MS, Waters, Milford, MA, USA) with an electro- spray 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 valor- isation; extraction from lab to pilot-scale cavitational reactors, FOODRES-D-18–01707R1 (2018) (In Press) [[1]](#_bookmark12).

**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 sheds 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 identiﬁ- cation. 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]](#_bookmark12).

1. **Experimental design, materials and methods**
	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]](#_bookmark12), Paragraph *2.3.1 US-assisted extraction*).

* 1. *Methods*
		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](#_bookmark4)) were normalised to the highest absorption intensity in each spectrum (in the ca. 3400 cm-1 range). Bands assignments are reported in [Table 1](#_bookmark5), according to wave numbers.



Fig. 1. Normalized FTIR spectra of the cocoa beans (black) and shells (red).

Table 1

Bands assignments in the FTIR spectra of the cocoa samples.

Wave number (cm-1) Assignment

3367 -OH stretching vibration

2918, 2851 C-H stretch in CH2 and CH3 groups, mainly in lipids

1735 C¼ O stretch in unconjugated esters, carboxylic acids, aldehydes and ketones

1660 C¼ C valence deformation in fatty acid plus C¼ O stretch in conjugated aryl ketones

1630 amide I in proteins (C¼ O stretch in amide)

1549 amide II in proteins (NH2 deformation vibration)

1510 aromatic skeletal vibrations, mainly phenolics

1444 deformation vibration of C-H in CH2 and CH3 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

* + 1. *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](#_bookmark6).

* + 1. *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]](#_bookmark13) 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 mm), and methyl α-*D*-gluco-

pyranoside as the internal standard.

Results were expressed as mannose (Man), galactose (Gal), glucose (Glc), rhamnose (Rha), arabi- nose (Ara) and xylose (Xyl) contents ([Table 2](#_bookmark7)).

* + 1. *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 1.00C2.00 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.

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 Tot Cellulose

Beans o 0.01 1.970.03 0.170.01 0.770.01 2.070.1 18.870.5 18.570.5 23.570.5 21.170.5

Shells 0.870.1 1.770.1 1.270.2 2.670.2 3.170.2 16.570.5 15.170.5 25.970.5 23.270.5

MS¼ monosaccharides, PS¼ polysaccharides

assess biomass sample composition ([Table 3](#_bookmark8)). Measurement error did not exceed 5% of the mean area value.

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., | Carbohydrates | Beans 37.21 | Shells 44.28 |
| Furan derive., Sugars, including: |  |  |  |
| 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-methyl-butanal | 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-cyclopentanedione | 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-cyclopentanedione | 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 þ Polyphenols | 7.70 | 7.76 |
| methyl-benzene | Pph | 0.93 | 0.61 |
| ethyl-benzene, | Pph | 0.33 | 0.45 |
| ethenyl-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 þ 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., | Carbohydrates | Beans 37.21 | Shells 44.28 |
| Furan derive., Sugars, including: |  |  |  |
| 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 |
| pentadecanoic acid, ethyl ester | FA | n.d. | 0.16 |
| octadecanoic acid, 2-propenyl ester | FA | 1.95 | 0.16 |
| n-hexadecanoic acid | FA | 0.87 | 1.06 |
| 2-nonadecanone | Lip | 0.19 | n.d. |
| cyclododecanemethanol | Lip | 1.28 | n.d. |
| octadecanoic acid, 2-propenyl ester, isomer | FA | 2.86 | 0.20 |
| hexadecanoic 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 þ 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 |  |  |  |

* + 1. *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](#_bookmark9)). 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 mm, 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](#_bookmark10)), available literature referencse are shown. A composition comparison is possible, referring to UHPLC-ESI-MS/MS analysis of cocoa shells extract, reported by Grillo et al. (see [Fig. 3](#_bookmark9) and Table 9 in Ref. [[1]](#_bookmark12), Paragraph. 3.3.2 *Extraction screening*).



Fig. 3. Total ion chromatogram (negative ionization) 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.

Table 4

Polyphenols detected in the UHPLC-ESI-MS/MS analysis of the conventional extracts obtained from cocoa shells ([Fig. 3](#_bookmark9)).

|  |  |  |  |
| --- | --- | --- | --- |
| Compound | Peak Nr. | [M-H], Main fragments | Ref. |
| Gluconic acid sodium salt/glucose acid | 1 | 195, 177, 129, 85, 75 | [[3]](#_bookmark14) |
| citric acid | 2 | 191, 111, 87 | [[3]](#_bookmark14) |
| protocatechuic acid | 3 | 153, 109, 65 | [[3]](#_bookmark14) |
| procyanidin tetramer | 4 | 1153, 577, 289 | [[4]](#_bookmark15) |
| *N*-caffeoyl-*L*-aspartate derivative | 5 | 276, 179, 131 | [[5]](#_bookmark16) |
| catechin or epicatechin with a cinnamic acid side-group | 6 | 633, 329, 305, 289, 267, 225 | [[6]](#_bookmark17) |
| 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]](#_bookmark14) |
| hydroxybenzoic acid sugar derivative | 10 | 299, 137 | – |
| linoleic acid | 11 | 279 | [[3]](#_bookmark14) |
| oleic acid | 12 | 281 | – |
| citric acid derivative | 13 | 191, 111, 87 | [[3]](#_bookmark14) |
| coumaric acid derivative | 14 | 163, 145 | [[7]](#_bookmark18) |
| procyanidin trimer | 15 | 865, 860, 577, 305, 289, 245 | [[4]](#_bookmark15) |

Table 5

FAMEs composition of the hexane phase from UAE extracts obtained using the ternary mixture, expressed as w/w percentage on the extract.

|  |  |
| --- | --- |
| FAMEs | w/w % |
| Me myristate-C14 | 0.7 |
| Me palmitate-C16 | 28.5 |
| Me palmitoleate-C16:1(n-7) | 0.8 |
| Me stearate-C18 | 31.6 |
| Me oleate-C18:1(cis,n-6) | 32.7 |
| Me hexadecenoate-C18:1(*cis*,n-9 o 5) | 0.6 |
| Me linoleate-C18:2(*cis*,n-6) | 1.0 |
| Me eicosanoate-C20 | 1.3 |
| Me 11-eicosaenoate-C20:1(*cis*,n-9) | 0.2 |
| Me arachidonate-C20:4(*cis*,n-6) | 0.1 |
| Me 5,8,11,14,17-eicosapentaenoate-C20:5(*cis*,n-3) | 0.1 |
| Me docosanoate-C22 | 0.5 |
| Me tetracosanoate-C24 | 0.1 |
| Me pentacosanoate-C25 | 0.2 |
| Me hexacosanoate-C26 | 0.3 |
| *Total* | *98.7* |

* + 1. *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]](#_bookmark12), 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]](#_bookmark19). GC–MS qualitative analyses 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 analyses 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 (around 10 mg) were derivatised before analysis [[8]](#_bookmark19).

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](#_bookmark11), showing an overall matching with cocoa butter content proﬁle, according to literature [[9]](#_bookmark20).

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