Quality characterisation of commercial Shea nuts using near infrared spectroscopy

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Introduction

The Shea tree (*Vitellaria paradoxa* C. F Gaertn, Sapotaceae family) is a major fruit tree in African agro-forestry systems. The native range of this long-lived (over 200 years) savannah tree species is a large belt 6000 km long from East (Senegal) to West (Uganda) and 600 km wide from north of the equator to south of the Sahara. The Shea tree has been exploited by African communities for about 3000 years and offers an opportunity for sustainable development in Sudanian countries.[1,2] Indeed, Shea butter extracted from fruit kernels provides an attractive potential for both the food and cosmetics industries. The estimated yield of dry kernel is about 600,000 tons per year and exports have increased over the last decade, reaching 350,000 tons today, mainly to the USA and Europe. Initial evaluations of Shea nut chemical composition throughout the natural range have shown great diversity particularly for fat content and fatty acid composition.[3,4] Those studies revealed fat content values ranging from 22.3% to 52.8%. Relative fatty acid compositions were found to vary, particularly for oleic acid (C18:1), ranging from 37.1% to 62.1%, and stearic acid (C18:0), from 25.6% to 50.2%.

End-use product quality depends on butter characteristics; in particular, oxidative and hydrolytic degradation of lipids represent high losses. Industrial applications require efficient and rapid nut quality control at an early marketing stage. This study was conducted under the European development project INNOVKAR,[5] with the specific objective of characterising the diversity of shea nuts in terms of fat content and fat composition using near infrared spectroscopy.

Materials and Methods

The sampling strategy was designed to ensure maximum coverage of the range of variation in fat composition. Samples were collected under uniform conditions over two years (2007 and 2008) in four West African countries (Senegal, Mali, Burkina Faso and Ghana) and one East African country (Uganda). Within each country, different sites were sampled based on a rainfall and temperature gradient; a total of 624 trees were sampled at 17 sites

Samples preparation

Unshelled Shea nuts were first ground (Thermomix Robot, Vorwerk. Nantes, France); raw powders were frozen at -20°C and re-ground (Valentin coffee grinder, Seb, Ecully, France) in order to obtain a final particle size between 0.5 and 0.8 mm. The final powder samples were stored at -20°C. Fifty-three samples were enriched in FFA by natural evolution during storage in climatic oven (28°C, 60%RH).

Near infrared spectroscopy

Samples were scanned from 400 to 2500 nm at 2 nm intervals in reflectance mode using a NIRS 6500 monochromator with a spinning cell module (Foss NlRSystems, Silver Spring, MD). Data were saved as the average of 32 scans and stored as log (1/R), where R was the reflectance at each wavelength and 1 the reflectance of a standard ceramic reference. Samples were scanned in random order with each sample being measured twice and the average spectrum stored.

Laboratory analyses

For each sample, moisture content (MC) was assessed by gravimetric analysis after drying at 103°C in an oven (Gefran 800, Chopin, Boulogne, France) for 16 hours. Fat content (FC) was solvent-extracted (petroleum ether) from powders using a semi-automatic Soxtec 2050 extractor (FOSS Analytical, Denmark). Fatty acid (FA) profiles were obtained after esterification of the oil using sodium methylate using gas chromatography using a Thermo Focus (Thermo Fisher Scientific, USA). For all laboratory measurements,

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the standard error of the laboratory (SEL) was estimated as the standard deviation (10 replicates) of a standard Shea sample. A total of 602 samples was analysed for MC, Fat and FA profiles. A subset of 205 samples (including 53 artificially enriched samples) was analysed for FFA content by neutralisation of the fat after extraction using an alcoholic hydroxide potassium solution (0.1 N) and phenolphthalein. FFA content was expressed as oleic acid equivalent (%/DM).

Data processing

Statistical analyses were performed using Win-ISI II software (Infrasoft International, Port Matilda, PA, USA), JUMP 7.01 (SAS Institute Inc., Cary, USA), Statgraphics Centurion XV (StatPoint Inc., USA) and XLstat software (Addinsoft, Paris, France).

Spectrum pretreatment

Spectra were mathematically corrected for light scattering using the standard normal variate and detrend correction. The second derivative was calculated on five datapoints and smoothed using Savitzky-Golay polynomial smoothing over five data points.

NIR calibration development

In order to assess the performance of the predictive equations, the data set was split into a calibration subset (cal) and a validation subset (val); the validation set was created by randomly selecting 10% of the samples. Calibration equations for MC, FAT and FA Profiles were constructed with the calibration subset using the modified partial least squares regression (mPLS) algorithm of WinISI software. Cross-validation (4 groups) was used during calibration development in order to select the optimum number of latent variables and to minimise over-fitting of the equations. The standard error of prediction (SEP) was estimated by predicting the validation subset using a model developed on the calibration subset. The ratio performance to deviation of prediction (RPD_p) was also calculated as $RPD_p=SD_{val}/SEP$ (where SD_{val} was the standard deviation of validation samples).

Results and Discussion

Prior to calibration development, a principal component analysis (PCA) was used to extract relevant information from the spectral matrix (n = 624). The generalised Mahalanobis distance (H) was calculated on the extracted PCs for each sample. This enabled deletion of 22 outlier samples with a Mahalanobis distance H>3; these samples had been tagged as mouldy on arrival at the laboratory.

Moisture content ranged from 2.25% to 8.37%, with an average value of 4.48%. Data dispersion was rather small (SD= 0.89%). Fat content was equal to 49.66% on average (dry matter basis) with a SD of 5.03% corresponding to relatively low dispersion (CV = 10.1%). Individual values ranged from 29.96% to 59.66%. Based on an examination of gas chromatography profiles, 7 FAs with relative percentages over 0.05% were adopted for the study; these comprised three saturated FAs (palmitic C16:0, stearic C18:0 and arachidic C20:0), two cis-monoenoic FAs (oleic C18:1 n-9 and cis-vaccenic C18:1 n-7) and two polyenoic FAs (linoleic C18:2 n-6 and g-linolenic C18:3 n-6). Fatty acid composition mainly consisted of stearic (overall average value 38.13%) and oleic (overall average value 48.58%) acids. The free fatty acid content ranged from 0.21% to 53.98% with an average value of 7.04%; data dispersion was rather large (SD= 9.97%). The 53 samples incubated in the climatic oven successfully filled the gap observed in the original samples between 7% and 20 % FFA. Of the 602 spectra, the samples (n=542) used for calibration (MC, FAT and FA) and the randomly selected samples (n=60) for validation were representative of the variation in terms of SD and range (Table 1) for each constituent.

Moisture content

Calibration for MC produced a value for both R^2 and R^2_p of 0.95. For this model, RPD_p was 4.45 and SEP was 0.23%. Given that commercial nuts must have a moisture content below 9%, our model was efficient enough for its control.

Fat content

The model developed for fat quantification was efficient with R^2 and R^2_p equal to 0.96 and 0.97 respectively and RPD_p equal to 5.61. Our calibration was usable for quality control of Shea nut fat content in producing countries for commercial purposes.

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Stearic and oleic acids

The R^2 values for calibrations were close to 1 for stearic acid (0.96) and oleic acid (0.98). High R^2 coefficients correspond to a very good data fit. These results were confirmed by estimating R^2_p on the validation set (stearic acid 0.98 and oleic acid 0.98). The RPD_p obtained for stearic and oleic models were 6.26 and 7.91 respectively. SEP values observed on the validation set for stearic and oleic acids were 1.19% and 0.90% respectively. The scatter plots of GC values and NIR-predicted values for the 602 samples are shown in Figures 1a and 1b.

Free fatty acids

The RPD_p obtained for the FFA model was 5.19 while the SEP value observed on the validation set was 1.38%. The slope of the fitted regression line between laboratory titration and NIR-predicted values was 1.04 (Figure 2). This model fitted the FFA range observed well but it could still be improved for FFA levels lower than 6% which is the maximum acceptable by the buyers. However, this model can be efficiently used for screening of shea nuts at the production sites.

Table 1. Descriptive statistics for calibration subsets, validation subsets and NIR equations.

		MC	Fat	Palmitic	Stearic	Oleic	Vaccenic	Linoleic	Linolenic	Arachidic
Calibration N=542	Mean	4.46	49.68	4.24	38.25	48.44	0.40	7.15	0.30	1.20
	Range	6.12	31.22	5.73	25.32	23.58	0.82	8.47	0.63	1.37
	SEL	0.1	0.79	0.19	0.98	0.66	0.09	0.34	0.12	0.05
	SD_{cal}	0.84	4.77	0.66	5.68	5.21	0.15	0.90	0.12	0.19
	SEC	0.18	1.00	0.41	1.06	0.74	0.11	0.55	0.07	0.12
	R^2	0.95	0.96	0.61	0.96	0.98	0.48	0.63	0.66	0.63
	SECV	0.20	1.08	0.46	1.14	0.81	0.11	0.62	0.08	0.13
	RPD	4.22	4.43	1.43	4.97	6.47	1.32	1.46	1.54	1.53
Validation N=60	Mean	4.44	50.40	4.49	36.69	49.68	0.41	7.28	0.31	1.17
	Range	4.65	31.38	3.06	24.16	23.15	0.69	9.11	0.49	0.87
	SD_{val}	1.02	5.88	0.69	7.43	7.11	0.19	1.33	0.13	0.21
	SEP	0.23	1.05	0.53	1.19	0.90	0.16	0.78	0.10	0.14
	R^2_p	0.95	0.97	0.45	0.98	0.99	0.23	0.68	0.39	0.57
	RPD_p	4.45	5.61	1.30	6.26	7.91	1.19	1.71	1.30	1.50

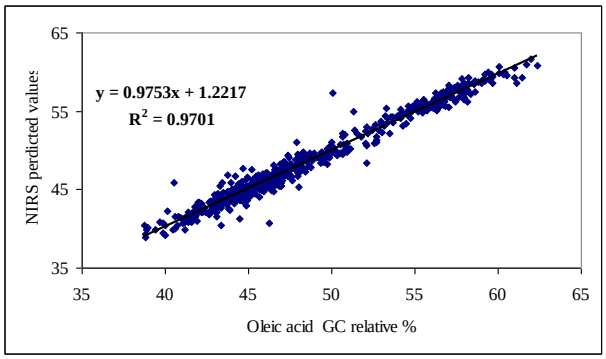

Figure 1a. Scatter plot of laboratory versus NIR-predicted oleic acid values (n=602)

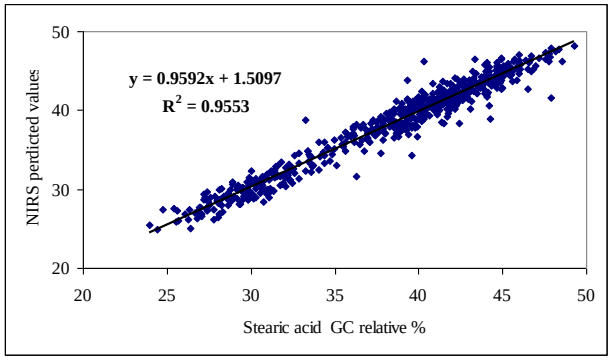

Figure 1b. Scatter plots of laboratory versus NIR-predicted stearic acid values (n=602)

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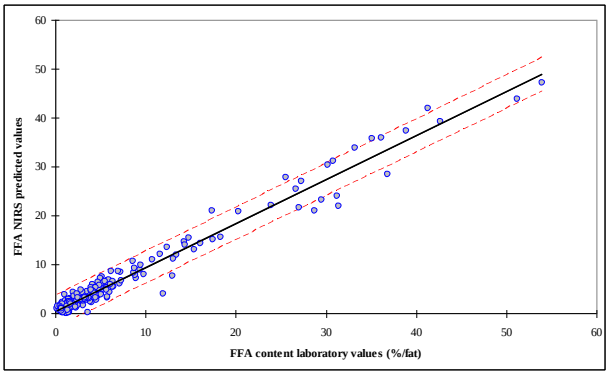

Figure 2. Scatter plots of laboratory versus NIR-predicted free fatty acid values (n=205)

Conclusion

In this study, we developed NIR models for highly accurate prediction of Shea nut stearic and oleic acids composition, fat and water content. Transferring these novel tools to producer countries will provide them with the opportunity to control and promote the quality of their production. In addition, for the food and cosmetic industries, this application will enable early selection of products according to their end-use. Accurately predicting the saturated:unsaturated FA ratio is relevant for Shea butter use as a cocoa butter equivalent (CBE) in the chocolate industry. The sampling was performed on a wide database (624 samples) covering the main ecological regions of shea production and was representative of agricultural practices. Sampling was completed by the use of "artificial" samples to increase FFA range. This strategy was successful for developing an efficient calibration; the FFA calibration can be applied to identify shea nuts with FFA content higher than 6 % which is the limit accepted by buyers.

Acknowledgements

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