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CHEMICAL COMPOSITION AND SPECIFIC LIPIDS PROFILE OF THE CASHEW APPLE BAGASSE

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ABSTRACT

Cashew bagasse is a non-upgraded agricultural byproduct. In this study, three categories of samples consist of red apple skin (R), yellow apple skin (Y), and a mixture of the pulps (P) from the two varieties. The skins were carefully removed by hand, and then washed with distilled water until obtaining a wash water with zero sugar content and then dried in a room protected from sunlight at room temperature. Finally, the dried samples were ground and screened through a sieve of 1 mm mesh and then stored in a hydroclimatic chamber. The lipids from the three samples were Soxhlet-extracted with hexane. The physicochemical characterizations gave: (i) moistures rate of 8.26 to 9.27% from the dry matter, (ii) cellulose content from 18 to 19.92%, (iii) content of lignin, hemicellulose, pectin, protein and lipids respectively from 3.65 to 4.98%, 41.12 to 51.65%, 8.56 to 10.11%, 16.31 to 18.20% and 7.59 to 12.06 %. The fatty acid profile of the lipid extracts revealed a majority of oleic (64.10 to 64.69%) and palmitic (19.36 to 20.77%) acids. The glyceric profile revealed free fatty acids, monoglycerides, diglycerides and triglycerides with contents of 44.06 to 57.11%, 1.55 to 3.71%, 19.77 to 26.84 % and 23.73 to 29.29 % respectively.

Keywords: cashew apple bagasse, skin, lipids, fatty acids, valuation, chemical composition.

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INTRODUCTION

Cashew apple (*Anacardium occidentale* L.) is grown for its economic potential in several countries around the word ¹. World production of cashew nuts was 3.7 million tons in 2014². Brazil which has the long been the leader with 95% of the world production³, is now overtaken by Côte d'Ivoire, which produced over 531 488 tons of cashew nuts in 2014². The cashew apple is 9-10 times heavier than the nut⁴ and nearly 7 million tons of cashew apples was produced in Côte d'Ivoire in 2015⁵. Cashew apple bagasse represents approximately 20% of the weight of this apple^{3,6}. This lignocellulosic material has been the subject of a few studies in Brazil for its conversion into second-generation bioethanol and more recently for xylitol production^{6,8}. According to other studies, the juice is very rich in vitamin C, in polyphenolic compounds and has a very diversified carotenoids profile^{1,9}. Contrary to Brazil, where cashew apple juice is used in the food sector, cashew apple is abandoned in the fields in Côte d'Ivoire with loss of the intrinsic value¹⁰. In recent years, our laboratory has been studying the valorization of waste from agro-resources where bioactive compounds have been isolated and identified from kernel seed cake of the mango (*Mangifera indica* Lam)¹¹. In order to find chemical substances of great interest for the valorization of the cashew apple bagasse, we describe in this study its chemical composition and specific lipids profile. To the best of our knowledge, such a study has not been undertaken on cashew apple from Côte d'Ivoire.

EXPERIMENTAL

Plant Materials

The plant material used consists of very mature red and yellow cashew apples harvested in a cultivated field of 11 hectares near Yamoussoukro, in the center of Côte d'Ivoire. The nuts were manually removed and the apples were immediately used.

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Preparation of the Samples

After collection, the skins were carefully extracted by hand and the three samples obtained consist of red skin (R), yellow skin (Y) and a mixture of the pulps (P) from the two varieties. The samples thus obtained were rapidly washed twice in distilled water at 60 °C, and then several times with distilled water at room temperature until the wash water was clear from sugar (°Brix 0), and then spread on a surface to air-dry in a room protected from light at room temperature (26±2 °C). Finally, the dried samples were ground and screened through a mesh of diameter less than 1 mm and then stored in a hydroclimatic chamber at 40 °C and relative humidity of 60%.

General Procedure

Chemicals and standards

Hexane for HPLC (97% GC purity), trimethylsulphonium hydroxide (TMSH) (0.2 mol/L solution in methanol), and tert-butyl methyl ether (MTBE) HPLC grade were respectively purchased from Sigma-Aldrich and Macherey-Nagel Scharlau Spain. They were stored at 4°C and used without further purification.

Characterization of Cashew Apple Bagasse

The water and volatiles content in the samples were determined according to French standard NF T 60-201. A mass of 5.0 g of the dry matter is taken to an oven at 105 ± 2 °C overnight. After removal from the oven, the sample is cooled in the desiccator and then weighed until the mass of the sample is stabilized. For the determination of ash content and organic matter, the samples were heated at 550 °C for 6 hours. The standards NF V 18-100 and NF V05-128 were used to determine the protein and pectin contents. The contents of lignin, hemicellulose and cellulose were determined using the Van Soest and Wine ADF/NDF method¹². The acid, iodine and saponification indices were respectively determined according to the NF EN ISO 660; NF EN ISO 3961 and NF EN ISO 3657 standards. All experiments were carried out in triplicate. The extraction of the specific lipids was carried out by the Soxhlet method using hexane for 7 hours (NF V03-908). The solvent was removed at 60 °C with a rotavapor and the resulting extract was stored in a colored hermetically closed bottle in obscurity at 4 °C until analysis.

The fatty acid profile was determined by gas chromatography. Oil (20 mg) was dissolved in 1 mL of tert-butyl methyl ether. Then 50 μ g reagents were added to 100 μ L of this solution¹³. Fatty acids (FAs) analyses were carried out on a Varian gas chromatograph. The analyzes were carried out under the conditions described by Elaloui et al.¹⁴

Triacylglycerols (TAG), diacylglycerols (DAG), monoacylglycerols (MAG) and free fatty acids (FFA) were separated by size exclusion chromatography according to standard NF EN ISO 17059. It was carried out by gas chromatography coupled to a flame ionization detector. Their profiles were obtained by gas chromatography coupled to a flame ionization detector. Compounds were identified by comparison of retention times with reference standards and quantification was performed by internal calibration. For this analysis, the characteristics of gas chromatograph (Perkin Elmer) coupled to the ionization detector were as follows: the carrier gas (helium at 15 psi pressure at the column head), the column (Rtx-5 (Restek) length 15 m, internal diameter 0.32 mm, film thickness 0.25 μ m), injection into the column (1 μ L, temperature at 55 °C for 0.5 min, then 200 °C/min to 340 °C and finally maintained at 340 °C for 40 min), the oven (temperature at 55 °C for 0.5 min, then 45 °C/min to 80 °C and finally 10 °C/min to 360 °C for 16 min) and the FID (temperature at 365 °C).

RESULTS AND DISCUSSION

Physicochemical Characterization of the Cashew Apple Bagasse

The results in Table 1 show that the water and volatiles content of the samples (P), (R) and (Y) are respectively $8.26 \pm 0.01\%$, $9.27\% \pm 0.03\%$ and 9.07 ± 0.06 of the dry matter. These results are substantially consistent (or identical) with those of Flávia et al. ¹⁵, which was $9.29\% \pm 0.07\%$ on Brazilian cashew apple bagasse. The small amount of water and volatiles still present in this matrix could give it a long shelf life and reduce the growth of microorganisms ¹⁶. The protein contents of the samples range from $16.31 \pm 0.08\%$

to $18.20 \pm 0.02\%$ for samples (P) and (Y) respectively. These values are higher than those of Lautié¹⁷ which range from 7 to 8%. These differences could be due to the geographical area of cultivation of these cashew apples and could lead to a new chemotype.

The cellulose contents range from $18.00 \pm 0.61\%$ to $19.92 \pm 0.36\%$ for (R) and (Y), respectively. These contents are similar to those of Correia et al. and Flávia et al. which are $20.56 \pm 2.10\%$ and $18.31 \pm 0.07\%$. The hemicellulose contents range from $41.12 \pm 0.24\%$ to $51.65 \pm 0.11\%$ for (P) and (R), respectively. The Samples contain large quantities of hemicellulose compared to those of Correia et al. Rocha et al. And Flávia et al. which range from $8.20 \pm 0.07\%$ to $27.18 \pm 0.01\%$.

The lignin contents range from $3.65 \pm 0.24\%$ for (Y) to $4.86 \pm 0.23\%$ for (P). These values are very low compared to those of Correia et al.⁶, Rocha et al.⁷ and Flávia et al.¹⁵, which vary between $23.91\% \pm 0.02\%$ and $35.26 \pm 0.9\%$. However, the lignin contents of cashew apple bagasse are much higher than those of Rice Hush where optimized content represents only 1.79% ¹⁸.

All three samples have pectin contents in the range of $8.56 \pm 0.39\%$ for (Y) and $10.11 \pm 0.48\%$ for (R). These values are substantially equivalent to one another. The pectin content in the apples bagasse usually varies between 10 and $15\%^{19-21}$. The use of pectin is increasing and apple pudding remains one of the main sources of supply^{19,22}. Bagasse of cashew apple, left at the harvest site as agricultural waste, could constitute a new source of pectin in the development of green products containing pectin. Indeed, fruit pectin is used today as gelling, thickening, texturing, emulsifiers and stabilizers agents in food processing, and in cosmetics and pharmaceutical industries 19,22-24. Due to its ability to bind heavy metals, pectin is used as a detoxifying agent²⁵. The cashew apple bagasse could, therefore, be used in the treatment of water loaded with heavy metals and this study is currently being carried out in the Ivorian laboratory.

Table-1: The Physicochemical Characterization of the Cashew Apple Bagasse. The Chemical Composition of the Samples is given on a Dry Matter Basis (9/100 g of Dry Sample)

Parameters Analysed	P	R	Y
Water and Volatiles	8.26 ± 0.01	9.27 ± 0.03	9.07 ± 0.06
Ash Content	3.71 ± 0.11	2.22 ± 0.06	2.20 ± 0.09
Protein	16.31 ± 0.08	16.83 ± 0.05	18.20 ± 0.02
Lipids	7.59 ± 0.37	10.47 ± 0.05	12.06 ± 0.23
Pectin	9.28 ± 0.77	10.11 ± 0.48	8.56 ± 0.39
Cellulose	19.19 ± 0.30	18.00 ± 0.61	19.92 ± 0.36
Hemicellulose	41.12 ± 0.24	$51,65 \pm 0.11$	51.10 ± 0.18
Lignin	4.86 ± 0.23	4.27 ± 0.41	3.65 ± 0.24
рН	4.30 ± 0.01	4.30 ± 0.01	4.40 ± 0.02

Fatty Acid Composition of Cashew Apple Bagasse

The lipid content ranges from $7.59\% \pm 0.37\%$ for (P) to $12.06\% \pm 0.23\%$ for Y (Table-1). These results show that the lipid content is higher in the skin than the pulp. We did not find a study in the literature on lipids from cashew apple bagasse as this study is new. The results in Table-2 show that these lipids are mainly unsaturated, this fraction represents $77.05 \pm 0.60\%$, $77.26 \pm 0.01\%$ and $75.64 \pm 0.07\%$ respectively for (P), (R) and (Y). The various fatty acids found in the lipids of the samples are found in olive pomace oils, *Hippophae rhamnoides* L. pulp²⁶⁻²⁹ and seeds of *Cucumis amaris*³⁰.

The fatty acid profile shows that the oleic and palmitic acids are the most abundant in the samples with respectively $64.44 \pm 0.06\%$ and $19.36 \pm 0.12\%$ for (P); $64.10 \pm 0.33\%$ and $20.61 \pm 0.33\%$ for (R); $64.69 \pm 0.15\%$ and $20.77 \pm 0.01\%$ for (Y). Oleic acid, with its many applications in the food industry, could be used as a tumoricidal agent³¹.

Palmitic acid is used to produce soaps, cosmetics and release agents and the production of palm oil greatly affects the environment and animals. Cashew apple bagasse could, therefore, be an alternative source of

production of this fatty acid as well as "METI" MUSSELS (*Batissa violacea* L. von Lamarck, 1818) which contains 30% of palmitic acid³².

Table-2: Fatty Acid Composition of Cashew Apple Bagasse

Fatty acids		Р	R	Y		
		%	%	%		
		Saturated				
C16:0	Palmitic	19.36 ± 0.12	20.61 ± 0.33	20.77 ± 0.01		
C18:0	Stearic	2.35 ± 0.16	2.56 ±0.40	1.98 ± 0.02		
C20:0	Arachidic	0.44 ± 0.02	0.76 ± 0.03	0.66 ± 0.01		
C22:0	Behenic	0.80 ± 0.01	0.81 ± 0.01	0.95 ± 0.26		
Total		22.94 ± 0.08	24.73 ± 0.19	24.34 ± 0.07		
Unsaturated						
C16:1n7c	Palmitoleic	1.33 ± 0.03	1.29 ± 0.04	1.45 ± 0.01		
C18:1n7c		3.94 ± 0.04	3.65 ± 0.11	3.69 ± 0.04		
C18:1n9c	Oleic	64.44 ± 0.06	64.10 ± 0.33	64.69 ± 0.15		
C18:2n6c	Linoleic	2.29 ± 0.06	2.15 ± 0.06	1.80 ± 0.01		
C18:3n3a	Linolenic	2.43 ± 0.03	1.90 ± 0.13	1.75 ± 0.01		
C20:1n9c	Eicosenoic	2.65 ± 0.01	2.20 ± 0.16	2.30 ± 0.02		
Total		77.06 ± 0.04	75.27 ± 0.19	75.66 ±0.04		
C18:3n3a C20:1n9c	Linolenic	2.43 ± 0.03 2.65 ± 0.01	1.90 ± 0.13 2.20 ± 0.16	2.30		

Composition of Glycerol Profile of Cashew Apple Bagasse

The results in Table-3 show that the lipids from cashew apple bagasse are rich in free fatty acids (FFA) in the range of 44.06 to 57.11% in the total fraction. This represents an opportunity in the valuation of cashew apple bagasse. Indeed, most of the lipids are in the form of triglycerides and obtaining the free fatty acids requires saponification. As the national cashew apple production in Côte d'Ivoire was more than 7 million tons in 2015⁶, the potential FFA could represent 9 000 tons per year.

Table-3: Composition of Glycerol Profile of Cashew Apple Bagasse

	Acylglycerols	P	R	Y
FFA	Free Fatty Acids total*	11.44	12.55	18.14
	% of General Total**	45.71	44.06	57.11
MAG	Total Monoglycerides*	0.93	0.45	0.49
	% of General Total**	3.71	1.59	1.55
DAG	Total Diglycerides*	6.72	7.14	6.28
	% of General Total**	26.84	25.07	19.77
TAG	Total Triglycerides*	5.94	8.34	6.85
	% of General Total**	23.74	29.29	21.58
	General Total	25.03	28.48	31.77

^{*} grams per 100 g of lipid extract

^{**} grams per 100 g of total glycerides

CONCLUSION

This study showed that the cashew apple bagasse abounds several chemical compounds to be valued. The skins and pulp have substantially the same physicochemical characteristics.

The varieties of apples of yellow and red color do not show enough differences in the parameters analyzed. The quantities of pectins in the bagasse and of fatty acids in the lipids show that this agro-resource has a high potential for recovery. The study of the different types of pectins contained in this bagasse is being carried out in our laboratory.

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