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Research Article

Valorization of cacao and rose waste for preparation of liqueurs

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Abstract

Cacao and rose waste, generated yearly by chocolate and rose-oil industry, respectively, pose to the manufacturers' difficulties for disposal. These by-products are underused and represent also sources of valuable substances: polyphenols, polysaccharides, aroma substances, etc. The aim of the present work was to characterize cacao waste and evaluate possibility for preparation of liqueurs with substituted cacao and aromatized with rose waste. The cacao waste was investigated for total dietary fibres (63.58±0.22% DW), proteins (15.80±0.11% DW), and hexane-soluble substances (13.39±0.08% DW). The most abundant essential amino acids were lysine, phenylalanine and threonine: 1.35±0.13, 1.00±0.08 and 0.73±0.11 g.100g^{-1} waste, respectively. Water, 50% and 95% ethanol extracts were obtained and the highest amount of polyphenols were extracted with 50% ethanol: 5.86±0.39 mg GAE.g^{-1} dry weight (DW) for cacao waste and 3.33±0.39 mg QE.g^{-1} DW for rose waste. The antioxidant activity of 50% ethanol extracts, evaluated by DPPH and FRAP (82.82±1.72 and 31.13±0.70 mM TE.g^{-1} DW cacao waste, respectively; and 14.53±0.35 and 13.42±0.64 mM TE.g^{-1} DW rose waste, respectively) suggested that cacao and rose wastes had a potential as antioxidant supplements. The most prevalent aroma substances in cacao ethanol (50%) extract was hexanal (10.33±0.12% of TIC) and for rose extract: β-phenylethyl alcohol (17.14±0.18% of TIC). A novel possibility for valorization of cacao and rose wastes was explored and liqueurs with substituted cacao powder with cacao waste and added rose waste extracts were obtained. Sensory evaluation revealed that cacao pod husks were a promising constituent for preparation of low-alcoholic beverages.

Keywords: *Theobroma cacao* L., cacao pod husks, *Rosa damascena* Mill, waste valorization, antioxidant activity, liqueurs

Abbreviations: GAE – Gallic acid equivalents; GC-MS – Gas chromatography-mass spectrometry; DPPH – 2,2-diphenyl-1-picrylhydrazyl; DW – Dry weight; FRAP – Ferric reducing ability of plasma; QE – Quercetin equivalents; RI – relative index; TE – Trolox equivalents; TDF – Total dietary fibres; TIC – total ion current.

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Introduction

Cacao (*Theobroma cacao* L.) is an important native tree grown in the tropical forests of the Andes. The name *Theobroma* (meaning "Food of the Gods) signifies the consideration of the local habitants for its divine origin and taste (Nair 2010). The Spanish were the first Europeans started drinking cacao based beverages and introduced it also in Europe. Nowadays, the cacao, together with tea and coffee are among the most significant crops, with major application in the confectionery industry and chocolate manufacturing. The world consumption of cacao increases approximately with 12% per year (Nair 2010). According to the statistical reports 3.97 million tons of cacao were produced worldwide for the 2015/2016 crop year (https://www.statista.com/statistics/262620/global-cacao-production/). This immense production leads to generation of huge amounts of wastes. The major waste materials are the pod husks, sweating, germ, and shell. Each ton of dry cacao beans generates approximately ten tons of cacao pod husks (Kalvatchev et al. 1998). The disposal of these large quantities of waste is a challenging problem for the cacao-manufacturers. Besides, the pod husks are a valuable source of biologically active and nutritional substances: crude protein 5.69-9.69%, fatty materials 0.03-0.15%, glucose 1.16-3.92%, sucrose 0.02-0.16%, pectin 5.30-7.06%, nitrogen-free extract 44.2-151.27%, and crude fibres 33.19-39.45% (Nambuthiri and Shivshankar 1987). Bulgaria is one of the major world producers of rose aroma products based principally on the beautiful *Rosa damascena* Mill. Distillation or extraction of the rose flowers leads to formation of large amounts of residual material which is underused but has a potential as source of polyphenols (Eren et al. 2015; Slavov et al. 2017), polysaccharides (Slavov et al. 2013; 2017), aroma products (Stefanov 2016), bio-sorbent (Rabbani et al. 2015; 2016), feed additive (Balev et al. 2015), etc. Alternative approaches are exploitation of novel methods for valorization of the cacao husks and rose wastes. Due to the lower theobromine content the pod husks could be incorporated in the cattle feed (Sampath et al. 1990). The pods were subject of different studies in order to find possible methods for valorization: the husks were utilized as source of pectins (Vriesmann et al. 2012), as source of dietary polyphenols with pronounced antioxidant activity (Manzano et al. 2017), for production of cacao vinegar, active carbon (Wijaya and Wiharto 2017), etc. Rose waste materials were successfully used as additive for functionalization and aromatization of bakery products (Slavov et al. 2018). New approaches for valorization of cacao pod husks and rose oil industry by-products could significantly contribute to the reduction and better utilization of the wastes. Therefore, the present study aims at determination of composition of industrial sample of cacao pod husks and investigation of the possibility to obtain beverages in which the cacao powder is substituted with cacao pod husks powder / extracts. Additionally, a combination of cacao pod husks powder (or extracts) and ethanolic extracts of waste rose biomass was explored as variant for obtaining of new aromatized liqueurs.

Materials and Methods

Materials

Raw materials. The waste cacao pod husks were provided by ANES 96 Ltd. (Plovdiv, Bulgaria). The waste rose materials (*Rose damascena* Mill.) were provided by EKOMAAT distillery, (Mirkovo, Sofia, Bulgaria: 2017 harvest). The wastes were inspected for impurities, dried under vacuum at 50°C, and then stored at -18°C. The commercial cacao powder and milk (3% fat) were purchased from the local market. The guar gum was obtained from KUK Bulgaria Ltd. All the solvents and reagents were of analytical grade.

Methods

Preparative methods. Extracts (50% and 95% ethanol, and water) of waste cacao pod husks were obtained (solid to liquid ratio 1:5 w/v) after overnight stirring of the mixture at 22±1°C (room temperature). Then the mass was filtered through filter paper.

The liqueurs composition is presented in Table 1 and they were produced according to the following procedure: the sugar was added to 25mL water preheated to 80°C at constant stirring; the guar gum was dissolved in 25mL water; both solutions were mixed and the other ingredients and extracts were added at constant stirring for 10 min (until homogenous mixture was achieved). The liqueurs were left to cool down at room temperature. The cacao pod husks extract used for liqueurs preparation was obtained as follow: 10g dry mass was extracted with 150mL 70% ethanol at 65°C for 1 h at constant stirring. The mass was left overnight at room temperature, filtered and the solid residue was extracted again with 50mL 70% ethanol under the same conditions. Both extracts were combined and further used. The waste rose biomass extract was obtained as follow: 45g dry waste was extracted 300mL 70% ethanol at 65°C for 1 h at constant stirring. The mass was left overnight at room temperature, filtered and the solid residue was extracted again with 150mL 70% ethanol using same conditions. Both extracts were combined.

Analytical methods. The protein content in the cacao pod husks was determined by the Kjeldahl method with automated nitrogen analyzer UDK152 (Velp Scientifica, Italia) using correction factor N×6.25 for calculation of total protein. Hexane soluble substances were determined according to AOAC 922.06 method by Soxhlet extraction with hexane (Fluka, Germany). The total dietary fibres (TDF) were determined by the enzymatic-gravimetric method, using the total dietary fibre assay kit Bioquant 1.12979.0001 (Merck, Germany) and the instructions provided by the manufacturer. The total polyphenol content of extracts was determined using the method described by Singleton and Rossi (1965). Total flavonoid content was determined using $Al(NO_3)_3$ reagent and measuring the absorbance at 415 nm according to Kivrak et al. (2009). The DPPH and FRAP assays were performed according to the procedure described by Slavov et al. (2017). The individual amino acids were determined after derivatization as described by Aronal et al. (2012) using an HPLC system ELITE LaChrome (Hitachi) equipped with diode array detector Elite LaChrome L-2455. The separation was performed on an AccQ-TagTM (3.9×150mm) column. The individual volatile compounds in the cacao waste ethanolic extracts were determined according to the following procedures: 1.0mL extract was extracted with 1.0mL dichloromethane (in triplicate). The combined organic layers were dried under vacuum at 30°C. The dry residue was dissolved in 100μL dichloromethane. For analysis 1.0μL from the solution was injected on gas chromatograph Agilent GC 7890 with mas-selective detector Agilent MD 5975 and column HP-5ms. The following temperature regimen was used – initial temperature was 40°C and then increased to 300°C with 5°C.min^{-1} (hold for 10 min); injector and detector temperatures – 250°C, helium was used as carrier gas at 1.0mL.min^{-1}. The scanning range of mass-selective detector was m.z^{-1} = 40 – 400 in splitless mode. The individual compounds were identified comparing the retention times and the relative index (RI) with those of standard substances and mas-spectral data from libraries of The Golm Metabolome Database and NIST'08 (National Institute of Standards and Technology, USA). The results were expressed as % of total ion current (TIC). The stability of the liqueurs was evaluated by visual observation of particles sedimentation of the beverages due to gravitation after 72 h at room temperature. The sensory evaluation of the liqueurs was performed by 10 member test panel using a scale of 1 to 10 (1-exremly dislike, 10-extremly like). The following parameters were evaluated: homogeneity, color, aroma, taste, after taste and aroma of cacao, after taste and aroma of roses and overall acceptance. The results were presented as mean values.

Statistical analysis. The analyses were performed in triplicate, and the data were given as mean values. Statistical significance was detected by analysis of variance (ANOVA, Tukey's test; value of $p<0.05$ indicated statistical difference).

Table 1. Combinations and ingredients of the liqueurs with cacao powder, waste cacao pod husks powder and waste rose biomass extract

Variant	Milk mL	Water, mL	Ethanol 70%, mL	Sugar, g	Cacao powder, g	Waste cacao pod husks powder, g	Cacao extract, mL	Waste cacao pod husks extract, mL	Waste rose biomass extract, mL	Guar gum, g
Control 1	25	50	25	30	5	-	-	-	-	0.3
Variant 1.1	25	50	25	30	-	5	-	-	-	0.3
Variant 1.2	25	50	12.5	30	-	2.5	-	-	12.5	0.3
Control 2	25	50	-	30	-	-	25	-	-	-
Variant 2.1	25	50	-	30	-	-	-	25	-	-
Variant 2.2	25	50	-	30	-	-	-	12.5	12.5	-

Results and Discussion

Proximate composition of cacao pod husks. Total polyphenols and flavonoids content, and determination of antioxidant activity of extracts of cacao and rose wastes. The waste cacao pod husks were rich source of TDF: 63.58±0.22% (Table 2). Besides, the cacao waste was also a good source of proteins (15.80±0.11%) and the highest concentrations of the essential amino acids were for lysine, phenylalanine and threonine: 1.35±0.13, 1.00±0.08 and 0.73±0.11 $g.100g^{-1}$ waste, respectively. In order to evaluate the total phenolic content and antioxidant activity of cacao pod husks and rose wastes three extracts with different solvents were obtained: 95% ethanol, water and 50% ethanol.

Table 2. Proximate composition of waste cacao pod husks

Parameter	Value
Moisture, %	4.72±0.15
Hexane-soluble substances, %	13.39±0.08
Crude cellulose, %	23.12±0.18
Total protein, %	15.80±0.11
TDF, %	63.58±0.22
Essential amino acids	
Valine, g/100g waste	0.52±0.07
Isoleucine, g/100g waste	0.39±0.12
Leucine, g/100g waste	0.06±0.02
Lysine, g/100g waste	1.35±0.13
Methionine, g/100g waste	0.17±0.02
Cysteine, g/100g waste	0.22±0.04
Threonine, g/100g waste	0.73±0.11
Phenylalanine, g/100g waste	1.00±0.08
Dispensable amino acids	
Alanine, g/100g waste	1.18±0.12
Arginine, g/100g waste	0.94±0.10
Aspartic acid, g/100g waste	1.76±0.14
Glycine, g/100g waste	0.24±0.04
Glutamic acid, g/100g waste	1.82±0.08
Proline, g/100g waste	0.79±0.09
Serine, g/100g waste	1.87±0.07
Tyrosine, g/100g waste	1.16±0.09

Data were expressed as Mean ± SD (n = 3).

This approach was used in order to evaluate also the extractability of biologically active substances by three solvents having in mind that different compounds could be better extracted using different vehicles or concentrations. The highest value of total polyphenols content was found in the 50 % ethanol extracts – 5.86±0.39 mg GAE.g^{-1} cacao waste and 3.33±0.09 mg GAE.g^{-1} rose waste, whereas in the 95% ethanol extracts dominated the total flavonoids: 1.09±0.02 mg QE.g^{-1} cacao waste and 0.82±0.03 mg QE.g^{-1} rose waste (Table 3). Water extracts showed the lowest levels of phenolic compounds and consequently: the lowest antioxidant activity. The higher level of total polyphenols in the ethanol extracts were in accordance with the observation of Valadez-Carmona et al. (2018) that ethanol extraction allowed increasing the amount of total phenols recovered from cacao by-products. In our study, the total phenolic compounds found in cacao waste were comparable with values for a carob flour (Petkova et al. 2017) and higher than in some medicinal plants (Wojdyło et al. 2007). Similar results for the extractability of phenolic compounds from rose waste were observed by Slavov et al. (2017). The highest antioxidant activities evaluated by both methods (DPPH and FRAP) demonstrated 50% ethanol extracts: 82.82±1.72 and 31.13±0.70 mM TE.g^{-1} for the cacao waste and 14.53±0.35 and 13.42±0.64 mM TE.g^{-1} for the rose waste, respectively.

Table 3. Total phenolics, flavonoids, and antioxidant activity of extracts of cacao and rose wastes

Material	Extracts	Total phenolics, mg GAE[1]/g waste	Total flavonoids, mg QE[2]/g waste	Antioxidant activity, mM TE[3]/g waste	
				DPPH	FRAP
Cacao waste	50% Ethanol	5.86±0.39^{a}	0.77±0.02^{a}	82.82±1.72^{a}	31.13±0.70^{a}
	Water	1.66±0.09^{b}	0.48±0.04^{b}	7.53±0.30^{b}	7.53±0.54^{b}
	95% Ethanol	0.94±0.11^{c}	1.09±0.02^{c}	4.22±0.08^{c}	4.27±0.61^{c}
Rose waste	50% Ethanol	3.33±0.09^{d}	0.68±0.05^{a}	14.53±0.35^{d}	13.42±0.64^{d}
	Water	1.34±0.11^{b}	0.39±0.04^{b}	8.55±0.09^{b}	9.06±0.71^{b}
	95% Ethanol	2.45±0.11^{e}	0.82±0.03^{a}	13.10±0.10^{e}	12.62±0.52^{d}

[1]GAE – gallic acid equivalent, [2]QE – quercetin equivalent, [3]TE – Trolox equivalent.
Data were expressed as Mean ± SD (n = 3).
[a, b, c ,d e,]- different letters indicated that values of the means in the columns are significantly different (p<0.05).

The higher amount of total phenolic content in this extracts contributed to increase in antioxidant activity especially the radical scavenging ability, evaluated by DPPH method. In addition, Manzano et al. (2017) published results for improving the quality parameters of cooking oils using polyphenols extracted from cacao bean shell. The obtained results showed the potential application of cacao wastes as source of polyphenols and antioxidants. In comparison with water extracts of carob flour, typically used as a cacao substitute (Petkova et al. 2017) 50% ethanol extract from cacao husk waste showed higher radical scavenging activity evaluated by DPPH method.

Aroma (volatile) substances in 50% ethanolic extracts of cacao and rose waste. One of the most valuable and treasured by the consumers' characteristics of the cacao (beside the stimulant activity due to theobromine and the pronounced antioxidant activity) is the pleasant aroma. The specific odor is formed during the fermentation and mostly due to the Maillard reaction during roasting (Voight 2012). Nevertheless that the main aroma compounds were found in the roasted beans, the cacao pod husks had also the distinguished and pleasant cacao aroma. Moreover, the rose waste is also characterized with agreeable rose odor, despite the fact that the flowers were already subjected to distillation and the majority of the aroma substances were removed. For this reason in the next experiments the aroma (volatile) profile of the cacao and rose waste was evaluated by GC-MS (Table 4). The odor of cacao is due to a great number of volatile substances but several compounds determined by GC-MS and GC-olfactometry could be identified as key odorants (Voight 2012). Mainly, these are isomers of saturated and unsaturated pentanals and hexanals. In our study we identified hexanal (10.33 % of TIC) as the most prevalent aroma substances in the 50% ethanol extract. Besides, other compounds also contributed to the complex flavor: 2-octanol and 3-octanol (earthy, mushroom), β-linalool (flowery-fresh odor, reminiscent of lily of the valley; present also in the rose extract), α- and β-phellandrene (peppery-minty; slightly citrusy), etc. This suggested that to a certain extent the waste cacao husks could be utilized in food products as a replacer of cacao powder. The variants (Variant 1.2 and 2.2) with added rose waste extract additionally were aromatized with distinctive rose odor due to the presence of β-phenylethyl alcohol (17.14±0.18 % of TIC), n-nonadecane (16.61±0.16% of TIC), citronellol (6.16±0.12 % of TIC), trans-nerolidol (4.36±0.15 % of TIC), nerol (3.42±0.10 % of TIC), geraniol (2.31±0.08 % of TIC), etc.

Table 4. Aroma (volatile) substances in 50% ethanolic extracts of waste cacao husks and waste rose flowers

Compound	Retention Index	Quantity (% of total ion current)	
		Waste cacao husks	Waste rose flowers
Hexanal	800	10.33±0.12	-*
Hexanol	864	4.71±0.15	-
α-Pinene	940	6.06±0.21[a]	0.79±0.12[b]
Benzaldehyde	961	2.67±0.10	-
Sabinene	976	8.83±0.12	-
β-Pinene	980	3.15±0.26[a]	0.55±0.08[b]
β-Myrcene	991	-	0.31±0.07
3-Octanol	993	0.65±0.09	-
2-Octanol	998	0.48±0.09	-
α-Phellandrene	1005	9.02±0.16	-
o-Cymene	1022	3.67±0.20	-
Limonene	1029	2.81±0.11	-
β-Phellandrene	1031	6.07±0.18	-
γ-Terpinene	1062	-	0.82±0.06
Terpinolene	1087	-	0.61±0.05
β-Linalool	1097	3.15±0.14[a]	2.44±0.11[b]
β-Phenylethyl alcohol	1110	-	17.14±0.18
cis-Rose oxide	1112	-	0.39±0.08
trans-Rose oxide	1127	-	0.23±0.06
Terpinen-4-ol	1178	-	1.23±0.09
β-Citronellol	1228	-	6.16±0.12
Nerol	1230	-	3.42±0.10
Geraniol	1255	-	2.31±0.08
Thymol	1289	1.00±0.11	-

Eugenol	1356	-	0.17±0.02
Geranyl acetate	1383	-	2.57±0.08
Neryl acetate	1365	-	1.89±0.07
β-Bourbonene	1383		2.86±0.15
β-Cubebene	1389	-	5.35±0.09
β-Elemene	1390	-	0.46±0.06
Methyl eugenol	1401	-	0.25±0.04
β-Caryophyllene	1419	1.26±0.10[a]	1.43±0.11[a]
α-Humulene	1554	-	0.31±0.07
Germacrene D	1479	-	0.36±0.05
α-Farnesene	1508	-	0.51±0.06
β-Bisabolene	1510	-	0.17±0.04
trans-Nerolidol	1564	-	4.36±0.15
Spathulenol	1575	-	1.48±0.12
Caryophyllene oxide	1580	-	0.29±0.10
γ-Eudesmol	1631	-	0.27±0.08
β-Eudesmol	1649	-	0.23±0.06
α-Eudesmol	1652	-	0.80±0.10
Farnesol	1714	-	0.31±0.06
n-Nonadecane	1901	-	16.61±0.16
n-Eicosane	2000	-	0.11±0.02
10-Heneicosene	2093	-	3.47±0.13
n-Heneicosane	2100	-	5.24±0.10
n-Docosane	2200	-	0.68±0.04
n-Tricosane	2300	-	4.04±0.11
n-Tetracosane	2400	-	1.45±0.12
n-Pentacosane	2500	-	1.28±0.09
n-Hexacosane	2600	-	1.27±0.10
Total		63.86±0.26[a]	94.62±0.18[b]

** – not determined in the extract;*
Data were expressed as Mean ± SD (n = 3);
[a ,b] - different letters indicated that values in the rows are significantly different (p<0.05).

Similar observations for presence of the main fragrance compounds, such as: of β-phenylethyl alcohol, citronellol, nerol and geraniol, were reported by Stefanov (2016) for aroma products obtained after valorization of waste rose biomass.

Preparation of liqueurs with substituted cacao powder and added extracts of Rosa damascena waste. Alcoholic emulsion systems (i.e. liqueurs) are well accepted beverages by the consumers. They are characterized with specific and mild sensory qualities and belong to elegant and luxurious alcoholic beverages that are preferred by a wide group of consumers. Based on the analyses for antioxidant activity, total phenolic content and aroma substances of the cacao pod husks and rose waste, in the next experiments liqueurs with substituted cacao powder were obtained. In order to additionally enhance the antioxidant activity and search for new aroma profile, ethanolic extract of

waste rose biomass (in combination with waste cacao husks) was also used for formulation of liqueur beverages. This approach allows for better utilization of the wastes generated by the essential oil industry (in particular, the rose oil industry), having in mind the polyphenol and aroma metabolites content in the rose waste (Slavov et al. 2017).
Four variants (according to Table 1) were tested and compared to control samples made with commercial cacao powder or its ethanolic extract. The stability tests of the liqueurs (Figure 1)

Figure 1. Liqueurs with cacao powder, waste cacao pod husks powder, and waste rose biomass extracts

The coding of the samples is according Table 1. A – after preparation; B – after 72h storage at room temperature suggested that the variants with added cacao or cacao pod husks powder (control 1, variants 1.1 and 1.2) were not stable with time even when stabilizer (guar gum) was added. The results from sensory evaluation were presented on Figure 2.

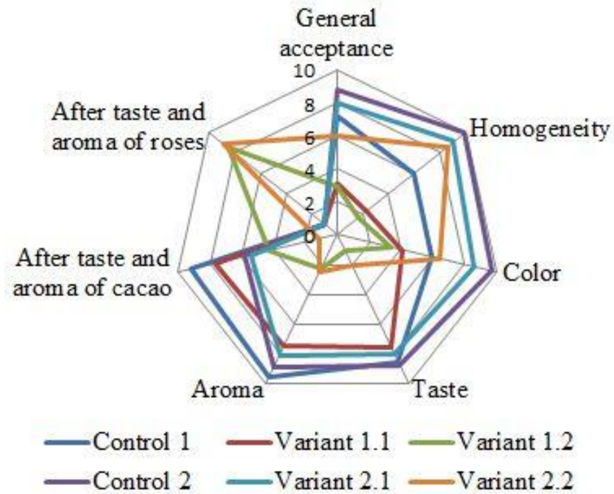

Figure 2. Sensory profile of liqueurs with cacao powder, waste cacao pod husks powder, and waste rose biomass extracts (data were expressed as mean values of the ratings of 10 participants of the sensory evaluation)

The test panel preferred mostly the combination with added cacao (control 2) or cacao pod husks (variant 2.1) extracts (not statistically significant results for the overall acceptability of both liqueurs). As a suggestion the test panelists commented that the combinations with added rose waste extracts should be reformulated and better balance of the aroma profile of liqueurs obtained

Conclusions

Cacao waste husks were investigated and it was found that they are rich source of TDF (63.58±0.22%), proteins (15.80±0.11%) and antioxidants (82.82±1.72 mM TE.g^{-1} by DPPH and 31.13±0.70 mM TE.g^{-1} waste by FRAP assay). Based on the aroma (volatile) metabolites profile and the specific odour of the cacao husks it was suggested that they could be successfully implemented as cacao replacer in low-alcoholic beverages. Besides, additionally for enhancement of antioxidant activity and in searching of new aroma profiles, mixed liqueurs with cacao pod husks and extract of waste rose biomass were formulated. The extracts of rose waste were investigated for polyphenols content (3.33±0.09 mg GAE.g^{-1} waste) and antioxidant activity by DPPH and FRAP (14.53±0.35 and 13.42±0.64 mM TE.g^{-1} waste, respectively). The main volatile compound in cacao pod husks extract (50%) was hexanal (10.33±0.12 % of TIC) and for the 50% rose extract: β-phenylethyl alcohol (17.14±0.18 % of TIC). Both substances contribute substantially to the specific aroma of the wastes and this was used for formulation of low-alcoholic beverages. Four variants of liqueurs were obtained: two with added extracts of cacao pod husks and waste rose biomass extracts and two with direct addition of solid waste cacao pod husks. The stability tests suggested that variants with added cacao extracts were more stable in time and had better and creamy structure. The sensory evaluation revealed that the best combinations were control 2 and variant 2.1. Both liqueurs had a balanced and well accepted overall appearance, taste, color and aroma but additional improvement of density of the beverages is necessary. The combinations 1.2 and 2.2 (with added waste roses) received relatively low scores and the panelists noted that the aroma of roses dominated (even described as intrusive, overpowering smell) over the cacao odour. In this case it seems that the amount of added waste rose extracts (having in mind that the mass was already distilled and much of the essential oils were removed) should be diminished. The control 1 was also positively evaluated by the consumers but the problem here was the precipitation of the cacao powder, and it seems also that this combination, as well as combination 1.1, was more suitable for cacao liqueurs without creamy structure.

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