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Chemical and Sensory Characterization of Carob Spirits According to Different Distillation Systems

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Abstract

Carob is the legume of the carob tree (*Ceratonia siliqua* L.), which is cultivated in many parts of the Mediterranean area. It is mainly used as animal feed and in the formulations of human foods. Due to the high concentration of sugars in carob pods, this fruit could be used as a raw material to produce distillates. In this study, the effect of the distillation system (Charantais alembic versus Charantais alembic with column) on the chemical and sensory characteristics, as well as on the ethanol yield of carob spirits, was analyzed. The ethanol recovery using Charantais alembic was 74.9%, and for Charantais alembic with column, it was 85.8%. Regarding the chemical composition, esters, furanic compounds, and alcohols were the most abundant compounds in the distillates. Principal component analysis was used to identify the different distillate fractions, first distillations, and residues. Nevertheless, the corresponding distillate fractions for both distillation systems were plotted near to each other due to the similar concentration of the volatile compounds. The spirits obtained from both distillation systems were not differentiated by organoleptic triangular and two-alternative forced-choice (2-AFC) tests according to the results of the semi-trained and professional panels. Both spirits were sensorial characterized as floral, fruity, and alcoholic.

Keywords: carob; distillates; spirits; distillation system; ethanol yield; sensorial analysis

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1. Introduction

Carob is the legume of the carob tree (*Ceratonia siliqua* L.), which has been cultivated since ancient times in many parts of the Mediterranean area to restore dryland areas. The carob tree can grow to a height of 12–15 m, with a productive life span of more than one hundred years. Carob is characterized by its low maintenance requirements, and it is drought-resistant [1]. The principal carob producers in the world are Spain, Italy, Portugal, Greece, Morocco, and Turkey [2]. The two principal parts of the carob are the pulp (deseeded pod, carob kibble, or flesh) and the seeds. Carob pulp, representing the 90% of the total weight, is mainly used as animal feed [3] and for the formulations of some human foods such as creams [4]. Only the carob seeds, the other 10% of the whole pod weight, are processed for producing a natural additive (E410) used as a stabilizer and thickener in food products [5,6]. In this case, the pulp could be used as a by-product, and therefore, the carob would be valorized [7]. Previous studies have analyzed the effect of

different maceration operating conditions of carob pods as a cheap source of sugar with the aim of producing bioethanol [8]. The interest in this natural source also increases due to its antioxidant properties correlated with the phenolic content, which would be considered for future studies as pharmaceutical and cosmetic utilizations [9].

Due to the high concentration of sugars (the main sugars are fructose, sucrose, and glucose) in carob pods ranging from 48% to 56% [10], this fruit could be used as a raw material to produce distillates. Yatmaz, 2019 studied continuous ethanol fermentation from a carob pod extract by free or immobilized Saccharomyces (S.) cerevisiae cells, determining the optimal hydraulic residence time of 8 h for a free cell and 6.67 h for immobilized cells [11].

Distillates are consumed worldwide and different techniques are used, such as liquid-state distillation, solid-state distillation, and equipment such as a copper Charantais alembic (French style) and batch distillation columns (German style). The contents of compounds responsible for the aroma of distillates will depend on their volatility and the solubility in ethanol and water. During the spirits distillation process, the distillate is divided into three parts (head, heart, and tail fractions) according to the concentration of compounds, organoleptic characteristics, and ethanol concentration [12].

To our knowledge, few studies about chemical and sensory characterization of carob spirits obtained directly from the distillation of fermented carob pods have been carried out. Mrvčić et al., 2022 studied different fermentation process conditions, such as the temperature and yeast strains of carob mash and the chemical and aromatic characteristics of carob spirits obtained by a copper still [13]. Other works published to date are focused on the study of the antioxidant capacity and phenolic content of carob macerates and carob liqueurs using a fig spirit base [14], as well as on the influence of maceration conditions, such as temperature, maceration time, solid/liquid ratio, on the physicochemical and aromatic characteristics of carob macerates [15].

The study of the production of carob distillates to be consumed is a relatively new fruit spirits area with a big lack in the literature. The aim of this work is to extend the knowledge on the carob distillate products by determination of the alcohol yield of the process and the chemical and sensorial characteristics of carob spirits obtained directly by two different distillation systems (Charantais alembic and alembic with column).

2. Materials and Methods

2.1. Reagents

To prepare the samples for the liquid–liquid extraction, sodium chloride and dichloromethane were obtained from Panreac (Barcelona, Spain) and ethanol from Scharlab S.L. (Barcelona, Spain). 2-octanol was obtained from Sigma-Aldrich (Steinheim, Germany), and type III water was used.

Chemical standards of carob wort and fermented carob wort for high-performance liquid chromatography (HPLC) analysis were fructose from Fisher Scientific (Loughborough, UK). Sucrose, malic acid, and succinic acid were purchased by Sigma-Aldrich (Steinheim, Germany). Glycerol was obtained from Thermo Fisher (Kandel, Germany) and methanol from Fisher Chemical (Geel, Belgium); ethanol was obtained from Scharlab S.L. (Barcelona, Spain). Glucose was purchased by Acros Organics (Geel, Belgium).

2.2. Carob Syrup and Fermentation

This study was carried out in the research laboratory of the Departament d'Enginyeria Química of the Universitat Rovira i Virgili (URV) using a carob syrup of 65 ºBrix supplied by Concentrats Pallejà SL (Riudoms, Spain).

The carob syrup was distributed homogeneously in 4 plastic containers/fermenters with a capacity of 30 L. In each fermenter, 4 L of carob syrup and 16 L of tap water were added, and then this obtained carob wort was inoculated with the yeast strain S. cerevisiae QA23 (Lallemand, Fredericia, Denmark). Before inoculation, the yeast strain was rehydrated in 240 mL of water at 38 °C for 20 min and then added to the fermenters at a concentration of 30 g of yeast/hL, following the recommendations of the manufacturer. Immediately after the inoculation, 7.5 g of the nutrients Vit (Lallemand, Fredericia, Denmark) was added to each fermenter (37.5 g/hL as a concentration within the range recommended by the manufacturer). The mixture was carefully mixed to ensure a homogeneous distribution of all the compounds in the carob wort. Then the containers were provided with a water trap to prevent the entry of air and allow the release of carbon dioxide during the fermentation. The fermentation was carried out at room temperature (average temperature of 22 °C), and the fermented wort was stored at 4 °C until distillation. Temperature and density of fermentation were measured once every day using a hydrometer until constant density.

2.3. Distillation Procedure

The procedure to obtain carob spirit was by double distillation. This is a process where a liquid/fermented raw material is distilled twice with the aim being to concentrate the desired alcohol in the first distillation and, in the second, to recover alcohol as well and refine the flavor.

2.3.1. First Distillation

In the first distillation, the fermented carob of each fermenter (approximately 20 L/fermenter) was separately distilled (4 replicates for the first distillation were carried out) in a 30 L copper Charantais alembic from Maritas Stills, S.L. (Palmeira, Spain) with the objective of recovering the maximum ethanol, and no separation of head, heart, and tail fractions was performed. The base of the boiler was heated by an electrical heating source, and tap water was used to cool the total condenser. The heater was set to obtain an average distillation rate of approximately 36 mL min^{-1}. The four distillates obtained were subsequently mixed.

2.3.2. Second Distillation

The total distillate obtained from the first distillation was 20.68 L. For analytical purposes, 2 L was stored. The rest of the distillate was divided into two individual batches to be distilled according to both distillation methods:

- Copper Charantais alembic from Maritas Stills, S.L. (Palmeira, Spain): 9 L of the first distillate was distilled in a 10 L copper Charantais alembic as an individual batch (1 replicate). The base of the boiler was heated by an electrical heating source and tap water was used to cool the total condenser. The heater was set to obtain an average distillation rate of approximately 25 mL min^{-1}. Based on the sensory analysis carried out by expert tasters of spirits, the distillation products were separated into three fractions: head, heart, and tail. The head fractions were defined as the first 300 mL; the following 2700 mL was collected as the heart fraction; and the following 1250 mL was collected as the tail fraction.
- Copper Charantais alembic with column from Maritas Stills, S.L. (Palmeira, Spain): 9 L of first distillate was distilled in a 10 L copper Charantais alembic with column as an individual batch (1 replicate). The base of the boiler was heated by an electrical heating source, and tap water was used to cool the total condenser. The heater was set to obtain an average distillation rate of approximately 26 mL min^{-1}. On the basis of

sensorial analysis, the distillation products were separated into three fractions: head, heart, and tail. The head fractions were defined as the first 200 mL; the following 3050 mL was collected as the heart fraction; and the following 1000 mL was collected as the tail fraction.

- Both distillation methods are characterized by similar operating parameters, such as energy consumption and processing time.

2.4. Chemical Analysis of Distillates

Ethanol content (%, v/v) was measured with an electronic densimeter (model DSA 5000M, Anton Paar GmbH, Graz, Austria).

Chemical composition with regard to acids, sugars, and alcohols of carob juice and fermented carob juice was determined by the high-performance liquid chromatography Agilent 1100 series system equipped with a refractive index detector (RID) and an ultraviolet diode array detector (UV-DAD) (Agilent, Waldbron, Germany). The separation was performed on a Pronto Gel H column with dimensions 300 × 8.0 mm at 50 °C (Scharlab, Barcelona, Spain). The mobile phase was H2SO4 0.5 mM, and the flow rate was 0.60 mL/min. The diode array detector was monitored at 210 nm. The sample injection volume was 20 µL. The standard solutions and the samples were filtered through 0.45 µm and 0.22 µm syringe filters prior to their injection into the HPLC system. The individual acids and sugars were identified by comparing their retention times to the retention times of commercial standards.

The heart fractions of all the distillates and the first distillate were analyzed by gas chromatography/mass spectrometry to determine and quantify the main aromatic compounds. The equipment employed was an Agilent 6890 series gas chromatograph coupled to a mass selective detector model Agilent 5973. The chromatographic separation was carried out in a capillary chromatographic column DB-FastFame (J&W Scientific, Folsom, CA, USA) (60.0 m × 250.00 µm i.d. × 0.25 µm film thickness). The column oven temperature program was 60 °C (3 min), 4.00 °C/min from 60 to 230 °C, and finally remained at 230 °C for 4.5 min. The carrier gas was helium at a column flow rate of 1.0 mL/min. The sample injection volume was 1 µL (the injection was in split mode 1:2). The injector temperature was 240 °C. The mass spectrometer was operated in the electronic impact ionization mode (70 eV) and in SCAN (mass-to-charge ratio (m/z) range: 35–400) and selected ion monitoring (SIM) (m/z = 59, 69, and 93) combined acquisition mode.

Identification of compounds was based on the mass spectrum comparison with the spectrum library National Institute of Standards and Technology (NIST) 2.0. Quantification of volatile compounds was carried out as concentration equivalent to the internal standard.

Sample Preparation for Liquid–Liquid Extraction for Gas Chromatography/Mass Spectrometry (GC/MS)

For the analysis of volatile compounds of distillates and residues, previously, liquid–liquid extractions were carried out. Briefly, 100 mL of distillate fraction (diluted at 40% v/v of alcohol), 200 mL of distilled water, 30 g of NaCl, 10 mL of dichloromethane, and 100 µL of 2-octanol with a concentration of 3900 mg/L as an internal standard were added to a 500 mL separating funnel and then stirred on an orbital shaker model SBS-LAB-125 (Steinberg Systems, Berlin, Germany), for one hour at 110 rpm. After mixing, the lower phase (dichloromethane extracts) was concentrated with a 20 cm Dufton column in a bain-marie at 50 °C to a volume of 0.5 mL. Dichloromethane extracts were stored in a freezer (−18 °C) until analysis. Extractions were conducted in duplicate.

2.5. Sensory Analysis

Samples obtained from both distillate systems were diluted with distilled water to an ethanol content of 40% v/v and kept at room temperature.

Sensory evaluation of the two different distillates was carried out to determine possible differences between them. Therefore, a triangular test was applied followed by a 2-AFC test.

Finally, a quantitative descriptive analysis was carried out. It consisted in the evaluation of the intensity of 20 agreed organoleptic descriptors: 13 aroma descriptors (fruity, floral, spicy, herbaceous, fusel/solvent/chemical, fatty, woody, cocoa, vanilla, coffee, rancid, burnt/smoky, nutty) and 7 taste descriptors (astringency, mellowness, sweet, alcoholic, prickling, harmony, persistence) for both carob distillates using a discontinuous scale from 0 to 5. A zero indicated that a descriptor was not detected, and a score of 5 indicated the highest intensity. The obtained values ranging from 0 to 5 were transformed by geometric means according to ISO 11035 scaled from 0 to 100 [16].

The samples were served in tasting glasses at room temperature (20 °C). The first panel consisted of a group of 24 students from the Enology Degree of the Universitat Rovira i Virgili (17 men and 7 women between 19 and 64 years old). This group was defined as a semi-trained panel and participated in the triangular and 2-AFC tests. The second panel was formed by 17 sensory professionals (5 women and 12 men between 24 and 66 years old) from the specific area of spirits production. This group carried out all three sensory tests.

2.6. Statistical Analysis

Two-way analysis of variance (ANOVA) was applied to the data of volatile composition (obtained with GC/MS) with the aim of determining whether there were significant differences (at a 5% level) among the different carob distillate fractions and the equipment used to produce them. Multiple comparisons of pairs were carried out to determine the value or values that differed, and Tukey's test was applied at a significance level of 95%.

The data from the 2-AFC test was analyzed using the table of paired comparison tests, two-tailed for difference, and the results for the triangular test were evaluated using the statistical table of binomial distribution [17]. All statistics were performed with significance at $p < 0.05$.

The geometric mean according to ISO 11035 was determined for each evaluated organoleptic descriptor for both types of distillates and represented in a spider diagram to visualize the differences between both distillate systems. Only one replicate was performed.

In addition, the Wilcoxon signed-rank test was applied to determine significant differences between both distillation systems regarding each organoleptic descriptor evaluated by the professional panel in one session (one replicate for the sample and taster).

All statistical analyses were carried out using MS Excel tool XLSTAT 2024.3 (Addinsoft Lumivero, Paris, France).

3. Results and Discussion

3.1. Carob Wort and Fermentation

The carob wort was fermented according to the procedure described in Section 2.2, and in Table 1 is shown the composition in g/L of the carob wort and fermented carob wort. The fermentation was completed after 9 days, and the sugar yield to ethanol was 77.2% (theoretical alcohol to be obtained after fermentation 7.47 L and real alcohol obtained, 5.76 L). The four fermentations showed the same behavior during the whole process.

Table 1. Carob wort and fermented carob wort composition prior to distillation by high-performance liquid chromatography (HPLC) analysis.

	Carob Composition Prior Distillation							
	Fructose (g/L)	**Sucrose (g/L)**	**Glucose (g/L)**	**Malic Acid (g/L)**	**Succinic Acid (g/L)**	**Glycerol (g/L)**	**Methanol (g/L)**	**Ethanol (g/L)**
Carob wort	71.83 ± 1.73	4.04 ± 0.08	69.89 ± 1.68	<LOD [a] (0.625)	<LOD [a] (0.625)	0.75 ± 0.03	n.d. [b]	n.d. [b]
Fermented carob wort	2.74 ± 0.09	3.28 ± 0.10	0.43± 0.01	2.55 ± 0.10	4.99 ± 0.16	6.22 ± 0.19	1.01 ± 0.02	60.46 ± 1.59

[a] LOD: limit of detection. [b] n.d.: not detected.

The main sugars identified in the carob wort were fructose, glucose, and sucrose with concentrations of 71.83 g/L, 69.89 g/L, and 4.04 g/L, respectively. This also confirms data documented by other authors, such as Papaefstathiou et al., 2018 [10] and Hanousek Čiča 2020 [15], but their relative proportions of sugar are different. This difference can be attributed to the hydrolysis effect over sucrose during the production of carob syrup used in this work (personal communication of producer). The concentration of malic and succinic acids in the carob wort was lower than 0.625 g/L (LOD), and the concentration of glycerol was 0.75 g/L.

The alcohol concentration in the fermented carob wort was 60.46 g/L (7.66% v/v), being the residual concentrations of fructose, glucose, and sucrose 2.74 g/L, 0.43 g/L, and 3.28 g/L, respectively. Glucose is the precursor of malic and succinic acids via the aerobic glycolyse channel [18]. The concentrations of malic acid and succinic acid were 2.55 g/L and 4.99 g/L, respectively. Malic and succinic acids were also found by Li et al., 2013 [19] and Duarte et al., 2010 [20] for mango wine and jaboticaba wine, respectively. The obtained malic acid concentration in our work is comparable to the concentration range determined in wines (0–4.0 g/L) by Regmi et al., 2012 [21]. For succinic acid, Ribéreau-Gayon et al., 2006 reference average concentrations lower than 1 g/L in wine [18].

The concentration of glycerol was 6.22 g/L. Comparable concentrations were determined in mango wine, 6.81 g/L [18], in plum wine, 5 g/L [22], and in cider, with the concentration being 3–6 g/L [23]. The methanol concentration in the fermented wort was 1.01 g/L. Methanol is from enzymatic hydrolysis of the methoxyl groups of pectins during fermentation [18]. A considerable amount of pectins were identified by Llompart et al., 2025 in the carob pulp [24]. A high concentration of methanol was determined as well in plume wine, being over 1 g/L [22]. Despite the high concentrations obtained, commercial wines cannot contain over 200–250 mg/L according to the regulations in different countries considering its toxic properties to humans [25]. Other fruit wines, such as apple wine and blackberry wine, contain relatively high methanol concentrations, being 120–250 mg/L and 100–250 mg/L, respectively [25]. Despite the high methanol concentrations determined in these works and in our work, the European Union (EU) limit for methanol can be up to 10 g methanol/L ethanol with regard to the type of distillates and products [26].

3.2. Ethanol Yield for Alembic and Alembic with Column Distillation Systems

Table 2 shows the ethanol balance of both distillation systems (Charantais alembic and Charantais alembic with column). The yield for the first distillation (alembic first distillation) was 94.9%, obtaining 20.76 L of distillate with an average alcoholic strength of 26.3% vol. for an initial amount of 79.1 L fermented carob (7.3% vol.). In the second distillation, 9 L of the first distillate was re-distilled on the 10 L copper Charantais alembic, obtaining a heart of 2.70 L with an alcoholic strength of 65.8% vol. Ethanol recovery in the heart fraction was 74.8%. The total ethanol yield also considering the ethanol in the

head and tail fractions was 97.1%, which was higher than the total ethanol yield of the first distillation of 94.9%. An amount of 9 L from the first distillate was also re-distillated but using a 10 L copper Charantais alembic with a packed column. In this case, it was a heart of 3.050 L with an alcoholic strength of 66.6%. Ethanol recovery in the heart fraction was 85.8%. The total recovery considering the head and tail fractions was 99.9%.

Table 2. Ethanol balance in both distillation systems.

Distillation Type	Amount Distilled (L)	Alcoholic Strength (% vol)	Distilled Volume (L)	Alcoholic Heart Strength (% vol)	Theoretical Ethanol Yield (L a.a.)	Absolute Heart Ethanol Yield (L a.a.)	Heart Ethanol Yield (%)
Alembic first distillation *	79.1 *	7.3 *	20.68 *	26.3 *	5.76 *	5.5 *	94.9 *
Heart alembic second distillation	9	26.4	2.70	65.8	2.4	1.8	74.8
Heart alembic with column second distillation	9	26.3	3.05	66.6	2.4	2.0	85.8

* No separation of head, heart, and tail fractions was performed in the first distillation.

Both distillation systems showed similar ethanol strength for heart fractions, being 65.8% vol and 66.6% vol for the Charantais alembic and Charantais alembic with column, respectively. Nevertheless, the distilled volume for the heart fractions in the second distillation was 10% higher in the Charantais alembic with column in comparison to the Charantais alembic, resulting in an ethanol yield for the Charantais alembic with column of 11% higher than the one for the Charantais alembic.

Garcia-Llobodanin et al., 2011 obtained a heart ethanol yield of 71.3% in the second distillation of pear fermented using a Charantais alembic, similar to the results obtained in our work of 74.8% [27]. The difference was that in the study by Garcia-Llobodanin et al., 2011 [27], only 79.0% of the alcohol from the fermentation was recovered, whereas in our work it was 94.9%.

Arrieta et al., 2014, for a single distillation, comparing an alembic and a column, the average ethanol yields in the heart were 51.1% and 79.6%, respectively, with an alcoholic strength of 44.9% v/v and 54.4% v/v [28]. Therefore, the heart ethanol yield was higher for the column distillation technique. In our work, comparing both distillation devices, the heart ethanol yield was also higher using the alembic with column, 85.8%, than that obtained using the Charantais alembic, 74.8%.

3.3. Carob Distillates Volatiles Content

Table 3 shows the average concentration in mg/L of volatile compounds for the carob spirits obtained with the Charantais alembic and Charantais alembic with column distillation systems. A total of 52 volatile compounds were identified and quantified in the Carob distilled fractions and residues. Two-way analysis of variance (ANOVA) was applied to the raw data of the volatile composition obtained with GC/MS to determine statistical differences with a significance level of 0.05. The results showed differences among the samples according to the distillation system and distillation fractions.

Table 3. Average concentration (mg/L) equivalent of the internal standard (2-octanol) of the identified compounds in each distillate fraction, residue, and first distillation.

Compound	1st Dist. ** 24	2nd Dist. Char. *** Head 24	2nd Dist. Char. Heart 24	2nd Dist. Char. Tail 24	2nd Dist. Char. Residue 24	2nd Dist. Char. Column Head 24	2nd Dist. Char. Column Heart 24	2nd Dist. Char. Column Tail 24	2nd Dist. Char. Column Residue 24
1-propanol [a]	0.22 ± 0.03	0.49 ± 0.02	0.49 ± 0.05	0.10 ± 0.01	n.d.	0.58 ± 0.00	0.54 ± 0.06	0.08 ± 0.01	n.d.
Isobutanol [a]	3.65 ± 0.58	10.38 ± 0.39	7.86 ± 0.36	0.31 ± 0.01	n.d.	12.66 ± 0.97	8.09 ± 0.76	0.26 ± 0.08	n.d.
1-Butanol [a]	n.d.	0.09 ± 0.00	0.10 ± 0.01	n.d.	n.d.	0.10 ± 0.01	0.11 ± 0.02	n.d.	n.d.
3-Methyl-1-pentanol [a,b,c]	n.d.	0.07 ± 0.00	0.07 ± 0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1-Hexanol [a]	n.d.	0.06 ± 0.00	0.07 ± 0.00	n.d.	n.d.	0.06 ± 0.00	0.07 ± 0.00	n.d.	n.d.
Phenylethyl alcohol [a,b,c]	28.71 ± 4.95	2.06 ± 0.43	9.08 ± 0.78	50.93 ± 2.02	19.00 ± 3.47	2.54 ± 0.04	9.59 ± 0.23	59.31 ± 1.09	27.91 ± 2.23
2-Heptanol [a,b,c]	0.09 ± 0.01	n.d.	n.d.	n.d.	n.d.	n.d.	0.14 ± 0.00	n.d.	n.d.
∑ Alcohols	32.67 ± 5.58	13.15 ± 0.85	17.66 ± 1.22	51.34 ± 2.05	19.00 ± 3.47	15.93 ± 1.03	18.54 ± 1.07	59.65 ± 1.18	27.91 ± 2.23
Ethyl acetate [a]	18.39 ± 1.18	89.27 ± 16.89	16.08 ± 1.26	1.18 ± 0.01	0.15 ± 0.15	99.95 ± 2.20	17.85 ± 0.40	2.18 ± 0.35	0.24 ± 0.01
Ethylbutanoate [a]	0.11 ± 0.01	1.10 ± 0.06	0.07 ± 0.00	n.d.	n.d.	1.40 ± 0.21	0.08 ± 0.00	n.d.	n.d.
Isobutylacetate [a,b,c]	n.d.	1.04 ± 0.04	n.d.	n.d.	n.d.	1.29 ± 0.01	n.d.	n.d.	n.d.
Ethyl hexanoate [a]	0.22 ± 0.00	3.19 ± 0.21	0.19 ± 0.01	0.04 ± 0.00	n.d.	3.65 ± 0.42	0.20 ± 0.00	n.d.	n.d.
Ethyl octanoate [a]	0.31 ± 0.02	4.89 ± 0.10	0.31 ± 0.06	0.11 ± 0.01	n.d.	4.78 ± 1.41	0.33 ± 0.03	0.13 ± 0.01	n.d.
Ethyl decanoate [a]	0.13 ± 0.02	3.29 ± 0.12	0.21 ± 0.07	0.05 ± 0.01	n.d.	2.21 ± 0.87	0.14 ± 0.01	0.03 ± 0.00	n.d.
Ethyl 9-decenoate [a]	n.d.	0.13 ± 0.00	n.d.	n.d.	n.d.	0.10 ± 0.04	n.d.	n.d.	n.d.
2-Phenylethyl acetate [a,b,c]	0.28 ± 0.01	0.21 ± 0.01	0.62 ± 0.02	0.39 ± 0.02	n.d.	0.11 ± 0.02	0.54 ± 0.03	0.17 ± 0.01	n.d.
Ethyl benzenepropanoate [a,b,c]	0.03 ± 0.00	n.d.	0.07 ± 0.00	n.d.	n.d.	n.d.	0.05 ± 0.00	n.d.	n.d.
Ethyl dodecanoate [a]	n.d.	0.27 ± 0.01	0.02 ± 0.01	n.d.	n.d.	0.17 ± 0.11	n.d.	n.d.	n.d.
Ethyl tetradecanoate [a,b,c]	n.d.	0.06 ± 0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ethyl 9-hexadecenoate [a,b,c]	n.d.	0.24 ± 0.00	0.05 ± 0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ethyl hexadecanoate [a]	n.d.	0.63 ± 0.02	n.d.	n.d.	n.d.	0.36 ± 0.25	0.03 ± 0.01	n.d.	n.d.
Ethyl isobutyrate [a]	n.d.	n.d.	n.d.	0.06 ± 0.00	n.d.	n.d.	n.d.	0.06 ± 0.01	n.d.
Diethyl succinate [a,b,c]	n.d.	n.d.	n.d.	0.03 ± 0.00 [a]	n.d.	n.d.	n.d.	n.d.	n.d.
Ethyl 2-hydroxy-4-methyl pentanoate [a,b,c]	n.d.	0.02 ± 0.00	0.03 ± 0.00	n.d.	n.d.	n.d.	0.03 ± 0.00	n.d.	n.d.
Ethyl lactate [a,b,c]	0.41 ± 0.07	0.11 ± 0.00	n.d.	0.99 ± 0.07	0.09 ± 0.09	n.d.	0.42 ± 0.02	1.03 ± 0.10	0.22 ± 0.05
∑ Esters	19.87 ± 1.30	104.45 ± 17.47	17.66 ± 1.45	2.85 ± 0.12	0.24 ± 0.24	114.01 ± 5.55	19.66 ± 0.51	3.60 ± 0.48	0.46 ± 0.07
cis-Linalooloxide [a,b,c]	0.87 ± 0.07	0.74 ± 0.01	1.64 ± 0.02	0.90 ± 0.03	n.d.	0.44 ± 0.05	1.71 ± 0.06	0.50 ± 0.00	n.d.
trans-Linalooloxide [a,b,c]	0.51 ± 0.05	0.30 ± 0.01	0.84 ± 0.01	0.86 ± 0.04	0.06 ± 0.02	0.16 ± 0.02	0.89 ± 0.00	0.60 ± 0.02	0.01 ± 0.01
p-Menth-1-en-9-al [a,b,c]	0.07 ± 0.01	n.d.	0.14 ± 0.00	0.08 ± 0.00	n.d.	n.d.	0.13 ± 0.01	n.d.	n.d.
D-nerolidol [a,b,c]	n.d.	n.d.	0.04 ± 0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,3-Dihydrofarnesol [a,c]	n.d.	n.d.	0.17 ± 0.03	n.d.	n.d.	n.d.	0.10 ± 0.01	n.d.	n.d.
Linalool [a,b]	n.d.	0.01 ± 0.00	0.01 ± 0.00	n.d.	n.d.	0.01 ± 0.00	0.01 ± 0.00	n.d.	n.d.
Alfa-Terpineol [a,c]	n.d.	0.04 ± 0.00 [a]	0.02 ± 0.00 [a]	0.01 ± 0.00 [a]	0.00 ± 0.00 *	0.03 ± 0.01	0.01 ± 0.00	0.02 ± 0.01	n.d.
∑ Terpenes	1.44 ± 0.13	1.09 ± 0.02	2.86 ± 0.07	1.84 ± 0.07	0.06 ± 0.02	0.64 ± 0.08	2.84 ± 0.08	1.12 ± 0.03	0.01 ± 0.01

Table 3. *Cont.*

Compound	1st Dist. ** 24	2nd Dist. Char. *** Head 24	2nd Dist. Char. Heart 24	2nd Dist. Char. Tail 24	2nd Dist. Char. Residue 24	2nd Dist. Char. Column Head 24	2nd Dist. Char. Column Heart 24	2nd Dist. Char. Column Tail 24	2nd Dist. Char. Column Residue 24
3-methylbutanal + 2-methylbutanal [a,b,c]	0.48 ± 0.02	5.20 ± 0.03	0.35 ± 0.04	n.d.	n.d.	7.21 ± 0.43	0.39 ± 0.01	n.d.	n.d.
Benzaldehyde [a,b,c]	0.09 ± 0.01	0.26 ± 0.01	0.45 ± 0.01	0.25 ± 0.01	0.03 ± 0.03	0.22 ± 0.03	0.45 ± 0.00	0.05 ± 0.01	0.08 ± 0.00
(E)-2-Hexenal [a,b,c]	n.d.	n.d.	n.d.	0.02 ± 0.00	n.d.	n.d.	n.d.	n.d.	n.d.
2-Cyclopentene-1,4-dione [a,b,c]	0.08 ± 0.01	n.d.	0.07 ± 0.00	0.17 ± 0.01	n.d.	n.d.	0.09 ± 0.00	0.10 ± 0.01	n.d.
∑ Aldehydes + Ketones	0.64 ± 0.04	5.46 ± 0.04	0.87 ± 0.05	0.45 ± 0.02	0.03 ± 0.03	7.43 ± 0.45	0.93 ± 0.02	0.15 ± 0.02	0.08 ± 0.00
Acetal [a]	9.53 ± 1.17	78.28 ± 7.38	16.70 ± 1.93	0.85 ± 0.07	1.55 ± 0.24	91.40 ± 1.68	17.65 ± 0.11	1.48 ± 0.33	1.28 ± 0.04
Isobutanal diethyl acetal [a]	n.d.	2.96 ± 0.18	0.14 ± 0.01	n.d.	n.d.	3.51 ± 0.46	0.14 ± 0.01	n.d.	n.d.
3-Methyl butanal diethyl acetal [a]	0.15 ± 0.01	3.31 ± 0.17	0.18 ± 0.01	n.d.	n.d.	3.80 ± 0.56	0.19 ± 0.01	n.d.	n.d.
2-Methylbutanal diethyl acetal [a]	n.d.	1.01 ± 0.03	n.d.	n.d.	n.d.	1.25 ± 0.19	0.05 ± 0.00	n.d.	n.d.
1,1,3-triethoxypropane [a,c]	0.04 ± 0.00	0.10 ± 0.00	0.05 ± 0.00	0.03 ± 0.00	n.d.	0.12 ± 0.01	0.05 ± 0.00	n.d.	n.d.
Phenylacetaldehyde diethyl acetal [a,b,c]	0.08 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	n.d.	n.d.	n.d.	0.04 ± 0.00	n.d.	n.d.
∑ Acetals	9.79 ± 1.19	85.70 ± 7.76	17.11 ± 1.95	0.88 ± 0.08	1.55 ± 0.24	100.08 ± 2.89	18.12 ± 0.14	1.48 ± 0.33	1.28 ± 0.04
Furfurylformate [a]	0.37 ± 0.03	1.36 ± 0.12	0.69 ± 0.04	0.32 ± 0.01	n.d.	1.61 ± 0.08	0.64 ± 0.02	0.25 ± 0.02	n.d.
Dihydro-2-methyl-3(2H)-furanone [a,c]	0.44 ± 0.06	0.26 ± 0.01	0.56 ± 0.09	0.91 ± 0.09	n.d.	n.d.	0.68 ± 0.03	0.98 ± 0.04	0.07 ± 0.01
1-(2-furanyl)-1-propanone [a,b,c]	0.17 ± 0.02	0.11 ± 0.01	0.27 ± 0.00	0.31 ± 0.00	n.d.	0.07 ± 0.01	0.30 ± 0.01	0.23 ± 0.00	n.d.
unknown/furanic [a]	0.22 ± 0.01	1.83 ± 0.09	0.92 ± 0.06	n.d.	n.d.	2.09 ± 0.20	0.91 ± 0.05	0.07 ± 0.01	n.d.
5-Methyl furfural [a,c]	1.78 ± 0.26	0.65 ± 0.03	1.89 ± 0.09	4.65 ± 0.12	0.23 ± 0.23	0.36 ± 0.02	2.25 ± 0.00	4.64 ± 0.02	0.31 ± 0.00
Furfural [a]	3.74 ± 0.59	2.16 ± 0.05	4.78 ± 0.41	7.07 ± 0.85	0.26 ± 0.26	1.82 ± 0.04	6.21 ± 0.06	7.66 ± 0.11	0.38 ± 0.06
Acetylfuran [a]	1.97 ± 0.30	0.83 ± 0.02	2.22 ± 0.12	4.50 ± 0.42	0.21 ± 0.21	0.55 ± 0.06	2.69 ± 0.03	4.77 ± 0.11	0.28 ± 0.02
Furfuryl alcohol [a,b,c]	0.32 ± 0.06	n.d.	n.d.	0.38 ± 0.03	0.08 ± 0.08	n.d.	0.13 ± 0.01	0.43 ± 0.02	0.27 ± 0.07
∑ Furanic compounds	9.02 ± 1.34	7.20 ± 0.33	11.34 ± 0.81	18.14 ± 1.53	0.79 ± 0.79	6.50 ± 0.40	13.80 ± 0.21	19.04 ± 0.34	1.31 ± 0.16
not identified [a]	n.d.	n.d.	n.d.	0.58 ± 0.07	n.d.	n.d.	n.d.	0.58 ± 0.00	n.d.
not identified [a,b,c]	0.09 ± 0.00	n.d.	0.11 ± 0.00	n.d.	n.d.	n.d.	n.d.	0.15 ± 0.01	n.d.
not identified/mixture [a,b,c]	n.d.	1.47 ± 0.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
∑ Not identified	0.09 ± 0.00	1.47 ± 0.08	0.11 ± 0.00	0.58 ± 0.07	n.d.	n.d.	n.d.	0.73 ± 0.01	n.d.

a: Significant differences ($p \leq 0.05$) between the concentrations for the compound for the second distillation due to head, heart, and tail distillation fractions. b: Significant differences ($p \leq 0.05$) between the concentrations for the compound for the second distillation due to the type of distillation method. c: Significant differences ($p \leq 0.05$) between the concentrations for the compound for the second distillation due to the interaction between distillation fractions and type of distillation. * Mean concentration for alfa-terpineol < 0.01 mg/L. ** Distillation (Dist.) *** Charantais (Char.) n.d.: not detected.

Esters were the most abundant with 17 compounds detected, followed by furanic compounds, eight; alcohols, seven; and terpenes, seven. Aldehydes and ketones were the least abundant.

3.3.1. Esters

From a total of 17 identified esters, only ethyl acetate was found in all the distilled fractions and residues. Ethyl acetate is in general the most abundant ester in spirits [29], and in this study, its concentration was significantly higher than the concentration of the rest of the esters for the majority of distilled fractions. Ethyl acetate is formed during the fermentation due to the reaction of acetic acid and ethanol and is mainly distilled in the head fractions. According to the results, the higher concentration was determined in the head fractions for both distillation systems (89.27 mg/L with alembic Charantais and 99.95 mg/L with alembic Charantais with column). Similar results were obtained by Wang, 2024 [29].

Ethyl octanoate and ethyl hexanoate were identified by other authors as the most abundant lower molecular weight ethyl esters in the carob spirits [13,15]. Both ethyl esters are produced during raw material fermentation and are distilled in first fractions during pot still distillation due to their better solubility in ethanol than water [30]. As expected, the results of this work showed higher concentrations of ethyl octanoate in first fractions (heads) for both distillation systems, Charantais alembic and Charantais alembic with column, being 4.89 mg/L and 4.78 mg/L, respectively. Levels for the heart fractions were much lower than in the head fraction: 0.31 mg/L and 0.33 mg/L for Charantais alembic and Charantais alembic with column, respectively. Similar behaviour was observed for ethyl hexanoate. Ethyl decanoate was the other linear ethyl ester with a relatively high concentration among the esters and is characterized by its distillation in head fractions [30], and it has also been detected in the carob macerates [15]. In our study, ethyl decanoate was mainly distilled in the head fractions for both distillation systems. In fig spirits, this ester is one of the most abundant [31]. Rodríguez-Solana et al., 2018 determined that ethyl decanoate concentration was higher than the concentration of ethyl octanoate and ethyl hexanoate for fig spirits and for other fruit spirits [32]. For these three linear esters, no concentration differences were observed due to the distillation system.

Among the minor esters, ethyl butyrate, ethyl dodecanoate, ethyl 9-decenoate, and ethyl hexadecanoate showed statistical differences in concentrations between fractions; however, the distillation system did not show a significant effect. For all of them, the contents were higher in head fractions than in the heart or tail fractions, and in several cases the compound was only detected in the head fraction. As the previous esters described, these compounds, due to their volatility and solubility in ethanol, tend to distillate with the first fractions [30].

Another group of esters is formed by 2-phenylethyl acetate, isobutyl acetate, ethyl benzenepropanoate, ethyl tetradecanoate, ethyl 2-hydroxy-4-methyl pentanoate, ethyl 9-hexadecenoate, diethyl succinate, and ethyl lactate. These compounds showed statistical differences due to the two factors studied (distillation system and fraction), and their interaction (distillation system x fraction) also showed a significant effect. In addition, the statistical analysis showed that all these compounds, except ethyl lactate and isobutyl acetate, tend to show lower contents in fractions obtained with the Charantais column system. With regard to the heart fraction, it is remarkable that benzenic compounds show the highest levels in this fraction for both distillation systems. Ethyl lactate, formed by the esterification of lactic acid with ethanol, is associated with the tail fractions. In our results, the concentrations in the tail fractions were the highest

3.3.2. Alcohols

From higher alcohols, straight-chain alcohols such as isobutanol, 1-propanol, 1-butanol, and 1-hexanol are produced during the alcoholic fermentation [30]. All these compounds showed statistical differences in concentrations between fractions.

For isobutanol, identified in all fractions, in the first distillation, except in the residue of Charantais alembic with column, the major concentration was in the head fractions of both distillation systems and was comparable, followed by the hearts concentration, which was similar between the distillation systems, showing no significant differences regarding the distillation system. This alcohol was identified by Mrvčić et al., 2022 in carob wine fermentation [13]. 1-Propanol is a typical compound found in spirits [30]. In our study, its higher concentration was determined in the head and heart fractions for both distillation systems and was comparable between them, showing no significant differences between distillation systems. Nevertheless, Mrvčić et al., 2022 identified 1-propanol only in carob wine fermentation [13].

1-Butanol was only identified in the head and heart fractions of both distillation systems with a similar concentration (approximately 0.1 mg/L, see Table 4). 1-Hexanol was only detected with clearly low concentrations of 0.06 mg/L and 0.07 mg/L in the head and heart fractions, respectively, for both distillation systems. Stanojevic et al., 2024 [33] also determined a low concentration of 1-hexanol in pear spirits, 2.9 mg/L, and it is considered relevant in apple pomace [34] and in apple ciders [35]. 1-hexanol, and its corresponding unsaturated trans/cis-3-hexen-1ol and trans/cis-2-hexen-ol, may have, in part, a varietal origin [36] and play a positive role in spirits, but when the concentration of 1-hexanol exceeds 12 g/hL a.a., it becomes unpleasant due to its strong herbaceous odor. López-Vázquez et al., 2012 determined a relatively high concentration of cis-3-hexen-1-ol, being 0.14 g/hL p.a. for kiwi distillates [37]. 1-Hexanol was also quantified by Diéguez et al., 2005 in considerably higher concentrations for different Galician orujo spirits (30.4–79.7 mg/L) [38].

The concentration of 3-methyl-1-pentanol, 2-heptanol, furfuryl alcohol, and phenyl ethyl alcohol showed significant differences according to the distillate fraction, distillation system, and the interaction of both.

3-Methyl-1-pentanol was only quantified in a low concentration in the head and heart fractions for the Charantais alembic distillation system, being 0.07 mg/L. 2-heptanol was identified in the first distillation with a concentration of 0.09 mg/L and in the heart fraction of the Charantais alembic with column system, being 0.14 mg/L. This alcohol was also identified by Mrvčić et al., 2022 as one of the minority alcohols in the carob spirits [13].

As expected, for the major concentration of phenylethyl alcohol, the typical tail compound was in the tail fractions for both distillations systems [39]. The concentration differences were significant between fractions, the distillation system, and their interaction (distillation system x fraction). According to the current literature, the compound phenylethyl alcohol was not identified in any previous work about carob liquors and distillates.

3.3.3. Terpenes

Linalool was detected only in the heart and head fractions for both distillation systems, showing similar contents in all of them. 2,3-Dihydrofarnesol was only identified in the heart fractions, with higher levels in the case of Charantais alembic without column with respect to the system with column (0.17 mg/L and 0.10 mg/L, respectively). D-nerolidol was only found in the heart fraction of Charantais alembic with a concentration of 0.04 mg/L. Alfa-terpineol was identified in all fractions of second distillations, showing statistical differences due to the fraction and its interaction with the distillation system. Levels of

the heart fraction were higher in the case of the column Charantais system; however, head fractions showed the contrary effect.

Table 4. Summary of principal characteristics of spirits obtained by both distillation systems (Charantais alembic and Charantais alembic with column).

	Charantais Alembic	**Charantais Alembic with Column**
Sensory properties	Slightly higher intensity in herbaceous and fusel/chemical/solvent notes.	Slightly higher intensity in spicy, woody, cocoa, coffee, and rancid notes.
	Both distillates are characterized by higher intensity in floral, fruity, and alcoholic notes. The effect of the distillation system did not show significant differences between both distillation products regarding their organoleptic properties.	
Heart Ethanol yield	74.8%	85.8%
Alcoholic heart strength	65.8%	66.6%
Chemical properties heart fractions	Alcohols concentration: 17.66 ± 1.22 mg/L 3-Methyl-1-pentanol detected 2-Heptanol not detected Esters concentration: 17.66 ± 1.45 mg/L Terpenes concentration: 2.86 ± 0.07 mg/L D-nerolidol detected Aldehydes and ketones concentration: 0.87 ± 0.05 mg/L Acetals concentration: 17.11 ± 1.95 mg/L Furanic compounds concentration: 11.34 ± 0.81 mg/L	Alcohols concentration: 18.54 ± 1.07 mg/L 3-Methyl-1-pentanol detected 2-Heptanol detected Esters concentration: 19.66 ± 0.51 mg/L Terpenes concentration: 2.84 ± 0.08 mg/L D-nerolidol not detected Aldehydes and ketones concentration: 0.93 ± 0.02 mg/L Acetals concentration: 18.12 ± 0.14 mg/L Furanic compounds concentration: 13.80 ± 0.21 mg/L

On the other hand, cis-linalooloxide, trans-linalooloxide, and P-Menth-1-en-9-al show statistical differences due to the distillation system, distillate fraction, and the interaction of the distillation system*distillate fraction. Cis-Linalooloxide, showed the highest concentration in heart fractions for both distillation systems (1.64 mg/L and 1.71 mg/L in the heart fraction for the Charantais alembic and the Charantais alembic with column, respectively). In the case of trans-linalooloxide, this trend is only observed for the column Charantais system. Spaho et al., 2021 also identified cis-linalooloxide in pear and apple distillates by double distillation using a copper pot still [30]. Finally, p-Menth-1-en-9-al also shows the highest levels in hearts fractions with similar values for both systems (0.14 mg/L and 0.13 mg/L for the Charantais alembic and the Charantais alembic with column, respectively).

3.3.4. Aldehydes and Ketones

Benzaldehyde is an important aromatic aldehyde, especially for stone fruit spirits. In our work, the benzaldehyde concentration was lower than 0.5 mg/L for all distilled fractions, the first distillation, and the residues for both studied distillation systems, showing significant differences due to the distillate fraction, distillation system, and interaction of both factors. Mrvčić et al., 2022 identified benzaldehyde and considered it to play the main role in the raw carob distillate [13]. According to Spaho, 2017 [30], benzaldehyde is

mainly distilled in the tail, regardless of the distillation system, but can also be present in high concentrations in the heart. However, in our studies, the main concentration was determined in the heart fractions for both distillation systems with similar levels.

Short-chain aliphatic aldehydes such as 3-methylbutanal are common head compounds [29]. Regarding our results the major concentration of the mixture of -3-methylbutanal and -2-methylbutanal was found in the head fractions for the Charantais alembic and Charantais alembic with column systems, being 5.20 mg/L and 7.21 mg/L. The concentrations of these compounds are statistically different due to the distillate fraction, distillation system, and interaction of both factors. The concentration of 2-Cyclopentene-1,4-dione was significantly different as well due to the three mentioned factors, with the highest concentration in the tail fractions of Charantais alembic, 0.17 mg/L, and Charantais alembic with column, 0.10 mg/L.

3.3.5. Acetals

Acetal was determined in all fractions for both distillation systems and was shown as a typical head compound [29]. The concentration was significantly different due to the distillate fraction, as well for isobutanal, diethyl acetal, 3-Methyl butanal diethyl acetal, and 2-methylbutanal diethyl acetal. 3-Methyl butanal diethyl acetal shows similar concentrations in the heart fractions for Charantais alembic and Charantais alembic with column, 0.18 mg/L and 0.19 mg/L, respectively. This compound and isobutanal diethyl acetal were identified and quantified by Rodríguez-Solana et al., 2018 in fig spirits [32]. 1,1,3-triethoxypropane concentration was significantly different due to the distillate fraction and interaction distillation system and distillate fraction. The highest concentrations were determined in the head fractions for both distillation systems and were similar in the heart fractions. This compound was also identified by Rodríguez-Solana et al., 2018 in fig spirits [32]. The phenylacetaldehyde diethyl acetal concentration in all fractions differs significantly due to the distillate fraction, distillation system, and interaction of both factors.

3.3.6. Furanic Compounds

Acetylfuran, furfuryl formate, and furfural showed significantly different concentrations due to the distillate fractions. Similar concentrations for acetylfuran were quantified in the tail fraction of Charantais alembic, 4.50 mg/L, and in the tail fraction of Charantais alembic with column, 4.77 mg/L. The levels for the heart fractions of both distillation systems were 2.22 mg/L for Charantais alembic and 2.69 mg/L for Charantais alembic with column.

Furfuryl formate was predominant in the head fractions of both distillate techniques (Charantais alembic: 1.36 mg/L and Charantais alembic with column: 1.61 mg/L). Furfural was identified in the first distillation, all distilled fractions, and residues. The concentrations for both distillation systems are comparable. This compound is produced during distillation due to dehydration of residual sugars. The high concentration could be explained, among other factors, due to the heating pre-treatment of the purchased carob syrup. Furfural distills mainly in the tail fraction due to its water solubility [30]. Regarding our results, the higher concentrations of furfural were also found in the tail fractions of the Charantais alembic technique and the Charantais alembic with column, being 7.07 mg/L and 7.66 mg/L, respectively.

Another group identified was formed by dihydro-2-methyl-3(2H)-furanone and 5-Methyl furfural. Statistical differences were determined in the concentrations of these compounds due to the distillate fraction and interaction of the distillation system*distillate fraction. The major concentration of dihydro-2-methyl-3(2H)-furanone was determined in the tails of both distillation systems. The determined concentrations of 5-Methyl furfural

for each distilled fraction and residues are comparable. For the furfural compound, the higher concentration was quantified in the tail fractions for both distillation techniques. Spaho et al., 2021 identified this compound in pear and apple spirits [40].

The last group identified was formed by 1-(2-furanyl)-1-propanone and furfuryl alcohol. Statistical differences were determined in the concentrations of these compounds due to the distillation system, distillate fraction, and interaction of the distillation system*distillate fraction. The higher concentrations for 1-(2-furanyl)-1-propanone were in the heart and tail fractions of both distillation systems. The amounts of 0.27 mg/L and 0.30 mg/L were quantified in the heart fraction of Charantais alembic and the heart fraction of Charantais alembic with column, respectively.

To our knowledge, no identified furfuryl alcohol was documented in previous works of carob liquors and carob spirits. Okaru et al., 2017 documented heating processes as the major source of furfuryl alcohol in foods and ageing of alcoholic beverages [41]. In our study, it could be produced due to the thermal treatment during the distillation. According to our results, the higher concentration of furfuryl alcohol was in the first distillation, in the tail fractions of the Charantais alembic and Charantais alembic with column and in the residues for both distillation systems, being 0.32 mg/L, 0.38 mg/L, 0.43 mg/L, 0.08 mg/L, and 0.27 mg/L, respectively.

3.3.7. Not Identified Compounds

From a total of 52 volatile compounds detected, 3 compounds could not be identified. They were found in a significantly low concentration (<1.5 mg/L) in the first distillation, tail fractions, head, and heart fractions (Table S1, Figures S1–S12 in the Supplementary Materials).

3.4. Principal Component Analysis (PCA)

Principal component analysis was applied to the 52 compounds shown in Table 3 using their raw data of composition obtained with GC/MS.

The first and second principal components (see Figure 1) explained 70.03% of the total variance. Principal component 1 (PC1) represented 47.33% of the total variance and clearly differentiated the head fractions of both distillation systems from the tail fractions of both distillation systems and first distillation. The loading factors are indicated in the Supplementary Materials, Table S2. As seen in Figure 1, the head fractions for both distillation systems were positioned in the positive axis region of the PC1 and were associated with ethyl acetate, acetal, isobutanal diethyl acetal, ethyl butanoate, 3-methyl butanal diethyl acetal, ethyl hexanoate, octanoic acid ethyl ester, and an unknown/furanic compound. On the other side, in the negative axis region of PC1, the tail fractions of both distillation systems were grouped according to the compounds phenylethyl alcohol, furfuryl alcohol, ethyl lactate, 2-cyclopentene-1,4-dione, 5-methyl furfural, and acetylfuran.

Principal component 2 (PC2) accounted for 22.70% of the total variance and distinguished the heart fractions of Charantais alembic and Charantais alembic with column from the residues of these two distillation systems. The heart fractions were in the positive region of PC2. Relevant characteristic compounds for these fractions were cis-Linalooloxide, acetic acid 2-phenylethyl ester, p-Menth-1-en-9-al, benzaldehyde, trans-Linalooloxide, benzenepropanoic acid ethyl ester, 1-(2-furanyl)-1-propanone, and 2,3-dihydrofarnesol. The residues were distributed in the bottom region covering the PC2 negative axis. Those associated compounds were phenylethyl alcohol, isobutylacetate, and furfuryl alcohol.

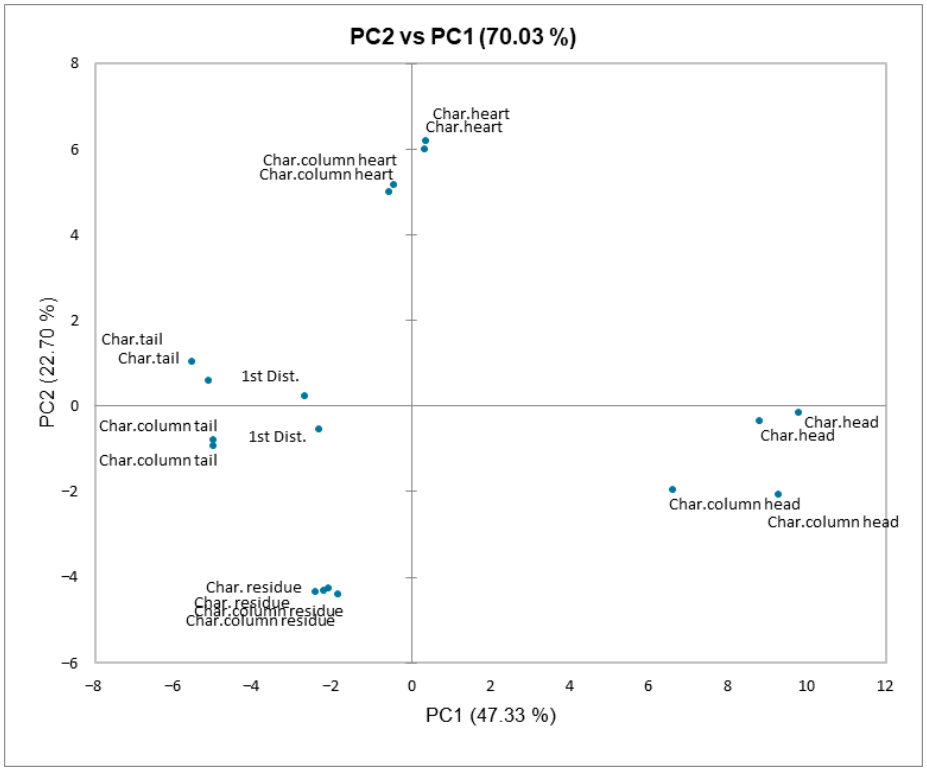


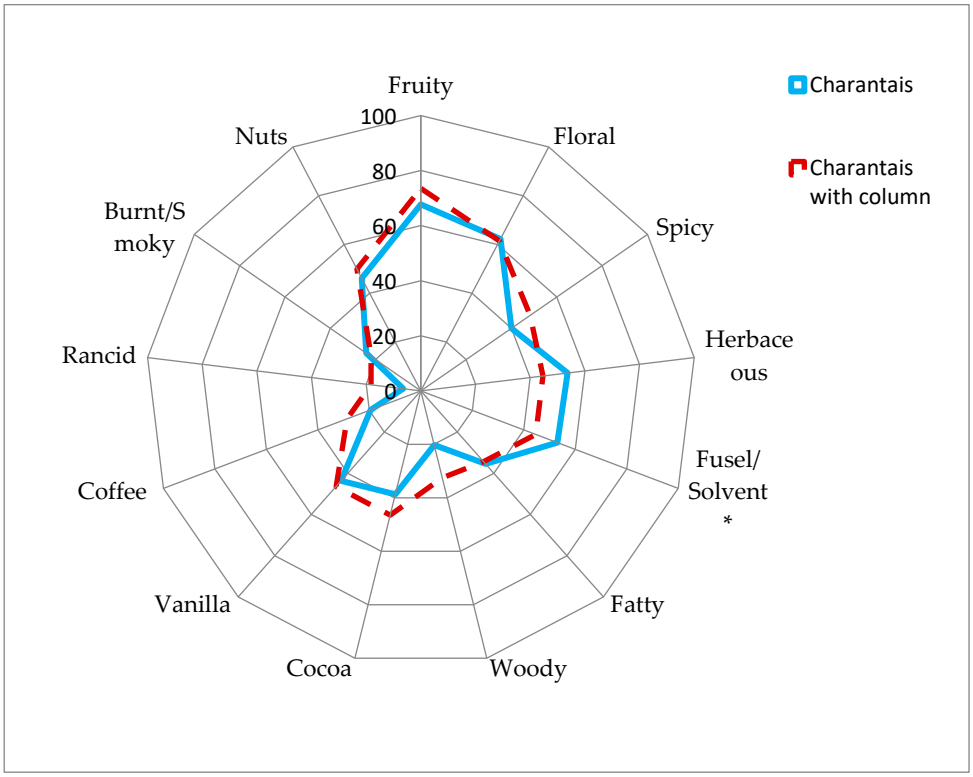
Figure 1. Principal component analysis of the distillate fractions, residues, and first distillations for Charantais alembic and Charantais alembic with column systems.

As seen in Figure 1, distillation systems using Charantais alembic and Charantais alembic with a column were not differentiated because both show a similar concentration/distribution of the compounds across the distillation fractions. Head fractions were primarily associated with esters, tails with furanic compounds and alcohols, and heart fractions with terpenes, and residues and first distillation were grouped with alcohols.

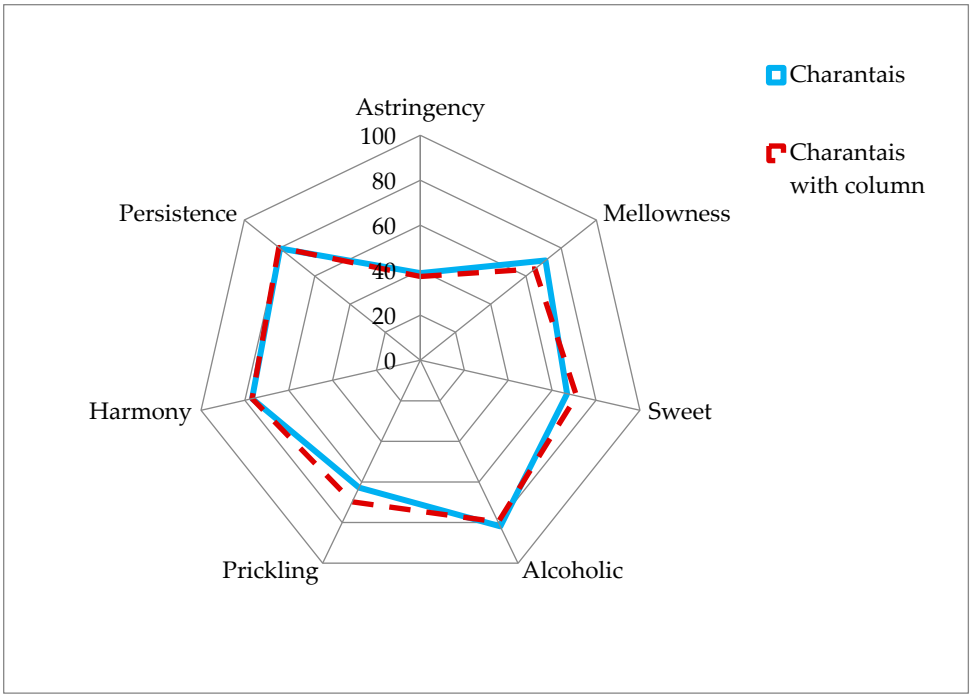
3.5. Sensory Results

The triangular test and the two-alternative forced-choice test did not show any significant taste and aroma difference among the distillates regarding the distillation system by the semi-trained panel of students. The panel of experts was also not able to differentiate the distillation system by performing these sensorial tests. Nevertheless, the professional panel characterized both distillates by applying a quantitative descriptive analysis (QDA).

For aroma (Figure 2A), the distillates produced by both distillation systems show similar sensory profiles obtained from the quantitative descriptive test. Nevertheless, it can be noted that the distillate obtained with Charantais alembic was characterized by slightly higher scores in herbaceous and fusel/solvent/chemical notes than Charantais alembic with column, whereas the distillate obtained with Charantais alembic with column was characterized by having slightly higher scores in spicy, woody, cocoa, coffee, and rancid notes. However, all these differences were not large enough to differentiate the distillates, and no organoleptic descriptor was determined to be significantly different according to the Wilcoxon signed-rank test results.



(**A**)



(**B**)

Figure 2. Spider diagram of descriptive sensory analysis for carob distillate obtained with Charantais alembic (continuous line) and carob distillate obtained with Charantais alembic with column (discontinuous line): (**A**) aroma profile and (**B**) taste profile. * Fusel/Solvent/Chemical. Geometric means according to ISO-11035 are represented for each organoleptic descriptor.

Both distillates are characterized by higher fruity and floral notes that may be explained by their high concentration of esters and terpenic compounds, such as cis-Linalooloxide and 2,3-Dihydrofarnesol.

High concentration of phenylethyl alcohol in both distillates can contribute to the higher fruity and floral notes. Another alcohol, such as 2-heptanol, characterized by its fruity and green odor, could explain the slight difference shown on the spider diagram, where the intensity of the fruity note is higher for the distillate obtained by Charantais alembic with column, which is affected by the distillation system.

3-Methyl-1-pentanol, associated with alcoholic and plant (herbaceous) notes [42], could explain the difference between the intensity of the herbaceous note, as seen in the spider diagram, as the concentration of this alcohol was significantly different between both distillation systems.

The spirits obtained by both distillation systems have low intensities in cocoa, nuts, and coffee notes, which can be associated with furanic and aldehyde compounds. In addition, the concentrations of furanic compounds were not significantly different due to the distillation system except only for 1-(2-furanyl)-1-propanone Therefore, it could explain the similar sensory profile for these notes for both distillation systems. The vanilla note was evaluated with low intensity values, although no compounds associated with this aroma were identified.

The spirits are characterized by a low intensity of spicy and herbaceous notes, which can be associated with compounds such as 1-hexanol, p-Menth-1-en-9-al, (E)-2-Hexenal, and Phenylacetaldehyde diethyl acetal, while the fusel/solvent/chemical, fatty, and burnt/smoky notes can be associated with alcohols, long chain esters, and some furanic compounds, respectively. The difference in intensity of rancid notes between the distillates produced by both distillation systems could be explained by different ethyl lactate concentrations [30].

The expert panel did not significantly differentiate the taste profile according to the distillation system (Wilcoxon signed-rank test), as shown in Figure 2B. These similar taste profiles may be explained by the similar concentrations of the volatile compounds in both tasted distillates (see Table 3). Only the distillate obtained with Charantais alembic was characterized by a slightly higher score in positive attributes, such as mellowness and slightly less prickling and sweetness than the distillate obtained by Charantais alembic with column. Both carob distillates were characterized by a high persistence in the mouth and alcoholic notes, balanced by low astringency and prickling and a notable mellowness and sweetness, thus giving them high harmony.

In Table 4 is shown a summary of the similarities and differences between the two distillation methods from both a chemical and sensory perspective.

4. Conclusions

In this study, the effect of two traditional distillation systems, Charantais alembic and Charantais alembic with column, on the ethanol yield as well as on the chemical and sensory characteristics of carob spirits was analyzed.

Chemical analysis shows that the ethanol recovery using both distillation systems was notably high; for Charantais alembic and for Charantais alembic with column, it was 74.9% and 85.8%, respectively. A total of 52 volatile compounds were detected, with the main volatile aromatic compounds being esters (17), furanic compounds (8), alcohols (7) and terpenes (7). Principal component analysis, with two components explaining 70.03% of the variance, was able to clearly identify the different distillate fractions, first distillations, and residues. Nevertheless, the corresponding distillate fractions for both distillation systems were plotted near to each other due to the similar concentrations of the volatile compounds. In addition, the carob spirits obtained from both distillation systems could not be differentiated by the organoleptic triangular test, and no organoleptic descriptor was significantly different with the 2-AFC test according to the results of the semi-trained

student panel and professional panel. In addition to this, similar sensory profiles for both distillates were determined by the professional panel. Both carob spirits were characterized mainly as floral, fruity, and alcoholic with persistence and overall harmony in the mouth.

These results were valuable to conclude that the Charantais alembic with column system is an excellent option to produce carob distillates due to its higher ethanol yield recovery compared to the Charantais alembic system. From a sensory perspective, the differences are minimal, such as a slight enhancement in fruity, cocoa, woody, and coffee notes, and a reduction in fusel/solvent/chemical notes for the Charantais alembic with column system. These results suggest that these distillates could enable valorization of the legume as a new source of sugar for the distillates area.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/beverages11040119/s1. Table S1: Retention times for unidentified and quantified compounds in the distillate fractions, Table S2: Loading factors obtained by principal component for the volatile compounds quantified in the first distillation, heart, head, and tail fractions, and residues produced by both distillation systems, Figure S1: Spectrum (A) and chromatogram (B) for the not identified compound (1) quantified in the tail fraction obtained with Charantais alembic in the second distillation (1st sample), Figure S2: Spectrum (A) and chromatogram (B) for the not identified compound (1) quantified in the tail fraction obtained with Charantais alembic in the second distillation (duplicate sample), Figure S3: Spectrum (A) and chromatogram (B) for the not identified compound (1) quantified in the tail fraction obtained with Charantais alembic with column in the second distillation (1st sample), Figure S4: Spectrum (A) and chromatogram (B) for the not identified compound (1) quantified in the tail fraction obtained with Charantais alembic with column in the second distillation (duplicate sample), Figure S5: Spectrum (A) and chromatogram (B) for the not identified compound (2) quantified in the first distillation (1st sample), Figure S6: Spectrum (A) and chromatogram (B) for the not identified compound (2) quantified in the first distillation (duplicate sample), Figure S7: Spectrum (A) and chromatogram (B) for the not identified compound (2) quantified in the heart fraction obtained with Charantais alembic in the second distillation (1st sample), Figure S8: Spectrum (A) and chromatogram (B) for the not identified compound (2) quantified in the heart fraction obtained with Charantais alembic in the second distillation (duplicate sample), Figure S9: Spectrum (A) and chromatogram (B) for the not identified compound (2) quantified in the tail fraction obtained with Charantais alembic with column in the second distillation (1st sample), Figure S10: Spectrum (A) and chromatogram (B) for the not identified compound (2) quantified in the tail fraction obtained with Charantais alembic with column in the second distillation (duplicate sample), Figure S11: Spectrum (A) and chromatogram (B) for the not identified compound/mixture (3) quantified in the head fraction obtained with Charantais alembic in the second distillation (1st sample), Figure S12: Spectrum (A) and chromatogram (B) for the not identified compound/mixture (3) quantified in the head fraction obtained with Charantais alembic in the second distillation (duplicate sample).

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Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding authors.

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Abbreviations

The following abbreviations are used in this manuscript:

2-AFC	Two-Alternative Forced Choice
S.	Saccharomyces
RID	Refractive Index Detector
UV-DAD	Ultraviolet Diode Array Detector
HPLC	High-Performance Liquid Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
m/*z*	Mass-to-charge ratio
SIM	Selected Ion Monitoring
NIST	National Institute of Standards and Technology
ANOVA	Analysis of Variance
ISO	Internal Organization for Standardization
EU	European Union
Dist.	Distillation
Char.	Charantais
PCA	Principal Component Analysis
PC1	Principal Component 1
PC2	Principal Component 2
QDA	Quantitative Descriptive Analysis

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