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Analysis of Volatile Flavor Compounds in Four Commercial Beverages Using Static Headspace Gas Chromatography/Mass Spectrometry: A Qualitative Approach

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Abstract: Understanding the volatile flavor compounds present in commercial beverages is crucial for the food and beverage industries as these compounds significantly influence product perception and consumer acceptability. This paper aims to comprehensively analyze the composition of volatile organic compounds in various commercial beverages using targeted gas chromatographic–mass spectrometry (GC/MS) approaches. The study employs a screening method based on the Headspace-GC/MS technique to efficiently extract and identify volatile organic compounds found in commercial beverages. This methodology provides a rapid and reliable system for assessing the volatile profile of these beverages. The analysis reveals the presence of a total of 40 volatile organic compounds, including esters, terpenes/terpenoids, alkenes, aldehydes, aromatic hydrocarbons, and alcohols. Medium-chain esters were found to dominate the volatile profile of the beverages, suggesting a significant contribution to their fragrance and taste. This study offers valuable insights into the volatile profile of commercial beverages, creating awareness among consumers about the flavor components present in these products. By understanding the volatile composition, consumers can make informed choices regarding their beverage consumption. The comprehensive analysis provided by this research serves as a foundation for further studies related to flavor characterization and optimization in commercial beverages.

Keywords: VOCs profile; Headspace-GC/MS; beverage; fragrances; screening method

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1. Introduction

The quality of food and drink composition is influenced by several variables, including the ingredients used in their production. Food Composition Databases (FCDBs) provide data on the content of commercial products. The main ingredients used to manufacture commercial drinks and foods are preservatives [1,2], sweeteners [3], color additives [1], nutrients [4], emulsifiers [5], binders [5], flavors and color [6], flavor enhancers [6], and many others. Flavors and flavor enhancers are added to most processed foods and drinks to provide a representative olfactory and taste sensory image [6].

Under European law, "natural flavor" represents in general a chemical substance obtained from animal or vegetation sources. Most of the products used as flavor additives in the food and beverage industry are identified from many natural sources and can be obtained by various extraction processes (distillation, supercritical fluid extraction, and Soxhlet extraction) [7–9]. However, large amounts of raw materials are needed to extract enough flavors to satisfy the market's demand. It means a process that consumes financial resources, is time-consuming, and leads to ecological problems. Therefore, flavors are

preferred to be produced synthetically, where the production costs are attractive, and the desired product yields are at their maximum, without wasting time.

Depending on the chemical structure, the compounds used as flavors in drinks are volatile organic compounds (VOCs) from different classes, such as: esters [10], terpenes/terpenoids [11], alkenes [12], ketones [12], fatty acids [13], aldehydes [12], alcohols [14], aromatic compounds [15], etc. Esters are responsible for the fruity aroma of drinks and foods [10]. Pineapple (Ethyl butyrate), banana (Pentyl acetate), and apricot (Pentyl butyrate) are among the most common flavors in the composition of beverages [16]. Alkenes are very rarely found in the composition of flavors in drinks. Therefore, few alkenes are found naturally in nature: 1-octene was identified in lemon oil [17], octadecene in Mandragora autumnalis fruits [18], and 1,3-pentadiene in roasted ground coffee [19,20]. Terpenes/terpenoids are also used as fragrances. These are universal natural products abundantly found in plants, coniferous and citrus species, flowers, and fruits. Alpha-pinene, d-limonene, and 3-carene are the most significant representatives of this class. Aldehydes and alcohols are essential flavoring compounds in many fresh and prepared food products. Alcohols offer a sweet and fruity aroma if short-chain alcohols are used, while spicy/vinous aromas are characteristic of long-chain alcohols. Compared to esters and alcohols, compounds commonly found in beverages and food due to their aroma stability, aldehydes such as acetaldehyde and benzaldehyde are used with difficulty. They are reactive and very volatile, which reduces or destroys their effect in an aroma [21].

In the detection of flavor substances in commercial beverages, gas chromatography coupled with mass spectrometry (GC/MS) has rapidly been established as an essential analysis technique [22,23]. Headspace (HS) analysis is the most effective technique for extracting volatile organic compounds in gas chromatography. There are three types of such analyses (static, dynamic, and headspace with solid phase microextraction). Using static-HS to determine volatile organic compounds (VOCs) presents several advantages, such as short sample preparation and analysis time, allowing continuous sampling without replacing the extraction head between samples [24].

Therefore, the aim of this paper was to identify volatile compounds in various commercial beverages using HS-GC–MS. The qualitative analysis of VOC flavors in local commercial (Romanian) beverages will begin to address the deficiency of information at the national level. The proposed technique offers a rapid, simple, and reliable approach for extracting and identifying VOCs, minimizing the loss of volatile flavors and cross-contamination. As a means of verifying the validity of the HS-GC/MS-based method, a qualitative comparison of VOC profiles from online databases was conducted. Following the identification of VOCs in the beverages, an aromatization/fragrance profile was established, and the primary compound sources were studied. The outcomes of this study will enhance our understanding of current commercial beverages and potentially contribute to the development of products with natural and safe flavors.

2. Materials and Methods

2.1. Materials

Anhydrous sodium chloride, ≥99% acquired from Merck (Darmstadt, Germany), was used to enhance headspace sample concentration. Four distinct varieties of commercial beverages (Table S1) were procured from local Romanian markets and anonymized as brands AJ, F, S, and CC. These samples represent four types of non-alcoholic drinks: concentrated apple juice, commercial tea, carbonated lemon drink, and flavored sparkling water (strawberry).

2.2. Sample Preparation

To prepare the samples for analysis, 10 mL of each commercial beverage was placed in headspace vials along with 2 g of sodium chloride and immediately injected for analysis using HS-GC/MS. Sodium chloride was added to aid in the transfer of the target compounds from the liquid phase to the gas phase. A blank sample was also analyzed simultaneously to

determine if the VOC compounds detected were specific to the target samples. Each sample was analyzed in triplicate. The headspace vials used in this study were standard 20 mL, screw-top clear glass vials purchased from Agilent Technologies (Waldbronn, Germany), equipped with magnetic caps, silicone septum, and PTFE to prevent volatile compound leakage.

2.3. Instrumental Analysis of Volatile Compounds and Peak Identification

The gas chromatography (GC) system utilized in this study consisted of a 7890B chromatograph (split/splitless injector) coupled with a QQQ 7010B mass spectrometer detection system (Agilent Technologies, Waldbronn, Germany) and featured a PAL RSI 85 static headspace autosampler (CTC Analytics AG, Zwingen, Switzerland). A 1 mL sample of headspace gas was injected using a heated (90 °C) gastight syringe (2.5 mL) in split mode (1:5, split flow 5 mL/min). The inlet temperature was set at 200 °C. Equilibration of the static headspace was carried out at 50 °C for 10 min, with gentle shaking at 250 rpm during sample heating. Separation of volatile compounds was achieved using a VF-1701-MS column (14% cyanopropylmethylpolysiloxane, 30 m length × 0.25 mm i.d. × 1 mm) from Agilent Technologies (Waldbronn, Germany). Helium 6.0 was used as carrier gas at a flow rate of 1 mL/min. The temperature gradient of the VF-1701-MS column started at 50 °C (2 min), increased from 50 °C to 200 °C at a rate of 10 °C/min, and then to 250 °C at a rate of 20 °C/min, with a final hold at 250 °C for 10 min. The mass spectrometer was configured for full-scan mode with a scan range set to m/z 30–350 amu, scan time of 100 ms, ionization source temperature set at 230 °C and transfer line at 250 °C, and an ionization energy of 70 eV.

The identification of volatile organic compound confirmation was conducted using MassHunter Qualitative Analysis software (version number B.07.06.2704), and the target compound identification was performed using the NIST Mass Spectral Libraries. Structural confirmation of detected compounds was obtained by comparing the resulting MS spectra with entries in the NIST spectral databases. Mass spectra were automatically assigned based on probability matching and manually reviewed by an experienced analyst. Chromatograms were recorded in full-scan mode.

3. Results and Discussion

3.1. Qualitative Identification of Flavor Compounds in Commercial Beverages

The screening method was applied to samples of commercial non-alcoholic beverages to generate a comprehensive fragrance/flavor profile. VOCs occurred in different patterns according to the analyzed non-alcoholic beverage, as shown in Figure S1. A total number of 40 volatile organic compounds were identified as a complex combination of different classes of substances, with esters (50%), followed by terpenes/terpenoids (25%), alkenes (12, 5%), aromatic hydrocarbons (5%), aldehydes (5%), and alcohols (2.5%). Thirty-five volatile organic compounds were unique, and five were found in many samples.

3.2. VOC Flavor Profile of Concentrated Apple Juice

Eleven VOCs were detected in the sample of concentrated apple juice (Table 1). MS profiles of the VOCs identified in the apple juice sample are shown in Figure S2. The profile was dominated by seven medium-chain esters that likely contributed substantially to the flavor. All VOCs were detected in the headspace air of the concentrated apple juice with a probability > 65% and a match factor score higher than 700.

Esters represent the main group of volatile compounds detected in commercial apple juice and are listed as pentyl acetate (amyl acetate) (rt = 4.428 min; top-priority three peaks of MS spectrum: 55, 61, 43), ethyl butyrate or ethyl butanoate (rt = 7.898 min; m/z= 43, 73, 88), butyl butyrate (m/z = 89, 43, 71; rt = 11.568), tetramethylene diacetate or 1,4-butanediol diacetate (rt = 8.250 min; three most significant peaks: 43, 61, 71), ethyl 2-methyl butyrate (rt = 8.775 min, m/z = 74, 102, 87), 2-methyl butyl acetate (rt = 9.490 min; three most prominent peaks: 70, 43, 45) and hexyl acetate, known as N-hexyl ethanoate (rt = 11.930 min; top-priority three peaks MS spectrum 69, 43, 61). Other compounds identified by the screening method were trans-2-pentene (rt = 7.562 min; three most significant peaks 55, 70, 42), 2,2-dimethyl-1-pentene (rt = 10.044 min;

three most significant peaks 69, 41, 55), 3-furaldehyde (rt = 10.200 min, three most significant peaks 95, 96, 67), and a-Pinene oxide (rt = 12.045 min; m/z = 67, 82, 55).

Table 1. VOCs identified in the concentrated apple juice.

Peak No.	RT (min)	Compound	CAS No.	Probability (%)	Flavor/Fragrance
1	4.428	Pentyl acetate	628-63-7	66.8	Banana/apple
2	7.562	trans-2-Pentene	646-04-8	65.2	-
3	7.898	Ethyl butyrate	105-54-4	73.0	Pineapple
4	8.250	Tetramethylene diacetate	628-67-1	70.6	Pineapple
5	8.775	Ethyl 2-methylbutyrate	7452-79-1	65.1	Strawberries
6	9.490	2-Methylbutyl acetate	624-41-9	68.7	Sweet banana
7	10.044	3,3-Dimethyl-1-pentene	3404-73-7	66.8	-
8	10.200	3-Furaldehyde	498-60-2	67.6	Woody
9	11.568	Butyl butyrate	109-21-7	69.0	Sweet pineapple
10	11.930	Hexyl acetate	142-92-7	75.4	Sweet pear/banana

Pentyl acetate is the most-often used flavor in the beverage industry and has been reported to have a persistent, ethereal banana/apple odor. It was detected in many fruits: blackberries (*Rubus*), pears (*Pyrus pyrifolia*), apples (*Malus pumila*), papaya (*Carica papaya*), and cocoa beans (*Theobroma cacao*) [25]. Ethyl butyrate is a flavoring ingredient in food and drinks with a strong sweet taste like pineapple and an intense fruity odor similar to butyl butyrate [26]. According to the Human Metabolome Database, ethyl butyrate naturally occurs in many fruits, e.g., apples, apricots, bananas, plums, and tangerines. Butyl butyrate is used most often to prepare alcoholic beverages [27]. It is naturally present in several fruits such as bananas, cherries, melons, and plums and in perennial plants such as common myrtle (*Myrtus communis* L.) [28].

Regarding tetramethylene diacetate, there are few known data related to the origin and the flavor it confers. Its presence is confirmed by headspace solid-phase microextraction and analyzed by Headspace-SPME-GC/MS from pineapple fruit [26]. The aroma of fruits such as strawberries, which can be among the spectrum of fruity tones, is most commonly associated with the presence of ethyl 2-methyl butyrate found in blueberries, apples, and obviously in strawberries. The profile of sweet aromas is completed by 2-methyl butyl acetate and hexyl acetate with apple and banana flavors. 2-Methylbutyl acetate is naturally found in perennial herbaceous plants such as Myrtus communis and Tagetes minuta and in vines (Vitis vinifera). In contrast, hexyl acetate is found in very high concentrations in blueberries, and is detected but not quantified in pears, oats, and cherries. Two alkenes are qualitatively identified in commercial apple juice (trans-2-pentene and 2,2- dimethyl-1-pentene). No scientific studies have been conducted regarding these volatile organic compounds' natural origin. However, the formation of trans-2-pentene was observed in a study of thermal degradation via HS-SPME-GC/MS of sugarcane juice [29]. This paper can be a source of confirmation of trans-2-pentene in concentrated apple juice from the related alcohol through thermal degradation during the detection process. The woody pine aroma is conferred by the presence of 3-furaldehyde (found in common species of spruce) and monoterpenoid a-Pinene oxide (a natural product found in carrots (*Daucus carota*). No studies were identified regarding detecting 3-furaldehyde in commercial non-alcoholic beverages, compared to a-pinene epoxide and its role in the fragrance formulation of products such as bacterial xenobiotic metabolite and human metabolite [PubChem database]. Another application of a-pinene oxide is as a food additive.

3.3. VOC Flavor Profile of Commercial Tea

Compared to the VOC flavor profile of concentrated apple juice, a considerably lower number of target compounds were identified in samples of commercial tea, but also a different structure of the proportions between the classes of compounds. Also, in this case, the flavor profile was dominated by compounds from the medium-chain ester class, with a

majority of four compounds, namely pentyl acetate (rt = 4.428 min; m/z = 55, 61, 43), ethyl butyrate (rt = 7.898 min; m/z = 43, 73,88), isopentyl acetate (rt = 9.449 min, m/z = 70, 55, 43), and pentyl butyrate (rt = 12.607, m/z = 70, 43, 89). The other compounds were identified as terpenes/terpenoids: two compounds (A-terpineol; rt = 12.756 min; top-priority m/z = 91, 93, 121) and A-pinene (rt = 13.839; top-priority m/z = 91, 93, 77)) and the alkene 1-methyl-cyclopentene (rt = 11.928, m/z = 67, 82, 41, Table 2). VOCs qualitatively identified by the proposed method have a probability higher than 67% and, respectively, a match factor score higher than 750. MS profiles of the VOCs identified in the commercial tea are given in Figure S3.

Table 2. VOCs identified in the commercial tea.

Peak No.	RT (min)	Compound	CAS No.	Probability (%)	Flavor/Fragrance
1	4.429	Pentyl acetate	628-63-7	70.3	Banana/apple
2	7.898	Ethyl butyrate	105-54-4	78.0	Pineapple
3	9.449	Isopentyl acetate	123-92-2	80.0	Banana/pear
4	11.928	1-Methylcyclopentene	693-89-0	70.1	-
5	12.607	Pentyl butyrate	540-18-1	67.7	Banana/apricot
6	12.756	α-Terpineol	586-62-9	72.6	Pine/woody
7	13.839	(+)-α-Pinene	80-56-8	74.7	Citrus/spicy

Pentyl acetate and ethyl butyrate were previously detected in the concentrated apple juice, giving the profile the sweet and intense flavor of apple and pineapple. Compared to pentyl acetate, its superior counterpart, isopentyl acetate is an ester with a strong and pungent smell similar to banana and pear [30]. It is found naturally in the banana plant, but it is also obtained synthetically through a condensation reaction, and the product is commercially also called banana oil. Isopentyl acetate is found naturally in the species of Vitis rotundifolia, but there are studies on its formation through the microbial proliferation of *C. albicans* and *S. aureus* [31]. A final ester detected in commercial tea that contributes to banana-like flavors is pentyl butyrate (amyl butyrate). It is found naturally in bananas, apples, and common apricot species. It has a smell reminiscent of pears and apricots, which makes it ideal in food flavoring and as an additive in cigarettes [10].

The alkene 1-methyl-cyclopentene is the only component in commercial tea. There are a lot of studies in the literature on 1-methyl-cyclopentene, but none attest to its use in the food or beverage industry. However, according to the PubChem database, it is a compound detected naturally in camphor (*Cinnamomum camphora*) and rice (*Oryza sativa*).

A-terpineol is a terpenoid with an intense woody odor, used most intensively in the flavors and fragrances industry and in medicine due to its multiple properties reported as biological agents (antimicrobial, anticarcinogenic, etc.). In nature, it is identified in many sources, such as flowers, fruits, vegetables, and herbs, but this compound is present in low concentrations (generally less than 1%). Moreover, although it can be extracted from natural sources by fractional distillation, in terms of commercial production, a-terpineol is generally obtained by chemical synthesis [32].

A-pinene completes the profile of intense woody aromas. It has a reminiscent smell of pine and turpentine with spicy citrus notes. It is found naturally in over 400 plants, spices, fruits (rosemary, coriander, lavender, lemon), and many coniferous trees (e.g., pine). It is used intensively in the flavor industries but is also a promising candidate in medicine due to its therapeutic effects. A-pinene is the synthesis precursor of a-terpineol and is also found naturally in low concentrations [33].

3.4. VOC Flavor Profile of Carbonated Lemon Drink

The volatile composition of carbonated lemon drink is shown in Table 3. All compounds were detected with a higher than 71% probability and a match factor score greater than 700. The MS spectra of the identified compounds are presented in Figure S4. Terpenes/terpenoids detected by gas chromatography were (+)-Sabinene (rt = 10.916;

m/z = 93, 91, 77), (+)-Limonene (rt = 11.770; m/z = 93, 91, 67), cis-Sabinene hydrate (rt = 12.175 min; m/z = 93, 91, 81), γ-Terpinene (rt = 12.274; m/z = 91, 93, 77), 3-Carene (rt = 15.723 min; m/z = 93, 91, 79), and α-Terpineol (rt = 12.756 min, m/z = 91, 93, 121). The aromatic compound identified was p-Cymene (rt = 12.058 min, m/z= 119, 91, 34).

Table 3. VOCs identified in the carbonated lemon drink.

Peak No.	RT (min)	Compound	CAS No.	Probability (%)	Flavor/Fragrance
1	10.916	(+)-Sabinene	3387-41-5	77.9	Herb
2	11.770	(+)-Limonene	5989-27-5	73.1	Fruity
3	12.058	p-Cymene	535-77-3	83.4	Fruity
4	12.175	cis-Sabinene hydrate	15537-55-0	77.5	Herb
5	12.274	γ-Terpinene	99-85-4	71.2	Turpentine odor
6	15.723	3-Carene	13466-78-9	72.2	Piney
7	12.756	α- Terpineol	586-62-9	81.3	Pine/Woody

(+)-Sabinene and its homologous alcohol (cis-Sabinene hydrate) belong to the class of bicyclic monoterpenes. These compounds have a very hydrophobic molecule, insoluble in water. They are often found in sage (Salvia verbenaca), nutmeg (Myristica fragrans), sweet marjoram, and spearmint. There are many studies in the literature regarding detecting and quantifying (+)-sabinene and cis-sabinene hydrate, especially in essential oils. The main field of application is aromatherapy [34–36].

Limonene presents an aromatic profile based on citrus and bitter notes. The primary botanical sources are citrus fruits, piney, rosemary, mint, fennel, and cannabis. According to the studies published so far, due to its pharmacological properties (antimicrobial, antioxidant), limonene is used as a flavoring compound in the food and beverage industry [11]. γ-terpinene, or 1,4-p-menthadiene, is an isoprenoid with a strong lemon smell and herbal taste. The GC-MS technique detected γ-terpinene in the leaves of Origanum vulgare [37] and citrus fruits, where the recovery percentage was 3–5% [38]. Besides its role as a flavoring agent, γ-terpinene has an antioxidant effect, making it an ideal candidate in medicine [39]. γ-terpinene has also been detected, but not quantified, in several different fruits and herbs, such as evergreen blackberries (*Rubus laciniatus*), saffron (*Crocus sativus*), and pepper (spice).

Natural sources in which 3-carene was identified are mango fruits and cannabis leaves. It is a monoterpene soluble in oils and fats and, similar to limonene, and has the same fruity notes—citrus and sweet. Published studies confirm through GC-MS analysis the presence of 3-carene in some alcoholic beverages, which was proven to be the dominant terpene compound [40].

The woody aroma, specific to a-terpineol, was also identified in the samples of commercial tea. P-Cymene is a compound from the class of aromatic compounds with a structure similar to monoterpenes, with a typical lemon aroma. It is a constituent of many essential oils, including cumin and thyme. GC-MS/MS quantitatively detected p-cymene in different parts of Eupatorium fortune [15]. Although p-cymene is the only natural geometric isomer, several methods have been scientifically published for preparing these isomers: 1) dehydrogenation of limonene produces p-cymene; dehydrogenation of 3-carene produces a mixture of p- and m-cymene [41].

3.5. VOC Flavor Profile of Flavored Sparkling Water

The total ion chromatogram (TIC) recorded for flavored sparkling water showed an impressive number of peaks: 15 were identified according to Figure S5 and are exemplified in Table 4. According to the retention time and the three most important peaks of the MS spectrum, the volatile organic compounds detected were esters such as methyl butyrate (rt = 6.423 min; m/z = 43, 74, 78), ethyl isobutyrate (rt = 6.978 min; m/z = 88, 43, 73), methyl 2-methyl butyrate (rt = 7.411 min; 88, 57, 101), ethyl butyrate (rt = 7.893 min; m/z = 43, 73, 88), ethyl 2-methyl butyrate (rt = 8.773 min; m/z = 74, 102, 87), ethyl hexanoate

(rt = 11,606 min; m/z = 73, 61, 55), propyl 3-methyl butyrate (rt = 12.417 min; m/z = 103, 57, 85), and trans-methyl cinnamate (rt = 18.700 min; m/z = 103, 131, 77). Other compounds identified were alcohols such as cis-2-hexenol (rt = 8.473 min; m/z = 67, 77, 72), trans-verbenol (rt = 13.397 min; m/z = 79, 91, 81), and cis- verbenol (rt = 13.713 min; m/z = 79, 91, 81); aldehydes such as trans-2-hexenal (rt = 10.032 min; m/z = 83, 69, 55); alkenes, for example, 3-menthene (rt = 15,407 min, m/z = 81, 95, 67) and 2-menthenes (rt = 16.569 min, m/z =95, 81, 67); and terpenes such as 3-carene (rt = 15.720 min, m/z = 93, 91, 79). All VOCs were detected in the headspace air of the flavored sparkling water with a probability > 70% and a match factor score higher than 700.

Table 4. VOCs identified in flavored sparkling water.

Peak No.	RT (min)	Compound	CAS No.	Probability (%)	Flavor/Fragrance
1	6.423	Methyl butyrate	623-42-7	71.7	Sweet apple/pineapple
2	6.978	Ethyl isobutyrate	97-62-1	77.0	Fruity
3	7.411	Methyl 2-methylbutyrate	868-57-5	83.5	Ethereal, fruity
4	7.893	Ethyl butyrate	105-54-4	71.4	Pineapple
5	8.473	cis-2-Hexenol	928-94-9	72.1	Fruity/green
6	8.773	Ethyl 2-methylbutyrate	7452-79-1	71.8	Strawberries
7	10.032	2-Hexenal	6728-26-3	78.1	Green apple
8	11.606	Ethyl hexanoate	123-66-0	75.7	Sweet apple/pineapple
9	12.417	Propyl 3-methylbutyrate	557-00-6	70.8	Sweet apple/fruity
10	13.397	trans-Verbenol	1820-09-3	89.4	Herbal
11	13.713	cis-Verbenol	1845-30-3	82.8	Herbal
12	15.407	3-Menthene	500-00-5	72.3	-
13	15.720	3-Carene	13466-78-9	76.1	Piny
14	16.569	2-Menthene	5256-65-5	79.5	-
15	18.700	trans-Methyl cinnamate	1754-62-7	83.9	Intense/aromatic

Like many other esters, methyl butyrate and ethyl hexanoate have a fruity apple or pineapple smell. Methyl butyrate was identified by GC-MS in strawberries [42], and ethyl hexanoate was isolated by HS-SPME-GC/MS [43]. It can be produced by distilling essential oils but also chemically synthesized for use in perfumes [44] and as a food flavor. Ethyl isobutyrate has a fruity smell and is used in the following products: disinfectants, washing and cleaning products, paints, and waxes, but also in the cosmetic and food industry as a flavoring agent [45].

Regarding Methyl 2-methyl butyrate, numerous brands of fresh and processed apple juices with a pungent, ethereal, and fruity smell use it. Specific strawberry and pineapple flavors for Ethyl butyrate and Ethyl 2-methyl butyrate esters were identified and discussed for the concentrated apple juice samples. Another compound that contributes to the fruity aroma of flavored sparkling water is propyl 3-methyl butyrate. It was isolated and detected from sea buckthorn juice by HS-SPME-GC/MS [46]. Moreover, the profile of ethereal aromas is completed by trans-Methyl cinnamate-ester derived from aromatic cinnamic acid. According to the PubChem database, it is found in olive oil, used in the perfume industry, and used as a food flavoring due to its intensely aromatic volatile component.

Trans-2-hexenal is one of the aldehydes similar in aroma to green apples. It is found naturally in other fruits, such as cherries and wild strawberries. It is only formed when crushed or chewed by very rapid enzymatic conversion of fatty acids. In addition to its usefulness as a flavoring agent, 2-hexenal is used in manufacturing brake fluid and motor lubricants and as a refrigerator cooling agent [47]. 3-menthene and 2-menthene are alkenes structurally similar to monoterpenes. No studies have been identified regarding their identification in food or their fields of application. According to the safety information provided by the Good Scents Company, 3-menthene is not recommended for fragrance or flavor use [48].

From the category of alcohols, 2-hexenol, cis-verbenol, and trans-verbenol were identified in flavored sparkling water. 2-hexenol gives commercial drinks a fruity, green smell similar to wine and a fresh sweet taste similar to apples and pears. Studies published in the literature show the natural presence of 2-hexenol in vine species (Vitis rotundifolia) and

yellow guava fruits (Psidium guajava), as well as in most apple species, citrus fruits, and ginger [49]. Cis-verbenol and trans-verbenol are terpene alcohols with a fresh pine smell and represent the main metabolites from the oxidative study of alpha-pinene. There is little information in the literature regarding the possibility of their use in the food industry, but they are applied in the agricultural industry due to their pheromone properties. Their presence was identified in a follow-up study of humans exposed to monoterpenes using a GC-MS/MS method by derivatization [50].

3.6. Flavor Compound Distribution in Commercial Beverages

The distribution pattern of VOC flavors proved to be different for each type of commercial beverage (Figure 1). Except for the carbonated lemon drink, ester compounds were the majority of flavors in all other three samples. In the apple juice sample, ester compounds were detected in 64%. Alkene compounds were the next predominant class of compounds (18%), followed by aldehydes and terpenes/terpenoids, which together amounted to 18% (Figure 1a). In the commercial tea, esters represented 57% of the total flavor compounds identified. Terpenes/terpenoids were also detected as a high percentage (29%), while alkenes represented only 14% (Figure 1b). A high percentage of esters were also detected in the flavored sparkling water (53%), while alkene and terpene/terpenoid compounds together were up to 20%. Unlike the other samples, alcohols and aldehydes were identified, totaling a significant percentage of up to 27% (Figure 1d). A totally different pattern was observed in the case of the carbonated lemon drink (Figure 1c). Terpenes/terpenoids were the majority of compounds identified in this sample, representing a percentage of 86%, with a difference of up to 100% being taken up by aromatic compounds.

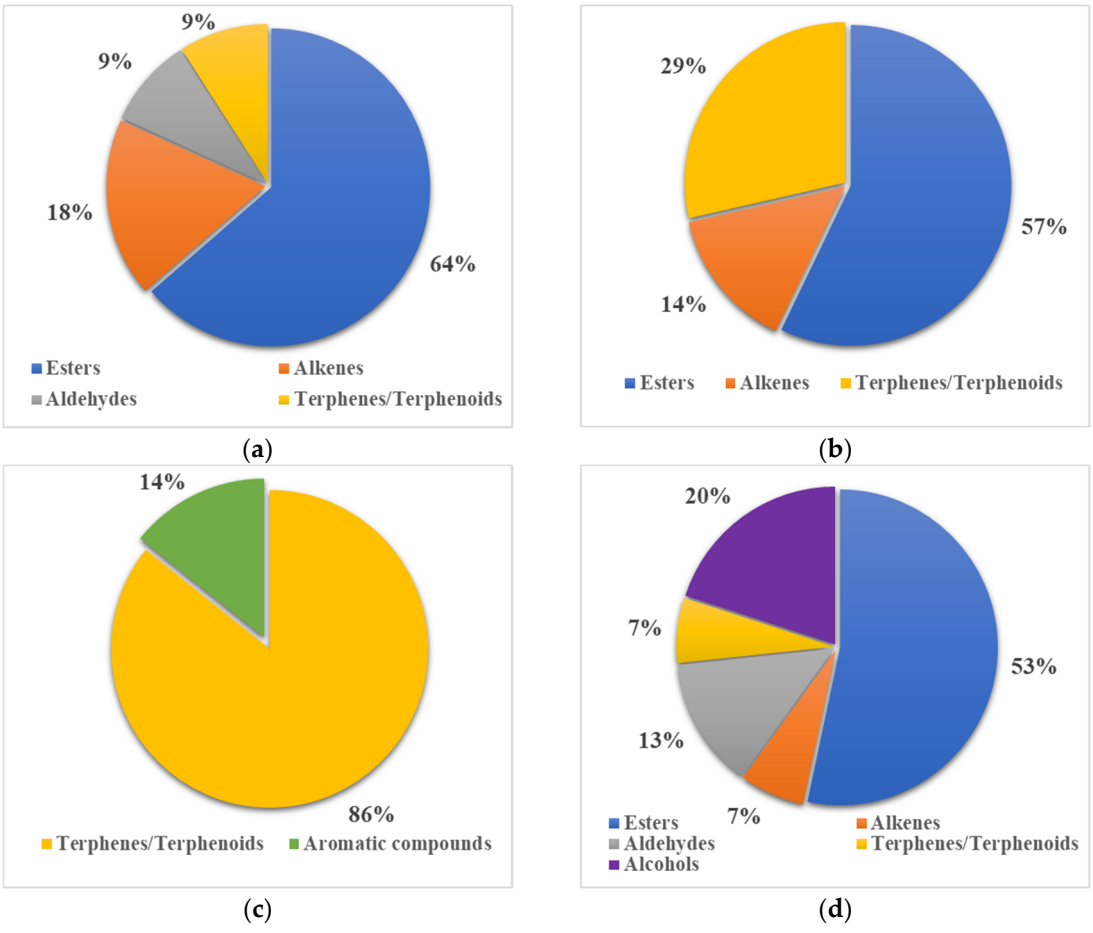

Figure 1. Percentage distribution of VOC flavors in (**a**) AJ, (**b**) F, (**c**) S and (**d**) CC samples.

3.7. Consumption of Commercial Drinks and Current Regulations

It is known that the consumer market for beverages and food sold tends to be oversaturated. Statistical studies carried out on the territory of Romania confirm this aspect. The last study published showed that in Romania, in 2021, more than 1600 tons of non-alcoholic beverages were produced [51]. Moreover, consumption is increasing every year. For this reason, traders prefer artificial ingredients and flavors due to cost and reduced production time.

Consequently, artificial flavors come with a series of restrictions, and ECHA (European Chemicals Agency) has classified several compounds identified in the drink samples under study in several hazard classes. Ethyl butyrate, ethyl 2-methyl butyrate, and hexyl acetate are included in the danger class as a warning in the REACH Regulations, classified as flammable liquid substances whose vapors cause severe eye irritation. Also, from the series of flammable substances that cause vapors, 2-methyl butyl acetate, pentyl acetate, isopentyl acetate, and propyl isobutyrate are included in the danger class as warnings.

Regarding ethyl isobutyrate, it is considered a dangerous substance according to the REACH Regulations, and the manufacture or import into the European Economic Area of less than 100 tons per year is limited, just as in the case of Ethyl hexanoate, having a consumption annually of less than 1000 tons per year [45]. Moreover, the alkenes in commercial drinks are classified as dangerous; trans-2-pentene irritates the eyes and skin and can cause respiratory problems. Lastly, 2-hexenal, according to REACH, is classified as a hazard for the aquatic environment with long-term effects, irritating the eyes and skin, and causing allergic reactions. Production/consumption in the European space is limited to 100 tons per year [47]. According to them, raising an alarm signal about the effects of excessive consumption of commercial drinks is necessary.

4. Conclusions

VOCs emitted in the headspace air of commercial beverages belong to different classes of compounds such as esters, alkenes, aldehydes, terpenes/terpenoids, alcohols, and aromatic compounds, which are used mostly as flavoring agents or as flavor enhancers in carbonated drinks. In the present study, a number of 40 volatile organic compounds were identified in the four types of commercial non-alcoholic beverages. Using static HS-GC/MS as an extraction and identification technique, a screening method was proposed that facilitated the creation of the VOC flavor profile. The main compounds identified were esters, which play a significant role in creating aromas. Although many compounds from the present study are confirmed as coming from natural sources, artificial flavors are used in the beverage industry to meet the needs of the economic space. Therefore, according to current regulations, a safety evaluation of any impurities and contaminants in artificial flavors should be performed. Reducing the consumption of commercial drinks due to the effects additives might potentially produce on health must be taken into account: allergic reactions, gastrointestinal disturbances, neurological effects, or carcinogenic concerns. Either natural or artificial flavors are added compounds which should be avoided since natural beverages without additives offer more potential health benefits. Another significant concern related to the consumption of synthetic flavors in non-alcoholic beverages is the potential for long-term exposure and the accumulation of these compounds in the various tissues and organs, which may result in adverse health effects. The cumulative exposure to synthetic flavors can increase the risk of developing chronic health conditions over time, as the body may struggle to metabolize and eliminate these substances efficiently. Additionally, the interaction of synthetic flavors with other compounds in the body or with medications could lead to unforeseen health complications.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app14051910/s1, Table S1: Commercial beverages involved in the qualitative study; Figure S1: Total ion chromatograms (TIC) for all non-alcoholic beverages tested: (a) apple juice, (b) commercial tea, (c) carbonated lemon drink, and (d) flavored sparkling water; Figure S2: The MS profiles of the VOCs identified in the apple juice sample; Figure S3: The

MS profiles of the VOCs identified in the commercial tea; Figure S4: The MS profiles of the VOCs identified in the carbonated lemon drink; Figure S5: The MS profiles of the VOCs identified in the flavored sparkling water.

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