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Review

Modern Analytical Techniques for Berry Authentication

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Abstract: The health-related properties attributed to berries and the subsequent interest awakened within the market of functional foods mean that these small fruits may be potential targets for food fraud. In this review, studies on berry authentication through modern analytical techniques are discussed in detail. Most of the studies reported to date are related to chemical approaches, mainly chromatographic techniques. Other chemical (NMR, NIR, and Raman spectroscopy), biomolecular, and isotopic methods have also delivered promising results in the field of berry authentication, although there is still limited information available in this respect. Despite the potential of the methods described in the present review, to date, there is no universal one. Therefore, combinations of different approaches in order to complement each other are increasingly used (e.g., HPTLC and mass spectrometry; Raman and IR spectroscopies; biomolecular and analytical techniques. . .). Considering that adulteration practices are increasingly evolving, continuous research in the field of food authentication is needed, especially in the case of berries, since there are still some berry species that have not yet been included in any authentication study.

Keywords: berries; authenticity; geographical origin; fingerprinting; chemometrics

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1. Introduction

There is a wide variety of plant species with berry fruits, although the most common belong to the *Rosaceae*, *Ericaceae*, *Myrtaceae*, *Berberidaceae*, and *Elaeocarpaceae* families, which are generally characterized by their small red to purple colorful fruits [1].

Berries are good sources of bioactive compounds, including phenolic and carotenoid compounds. Their phenolic compounds include phenolic acids, such as hydroxybenzoic and hydroxycinnamic acid conjugates, and flavonoids, such as flavonols, flavanols, and anthocyanins. Likewise, tannins, condensed tannins (proanthocyanidins), and hydrolysable tannins have been reported as important bioactive compounds in berries [2–4]. In addition to the aforementioned bioactive compounds, antioxidant vitamins (such as ascorbic acid) and minerals have been also found in berries [2]. These bioactive compounds are associated with the most significant health benefits of berries, such as anti-inflammatory, anticancer, or antimicrobial activities [1]. Food technologists have shown growing interest in these small fruits as ingredients of functional foods [1], which explains the increasing levels of worldwide demand for berries.

Strawberry, raspberry, blackberry, blueberry, or cranberry are among the species that contain higher amounts of bioactive compounds [2]. However, berry composition is not only species related, as geographical origin plays a key role in food quality. Local differences associated with the climate, the soil, and their cultivation can affect the chemical composition of a plant [5]. In this sense, labels such as "protected designation of origin" have been approved, in order to highlight the geographical component in food quality, since consumers have expressed greater interest in foods associated with a specific place of origin.

Therefore, the determination of quality features (i.e., species identification and/or geographical origin) has become increasingly essential in order to avoid food fraud or adulterations [6]. Unfortunately, mislabeled or adulterated berry products have been found on the market [7]. In this scenario, authentication emerges as a fundamental tool to guarantee transparency and food safety to the consumers [8]. Food authentication could be defined as the process through which a food is tested, in order to verify that it is what it is claimed to be. It encompasses issues such as mislabeling, adulteration, or misleading statements related to origin (e.g., cultivar, geographical origin), production method (e.g., conventional vs. organic), or processing. A wide variety of methods have been developed for food authentication. Specific information on food composition, geographical origin, species used in the production procedure, or presence of adulterants can be obtained from each method [8]. In this sense, traditional methods for the identification of berry quality or origin involved phenotypical characteristics such as shape, color, size, or tasting flavors, among others [9]. However, these methods lack accuracy and universality, so the focus of current research has turned to analytical methodologies. Therefore, modern analytical techniques are currently used for food authentication. Accurate determination is essential for discriminatory purposes, and for the subsequent identification of potent quality marker compounds [10].

Several modern analytical techniques are at present used for food quality assessment: (i) chemical approaches (i.e., chemical compound contents, compound profiling, metabolic fingerprinting); (ii) biomolecular approaches (i.e., DNA or protein composition); and (iii) isotopic approaches (i.e., stable isotopic composition of individual atoms) [10]. These analytical techniques usually generate complex and large sets of data, which make mandatory the use of chemometric tools in order to extract the maximum amount of information from the raw data. Chemometrics refers to the branch of chemistry concerned with the analysis of chemical data. It is based on the application of mathematical and statistical methods to establish the relationships among variables. Therefore, these tools allow the construction of statistical models able to interpret the characteristics of the system. These models are subsequently employed for discrimination, classification, and prediction purposes [11]. Multivariate data analysis, which measures the relations between multiple variables, is widely used in chemometrics. Three general categories of analysis are commonly used in chemometrics [12]: (i) exploratory analysis, (ii) discriminant/classification analysis, and (iii) prediction models/regression analysis. The most common unsupervised exploratory approaches are hierarchical clustering analysis (HCA) and principal component analysis (PCA); alternative approaches are soft independent modelling of class analogy (SIMCA) and k-nearest neighbors (kNN). Supervised methods, such as discriminant analysis (linear discriminant analysis, LDA; partial least squares DA, PLS-DA, among others) and regression analysis (multiple linear regression, MLR; principal components regression, PCR; and PLS, among others) are used for discriminative or classification analyses [13]. More than one of the aforementioned tools are usually applied for food authentication; fruit juices, wine, and other alcoholic beverages, or coffee and tea, are matrices where these chemometric tools have been successfully applied [14].

In view of the above, the recent literature related to berry authentication protocols using modern analytical techniques are discussed in detail in this review.

2. Chemical Approaches

Several chemical techniques have, to date, been used for berry authentication. High-performance liquid chromatography (HPLC), high-performance thin-layer chromatography (HPTLC), gas chromatography (GC), nuclear magnetic resonance (NMR) spectroscopy, near-infrared (NIR) spectroscopy, Raman spectroscopy, and inductively coupled plasma (ICP) are described in detail in this section.

2.1. High-Performance Liquid Chromatography (HPLC)

High-performance liquid chromatography (HPLC) is a powerful technique mainly used for the separation of low volatility compounds. Different berries, such as bilberry [15], blueberry [16], cranberry [16,17], elderberry [18], ginseng berry [19], goji berry [20–23], grape berry [24,25], lingonberry [17], myrtle berry [26,27], sea buckthorn berry [28], and strawberry [29] fruits were authenticated through HPLC coupled to chemometric tools (Table 1).

Table 1. Liquid chromatographic methods for berry authenticity assessment.

Berry Type	Genotype/Origin	Instrument/Chemometrics	Discriminating Marker(s)	Reference
Bilberry (*Vaccinium myrtillus* L.)	Bilberries from 10 wild populations in Turkey and 20 wild populations in Finland.	HPLC-DAD and logistic regression model	Anthocyanin glycosides.	[15]
Blueberry (*Vaccinium* spp.) and Cranberry (*Vaccinium* spp.)	Blueberry and cranberry juices adulterated with apple and grape juices.	LC-qTOF-MS and PCA-DA	Anthocyanins and other flavonoids such as myricetin, together with several nonphenolic compounds.	[16]
Cranberry (*Vaccinium macrocarpon*) vs. Lingonberry (*Vaccinium vitis-idaea*)	Different cultivars of cranberries (Pilgrim, Howes, Ben Lear, McFarlin and Stevens) and lingonberries (Koral, Sussi, Linnea, Ida, Runo Bielawskie and Sanna).	UHPLC-qTOF and PLS-DA	Cranberries: glycosylated peonidins and flavonols (myricetin 3-*O*-glucoside and myricetin 3-*O*-arabinoside). Lingonberries: catechin and ferulic acid. Glycerophospholipids upregulated.	[17]
Elderberry (*Sambucus nigra* L.)	Elderberries obtained from 4 herbal manufacturers in Poland.	HPLC-UV and PCA, cluster analysis	Phenolic compounds (flavonols and phenolic acids).	[18]
Ginseng berry (*Panax ginseng*)	Berries from 7 different cultivars of ginseng (Korea): Chunpoong, Chungsun, Kumpoong, Yunpoong, Gopoong, Sunun, Sunwon.	UPLC-qTOF/MS	Ginsenosides.	[19]
Goji berry (*Lycium barbarum*)	4 goji berries from different geographical origins (Tibet, Mongolia and North of China).	LC-PDA-qTOF-MS and PCA, PLS-DA	Mongolian berries: higher quercetin, kaempferol, and isorhamnetin derivatives, and coumaric acid. Chinese berries: citric acid and N-hydroxy-L-tyrosine, a dopamine derivative and a pesticide.	[20]
	23 goji berries from different geographical origins (Italian vs. Asian).	HPLC-DAD-MS and PCA, cluster analysis and Forward Stepwise DA	Total carotenoid content and zeaxanthin palmitate.	[21]
	Zhongning goji berries (ZNG) and non-Zhongning goji berries (NZGB).	UHPLC-qTOF and PCA, PLS-DA	Succinic acid, N-methylcalystegine C1, N-*trans*-feruloyloctopamine, N-*trans*-feruloyltyramine, quercetin, gingerglycolipid B, glycoside of pyrrolidine alkaloid.	[22]
	32 berries from 4 different regions in China	HPLC/UPLC-DPPH-PDA-ESI-TOF/MS and PCA, PLS-DA	Rutin, rutin di-hexose, p-coumaric acid tri-hexose, dicaffeoylquinic acid isomer, quercetin-rhamno-di-hexoside	[23]
Grape (*Vitis vinifera* L.)	4 red grape varieties: Aglianico, Negroamaro, Uva di Troia, and Primitivo from southern Italy.	HPLC-DAD, UV and PCA	Acetylated forms of anthocyanins, cyanidin-3-*O*-glucoside, trans-coutaric and trans-caftaric acids; also, glucosidic precursors of several terpene families and shikimic acid.	[25]

Table 1. *Cont.*

Berry Type	Genotype/Origin	Instrument/Chemometrics	Discriminating Marker(s)	Reference
	Moribel and Tinto Fragoso red grape genotypes, and Tempranillo variety.	HPLC-DAD-ESI-MS/MS, HPLC-MS-MRM and PCA	Tempranillo: higher acylated delphinidin and petunidin derivatives. Moribel and Tinto Fragoso: greater malvidin 3-glucoside. Tinto Fragoso: higher galloylated flavan-3-ols and stilbenes in seeds. Moribel: greater quercetin-type flavonols and procyanidin B2 in seeds.	[24]
Myrtle berry (*Myrtus communis*)	Different varieties of myrtle berry seeds collected from different geographic areas of Sardinia, and grown under similar experimental conditions (Sardinia, Italy).	LC–ESI–FT-(Orbitrap)-MS/MS and PCA	Delphinidin-3-*O*-glucoside, peonidin-3-*O*-glucoside and cyanidin-O-glucoside.	[26]
	2 cultivars of myrtle berry seeds collected from the geographic area of Sassari and Cagliari (Sardinia), and grown under similar experimental conditions (Sardinia, Italy).	LC-ESI-Orbitrap-MS and PCA	Anthocyanins and flavonoids (mainly in pulp and peel).	[27]
Sea buckthorn berries (*Hippophae rhamnoides* L., ssp. *Carpatica*)	6 Romanian varieties (Victoria, Tiberiu, Sf. Gheorghe, Serpenta, Serbanesti 4 and Ovidiu) of sea buckthorn berries.	UHPLC-PAD-ESI-MS and PCA	Zeaxanthin di-palmitate, zeaxanthin-palmitate, zeaxanthin-palmitate myristate, lutein-palmitate-myristate, lutein-palmitate, lutein di-palmitate, lutein di-myristate, b-carotene, and 15,15-cis b-carotene.	[28]
Strawberry (*Fragaria vesca*)	Strawberries from two different locations in southern Italy (Petina and Sarno).	LC-ESI-Orbitrap-MS and PCA	Polyphenols. Berries from Petina: overexpressed cyanidin derivatives.	[29]

HPLC: high performance liquid chromatography; UHPLC: ultra-high performance liquid chromatography; UV: ultraviolet detector; DAD: diode array detector; PDA: photodiode-array; MS: mass spectrometry; Qtof: quadrupole time-of-flight; ESI: electrospray ionization; FT: Fourier transform; MRM: multiple response monitoring; PCA: principal component analysis; DA: discriminant analysis; PLS-DA: partial least squares-discriminant analysis.

Both targeted and untargeted metabolic profiling have, to date, been used to test berry authenticity using liquid chromatographic techniques. In this respect, targeted analyses have mainly been focused on the identification and the quantification of phenolic compounds, since these phytochemicals have been widely found as good markers to determine berry authenticity. Pérez-Navarro et al. [24] studied the use of the phenolic profile of Spanish grape berries as a tool for cultivar differentiation and authentication, using HPLC-MS followed by a PCA. The results showed that the Tempranillo cultivar differed from the novel genotypes (Moribel and Tinto Fragoso), due to a higher content of acylated delphinidin and petunidin derivatives. In contrast, Moribel and Tinto Fragoso presented higher contents of malvidin 3-glucoside. Tinto Fragoso showed a higher proportion of galloylated flavan-3-ols and stilbenes in seeds. A greater proportion of quercetin-type flavonols (mainly quercetin 3-glucuronide) and seed procyanidin B2 was found in Moribel grapes. Similarly, another study [25] was conducted on four different Italian grape cultivars, harvested at two different times, using HPLC-DAD and PCA. The results showed that acetylated forms of anthocyanins, cyanidin-3-*O*-glucoside, *trans*-coutaric, and *trans*-caftaric acids were useful varietal discriminating factors, although the authors also highlighted the key role of glucosidic precursors of several terpene families, and shikimic acid as decisive contributors to varietal differentiation [25]. Primetta et al. [15] evaluated the usefulness of anthocyanin (aglycones and sugar moieties) fingerprinting using an HPLC-DAD system, followed by a logistic regression analysis to discriminate bilberries from Turkish and Finnish populations. The results showed that bilberries from Turkey and Finland significantly differed in the proportions of sugar moieties, which could be used as a discriminating factor for distinguishing different origins of bilberries. The authors

presented a logistic regression model based on glucoside proportions that they used to classify samples by geographical region with success rates of up to 96.7%. In contrast, the aglycone content of the berries from different origins were similar, which could be used as a feature for the identification of bilberries. In another study, Viapina and Wesolowski [18] developed an efficient method based on combining a reference HPLC fingerprint, some phenolic compound quantifications, and a chemometric tool for monitoring the quality of commercial elderberry samples from various manufacturers.

Aside from polyphenols, carotenoids have also been investigated as marker compounds for berry authentication. Among various authors, Pop et al. [28] analyzed six Romanian varieties of sea buckthorn berries using UHPLC-PAD-ESI-MS followed by a PCA. Zeaxanthin di-palmitate, zeaxanthin-palmitate, zeaxanthin-palmitate myristate, lutein-palmitate-myristate, lutein-palmitate, lutein di-palmitate, lutein di-myristate, b-carotene, and 15,15-cis b-carotene were identified as major carotenoid biomarkers for the authentication of Carpathian sea buckthorn berries from Romania. In another study, 23 goji berries from different geographical origins (Italian vs. Asian) were studied through HPLC-MS followed by multivariate analysis. The results showed higher total carotenoid contents for Italian berries, and the discriminant analysis successfully classified the berries according to their geographical origin, based on total carotenoid content and zeaxanthin palmitate (although this study also included other compounds in the multivariate analyses, such as minerals and stable isotopic ratios determined with analytical techniques outside the scope of this section) [21].

Aside from polyphenols and carotenoids, Yoon et al. [19] conducted a targeted analysis to profile the ginsenosides of seven ginseng berry cultivars using UPLC-QTOF/MS. The heatmap analysis of the 26 ginsenosides that had previously been identified, revealed that Kumpoong and Sunwon cultivars presented patterns unlike the other analyzed cultivars, whereas Chunpooong and Yunpoong cultivars showed similar patterns to each other.

In contrast, nontargeted analyses are used to investigate the entire "chemical fingerprint" of the samples and, by doing so, identify other marker compounds useful for berry authentication, besides the aforementioned phytochemicals. In this respect, Bondia-Pons et al. [20] used HPLC coupled to a quadrupole time of flight (qTOF) mass spectrometer to perform a nontargeted analysis of four goji berries (*Lycium barbatum*) of varied geographical origin (Tibet, Mongolia, and North China). The data were analyzed with PCA and PLS-DA. The results indicated that Mongolian goji berries were characterized by significantly higher levels of several flavonol derivatives, such as quercetin, kaempferol, and isorhamnetin derivatives, and phenolic acids, such as coumaric acid. These authors also found differences in organic acids, amino acids, and fatty acids. Citric acid and N-hydroxy-L-tyrosine were shown as discriminant metabolites in the Chinese goji berries; myristic acid showed significant differences between groups. In addition to the phytochemical metabolites identified, a dopamine derivative and a pesticide appeared as two discriminant markers of Chinese goji berries. In another untargeted metabolomic approach, D'Urso et al. [27] used an LC-ESI-Orbitrap-MS metabolic profiling tool to discriminate between two cultivars of myrtle berry, whose seeds had been collected from different geographical areas (Sassari and Cagliari) of Sardinia (Italy). The results highlighted that the phenolic compounds such as anthocyanins and other flavonoids, mainly present in the pulp and peel, were good marker compounds of the cultivars and of greater influence than the metabolites present in the seeds, such as gallotannin derivatives. In contrast, another study from the above research group [26] reported the analysis of myrtle berry seeds from six different geographical areas (Oristano, Sassari, Olbia, Nuoro, Cagliari, and other areas) of Sardinia (Italy), using the same LC-MS profiling tool. The results led the authors to conclude that untargeted metabolomics could not be used to discriminate between myrtle berry seeds collected from different geographical areas of Sardinia and grown under the same experimental conditions. However, a pseudo-targeted approach was also useful to assess the geographical origin of the seeds that mainly distinguished between the areas of Sassari and Cagliari. Anthocyanins were the main chemical markers of the geographical origin of the

myrtle berry seeds, highlighting delphinidin-3-*O*-glucoside, peonidin-3-*O*-glucoside, and cyanidin-*O*-glucoside as the most influential compounds. Myricetin was also influential among the flavonoids [26].

Hurkova et al. [17] employed a metabolomic fingerprinting approach using a U-HPLC-HRMS/MS system to discriminate between two Vaccinium berry species: cranberries and lingonberries. Characteristic markers were identified from the analysis of 33 samples from two harvest years. Glycosylated peonidins and glycosylated flavonoids, such as myricetin 3-*O*-glucoside and myricetin 3-*O*-arabinoside, were characteristic markers of cranberries. Catechin and ferulic acid were the two phenolic compounds mainly associated with lingonberries. Polyphenols and glycerophospholipids were also identified as significant markers, where phosphatidylcholines were upregulated in lingonberries.

Lv et al. [22] identified biomarkers to distinguish Zhongning goji berries (ZNG), traditionally considered to be good quality, from non-Zhongning goji berries (NZNG), using a nontargeted metabolomic technique based on UHPLC-Q-TOF-MS combined with chemometric analysis. The differential biomarkers associated with ZNG were mainly flavonoids, organic acids, alkaloids, and sugar esters. Particularly, seven biomarkers were suggested as good discriminants for goji berry authentication: succinic acid, N-methylcalystegine C1, N-*trans*-feruloyloctopamine, N-*trans*-feruloyltyramine, quercetin, gingerglycolipid B, and glycoside of pyrrolidine alkaloid.

A combination of targeted and untargeted analyses has also proven its usefulness for berry authentication. Zhang et al. [16] developed an LC-QTOF-MS-based metabolomic approach as a useful tool for the authentication of berry fruit juices using both targeted and untargeted analyses. A total of 18 biomarkers (wherein 7 anthocyanins and other flavonoids such as myricetin, together with several nonphenolic compounds) were identified to detect adulteration of blueberry and cranberry juices. The LC-ESI-Orbitrap-MS metabolic profiling approach was also used to discriminate the origin of wild strawberries in a study aimed at assessing whether strawberry composition was affected by germplasm (autochthonous vs. nonautochthonous), growing conditions (spontaneous vs. cultivated), and geographical location (Petina vs. Sarno) [29]. The results showed that both untargeted and targeted analyses were capable of discriminating between the samples. Polyphenols had a primary role in the discrimination of the samples. Cyanidin derivatives were overexpressed in samples from the area of Alburni. Wild strawberries from this area presented higher anthocyanin contents.

In view of the above, hardly any of the studies available have addressed the relationship between chemical compounds and bioactivity. In this sense, an online UPLC-DPPH-PDA-ESI-Q-TOF/MS technology coupled with multivariate analysis (PCA and PLS-DA) has been recently presented as a strategy for the discrimination among Goji berry geographical origins based on an antioxidant fingerprint [23].

2.2. High-Performance Thin-Layer Chromatography (HPTLC)

Compared to HPLC, HPTLC is an eco-friendly (a low volume of solvent is used), rapid (less time for analysis), and low-cost technique [30]. Therefore, HPTLC is a good analytical method for plant-based food characterizations. It performs rapid and simultaneous sample authentications based on chromatographic fingerprints, and can be used to identify several types of compounds with less effort than HPLC [30]. Several HPTLC methods have been developed for the assessment of bioactive compounds in berries. In this sense, Krüger et al. [31] demonstrated that HPTLC is suitable for the quantitation of anthocyanins in elderberry. Moreover, the same authors highlighted that HPTLC coupled with mass spectrometry and bioassays could be useful for fingerprinting, pattern recognition, and bio-profiling of elderberries, furthering the development of potential quality controls of raw materials, and for the detection of falsifications. Gonzalez et al. [32] used HPTLC fingerprinting to visualize the flavonoid composition and radical scavenging DPPH activity of maqui berries from four cultivated clones collected from wild populations at different ripening stages: San Fernando, Puerto Montt, San Clemente, and Entrelagos. The results showed

that clones from San Fernando, San Clemente, and Entrelagos presented a higher radical scavenging activity than those from Puerto Montt and concluded that HPTLC flavonoid and DPPH fingerprints of maqui berries were useful tools for selecting high-quality raw materials. Aside from berry fruits, the potential of HPTLC and multivariate analysis (PCA and PLS-DA) has been recently proven for the intercultivar discrimination of berry seeds. In this sense, the phenolic profiles of 45 berry seeds from nine Serbian species (raspberry, strawberry, black currant, blackberry, gooseberry, blueberry, chokeberry, cape gooseberry, and goji berry) showed a good differentiation based on botanical origin [33]. In view of the above, HPTLC might be used as a reliable and simple untargeted approach to quickly discriminate among geographical origins. Moreover, when combined with LC–HRMS, the metabolites responsible for the discrimination of the samples can be identified [34].

2.3. Gas Chromatography (GC)

Gas chromatography may be used for the identification of targeted individual molecules and their quantification for the characterization of berry extracts. Moreover, untargeted GC analyses may also be applied to raw chromatogram data in order to obtain discrimination between the samples.

Parker et al. [35] identified and quantified the marker compound for 'pepper' aroma and flavor in Shiraz grape berries (*Vitis vinifera* L.) using gas chromatography–mass spectrometry (GC–MS) combined with PCA and PLS. Chemometric methods were successfully used to differentiate between both the samples from different vineyards (South Australia and Victoria) and the samples from the vineyards collected at different vintages. Moreover, α-ylangene, a tricyclic sesquiterpene, was identified as the marker of the 'pepper' aroma and flavor of the Shiraz grape. In another study [25], glycosidic aroma precursors of nonaromatic red grapes (*V. vinifera* L.) from southern Italy (Aglianico, Negroamaro, Primitivo, and Uva di Troia) were analyzed using GC–MS together with PCA. The relative amounts of grape glycosidic precursors from diverse terpene families have been reported as useful markers for discrimination. Aglianico was characterized by the presence of glycosidic precursors from the alpha-terpineol and linalool families, while the contents of those families were the highest in Negroamaro. Uva di Troia grapes were characterized by the high content of alpha-terpineol family derivatives. Similar patterns were also recorded for Primitivo grapes, together with a lack of aglycons derived from norisoprenoid and geraniol groups [25]. Deng et al. [36] determined the volatile compounds of five new Muscadine grape cultivars (Alachua, Carlos, Fry, Granny Val, and Noble) using HS-SPME-GC/MS combined with chemometrics. A comprehensive identification and relative quantification of 44 compounds, including esters, aldehydes, alcohols, fatty acids, terpenes, ketones, and furan, was successfully conducted. PCA and PLS-DA effectively differentiated the five cultivars by utilizing their volatile profiles. Geraniol and cinnamyl alcohol were found to be crucial in defining the characteristics of the Alachua cultivar, while ethyl trans-2-butenoate and propyl acetate were identified as significant compounds in characterizing the Noble cultivar. Moreover, 2-Ethyl-1-hexanol, (Z)-3-hexenal, and (E)-2-hexenol were found to exhibit strong associations with the Carlos, Fry, and Granny Val cultivars, respectively. Another recent study [37] analyzed the volatile profile of Molixiang grapes from three different regions of China (Ningbo, Beizhen, Zhangzhou) using headspace gas chromatography-ion mobility spectrometry (HS-GC-IMS) coupled with PCA. Grapes sampled from Ningbo were primarily characterized by the presence of butyl lactate, E-2-octenal, and Z-2-pentanol, while grapes collected from Beizhen were found to contain p-cymene, styrene, and γ-terpinene. Furthermore, grapes sampled from Zhangzhou were prominently enriched with benzaldehyde and methyl benzoate. The PCA analysis demonstrated successful discrimination of samples from various geographical origins using the information obtained from GC-IMS [37].

Aside from grape berries, volatile components from other berries such as lingonberry (*Vaccinium vitis-idaea* L.) [38], sea buckthorn berry (*Hippophae rhamnoides* L.) [39,40], elderberry (*Sambucus nigra* L.) [41], Madeira blueberry (*Vaccinium padifolium* L.) [42], and goji

berry (*Lycium barbarum* L.) [43,44] were also assessed, in order to determine their authenticity. Accordingly, [38] analyzed triterpenoids in lingonberry (*V. vitis-idaea* L.) fruits and leaves from Finland and Poland using GC–FID and GC–MS. The lingonberries collected from two different countries showed differences in their triterpenoid levels. In particular, fernenol and taraxasterol were found to be the main compounds in lingonberry samples from Finland and Poland, respectively. In another study, Socaci et al. [39] performed GC–MS analysis to discriminate 12 wild and cultivated sea buckthorn berries (*H. rhamnoides* L. ssp. *Carpatica*) based on their volatile compounds. As a result, PCA analysis demonstrated a good separation between the samples. The predominant compounds were reported as ethyl esters of 2-methylbutanoic acid, 3-methylbutanoic acid, hexanoic acid, octanoic acid, butanoic acid, 3-methylbutyl 3-methylbutanoate, 3-methylbutyl 2-methylbutanoate, and benzoic acid ethyl ester. Singh and Sharma [40] also performed GC–MS analysis for metabolic profiling of sea buckthorn berries from the Himachal Pradesh (Lahaul and Spiti) and Jammu and Kashmir (Leh, Nubra, and Kargil) regions of the Indian Himalayas. The heat map of metabolite expression profiles clearly showed two separate clusters of sea buckthorn berries, one originating from Himachal Pradesh and the other from Jammu and Kashmir. Notably, a significant negative correlation was observed between altitude and the quantities of certain metabolites, including amides, alkyl esters, alcohols, sugars, and sugar esters. Conversely, temperature exhibited a strong positive correlation with ketone and alkyl ether levels. In a study carried out by Salvador et al. [41], fingerprinting of volatile terpenoids and norisoprenoids in three cultivars of elderberry (*S. nigra* L.) was performed throughout ripening. Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC X GC-TOF-MS) combined with chemometric tools revealed that the ripening stage was the most influential factor in the profile of volatile compounds. In all three cultivars, the higher metabolite concentrations of the unripe berries gradually diminished throughout the ripening stages. Two major monoterpenic compounds were detected, limonene and p-cymene, whereas aromadendrene and β-caryophyllene were reported as the main sesquiterpenic compounds. For norisoprenoids, dihydroedulan was identified as the major compound. Porto-Figueira et al. [42] investigated the volatile composition of Madeira blueberry (*V. padifolium* L.), locally called Uveira, at different ripening stages using headspace solid-phase microextraction (HS-SPME) coupled to gas chromatography–quadrupole mass spectrometry (GC–qMS). The data subjected to multivariate statistical analysis revealed that ethyl caprylate, trans-geraniol, ethyl isovalerate, and benzyl carbinol were the key parameters in the discrimination of Uveira berries by ripening stages. Another research group [43] applied PCA to the data obtained with GC–MS, in order to study the variability of volatile compounds in two goji berry varieties (*Lycium barbarum* and *Lycium chinense*). However, the authors were unable to differentiate between the two goji berry varieties, and suggested the products could have been mislabeled [43]. A similar study on goji berries (*L. barbarum*) [44] used gas chromatography-isotope ratio mass spectrometry (GC-IRMS) with HS-SPME in order to discriminate samples from different provinces of China (Gansu, Ningxia, Qinghai) based on their volatile compounds (geranylacetone, β-ionone, limonene, safranal, tetramethylpyrazine). As a result, the geographical origin of goji berries was determined using linear discrimination analysis (LDA) at accuracy rates of 86–89% [44].

In addition to the above, a number of gas chromatographic protocols have been employed for the authentication and traceability of various berries through fingerprinting of fatty acids [28,45,46]. For example, Socaciu et al. [45] analyzed the fatty acid profile of sea buckthorn berry (*H. rhamnoides* L.) oils from Romania in an evaluation of their authenticity. GC–FID results showed that sea buckthorn oil was rich in palmitic acid (32%), palmitoleic acid (25%), and oleic acid (23%), which differed significantly from sunflower oil. Later on, the same research group [28] analyzed the fatty acid composition of six Romanian sea buckthorn berry varieties (Victoria, Tiberiu, Sf. Gheorghe, Serpenta, Serbanesti 4, and Ovidiu) using GC–MS. Confirming the results of their previous study [45], the major fatty acids were determined as palmitic (28–44%), palmitoleic (21–28%), and

oleic (17–34%) acids, which were unique for each berry variety [28]. In another study [46], the fatty acids of 46 saw palmetto berry (*Serenoa repens*) products from different countries, including Canada, Finland, Germany, the Netherlands, the United Kingdom, South Korea, Spain, Switzerland, and the United States, were quantified using GC–FID. Among the fatty acids, lauric acid, capric acid, caprylic acid, myristic acid, palmitic acid, linolenic acid, oleic/linoleic acid, and stearic acid were analyzed, which comprised > 95% of the fatty acids present in the saw palmetto berries. The results showed wide variations in the fatty acid content of saw palmetto berry products: differences that were in the order of a factor of 177 and 38, between the minimum and the maximum concentrations in mono products and in combined products, respectively. Overall, GC analysis enabled the identification of products with elevated levels of specific fatty acids commonly linked to adulteration [46].

In addition to volatile compounds and fatty acids, profiling of primary compounds such as amino acids, organic acids, and simple sugars has also been performed in berry fruits using GC. For example, Dumont et al. [47] analyzed the primary compounds in two goji (*L. barbarum* and *L. chinense*) fruits using GC–MS. Chemometric tools revealed metabolic markers discriminating Lycium species. In *L. barbarum* berries, lycibarbarphenylpropanoids A-B, fructose, and glucose were abundant, whereas *L. chinense* fruits accumulated high levels of asparagine. Similarly, Lee et al. [48] investigated ginseng berries (*Panax ginseng)* at five different maturation stages including immature, mature, partially red, fully red, and overmature red using GC–MS combined with PCA and partial least squares-discriminant analysis (PLS-DA). PLS-DA applied to the GC–MS data could usefully discriminate between preharvest (immature and mature) and harvest/postharvest (partially red, fully red, and overmature red) fruits. In total, 43 metabolites played a major role in the distinction of five developmental stages. Amino acids, organic acids, 5-C sugars, purines, ethanolamines, and palmitic acid were found to predominate in preharvest berries, whereas 6-C sugars, phenolic acid, and oleamide levels were more abundant in harvest/postharvest berries.

The studies investigating the authenticity of berries using gas chromatographic methods are summarized in Table 2. In summary, the union of GC and chemometric tools is a demonstrated technique that categorizes berry fruits by origin, genotype, maturity, and cultivation season for their discrimination.

Table 2. Gas chromatographic methods for berry authenticity assessment.

Berry Type	Genotype/Origin	Instrument/Chemometrics	Discriminating Marker(s)	Reference
Elderberry (*Sambucus nigra* L.)	3 cultivars of elderberry at different ripening stages.	GCXGC–TOF-MS and PCA	Limonene, *p*-cymene, aromadendrene, *β*-caryophyllene, dihydroedulan.	[41]
Ginseng berry (*Panax ginseng*)	Ginseng berries at 5 maturation stages: immature, mature, partially red, fully red, overmature red.	GC–MS and PCA, PLS-DA	Preharvest berries: amino acids, organic acids, 5-C sugars, purines, ethanolamines, palmitic acid. Harvest/postharvest berries: 6-C sugars, phenolic acid, oleamide.	[48]
Goji berry (*Lycium* spp.)	2 goji berry fruit varieties: *L.* barbarum, *L. chinense.*	GC–MS and PCA	None.	[43]
	Goji berries from 3 provinces in China: Gansu, Ningxia, Qinghai.	HS–SPME coupled to GC-IRMS and LDA	Compounds geranylacetone, *β*-ionone, limonene, safranal, tetramethylpyrazine.	[44]
	2 goji berry fruit varieties: *L.* barbarum, *L. chinense.*	GC–MS and PCA, PLS-DA	*L. barbarum*: lycibarbarphenylpropanoids A-B, fructose, glucose; *L. chinense*: asparagine.	[47]
Grape (*Vitis vinifera* L.)	Various vintages of Shiraz grapes from vineyards in South Australia and Victoria.	GC–MS and PCA, PLS	Alpha-ylangene was responsible for 'pepper' aroma and flavor.	[35]

Table 2. *Cont.*

Berry Type	Genotype/Origin	Instrument/Chemometrics	Discriminating Marker(s)	Reference
	Red grapes of southern Italy: Aglianico, Negroamaro, Primitivo, Uva di Troia.	GC–MS and PCA	Glycosidic precursors from the alpha-terpineol and linalool families.	[25]
	5 Muscadine grape cultivars from China: Alachua, Carlos, Fry, Granny Val, Noble.	HS-SPME-GC/MS and PCA, PLS-DA	Alachua: Geraniol, cinnamyl alcohol; Noble: trans-2-butenoate and propyl acetate; Carlos: 2-Ethyl-1-hexanol; Fry: (Z)-3-hexenal; Granny Val: (E)-2-hexenol.	[36]
	Molixiang table grapes from 3 different regions of China: Ningbo, Beizhen, Zhangzhou.	HS-GC-IMS and PCA	Ningbo: Butyl lactate, E-2-octenal, Z-2-pentanol; Beizhen: p-cymene, styrene, γ-terpinene; Zhangzhou: benzaldehyde, methyl benzoate.	[37]
Lingonberry (*Vaccinium vitis-idaea* L.)	Lingonberry fruits and leaves from Finland and Poland.	GC–FID, GC–MS	Finnish berries: fernenol; Polish berries: taraxasterol.	[38]
Madeira blueberry (*Vaccinium padifolium* L.)	Uveira berries from Portugal at 3 ripening stages: green, breaker, ripe.	HS–SPME coupled to GC–qMS and PLSR	Ethyl caprylate, *trans*-geraniol, ethyl isovalerate, benzyl carbinol.	[42]
Saw palmetto berry (*Serenoa repens*)	46 saw palmetto berry products from Canada, Finland, Germany, the Netherlands, the United Kingdom, South Korea, Spain, Switzerland, and the United States.	GC–FID	Lauric acid, capric acid, caprylic acid, myristic acid, palmitic acid, linolenic acid, oleic/linoleic acid, stearic acid.	[46]
Sea buckthorn berry (*Hippophae rhamnoides* L.)	Sea buckthorn berry oils from Romania.	GC–FID	Palmitic acid, palmitoleic acid, oleic acid.	[45]
	12 wild and cultivated sea buckthorn berries.	GC–MS and PCA	Ethyl esters of 2-methylbutanoic acid, 3-methylbutanoic acid, hexanoic acid, octanoic acid, butanoic acid, 3-methylbutyl 3-methylbutanoate, 3-methylbutyl 2-methylbutanoate, benzoic acid ethyl ester.	[39]
	6 sea buckthorn berry varieties from Romania: Victoria, Tiberiu, Sf. Gheorghe, Serpenta, Serbanesti 4, Ovidiu.	GC–MS	Palmitic acid, palmitoleic acid, oleic acid.	[28]
	Berries from Himachal Pradesh and Jammu and Kashmir regions of the Indian Himalayas.	GC–MS and PCA, HCA	Amides, alkyl esters, alcohols, sugars, sugar esters, ketone, alkyl ether.	[40]

GC–FID: gas chromatography–flame ionization detector; GC-IRMS: gas chromatography-isotope ratio mass spectrometry; GC–MS: gas chromatography–mass spectrometry; GC–qMS: gas chromatography–quadrupole mass spectrometry; GCXGC-TOF-MS: two-dimensional gas chromatography with time-of-flight mass spectrometry; HS-SPME: headspace-solid phase microextraction; LDA: linear discrimination analysis; PCA: principal component analysis; PLS: partial least-squares; PLS-DA: partial least squares-discriminant analysis; PLSR: partial least squares regression.

2.4. Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectroscopy is an analytical method based on the magnetic properties of certain nuclei that provides structural and quantitative information on molecules in a nondestructive, effective, and rapid way [49]. Several studies have recently applied NMR spectroscopy for the authentication of different food products [14,50–52]. In the case of berries, NMR spectroscopy coupled with chemometric tools has been used to evaluate the influence of soil, vintage, growing areas, and growing systems on the metabolic profile of grape berries. Accordingly, Pereira et al. [53] determined the metabolic profile of three grape berry cultivars (Merlot noir, Carbernet Franc, and Cabernet Sauvignon), harvested in three vintages (2002–2004) in different geographical origins from Bordeaux (France) using 1H NMR analyses. PCA and PLS multivariate analysis showed a good separation of samples according to vintages, which highlights the potential of this method to discriminate berries grown under different climatic conditions. Several metabolites such as sugars, organic acids, and amino acids contributed to the differences that were observed. A similar approach was

used to evaluate the metabolic variations among grapes from different regions of South Korea [54]. The multivariate analysis applied in this study highlighted citrate, malate, alanine, proline, threonine, and trigonelline as the main discriminatory compounds to trace the geographical origin of the grapes. PCA and PLS-DA associated with 1H NMR has also proven useful when differentiating between four development stages in three Portuguese grape berries cultivars (Trincadeira, Aragonês, and Touriga Nacional). The phenolic profile, together with organic acid and sugar contents, were the main discriminants throughout the stages of early growth [55]. Picone et al. [56] developed a foodomics study using 1H NMR spectroscopic data under multivariate analysis to confirm differences in the molecular composition of grape berries grown under different production systems (biodynamic versus organic). Biodynamic grapes were differentiated according to their higher γ-aminobutyric acid (GABA) content and lower sugar, coumaric, and caffeic acid contents.

In addition to grape berries, sea buckthorn berries have also been authenticated through NMR spectroscopy [57–60]. In this sense, Kortesniemi et al. [58] used 1H NMR metabolomics to study two cultivars of sea buckthorn berries (*Hippophaë rhamnoides* ssp. *Rhamnoides*) (Terhi and Tytti) grown in different geographical locations of Finland and Canada. The results pointed out differences between cultivars and growing locations. Tytti berries were characterized by the presence of higher levels of O-ethyl b-D-glucopyranoside, while Terhi berries showed stronger quinic acid signals. The metabolic profile of northern berries was different from their southern counterparts. Northern growth conditions induced the production of compounds with a protective role against high-latitude related abiotic stress factors, such as vitamin C, together with quinic acid, glucose, and L-quebrachitol. In a study from the same group [59], a similar NMR metabolomic technique was applied to sea buckthorn berries from different locations in Finland and China. A multivariate analysis confirmed the effectiveness of this method for the identification of the geographical origin of the berries (lower contents of ascorbic, malic, and quinic acids, and higher levels of O-ethyl b-D-glucopyranoside in the southern berries).

Other berries such as cranberry, blueberry, goji berry, golden berry, raspberry, and maqui berry have been also authenticated through NMR-based metabolomics, confirming the useful role of compounds such as sugars, amino acids, and organic acids as biomarkers for the assessment of berry quality [61].

2.5. Near-Infrared (NIR) Spectroscopy

Near-infrared spectroscopy is based on the vibrational characteristics of the chemical bonds C–H, O–H, and N–H, and uses the infrared region of light to identify both the chemical and the physical properties of a sample [62]. Compared to traditional methods, NIR spectroscopy is a proven alternative for the quantification and the identification of food components that is easy to handle, rapid, nondestructive, and environmentally friendly [63].

Several compounds such as soluble sugars, micronutrients (i.e., P, K, Mg, Ca, Mn, Cu, Fe, Zn; in this case, minerals linked to an organic matrix), anthocyanins, and organic acids have been quantified in berries using NIR spectroscopy [64–69]. This analytical method has also been used as a chemical fingerprinting tool to assess grape smoke contamination, as any wildfires close to a vineyard may alter both berry quality and, therefore, the characteristics of the wines (smoky aromas and undesirable flavors) [70]. NIR spectroscopy combined with chemometrics has proven useful both for assessing blueberry ripeness and for classifying grape berries according to their developmental stage [71,72].

Moreover, NIR spectroscopy has recently been applied to trace the geographical origin of berries. Accordingly, Tingting et al. [73] analyzed goji berries (*Lycium barbarum* L.) from four different topographical regions in China (North China Plain, Loess Plateau, Northeast China Plain, and the Northwest Basin) using NIR spectroscopy and chemometrics. PCA was applied to analyze the pretreated spectra, and then three different discrimination models were compared: least-squares support vector machine (LS-SVM), back propagation artificial neural network (BP-ANN), and K-nearest neighbors (KNN). The results showed

that, compared with BP-ANN and KNN LS-SVM, LS-SVM is an excellent chemometric tool to classify goji berry geographical origins based on NIR spectra (96.67–100% discrimination rates). In a study of the same research group [74], a similar approach was applied to determine the geographical origin in five varieties of black goji berry (*Lycium ruthenicum* Murr.). The recognition rate of LS-SVM was higher than 98.18%, meaning that this method provided excellent classification of the geographical origin of black goji berries. The authors also proved that NIR spectroscopy combined with synergy interval PLS (Si-PLS) can accurately predict the anthocyanin content of these berries.

In addition to berries, wines have also been authenticated using NIR spectroscopy. In this respect, Zaukuu et al. [75] developed a method to discriminate lower-grade Tokaj wines (Hungarian wines adulterated with grape must concentrate, so their sugar content was equal to high-grade wines) using NIR spectroscopy and an e-tongue coupled to chemometrics (PCA, LDA, PLSR, and aquaphotomics). The results showed that PCA gave a good separation pattern, although 100% classification of adulterated and nonadulterated wines was obtained when an e-tongue combined with LDA was used. PLRS models also showed high determination coefficients (0.87–0.98) with both methods, and the aquagrams revealed water absorption bands as good markers for wine quality, which highlights the potential of aquaphotomics as a novel approach in this field.

2.6. Raman Spectroscopy

Interest has recently been growing in Raman spectroscopy, a fast, nondestructive, eco-friendly, and highly sensitivity analytical technique for the identification and quantification of food microconstituents [76,77]. Foods may therefore be classified with Raman spectroscopic information in combination with chemometric tools [77].

So far, few studies have applied Raman spectroscopy for the study of berry features. Khodabakhshian [78] investigated the feasibility of Raman spectroscopy to differentiate four stages of pomegranate fruit maturity (immature stage, fairly half-ripe stage, half-ripe stage, and full ripe stage) on the basis of tannin changes. The results showed that Raman spectroscopy is a useful tool for the detection of tannin as an indicator of pomegranate maturity. Similarly, in another study from the same research group [79], Fourier transform (FT) Raman spectroscopy was combined with unsupervised (PCA) and supervised (PLS-DA and SIMCA) pattern recognition methods in order to distinguish the stage of pomegranate maturity. The results confirmed that PCA successfully classified the Raman spectra of the samples. In addition, SIMCA could differentiate the four pomegranate maturity stages with good accuracy (82%), and PLS-DA also showed a high discrimination power (95%). Therefore, these studies demonstrated the feasibility of Raman spectroscopy as an automated, nondestructive, and rapid technique for the quality control of berries. However, as far as we are concerned, there is still no research dealing with the application of Raman spectroscopy to trace the geographical origin of berries, although some applications have been described for berry-derived products. In this respect, Magdas et al. [80] used FT-Raman spectroscopy associated with chemometric tools to discriminate wines based on variety, geographical origin, and vintage. The authors analyzed 30 wines (Feteasca Regala and Sauvignon Blanc), produced from five vintages within three regions of Romania. The results showed a 100% discrimination of wine according to grape variety and geographical origin, which highlights the potential of Raman spectroscopy for the authentication of berry-based products.

Vibrational spectroscopy analysis (FTIR and Raman) combined with multivariate analysis has been also successfully applied to differentiate grapes coming from conventional and organic agriculture [81].

2.7. Inductively Coupled Plasma (ICP)

Many studies investigated the relationship between the elemental compositions of grape berries (*Vitis vinifera* L.) and soil/leaves, in order to trace their geographical origin. Most of them examined the distribution of major and trace elements using induc-

tively coupled plasma–mass spectrometry (ICP–MS) and/or atomic emission spectroscopy (ICP–AES) [82–86]. Accordingly, Cugnetto et al. [82] used ICP–AES for the analysis of 20 elements in 39 grape samples (Nebbiolo and Barbera varieties) from 8 different sites in northwestern Italy (Agliè, Briona, Mezzomerico, Monforte, Pont S. Martin, Sinio, Sondrio, and Treiso). Principal component analysis (PCA) was applied to the data after ICP–AES analysis, in order to distinguish between the different sites. The results pointed to Ba, Mn, Si, Sr, and Ti as the main discriminating markers for the samples from different sites, whereas Ba and Sb played a major role in the differentiation of the two varieties. Similarly, Pepi et al. [83] analyzed the concentrations of major and trace elements in soil and grape berries of the 'Negroamaro' cultivar from Apulia, southern Italy, using ICP–MS combined with linear discriminant analysis (LDA). As a result, discrimination was possible with LDA between berries grown under three different soil management regimes. Later, the same research group [84] investigated the relationship between geochemical elements in another Italian grape cultivar 'Glera' and soil using ICP–MS and LDA. Samples taken from different wineries in Veneto were differentiated from each other by considering the concentrations of Al, B, Ba, Ca, Co, K, Mg, Ni, Sr, and Zn. In particular, Sr was found as a key indicator of geochemical correlation between soil and 'Glera' grapes [84]. The major and trace elemental composition of another Italian grape cultivar 'Cannonau' was also studied by the same research group [85]. PCA was applied to the data from ICP–MS analysis, in order to establish the relation between the geochemical attributes of soil, leaves and 'Cannonau' grape berries from two study areas. The results showed that B, Sr, and Zr were the key markers that confirmed a correlation between the soil and leaves and grape berries of the Cannonau variety [85]. In a more recent study, Gao et al. [86] analyzed 46 elements in Chinese grapes using ICP–MS to discriminate their geographical origin. According to chi-squared test, K, Na, Cs, V, Li, Sc, In, Mn, Mg, Al, and Li were determined as characteristic parameters to distinguish grape origin. Furthermore, chemometric approaches including feed-forward neural network (FNN), random forest (RF), and SVM achieved accuracy rates of 98.33%, 96.67%, and 100%, respectively, in differentiating the geographical origin of the grapes.

There are also a few studies on the determination of concentrations of rare earth elements (REEs) in grape berries from various geographical origins [87–89]. The REEs are commonly known as lanthanum (La) and the 14 elements comprising the lanthanide series: cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). These elements can be classified into three groups: (i) light rare earth elements (LREEs) from La to Nd, (ii) medium rare earth elements (MREEs) from Sm to Gd, and (iii) heavy rare earth elements (HREEs) from Tb to Lu [90]. In a study conducted by Pepi et al. [87], the distribution of REEs in grape berries and soil of V. vinifera cv. 'Glera' was investigated using ICP–MS. In this study, the grape cultivar 'Glera' grown in five wineries (Bottazzo, Gaiarine, Lonigo, Nardin and Pattarello) in the Veneto region of Italy was collected. The bioaccumulation index, which is the ratio between the concentration of a given element in a plant and the concentration of the same element in soil, was calculated in order to determine the assimilation of REEs from soil to berries. The results revealed that higher accumulation of REEs was detected in solid grape berry residues compared to the juice. Each vineyard showed a different bioaccumulation index for REEs. Regarding the LREEs, the highest bioaccumulation index was found in solid grape berry residues from Gaiarine, followed by Lonigo, Bottazzo, Nardin, and Pattarello. In another study by the same research group [88], the distribution of REEs in six grape varieties grown around Mount Etna, Sicily, Italy (Carricante, Grecanico, Inzolia, Merlot, Nerello Cappuccio, Nerello Mascalese) was investigated. Different parts of the plants including leaves, seeds, juice, and skin along with the soil were examined using ICP–MS combined with PCA and LDA. The highest REE concentrations were detected in the leaves, whereas skins and juices showed lower concentration values, which further decreased in seeds. Overall, the multivariate statistical analysis provided data for the discrimination of different grape varieties [88]. In another study [89], concentrations of

34 mineral elements including REEs were determined in *V. vinifera* cv 'Corvina' berries from 11 vineyards located in 3 different macro-areas of the Verona region in Italy (Bardolino, Soave, and Valpolicella). After ICP–MS analysis, PCA was applied to the data. When only REEs were considered for PCA, the samples formed two distinct clusters: (i) samples from Bardolino and Valpolicella vineyards, and (ii) samples from Soave vineyards [89].

In addition to grape berries, the authenticity of other berries such as bilberry (*Vaccinium myrtillus* L.), black currant (*Ribes nigrum*), blackberry (*Rubus fruticosus* L. and *R. allegheniensis* L.), blueberry (*Vaccinium corymbosum* L.), chokeberry (*Aronia arbutifolia*), goji berry (*Lycium barbarum* L.), goldenberry (*Physalis peruviana*), gooseberry (*Ribes uva-crispa* L.), raspberry (*Rubus idaeus* L.), and strawberry (*Fragaria ananassa* Duch.) were also investigated through elemental fingerprinting [91,92]. Covaciu et al. [91] examined the elemental concentrations of wild and cultivated berries from Transylvania using ICP–MS combined with LDA. The model classified 72.5% of the species correctly, and the most effective discrimination markers for the differentiation of species were determined as Ba, Ca, Na, P, and Zn. Moreover, the cultivated and wild bilberries and raspberries were 100% correctly classified with initial and cross-validation. The concentration of Mg was found to be low in cultivated bilberries and raspberries, due to the nutrient deficiency in the soil where they were cultivated. In another study [92], ICP–AES and ICP–MS were utilized to identify and quantify 20 macro, micro, and trace elements in the seeds of wild and cultivated berries. PCA applied to the classification of the berries revealed three distinct clusters. The first cluster included blackberry, blueberry, and raspberry seeds, which were abundant in Al, Mn, and Na. Currants and gooseberries with high K, Mg, P, and sulfur (S) content were clustered in the second group. The third group separated from the first two groups included chokeberry, goji berry, goldenberry, and strawberry samples with high concentrations of Cd, Co, Cr, Cu, Hg, Pb, and Zn. Furthermore, in general, Ba, Pb, and Sr contents were found to be significantly higher in wild fruits, whereas Fe, Mg, Mn, Ni, and Zn were more abundant in cultivated fruits [92].

3. Biomolecular Approaches

Although the chemical approaches based on chemical components that have been described above are common choices for the authentication of plant-based foods, it is important to take into account that metabolite profiles can be influenced by external factors such as light and any other storage conditions. With regard to species identification, DNA-based authentication methods could therefore determine the biological origin of a food in a more reliable way, since the taxonomic identity of a species is mainly determined by its genetic information [93].

These biomolecular approaches have also been applied to berry authentication, using mainly PCR- and sequencing-based methods, although the latter are replacing the PCR-based methods (traditional and quantitative PCR—qPCR), since there is an increase in DNA sequencing that allows the search for DNA barcodes applicable in the field of food authentication. Jaakova et al. [94] developed a method based on DNA barcodes (short sequences of DNA universally amplifiable and used to differentiate species) and high-resolution melting (HRM) of amplicons, for the identification of bilberry (*Vaccinium myrtillus* L.) samples from other berry species that usually appear mixed in the market: lingonberry (*V. vitis-idaea* L.), bog bilberry (*V. uliginosum* L.), blueberry (*V. corymbosum* x *V. angustifolium)*, crowberry (*Empetrum nigrum* L.), gooseberry (*Ribes uva-crispa* L.), honeysuckle (*Lonicera caerulea* L.), and mountain shadbush (*Amelanchier bartramiana* (Tauch) M. Roem.). According to the results, the proposed method is a useful tool to identify closely related berries of commercial interest. In addition, the method that only requires DNA isolation and common PCR steps can be performed in few hours. In a similar study, Wu et al. [95] also used DNA barcoding technology (Sanger sequencing-based DNA barcoding) for the authentication of small berry fruit samples (different species of 10 categories: blueberry, cranberry, lingonberry, blackcurrant, mulberry, raspberry, grape, duchesnea, wolfberry, and lantern fruit) in various nonprocessed and processed products (dried berry fruit, fruit jam, and fruit juice). The

authors investigated seven different barcodes, and the results confirmed that the MatK, rbcL, and psbA-trnH could successfully discriminate small berries (10 categories—100% correctly identified) in fresh, pasteurized, and high-temperature treated small berry fruit juice. The authors finally applied their method to commercial small berry products available in the market, and surprisingly found that almost half (45.4%) of the products analyzed were inconsistent with the label. Although useful to detect fraud in food products, most of the DNA barcoding methods used for authentication are qualitative and, therefore, they cannot quantify the amount of authentic over fraud materials. In this sense, digital PCR (dPCR) allows the absolute quantification of the DNA copy number and, compared to qPCR, is a more sensitive technique [96]. A dPCR method has been recently optimized to discriminate between American cranberry and lingonberry DNA, which is also able to quantify the DNA copy numbers in mixed samples [97].

On the other hand, DNA methylation, which belongs to a type of epigenetic tools by which the gene expression of a plant can be altered, could be changed as a consequence of different environmental conditions or cultivation practices [98]. Reasonable evidence is therefore forthcoming from DNA methylation as a tool to trace the geographical origin of a plant. Accordingly, in a recent study, Barankova et al. [99] collected grape berry (Merlot and Pinot Noir) samples grown under very dissimilar climatic conditions at vineyards some 2000 km apart (Czech Republic and Armenia). They analyzed their DNA methylation pattern through a methylation sensitive amplified polymorphism (MSAP) method. The results showed that the DNA methylation profiles of the samples originating from the same vineyard were unique. In addition, different climate conditions of individual vineyards contributed significantly to variability in the DNA methylation pattern. Although yielding promising results, further studies at varied geographical locations are still needed to confirm whether the DNA methylation landscape will represent a successful strategy to trace the geographical origin of berries.

Moreover, the role that the microbiome could play in addressing the geographical origin of a plant has been suggested in recent research. In this respect, Mezzasalma et al. [100] characterized the soil and grape microbiome by 16s rRNA high throughput sequencing (HTS) of three different cultivars (Cabernet Sauvignon, Sauvignon Blanc, and Syrah) grown at three geographical locations (North Italy, Italian Alps, and Northern Spain) with varied environmental conditions. The results confirmed that almost 60% of bacterial genera were shared between soil and berry. Although all berries shared some bacterial taxa, there were some operational taxonomic units (OTUs) that could serve as geographical origin markers, and even serve as cultivar fingerprints. The geographical origin and grape cultivar could be predicted with high levels of accuracy (9 out of 12 cases assessed) according to the machine learning analysis that was performed.

4. Isotopic Approaches

Increasing interest is also evident in stable isotope ratio mass spectrometry (IRMS) to trace food geographical origin and authenticity on the basis that the stable isotopic ratio of an organism is an indicator of the features of specific growing conditions or nutritional profile [101].

To date, the stable isotope ratios of different berries have been explored. Li et al. [102] analyzed the carbon, nitrogen, hydrogen, and oxygen isotope compositions of blackcurrants collected from four different cultivation regions of China. The results indicated that blackcurrant berries from different cultivation sites could be discriminated based on a combination of the stable nitrogen, hydrogen, and oxygen isotope ratios, whereas the carbon isotope ratio added no useful information in relation to blackcurrant geographic origin. In another study, Perini et al. [103] evaluated the H, C, N, and O isotopic ratios of several berries (strawberries, raspberries, blueberries, blackberries, and currants) produced in different regions (north Italy, Romania, and Poland) over three harvest years. The results confirmed that δ13C and δ15N of the pulp, and δ18O of the juice could serve as effective markers to discriminate between different geographical origins of the berries. In a recent

study, Klavins et al. [104] determined the stable isotope ratios of various blueberry and bilberry varieties from different geographical origins (Norway and the Baltic Sea region: Latvia, Lithuania, and Finland). The results showed that IRMS analysis of the berries revealed significant differences in isotope ratios according to the place of origin, supporting the possibility of using this analytical tool for berry authentication purposes.

On the other hand, a novel GC-IRMS method for compound-specific isotope analysis (CSIA) of volatile compounds has recently been developed and applied to goji berries [44]. The authors analyzed 52 berries from three Chinese provinces (Gansu, Ningxia, and Qinghai). Their results showed that the δ13C compound-specific isotope analysis of volatile compounds delivered reliable results for the discrimination of the geographical origin of Chinese goji berries (LDA differentiate with an accuracy of 89.16%, 87.77%, and 85.87% for the three provinces, respectively).

5. Conclusions

Studies on berry authentication using modern analytical techniques (chemical, biomolecular, and isotopic approaches) have been discussed in detail in this review. Most of the studies reported to date are related to chemical approaches, mainly chromatographic techniques. Polyphenols are the major discriminating markers analyzed with liquid chromatography, whereas gas chromatography is generally used for the determination of volatile compounds and fatty acids. Many studies have also investigated the authenticity of berries using ICP–MS. Both chromatographic and elemental ICP–MS fingerprinting combined with chemometric methods are useful tools for the authentication and traceability of berries. Other chemical (NMR, NIR, and Raman spectroscopy), biomolecular, and isotopic methods have also delivered promising results in the field of berry authentication, although there is still limited information available in this respect.

In any case, and despite the potential of the methods described in the present review, to date, there is no universal one. Therefore, combinations of different approaches in order to complement each other are increasingly used (e.g., HPTLC and mass spectrometry; Raman and IR spectroscopies; biomolecular and analytical techniques. . .).

Taking into account that adulteration practices are increasingly evolving, continuous research in the field of food authentication is needed, especially in the case of berries, since there are still some berry species that have not been yet included in any authentication study (i.e., boysenberries, acai berries, huckleberries, or hackberries, among others). In addition, more practical management tools should be developed, since the application of the available approaches for industrial purposes is still a challenge.

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