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Article

Relationships Between Chemical Compounds and Sensory Properties of Virgin Olive Oil in the US and Israel: Development of a Prediction Model for Defects

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ABSTRACT: Virgin olive oil (VOO) quality is defined by both chemical and sensory parameters. While the chemical parameters are objective and measured using instrument-based methods, sensory quality evaluation is based upon human panels, which can be subjective, have less repeatability, suffer from fatigue, and require long and costly training. Tasting biases could be minimized by a trained panel, but using humans as a testing instrument is inevitably prone to various psychological biases, stimulus-related factors, and carry-over effects. The objectives of this study were to evaluate instrumental methodologies that will assist the existing human panel in assessing the sensory characteristics of VOO and to develop chemistry-based predicting models for sensory properties in the oil using VOO samples originating from the US and Israel. Our results indicated that oil rancidity highly correlated with the contents of chemical components contents; 1-penten-3-one, 3-hexen-1-ol, (*E*)-2-pentanal, and 1-octen-3-ol are the major volatiles associated with rancidity defects (low concentrations of these compounds). Positive sensory attributes, such as fruitiness, correlated with 1-acetoxypinoresinol and hexanal, while bitterness correlated with pinoresinol, the aldehydic form of oleuropein aglycones, and the dialdehydic form of oleuropein aglycone. The random forest model suggested that luteolin, (*E*)-2-hexenal, 1-penten-3-one, and C18:0 are the most useful measurements in predicting the occurrence of sensory defects in the olive oil samples included. In other words, when these compounds are below or above a certain threshold, a defect, such as rancidity, is more likely to be found by the sensory panel.

KEYWORDS: *virgin olive oil, sensory, chemical quality, phenolics, volatiles*

INTRODUCTION

Virgin olive oil, a key component of the Mediterranean diet, is celebrated for its distinctive flavor and aroma, which are intrinsically linked to its chemical composition. Numerous studies have highlighted the benefits of incorporating extra virgin olive oil into the diet, particularly within the context of the Mediterranean diet.[1−3] Additionally, olive oil consumption is associated with a reduced risk of heart disease and certain types of cancer, likely due to its high content of monounsaturated fatty acids and phenols.[4,5] The primary component of olive oil is fatty acids, which contribute to its health benefits, oxidative stability, and mouthfeel. Monounsaturated fatty acids, particularly oleic acid, dominate its composition. Higher levels of monounsaturated fatty acids result in a smoother, more fluid texture, while saturated fatty acids, such as palmitic acid, can lead to a slightly waxy or thicker texture. The perception of texture is a complex sensory experience influenced by the concentrations and ratios of these compounds and their interactions (Cecchi et al., 2021).[6]

Virgin olive oil is obtained solely through mechanical means from olives (*Olea europaea* L.), without solvent extraction, allowing the oil to retain its natural flavors and potential health benefits.[7] The chemical and sensory properties of virgin olive oil are influenced by numerous factors, including cultivars, geographical origins, climatic conditions, ripeness at harvest, and processing practices.[8] Within the virgin olive oil category, there are three subcategories suitable for consumption: extra virgin olive oil, virgin olive oil, and ordinary virgin olive oil. There is also lampante virgin olive oil, which is not suitable for consumption without refining (COI/T.15/NC No 3/Rev.19). Extra virgin olive oil is of the highest quality, with a premium economic value.

High temperatures during olive oil processing and storage significantly accelerate oxidative reactions and degrade oil quality. These oxidative processes, particularly lipid peroxidation, lead to the formation of undesirable compounds, such as hydroperoxides, aldehydes, and ketones, which negatively affect the oil's flavor, nutritional value, and shelf life.[9] Furthermore, studies have shown that high temperatures during malaxation promote the degradation of phenolic compounds, thereby reducing its antioxidant capacity and oxidative stability in the oil.[10,11]

Phenolic compounds contribute significantly to the bitterness and pungency of virgin olive oil. Oleuropein and ligstroside

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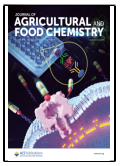

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derivatives, such as aldehydic forms of oleuropein aglycone and ligstroside aglycone, contribute to bitterness, while oleocanthal and oleacein are responsible for the pungent, throat-irritating sensation.[12,13] The concentrations of these compounds and their interactions play a crucial role in the unique and complex sensory profile of each virgin olive oil.

Many studies have explored the relationships between sensory attributes and chemical compounds in virgin olive oil to understand the interplay between these parameters and the factors that affect them. Researchers have investigated the influence of volatile compounds, such as aldehydes, alcohols, and esters, on the aroma profile of olive oil.[6,14] Common aroma attributes of virgin olive oil include fruity and grassy, along with other positive notes, such as apple, banana, citrus, floral, and tomato leaf. Aldehydes like hexanal and (*E*)-2-hexenal, contribute to green, fruity, almond, artichoke, and grassy aromas; alcohols like 1-hexanol, (*Z*)-3-hexen-1-ol, and (*E*)-2-hexen-1-ol are associated with green, fruity, and banana-like aromas, while esters like hexyl acetate impart fruity and green apple notes.[15,16]

Sensory analysis is an official method for determining the quality of virgin olive oil, involving humans as a measurement instrument. However, given the high cost and inevitable human bias, there is an urgent need for analytical methodologies that can reliably measure chemical compounds in virgin olive oil to prescreen and support the official panel test.[17] Most studies on the relationship between chemical and sensory properties of virgin olive oil have been conducted in Southern Europe on locally produced olive oil.[8,18−25] Only one published study outside Europe, conducted in Brazil, examined 12 locally produced virgin olive oil samples.[26] While these studies have significantly contributed to our understanding of the chemical basis of sensory properties in virgin olive oil, there is a gap in the literature regarding the specific relationships between chemical compounds and sensory attributes in the US and Israel. These two countries, with their distinct climatic conditions and olive cultivars, present unique opportunities to explore these relationships. Olives have been grown in Israel for more than 7,000 years, making it one of the regions with the longest tradition of olive oil production.[27] Although olives were brought to California in 1769 by the Mission padres at Mission San Diego, industrial olive oil production only began in the last two decades, thanks to the development of medium-, high-, and super high-density plantations.[28] Both countries currently produce a similar volume of olive oil, with average production for 2019−2021 at 14800 tons in Israel and 16000 tons in the US (FAOSTAT).

In this study, we evaluated the relationship between sensory and chemical properties of 230 samples obtained from the US and Israel. We assessed basic chemical quality parameters, such as free fatty acidity (FFA), peroxide value (PV), specific UV absorbances, total phenol content, diacylglycerols (DAGs), and pyropheophytins (PPP), as well as specific compounds relevant to olive oil characteristics, such as fatty acids, phenolic compounds, and volatiles. Concurrently, trained sensory panels evaluated the same oil samples using a standardized methodology established by the International Olive Council (IOC). We utilized a random forest model, known for its high prediction accuracy in classification tasks, to rank the top models for prediction accuracy.[29] This model consists of a collection of classification and regression trees that use binary splits on predictor variables to make outcome predictions.[30] This ensemble approach often results in higher accuracy compared to a single decision tree model while retaining interpretability benefits, such as elucidating relationships between predictors and outcomes.[31] Variable selection within the random forest framework is crucial for many applications, particularly with an aim to support decision-making in complex problems. This aligns with our goal of prediction modeling, where a dataset is used to develop a model to predict whether the oil will have a sensory defect to ease the burden of sensory panels. By utilizing the rich data set generated from both analytical measurements and sensory evaluations, the random forest model can capture intricate patterns and correlations that may exist between various chemical compounds and sensory attributes of olive oil.

MATERIALS AND METHODS

Chemicals. Ethanol, sodium hydroxide, sodium thiosulfate, isooctane, acetic acid, phenolphthalein, Folin-Ciocalteu reagent, sodium carbonate, petroleum ether, diethyl ether, toluene, hexane, methanol, and acetonitrile were purchased from Fisher Scientific (Hampton, NH, US). Caffeic acid, *p*-hydroxyphenyl-acetic acid, Supelco 37 Component fatty acid methyl ester (FAME) Mix, and 1-methyl imidazole were obtained from Sigma-Aldrich (St Louis, MO, US). The derivatization reagent *N*-methyl-*N*-trimethylsilyl-heptafluorobutyramide (MSHFBA) for DAGs analysis was purchased from Macherey−Nagel (Bethlehem, PA, US). Nanopure water was prepared with a Milli-Q system (Millipore, Bedford, MA, US). Samples were stored at 4 °C, as previous works have shown that this temperature is effective in preventing oil oxidation, with preservation effects comparable to those at freezing temperature (−18 °C).

Olive Oil Samples. We obtained 230 samples of virgin olive oil from California and Israel for this study. We aimed to have a wide diversity of samples, including those with typical sensory defects. The following set of samples was included (also see Supporting Information):

1. Samples of "Barnea", "Souri", and "Arbequina" EVOO originated from Geshur Olive Farm in northern Israel. The samples were in 1 L bottles and placed on a shelf at room temperature. Half of the bottles were left closed while half were left open to accelerate oil oxidation. Every two months, a subsample from each combination cultivar × open/close was transferred to refrigerators and kept until analysis. Hence, we had oil samples stored at room temperature (closed or open) for 0, 2, 4, 6, 8, 10, and 12 months. In total, we had 144 samples from this set (RUN code).
2. Samples collected from the supermarkets in California (CA) of locally produced and imported virgin olive oil, 35 samples (COM-CA code).
3. Samples collected from the supermarkets in Israel (IL) of locally produced and imported virgin olive oil, 15 samples (COM-IL code).
4. Samples originating from olives infested with Olive Fly (*Bactrocera oleae*) at increasing degrees of infestation: 0, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100%. The oil was extracted with an Abencor laboratory-scale olive mill (mc2 Ingenieria y Sistemas, Seville, Spain) in Israel, 11 samples (FUS code).
5. Samples of the Barnea cultivar originating from olives that were artificially exposed to freezing temperatures (for at least 24 h at −4 °C) after harvesting (to simulate frostbitten sensory defect). The oil was extracted using a laboratory-scale Abencor Mill, 3 samples (FBR code).

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6. Samples originating from olives harvested in November in IL were stored in a sack for different time periods (3 and 7 days) under different temperatures (4 °C, room temperature). The oil was extracted using a laboratory-scale Abencor Mill, 7 samples (MHF code).

7. Samples were collected in the olive mills from the bottom of the oil tank after a few months of sedimentation and were exposed to the sediments and oil samples that were identified as containing sensory defects by the packing house during their primary sorting of oils. A total of 15 samples (OM code) were collected.

Chemical Quality Parameters. FFA, PV, and specific UV absorbances at 232 nm (K_{232}) and 268 nm (K_{268}) were determined following the AOCS official method Ca 5a-40, Cd 8b-90, and Ch 5−91, respectively. PPP was evaluated on Agilent 1290 LC-DAD (Santa Clara, CA, US) following the ES International Organization for Standardization (ISO) 29841:2012 standard method, with modifications described previously by Li et al.[32] DAGs were determined on a Varian 450 GC-FID based on the ISO standard method (ISO 29 822:2012) with modifications provided by Polari et al.[33]

Induction Time. Oxidative stability analysis was performed on a Metrohm 892 Rancimat instrument (Herisau, Switzerland) following the AOCS official method Cd 12b-92. Briefly, 2.5 g of oil was measured into a reaction vessel and heated under 120 °C with a constant air flow of 20 L/h until the induction time was reached.

Total Phenol Content and Phenolic Compounds Profile. Total phenol content was determined using the Folin-Ciocalteu method with modifications from Polari et al.[33] Two grams of olive oil in 1 mL of hexane were extracted three times with 2 mL of methanol/water (60:40, v/v). Supernatants were combined in a single tube after three centrifugations (4000 rpm, 10 min), and 0.5 mL of the extract was diluted with DI water to 5 mL for the subsequent reaction with 0.5 mL of Folin-Ciocalteu reagent and 1 mL of 35% sodium carbonate. The sample was incubated in the dark for 2 h before absorbance was measured at 725 nm. Results were expressed as caffeic acid equivalents.

Phenolic compounds were obtained using solid-phase extraction and separated on LC-DAD following Mateos et al.[34] Briefly, 2.5 g of oil and 0.5 mL of internal standard, *p*-hydroxyphenylacetic acid (6.75×10^{-2} mg/mL methanol), were combined and dissolved in 6 mL of hexane, followed by a 30 s of vortex. The mixture was then loaded onto a 1000 mg/6 mL diol-bonded cartridge (Thermo Scientific, Waltham, MA, US), washed twice with 6 mL hexane and once with 6 mL hexane/ethyl acetate (90:10, v/v), before eluted with 10 mL of methanol. The solvent was evaporated on a Buchi E-300 (Flawil, Switzerland) to dryness, and the residue was reconstituted in 1 mL methanol/water (1:1, v/v) for LC injection. The separation was achieved on an Agilent Zorbax Eclipse Plus C18 column (4.6 mm × 250 mm x 5 μm). The injection volume was 20 μL and the flow rate was 1 mL/min. Mobile phase A was water/acetic acid (97:3, v/v) and mobile phase B was methanol/acetonitrile (50:50 v/v). The solvent gradient changed from 95% A−5% B to 70% A−30% B in 25 min; to 65% A−35% B in 10 min; to 60% A−40% in 5 min; to 30% A−70% B in 10 min; and to 100% B in 5 min. DAD was set at 240, 280, and 340 nm. Peak identification was done by comparing retention times with those of commercially available standards and with the elution pattern in Mateos et al.[49] Quantification was done using the relative concentration to the concentration of the internal standard.

Volatile Organic Compounds (VOCs). Olive oil volatiles were measured following the same protocol used by Polari et al.[33] One gram of oil was spiked with 4-methyl-2-pentanol as an internal standard (2.5 mg/kg) in a 20 mL glass vial with a PTFE/silicone septum. After 10 min of equilibrium at 40 °C, a solid-phase microextraction (SPME) fiber (2 cm, DVB/CAR/PDMS, Sigma-Aldrich, St. Louis, MO, US) was exposed to the sample headspace for 40 min for volatile absorption. Volatile analysis was performed on a Varian 450 GC equipped with a Varian 220 MS ion trap using a Supelcowax 10 column (30 m × 0.25 mm × 0.25 μm, Sigma-Aldrich). The SPME fiber was thermally desorbed in the GC injector for 5 min at 260 °C. The temperature gradient in the GC oven started at 40 °C and ramped at 3 °C/min after 10 min to a final temperature of 200 °C. Helium was used as the carrier gas at a flow rate of 1 mL/min. The ionization energy was 70 eV, and ions were analyzed in the m/z range from 40 to 400. Volatile compounds were identified by comparing their mass spectra with commercial standards, the NIST library, and the Kovatz retention index (KI). Volatile concentrations were expressed as relative concentrations to IS in ppb (μg/kg).

Fatty Acid Profile. The fatty acid profile was obtained following the International Olive Council (IOC) official method (COI/T.20/Doc. no. 24−2001) with modifications as described in Li et al.[32] Approximately, 0.01 g of oil was dissolved in 0.4 mL of toluene, followed by the addition of 3 mL of methanol and 0.6 mL of methanol/HCl (80:20, v/v). The sample was heated at 80 °C for an hour before 1.5 mL of hexane and 1 mL of nanopure water were added and vortexed. The upper layer was decanted and dried with anhydrous sodium sulfate before GC injection. Separation was conducted on an Agilent DB-5 capillary column (30 m × 0.25 mm × 0.1 μm) using a Varian 450 GC-FID. The injector was held at 240 °C at a split ratio of 150. The GC oven was initially held at 80 °C for 5 min; then ramped at 10 °C/min to 230 °C and held for 5 min, and finally ramped at 20 °C/min and held for 10 min. The FID was set at 260 °C. The detector gas consisted of helium make-up gas (25 mL/min), hydrogen (30 mL/min), and air (300 mL/min). A Supelco 37 Component FAME standard mixture was used for peak identification.

Sensory Analysis. Sensory assessment was performed by two sensory panels: Israel's Southern Panel (an IOC-recognized panel in Israel) and the Applied Sensory Panel (an AOCS-recognized panel in Fairfield, CA, USA) following the IOC COI/T.20/Doc. No 15/Rev method regulation.

Statistical Analysis. Different oils from the US and Israel were considered in this study (n = 230). Pearson correlation coefficients between quality measurements and sensory attributes, phenolic compounds with VOCs and sensory attributes, and fatty acids and quality measurements were determined. This coefficient describes the strength of the linear relationship between two quantitative variables at $p < 0.05$. Discrimination between the evaluated parameters was achieved by Principal Component Analysis (PCA) using the Pearson correlation matrix. Additionally, Pearson correlation coefficient was calculated between the sensory attributes and evaluated chemical quality parameters, phenolic compounds, VOCs, and fatty acids. These correlations are represented with a heatmap. Machine learning model random forest was used to predict the defects (response variable) in oil from the chemical quality parameters, phenolic compounds, fatty acids, and VOCs (predictor variables).

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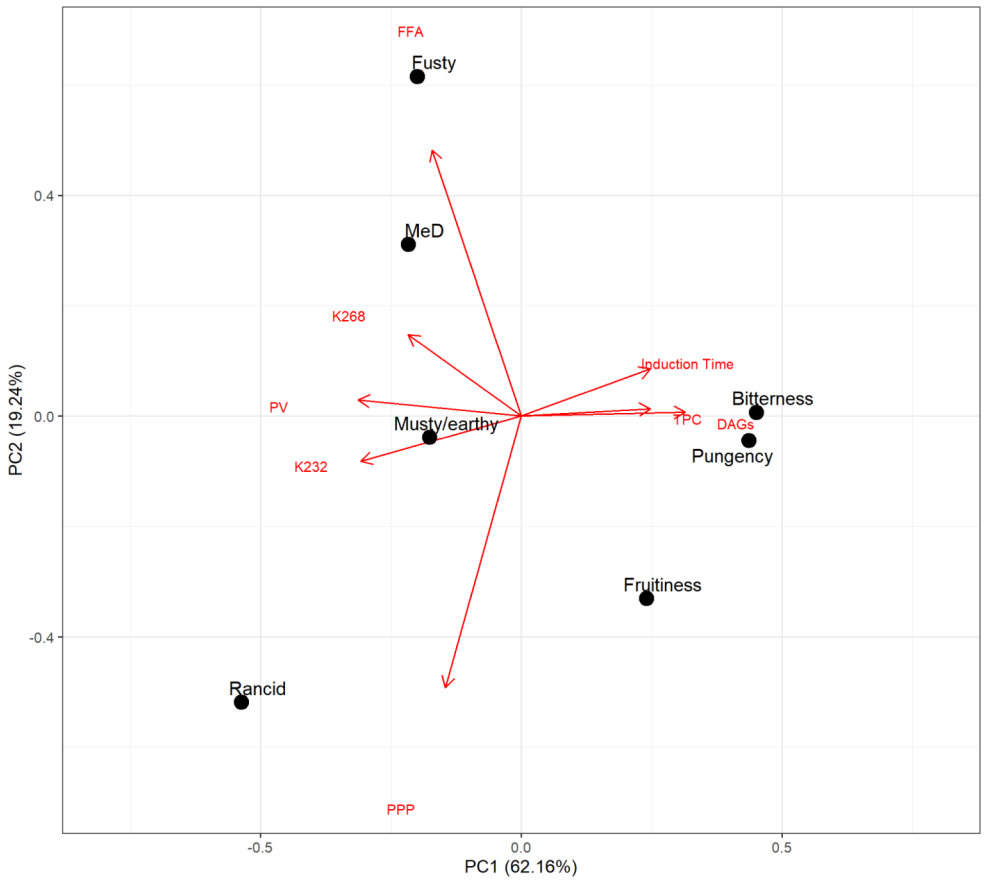

Figure 1. Principal Component Analysis (PCA) where a correlation matrix was used to represent associations between the evaluated chemical parameters. The PCA consisted of the loading plot of PC1 to PC2, the score plot, and the distribution of the samples in the consensus space. DAGs: Diacylglycerols (%); FFA: Free fatty acidity (%m/m oleic acid); K_{232}: Specific absorbance at 232 nm; K_{268}: Specific absorbance at 268 nm; PPP: Pyropheophytins (%); PV: Peroxide value (meq O_2/kg); TPC: Total Phenol Content (mg of caffeic acid equivalent/kg olive oil); MeD: Median of defect, defined as the median of the defect perceived with the greatest intensity.

The confusion matrix values used to determine the effectiveness of the model, the accuracy (1) is computed by adding up all the correct predictions and then dividing by the total data set size:

$$\text{Accuracy} = (\text{TP} + \text{TN}) \div (\text{TP} + \text{TN} + \text{FP} + \text{FN}) \quad (1)$$

Sensitivity (3) is calculated as the ratio of true positives to the sum of true positives and false negatives:

$$\text{Sensitivity} = \text{TP} \div (\text{TP} + \text{FN}) \quad (2)$$

Similarly, specificity (3) is determined by the ratio of true negatives to the sum of true negatives and false positives:

$$\text{Sensitivity} = \text{TN} \div (\text{TN} + \text{FP}) \quad (3)$$

Where TP, TN, FP, and FN represent true positives, true negatives, false positives, and false negatives, respectively.

Receiver Operating Characteristic (ROC) curve analysis was used to determine the cutoff value in the response variable. The ROC curve is created by plotting the true positive rate (sensitivity) against the false positive rate (1 − specificity) for different threshold values of the classification model. Each point in the ROC curve represents a different threshold value. The threshold at which the response variable changes its value was calculated by Youden's J statistic, which is defined as sensitivity + specificity −1. The threshold that maximizes Youden's J statistic corresponds to the optimal cutoff point.

The statistical analysis was carried out using R software (R core team, 2023, version 1.1.463−2009−2018 R-studio, Inc.).

RESULTS AND DISCUSSION

The commercial categories of virgin olive oil are currently based on chemical, physical, and sensory parameters, following official methods. Studies have shown that consumers consider sensory characteristics to be one of the most important purchasing factors.[35] Considering the limited number of oil samples that can be analyzed daily by a sensory panel, an instrumental screening tool could help reduce the panel members' workload and improve their performance. In this study, we attempted to identify the most useful chemical measurements that may predict sensory defects.

Quality Measurements and Sensory Attributes. PCA was performed on a dataset comprising sensory attributes and major chemical quality parameters. Prior to PCA analysis, a Pearson correlation coefficient matrix was computed to assess the linear relationships between variables. In Figure 1, the analysis revealed that 81.4% of the total variance in the data was accounted for by the principal components, with Component 1 explaining 62.16% and Component 2 explaining 19.24%. Component 1 appeared to capture predominant patterns or correlations between sensory attributes and chemical parameters, exerting a significant influence on the overall observed variability.

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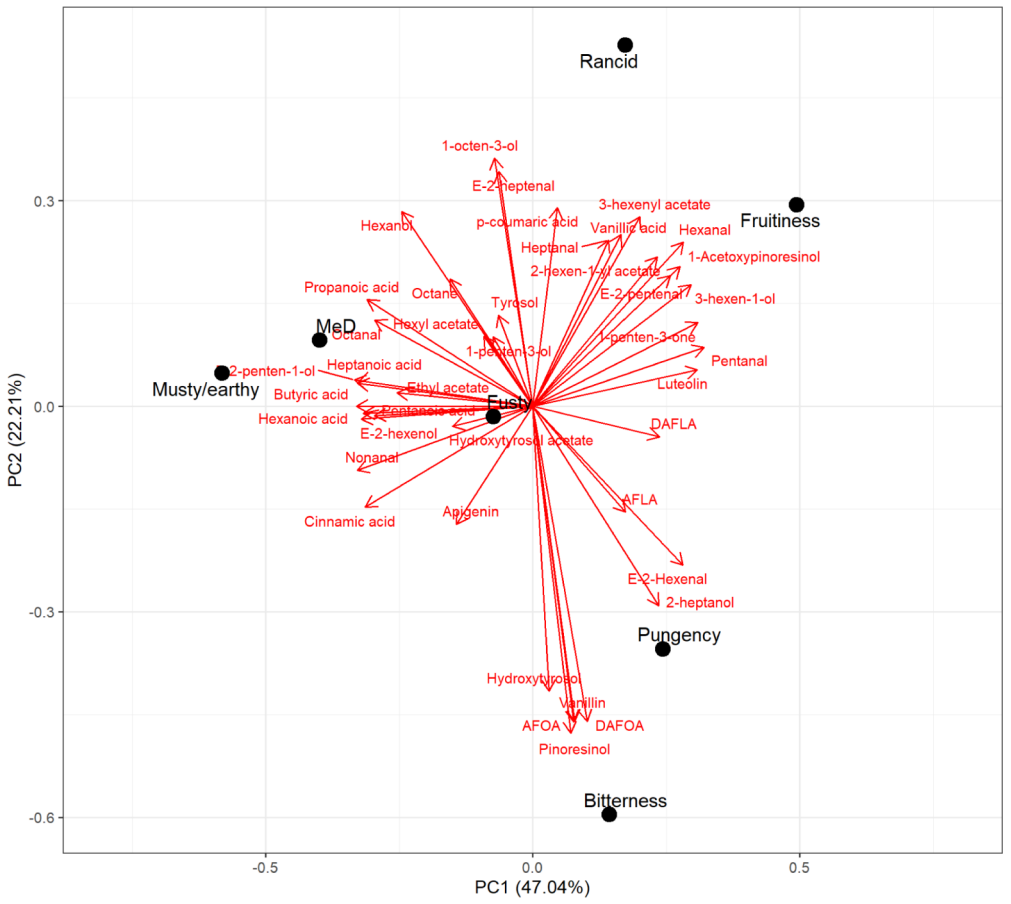

Figure 2. Principal Component Analysis (PCA) where a correlation matrix was used to represent associations between the evaluated VOCs and phenolic compounds. The PCA consisted of the loading plot of PC1 to PC2, the score plot, and the distribution of the samples in the consensus space. AFLA: aldehydic form of ligstroside aglycone; DAFLA: dialdehydic form of ligstroside aglycone; AFOA: aldehydic form of oleuropein aglycone; DAFOA: dialdehydic form of oleuropein aglycone; MeD: Median of defects.

Several observations were noted from Figure 1. First, the primary and secondary oxidation products (K_{232} and K_{268}, respectively), along with the peroxide value (PV), exhibit stronger associations with musty and earthy aromas, which is consistent with the findings of Cinquanta et al.[36] The musty defect is generally associated with storage of olives prior to milling under poor conditions (high humidity and anaerobic environments) which allow the development of microbial populations and fruit rotting.[19] Interestingly, this defect was detected in the current study, mainly in commercial virgin olive oil samples collected from supermarkets in both Israel and the US (samples set #2 and 3, see Material and Methods/olive oil samples) and not in samples originating from olives that were stored for a long time in unventilated sacks (sample set # 6). It is possible that olives used in producing commercial olive oil had a much stronger musty defect (i.e., longer storage time and higher storage temperatures) than the laboratory produced olive oil in which musty defect was not significant.

Free fatty acidity content is one of the most fundamental parameters used to evaluate the quality of olive oil.[37] Still, there are not many studies that examine the relationship between sensory defects and FFA. Our results showed that there was a strong correlation between them, especially for fusty defects (Figure 1). A slight association with PPP was observed for the rancid aroma. On the negative side of PC1, which accounts for the highest variance explained, off-flavors predominantly reside. Conversely, positive aromas are situated on the positive side of PC1, where bitterness and pungency show connections with higher induction time, elevated DAGs, and total phenolic content (TPC) (Figure 1). The relationship between sensory attributes and total phenolic compounds observed in this study agrees with previous studies, including those from Pedan et al., which reported the same trends.[38] In accordance with those standards, 72% of the tested VOO samples in the current study were considered nonbitter, 18% slightly bitter, 6% bitter, and 3% very bitter. Nevertheless, the correlation between TPC and bitterness is represented by an R^2 of 0.52 (Table S1). The increased phenol levels in those pungent and bitter oils correlated with increased oil stability, i.e., the induction time. Some phenolic compounds have high antioxidant activity, and hence, improve VOO stability.[39] Although fruitiness lacks direct correlation with any variable in the loading plot, it is closely positioned to positive attributes and is notably distant from off-flavors.

Phenolic Compounds, Volatiles, and Sensory Attributes. PCA was also conducted on a dataset comprising sensory attributes andphenolic compounds along with VOCs. In Figure 2, the analysis disclosed that 69.25% of the total variance in the data was elucidated by the principal components, with Component 1 accounting for 47.04% and Component 2 for 22.21%. Component 1 appeared to capture prevalent patterns or correlations between sensory attributes and chemical parameters, exerting a notable influence on the overall observed variability.

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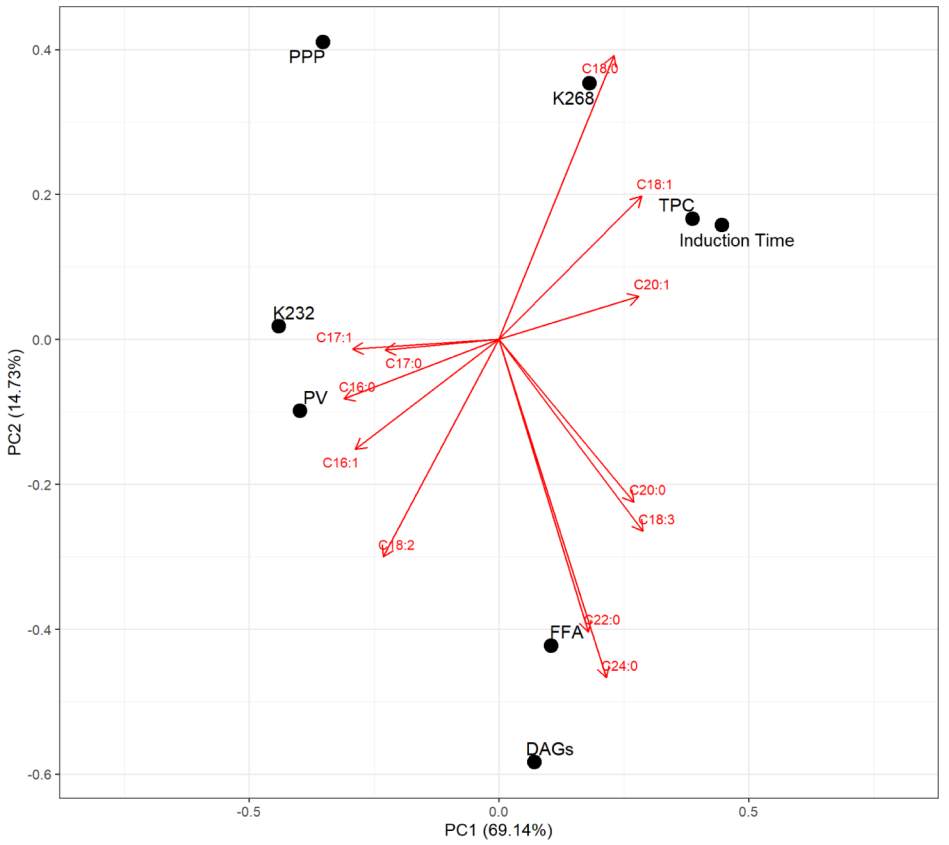

Figure 3. Principal Component Analysis (PCA) where a correlation matrix was used to represent associations between the evaluated fatty acids and the sensory attributes. The PCA consisted of the loading plot of PC1 to PC2, the score plot, and the distribution of the samples in the consensus space. DAGs: Diacylglycerols (%); FFA: Free fatty acidity (%m/m oleic acid); K_{232}: Specific absorbance at 232 nm; K_{268}: Specific absorbance at 268 nm; PPP: Pyropheophytins (%); PV: Peroxide value (meq O_2/kg); TPC: Total Phenol Content (mg of caffeic acid equivalent/kg olive oil).

As expected, phenolic compounds were correlated mainly with bitterness and pungency, while volatile compounds were associated with sensory defects and VOO fruitiness (Figure 2).

The fruitiness level was found in our study to be correlated to hexanal levels (Figure 2). Hexanal is known for its positive contribution to VOO sensory attributes and its aroma described as green apple and grassy.[15] Previous studies showed that a lower amount of hexanal is associated with positive virgin olive oil flavor (green and grassy) in the early stages of olive oil flavor development.[40,41] In our study, hexanal was found to be correlated to the fruitiness level, as discussed in Figure 2. We did not observe a strong correlation between hexanal and defects. 1-Acetoxypinoresinol levels also correlated with oil fruitiness level (Figure 2). 1-Acetoxypinoresinol and pinoresinol degrade during fruit ripening and might describe better with "green oil" and less with "ripe".[42] Those lignans are transferred from the olive fruit during crushing and malaxing into olive oils due to their lipophilic character.[38,43] 3-Hexen-1-ol also correlated to VOO fruitiness (Figure 2) and was reported as one of the major components related to the "green fruity" aroma in VOO.[44]

We found a correlation between hydroxytyrosol, the aldehydic form of ligstroside aglycone, and the dialdehydic form of ligstroside aglycone with VOO bitterness which is consistent with the findings of Garcia et al., showing a significant correlation between the content of secoiridoid derivatives of hydroxytyrosol and VOO bitterness intensity.[45] Pinoresinol was also found to be positively correlated with bitterness. It is commonly known that the compound oleuropein contributes to the pungency of EVOO.[46,47] We found a correlation between pungency and the aldehydic form of oleuropein aglycone and the dialdehydic form of oleuropein aglycone, though both compounds showed a stronger correlation to bitterness. We also observed a strong correlation between 2-heptanol and pungency; however interestingly, this compound is generally known as a source of mold-humidity sensory defect.[48]

Fusty defects are caused by esters and acids formed when olives are stored in piles that have undergone anaerobic fermentation. Butyl acetate and ethyl propanoate are generally known to be responsible for this defect.[49] Propionic acid was reported in the past to be associated with fusty sensory defect, though it also appeared to be associated with a musty sensory defect in this study.[16] Other compounds, such as heptanoic acid and butyric acid, were also found to correlate with musty and earthy defects.

Quality Measurements and Fatty Acid Profile. Chemical parameters and evaluated fatty acids are represented in Figure 3—PCA, following the computation of a correlation matrix to gauge their interrelationships. The analysis revealed that 83.87% of the overall variability is explained by the principal components, with Component 1 clarifying 69.14% and Component 2 elucidating 14.73% of this variance. Component 1 likely amalgamates sensory attributes and fatty acid profiles that significantly contribute to the dataset's variability, while Component 2 captures additional variability not fully accounted for by Component 1.

In Figure 3, the peroxide value and primary oxidation products display positive correlations with C16:0, C17:0, and C17:1. FFA exhibited associations with saturated C22 and C24

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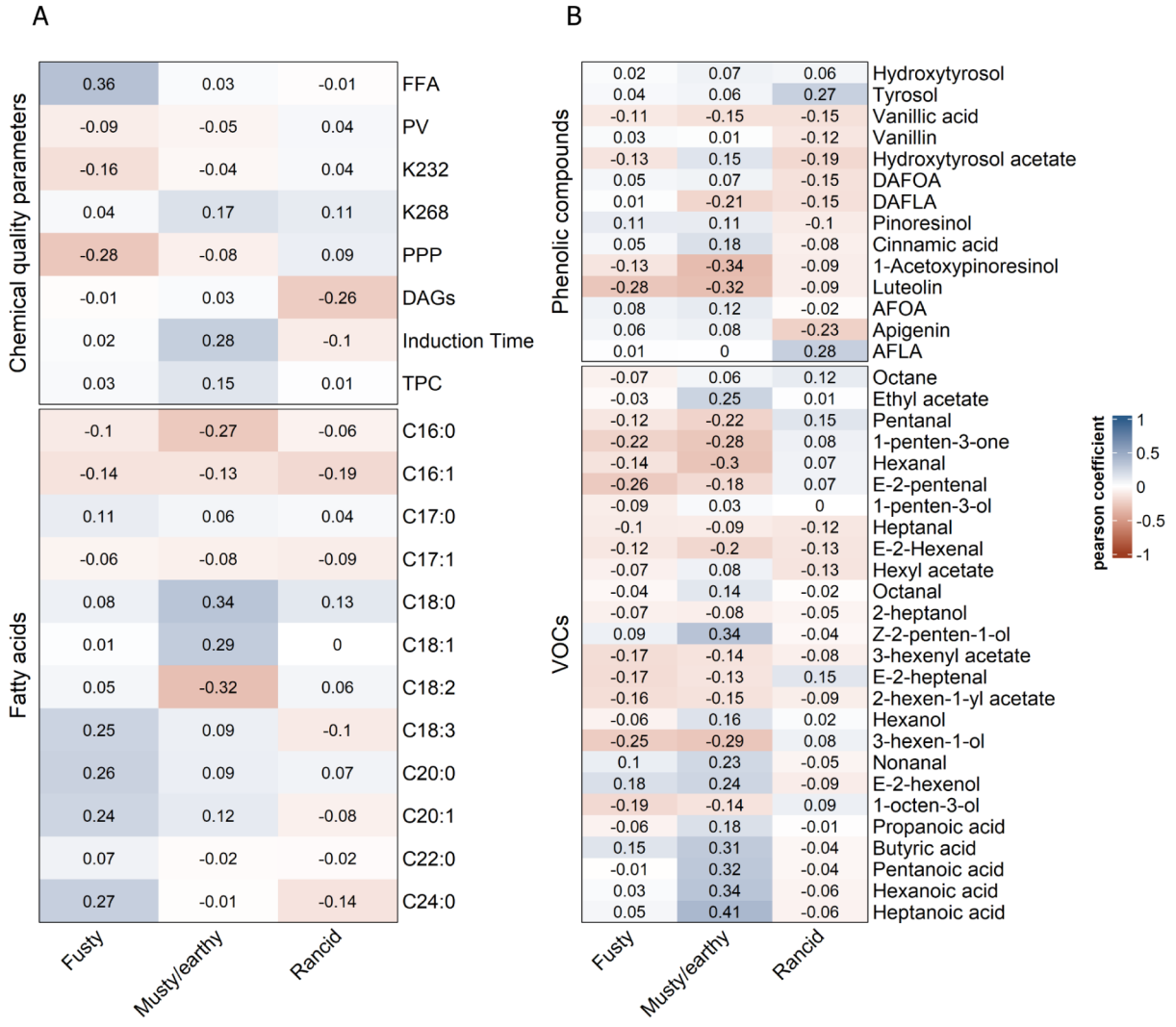

Figure 4. Heatmap representing Pearson's correlation coefficient between chemical quality parameters and fatty acids (Figure 4A) and VOCs and phenolic compounds (Figure 4B). DAGs: diacylglycerols (%); FFA: free fatty acidity (%m/m oleic acid); K_{232}: Absorbance at 232 nm; K_{268}: Absorbance at 268 nm; PPP: Pyropheophytins (%); PV: Peroxide value (meq O_2/kg); TPC: Total Phenol Content (mg of caffeic acid equivalent/kg olive oil). AFLA: Aldehydic form of ligstroside aglycone; DAFLA: Dialdehydic form of ligstroside aglycone; AFOA: Aldehydic form of oleuropein aglycone; DAFOA: Dialdehydic form of oleuropein aglycone.

fatty acids and elevated DAGs. Both FFA and DAGs are products of fatty acid hydrolysis, therefore, it is reasonable that they are correlated. Long-chain monounsaturated fatty acids, such as eicosenoic acid (C20:1) and oleic acid (C18:1), demonstrated positive correlations with heightened total phenol content and extended induction time. This finding is not surprising since C18:1 is considered relatively stable and is known to be as an important component in reducing VOO oxidation.[20] Remarkably, a high stearic acid level strongly correlated with increased secondary oxidation products. PPP appeared unaffected by variations in fatty acid composition. These new insights show the interplay between lipid profiles, oxidative stability and freshness markers such as DAGs and PPP.

Sensory Defects and Their Relationship with Chemical Parameters, Fatty Acids, Volatiles, and Phenolic Compounds. As shown in Figure 4A, there is a positive correlation between the fusty defect and FFA (correlation coefficient 0.36) and fatty acids C18:3, C20:0, C20:1, and C24:0, with a low correlation values of 0.25, 0.26, 0.24, and 0.27, respectively. The "fusty" attribute in olive oils is often associated with the growth of microorganisms and the breakdown of olive pulp, leading to the development of unpleasant flavors.[49,50] There is no direct evidence suggesting that it is caused by a higher presence of long-chain fatty acids; instead, the fusty defect is more closely related to the overall quality of the olives and the conditions under which they are stored and processed.[50,51] In contrast, the musty/earthy defect shows a negative correlation with C18:2 (0.32) and positive correlations with fatty acids C18:0 (0.34) and C18:1 (0.29), as well as with induction time (0.28). However, rancidity does not seem to have a strong correlation with any of the evaluated chemical parameters and fatty acids, apart from a slight negative correlation with DAGs (0.26).

In general, rancidity defects exhibited a much stronger correlation with volatiles and phenolic compounds (Figure 4B) compared to chemical quality parameters (FFA, PV, K232, K268, PPP, DAGs, induction time, and TPC) and fatty acids (Figure 4A). Luteolin, (*E*)-2-pentenal, and 3-hexen-1-ol showed a negative correlation with the fusty attribute. The musty/earthy defect positively correlated with heptanoic acid (0.41), (*Z*)-2-penten-1-ol (0.34), hexanoic acid (0.34), pentanoic acid (0.32), butyric acid (0.31), ethyl acetate (0.25), (*E*)-2-hexenol (0.24), and nonanal (0.23). Additionally, negative correlations were

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found for 1-acetoxypinoresinol (0.34), luteolin (0.32), hexanal (0.3), 3-hexen-1-ol (0.29), 1-penten-3-one (0.28), pentanal (0.22), and DAFLA (dialdehydic form of ligstroside aglycone) (0.21). Butyric acid was found in the current study to be correlated to musty/earthy sensory defect (Figure 2), opposing previous study that found this compound responsible for VOO winey-vinegary defects.[52] However, the correlation coefficient was relatively low (0.25, Figure 4B), which is too low to be used as a chemical marker for this defect. The compounds that had the highest positive correlations with rancidity were tyrosol (0.27) and AFLA (aldehydic form of ligstroside aglycone) (0.28). There is evidence that some phenolic compounds, such as tyrosol, and oxidized derivatives of secoiridoids, remain in the oil mostly in unchanged form during storage.[53] This might indicate the poor antioxidant activity of these compounds.[54]

Butyric, pentanoic, hexanoic, and heptanoic acids are linked to the development of off-flavors in olive oil, contributing to sensory defects, such as musty or earthy characteristics. Butyric acid, a short-chain fatty acid, has a strong, unpleasant smell reminiscent of rancid butter or vomit and can develop in olive oil due to anaerobic fermentation and poor postharvest storage conditions. Pentanoic acid (valeric acid) has a pungent, unpleasant odor that can contribute to musty or rancid flavors in olive oil, often resulting from microbial activity and improper handling. Hexanoic acid, known for its sour, cheesy, and sweaty odor, can contribute to undesirable sensory attributes in olive oil, indicating microbial contamination or spoilage. Heptanoic acid is associated with musty or earthy off-flavors in olive oil and often points to oxidative degradation or microbial activity.[55−58]

Generally, phenolic compounds are negatively correlated with the increase in rancidity, which is consistent with studies by Hrncirik and Fritsche, Nieto et al., and Pierguidi et al.− indicating that a high concentration of phenolic compounds is associated with greater oxidative stability and reduced oxidative lipid deterioration, thereby preventing the development of sensory defects such as rancidity.[59−61] As anticipated, the rancid oil (Figure 1C) exhibits a very low phenol content, a result of the autoxidation process that causes this defect and leads to the degradation of phenols.[62]

The compounds that were generally more correlated with the presence and level of defects (MeD) in VOO samples were ethyl acetate (0.41), AFLA (0.35), and octane (0.35) (Figure 4B). These values are too low to be used as sole chemical indicators for sensory defects; instead, their combination needs to be considered. Ethyl acetate is generally related to a "winey-vinegar" off-flavor, while octane is related to a fusty sensory defect.[15,63] However, octane, at low levels, is related to the positive attribute of "green fruitiness".[64]

Development of Prediction Model for Sensory Defects. Defects evaluation in olive oil is crucial for maintaining its quality and ensuring consumer satisfaction. In this context, a Random Forest model can be an effective tool for classification and prediction tasks. For tasks with two classes (defective and nondefective oil), accuracy provides valuable insights. The confusion matrix (Table 1) offers a comprehensive assessment, showing the types of errors made (false positives or negatives) with columns representing predicted values and rows representing actual values. In this work, accuracy quantifies the proportion of correct predictions of oil defects. Sensitivity measures the classifier's ability to detect positive examples, while specificity measures its accuracy in identifying negative instances. Integrating these metrics gives a comprehensive understanding of the algorithms' performance. Accuracy, sensitivity, and specificity range from 0 to 1, where higher values indicate better performance. Accuracy values above 0.8 are generally considered good; sensitivity values above 0.7 indicate strong detection of true positives, while specificity values above 0.7 indicate strong identification of true negatives. High values for these metrics suggest effective defect detection in oil. The Kappa value measures inter-rater reliability, ranging from −1 (total disagreement) to 1 (perfect agreement).[65]

Table 1. Statistics and Confusion Matrix Obtained from the Random Forest Model[abcdefgh]

Statistics of the model		Confusion Matrix		
Accuracy	0.8667	Prediction	Reference	
Sensitivity	0.9394		Actual negative	Actual positive
Specificity	0.6667	Predicted Negative	31 (TN)	4 (FN)
Kappa	0.64	Predicted Positive	2 (FP)	8 (TP)

[a]Accuracy: quantifies the proportion of correct predictions of oil defects. [b]Sensitivity: measures the classifier's ability to detect positive examples. [c]Specificity: measures its accuracy in identifying negative instances. [d]Kappa: measures inter-rater reliability, ranging from −1 (total disagreement) to 1 (perfect agreement). [e]TP (True Positive): the number of instances where the model correctly predicted the positive class. [f]FP (False Positive): the number of instances where the model incorrectly predicted the positive class, but the actual value was negative (Type I error). [g]TN (True Negative): the number of instances where the model correctly predicted the negative class. [h]FN (False Negative): the number of instances where the model incorrectly predicted the negative class, but the actual value was positive (Type II error).

The Random Forest model demonstrated good performance with an overall accuracy of 86.67% and high sensitivity (93.94%), indicating that it was effective at identifying oils with "No" sensory defects. However, the specificity (66.67%) was lower, suggesting some room for improvement in identifying oils with "Yes" defects. The Kappa value of 0.64 indicated substantial agreement between the predicted and actual classifications, adjusted for chance. Overall, the model appeared to be reliable but it could benefit from further refinement to improve the specificity. 80% of the samples in the dataset were used to build the model, while the remaining 20% were used to test it.

MeanDecreaseAccuracy (MDA in Figure 5A) measures how much the accuracy of the Random Forest model drops when the values of a particular variable are randomly permuted. If a variable is important, permuting its values will significantly reduce the model's accuracy. A high MDA value indicates that the variable is crucial for the model's predictive accuracy. MeanDecreaseGini (MDG in Figure 5B) measures the reduction in Gini impurity caused by each variable across all trees in the Random Forest. Gini impurity assesses the likelihood of incorrect labeling of a randomly chosen element. A high MDG value indicates that the variable is essential for creating splits that result in purer, more homogeneous nodes, improving the quality and structure of the decision trees.

As shown in Figure 5, luteolin, (*E*)-2-hexenal, 1-penten-3-one, and C18:0 emerge as pivotal factors in predicting the occurrence of defects within olive oil samples. These variables exhibit a pronounced influence, suggesting their significant contribution to the model's predictive accuracy. The prominence of these specific compounds underscores their potential as key indicators in discerning the quality and integrity of olive oil, providing

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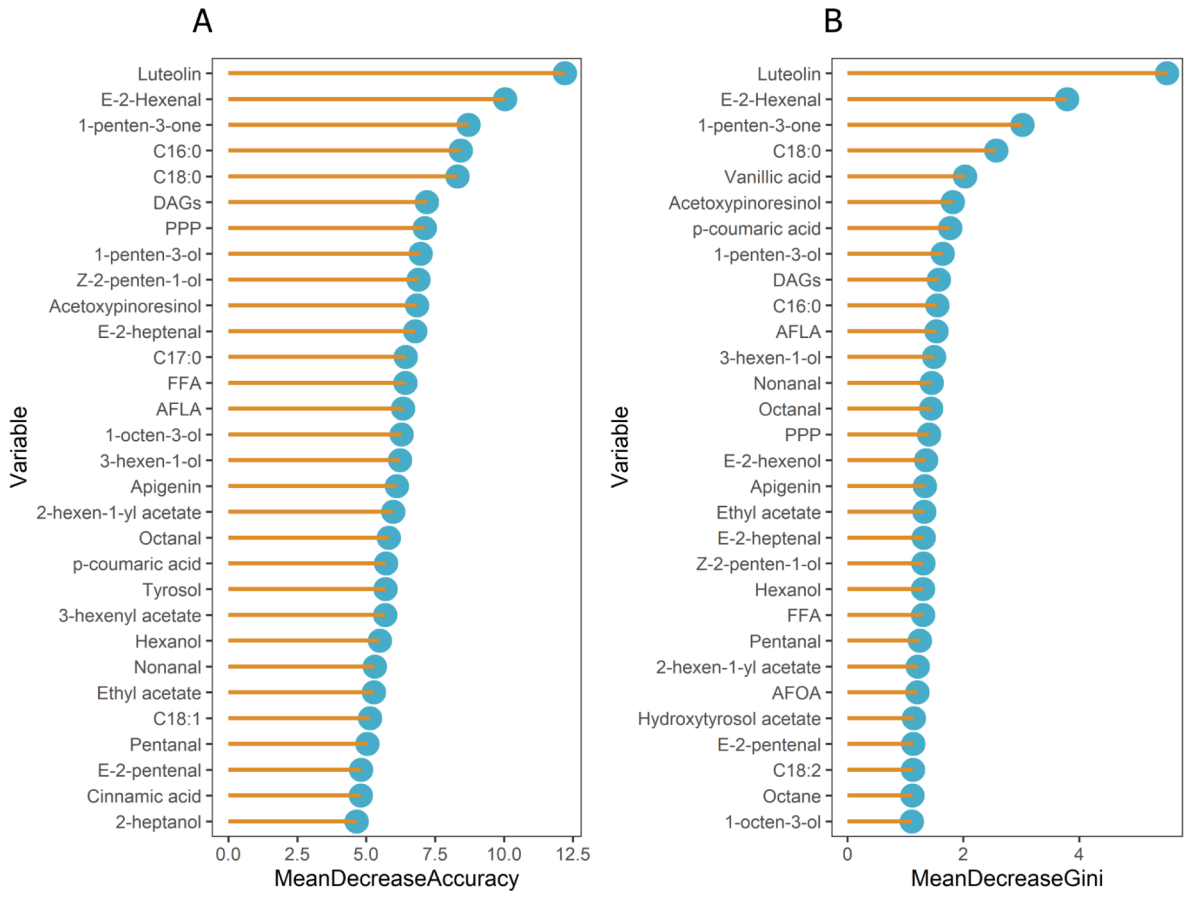

Figure 5. MeanDecreaseAccuracy and MeanDecreaseGini have been calculated after the Random Forest model where Defect has been used as the response variable, whereas the detected compounds have been used as predictor variables.

valuable insights for quality evaluation. Previous research by de los Angeles Fernandez et al., Kalogiouri et al., KadiroĞlu et al., and Tome-Rodriguez et al. efficiently detected luteolin, (*E*)-2-hexenal, and 1-penten-3-one as crucial compounds shaping the aroma of olive oil using random forest model.[66−69] The evaluated data suggest that these compounds are the best predictors when their values are below or above certain thresholds; a defect, such as rancidity, was more likely to occur in the oil.

Receiver operating characteristic (ROC) curve analysis evaluates the performance of binary classification models, particularly in distinguishing between two classes. The ROC curve is a graphical representation of the trade-off between the true positive rate (sensitivity) and the false positive rate (1−specificity) for different threshold values. The area under the ROC curve (AUC) is a summary measure of the performance of the classification model. AUC ranges from 0 to 1, where a value of 0.5 indicates a model with no predictive power (random guessing), and a value of 1 indicates a perfect classifier. Luteolin emerges as the best classifier, with the highest AUC, followed by 1-penten-3-one, C18:0, and (*E*)-2-hexenal.

Table 2 presents the threshold values at which the prediction model differentiates defective olive oil from nondefective oil. According to Figure 4, for luteolin, values below 12.02 mg/kg indicate a high likelihood of the oil being defective. Similarly, for 1-penten-3-one, a relative concentration of 648 μg/kg serves as the threshold, and for (*E*)-2-hexenal, the threshold is a relative concentration of 10512.5 μg/kg. Based on this work, if an oil has C18:0 content exceeding 2.15%, it may be more likely to be defective. However, we need to acknowledge that natural variables, such as genetics, climate, and maturation, have an influence on these compounds, and that this model will likely need improvement with more and diverse data.

Table 2. Cut-Off Value Obtained by the Receiver Operating Characteristic, Where the Prediction Model Distinguishes The two Classes of the Predicted Variable

Compound	Threshold	AUC
Luteolin	12.02 (mg/kg)	0.8188
1-penten-3-one	648 (μg/kg)	0.7293
C18:0	2.15%	0.7234
(*E*)-2-hexenal	10512.5 (μg/kg)	0.6727

By integration of analytical and sensory data, a predictive model can serve as a quality screening tool for olive oil. It can assist in the early detection of potential defects, allowing producers to take proactive measures to maintain product quality and consistency. Additionally, by providing objective assessments alongside traditional sensory evaluations, the model can help validate and reinforce the findings of sensory panels, thereby helping with sensory assessments. However, olive oil chemistry and sensory evaluations are complicated, and more data points are needed, especially from samples that cover natural variables, such as cultivars, maturation, farming and processing practices, and growing regions, to improve the accuracy and sensitivity of the model that can be reliably used to screen for defects.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jafc.4c06012.

Fatty acid profile data (XLSX)
Phenolics data (XLSX)
Volatiles data (XLSX)
Other chemical parameters data (XLSX)

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Notes

The authors declare no competing financial interest.

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