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Characterization of hazelnut kernel responses to brown marmorated stink bug [*Halyomorpha halys* Stal (Hemiptera: Pentatomidae)] infestations: Changes in bioactive compounds and fatty acid composition

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ABSTRACT

The brown marmorated stink bug (BMSB) (*Halyomorpha halys* Stal) has become a global threat to hazelnut yield and quality in the last decade by establishing a considerable population in hazelnut orchards in some countries. For the first time ever, we conducted an analysis on metabolic response of a necrotic hazelnut kernel, which is one of the most important damage types caused by BMSB feeding. In the present study, we investigated how hazelnut kernels respond to BMSB infestations in terms of the individual phenolics and fatty acid compositions in four different kernel types [i.e., control/healthy kernel (HK), whole of damaged kernel (WDK), healthy part of damaged kernel (HPDK), necrotic part of damaged kernel (NPDK)]. Individual phenolics were significantly affected by BMSB. Especially, epicatechin and catechin from flavan-3-ols, rutin from flavonol, and caffeic from phenolic acids increased significantly in kernel injured by BMSB. Major fatty acids were significantly affected by BMSB, except for palmitic. Oleic acid decreased in kernel injured by BMSB (WDK, HPDK and NPDK) compared with the HK, while palmitic, stearic, and linoleic acids increased. As from our results, it was revealed that BMSB affected the secondary metabolites in hazelnut and had a remarkable effect on epicatechin, rutin, caffeic acid and *p*-coumaric acid.

1. Introduction

The brown marmorated stink bug (BMSB), *Halyomorpha halys* (Stål) (Hemiptera: Pentatomidae), an invasive pest native to Asia, was first recorded in Pennsylvania, USA, in 1996 (Hoebeke and Carter, 2003). By the year 2020, it had spread to 46 states in the USA and 4 provinces in Canada (StopBMSB, 2020). It was discovered in Europe for the first time in 2004 in Switzerland (Haye et al., 2015) and was afterwards recorded in many other European countries (Maistrello et al. 2018), in Türkiye (Cerci and Kocak, 2017) and the Caucasus (Musolin et al., 2018). The lack of natural enemies, worldwide trade and climate change are among the reasons that contribute to the insect's rapid spread and invasive nature.

The BMSB is a polyphagous pest with a wide host range (~300 plant species), including agricultural crops such as fruits, tree nuts, field crops, vegetables and ornamental plants. The potential to damage agricultural crops is quite high (Nielsen and Hamilton, 2009). By sucking and piercing fruits, the nymphs and adults of BMSB cause economic damage, rendering it unmarketable and resulting in decreased yield and quality (Lee et al., 2013). BMSB populations are supported by natural vegetation, and their high flight and reproductive capacity allow for quick invasion of the region, a significant economic impact on crops, and population establishment in new areas (Rice et al., 2014; Nielsen et al., 2016).

Abbreviations: BMSB, Brown marmorated stink bug; HK, Control/healthy kernel; WDK, Whole of damaged kernel; HPDK, Healthy part of damaged kernel; NPDK, Necrotic part of damaged kernel.

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BMSB has become a global threat to hazelnuts in the last decade by establishing a considerable population in hazelnut orchards in countries such as USA (Hedstrom et al., 2014), Italy (Bosco et al., (2018)), Georgia (Murvanidze et al., 2018) and Türkiye (Ozdemir and Tuncer, 2021). Especially in Türkiye, which is the world's largest hazelnut producer (62%) and exporter (~75%) (FAO (2022)), it has expanded throughout the Black Sea coastline, where hazelnut cultivation is dense, like west of Istanbul and east of Artvin, from its first discovery until now (Ozdemir and Tuncer, 2021; Ak et al., 2023). The potential distribution map prepared by taking the BMSB's ecological requirements into consideration indicates that the most favorable distribution area for this insect in Türkiye is the coast (Haye et al., 2015; Kistner, 2017), and the bug completes its entire life cycle on the hazelnut, the region's cultivated predominant plant. Its nymphs and adults cause different types of injury depending on the stage of the nut, either by sucking or piercing the hazelnut. The feeding could cause blank nuts during shell expansion, malformed/shriveled kernels throughout kernel development, and necrotic/corked kernels throughout the kernel maturing/nearly mature stage (Hedstrom et al., 2014). This invasive species, which has a high reproductive ability, causes a significant increase in damage in the short term and thereby lead to significant economic losses (Ozdemir and Tuncer, 2021; Ak et al., 2023), in addition to the kernel quality problems caused by *Palomena prasina* (Hemiptera: Pentatomidae) (Ak et al., 2018), which is another bug species causing damage to hazelnut. Injured kernels have distinct characteristics like changes in color form and aroma as compared to healthy kernels. They are mostly used in hazelnut flour production. Hazelnut exporters are struggling to market products with lower internal quality, and this causes them to lose economically (Tuncer et al., 2005).

The watery saliva of some Hemiptera insects, such as BMSB, serves as a vehicle for the transmission of hydrolyzing enzymes, including protease, amylase, esterase, and lipase (Vaccino et al., 2008). Injecting toxic saliva of stink bugs into plant tissues results in further tissue injury, discoloration in necrotic kernels, and even abortive nut formation (Ni et al., 2010; Silva et al., 2012). Higher plants that have been infested by pests as a result of such circumstances possess several defense mechanisms (Yactayo-Chang et al., 2020). Many plants produce a wide range of secondary metabolites, such as terpenoids, phenols, anthocyanins, quinones, and alkaloids, which have hazardous, repellant, and/or anti-feedant impacts on herbivorous insects (War et al., 2012). The jasmonate pathway regulates phenolic induction in plants. It has been reported that the saliva secreted by BMSB during fruit damage reveals jasmonate-inducible genes and activates the jasmonate pathway, resulting in an increase in phenolic content (Peiffer and Felton, 2014). Higher phenolic content has been reported in hazelnut kernel (Turan, 2021) caused by green shield bug, and fruit species such as blueberry (Zhou et al., 2016), strawberry (Weber et al., 2021) and olive (Ivancic et al., 2022) damaged by BMSB. Flavan 3-ols such as catechin and epicatechin, act as an anti-feedant against some insects, and their levels rise in response to insect damage (War et al., 2012; Weber et al., 2021; Li et al., 2023). There is a significant correlation between biotic stress factors like insect infestation and antioxidant activity in plants (Reyes et al., 2007). The infestation of various pests such as *P. prasina* and *Curculio nucum* L. (Coleoptera: Curculionidae) on hazelnut has been reported to increase antioxidant enzyme activity (Ozdemir et al., 2023; Li et al., 2023). Furthermore, fatty acids, particularly oleic acid, play a crucial function in plant stress resistance. Indeed, it was revealed in several studies that the oleic acid content of hazelnuts decreased against insect infestation while the linoleic and linolenic acid concentrations increased (Bouali et al., 2013; Memoli et al., 2017).

For the first time ever, we conducted an analysis of the metabolic response of hazelnut kernels to the damage caused by BMSB feeding. The damage has previously not been thoroughly studied and reported. In the present study, we investigated how hazelnut kernels respond to BMSB infestations in terms of the bioactive compounds, individual phenolics, and fatty acid compositions. We also investigated whether the feeding of this invasive pest affected the entire kernel or just the part where the necrotic wound was located.

2. Material and methods

2.1. Plant materials

Plant materials studied consisted of the Palaz hazelnut cultivar (*Corylus avellana* L.), which is commonly grown in Türkiye. Fig. 1 shows the climatic data for the study region.

2.2. Reagents and standards

4-Aminobenzoic acid (≥99%), (+)-catechin (≥99%), caffeic acid (≥98%), (-)-epicatechin (≥90%), *p*-coumaric acid (≥98%), protocatechuic acid (97%), chlorogenic acid (≥95%), ferulic acid (99%), rutin (≥95%), potassium methoxide solution (95%), sulfuric acid (25%), and FAME standard mix obtained from Sigma-Aldrich. 4-Hydroxybenzoic acid (≥99%) was purchased from Carl Roth.

2.3. Obtaining necrotic kernels and growing conditions

In order to obtain the necrotic hazelnut kernels caused by BMSB and healthy kernels, 20 'ocak' (multi-stemmed bushes) were selected in a 12-year-old orchard established with the "Palaz" cultivar. Two branches containing at least 10 hazelnut clusters were determined from each "ocak". These branches were caged as of May 1, 2021, with 50 × 100 cm fine mesh cages (a total of 40 cages). These two exclusion cages were set on two different branches of each chosen "ocak" and appointed as controls (20 cages for the healthy/no insect-damaged kernels) and cages with insects (20 cages for obtaining the necrotic kernels). On June 25, 2021, 4 adult BMSBs were placed in each cage assigned "with insect" and exposed to the bug feeding. The BMSB adults collected from the selected orchard for the cages in Ardeşen district in Rize province (41°13′47.82 N latitude, 41°5′47.96 E longitude, and 144 m) were kept

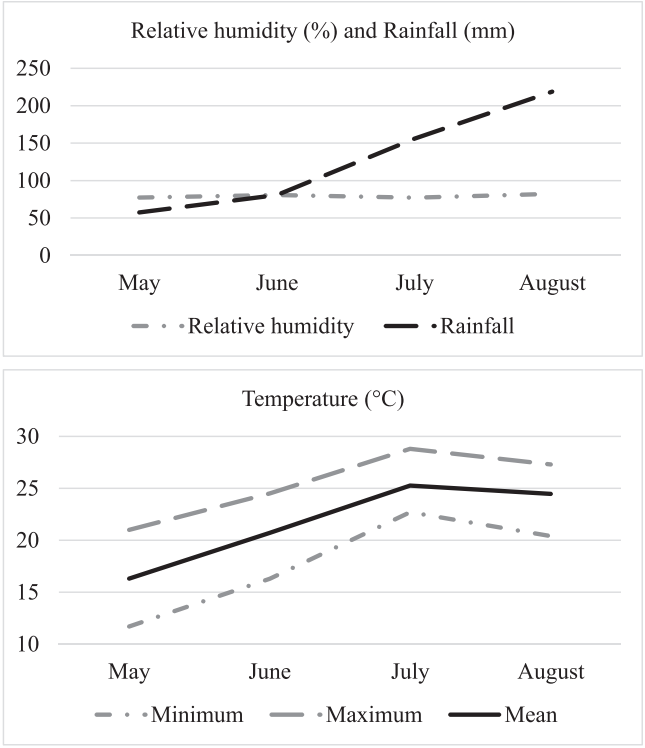

Fig. 1. Relative humidity (%), rainfall (mm), and temperature values (°C) during nut development.

in the cages until harvest (Ozdemir et al., 2023). At harvest (on August 3), the hazelnuts in the cages were hand-harvested and were transported to the laboratory labeled as insect-damaged or healthy.

2.4. Preparing hazelnut kernels for analysis

The hazelnuts transported to the laboratory were placed on the bench under ventilated laboratory conditions to dry at 25 ± 1 °C and 60–70% humidity for 10 d and removed by hand from their husks. After drying (approximately moisture 6%), the specimens were kept at + 4 °C until analysis. The kernels were separated into four groups [i.e., control/healthy kernel (HK), whole of damaged kernel (WDK), healthy part of damaged kernel (HPDK), necrotic part of damaged kernel (NPDK)]. Approximately 100 g of the kernels in each group were obtained for further analysis. The target parts of the hazelnut kernels were scraped with a scalpel and whole kernels/target parts placed in sterile tubes for analysis.

Chemical analyses were performed in healthy/no insect-damaged kernels, whole of damaged kernel, healthy part of damaged kernel, and necrotic part of damaged kernel (Fig. 2). Individual phenolics were determined in defatted kernel samples. Oil extraction from the kernel samples was performed by using the Soxhlet method. Obtained oils were used to determine the fatty acids composition of samples.

2.5. Individual phenolic compounds

A defatted hazelnut sample (3 g) was extracted along with 15 mL methanol. Prepared solution was centrifuged at 5000 rpm for 15 min, and then kept at 4 °C. The individual phenolics of defatted hazelnut kernel were detected by high-performance liquid chromatography (HPLC) by modifying the method of Altun et al. (2013). HPLC (Thermo Scientific, Ultimate 3000, USA), Hypersil GD phenyl column (Thermo Scientific, Waltham, MA) and UV detector (DAD-3000) (at 280 nm) were used to determine the individual phenolics of defatted hazelnut kernel. Prepared extracts were filtered through a 0.45 μm membrane filter. Methanol (A) and ultrapure water 2.5% formic acid (B) were used as mobile phases. The flow rate, injection volume and total analysis time were 1 mL min^{-1}, 20 μL and 50 min, respectively. 4-Aminobenzoic acid, (+)-catechin, protocatechuic acid, caffeic acid, 4-hydroxybenzoic acid, (−)-epicatechin, *p*-coumaric acid, chlorogenic acid, ferulic acid, and rutin as individual phenolics were detected. 4-Aminobenzoic acid and ferulic acid were used as internal standards. Curve equations of individual phenolics detected are shown in Table S1. The results were expressed as mg kg^{-1}.

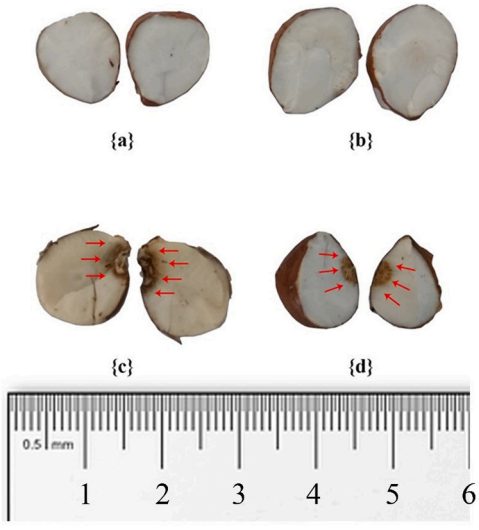

Fig. 2. a, b) healthy kernel, **c, d)** Whole of damaged kernel (necrosis is shown by black arrows, and the healthy part represents the remaining tissue in the kernel).

2.6. Fatty acid composition

The fatty acid composition was detected by GC (gas chromatography) by modifying the method of Karakaya (2023). GC (GC-2010 Plus; Shimadzu, Kyoto, Japan), capillary column (TR-CN100, 100 m × 0.25 mm × 0.2 μm; Teknokroma Analítica S.A., Barcelona, Spain) and flame ionization detector (FID) were used to determine the fatty acid composition of hazelnut oils. The oils' fatty acids content was determined using the DGF standard methods C-VI 10 a and C-VI 11 d. The oils obtained from hazelnut kernels were derivatized to fatty acid methyl esters using potassium methoxide solution in methanol. Then, for neutralization, 25% sulfuric acid was added (DGF, 1998). Prepared samples were injected into a capillary column. The column temperature was set at 140 °C, raised to 240 °C with a rate of 4 °C min^{-1} and held at 240 °C for 20 min. The detector and injector temperatures were 250 °C. The flow rate, injection volume and split ratio were 0.94 mL min^{-1}, 1 μL and 1:100, respectively. Helium was provided as the carrier gas. Fatty acids peaks were identified by comparing the retention time of fatty acid methyl esters (FAMEs) (Supelco 37 Component FAME Mixture, 47885 U, Merck, Germany). The results were expressed as percentage of the peak area of identified fatty acids.

2.7. Statistical analysis

The data were evaluated using JMP 14.0 (trial) statistic packet program. Differences were determined with LSD multiple comparison test at %5 significant level.

3. Results

3.1. Individual phenolics

The changes elicited by BMSB on individual phenolics was significant ($p < 0.05$). 4-Aminobenzoic acid, protocatechuic acid, (+)-catechin, caffeic acid, *p*-coumaric acid and rutin were significantly increased in damaged kernel (WDK, HPDK and NPDK) as compared to HK. The highest, protocatechuic acid (1.47 mg kg^{-1}), caffeic acid (19.16 mg kg^{-1}) and rutin (17.73 mg kg^{-1}) were determined in NPDK, with the lowest in HK (0.48, 1.02 and 0.89 mg kg^{-1}, respectively). NPDK had the highest 4-Hydroxybenzoic acid (0.91 mg kg^{-1}) and (−)-epicatechin (50.19 mg kg^{-1}), while HPDK had the lowest (0.22 and 13.73 mg kg^{-1}, respectively). The highest 4-Aminobenzoic acid (3.54 mg kg^{-1}) and (+)-catechin (36.31 mg kg^{-1}) were determined in HPDK, the lowest in HK (1.54 and 30.18 mg kg^{-1}, respectively). HPDK had the highest chlorogenic acid (1.76 mg kg^{-1}) and ferulic acid (7.83 mg kg^{-1}), NPDK had the lowest (0.41 and 5.81 mg kg^{-1}, respectively). The highest *p*-coumaric acid (27.72 mg kg^{-1}) was found in WDK, the lowest in HK (3.81 mg kg^{-1}). The rutin, caffeic acid, *p*-coumaric acid, 4-Hydroxybenzoic acid, protocatechuic acid and (−)-epicatechin contents of the NPDK kernel injured by BMSB also increased by 19.9, 18.8, 5.3, 4.0, 3.1 and 2.3 times, respectively, as compared with the HK (Table 1).

3.2. Fatty acids composition

Ten fatty acids were detected in the analyzed kernels. Oleic, linoleic, palmitic and stearic were determined as major fatty acids, with palmitoleic, heptadecanoic, *cis*-10-heptadecenoic, arachidic, *cis*-11-eicosenoic and linolenic as minor fatty acids. BMSB significantly affected the oleic, linoleic, stearic and arachidic content. However, it had no effect on palmitic acid, palmitoleic acid, heptadecanoic acid, *cis*-10-heptadecenoic acid, *cis*-11-eicosenoic acid, or linolenic acid ($p < 0.05$). HK had the highest oleic (83.99%) and the lowest linoleic (7.01%). On the contrary,

Table 1
Individual phenolics of healthy and insect-damaged kernels in Palaz hazelnut cultivar.

Individual phenolic compounds (mg kg^{-1})	HK	WDK	HPDK	NPDK	Significance	LSD (0.05)
4-Aminobenzoic acid	1.54dz	1.88c	3.54a	2.90b	* **	0.25
Protocatechuic acid	0.48d	1.29b	1.09c	1.47a	* **	0.08
4-Hydroxybenzoic acid	0.23c	0.70b	0.22c	0.91a	* **	0.08
(+)-Catechin	30.18c	30.55c	36.31a	34.52b	* **	0.91
Chlorogenic acid	1.47b	1.09c	1.76a	0.41d	* **	0.22
Caffeic acid	1.02c	1.04c	3.12b	19.16a	* **	1.40
(–)-Epicatechin	21.50c	35.50b	13.73d	50.19a	* **	2.98
p-Coumaric acid	3.81d	27.72a	10.94c	20.21b	* **	2.35
Ferulic acid	6.48b	7.01b	7.83a	5.81c	* **	0.57
Rutin	0.89c	9.41b	1.60c	17.73a	* **	1.17

z: Differences among mean values shown on the same row with the same letter are not significant ($p < 0.05$). * ** : significant at $p < 0.001$
HK: Healthy kernel; WDK: Whole of damaged kernel; HPDK: Healthy part of damaged kernel; NPDK: Necrotic part of damaged kernel

WDK had the lowest oleic (81.43%) and the highest linoleic (9.45%). The highest stearic (3.04%) and arachidic (0.18%) were determined in NPDK, the lowest in WDK and HK (2.71% and 0.13%, respectively; Table 2).

4. Discussion

All plants have sufficient capacity to increase secondary metabolite production as a defensive strategy against biotic and abiotic stressors (Yactayo-Chang et al., 2020). Secondary metabolites have the potential to both disrupt and deter herbivore insects. Plants react against many insects by boosting the phenolic and flavonoid production in response to the stress, attempting to prevent insects' damage of feeding on various fruits (War et al., 2012; Weber et al., 2021).

The jasmonate pathway regulates phenolic induction in plants. It has been observed that BMSB saliva released after fruit damage reveals jasmonate-inducible genes and increases phenolics, stimulating the jasmonate pathway (Peiffer and Felton, 2014). Additionally, stink bugs infest plant tissues and cause an increase in phenolic compounds by releasing proteinases that break down proteins into amino acids such as tyrosine, phenylalanine, and tryptophan (Buchanan et al., 2015). Flavonoids are also known as plant defense molecules (Soriano et al., 2004). Flavonoids that impact plant flavor and nutritional value and can serve as toxins to protect the plants by repelling sucking insects (Mierziak et al., (2014)).

Our study showed that BMSB has a considerable impact on individual phenolics. In particular, the 4-Aminobenzoic acid, (+)-catechin, protocatechuic acid, caffeic acid, (−)-epicatechin, *p*-coumaric acid, and rutin contents were significantly higher than HK (control) in the kernels with BMSB feeding damage (WDK, HPDK, and NPDK) (Table 1). Individual phenolics have been found to be higher in fruit with BMSB feeding damage than in healthy fruit in blueberry (Zhou et al., 2016), strawberry (Weber et al., 2021), and olive (Ivancic et al., 2022). Furthermore, (+)-catechin, (−)-epicatechin, *p*-coumaric acid, and ferulic acid were determined as major individual phenolics in the current study, as previously reported by other researchers in hazelnut (Jakopic et al., (2011); Wani et al., 2020). Of these, flavan-3-ols such as catechin and epicatechin act as nutritional inhibitors against some insects (*Curculio nucum*, *Euproctis chrysorrhoea* L., *Lymantria dispar* L. and *Operophtera brumata* L.) and their amounts increase against insect damage (War et al., 2012; Weber et al., 2021; Li et al., 2023). As a matter of fact, apple fruits with BMSB damage had higher catechin and epicatechin contents than healthy apples (Zamljen et al., 2021). Similarly, catechin and epicatechin (Veluri et al., 2004; Ullah et al., 2017), which have antifungal, antimicrobial, and insect repellent properties, were found to be higher in strawberries with BMSB feeding damage (Weber et al., 2021). Catechin and epicatechin from flavan-3-ols, and rutin from flavonol, which are key compounds, have been found to be significantly higher in damaged kernels caused by BMSB (WDK, HPDK, and NPDK) than in HK (control) in our study. It is assumed that they act as a deterrent for sucking insects, particularly epicatechin, catechin, and rutin, which are found in higher amounts in kernels with feeding damage (WDK, HPDK, and NPDK) than in HK. Flavonoids are also stress defense molecules in plants that protect the plant from pathogen harm (Winkel-Shirley, 2002; Soriano et al., 2004; Li et al., 2023). Reports that flavonoids in hazelnuts are potential compounds with a protective effect against *C. nucum* (Li et al. 2023) confirms this hypothesis. In addition, it was revealed that caffeic acid was higher in cultivars resistant to hazelnut aphid (*Myzocallis coryli* G.), and caffeic acid was produced against insect damage (Gantner et al., 2019). Similarly, the findings of our studies determined that damaged kernels (WDK, HPDK and NPDK) had higher caffeic acid content than HK (control).

Hazelnut is an important source of oil and rich in terms of fatty acids. Oleic is the major fatty acid in hazelnut. This is followed by linoleic, palmitic, and stearic acid, in that order (Balta et al., 2006; Cetin et al., 2020). In our current study, oleic, linoleic, palmitic and stearic acids

Table 2
Fatty acids composition of healthy and insect-damaged kernels in Palaz hazelnut cultivar.

Fatty acids composition (%)	HK	WDK	HPDK	NPDK	Significance	LSD (0.05)
Oleic acid	83.99a	81.43b	82.65ab	82.40ab	*	2.11
Linoleic acid	7.01c	9.45a	7.91b	7.87b	* **	0.41
Palmitic acid	5.64a	5.71a	5.91a	5.87a	ns	0.36
Stearic acid	2.72b	2.71b	2.84ab	3.04a	*	0.30
Arachidic acid	0.13b	0.15b	0.16ab	0.18a	*	0.03
Palmitoleic acid	0.16a	0.16a	0.17a	0.17a	ns	0.03
Linolenic acid	0.06a	0.07a	0.07a	0.07a	ns	0.02
Heptadecanoic acid	0.04a	0.05a	0.05a	0.05a	ns	0.02
cis-10-Heptadecanoic acid	0.06a	0.06a	0.06a	0.06a	ns	0.02
cis-11-Eicosenoic acid	0.17a	0.18a	0.18a	0.18a	ns	0.02

z: Differences among mean values shown on the same line with the same letter are not significant ($p < 0.05$). * : significant at $p < 0.05$; * ** : significant at $p < 0.001$; ns: not significant
HK: Healthy kernel; WDK: Whole of damaged kernel; HPDK: Healthy part of damaged kernel; NPDK: Necrotic part of damaged kernel

were determined as major fatty acids. In addition, biotic (pathogenic attack) (Memoli et al., 2017) and abiotic (low and high temperature, drought, and ultraviolet light) factors, genetic structure, ecological conditions, cultural practices, and technical practices all affect the composition of fatty acids in hazelnuts (Balta et al., 2006; Karakaya et al., 2023).

While the damage caused by BMSB on linoleic, stearic, and arachidic acid were found to be significant in this research ($p < 0.05$), the other fatty acids were not significantly affected. In the damaged kernel types (WDK, HPDK, and NPDK), oleic of the major fatty acids decreased while stearic and linoleic increased, compared to HK kernels (Table 2). The decrease in oleic acid content can be attributed by the conversion of oleic acid, which plays a significant role in the synthesis of linoleic and linolenic acid, into these acids (Bouali et al., 2013; Memoli et al., 2017). The decreased oleic content associated with increased linoleic and linolenic contents in damaged fruits suggests the key role of oleic acid metabolism in plant defense. Similarly, Memoli et al. (2017) reported low oleic, high linoleic, and linolenic acid in stink bug-damaged hazelnut kernels compared to healthy kernel. Turan (2021) found similar results on damaged kernel caused by *P. prasina* feeding in hazelnuts. Furthermore, Memoli et al. (2017) reported decreased palmitic, stearic, and heptadecanoic values in stink bug-damaged hazelnuts compared to healthy kernels, while finding higher arachidic and *cis*-11-eicosenoic values. Turan (2021) demonstrated a reverse effect in necrotic kernel caused by *P. prasina*. Both studies found that palmitoleic acid content were higher in damaged kernels.

The results obtained in the current study in terms of palmitic, stearic, and heptadecanoic were consistent with the findings of Turan (2021), while the results obtained in terms of arachidic and *cis*-11-eicosenoic in our study were consistent with the findings of Memoli et al. (2017). Some of the differences observed are thought to be attributable to hazelnut cultivar and insect species.

5. Conclusion

In the study, metabolic reaction of hazelnut against BMSB feeding damage (necrotic kernel) was examined in detail. Generally, individual phenolics were significantly increased in damaged kernels (WDK, HPDK and NPDK) compared to HK. Epicatechin from flavan-3-ols, rutin from flavonol, and caffeic acid from phenolic acids increased significantly in necrotic kernels. These compounds probably increased as a result of the hazelnut plant's natural defense mechanism against stress. BMSB significantly affected major fatty acids of kernel. Oleic acid decreased in damaged kernel compared with the HK (control). On the contrary, linoleic and stearic acids increased. These findings give us a better understanding of how hazelnut metabolically responds to BMSB damage and show that BMSB feeding damage has a significant effect, especially on epicatechin, rutin, caffeic acid, and *p*-coumaric acid.

CRediT authorship contribution statement

Ismail Oguz Ozdemir: Investigation, Visualization, Conceptualization, Methodology, Data analyzing, Supervision, Writing – original draft. **Orhan Karakaya:** Investigation, Visualization, Data analyzing, Writing – original draft. **Umut Ates**: Analysis, Data collections. **Burhan Ozturk:** Methodology, Supervision, Writing – review & editing. **Mansur Uluca:** Investigation, Samples collections. **Celal Tuncer:** Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

Data Availability

Since this article already contains all newly created data, data sharing is not applicable to it.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2023.105696.

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