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Ex situ volatile survey of ground almond and pistachio hulls for emission of spiroketals: Analysis of hull fatty acid composition, water content, and water activity

Noreen E. Mahoney [a], Wai S. Gee [a], Bradley S. Higbee [b], John J. Beck [a,*]

[a] Plant Mycotoxin Research, Western Regional Research Center, Agricultural Research Service, United States Department of Agriculture, 800 Buchanan Street, Albany, CA 94710, United States
[b] Paramount Farming Company, 33141 E. Lerdo Highway, Bakersfield, CA 93308, United States

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ABSTRACT

The spiroketal conophthorin has recently been implicated as an important semiochemical of the navel orangeworm moth (*Amyelois transitella*), a major insect pest to California tree nuts. Additionally, new evidence demonstrates that fungal spores in the presence of linoleic acid produce conophthorin. Numerous investigations have analyzed the volatile emissions of almonds and pistachios under varying conditions, yet there are few reports of conophthorin as a volatile component. Previous studies by our laboratories have suggested almond hulls may be a source of conophthorin production. Accordingly, the volatile emissions of ex situ almond and pistachio ground hulls were surveyed at several developmental stages. Each ground sample was analyzed at various intervals to determine if conophthorin was produced. The almond and pistachio samples were presumed to have a natural fungal bouquet present. Additionally, the fatty acid composition, water content, and water activity of the hulls were analyzed for each sample. Conophthorin and the structurally similar compound chalcogran were detected from almond hulls and shells, but not from the pistachio samples. The almond and pistachio hulls were investigated for four fatty acid components – palmitic, oleic, linoleic, and linolenic. The fatty acid composition of almond hulls varied greatly throughout the growing season, whereas the composition of pistachio hulls remained relatively constant. Both water content and activity were constant in early stages of almond growth then dropped in the later stages of hull split. Spiroketal emission along with other associated volatiles is discussed. This is the first report of the fatty acid composition, water content, and water activity of developing almond and pistachio hulls.

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1. Introduction

The structurally simple spiroketal conophthorin (7-methyl-1,6-dioxaspiro[4.5]decane, **1** in Fig. 1) has recently been reported as an active component in a blend of host plant volatiles that attract both male and female navel orangeworm (*Amyelois transitella*) moths (Beck et al., 2012a). *A. transitella* is a major insect pest that inflicts significant economic loss to California almonds, pistachios, and walnuts (Campbell et al., 2003). Moreover, *A. transitella* larvae are purported to vector toxigenic aspergilli to almonds (Palumbo et al., 2008). Yet, conophthorin and the isomeric chalcogran (2-ethyl-1,6-dioxaspiro[4.4]nonane, **2** in Fig. 1) have long histories as semiochemicals of scolytid beetles with insect and plant origins (Francke and Kitching, 2001). Compared to the history of these spiroketals and scolytid beetles, reports of conophthorin (**1**) and chalcogran (**2**) from almonds are relatively new. As an example, recent investigations reported compound **1** from almonds at hull split (Beck et al., 2012a) and both **1** and **2** from mechanically damaged almonds (Beck et al., 2008). More recent was a report of **1** and **2** from various fungal spores on fatty acids common to almond and pistachio (Beck et al., 2012b).

What was interesting regarding the recent detection of **1** and **2** from almonds (all components present – hull, shell, and kernel) was their lack of detection in a number of investigations that reported on the volatile emissions of almonds or pistachios under varying conditions. For instance, spiroketal **1** or **2** was not detected from the following: the vacuum steam volatiles of almond hulls (Buttery et al., 1980); in situ intact and undamaged almonds (Beck et al., 2009); ambient almond orchard volatiles (Beck et al., 2011a); intact ex situ *Pistacia* spp. (Roitman et al., 2011); and, almond kernels naturally contaminated with orchard fungi (Beck et al., 2011b).

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* Corresponding author. Tel.: +1 510 559 6154; fax: +1 510 559 6493.
E-mail address: john.beck@ars.usda.gov (J.J. Beck).

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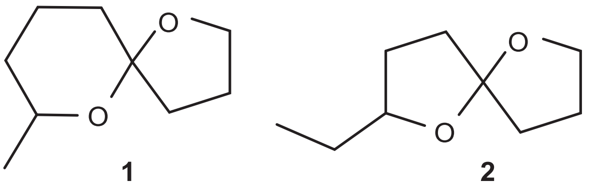

Fig. 1. Conophthorin (7-methyl-1,6-dioxaspiro[4.5]decane) (**1**) and chalcogran (2-ethyl-1,6-dioxaspiro[4.4]nonane) (**2**).

The present investigation was initiated to help delineate the true origin of conophthorin from almonds, and to determine if pistachios were a possible source. This is important for a number of reasons: the inconsistent detection of spiroketals in the aforementioned studies; the rich history of spiroketals and scolytid beetles; the recent assessment that conophthorin (**1**) is a semiochemical of *A. transitella*; and, the recent study that demonstrated spores produce both spiroketals (Beck et al., 2012b). Despite the mounting evidence, the question remains – is conophthorin produced by fungi, the host plant, or both? The fungal spore study demonstrated that spores were capable of producing both conophthorin (**1**) and chalcogran (**2**), but did not decisively eliminate the plant as an active participant – not just a carbon source for the spores.

Anecdotal evidence from previous volatile emission studies and preliminary exploratory experiments suggested we turn our attention to the hulls of almonds and pistachios as a possible source of compounds **1** and/or **2**. Thus, the objectives of this study were to: (1) monitor the volatiles emitted from ground almond and pistachio components, primarily the hulls, to determine a condition for consistent spiroketal production; (2) determine the corresponding fatty acid profiles of the hulls at progressive stages of hull development; and, (3) determine the water content and water activity of the hulls at the varying stages of hull development.

2. Results and discussion

The objectives of determining the relative fatty acid composition, water content, and water activity of the hulls were successfully met. Furthermore, both spiroketals were observed from ground almond hulls and shells at varying times and amounts (Table 1), yet no spiroketals were observed from the ground almond kernel treatments or any of the pistachio material. The objective of determining specific conditions for consistent spiroketal production was more elusive; however, based on our results various plausible mechanisms/conditions for spiroketal genesis can be considered.

The relative percentage of the four major fatty acids in the almond and pistachio hulls was evaluated at regular intervals throughout the growing season. The fatty acid data for almond hulls (Fig. 2) were surprising when compared to the fatty acid content of developing almond kernels (Soler et al., 1988). Several differences in fatty acid composition were noted. First, for hulls the major component was palmitic, whereas palmitic in kernels is on average the second lowest. In hulls, palmitic acid started at ca. 30% and steadily increased to ca. 46% of the fatty acid composition. This is in contrast to kernels where palmitic acid starts at 19% and decreases to ca. 7%. Second, oleic acid, normally the predominant fatty acid on average in kernels, starts as the lowest fatty acid in hulls at ca. 13% gradually increases to ca. 28% by August then decreases to 16% by mid-September. Third, linoleic acid, the second most predominant fatty acid in kernels, starts as the major component in hulls, decreases at the start of hull split, then increases slightly to about 20%. Finally, linolenic acid, which is a minor to trace component in kernel development shows as a consistent composition in hulls, starting off at ca. 25% and gradually decreasing to ca. 20% by mid-September.

The fatty acid composition in pistachio hulls also provided a distinct difference when compared to the fatty acid composition in the developing pistachio kernel (Chahed et al., 2006). Pistachio kernel fatty acid composition is similar to that of almond kernels. For example, oleic and linoleic also change relative percent compositions during the early stage of development to end with oleic acid as the highest (ca. 70%) and linoleic approximately the next highest at ca. 12%. Also in pistachio kernels, linolenic starts as a minor component and ends as a trace fatty acid, and palmitic gradually decreases from ca. 20% to ca. 12% of the composition (derived from Chahed et al., 2006 and Soler et al., 1988). The fatty acid composition of developing pistachio hulls (Fig. 3) was consistent in its relative percentages. Linoleic was the predominant fatty acid and showed a gradual decrease from ca. 45% in June to 34% in September. Palmitic was the second highest fatty acid with a slight increase from ca. 27% to ca. 30%. Oleic and linolenic were approximately equal; with oleic slightly favored over linolenic, both starting at ca. 15% and increasing to ca. 18%. Unlike almond hulls and kernels, or pistachio kernels, the pistachio hull fatty acid compositions did not undergo any crossing of relative percentages.

The water content and water activity (a_w) of the developing almond and pistachio hulls (Figs. 4 and 5) were measured to provide an overview of the growth environment for ubiquitous fungi present on the intact nuts. For both matrices there was a high Pearson product-moment correlation coefficient value between water content and a_w. For almond the Pearson's $r = 0.94$ and for pistachio $r = 0.96$. Water content is an important factor for water activity, a vital parameter for fungal growth (Ayerst, 1969). Non-xerophilic fungi prefer a_w values above 0.85 for optimal growth (Hocking, 2001). Interestingly, a surprising number of aspergilli common to tree nut orchards (Bayman et al., 2002) are considered xerophilic and thus can grow at relatively low a_w values (Hocking, 2001). For example, *Aspergillus niger* needs a minimum $a_w = 0.77$ for growth, and *A. flavus* and *A. parasiticus* need $a_w = 0.80$ for growth. Results from the fungal spores on fatty acids study (Beck et al., 2012b) showed spiroketal emission may be from the spores and not necessarily fungal growth; thus, water and fatty acid conditions in the hulls should be optimal in order for spores to undergo transition from resting to germination.

In almond hulls the a_w values remained fairly high (mean $a_w = 0.992$) for the first six samples, which is fairly surprising given the amount of hull split seen in the pictures in Table 1. These values would fully support fungal growth for the vast majority of microbes (Ayerst, 1969; Hocking, 2001). The sample labeled 8/31 ($a_w = 0.799$) showed a significant ($P < 0.0001$; all pairwise comparisons are oneway ANOVA followed by Tukey–Kramer HSD) drop in water activity when compared to the 8/17 sample ($a_w = 0.987$). The 8/31 sample $a_w = 0.799$ is a value likely to support fungal activity of the noted xerophilic aspergilli. The final sample, 9/14 ($a_w = 0.454$), showed another significant drop ($P < 0.0001$) from the 8/31 sample ($a_w = 0.799$). The $a_w = 0.454$ value is low enough that xerophilic fungi common to California tree nut orchards will not develop.

Like almonds, pistachio hull a_w values for the time period between 6/6 and 10/6 also remained high (mean $a_w = 0.989$), but for a longer period. The last pistachio sample analyzed on 10/21 ($a_w = 0.840$) showed a significant drop ($P < 0.0001$) from the previous 10/6 ($a_w = 0.989$). Unfortunately, the a_w values beyond the 10/21 sampling were not performed, but as of that date the a_w value was high enough to accommodate fungal growth of the noted xerophilic fungi.

Analysis of the volatile emission data from the ground almond and pistachio hulls was primarily focused on the presence or

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