Evaluation of a quasi-dimeric eugenol derivative as repellent against the stored grain insect pest *Sitophilus oryzae* (Coleoptera Curculionidae)

Linda Abenaim,*a* Alessandro Mandoli,*b* Francesca Venturi,*a* Stefano Bedini* a* and Barbara Contia

Abstract

BACKGROUND: Essential oils (EOs) and their chemical components are often proposed as an alternative to synthetic pesticides for pest control of foodstuff insect pests. However, their low persistence and strong, spicy odour, make them poorly suitable for use to protect food. Modification of the EOs components molecules increases their molecular weight and reduce their volatility. However, the effectiveness of such modified molecules has, so far, not been tested against stored food insect pests. In this study, the intensity and the duration of the repellence against the insect pest *Sitophilus oryzae* of a recently synthesized quasi-dimeric eugenol derivative (ED) (C_{18}H_{20}O_{4}) were compared to those of eugenol and three eugenol related compounds. The hypothesis tested was that by its higher molecular weight and two functional groups the ED would overcome the low persistence and strong and spicy odour drawback of eugenol without compromising the repellence against insects.

RESULTS: The insect behavioural tests showed a greater repellence and persistence of ED than eugenol and the three eugenol related compounds against *S. oryzae*. The sensory analysis of ED by panel test indicated that ED is significantly less odorous than eugenol without any spicy nor balsamic nuances in its smell profile.

CONCLUSIONS: Because of its high repellence against insects and its low smell intensity for humans, ED could represent a valid repellent for the control of foodstuffs insect pests.

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Keywords: eugenol; foodstuff insects; repellence; olfactometer; panel test

1 INTRODUCTION

Aromatic plant essential oils (EOs) are promising alternatives over the use of synthetic repellents and insecticides currently used to prevent post-harvest losses of stored food. EOs are a complex mixture of monoterpenes, sesquiterpenes, and oxygenated compounds1 extracted from various parts of plants, rich in sebaceous glands, including pulp, leaves and stems. The composition and bioactivity of EOs and their constituents have been extensively studied in recent years also as a protectant against insects of stored foodstuffs.2–4 Contrary to synthetic chemicals that pose many problems, such as toxic residues in food, environmental impact, worker safety, insect resistance,2 EOs are regarded as environmentally friendly, biodegradable, non-polluting for soil and water, and have low toxicity.1 However, despite their very appealing characteristics, the use of EOs has still not found a widespread application in real life because of some drawbacks among which, one of the main ones is the variability of composition. In fact, EOs composition may vary in function of biotic and abiotic factors that act on the plant. Since the repellent/toxicity activity of EOs is a consequence of the bioactivity of its single components, a possible strategy to avoid this problem may be to utilize a single or few pure chemical components in order to have a stable composition of the repellent/toxic. Actually, monoterpenes and sesquiterpenes, characterized by chains linked to isoprene (C_{5}H_{8}) are some of the most effective repellents for insects. However, their high volatility and consequent low persistence7 may limit their protection time and cause strong odour5,8 that may affect the organoleptic characteristic of food.9 To avoid such effects, a possible strategy is to modify the molecule structure in order to increase the molecular weight, reduce the...
volatility and as a consequence improve the duration of the bioactivity and reduce the intensity of the odour.\textsuperscript{10}

In this study, we tested the repellent activity of a recently synthesized quasi-dimeric eugenol derivative (ED) (C\textsubscript{18}H\textsubscript{20}O\textsubscript{4}) characterized by two 2-methoxyphenol groups per molecule and higher molecular weight than eugenol (300.3 versus 164.2 g mol\textsuperscript{-1}). The ED repellent activity was tested against the food insect pest Sitophilus oryzae (Coleoptera Curculionidae) in comparison to eugenol and the two standard insect repellents DEET and MR08. Finally, the olfactory characteristics of both ED and eugenol were described by sensory analysis performed by a panel of experts.

2 MATERIALS AND METHODS

2.1 Rearing conditions

S. oryzae population was reared under laboratory conditions (25 °C, 60–70% RH and in the dark) at the entomology laboratory of the Department of Agriculture, Food and Environment of the University of Pisa. The rearing was carried out in plastic boxes (29 × 18 × 9 cm) containing barley. The bioassays were conducted on insects homogeneous in age, obtained by removing daily the adults present in the rearing box by sieving of barley.

2.2 Chemical compounds

A preliminary selection of chemical compounds was performed among fourteen of the most common EOs constituents (Table 1).

2.3 Pure compounds preliminary screening

Preliminary screenings were carried out on some main EOs constituents with the Area Preference Method, as described by Taponджou et al.\textsuperscript{11} In detail, half discs of filter paper (filter paper Whatman n. 1.8 cm Ø) were used for tests. Half filters were treated with 500 μL of different solutions 10 mM for each constituent in ethanol. The other half were treated with 500 μL of ethanol alone. The constituents tested were compared with the two synthetic repellents MR08 (Menthol propylene glycol carbonate) and DEET (N,N-Diethyl-meta-toluamide). After ethanol evaporation, two half filter paper discs were put in the bottom of a polystyrene Petri dish (8 cm Ø). Twenty unsexed adult insects were introduced in each Petri dish, and the lid was sealed with self-sealing film (Parafilm). The Petri dishes were maintained at 25 ± 1 °C, 65% RH, in the dark. The insects in the two halves of the Petri dishes were recorded 24 h from the beginning of the test. Five replicates were performed for each assay, and the insects were used only once. The per cent repellence (PR) of each volatile was calculated by the formula: PR (%) = [(NT − T)/(NT + T)] × 100 where NT is the number of insects present in the no treated half paper and T the number of insects present in the treated one.

2.4 Behavioural assay

The bioactivity of the selected compound from the previous screenings (eugenol) was then tested in comparison to four eugenol analogues, three commercially available (vanillyl alcohol, homovanillyl alcohol, homovanillyl acid C\textsubscript{9}H\textsubscript{12}O\textsubscript{3}; homovanillyl alcohol C\textsubscript{9}H\textsubscript{12}O\textsubscript{3}; homovanillyl acid L\textsubscript{2}C\textsubscript{8}H\textsubscript{16}O\textsubscript{4}) (Fig. 1).

The attractiveness or repellence responses of S. oryzae towards eugenol, ED, vanillyl alcohol, homovanillyl alcohol and homovanillyl acid were evaluated in a two-way static olfactometer as described by Romani et al.\textsuperscript{6} The arena (15 × 15 × 1 cm), made of polymethylmethacrylate, consisted of three circular chambers (4 cm Ø). Two lateral chambers were connected to a central one (release chamber) by linear paths, forming a 90 ° angle. The top of the arena was covered through a removable glass panel. In each replicate a square of filter paper (0.5 × 0.5 mm) was treated with 3 μL of solution 1 mM in ethanol for each compound. All solutions were tested at 0.2–1.2–2.4–3.6–4.8 – 6.0–11.9 pmol cm\textsuperscript{-3}.

After ethanol evaporation, the treated filter paper was placed in one of the lateral chambers (treaty chamber). A second square of filter paper (0.5 × 0.5 mm) was treated with 3 μL of ethanol only and was placed, after ethanol evaporation, in the other lateral

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**Table 1. Chemical constituents chosen for preliminary screening**

| Chemical constituents | Component class | Essential oils |
|-----------------------|-----------------|----------------|
| 2-undecanone          | Ketone          | Ruta chalepensis (Rutaceae) |
| α-pinene              | Alkene          | Myrtus communis (Myrtaceae) |
| β-pinene              | Alkene          | Cannabisc sativa (Cannabaceae) |
| Borneol               | Alcohol         | Blumea balsamifera (Asteraceae) |
| Carvacrol             | Alcohol         | Origanum vulgare (Lamiaceae) |
| Citronellial          | Aldehyde        | Cymbopogon citratus (Poaceae) |
| Cuminaldehyde         | Aldehyde        | Cuminum cymum (Apiaceae) |
| Eugenol               | Phenol          | Eugenia caryophylla (Myrtaceae) |
| Fenchone              | Ketone          | Foeniculum vulgare (Apiaceae) |
| Geraniol              | Alcohol         | Pelargonium graveolens (Geraniaceae) |
| Limonene              | Alkene          | Citrus reticulata (Rutaceae) |
| Menthone              | Ketone          | Mentha piperita (Lamiaceae) |
| Terpineol             | Alcohol         | Thymus vulgaris (Lamiaceae) |
| Thymol                | Phenol          | Thymus vulgaris (Lamiaceae) |

**Figure 1. Structures of eugenol, ED, and the vanilloid compounds, with the common 2-methoxyphenol moiety evidenced by the dashed boxes.**

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At the beginning of the test, an adult of *S. oryzae* was transferred to the release chamber with tweezers. The choice was considered valid when it entered one of the two lateral chambers after at least 20 s and remained in the chamber for at least 30 s, for a total observation of 6 min. The insects that did not choose within 6 min from the release were discarded. For each replicate we recorded: the latency time (i.e., the time between the insect release and the entering in one of the chambers); the choice made (treatment or control); the permanence time (i.e., the time spent in the chosen chamber). After each test, the arena was rotated 90° clockwise to avoid positional effects, and a new insect was placed in the centre of the arena. After three consecutive tests, the arena and the glass lid were washed for about 30 s with ethanol, then with warm water at 35–40 °C and a mild soap for about 5 min, rinsed with hot water for about 30 s and finally, rinsed with distilled water at room temperature. For each concentration, the test was replicated until three groups of 10 unsexed adults made a valid choice.

Bioassays were conducted under laboratory conditions (25 ± 1 °C, 65% RH) in a room uniformly lit with fluorescent tubes (Philips 30 W/33). Light intensity was approximately 1000 lx.

2.5 Duration of the bioactivity

The duration in time of the repellent activity of the different compounds was assessed in the two-way static olfactometer above described. The compounds were tested at the highest concentration utilised in the behavioural tests. Eugenol, its quasi-dimer ED and the three vanilliods were tested at 11.9 pmol cm⁻³, while the positive controls MR08 and DEET were tested at 35.8 pmol cm⁻³. The repellence activity of all compounds towards *S. oryzae* was evaluated after 0, 24, 48 and 72 h from the treatment with the same methodology previously described.

2.6 Eugenol ED chemical synthesis

The quasi-dimeric eugenol derivative ED, (E,Z)-4,4′-(but-2-ene-1,4-diy)bis(2-methoxyphenol), was obtained by a modification of the reported procedure 12 (Fig. 2).

A 25 mL two-neck, round bottom flask, fitted with a reflux condenser and magnetic stirring bar, was charged under Ar with eugenol (0.177 g, 1.1 mmol), dry CH₂Cl₂ (1.0 mL), and the first-generation Grubbs catalyst G1 [dichloro(benzylidene)bis(tricyclohexylphosphine) ruthenium(II)], 0.0155 g, 19 μmol, 1.7 mol%]. The resulting burgundy solution was heated to gentle reflux overnight and then allowed to cool to room temperature before being filtered through a small pad of silica -gel. The filtrate was concentrated to dryness (10 mbar down to 0.1 mbar), to give a dark residue that was subjected to automatic flash chromatography (Isolera One system, 5–40% AcOEt in *n*-hexane). The fractions containing only the component at Rf = 0.22 (AcOEt: *n*-hexane = 1:4) were concentrated with a rotary evaporator (40 °C, 10 mbar), obtaining the ED (0.113 g, 70% yield) as off-grey platelets. A nearly colourless sample was obtained by dissolving the solid in boiling *n*-heptane: acetone, filtering through a 0.45 μm PTFE membrane to remove some dark insoluble matter, and allowing the yellow filtrate to crystallize overnight at −20 °C. After evaporation of the volatiles under high vacuum (0.1 mbar) the title product was obtained as an (E): (Z) = 5:4:1 mixture (from the integration of the proton resonances at δ = 3.30 ppm and δ = 3.45 ppm, respectively). The NMR spectroscopic constants of the specimen were in accordance with the published ones.12

(1H NMR (401 MHz, CDCl₃) δ 6.89–6.80 (m, 2H), 6.76–6.66 (m, 4H), 5.65 (tt, J = 3.8, 1.6 Hz, 2H), 5.51 (s, 2H), 3.86 (s, 6H), 3.30 (dd, J = 3.9, 1.6 Hz, 4H).

13C NMR (101 MHz, CDCl₃) δ 146.53, 143.95, 132.82, 130.70, 121.15, 114.34, 111.22, 55.97, 38.72.

(Z)-ED.

1H NMR (401 MHz, CDCl₃) δ 5.70 (dd, J = 5.8, 4.6, 1.2 Hz, 2H), 3.84 (s, 6H), 3.45 (d, J = 5.3 Hz, 4H) (some signals were not observed due to the overlapping with those of the major E-diastereoisomer).

13C NMR (101 MHz, CDCl₃) δ 146.60, 129.35, 121.01, 114.40, 111.06, 33.16 (some signals were not observed due to the overlapping with those of the major E-diastereoisomer).

2.7 Sensorial analysis

The sensorial features of eugenol and compound ED were evaluated and compared in blind odour tests by a panel of 10 trained assessors, 6 females and 4 males, aged between 25 and 60 years (`expert panel', Department of Agriculture, Food and Environment, University of Pisa). All assessors had previous experience in sensory descriptive analysis, mainly in food and EOs and their component evaluation.9,13 All assessors were provided with a sensory sheet consisting of an unstructured, descriptive parametric score chart specifically developed during a preliminary consensus panel of two substances to generate a set of main descriptors and their definitions. To give a quantitative measure (score) of each descriptor, the panellists were asked to refer to a continuous scale (0 to 10). Furthermore, the assessors were also asked to quantify smell intensity together with smell pleasantness as a hedonic parameter.

The blind odour test was performed in the morning, in a well-ventilated, quiet room and in a relaxed atmosphere. Each panellist was provided with a fragrance tester strip soaked in 10 μL of an unknown compound (corresponding to 11.9 pmol cm⁻³) labelled with a random three-digit code. To avoid cross-contamination, the samples were separately assessed in the same morning (with a 15 min break between assessments). Each assessment was randomly repeated twice.

Figure 2. Synthesis of the eugenol derivative (ED).
2.8 Data analysis

The reliability of the sensory data collected during the panel test was evaluated by Big Sensory Soft (BSS®), software specifically developed by the Centro Studi Assaggiatori (Brescia (BS), Italy) to process sensory data from panel tests. Sensory data were analysed by two-way ANOVA, with panelists and samples as main factors. Data from the preliminary screenings of the repellent effect of EOs constituents were processed by Kruskal-Wallis test. Medians were separated by Dunn-Bonferroni pairwise comparisons. The proportion of individuals choosing the EO-treated chamber in the two-choice behavioural assays was compared by means of a likelihood-ratio chi-square test, with a null hypothesis of a 50:50 chance of insects choosing the control chamber (NT) vs the EO-treated chamber (T). To compare the repellent activity of the compounds (and in the meantime to provide a more synthetic output of the results), behavioural assays data were also processed by one-way between-groups univariate analysis of covariance (ANCOVA), with the chemical compound as a fixed factor and the concentration as a covariate to control its effects in the model. The mean response for each factor (chemical compound), adjusted for the concentration, was reported as estimated marginal (EM) means, and significant differences among them were determined by post hoc comparisons using Bonferroni corrections for multiple comparisons.

Figure 3. Mean repellence (%) of some main EOs chemical constituents and of the synthetic repellents MR08 and DEET against *Sitophilus oryzae* adults. Bars represent standard error. Different letters indicate significant differences among treatments (Dunn-Bonferroni *P* ≤ 0.05).

Figure 4. Behaviour of adults of *Sitophilus oryzae* in the presence of eugenol. Histograms represent the percentage of insects that chose the control chamber. Asterisks indicate significant differences in the number of the choosing insects (*χ*² test; *, *P* < 0.05; ***, *P* < 0.001).
3 RESULTS

3.1 Preliminary screening
The preliminary screening showed a clear repellent activity of the single chemical components of EOs with significant differences among the compounds (χ² = 32.493; df = 16; P = 0.009). The recorded repellence varied from 4.0 ± 4.0 to 90.0 ± 5.5% for β-pinene and eugenol, respectively. The repellent activity of eugenol was also stronger than the one of the two reference repellents MR08 and DEET (repellence, 60 ± 12.2 and 62 ± 8.6%, respectively) (Fig. 3).

3.2 Behavioural assay
Tests performed in the two-way olfactometer confirmed the repellent effect of eugenol against S. oryzae, previously found by the preliminary screening. In the behavioural assay, the eugenol exerted a significant repellent effect starting from the 6.0 pmol cm⁻³ (χ² = 4.800, p = 0.028), and resulting highly significant at 11.9 pmol cm⁻³ (χ² = 13.333, p < 0.001) (Fig. 4).

The ED showed a significant repellent effect starting from a lower concentration than eugenol (2.4 pmol cm⁻³, χ² = 4.829, p = 0.028), and resulted very significant from 4.8 pmol cm⁻³ (χ² = 8.533, p = 0.003) (Fig. 5).

On the contrary, vanillyl and homovanillyl alcohol, did not show any significant repellent or attractive effect on S. oryzae, while the homovanillyl acid showed a significant attractive effect starting from the concentration of 4.8 pmol cm⁻³ (χ² = 4.800, p = 0.028) (Fig. 6).

ANOVA indicated statistically significant differences among the chemical compounds (F₁,120 = 13.137, P < 0.001). Estimates marginal (EM) means showed that the most effective compound was the eugenol derivative (ED) (Table 2).

In particular, the post-hoc tests indicated no differences between the repellent activity of ED and eugenol (Bonferroni pairwise comparison, P = 1.000) and a significant difference between them and the other compounds (Bonferroni pairwise comparison, P = 0.002) (Table 2).

3.3 Repellent activity duration test
The tests carried out in the two-way olfactometer showed that the ED showed the longest-lasting effect among the compounds tested remaining repellent to S. oryzae even after 72 h. On the contrary, the repellent activity of eugenol decreases considerably after 24 h and was ineffective after 48 h. Such behaviour was very similar to that observed for the MR08 and the DEET, while vanillyl alcohol, homovanillyl alcohol and homovanillyl acid showed the fastest loss of bioactivity, being virtually ineffective already after 24 h (Fig. 7).

3.4 Sensorial analysis
According to the ANOVA the sensory parameters of the smell profile of ED is significantly different than the eugenol ones with also a significantly reduced smell intensity (Fig. 8). In particular, panelists described the smell profile of ED as weakly pharmaceutical without any of the spicy and balsamic nuances detected in the eugenol.

4 DISCUSSION
Monoterpenes and sesquiterpenes are characterized by chains linked to isoprene (C₅H₈) and are one of the most important groups of repellents for insects. Among those compounds, the highest repellent activity was observed for the oxygenated compounds, as the hydroxyl group showed the best activity compared to other functional groups. The results of the present study show that the monoterpene eugenol is the most effective chemical compound among the tested EOs constituents as an insect repellent and that it is possible to modify its molecular structure in order to reduce its volatility without affecting its bioactivity. In agreement with our results, previous studies showed that eugenol is a very effective compound in repelling also other foodstuff insect pests as Sitophilus zeamais (Coleoptera Curculionidae), Tribolium castaneum (Coleoptera Tenebrionidae), Oryzaephilus surinamensis (Coleoptera Silvanidae) and Rhyzopertha dominica (Coleoptera Bostrichidae). In addition, eugenol is recognized...
as a food ingredient safe for humans (GRAS) and as an active substance with no maximum residue level (MRL) required in various food applications and is approved by the European Commission. However, despite its strong repellent activity, in this study, we observed that the eugenol bioactivity decreases very rapidly due to its volatility, reducing its repellence by about ten-fold after 24 h and disappearing completely after 48 h. Such high volatility, typical of the active EOs compounds, is confirmed also by the findings of Al-Harbi et al. and represent a strong limitation of their practical use. In line with our findings, Ngamo et al. tested the persistence of five aromatic plants and observed that their repellent effect decreases significantly over time, despite the strong bioactivity shown on the first day of application. Similarly, Obeng-Ofori & Reichmunth observed a significant loss of eugenol activity after 24 h of application leading to the reduction of the protective effect of stored products.

In this study, to overcome the drawback of the loss of bioactivity of compounds due to their high volatility, we tested a new compound, the ED, obtained by modifying the molecular structure of eugenol in order to obtain a new insect repellent with a higher molecular weight. In previous work, Lovinella modified the structure of the monoterpene menthone by adding bulky groups. The derivative obtained (menthone 2-ethyl-1,3-hexanediol ketal) showed no reduction of its efficacy as a repellent towards mosquitoes and long persistence on the human skin.

In line with this rationale, the ED was designed with the idea of abating the volatility of eugenol, yet keeping the functional groups deemed essential for its bioactivity. In this regard, the ruthenium-catalysed homo-metathesis reaction of eugenol was especially well-suited, as it could lead to nearly doubling of the molecular weight of the parent compound (300.3 g mol\(^{-1}\)) without affecting the phenol and ether moieties in the latter. In addition, the presence of two hydrogen-bonding hydroxy groups, increasing its persistency in time. The assumptions above were confirmed by our findings, which showed that the ED not only is much longer-lasting than eugenol but has slightly higher repellence activity that could be due to the presence of two 2-methoxyphenolic units per molecule instead of one in eugenol.

Compounds with lower volatility have the additional advantage of a weaker odour, a characteristic often desired when using essential oils. Actually, the results of the panel test indicate that in ED the strong spicy and balsamic character generally attributed to eugenol is not detectable and the overall intensity of the smell is significantly reduced.

Interestingly, despite the common 2-methoxyphenol structural motif in the nearly dimeric structure of ED, was expected to reduce further the volatility of the compound, thereby contributing a decrease in the typical odour of the phenol compound and extending its persistency in time. The assumptions above were confirmed by our findings, which showed that the ED not only is much longer-lasting than eugenol but has slightly higher repellence activity that could be due to the presence of two 2-methoxyphenolic units per molecule instead of one in eugenol.

Compounds with lower volatility have the additional advantage of a weaker odour, a characteristic often desired when using essential oils. Actually, the results of the panel test indicate that in ED the strong spicy and balsamic character generally attributed to eugenol is not detectable and the overall intensity of the smell is significantly reduced.

Interestingly, despite the common 2-methoxyphenol structural motif (Fig. 7), very little bioactivity was observed for vanillyl alcohol, homovanillyl alcohol and homovanillyl acid, with the latter compound actually behaving as an attractant at the highest

![Figure 6. Behaviour of adults of Sitophilus oryzae in the presence of vanillyl alcohol, homovanillyl alcohol and homovanillyl acid. Histograms represent the percentage of insects that chose the control chamber. Asterisks indicate significant differences in the number of the choosing insects.](image-url)
Therefore, the presence of an apolar (hydrocarbon) substituent at the C-4 position of the aromatic ring seems to be essential for exerting the sought biological effect (i.e., repellence). As a matter of fact, such structural feature of eugenol is nicely preserved in the ED, thereby confirming the convenience of the quasi-dimerization approach adopted herein as a means for reducing the strong odour of the parent compound without impairing (and, in fact, improving in terms of persistence) its desired properties.

Finally, it is interesting to note that, the two commercial synthetic repellents MR08 and DEET showed a lower repellent effect than eugenol and ED at the tested concentrations. This finding is consistent with other studies that found that EOs and their compounds may show repellent efficacy equal to or greater than commonly used synthetic repellents.21–23

**CONCLUSIONS**

Eugenol structure modification reduced the volatility of the compound and, consequently, also its strong and characteristic odour without any significant reduction of its bioactivity. The eugenol derivative could be considered a good candidate for practical applications in preventing the onset of insect pests in the storage and packaging of cereals and grain products. Deterring insect pests from stored products will reduce the quantitative and qualitative losses caused by insects. In this regard, the structural modification of the chemical components of the EOs could represent a valid method to overcome some of the most problematic drawbacks of the EO such as the variability of the composition, volatility and strong smell and therefore, to allow the development of valid alternatives to synthetic repellents for the control of food insects.

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**DATA AVAILABILITY STATEMENT**

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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