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Short Communication

Transformation of β-damascone to (+)-(*S*)-4-hydroxy-β-damascone by fungal strains and its evaluation as a potential insecticide against aphids *Myzus persicae* and lesser mealworm *Alphitobius diaperinus* Panzer

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ABSTRACT

Microbial conversion of β-damascone (**1**) into 4-hydroxy-β-damascone (**2**) was studied. The results showed the potential of the tested biocatalysts for the regio- and enantioselective hydroxylation of substrate **1**. The highest enantioselectivity was exhibited by strain *Mortierella isabellina* AM212. β-Damascone (**1**) was a relatively good deterrent towards *Alphitobius diaperinus* and it was behaviorally inactive to *Myzus persicae*. The racemic compound **2** and its (+)-(*S*)-enantiomer were stronger antifeedants against *A. diaperinus* than β-damascone (**1**), in the case of *M. persicae* only (+)-(*S*)-(**2**) exhibited the deterrent properties.

1. Introduction

Damascones are a class of norisoprenoids defined as rose ketones, which were discovered in the Bulgarian rose oil [1]. They are widely used in fragrance and cosmetic industry [2,3]. In the center of commercial interest are also the hydroxyderivatives of damascones, naturally occurring in tobacco plants [4,5]. Chiral 4-hydroxy-β-damascone was found to be suitable as a flavoring and plays a role of a building block in the synthesis of biologically active compounds, for example decalins [6,7]. Chemical synthesis of 4-hydroxy-β-damascone was the subject of many studies, but turned out to be complicated due to the formation of a variety of side products and lack of a selectivity. In this aspect, the enzymatic transformation seems to be a powerful tool for the production of optically pure or enantioenriched hydroxylated derivatives. Additionally, the products obtained by the transformation of natural compounds using microorganisms can be legally labeled also as 'natural' ones [8]. From that reasons the catalytic potential of fungi *Botrytis*, *Aspergillus*, *Botryosphaeria* and *Lasiodiplodia*, and the isolated enzymes of bacteria to the biooxidation of β-damascone (**1**) has been investigated [6,9–12]. The microbial or enzymatic hydroxylation of β-damascone (**1**) afforded mainly products of incorporation of a hydroxy group into the cyclohexane ring at C-3 rather than products with a hydroxy group in the allylic position. Moreover, during biooxidation processes 4-hydroxy-β-damascone (**2**) was isolated in low yields in a mixture with other hydroxyderivatives.

Presented studies make a substantial contribution to the research area concerning the microbial hydroxylation of damascones. Our studies were focused on testing 15 microbial strains towards the hydroxylation reaction. 4-Hydroxy-β-damascone (**2**) found as a major product, occurs in plants and contributes to the fragrance of many essential oils. Evaluating of its antifeedant activity we tried to find an answer if it plays other important role in a metabolism of plants. In 2010 Kaufman et al. found that β-damascone (**1**) is a potential agent for controlling multiple arthropod species [13]. Inspired also by the previous results of biological tests for hydroxyderivatives of natural compounds *e.g.* jasmonates [14] carried out in our research group we expected that the incorporation of a hydroxy group into the structure of β-damascone (**1**) would confirm that the product (**2**) is useful in the control of pests. In biological tests we focused on two insect species of economic importance that differ in the feeding habits and food preferences: peach potato aphid (*Myzus persicae*) and lesser mealworm (*Alphitobius diaperinus*). These insect pests represent two different groups with respect to the practical application of feeding deterrents targeted at contact chemoreceptory organs: the aphid possess sucking-piercing mouthparts that lack external taste receptors, while the taste sensilla of larvae and adults of *A. diaperinus* are located on their biting–chewing mouthparts. Consequently, the aphids require the ingestion of plant sap samples to evaluate food quality in contrast to the lesser mealworm beetles and larvae that can examine food at the preingestional phase.

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2. Materials and methods

2.1. Analytical methods

A course of microbial transformation was monitored by TLC technique on DC-Alufolien Kieselgel 60 F_{254} silica gel (0.2 mm; Merck). Chromatograms were developed using hexane: acetone (2:1, v/v) system. Visualization was effected with a solution of $Ce(SO_4)_2$ (10 g) and $H_3[P(Mo_3O_{10})_4]$ (20 g) in 10% H_2SO_4 (1 L), followed by heating to 120–200 °C. The eluent used in the TLC technique was also used for the preparative column chromatography performed on silica gel (Kieselgel 60, 230–400 mesh ASTM, Merck). Gas chromatography (GC) analysis was performed using an Agilent Technologies 6890N (Network GC System) instrument fitted with a flame ionization detector (FID) and HP-5 column (30 m × 0.32 mm × 0.25 μm) with hydrogen as a carrier gas. Temperature program was as follows: injector 250 °C, detector (FID) 250 °C, column temperature: 100 °C, 100–300 °C (rate 30 °C min^{-1}), 300 °C (hold 2 min). The chiral capillary column CP-cyclodextrin-B (25 m × 0.25 mm × 0.25 μm) was used to determine the enantiomeric compositions of the obtained products. Temperature program was as follows: 70 °C, 100–200 °C (rate 2 °C min^{-1}), and 200 °C (hold 2 min). Optical rotation was determined on JASCO P-2000-Na polarimeter in a version with iRM controller using dichloromethane as a solvent, concentration denoted in g/100 mL. Nuclear magnetic resonance (NMR) spectra were recorded with a AMX 300-MHz Bruker spectrometer and measured in $CDCl_3$.

2.2. Substrate and strains

The substrate used for biotransformation experiments was β-damascone (**1**) purchased from Sigma Aldrich (90% purity). The microorganisms were maintained on Sabouraud 4% dextrose-agar slopes at 4 °C and freshly subcultured before use in the transformation experiments. The following 15 fungal and yeast strains were used in the presented studies: *Fusarium oxysporum* AM13, *Penicillium purpurogenum* AM80, *Rhodotorula rubra* AM82, *Penicillium camemberti* AM83, *Syncephalastrum racemosum* AM105, *Penicillium lilacinum* AM111, *Penicillium chermesinum* AM113, *Mortierella vinaceae* AM149, *Mortierella isabellina* AM212, *Absidia cylindrospora* AM336, *Aspergillus ochraceus* AM456, *Cunninghamella japonica* AM472, *Aspergillus niger* MB, *Chaetomium* sp. KCh6651 and *Didymosphaeria igniaria* KCh6670. All microorganisms were from the collection of Department of Chemistry, Wroclaw University of Environmental and Life Sciences.

2.3. Microbial transformations

For the analytical tests the cultures were cultivated in Erlenmeyer flasks (300 mL) containing 100 mL of medium (3 g glucose, 1 g aminobac in distilled water (100 mL)). After full growth 10 mg of β-damascone (**1**) dissolved in 1 mL of acetone was added to the shaken cultures (150 rpm at 25 °C). After 1, 2, 4, 6 and 8 days 5 mL of the transformation mixture were taken and the products were extracted with dichloromethane (3 × 4 mL). The extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The residues were dissolved in 1 mL of acetone and analyzed by TLC and GC. All experiments were repeated three times. Additionally, two control flasks were used for each experiment: one only with microorganism's culture in the medium for determining the secondary metabolites and one with substrate in a growth medium for determining the stability of substrate.

For the preparative-scale biotransformation the substrate (150 mg of β-damascone (**1**) dissolved in 10 mL of acetone) was added to the cultures of selected strains cultivated in 2 L flasks (each containing 500 mL of the cultivation medium). After 2–8 days of incubation the products were extracted with dichloromethane. Organic solutions were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The transformation products were separated by column chromatography.

All experiments were carried out in triplicates. Results in Fig. 1 are reported as means of triplicate experiments ± standard deviations (SD).

Spectroscopic data of the obtained product, 4-hydroxy-β-damascone (**2**) were in accordance with those presented by More and Bhat [19]: 1H NMR (300 MHz, $CDCl_3$) δ: 1.02 (s, 6H, $(CH_3)_2C<$), 1.25–1.54 (m, 4H, CH_2-3, CH_2-2), 1.63 (s, 3H, CH_3-13), 1.84 (s, 1H, OH) 1.92 (dd, $J = 6.8$ and 1.2 Hz, 3H, CH_3-10), 3.99 (t, $J = 4.9$ Hz, 1H, H-4), 6.15 (dd, $J = 15.7$ and 1.8 Hz, 1H, H-8), 6.77 (dq, $J = 15.7$ and 6.8 Hz, 1H, H-9); 13C NMR (151 MHz, $CDCl_3$) δ: 201.3 (C-7), 146.6 (C-5), 143.6 (C-9), 135.1 (C-6), 133.9 (C-8), 69.0 (C-4), 34.7 (C-3), 34.6 (C-1), 29.8 and 27.7 (C-11 and C-12), 28.6 (C-2), 18.5 (C-10), 17.9 (C-13); IR (film, cm^{-1}): 3422 (s), 2928 (s), 2856 (s), 1716 (m), 1645 (s), 1442 (m).

2.4. Biological studies

The lesser mealworm (*A. diaperinus*) culture and feeding deterrence bioassays have been previously described [15,16]. Activity of the tested

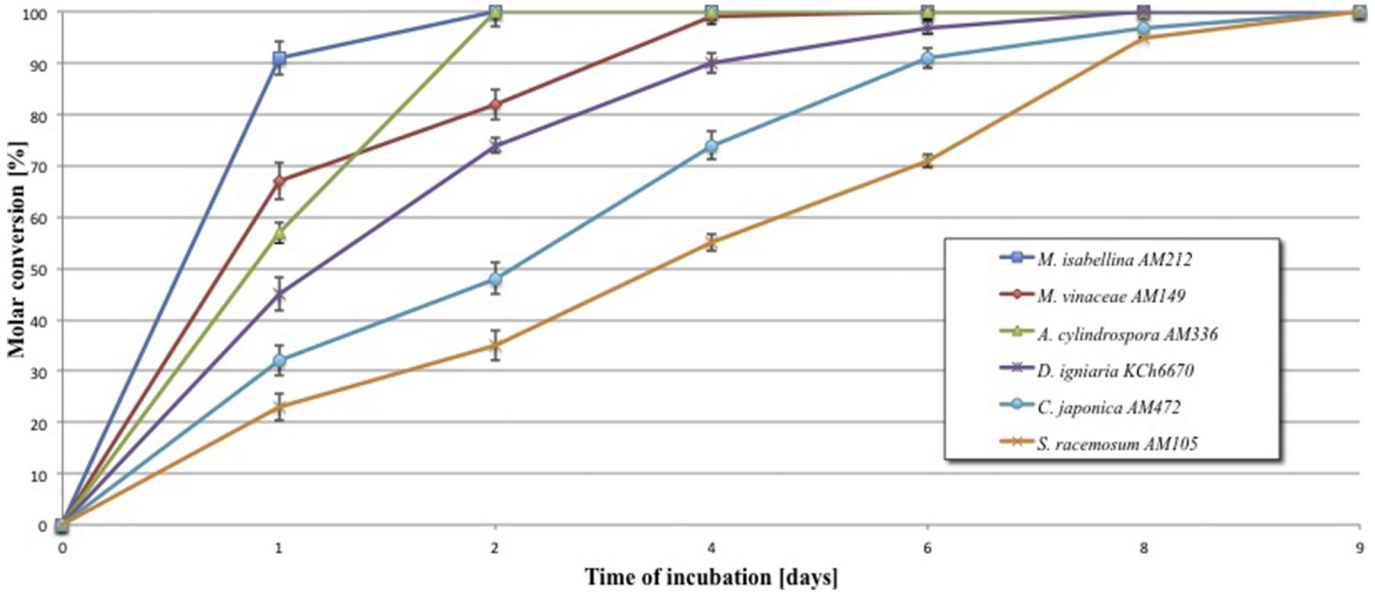

Fig. 1. Time course of the transformation of β-damascone (**1**) to 4-hydroxy-β-damascone (**2**) by selected fungal strains.

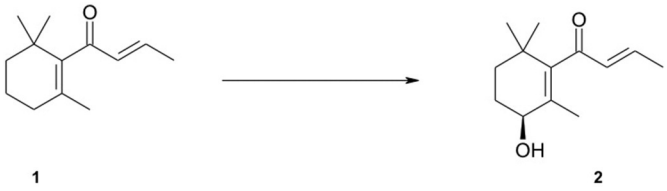

Fig. 2. Hydroxylation of β-damascone (**1**) by selected fungal strains.

compounds was evaluated by the standard method of choice test. The deterrence index (DI) was calculated using the formula: DI = (C − T) / (C + T) × 100 where C and T are the weights of the control and treated foods consumed by the insects, respectively [17]. Compounds with deterrence index of 75–100 are classified as very strong deterrents, those with values of 50–74 as good deterrents, whereas those with values of 25–49 have medium activity. [18]. The mean values of the deterrence coefficients and percentage of consumption were compared by means of one-way analysis of variance (ANOVA) followed by Tukey's test at a level of $P < 0.05$.

Application of compounds, culture of aphids (*M. persicae*) and their settling (choice-test) has been previously described by Gliszczyńska et al. [14]. The data were analyzed using one way ANOVA (STATISTICA 6.1. package). If aphids showed clear preference for the leaf treated with the tested compound ($P < 0.05$), the compound was described as having attractant properties. If aphids settled mainly on the control half of the leaf ($P < 0.05$), the compound tested in the respective choice-test was stated as a deterrent. From the data thus obtained the relative index of deterrence (DI) was calculated: DI = (C − T) / (C + T) where C is the number of aphids settled on control half of the leaf and T denotes the number of aphids settled on the treated half of the leaf. The value of DI ranges between 1 (ideal deterrent) and −1 (ideal attractant).

3. Results and discussion

3.1. Screening experiments for biotransformations of β-damascone (*1*)

In our studies we applied fungi to obtain hydroxyderivatives of β-damascone (**1**) with high enantiomeric excess. The screening of fifteen fungal strains let us to select six of them: *M. isabellina* AM212, *M. vinaceae* AM149, *C. japonica* AM472, *S. racemosum* AM105, *A. cylindrospora* AM336 and *D. igniaria* KCh6670 that were able to catalyze the conversion of β-damascone (**1**) (Fig. 1). It is worth to notice that in all cases formation of only one hydroxylation product was observed which evidence is a representative chromatograms obtained after biotransformation catalyzed by *M. isabellina* AM212 (S2 Fig. 1). No further oxidation products were detected in the biotransformation mixtures even after 9 days of process. Nine strains did not produce any products and only substrate was observed in the reaction mixture even after 12 days of reaction.

3.2. Identification of transformations product

All selected microorganisms converted β-damascone (**1**) into known 4-hydroxy-β-damascone (**2**), which was formed by oxidation of the allylic C-4 position of cyclohexene ring (Fig. 2). The structure of this product was fully confirmed by its spectral data, which were in accordance with these reported previously by More and Bhat [19].

Wide absorption band at 3422 cm^{-1} in the IR spectrum confirmed the presence of hydroxy group in the product **2** (S4 Fig. 3). The presence of triplet at 3.99 ppm with coupling constant $J = 4.9$ Hz from proton H-4 shifted to higher field (compared to the spectrum of the substrate) proved the location of hydroxy group.

The absolute configuration at C-4 was assigned as *S* by the comparison of the specific rotation sign determined for this compound with that reported by More and Bhat [19]. Depending on the fungus employed the enantiomeric excesses and the yields of 4-hydroxy-β-damascone (**2**) were different (Table 1).

3.3. The course of biotransformation of β-damascone by selected fungal strains

Table 2 shows the reaction rates during hydroxylation of β-damascone (**1**) by six active microorganisms. In the first 24 h of the incubation of substrate with the selected strains the highest rate was observed for the reaction catalyzed by *M. isabellina* AM212 (Table 2, entry 1). After that time the reaction mixture contained only 9% of unreacted substrate and 91% of product **2** (Fig. 1). During the next day the substrate **1** was fully converted to (+)-(*S*)-4-hydroxy-β-damascone (**2**) although reaction rate decreased significantly. The product was isolated in 35% yield and its enantiomeric excess (ee = 54%) was determined by chiral GC (S3 Fig. 2B).

Lower reaction rate was observed for *M. vinaceae* AM149 (Table 2, entry 2). After 24 h of incubation of substrate **1** the products mixture contained 33% of unreacted substrate and 67% of product **2** (Fig. 1). In the next days the reaction rate was reduced and conversion of substrate reached 99% after four days. The (+)-(*S*)-hydroxyderivative **2** was isolated in high yield (53%) but with significantly lower enantiomeric excess (ee = 12%).

The enzymatic system of *A. cylindrospora* AM336 transformed β-damascone **1** into the product **2** within two days at nearly constant rate (Table 2, entry 3). The process was carried out under the same experimental conditions as applied before but this time the racemic mixture of product **2** (S3 Fig. 2A) was obtained in 17% yield.

The strains *D. igniaria* KCh6670 and *C. japonica* AM472 catalyzed the process of biohydroxylation at significantly lower rates (Table 2, entries 4 and 5) than three cultures of microorganisms described above. After 24 h of the incubation of **1** with *C. japonica* AM472 the degree of conversion was 32% and increased proportionally in the next two days. After this time the reaction rate was reduced and the process proceeded slowly affording finally 97% of the product **2** in the reaction mixture after eight days (Fig. 1). Product **2** was isolated in 39% yield as (+)-(*S*)-enantiomer with ee = 20%. Process of biotransformation carried out by *D. igniaria* KCh6670 proceeded similarly (Fig. 1) and after eight days (+)-(*S*)-enantiomer of product **2** was isolated in 22% yield with ee = 30%.

S. racemosum AM105 transformed substrate **1** with a lowest reaction rate (Table 2, entry 6). After one day 23% of 4-hydroxy-β-damascone (**2**) was identified in the reaction mixture (Fig. 1). In the next days the rate of reaction was lower but the growing conversion of substrate **1** was observed to achieve 100% after 9 days. The product **2** was isolated in 47% yield as enantiomerically enriched (+)-(*S*)-enantiomer with ee = 48%.

Table 1
Results of preparative biotransformation of β-damascone (**1**) by selected fungal strains.

Microorganism	Time of transformation (days)	Isolated yield of product (**2**) (%)	ee of product (**2**) (%)	$[\alpha]_D^{20}$ (lit. + 3.7 (c = 1.8, EtOH))
M. isabellina AM212	2	35	54	+14.74 (c = 1.3, CH_2Cl_2)
M. vinaceae AM149	4	53	12	+3.98 (c = 1.4, CH_2Cl_2)
A. cylindrospora AM336	2	17	0	–
D. igniaria KCh6670	8	22	30	+8.19 (c = 1.5, CH_2Cl_2)
C. japonica AM472	8	39	20	+5.46 (c = 1.6, CH_2Cl_2)
S. racemosum AM105	8	47	48	+13.10 (c = 1.3, CH_2Cl_2)

Table 2
The reaction rates of production of hydroxyderivative **2** by different strains.

Entry	Microorganism	Transformation period [days]	Reaction rate [mg/h] of product
1	*M. isabellina* AM212	1	3.8×10^{-1}
		2	3.3×10^{-2}
		4	Full conversion
		6	Full conversion
		8	Full conversion
		9	Full conversion
2	*M. vinaceae* AM149	1	2.8×10^{-1}
		2	6.3×10^{-2}
		4	3.5×10^{-2}
		6	2.1×10^{-3}
		8	Full conversion
		9	Full conversion
3	*A. cylindrospora* AM336	1	2.4×10^{-1}
		2	1.8×10^{-1}
		4	Full conversion
		6	Full conversion
		8	Full conversion
		9	Full conversion
4	*D. igniaria* KCh6670	1	1.9×10^{-1}
		2	1.2×10^{-1}
		4	3.3×10^{-2}
		6	1.5×10^{-2}
		8	6.3×10^{-3}
		9	Full conversion
5	*C. japonica* AM472	1	1.3×10^{-1}
		2	6.7×10^{-2}
		4	5.4×10^{-2}
		6	3.5×10^{-2}
		8	1.3×10^{-2}
		9	1.3×10^{-2}
6	*S. racemosum* AM105	1	9.6×10^{-2}
		2	5.0×10^{-2}
		4	4.2×10^{-2}
		6	3.3×10^{-2}

3.4. Antifeedant activity

Behavioral bioassays showed that the β-damascone (**1**) was a good feeding deterrent towards the lesser mealworm. Both, larvae and adults of *A. diaperinus* were eating in the choice test less than 30% of treated food compared to the control (Table 3).

The deterrent activity of oxyderivative of β-damascone (**1**) depended on its enantiomeric purity. (+)-(*S*)-4-Hydroxy-β-damascone (**2**) with ee = 54% exhibited significantly stronger activity towards adults of lesser mealworm than its larvae. Racemic 4-hydroxy-β-damascone (**2**) was characterized by very strong antifeedant properties against both developmental stages of *A. diaperinus*. Food treated with the racemic compound was eaten in small quantities and made up only 7.29% (larvae) and 4.81% (adults) of control consumption. In comparison with the starting β-damascone (**1**), the significant improvement of activity was observed.

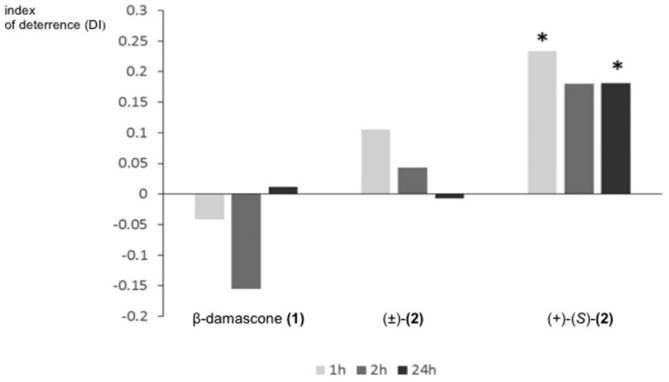

Fig. 3. The effect of β-damascone and its derivatives on settling preferences of *Myzus persicae* in the choice test. The data are expressed as values of indices of deterrence (*DI*). The standard error is indicated on the bar *P < 0.05 (Student's t-test).

β-Damascone (**1**) appeared to be a weak attractant for aphids during the initial contact with the treated leaves in the choice test, as it was observed that although the first probe was delayed in comparison to the control, further probing was rarely interrupted. The exposure of *M. persicae* to the racemic 4-hydroxy-β-damascone (**2**) resulted in the initial avoidance of the treated leaves by freely moving aphids in the choice-test. However, the antifeedant effect of racemic mixture of 4-hydroxy-β-damascone (**2**) significantly decreased in the next hours. The highest activity was observed for (+)-(*S*)-4-hydroxy-β-damascone (**2**) with ee = 54%. Aphids clearly avoided leaves treated with this enantiomer. The deterrent effect was observed 1 h after the exposure and it was maintained until the end of the experiment (24 h) (Fig. 3).

4. Conclusions

The selected fungal strains: *M. isabellina* AM212, *M. vinaceae* AM149, *C. japonica* AM472, *S. racemosum* AM105 and *D. igniaria* KCh6670 converted β-damascone (**1**) to (+)-(*S*)-4-hydroxy-β-damascone (**2**) whereas only *A. cylindrospora* AM336 produced the racemic mixture. The hydroxylation of β-damascone (**1**) was highly regioselective. The most efficient transformation (53% isolated yield) was observed in the case of *M. vinaceae* AM149 strain but the product obtained in the culture of *M. isabellina* AM212 was characterized by the highest enantiomeric excess (ee = 54%).

It is the first report on a regioselective microbial incorporation of a hydroxy group into the structure of β-damascone (**1**) by fungi species: *Mortierella*, *Cunninghamella*, *Syncephalastrum*, *Absidia* and *Didymosphaeria* that leads to the optically active product with increased antifeedant activity. The biological studies have shown that the incorporation of a hydroxy group into the structure of β-damascone (**1**) increases the antifeedant activity of the hydroxyderivative towards *A. diaperinus*. It proves a high sensory sensitivity of this insect to a hydroxy group introduced into the molecule. Likewise, the transformation of β-damascone (**1**) into 4-hydroxy-β-damascone (**2**), caused also a significant change in the peach potato aphid behavior. While β-damascone (**1**) appeared a behaviorally inactive compound, 4-hydroxy-β-

Table 3
Antifeedant activity of β-damascone (**1**) and its metabolites against *A. diaperinus*[a].

Compound	Larvae		Adults	
	DI[b] ± SE	Consumption[c] ± SE	DI ± SE	Consumption[c] ± SE
β-Damascone (**1**)	55.59 ± 3.41 a	28.73 ± 2.89 a	56.94 ± 4.49 a	27.82 ± 4.04 a
(+)-(*S*)-4-hydroxy-β-damascone (ee = 54%)	45.83 ± 2.27 a	37.25 ± 2.18 a	82.81 ± 4.52 b	9.61 ± 2.76 b
(±)-4-hydroxy-β-damascone	86.46 ± 1.63 b	7.29 ± 0.95 b	90.89 ± 2.06 b	4.81 ± 1.15 b

Means within a column followed by the same letter are not significantly different (one-way ANOVA followed by Tukey's test: P < 0.05).
[a] Deterrence index.
[b] Values are the mean of the four replicates, each set up with ten larvae or adults (n = 40).
[c] Data are expressed as percentage of control consumption.

damascone (**2**) caused the avoidance of treated leaves by free aphids in a choice-test. However, the level of activity depended on the enantiomeric purity of the compound and (+)-(*S*)-4-hydroxy-β-damascone (**2**) generated a significantly stronger deterrent effect against aphids than its racemic mixture.

Further studies are in progress to optimize the enantioselective hydroxylation of β-damascone (**1**) to 4-hydroxy-β-damascone (**2**) with selected fungal strain to obtain higher yield and enantiopurity of the product (**2**).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2016.03.018.

References

[1] E. Demole, P. Enggist, U. Sauberli, M. Stoll, E. Sz, Kovats, Helv. Chim. Acta 53 (1970) 541–551.
[2] K. Bauer, D. Garbe, H. Surburg, Common Fragrance and Flavor Materials, 2. Aufl. Weinheim, VCH Verlagsgesellschaft, 1990.
[3] E. Brenna, C. Fuganti, S. Serra, Tetrahedron: Asymmetry, 142003 1–42.
[4] Q. Hu, W. Boland, J.-K. Liu, Z. Naturfors, 60c, 2005 1–4.
[5] G. Krammer, P. Winterhalter, M. Schwab, P. Schreier, J. Agr, Food Chem. 39 (1991) 778–781.
[6] V. Krasnobajew, Biotechnology Vol. 6a, Biotransformations, Verlag Chemie, Weinheim, 1984.
[7] C. Fehr, J. Galindo, O. Guntern, Tetrahedron Lett. 28 (1990) 4021–4024.
[8] D.W. Armstrong, B. Gillies, H. Yamazaki, Flavor chemistry. Trends and developments, in: R. Teranishi, R.G. Buttery, F. Shahidi (Eds.), A-C-S-Symo-Ser-Am-Chem-Soc, 388, The society, Washington, D.C, 1989.
[9] E. Schoch, I. Benda, P. Schreier, Appl. Environ. Microbiol. 57 (1991) 15–18.
[10] E. Schwab, P. Schreier, I. Benda, Z. Naturfors, 43c, 1991 395–397.
[11] M. Ma, S.G. Bell, W. Yang, Y. Hao, N.H. Rees, M. Bartlam, W. Zhou, L.-L. Wong, Z. Rao, Chembiochem 12 (2011) 88–99.
[12] E. Hall, S.G. Bell, RSC Adv. 5 (2015) 5762–5773.
[13] P.E. Kaufman, R.S. Mann, J.F. Butler, Pest Manag. Sci. 67 (2011) 26–35.
[14] A. Gliszczyńska, W. Gładkowski, K. Dancewicz, B. Gabryś, Curr. Microbiol. 71 (2015) 83–94.
[15] M. Szczepanik, A. Grudniewska, B. Zawitowska, C. Wawrzeńczyk, Pest Manag. Sci. 70 (2014) 953–958.
[16] A. Gliszczyńska, K. Dancewicz, M. Hnatejko, M. Szczepanik, B. Gabryś, RSC Adv. 4 (2014) 39248–39256.
[17] O. Koul, Bioassays, in Insect Antifeedants, CRC Press, London/NewYork/Washington, 2004 25–42.
[18] B. Szołyga, R. Gniłka, M. Szczepanik, A. Szumny, Entomol. Exp. Appl. 151 (2014) 1–10.
[19] G.P. More, S.V. Bhat, Tetrahedron Lett. 54 (2013) 4148–4149.