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Synthesis, Absolute Configurations, and Biological Activities of Floral Scent Compounds from Night-Blooming Araceae

Patrick Stamm, Florian Etl, Artur Campos D. Maia, Stefan Dötterl, and Stefan Schulz*

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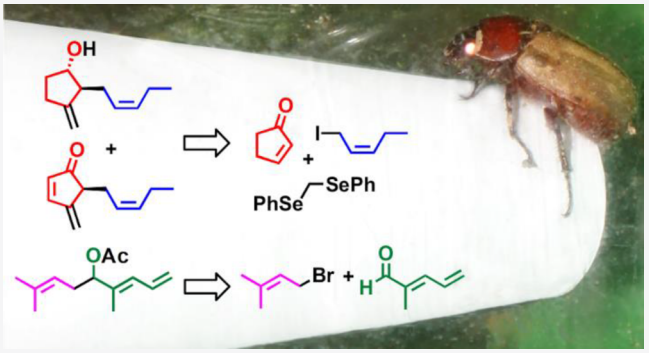
ABSTRACT: The uncommon jasmone derivatives dehydrojasmone, isojasmol, and isojasmyl acetate, floral scent compounds from night-blooming Araceae, were synthesized in a scalable synthesis employing conjugate addition with a selenoacetal as the key step. The stereoselective strategy with subsequent enzymatic kinetic resolution allowed determining the absolute configuration of the natural compounds by GC on a chiral phase. The homoterpene (*E*)-4,8-dimethyl-1,3,7-nonatrien-5-yl acetate, another uncommon scent compound, was obtained by α-regioselective aldehyde prenylation. The biological activities of dehydrojasmone and isojasmol were investigated in field assays, showing that these unique volatiles are able to selectively attract specific cyclocephaline scarab beetle pollinators.



INTRODUCTION

Night-blooming neotropical angiosperms of different plant lineages rely on single or simple combinations of specific floral volatile organic compounds[1] to selectively attract certain species of specialized cyclocephaline scarab beetle pollinators,[2] a mechanism assumed to play a key role in the reproductive isolation and species diversification of these plants. In 2019, we reported the discovery of three new floral scent compounds and one related compound[3] from headspace extracts of the South American scarab beetle-pollinated Araceae species *Thaumatophyllum mello-barretoanum*, *Xanthosoma hylaeae*, and *Philodendron squamiferum*.[4] After isolation by preparative gas chromatography, their structures were elucidated using high-resolution mass spectrometry and NMR spectroscopy, with their relative and absolute configurations still to be assigned (Scheme 1). The new compounds were found to be derived from more common floral scents, likely through biosynthetic "post-processing": isojasmol (**3**, isolated from *T. mello-barretoanum*, also produced by *X. hylaeae*, and *Ludovia lancifolia*[3]) and isojasmyl acetate (**4**, isolated from *X. hylaeae*) are reduction products of (*Z*)-jasmone (**1**), a widespread plant volatile produced from linolenic acid along the jasmonic acid cascade, which plays a role in attracting pollinators, antiherbivore defense, and intra- and interspecific control of gene expression.[5] The dienone dehydrojasmone (**2**, isolated from *T. mello-barretoanum*) is an oxidation product of (*Z*)-jasmone (**1**), with the endocyclic double-bond being shifted to the semicyclic position in all three compounds. The fourth compound, (*E*)-4,8-dimethyl-1,3,7-nonatrien-5-yl acetate (**6**, isolated from *P. squamiferum*), is an oxidation product of the homoterpene (*E*)-4,8-dimethyl-1,3,7-nonatriene (DMNT, **5**), another common plant volatile known to be involved in pollinator attraction and chemical defense.[3,6]

Herein, we report the synthesis of the jasmone derivatives **2**−**4** and homoterpene **6** by a scalable synthesis, the assignment of their absolute configurations, and results of field tests of their activities as attractants for scarab beetle pollinators.

RESULTS AND DISCUSSION

Synthesis of Jasmone Derivatives 2−4. Flowers and inflorescences of tropical plants pollinated by cyclocephaline scarab beetles emit large amounts of volatiles.[7] Therefore, we assumed that about 40 mg of material would be required for testing the attractiveness of these compounds in the field. Consequently, we were looking for a synthesis that could reliably yield the target compounds in the 100 mg range. Initial attempts using alkylation reactions starting from 1,3-cyclopentanedione were hampered by sometimes low yields and isomerizations. Subsequently, we opted for a late introduction of the double-bonds and 2-cyclopentenone as the starting material.

Similar to the classic three-component coupling prostaglandin synthesis developed by Noyori et al.,[8] a conjugate addition-

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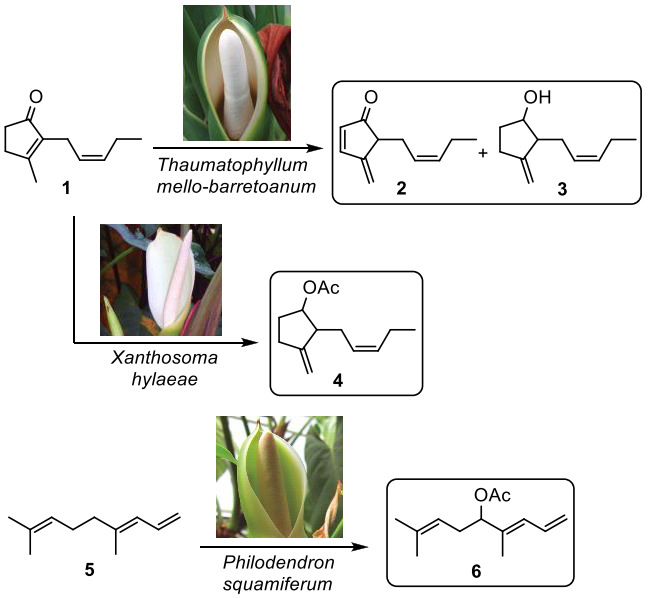
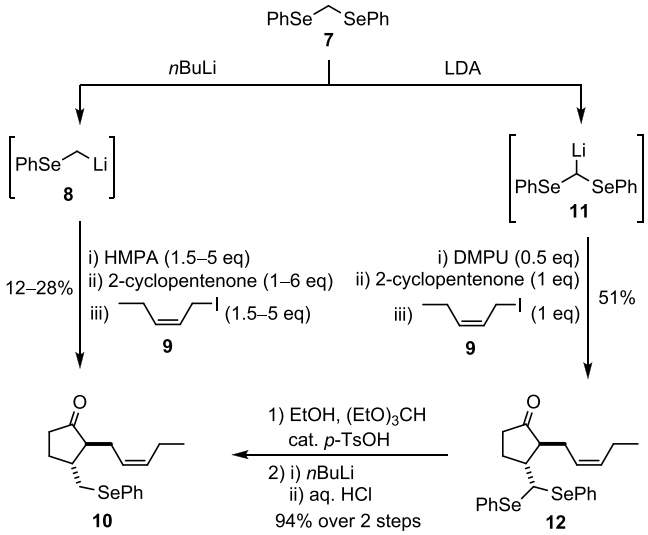
Scheme 1. Structures, Source Plants, and Assumed Biosynthetic Precursors of the Floral Scent Compounds Dehydrojasmone (2), Isojasmol (3), Isojasmyl Acetate (4), and (*E*)-4,8-Dimethyl-1,3,7-nonatrien-5-yl acetate (6). Photos from Top to Bottom by *A. Maia*, E. G. Gonçalves, and D. Scherberich[4]



enolate trapping strategy was anticipated to allow for an efficient construction of the carbon skeleton of jasmone derivatives **2**–**4**. The nucleophile used thereby should be suitably functionalized to later enable the facile introduction of the semicyclic double-bond. Organolithium reagents bearing an α-phenylselenyl group caught our interest as heterosubstituted organometallics of this kind are known to selectively undergo conjugate addition to α,β-unsaturated carbonyl systems in the presence of polar-aprotic co-solvents like HMPA or DMPU.[9−11] Unlike the enolates typically obtained from copper-based conjugate additions, the resulting lithium enolates are reactive enough to be directly alkylated.[12]

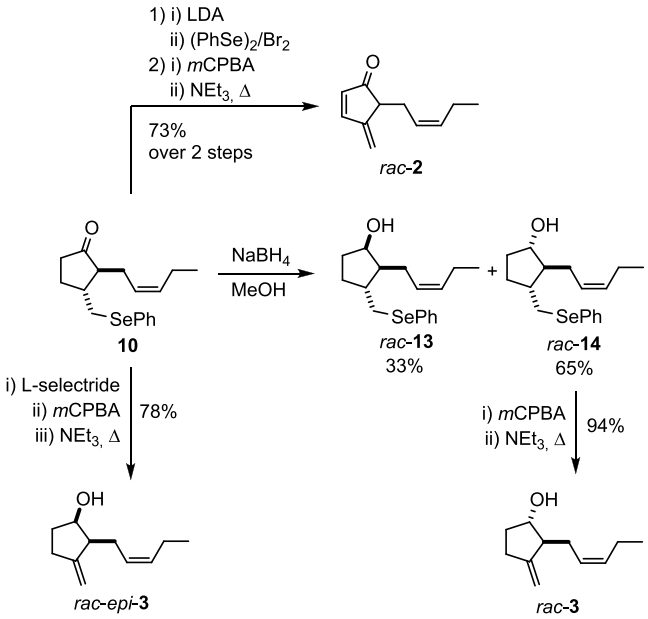
Thus, $(PhSe)CH_2Li$ (**8**), which can be generated via selenium-lithium exchange from selenoacetal **7**,[13] itself readily available from diphenyl diselenide and dibromomethane,[14] was selected as the nucleophile of first choice (Scheme 2). Despite extensive optimization attempts, its reaction with 2-cyclopentenone and allylic iodide **9**, accessible by iodination of the respective commercially available alcohol,[15] produced only low and variable yields of the desired coupling product **10**. As expected, the presence of excess HMPA was observed to suppress 1,2-addition but presumably also promotes competing deprotonation of the enone by exalting the basicity of organolithium reagent **8**. However, when treated with LDA instead of *n*-BuLi, selenoacetal **7** is deprotonated to yield the alternative nucleophile $(PhSe)_2CHLi$ (**11**), which compared to **8** exhibits a lower basicity and higher tendency toward conjugate addition due to stabilization of the carbanionic center by the second PhSe-group.[13] This nucleophile proved to be better suited for the addition, enabling the synthesis of the respective coupling product **12** in a fair yield on a 15 g scale. Compound **12** could then be efficiently transformed into the originally targeted key intermediate **10** by short-term protection of the keto group as the diethyl acetal followed by removal of one PhSe-group via selenium-lithium exchange.

Scheme 2. Synthesis of Key Intermediate 10 by Conjugate Addition of Selenium-Stabilized Organolithium Reagents 8/11 Followed by Enolate Trapping



From ketone **10**, racemic dehydrojasmone (*rac*-**2**) was smoothly obtained by α-selenylation of the keto group (LDA, $(PhSe)_2/Br_2$) followed by oxidative elimination of both selenyl groups using *m*CPBA (Scheme 3).[16,17] En route to isojasmol

Scheme 3. Synthesis of Racemic Dehydrojasmone (*rac*-2), Isojasmol (*rac*-3), and *epi*-Isojasmol (*rac-epi*-3) via Oxidative and Reductive Transformations of Ketone 10



(**3**), the reduction of ketone **10** produced two chromatographically separable diastereomers *rac*-**13** and *rac*-**14**. Like known for analogous substrates,[18] sodium borohydride was observed to exhibit a moderate 2:1 diastereoselectivity toward the 1,2-*trans*-product *rac*-**14**, while the addition of cerium trichloride promotes the 4:1 formation of 1,2-*cis*-product *rac*-**13** ($NaBH_4$, $CeCl_3{\cdot}7H_2O$, EtOH, −10 °C). Complete 1,2-*cis*-selectivity was obtained by the use of the hindered reducing agent L-selectride, in which case the oxidative workup generally

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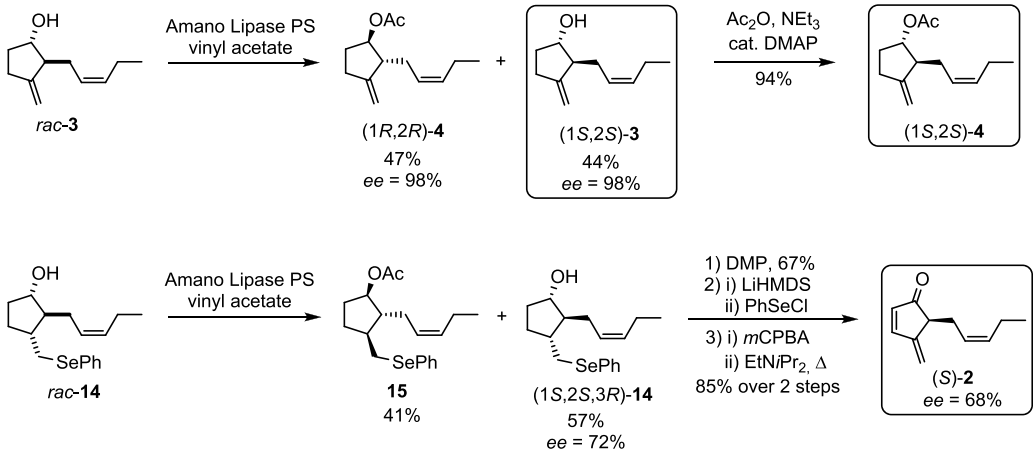
Scheme 4. Enantioselective Synthesis of Target Compounds 2−4 via Lipase-Catalyzed Kinetic Resolution



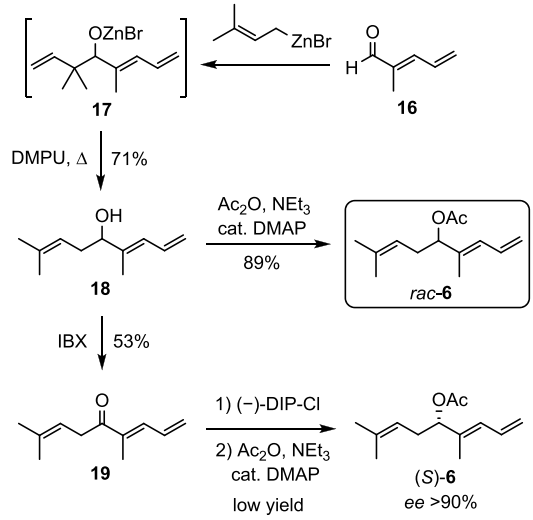
necessary for this reagent caused the concomitant oxidation of the PhSe-group, offering the possibility to perform the reduction of the keto group and selenoxide elimination efficiently as a one-pot reaction. Finally, the PhSe-group of 1,2-*trans*-diastereomer *rac*-**14** was eliminated in high yield under high-dilution conditions (*m*CPBA, hexane/NEt_3, Δ). Comparison of the two synthetic epimers *rac*-**3** and *rac-epi*-**3** with natural isojasmol by GC/MS, TLC, and NMR spectroscopy showed the natural relative configuration to be *trans*.

To give access to the enantioenriched target compounds and allow for the assignment of their natural absolute configurations, a lipase-catalyzed kinetic resolution[18] of *rac*-**3** (Amano lipase PS, vinyl acetate) was employed (Scheme 4). After approximately 50% conversion (∼4 days), both the product acetate and starting alcohol were obtained in high enantiomeric excess (98%). By synthesis and analysis of the Mosher esters[19] (see the Supporting Information), the slower acetylated enantiomer of isojasmol was shown to possess the (1*S*,2*S*)-configuration, confirming the selectivity predicted by Kazlauskas' rule.[20] By comparing the synthetic and natural samples via GC on a chiral stationary phase, (1*S*,2*S*) was revealed to be the configuration of both natural isojasmol (**3**) (Figure S2) and its acetate (**4**) (Figure S4). (1*S*,2*S*)-Isojasmyl acetate ((1*S*,2*S*)-**4**) was finally obtained via acetylation with acetic anhydride from (1*S*,2*S*)-**3**.

Attempts to transform (1*S*,2*S*)-**3** into enantioenriched dehydrojasmone (**2**) via oxidation to the corresponding ketone followed by α-selenylation/selenoxide elimination were unsuccessful, owing to the high tendency of the semicyclic double-bond to migrate into conjugation to the newly formed keto group. This could be overcome by performing the kinetic resolution before the formation of the semicyclic double-bond, although in this case the enzymatic reaction proceeded considerably slower (57% alcohol recovered after 8 days). Cyclopentanol (1*S*,2*S*,3*R*)-**14** was obtained with an enantiomeric excess of 72% and readily transformed into (*S*)-dehydrojasmone ((*S*)-**2**, ee = 68%) via oxidation to the ketone with Dess−Martin periodinane (DMP) followed by α-selenylation/selenoxide elimination. GC analysis on a chiral phase revealed (*S*) to be the natural configuration of dehydrojasmone, although the enantiomeric excesses observed in natural samples were low (29% in a sample from *Dieffenbachia aurantiaca*, 4% in a sample from *T. mello-barretoanum*), hinting toward a high tendency of **2** to racemize (Figure S3).

Synthesis of Homoterpene 6. The construction of the carbon skeleton of homoterpene **6** is efficiently accomplished via prenylation of the unsaturated aldehyde **16**, itself accessible from commercially available 3-ethoxymethacrolein and vinylmagnesium bromide (Scheme 5).[21] Typically, unsymmetrically

Scheme 5. Synthesis of Homoterpene 6 via α-Regioselective Prenylation



substituted allylic organometallics, e.g., prenyl Grignard reagents, add to carbonyl compounds with the higher substituted terminus (γ-addition), thus necessitating special methods for the synthesis of the desired α-addition product **18**.[22] Methods successfully used in the synthesis of the related natural product rosiridol include the BCl_3-mediated addition of a prenyl stannane[23] and a Ti(III)-catalyzed Barbier-type prenylation;[24] however, in the present synthesis, these procedures led to mixtures of α- and γ-isomers in low yields.

Eventually, satisfactory yields of alcohol **18** were obtained by the addition of prenylzinc bromide to aldehyde **16**. This method, used for the synthesis of rosiridol by Hong et al.[25] and then further developed by Zhao et al.,[26,27] involves the primary formation of the γ-addition product **17** followed by an *in situ* rearrangement to the thermodynamically more stable α-isomer induced by heating in polar-aprotic solvents such as HMPA or

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DMPU. From alcohol **18**, the racemic target compound *rac*-**6** was uneventfully obtained by acetylation with acetic anhydride.

Analogous to the synthesis of jasmone derivatives **2**−**4**, a lipase-catalyzed kinetic resolution was tested to synthesize natural product **6** in enantioenriched form; however, alcohol **18** showed little reactivity in the presence of various screened lipases (Amano lipase PS, lipase B from *Candida antarctica* immobilized on Immobead 150, Novozym 435, lipase from *C. rugosa*). Hence, the strategy used in the rosiridol synthesis by Schöttner et al., involving the IBX-oxidation of the racemic alcohol to the respective ketone **19** and subsequent enantioselective reduction with diisopinocampheylchloroborane (DIP-Cl), was adopted.[23] Although the reduction did not proceed in synthetically useful yield, a highly enantioenriched sample of acetate **6** was obtained that was used as reference in GC experiments on a chiral stationary phase (see the Supporting Information). Based on the transition-state model by Brown et al.[28] and the selectivity reported by Schöttner et al.,[23] we tentatively assign the (*S*)-configuration to the product obtained via the reduction with (−)-DIP-chloride. However, GC analysis on a chiral phase revealed that the natural compound is a racemic mixture or, at the most, might possess a low enantiomeric excess of the presumed (*S*)-enantiomer (Figure S5).

Biological Activities. In field bioassays in Costa Rica, the two compounds *rac*-dehydrojasmone (*rac*-**2**) and (1*S*,2*S*)-isojasmol ((1*S*,2*S*)-**3**) were highly specific attractants, each to a single distinct species of pollinating cyclocephaline scarab beetle. When tested on filter paper against filter paper alone (n = 3 each), 40 mg of isojasmol attracted overall 12 individuals of *Cyclocephala amblyopsis* Bates, 1888, while the same amount of dehydrojasmone attracted three individuals of *C. gravis* Bates, 1888. No other species of cyclocephaline scarab beetle responded to the scented baits. The negative control did not attract insects.

The specificity of each substance was further confirmed by paired testing (n = 2). Again, isojasmol specifically attracted *C. amblyopsis* (six individuals) and dehydrojasmone, *C. gravis* (three individuals). The lower number of *C. gravis* attracted to the scented baits appears to represent a natural trend as this species is less abundant at the study location than *C. amblyopsis* (Etl et al., unpublished data). Overall, these results show that both dehydrojasmone and isojasmol are bioactive and involved in the chemical communication between night-blooming Araceae and their specific pollinators. We expect that further studies will elucidate the role of these substances in the reproductive isolation of syntopic species through scent-mediated pollinator partitioning.

CONCLUSIONS

In summary, we establisehd an efficient strategy for the scalable synthesis of the new jasmone derivatives **2**, **3**, and **4** and determined their absolute configurations. These specific jasmone derivatives exhibit high and selective attractivity to specialized pollinating cyclocephaline scarab beetles.

EXPERIMENTAL SECTION

General Information. Natural dehydrojasmone (**2**) and natural (*E*)-4,8-dimethyl-1,3,7-nonatrien-5-yl acetate (**6**) were available in samples of *T. mello-barretoanum* and *P. squamiferum*, respectively, both from our previous work.[3] Natural dehydrojasmone (**2**) was also obtained from a dynamic headspace sample of *D. aurantiaca*. Natural isojasmol (**3**) and isojasmyl acetate (**4**) were available in a dynamic headspace sample collected from *P. grandipes*. Scents from inflorescences of *D. aurantiaca* and *P. grandipes* were collected at La Gamba, Costa Rica, on adsorbent tubes filled with Tenax TA/Carbotrap B (both Supelco, USA). To obtain the samples finally used for the present work, adsorbent tubes were eluted with 1 mL of acetone (p.a., Sigma-Aldrich, USA) (for more details, see elsewhere[29]).

Commercially available chemicals were purchased from Sigma-Aldrich, TCI, Fisher Scientific, and abcr and were used without further purification unless stated otherwise. Water- and air-sensitive reactions were carried out in heat-dried glassware under a nitrogen atmosphere. Solvents were dried by conventional methods. A silicone oil bath was used as a heat source for reactions that require heating. A Kugelrohr distillation apparatus (Büchi GKR-51) was used for the distillation of compound **16**. Flash column chromatography was performed using silica gel 60 (Fluka, particle size 0.040−0.063 mm, mesh 230−440 ASTM) as the stationary phase and redistilled technical solvents (pentane, diethyl ether) as eluents. TLC was performed on Polygram-SIL-G/UV254 silica plates (Macherey-Nagel). Molybdatophosphoric acid (10% in EtOH) was used for staining. NMR spectra were recorded on Avance III HD 300 N and Avance III 400 instruments (Bruker) at room temperature using tetramethylsilane as an internal standard (0 ppm). Signal multiplicities are denominated as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). Structural assignments were made with additional information from gCOSY, gHSQC, gNOESY, and gHMBC experiments.

EI-MS spectra (70 eV) were obtained by GC/MS on HP 6890/MSD 5973 and HP 7890A/MSD 5975 combinations (Agilent) using helium as carrier gas and HP-5MS fused-silica capillary columns (Agilent, 30 m × 250 μm × 0.25 μm). EI-HRMS spectra were obtained by GC/MS under the following conditions: An Agilent 6890 gas chromatograph was equipped with a 30 m analytical column (Phenomenex ZB1-MS, 30 m × 0.25 mm ID, tf = 0.25 μm). A split injection port at 270 °C was used for sample introduction, and the split ratio was set to 10:1. The temperature program was 50 °C (3 min)−10 °C/min−310 °C (3 min). Helium was used as carrier gas and was set to a 1.0 mL/min flow rate (constant flow mode). The transfer line was kept at 270 °C. A JMS-T100GC (GCAccuTOF, JEOL, Japan) time-of-flight mass spectrometer in electron ionization (EI) mode at 70 eV was used as the detector together with JEOL MassCenter workstation software. The source and transfer line temperatures were set at 200 and 270 °C, respectively. The detector voltage was set at 2050 V. The acquisition range was from m/z 41 to 600 with a spectrum recording interval of 0.4 s. The system was tuned with PFK to achieve a resolution of 6000 (FWHM) at m/z 292.9824. CI-HRMS spectra were obatined by GC/MS under the following conditions: A TRACE 1310 Series GC coupled to an Exactive GC Orbitrap mass spectrometer (Thermo Scientific) was used. Samples were injected (1 μL) in the gas chromatograph system with a split inlet of 1:20 and an injector temperature of 270 °C. The system was equipped with a ZB5MS capillary column (30 m × 25 mm ID × 0.25 μm f.t.; Phenomenex, Aschaffenburg, Germany), and helium was used as carrier gas at a flow rate of 1.0 mL/min. The temperature gradient used was 50 °C (3 min)−10 °C/min−310 °C (3 min). Mass spectral data were acquired in full scan mode (40−650 m/z), and the automatic gain control (AGC) was set to 1E6. The ion source and transfer line temperatures were set at 250 and 290 °C, respectively. The analyzer resolution settings were 60,000 at m/z 200 (full width at half-maximum (FWHM)) and 2 microscans averaging. For positive chemical ionization (CI) high-purity methane (99.995%; Westfalen AG) as CI-reagent gas was used at a flow rate of 1.7 mL/min. Internal lock masses (149.02332 or 207.03235) were used for spectrum mass correction. Xcalibur software V 4.4 (Thermo Scientific) was used for data processing. ESI-HRMS spectra were obtained using a linear ion trap coupled with an Orbitrap mass analyzer (LTQ-Orbitrap Velos, ThermoFisher Scientific (Bremen, Germany)) at a resolution of 100,000 FWHM at m/z 400. The acquisition range was m/z 130−2000 resulting in an acquisition time of 1.6 s per cycle. Electrospray measurements were performed in direct infusion mode using a

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custom-made microspray device mounted on a Proxeon nanospray ion source. The microspray device allows for the sample infusion through a stainless steel capillary (90 μm ID). The typical spray voltage was 2.3−2.8 kV in positive mode. Accurate mass measurements in the Orbitrap were performed using the lock mass option of the instrument control software using the cation of tetradecyltrimethylammonium bromide (256.29988 amu) as internal mass reference.

Enantiomer separation of isojasmol (**3**) and dehydrojasmone (**2**) was achieved by GC/FID on 7890A and 7820A gas chromatographs (Agilent) using hydrogen as carrier gas and a β-DEX 225 capillary column (Supelco, 30 m × 0.25 mm × 0.25 μm film thickness). In a typical temperature program, a starting temperature of 90 °C was held for 45 min. Then, the temperature was raised at a rate of 20 °C/min to 220 °C. Enantiomeric separation of homoterpene alcohol **18** was achieved by GC/FID on a 7820A gas chromatograph (Agilent) using hydrogen as carrier gas and a hydrodex β-6TBDM capillary column (Macherey-Nagel, 25 m × 0.25 mm ID). A starting temperature of 65 °C was held for 150 min. Then, the temperature was raised at a rate of 0.8 °C/min to 85 °C and eventually at a rate of 40 °C/min to 230 °C. IR spectra were recorded on a Bruker Tensor 27 (diamond ATR). Deviating from this, the IR spectrum of compound **6** was obtained using a GC/IR instrument, consisting of an Agilent 7890B gas chromatograph coupled to a Dani DiscovIR-GC. The band intensities are denominated as strong (s), medium (m), weak (w), and broad (br). Optical rotation values were measured on an MCP150 Modular Circular Polarimeter (Anton Paar).

Bis(phenylselenyl)methane (7). Using a modified procedure by Ribaudo et al., sodium borohydride (6.3 g, 167 mmol, 2.6 equiv.) was slowly added in portions to a suspension of diphenyl diselenide (20.0 g, 64 mmol, 1 equiv.) in abs. EtOH (700 mL) at 0 °C.[14] The reaction mixture was stirred at 0 °C for 30 min, giving a clear decolorized solution, and dibromomethane (4.5 mL, 11.1 g, 64 mmol, 1 equiv.) was added. The solution was stirred at room temperature for 20 h. The solvent was removed under reduced pressure, and the residue was partitioned between water and diethyl ether. The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over $MgSO_4$. After removal of the solvent under reduced pressure, selenoacetal **7** was obtained as a yellow oil/low-melting solid (19.7 g, 60.4 mmol, 94%).

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.52−7.45 (m, 4H), 7.24−7.19 (m, 6H), 4.16 (s, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ [ppm] = 132.7 (CH), 130.7 (C_q), 129.0 (CH), 127.3 (CH), 20.9 (CH_2); EI-MS (70 eV): *m*/*z* (%) = 328 (25, $[M]^+$), 326 (23), 324 (14), 173 (15), 171 (73), 169 (41), 167 (17), 157 (14), 93 (21), 91 (100), 77 (23), 65 (13), 51 (19); IR (ATR, neat): ν~ [cm^{-1}] = 3056 (w), 1574 (m), 1472 (m), 1433 (m), 1130 (m), 1065 (m), 1020 (m), 728 (s), 681 (s), 620 (m).

(*Z*)-1-Iodo-2-pentene (9). Using a modified procedure by Kurashina et al., (*Z*)-2-penten-1-ol (7.3 mL, 6.2 g, 72 mmol, 1 equiv.) was added at 0 °C to a solution of sodium iodide (21.6 g, 144 mmol, 2 equiv.) in acetonitrile (150 mL). The boron trifluoride-diethyl ether-complex (18.2 mL, 20.4 g, 144 mmol, 2 equiv.) was added dropwise, and the dark solution was stirred at 0 °C for 35 min.[15] The reaction mixture was poured into a mixture of sat. aq. $NaHCO_3$ and sat. aq. $Na_2S_2O_3$, and the aqueous and acetonitrile layers were extracted two times with pentane. The combined pentane extracts were dried over $MgSO_4$, and the solvent was removed under reduced pressure to yield crude allylic iodide **9** as a colorless liquid (12.4 g, 63.2 mmol, 88%). During synthesis and handling, this sensitive and lachrymatory compound was protected from light to avoid decomposition/isomerization. It was used immediately in the next step or stored in the freezer for short time periods.

EI-MS (70 eV): *m*/*z* (%) = 196 (8, $[M]^+$), 127 (14), 70 (7), 69 (100), 67 (7), 54 (13), 53 (10), 41 (71), 39 (23); ^{1}H and $^{13}C\{^1H\}$ NMR data: see elsewhere.[15]

(2*RS*,3*SR*)-3-(Bis(phenylselenyl)methyl)-2-((*Z*)-2-penten-1-yl)cyclopentan-1-one (12). A solution of *n*-butyllithium (1.6 M in hexanes, 41 mL, 66 mmol, 1.1 equiv.) was added at −80 °C to a solution of diisopropylamine (9.6 mL, 6.9 g, 69 mmol, 1.15 equiv.) in abs. THF (300 mL). After stirring for 5 min, a solution of selenoacetal **7** (19.5 g, 60 mmol, 1 equiv.) in THF (20 mL) was added, and the reaction mixture was stirred at −80 °C for another 1 h. DMPU (4.0 mL, 4.2 g, 33 mmol, 0.55 equiv.) and 2-cyclopentenone (5.0 mL, 4.9 g, 60 mmol, 1 equiv.) were added dropwise in short succession (2 min). After an additional 2 min, allylic iodide **9** (12.4 g, 63 mmol, 1.05 equiv.) was added. The mixture was warmed to −40 °C and stirred for 2 h at this temperature. The reaction was quenched by the addition of 1 M aq. HCl. The layers were separated, and the aqueous layer was extracted two times with diethyl ether. The combined organic layers were successively washed with a mixture of sat. aq. $NaHCO_3$/sat. aq. $Na_2S_2O_3$, sat. aq. NaCl and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica (pentane/diethyl ether 10:1) to yield cyclopentanone **12** as a yellowish oil (14.5 g, 30.4 mmol, 51%).

R_f (pentane/diethyl ether 10:1) = 0.27; ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.56−7.50 (m, 4H), 7.33−7.22 (m, 6H), 5.24−5.14 (m, 1H), 4.97−4.87 (m, 1H), 4.71 (d, *J* = 2.8 Hz, 1H), 2.57−2.49 (m, 1H), 2.46−2.26 (m, 3H), 2.16−1.99 (m, 3H), 1.85−1.63 (m, 3H), 0.84 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ [ppm] = 218.3 (C_q), 134.7 (CH), 134.2 (CH), 133.6 (CH), 130.7 (C_q), 130.1 (C_q), 129.2 (CH), 129.1 (CH), 128.2 (CH), 128.1 (CH), 124.9 (CH), 52.9 (CH), 50.4 (CH), 47.2 (CH), 37.3 (CH_2), 25.0 (CH_2), 24.4 (CH_2), 20.3 (CH_2), 14.1 (CH_3); HRMS (EI-TOF) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{26}OSe_2$: 478.0314; Found 478.0297; EI-MS (70 eV): *m*/*z* (%) = 478 (5, $[M]^+$), 476 (4), 321 (22), 319 (12), 253 (55), 251 (30), 163 (100), 157 (28), 155 (17), 145 (16), 135 (32), 121 (26), 119 (37), 96 (50), 91 (36), 79 (29), 77 (36), 69 (22), 67 (13), 55 (18), 41 (28); IR (ATR, neat): ν~ [cm^{-1}] = 3060 (w), 2962 (m), 2870 (w), 1736 (s), 1576 (m), 1470 (m), 1439 (m), 1266 (w), 1149 (m), 1066 (m), 1021 (m), 910 (m), 805 (m), 733 (s), 687 (s).

(2*RS*,3*SR*)-2-((*Z*)-2-Penten-1-yl)-3-((phenylselenyl)methyl)-cyclopentan-1-one (10). *p*-Toluenesulfonic acid monohydrate (56 mg, 0.3 mmol, 1 mol %) was added at room temperature to a solution of cyclopentanone **12** (14.1 g, 29.7 mmol, 1 equiv.) in abs. EtOH (200 mL). After dissolution, triethyl orthoformate (21 mL, 18.7 g, 126 mmol, 4.4 equiv.) was added, and the reaction mixture was stored in a refrigerator overnight. The solvent was removed under reduced pressure, and the crude diethyl acetal was dried in high vacuum.

The acetal was dissolved in THF (250 mL), and *n*-butyllithium (1.6 M in hexanes, 44 mL, 70 mmol, 2.4 equiv.) was added dropwise at −80 °C. After stirring for 50 min at −80 °C, EtOH (10 mL) was added, and the reaction mixture was warmed to room temperature. 1 M aq. HCl (150 mL) was added, and the biphasic mixture was stirred vigorously for 1 h. The layers were separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with sat. aq. $NaHCO_3$ and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica (pentane/diethyl ether 10:1) to yield cyclopentanone **10** as a yellowish oil (8.94 g, 27.8 mmol, 94%).

R_f (pentane/diethyl ether 10:1) = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.55−7.48 (m, 2H), 7.30−7.23 (m, 3H), 5.44−5.36 (m, 1H), 5.22−5.14 (m, 1H), 3.32 (dd, *J* = 12.2 Hz, 3.9 Hz, 1H), 2.90 (dd, *J* = 12.2 Hz, 8.4 Hz, 1H), 2.40−1.94 (m, 9H), 1.58−1.49 (m, 1H), 0.92 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ [ppm] = 219.2 (C_q), 133.9 (CH), 132.7 (CH), 130.3 (C_q), 129.1 (CH), 127.0 (CH), 125.1 (CH), 54.7 (CH), 41.8 (CH), 37.7 (CH_2), 33.1 (CH_2), 27.4 (CH_2), 25.4 (CH_2), 20.5 (CH_2), 14.1 (CH_3); HRMS (EI-TOF) *m*/*z*: $[M]^+$ Calcd for $C_{17}H_{22}OSe$: 322.0836; Found 322.0849; EI-MS (70 eV): *m*/*z* (%) = 322 (46, $[M]^+$), 320 (24), 254 (22), 252 (11), 172 (100), 170 (50), 165 (33), 158 (25), 157 (28), 151 (42), 147 (16), 135 (23), 123 (18), 109 (38), 97 (91), 95 (33), 93 (30), 91 (53), 83 (35), 81 (62), 79 (42), 77 (46), 69 (29), 67 (48), 55 (56), 41 (61); IR (ATR, neat): ν~ [cm^{-1}] = 3062 (w), 3006 (w), 2962 (m), 2927 (w), 2872 (w), 1736 (s), 1578 (m), 1470 (m), 1437 (m), 1409 (w), 1157 (m), 1070 (m), 1022 (m), 914 (w), 805 (w), 733 (s), 690 (s).

***rac*-4-Methylene-5-((*Z*)-2-penten-1-yl)-2-cyclopenten-1-one (*rac*-2).** At −80 °C, *n*-butyllithium (1.6 M in hexanes, 5.6 mL, 9.0 mmol, 1.2 equiv.) was added to a solution of diisopropylamine (1.36

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mL, 0.98 g, 9.7 mmol, 1.3 equiv.) in abs. THF (50 mL). After 3 min, cyclopentanone **10** (2.40 g, 7.47 mmol, 1 equiv.) in THF (5 mL) was added dropwise, and the reaction mixture was stirred for 1 h at −80 °C. In a separate flask, bromine (0.25 mL, 0.78 g, 4.9 mmol, 0.65 equiv.) was added dropwise to a solution of diphenyl diselenide (1.52 g, 4.86 mmol, 0.65 equiv.) in THF (5 mL). The resulting dark PhSeBr-solution was rapidly added to the enolate solution (decoloration). The reaction mixture was transferred to a separation funnel and partitioned between diethyl ether and 1 M aq. HCl. The aqueous layer was extracted with diethyl ether, and the combined organic layers were washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl and dried over $MgSO_4$.

The solvent was removed under reduced pressure, and the crude α,δ-bis(phenylselenyl)ketone was dissolved in DCM (50 mL). At −60 °C, mCPBA (70−75%, 4.27 g, 17.3−18.6 mmol, 2.3−2.5 equiv.) in DCM (20 mL) was added dropwise, and the reaction mixture was stirred at −60 °C for 30 min. Triethylamine (6.2 mL, 4.5 g, 45 mmol, 6 equiv.) was added, and the mixture was poured into refluxing DCM (400 mL). After 5 min in reflux, the solution was cooled to room temperature and washed with sat. aq. $NaHCO_3$. The aqueous layer was extracted with DCM, and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica (pentane/diethyl ether 20:1 → 10:1) to yield *rac*-dehydrojasmone (*rac*-**2**, 0.89 g, 5.49 mmol, 73%) as a yellowish liquid with a fruity odor. The compound is best stored in solution in a freezer. When left neat at room temperature, it decomposes overnight.

R_f (pentane/diethyl ether 10:1) = 0.26; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.72 (d, *J* = 5.6 Hz, 1H), 6.27 (dd, *J* = 5.5 Hz, 1.4 Hz, 1H), 5.45−5.38 (m, 1H), 5.40−5.39 (m, 1H), 5.35−5.34 (m, 1H), 5.26−5.19 (m, 1H), 2.87−2.83 (m, 1H), 2.59−2.47 (m, 2H), 2.07−2.00 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 208.6 (C_q), 159.0 (CH), 148.8 (C_q), 134.2 (CH), 134.0 (CH), 124.0 (CH), 113.0 (CH_2), 47.7 (CH), 27.1 (CH_2), 20.6 (CH_2), 14.1 (CH_3);); HRMS (EI-TOF) *m*/*z*: $[M]^+$ Calcd for $C_{11}H_{14}O$: 162.1045; Found 162.1060; EI-MS (70 eV): *m*/*z* (%) = 162 (17, $[M]^+$), 147 (10), 133 (50), 119 (18), 115 (9), 107 (11), 105 (25), 103 (7), 94 (100), 91 (36), 79 (15), 77 (23), 69 (7), 65 (12), 55 (13), 51 (11), 41 (19), 39 (17); GC: *I* = 1300 (HP-5MS); IR (ATR, neat): ν∼ [cm^{-1}] = 3009 (w), 2965 (w), 2876 (w), 1704 (s), 1639 (w), 1546 (m), 1455 (w), 1267 (w), 1166 (m), 1075 (w), 901 (m), 837 (m), 726 (w), 689 (w).

(1*RS*,2*SR*,3*RS*)-2-((*Z*)-2-Penten-1-yl)-3-((phenylselenyl)-methyl)cyclopentan-1-ol (*rac*-13) and (1*RS*,2*RS*,3*SR*)-2-((*Z*)-2-Penten-1-yl)-3-((phenylselenyl)methyl)cyclopentan-1-ol (*rac*-14). *Variant A (NaBH$_4$).* At room temperature, sodium borohydride (21 mg, 0.55 mmol, 1.5 equiv.) was added to a solution of cyclopentanone **10** (116 mg, 0.361 mmol, 1 equiv.) in abs. MeOH (5 mL). After stirring for 40 min, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica (pentane/diethyl ether 4:1) to yield 1,2-*trans*-cyclopentanol *rac*-**14** (75.5 mg, 0.234 mmol, 65%) and 1,2-*cis*-cyclopentanol *rac*-**13** (39 mg, 0.12 mmol, 33%) as colorless oils.

Variant B (NaBH$_4$/CeCl$_3$). At −10 °C, sodium borohydride (3.1 mg, 0.081 mmol, 1.1 equiv.) was added to a solution of cyclopentanone **10** (23.6 mg, 0.073 mmol, 1 equiv.) and cerium trichloride heptahydrate (30.1 mg, 0.081 mmol, 1.1 equiv.) in abs. EtOH (2 mL). The reaction mixture was warmed to room temperature over the course of 2 h. The reaction was quenched by the addition of sat. aq. $NaHCO_3$, and the aqueous layer was extracted two times with diethyl ether. The combined organic layers were dried over $MgSO_4$. GC analysis of the crude product showed the diastereomeric ratio **14**/**13** to be 1:4.

1,2-cis-Diastereomer rac-13. R_f (pentane/diethyl ether 2:1) = 0.46; ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.51−7.46 (m, 2H), 7.28−7.18 (m, 3H), 5.47−5.30 (m, 2H), 4.23 (td, *J* = 4.8 Hz, 2.0 Hz, 1H), 3.21 (dd, *J* = 11.6 Hz, 3.9 Hz, 1H), 2.82 (dd, *J* = 11.6 Hz, 8.5 Hz, 1H), 2.23−2.00 (m, 6H), 1.95−1.82 (m, 1H), 1.67−1.49 (m, 2H), 1.47 (s, 1H), 1.46−1.33 (m, 1H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ [ppm] = 132.8 (CH), 132.3 (CH), 130.9 (C_q), 129.0 (CH), 127.3 (CH), 126.6 (CH), 74.8 (CH), 51.4 (CH), 42.3 (CH), 33.8 (CH_2), 33.1 (CH_2), 29.8 (CH_2), 25.7 (CH_2), 20.6 (CH_2), 14.2 (CH_3); EI-MS (70 eV): *m*/*z* (%) = 324 (39, $[M]^+$), 322 (19), 172 (100), 170 (51), 167 (36), 158 (51), 153 (88), 149 (44), 119 (30), 107 (55), 93 (71), 91 (70), 81 (93), 79 (72), 77 (54), 69 (73), 67 (59), 55 (74), 41 (88); IR (ATR, neat): ν∼ [cm^{-1}] = 3403 (br), 3064 (w), 2957 (m), 1578 (w), 1470 (m), 1437 (m), 1303 (w), 1213 (w), 1070 (m), 1025 (m), 936 (w), 886 (w), 732 (s), 688 (s).

1,2-trans-Diastereomer rac-14. R_f (pentane/diethyl ether 2:1) = 0.32; ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.51−7.45 (m, 2H), 7.28−7.18 (m, 3H), 5.50−5.31 (m, 2H), 3.93−3.85 (m, 1H), 3.19 (dd, *J* = 11.7 Hz, 4.8 Hz, 1H), 2.90 (dd, *J* = 11.8 Hz, 8.5 Hz, 1H), 2.22−1.98 (m, 4H), 1.92−1.78 (m, 3H), 1.75 (s, 1H), 1.67−1.51 (m, 3H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ [ppm] = 133.5 (CH), 132.3 (CH), 130.8 (C_q), 129.0 (CH), 126.7 (CH), 126.6 (CH), 78.7 (CH), 54.3 (CH), 43.7 (CH), 34.3 (CH_2), 33.2 (CH_2), 30.2 (CH_2), 29.4 (CH_2), 20.6 (CH_2), 14.2 (CH_3); HRMS (EI-TOF) *m*/*z*: $[M]^+$ Calcd for $C_{17}H_{24}OSe$: 324.0992; Found 324.1009; EI-MS (70 eV): *m*/*z* (%) = 324 (16, $[M]^+$), 322 (8), 306 (9), 158 (29), 149 (100), 135 (9), 133 (10), 119 (25), 107 (41), 93 (52), 91 (41), 81 (57), 79 (46), 69 (50), 67 (38), 55 (44), 41 (57); IR (ATR, neat): ν∼ [cm^{-1}] = 3350 (br), 3064 (w), 2957 (m), 1578 (w), 1470 (m), 1437 (m), 1342 (w), 1214 (w), 1072 (m), 1023 (m), 973 (m), 909 (w), 731 (s), 688 (s).

(1*RS*,2*SR*)-3-Methylene-2-((*Z*)-2-penten-1-yl)cyclopentan-1-ol (*rac-epi*-3). L-Selectride (1 M in THF, 1.0 mL, 1.0 mmol, 1.3 equiv.) was added dropwise to a solution of cyclopentanone **10** (246 mg, 0.77 mmol, 1 equiv.) in abs. THF (15 mL) at −80 °C. The reaction mixture was allowed to warm to −25 °C over the course of 1.5 h. Then, a solution of mCPBA (70−75%, 1.04 g, 4.22−4.52 mmol, 5.5−5.9 equiv.) in THF (5 mL) was added dropwise, and the mixture was allowed to warm to −10 °C over the course of 1 h. The solution was poured into a refluxing mixture of hexane (100 mL) and triethylamine (10 mL). After 5 min in reflux, the reaction mixture was cooled to room temperature and washed with sat. aq. $NaHCO_3$. The aqueous layer was extracted two times with ethyl acetate, and the combined organic layers were washed with sat. aq. NaCl and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica (pentane/diethyl ether 10:1 → 5:1) to yield *epi*-isojasmol (*rac-epi*-**3**) as a yellowish liquid (100 mg, 0.60 mmol, 78%).

R_f (pentane/diethyl ether 2:1) = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 5.51−5.42 (m, 2H), 5.00−4.98 (m, 1H), 4.90 (q, *J* = 2.3 Hz, 1H), 4.26 (q, *J* = 3.2 Hz, 1H), 2.61−2.50 (m, 1H), 2.47−2.33 (m, 3H), 2.28−2.19 (m, 1H), 2.15−2.08 (m, 2H), 1.81−1.76 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 153.1 (C_q), 132.9 (CH), 127.2 (CH), 106.2 (CH_2), 74.1 (CH), 49.7 (CH), 32.4 (CH_2), 29.5 (CH_2), 25.0 (CH_2), 20.6 (CH_2), 14.2 (CH_3); EI-MS (70 eV): *m*/*z* (%) = 165 (6, $[M-H]^+$), 148 (13), 137 (11), 133 (15), 122 (28), 119 (100), 109 (22), 105 (31), 96 (31), 93 (46), 91 (97), 83 (32), 81 (46), 80 (90), 79 (85), 77 (42), 69 (39), 67 (48), 55 (29), 53 (23), 41 (87); GC: *I* = 1304 (HP-5MS); IR (ATR, neat): ν∼ [cm^{-1}] = 3373 (br), 3073 (w), 3006 (w), 2961 (s), 2932 (m), 1654 (m), 1456 (m), 1299 (w), 1255 (w), 1153 (m), 1077 (m), 1022 (m), 976 (m), 877 (s), 794 (m), 735 (s), 675 (m), 607 (w).

(1*RS*,2*RS*)-3-Methylene-2-((*Z*)-2-penten-1-yl)cyclopentan-1-ol (*rac*-3). At 0 °C, mCPBA (70−75%, 3.79 g, 15.4−16.5 mmol, 1.0−1.1 equiv.) was added to a solution of 1,2-*trans*-cyclopentanol *rac*-**14** (4.97 g, 15.4 mmol, 1 equiv.) in DCM (50 mL). After stirring for 15 min at 0 °C, the reaction mixture was poured into a refluxing mixture of hexane (1.5 L) and triethylamine (50 mL). After 1 h in reflux, the reaction mixture was cooled to room temperature and washed with sat. aq. $NaHCO_3$. The aqueous layer was extracted two times with diethyl ether. The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica (pentane/diethyl ether 4:1 → 2:1) to yield *rac*-isojasmol (*rac*-**3**) as a yellowish liquid (2.41 g, 14.5 mmol, 94%).

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R_f (pentane/diethyl ether 2:1) = 0.31; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 5.54−5.44 (m, 2H), 4.94−4.91 (m, 1H), 4.90−4.87 (m, 1H), 3.91 (q, J = 6.1 Hz, 1H), 2.54−2.45 (m, 1H), 2.35−1.95 (m, 7H), 1.75 (br s, 1H), 1.67−1.57 (m, 1H), 0.98 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 152.8 (C_q), 133.5 (CH), 126.8 (CH), 106.7 (CH_2), 77.9 (CH), 52.3 (CH), 32.5 (CH_2), 29.8 (CH_2), 29.2 (CH_2), 20.7 (CH_2), 14.2 (CH_3); HRMS (CI-Orbitrap) m/z: [M + H]$^+$ Calcd for $C_{11}H_{19}O$ 167.1436; Found 167.1431; EI-MS (70 eV): m/z (%) = 166 (4, [M]$^+$), 165 (14, [M−H]$^+$), 151 (11), 148 (13), 137 (25), 133 (15), 122 (32), 119 (91), 109 (42), 107 (25), 105 (25), 97 (45), 96 (71), 95 (47), 93 (63), 91 (76), 83 (53), 81 (56), 80 (64), 79 (81), 77 (52), 69 (57), 67 (64), 55 (43), 53 (33), 43 (24), 41 (100), 39 (44); GC: I = 1296 (HP-5MS); IR (ATR, neat): $\nu\sim$ [cm^{-1}] = 3333 (br), 3073 (w), 2960 (s), 2875 (m), 1654 (m), 1442 (m), 1343 (w), 1067 (s), 961 (m), 881 (s), 727 (m), 682 (m).

(1*S*,2*S*)-3-Methylene-2-((*Z*)-2-penten-1-yl)cyclopentan-1-ol ((1*S*,2*S*)-3) and (1*R*,2*R*)-3-Methylene-2-((*Z*)-2-penten-1-yl)-cyclopentyl Acetate ((1*R*,2*R*)-4). Amano Lipase PS (2.36 g) was added to a solution of *rac*-isojasmol (*rac*-**3**, 1.48 g, 8.88 mmol, 1 equiv.) in diethyl ether (50 mL), pentane (50 mL), and vinyl acetate (50 mL). The reaction mixture was stirred vigorously at room temperature for 91 h (progress monitored by chiral GC). Then, the mixture was filtered, and the filter cake was washed extensively with diethyl ether. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica (pentane/diethyl ether 10:1 → 2:1). After evaporation, the combined isojasmol fractions were redissolved in diethyl ether/pentane 1:1 and washed two times with sat. aq. K_2CO_3 to remove co-eluted acetic acid. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. (1*S*,2*S*)-Isojasmol ((1*S*,2*S*)-**3**, 648 mg, 3.90 mmol, 44%) and (1*R*,2*R*)-isojasmyl acetate ((1*R*,2*R*)-**4**, 879 mg, 4.22 mmol, 47%) were obtained as yellowish liquids.

To allow for the determination of the enantiomeric excess by GC on a chiral stationary phase, a sample of (1*R*,2*R*)-isojasmyl acetate was transformed back into isojasmol by deacylation: Sodium ethoxide (21 wt % in EtOH, 1.6 equiv.) was added to a solution of (1*R*,2*R*)-**4** in EtOH (0.05 M), and the mixture was left at room temperature for 4 h. Water was added, and the mixture was extracted two times with diethyl ether. After drying over $MgSO_4$, the crude isojasmol solution was directly analyzed.

*(1S,2S)-Isojasmol ((1S,2S)-**3**).* $[\alpha]_D^{25}$ = −54.8 (*c* 0.93, EtOH); ee = 98% (GC); the spectroscopic data were identical to those reported for *rac*-isojasmol (*rac*-**3**).

*(1R,2R)-Isojasmyl Acetate ((1R,2R)-**4**).* R_f (pentane/diethyl ether 10:1) = 0.50; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 5.48−5.33 (m, 2H), 4.97−4.95 (m, 1H), 4.93−4.87 (m, 2H), 2.56−2.44 (m, 2H), 2.40−2.31 (m, 1H), 2.28−2.12 (m, 2H), 2.09−1.99 (m, 3H), 2.02 (s, 3H), 1.75−1.66 (m, 1H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 170.8 (C_q), 152.0 (C_q), 133.2 (CH), 125.9 (CH), 106.9 (CH_2), 79.8 (CH), 49.5 (CH), 30.02 (CH_2), 20.99 (CH_2), 29.96 (CH_2), 21.3 (CH_3), 20.6 (CH_2), 14.1 (CH_3); HRMS (ESI-Orbitrap) m/z: [M + Na]$^+$ Calcd for $C_{13}H_{20}O_2Na$ 231.1361; Found 231.1356; EI-MS (70 eV): m/z (%) = 166 (1), 148 (61), 133 (27), 119 (100), 106 (36), 105 (33), 97 (16), 93 (16), 92 (16), 91 (59), 81 (19), 80 (73), 79 (55), 77 (23), 69 (16), 67 (15), 55 (10), 53 (11), 43 (75), 41 (39), 39 (14); GC: I = 1410 (HP-5MS); IR (ATR, neat): $\nu\sim$ [cm^{-1}] = 3074 (w), 2964 (m), 2875 (w), 1736 (s), 1657 (w), 1441 (w), 1369 (m), 1236 (s), 1040 (m), 965 (w), 886 (m), 725 (w), 608 (w); $[\alpha]_D^{25}$ = +32.5 (*c* 1.07, EtOH); ee = 98% (GC after derivatization).

Mosher Esters of (1*S*,2*S*)-Isojasmol ((1*S*,2*S*)-3). Following the procedure by Ward and Rhee for the microscale preparation of Mosher's acid chloride, oxalyl chloride (0.04 mL, 57 mg, 0.45 mmol, 10 equiv.) was added dropwise to a solution of (*S*)-Mosher's acid (20.9 mg, 0.089 mmol, 2 equiv.) and DMF (7 μL, 6.5 mg, 0.089 mmol, 2 equiv.) in abs. hexane (5 mL).[30] After stirring for 1 h at room temperature, the mixture was decanted, and the solvent and excess oxalyl chloride were removed under reduced pressure. The residue was dissolved in abs. DCM (2 mL), and triethylamine (0.02 mL, 18 mg, 0.18 mmol, 4 equiv.), (1*S*,2*S*)-isojasmol ((1*S*,2*S*)-**3**, 7.4 mg, 0.045 mmol, 1 equiv.), and DMAP (3 mg, 0.02 mmol, 0.5 equiv.) were added successively. The mixture was stirred overnight at room temperature and then directly subjected to column chromatography on silica (pentane/diethyl ether 20:1) to yield the (*S*)-Mosher ester (12.3 mg, 0.032 mmol, 72%) as a colorless oil/solid.

In an analogous experiment, the (*R*)-Mosher ester (19.9 mg, 0.052 mmol, 93%) was obtained from (*R*)-Mosher's acid (26.2 mg, 0.112 mmol) and (1*S*,2*S*)-isojasmol ((1*S*,2*S*)-**3**, 9.3 mg, 0.056 mmol).

(1S,2S)-Isojasmyl (S)-Mosher Ester. R_f (pentane/diethyl ether 20:1) = 0.47; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.54−7.50 (m, 2H), 7.43−7.36 (m, 3H), 5.52−5.35 (m, 2H), 5.13 (q, J = 4.4 Hz, 1H), 4.97 (q, J = 2.1 Hz, 1H), 4.93 (q, J = 2.1 Hz, 1H), 3.56−3.54 (m, 3H), 2.69−2.62 (m, 1H), 2.50−2.33 (m, 2H), 2.30−1.99 (m, 5H), 1.79−1.71 (m, 1H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 166.1 (C_q), 151.3 (C_q), 133.7 (CH), 132.4 (C_q), 129.5 (CH), 128.3 (CH), 127.3 (CH), 125.5 (CH), 123.3 (q, J = 288 Hz, CF_3), 107.4 (CH_2), 84.5 (q, J = 27.5 Hz, C_q), 82.5 (CH), 55.4 (CH_3), 49.4 (CH), 30.2 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 20.7 (CH_2), 14.2 (CH_3).

(1S,2S)-Isojasmyl (R)-Mosher Ester. R_f (pentane/diethyl ether 20:1) = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.55−7.50 (m, 2H), 7.42−7.36 (m, 3H), 5.47−5.39 (m, 1H), 5.36−5.28 (m, 1H), 5.12 (q, J = 4.9 Hz, 1H), 4.95 (q, J = 2.0 Hz, 1H), 4.89 (q, J = 2.1 Hz, 1H), 3.54−3.53 (m, 3H), 2.62−2.56 (m, 1H), 2.54−2.34 (m, 2H), 2.28−2.10 (m, 3H), 2.01 (quin, J = 7.4 Hz, 2H), 1.86−1.77 (m, 1H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 166.1 (C_q), 151.0 (C_q), 133.6 (CH), 132.3 (C_q), 129.5 (CH), 128.3 (CH), 127.4 (CH), 125.4 (CH), 123.3 (q, J = 288 Hz, CF_3), 107.4 (CH_2), 84.5 (q, J = 27.7 Hz, C_q), 82.2 (CH), 55.3 (CH_3), 49.2 (CH), 30.1 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 20.7 (CH_2), 14.2 (CH_3).

(1*S*,2*S*)-3-Methylene-2-((*Z*)-2-penten-1-yl)cyclopentyl Acetate ((1*S*,2*S*)-4). Acetic anhydride (0.11 mL, 120 mg, 1.2 mmol, 2 equiv.) and DMAP (7 mg, 0.06 mmol, 10 mol %) were added at room temperature to a solution of (1*S*,2*S*)-isojasmol ((1*S*,2*S*)-**3**, 100 mg, 0.60 mmol, 1 equiv.) and triethylamine (0.33 mL, 240 mg, 2.4 mmol, 4 equiv.) in abs. DCM (10 mL). After stirring for 16 h at room temperature, the reaction mixture was diluted with diethyl ether, washed with 1 M aq. HCl, sat. aq. $NaHCO_3$, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and (1*S*,2*S*)-isojasmyl acetate ((1*S*,2*S*)-**4**, 118 mg, 0.57 mmol, 94%) was obtained as a yellowish liquid.

$[\alpha]_D^{25}$ = −29.3 (*c* 1.05, EtOH); the spectroscopic data were identical to those reported for (1*R*,2*R*)-isojasmyl acetate ((1*R*,2*R*)-**4**).

(1*S*,2*S*,3*R*)-2-((*Z*)-2-penten-1-yl)-3-((phenylselenyl)methyl)-cyclopentan-1-ol ((1*S*,2*S*,3*R*)-14) and (1*R*,2*R*,3*S*)-2-((*Z*)-2-Penten-1-yl)-3-((phenylselenyl)methyl)cyclopentyl Acetate (15). Amano Lipase PS (0.72 g) was added to a solution of *rac*-1,2-*trans*-cyclopentanol *rac*-**14** (0.87 g, 2.69 mmol, 1 equiv.) in diethyl ether (15 mL), pentane (15 mL), and vinyl acetate (15 mL). The reaction mixture was stirred vigorously at room temperature for 7 days. Then, the mixture was filtered, and the filter cake was washed extensively with diethyl ether. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica (pentane/diethyl ether 2:1) to yield (1*S*,2*S*,3*R*)-cyclopentanol (1*S*,2*S*,3*R*)-**14** (498 mg, 1.54 mmol, 57%) and (1*R*,2*R*,3*S*)-cyclopentyl acetate **15** (404 mg, 1.11 mmol, 41%) as yellowish oils.

To allow for the determination of the configuration and enantiomeric excess by GC on a chiral stationary phase, a sample of (1*S*,2*S*,3*R*)-cyclopentanol (1*S*,2*S*,3*R*)-**14** was transformed into isojasmol by selenoxide elimination analogous to the preparation of *rac*-isojasmol (*rac*-**3**).

*(1S,2S,3R)-Cyclopentanol (1S,2S,3R)-**14**.* $[\alpha]_D^{25}$ = −45.1 (*c* 0.97, DCM); ee = 72% (GC after derivatization); the spectroscopic data were identical to those reported for *rac*-1,2-*trans*-cyclopentanol *rac*-**14**.

*(1R,2R,3S)-Cyclopentyl Acetate **15**.* R_f (pentane/diethyl ether 2:1) = 0.67; ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.51−7.45 (m, 2H), 7.28−7.20 (m, 3H), 5.46−5.36 (m, 1H), 5.33−5.23 (m, 1H), 4.83

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(dt, J = 8.0 Hz, 3.1 Hz, 1H), 3.17 (dd, J = 11.7 Hz, 4.8 Hz, 1H), 2.88 (dd, J = 11.7 Hz, 8.4 Hz, 1H), 2.22−1.47 (m, 10H), 2.01 (s, 3H), 0.92 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ [ppm] = 170.6 (C_q), 133.4 (CH), 132.4 (CH), 130.6 (C_q), 128.9 (CH), 126.6 (CH), 125.8 (CH), 80.6 (CH), 51.3 (CH), 43.5 (CH), 33.9 (CH_2), 31.0 (CH_2), 30.3 (CH_2), 29.8 (CH_2), 21.3 (CH_3), 20.5 (CH_2), 14.2 (CH_3); HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{19}H_{26}O_2Se$ 366.1098; Found 366.1073; EI-MS (70 eV): m/z (%) = 366 (17, $[M]^+$), 364 (9), 306 (19), 304 (10), 238 (9), 171 (9), 157 (19), 149 (100), 135 (8), 133 (12), 119 (32), 107 (49), 93 (57), 91 (50), 81 (55), 79 (56), 77 (32), 69 (30), 67 (33), 55 (24), 43 (81), 41 (44); IR (ATR, neat): $\nu\sim$ [cm^{-1}] = 3063 (w), 3006 (w), 2961 (m), 2930 (w), 2872 (w), 1732 (s), 1578 (w), 1470 (w), 1437 (m), 1367 (m), 1239 (s), 1022 (s), 970 (w), 734 (s), 690 (m), 607 (w); $[\alpha]_D^{25}$ = +39.3 (c 1.17, DCM).

(*S*)-4-Methylene-5-((*Z*)-2-penten-1-yl)-2-cyclopenten-1-one ((*S*)-2). *(2S,3R)-2-((Z)-2-Penten-1-yl)-3-((phenylselenyl)methyl)-cyclopentan-1-one ((2S,3R)-**10**).* Dess−Martin periodinane[31] (354 mg, 0.84 mmol, 2 equiv.) was added to a solution of (1*S*,2*S*,3*R*)-cyclopentanol (1*S*,2*S*,3*R*)-**14** (135 mg, 0.42 mmol, 1 equiv.) in DCM (8 mL). The turbid reaction mixture was stirred for 2 h at room temperature. Then, a mixture of sat. aq. $NaHCO_3$ and sat. aq. $Na_2S_2O_3$ was added. After stirring for 5 min, the phases became clear. The mixture was extracted two times with diethyl ether. The combined organic layers were washed with sat. aq. $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by filtering through a short column of silica (pentane/diethyl ether 2:1). (2*S*,3*R*)-Cyclopentanone (2*S*,3*R*)-**10** (90 mg, 0.28 mmol, 67%) was obtained as a colorless oil and directly used in the next step.

*(S)-4-Methylene-5-((Z)-2-penten-1-yl)-2-cyclopenten-1-one ((S)-**2**).* At −80 °C, LiHMDS (1 M in THF, 0.34 mL, 0.34 mmol, 1.2 equiv.) was added dropwise to a solution of (2*S*,3*R*)-cyclopentanone (2*S*,3*R*)-**10** (90 mg, 0.28 mmol, 1 equiv.) in abs. THF (5 mL). After stirring for 1 h at −80 °C, phenylselenyl chloride (70 mg, 0.36 mmol, 1.3 equiv.) in THF (2 mL) was added. Then, the reaction mixture was transferred to a separation funnel and partitioned between diethyl ether and 1 M aq. HCl. The aqueous layer was extracted with diethyl ether, and the combined organic layers were washed with sat. aq. $NaHCO_3$ and dried over $MgSO_4$.

The solvent was removed under reduced pressure, and the crude α,δ-bis(phenylselenyl)ketone was dissolved in DCM (3 mL). At −60 °C, mCPBA (70−75%, 166 mg, 0.67−0.72 mmol, 2.4−2.6 equiv.) in DCM (2 mL) was added dropwise, and the reaction mixture was stirred at −60 °C for 30 min. *N*,*N*-Diisopropylethylamine (0.29 mL, 220 mg, 1.7 mmol, 6 equiv.) was added, and the mixture was diluted with warm DCM (40 mL) and briefly heated to reflux. Then, the solution was cooled to room temperature, successively washed with 1 M aq. HCl and sat. aq. $NaHCO_3$, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica (pentane/diethyl ether 10:1) to yield (*S*)-dehydrojasmone ((*S*)-**2**, 39 mg, 0.24 mmol, 85%) as a yellowish liquid.

$[\alpha]_D^{25}$ = −16.5 (c 0.97, DCM); ee = 68% (GC); the remaining spectroscopic data were identical to those reported for *rac*-dehydrojasmone (*rac*-**2**).

(*E*)-2-Methyl-2,4-pentadienal (16). A modified procedure by Spangler et al. was used.[21] At 0 °C, a solution of vinylmagnesium bromide (1 M in THF, 63 mL, 63 mmol, 1.3 equiv.) was added to abs. diethyl ether (100 mL), forming a turbid mixture. 3-Ethoxymethacrolein (5.8 mL, 5.6 g, 49 mmol) was added dropwise, and the clear yellow solution was stirred for 30 min at room temperature. Then the solution was poured into a mixture of crushed ice and sat. aq. NH_4Cl, 3 M aq. HCl (7 mL) was added, and the mixture was stirred vigorously for 5 min. The layers were separated, and the aqueous layer was extracted two times with diethyl ether. The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by short-path distillation (32 mbar, 100−125 °C oven temp.) to yield dienal **16** (2.72 g, 28.3 mmol, 58%) as a colorless liquid. The compound is best stored in a freezer to avoid rapid degradation.

(*E*)/(*Z*) = 93:7 (NMR); ^1H NMR (300 MHz, $CDCl_3$): δ [ppm] = 9.48 (s, 1H), 6.92−6.77 (m, 2H), 5.78−5.48 (m, 2H), 1.88−1.85 (m, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ [ppm] = 195.1 (CH), 148.5 (CH), 138.4 (C_q), 131.9 (CH), 126.2 (CH_2), 9.5 (CH_3); EI-MS (70 eV): m/z (%) = 96 (83, $[M]^+$), 95 (37), 67 (100), 65 (30), 63 (10), 53 (43), 51 (11), 41 (48), 39 (18).

(*E*)-4,8-Dimethyl-1,3,7-nonatrien-5-ol (18). Zinc was activated according to Knochel et al.[32] 1,2-Dibromoethane (0.30 mL, 0.66 g, 3.5 mmol, 0.15 equiv.) was added to a suspension of zinc powder (5.88 g, 90 mmol, 3.9 equiv.) in abs. THF (50 mL), and the mixture was briefly heated to reflux. Trimethylsilyl chloride (0.37 mL, 0.31 g, 2.9 mmol, 0.13 equiv.) was added, and the mixture was stirred at room temperature for 15 min. The mixture was cooled to 0 °C, and prenyl bromide (5.2 mL, 6.7 g, 45 mmol, 1.9 equiv.) was slowly added over the course of 30 min. After stirring for 1 h at room temperature, the excessive zinc was removed by filtration through a glass frit, and dienal **16** (2.23 g, 23.2 mmol, 1 equiv.) in THF (3 mL) was added dropwise. After 30 min, DMPU (40 mL) was added and THF was removed under reduced pressure (Schlenk line). The reaction mixture was heated to 100 °C for 5 h. After cooling to room temperature, the mixture was partitioned between dil. aq. NH_4Cl and diethyl ether. The aqueous layer was extracted two times with diethyl ether, and the combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica (pentane/diethyl ether 10:1 → 4:1) to yield homoterpene alcohol **18** (2.76 , 16.6 mmol, 71%) as a colorless liquid.

R_f (pentane/diethyl ether 10:1) = 0.12; ^1H NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.59 (ddd, J = 16.8 Hz, 10.8 Hz, 10.2 Hz, 1H), 6.08 (d, J = 11.0 Hz, 1H), 5.20 (dd, J = 16.9 Hz, 1.9 Hz, 1H), 5.15−5.07 (m, 2H), 4.04 (t, J = 6.5 Hz, 1H), 2.31−2.24 (m, 2H), 1.77 (d, J = 1.1 Hz, 3H), 1.73 (d, J = 1.3 Hz, 3H), 1.65 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ [ppm] = 140.0 (C_q), 135.1 (C_q), 132.7 (CH), 125.6 (CH), 119.8 (CH), 116.9 (CH_2), 76.6 (CH), 34.2 (CH_2), 25.8 (CH_3), 17.9 (CH_3), 12.5 (CH_3); HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{11}H_{18}O$ 166.1358; Found 166.1353; EI-MS (70 eV): m/z (%) = 166 (2, $[M]^+$), 148 (7), 133 (4), 105 (9), 97 (100), 79 (19), 77 (11), 70 (16), 69 (22), 55 (17), 53 (11), 43 (27), 41 (45), 39 (17); IR (ATR, neat): $\nu\sim$ [cm^{-1}] = 3372 (br), 3084 (w), 2972 (m), 2918 (m), 1649 (w), 1600 (w), 1444 (m), 1379 (m), 1042 (s), 987 (s), 901 (s), 838 (w), 660 (m), 569 (m).

(*E*)-4,8-Dimethyl-1,3,7-nonatrien-5-yl Acetate (*rac*-6). Acetic anhydride (0.05 mL, 56 mg, 0.55 mmol, 2 equiv.) was added to a solution of homoterpene alcohol **18** (45 mg, 0.28 mmol, 1 equiv.) and triethylamine (0.15 mL, 111 mg, 1.1 mmol, 4 equiv.) in DCM (1 mL). Then, DMAP (7 mg, 0.06 mmol, 0.2 equiv.) was added. After 30 min, the reaction mixture was diluted with diethyl ether, washed successively with 1 M aq. HCl, sat. aq. $NaHCO_3$, and dried over $MgSO_4$. After removal of the solvent under reduced pressure, homoterpene acetate *rac*-**6** (51 mg, 0.25 mmol, 89%) was obtained as a yellowish liquid.

R_f (pentane/diethyl ether 10:1) = 0.39; ^1H NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.55 (ddd, J = 16.8 Hz, 10.9 Hz, 10.2 Hz, 1H), 6.05 (dm, J = 10.9 Hz, 1H), 5.22 (dd, J = 16.8 Hz, 2.0 Hz, 1H), 5.16−5.11 (m, 2H), 5.01 (tm, J = 7.2 Hz, 1H), 2.44−2.35 (m, 1H), 2.33−2.25 (m, 1H), 2.04 (s, 3H), 1.76 (d, J = 1.3 Hz, 3H), 1.68 (d, J = 1.0 Hz, 3H), 1.61 (br s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ [ppm] = 170.2 (C_q), 135.8 (C_q), 134.4 (C_q), 132.3 (CH), 127.7 (CH), 118.9 (CH), 117.7 (CH_2), 78.5 (CH), 31.7 (CH_2), 25.7 (CH_3), 21.2 (CH_3), 17.9 (CH_3), 12.7 (CH_3); HRMS (CI-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{13}H_{21}O_2$ 209.1542; Found 209.1536; EI-MS (70 eV): m/z (%) = 208 (<1, $[M]^+$), 166 (3), 148 (4), 139 (21), 97 (100), 91 (6), 79 (16), 69 (12), 43 (37), 41 (18); GC: I = 1381 (HP-5MS); IR (GC-IR): $\nu\sim$ [cm^{-1}] = 3085 (w), 2975 (m), 2920 (m), 1734 (s), 1447 (m), 1368 (m), 1239 (s), 1020 (m), 903 (m).

(*E*)-4,8-Dimethyl-1,3,7-nonatrien-5-one (19). Homoterpene alcohol **18** (100 mg, 0.60 mmol, 1 equiv.) in DMSO (1 mL) was added to a solution of IBX (252 mg, 0.90 mmol, 1.5 equiv.) in DMSO

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(3 mL). After stirring for 1.5 h at room temperature, the reaction mixture was poured into an aq. pH 7 buffer solution (KH_2PO_4/Na_2HPO_4). The turbid mixture was extracted three times with pentane/diethyl ether 2:1. The combined organic layers were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica (pentane/diethyl ether 20:1) to yield homoterpene ketone **19** (52.6 mg, 0.32 mmol, 53%) as a colorless liquid.

R_f (pentane/diethyl ether 5:1) = 0.59; ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.03 (d, J = 10.9 Hz, 1H), 6.75 (dt, J = 16.7 Hz, 10.5 Hz, 1H), 5.61 (d, J = 16.7 Hz, 1H), 5.50 (d, J = 10.0 Hz, 1H), 5.37−5.29 (m, 1H), 3.42 (d, J = 6.9 Hz, 2H), 1.91 (s, 3H), 1.75 (s, 3H), 1.67 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ [ppm] = 200.4 (C_q), 138.4 (CH), 136.5 (C_q), 134.8 (C_q), 132.8 (CH), 124.5 (CH_2), 117.0 (CH), 37.4 (CH_2), 25.6 (CH_3), 18.1 (CH_3), 11.8 (CH_3); HRMS (EI-TOF) m/z: [M]$^+$ Calcd for $C_{11}H_{16}O$ 164.1201; Found 164.1194; EI-MS (70 eV): m/z (%) = 164 (4, [M]$^+$), 96 (8), 95 (100), 67 (61), 65 (15), 53 (4), 51 (3), 41 (37), 39 (17); IR (ATR, neat): $\nu\sim$ [cm^{-1}] = 3088 (w), 2972 (w), 2922 (m), 1662 (s), 1627 (w), 1586 (w), 1445 (m), 1354 (m), 1267 (m), 1238 (m), 1139 (m), 1063 (m), 988 (s), 922 (s), 846 (m), 788 (m), 653 (m), 606 (w).

(*S*,*E*)-4,8-Dimethyl-1,3,7-nonatrien-5-yl Acetate ((*S*)-6). (−)-Diisopinocampheylchloroborane (81 mg, 0.25 mmol, 1.5 equiv.) was rinsed with abs. diethyl ether (1 mL) into a solution of (*E*)-4,8-dimethyl-1,3,7-nonatrien-5-one (27.5 mg, 0.17 mmol, 1 equiv.) in 0.4 mL diethyl ether. After stirring for 6 h at room temperature, the reaction mixture was cooled to 0 °C, and acetaldehyde (redistilled, 21 μL, 0.37 mmol, 2.2 equiv.) was added.[33] The solution was allowed to warm to room temperature overnight. Then, the solution was diluted with diethyl ether, 1 M aq. NaOH was added, and the mixture was stirred vigorously for 10 min. The layers were separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. After column chromatography on silica (pentane/diethyl ether 5:1), homoterpene alcohol (*S*)-**18** was obtained in low yield and purity. The enantiomeric excess was determined to be >90% by GC on a chiral stationary phase.

Triethylamine (80 μL) and acetic anhydride (25 μL) were added to a solution of the crude alcohol in $CDCl_3$ (0.5 mL). A crumb of DMAP was added, and the reaction mixture was left at room temperature for 3 h. Then, the solution was diluted with diethyl ether, washed subsequently with sat. aq. NH_4Cl and sat. aq. $NaHCO_3$, and dried over Na_2SO_4. After column chromatography on silica (pentane/diethyl ether 20:1), crude enantioenriched homoterpene acetate (*S*)-**6** suitable for the GC experiments on a chiral phase (see the Supporting Information) was obtained.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00145.

Stereochemical analysis, mass spectra, NMR spectra, TIC chromatograms, and field bioassays (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Stefan Schulz − *Institute of Organic Chemistry, Technische Universität Braunschweig, 38106 Braunschweig, Germany*; orcid.org/0000-0002-4810-324X; Email: stefan.schulz@tu-bs.de

Authors

Patrick Stamm − *Institute of Organic Chemistry, Technische Universität Braunschweig, 38106 Braunschweig, Germany*

Florian Etl − *Department of Botany and Biodiversity Research, University of Vienna, 1030 Vienna, Austria*

Artur Campos D. Maia − *Department of Systematics and Ecology, Federal University of Paraíba, 58051-900 João Pessoa, Brazil*

Stefan Dötterl − *Department of Biosciences, Paris-Lodron University of Salzburg, 5020 Salzburg, Austria*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.1c00145

Author Contributions

The manuscript was written through contributions of all authors, i.e., the chemistry part by P.S. and S.S., the bioassay part by A.C.D.M., F.E., and S.D. The syntheses were performed by P.S., and the behavioral assays were performed by F.E.. All authors commented on previous versions of the manuscript. The concept of the study was developed by all authors, which also gave approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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