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Enantio- and diastereo-convergent synthesis of (2*R*,5*R*)- and (2*R*,5*S*)-Pityol through enzyme-triggered ring closure

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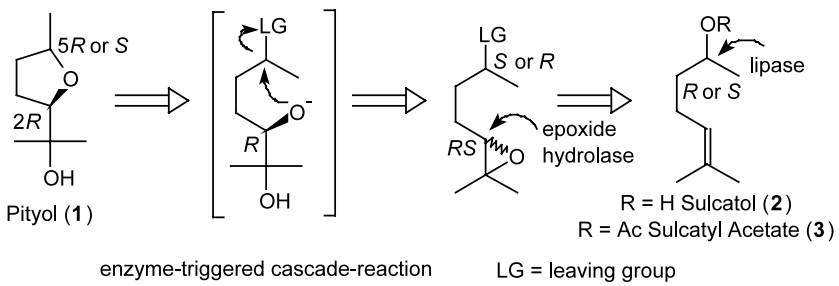
Abstract—A short chemoenzymatic synthesis of the (2*R*,5*S*)- and (2*R*,5*R*)-stereoisomer of the bark beetle pheromone Pityol **1** was achieved from (±)-Sulcatol **2** in an enantio- and diastereo-convergent fashion without the formation of any 'unwanted' stereoisomer. The key steps include: (i) lipase-catalyzed deracemization of (±)-**2** using kinetic resolution coupled to an in-situ inversion or, alternatively, dynamic resolution using combined lipase- and Ru-catalysis; and (ii) creation of the second stereogenic center by an epoxide hydrolase-catalyzed diastereo-convergent hydrolysis of a haloalkyl oxirane, followed by spontaneous ring closure to form **1** in a stereoselective fashion. © 2001 Published by Elsevier Science Ltd.

1. Introduction

Two of the four possible stereoisomers of Pityol (Scheme 1) are naturally occurring pheromones.[1] The (2*R*,5*S*)-isomer serves as the male-specific attractant for the spruce bark beetle *Pityophorus pityographus* and (2*R*,5*R*)-**1** was identified as the aggregation pheromone of the elm bark beetle *Pteleobius vitattus*.

Several approaches towards the stereoselective synthesis of Pityol have been investigated: alkene-epoxidation of (±)-Sulcatol **2** in the presence of titanium–silicate molecular sieves led to cyclisation to give a mixture of all four stereoisomers of **1**,[2] whereas Re-oxidation gave good access to both (±)-*trans*-isomers.[3–5] Both (±)-*cis*- and (±)-*trans*-isomers could be obtained from a bicyclic starting material depending on the conditions used.[6,7] Non-racemic *trans*-[8] and *cis*-isomers[9] were synthesized from non-racemic 3-hydroxybutanoate together with the corresponding six-membered ring analogues as by-products. Biocatalytic approaches based on diastereoselective microbial epoxidation using *Aspergillus niger*[10] selectively led to (2*R*,5*S*)-**1** in 7% overall yield, whereas lipase-initiated ring closure of an epoxide[11] gave a diastereomeric mixture of (2*R*,5*R*)-**1** and (2*S*,5*R*)-**1** which could be separated by column chromatography.

Retrosynthetic analysis (Scheme 1) indicated that the tetrahydrofuran ring might be obtained from a trisubstituted oxirane via an enzyme-triggered cascade reaction, which was recently demonstrated for 2,3-disubstituted halo-alkyl oxiranes.[12] This sequence shows the advantage that both stereoisomers of the (±)-epoxide can be hydrolyzed by a bacterial epoxide



Scheme 1. Retrosynthetic analysis.

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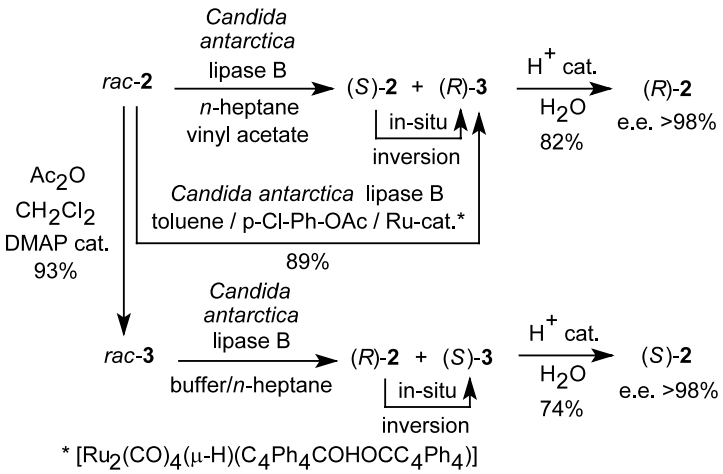
hydrolase in a stereo-convergent fashion forming a single stereoisomeric dihydroxy-intermediate, which spontaneously undergoes cyclization. The remaining stereogenic center would be obtained through deracemization of (±)-Sulcatol **2** via a lipase-catalyzed dynamic (kinetic) resolution leading to (*S*)-**2**, or, alternatively, via an in-situ inversion protocol for (*R*)-**2**.

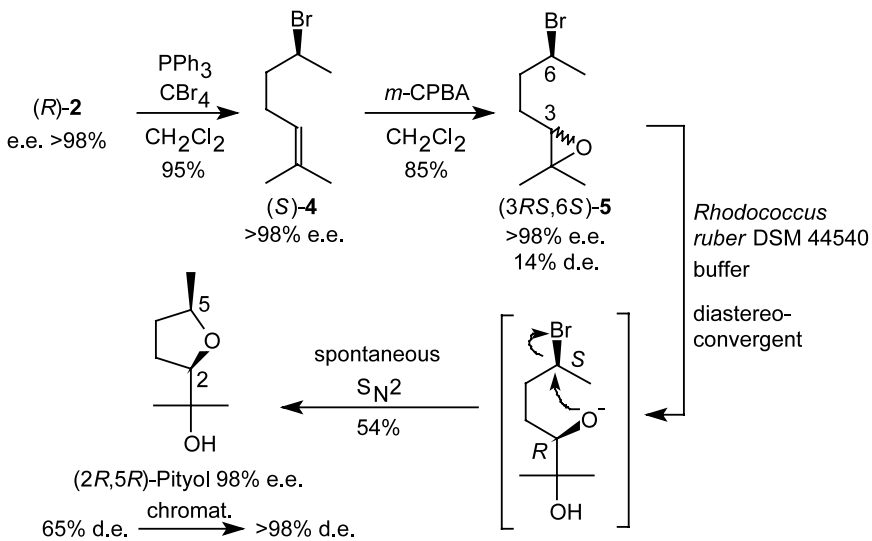
2. Results and discussion

Both enantiomers of Sulcatol **2** were obtained in enantiopure form via *Candida antarctica* lipase B-catalyzed kinetic resolution via an acyl-transfer (for (*R*)-**2**) or ester hydrolysis (for (*S*)-**2**) (Scheme 2). In order to avoid the occurrence of an undesired stereoisomer, both approaches were made enantioconvergent by Mitsunobu-type in-situ inversion[13] to furnish (*R*)-**2** and (*S*)-**2** in >98% e.e. from the racemate in 82 and 80% yield, respectively. Alternatively, highly efficient dynamic resolution of (±)-**2** was achieved via *C. antarctica* lipase B-catalyzed acyl transfer (using 4-chlorophenyl acetate as acyl donor) with Ru-catalyzed racemization of the non-reacting substrate enantiomer to furnish (*R*)-**3** in >98% e.e. and 89% yield.[14]

In order to introduce a suitable leaving group for the ring-closure reaction, (*R*)-**2** was stereoselectively transformed into the corresponding *sec*-bromide (*S*)-**4** with inversion of configuration via Appel-halogenation in 95% yield (Scheme 3).[15] Epoxidation of the latter material using *m*-chloroperbenzoic acid led to a diastereomeric mixture of (3*RS*,6*S*)-**5** in 64% yield and a (marginal) d.e. of 12%. For the enzyme-triggered cascade reaction, several bacterial strains, which were recently shown to be able to accept sterically demanding trisubstituted oxiranes,[16] were screened on an analytical scale (5 μL substrate).[17] The selectivities displayed in Table 1 reveal that high activities are found in particular among *Rhodococci* spp. In the majority of cases, the hydrolysis proved to be stereoconvergent, i.e. both diastereomers (with respect to the oxirane carbon atom) were hydrolyzed to form an (*R*)-configured *sec*-alcohol stereocenter, affording



Scheme 2. Enantio-complementary deracemization of Sulcatol through in-situ inversion or dynamic resolution.



Scheme 3. Synthesis of (2*R*,5*R*)-**1**.

Table 1. Biocatalytic diastereo-convergent hydrolysis/rearrangement of bromoalkyl oxiranes (3*RS*,6*R*)-**5** and (3*RS*,6*S*)-**5**

Substrate	(3*RS*,6*R*)-**5**				(3*RS*,6*S*)-**5**			
Biocatalyst	Conversion[a] (%)	D.e.$_S$[b] (%)	D.e.$_P$[c] (%)	Abs. config.[d]	Conversion[a] (%)	D.e.$_S$[b] (%)	D.e.$_P$[c] (%)	Abs. config.[d]
R. ruber DSM 44541	>98	>99	31	(2*R*,5*S*)	>98	>99	45	(2*R*,5*R*)
R. ruber DSM 44540	>98	>99	78	(2*R*,5*S*)	>98	>99	79	(2*R*,5*R*)
R. ruber DSM 44539	>98	>99	76	(2*R*,5*S*)	>98	>99	75	(2*R*,5*R*)
R. ruber DSM 43338	75	>99	31	(2*R*,5*S*)	n.d.	n.d.	n.d.	(2*R*,5*R*)
Arthrobacter sp. DSM 312	55	6	57	(2*R*,5*S*)	n.d.	n.d.	n.d.	(2*R*,5*R*)
Streptomyces sp. SM 4165	40	13	53	(2*R*,5*S*)	n.d.	n.d.	n.d.	(2*R*,5*R*)
Rhodococcus R312 CBS 717.73	48	31	70	(2*R*,5*S*)	n.d.	n.d.	n.d.	(2*R*,5*R*)

[a] Conversion after 47 h.
[b] D.e. of substrate **4**.
[c] D.e. of product **1**.
[d] Absolute configuration of product **1**; n.d., not determined.

(2*R*,5*R*)-Pityol in up to 79% d.e. at complete conversion.

For the preparative-scale biotransformation, 235 mg of bromo-oxirane (3*RS*,6*S*)-**5** was hydrolyzed using resting cells of *Rhodococcus ruber* DSM 44540 to give (2*R*,5*R*)-**1** in 54% isolated yield and 65% d.e. at a conversion of >97%, which indicated that this process was diastereo-convergent. After separation of the minor diastereomer (2*S*,5*R*)-**1** (formed in 12% yield) by column chromatography, (2*R*,5*R*)-**1** was obtained in 54% yield in >98% e.e. and >98% d.e. Since each of the stereogenic centers was created with maximum efficiency (i.e. product was obtained without the formation of an unwanted stereoisomer), the overall yield of the total synthesis is a respectable 36%.

The other bioactive Pityol stereoisomer (2*R*,5*S*)-**1** was prepared via the same sequence using (*S*)-**2** as starting material. In this case, biohydrolysis of haloalkyl oxirane (3*RS*,6*R*)-**4** followed by spontaneous ring closure led to (2*R*,5*S*)-**1** in >98% e.e. and 65% d.e. at complete conversion. After chromatographic separation of the minor (2*S*,5*S*)-stereoisomer (12%), (2*R*,5*S*)-**1** could be obtained in 43% yield with >98% d.e. and >98% e.e. (overall yield 17%).

3. Experimental

3.1. General remarks

NMR spectra were recorded in $CDCl_3$ using a Bruker AMX 360 at 360 (^{1}H) and 90 (^{13}C) MHz, and a Bruker DMX Avance 500 at 500 (^{1}H) and 125 (^{13}C) MHz. Chemical shifts are reported relative to TMS (δ 0.00) with $CHCl_3$ as internal standard (δ 7.23 (^{1}H) and 76.90 (^{13}C)), coupling constants (J) are given in Hz. GC analyses were carried out on a Varian 3800 gas chromatograph equipped with FID and either a HP1301 or a HP1701 capillary column (both 30 m, 0.25 mm, 0.25 μm film, N_2). Enantiomeric purities were analyzed on a Varian 3800 gas chromatograph equipped with FID, using a CP-Chirasil-DEX CB (column A, 25 m, 0.32 mm, 0.25 μm film) Astec Chiraldex G-PN (column B, 30 m, 0.25 mm) with H_2 as carrier gas.

TLC analyses were run on silica gel Merck 60 (F_{254}) and compounds were visualized by spraying with Mo-reagent [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (100 g/L), $Ce(SO_4)_2\cdot 4H_2O$ (4 g/L) in H_2SO_4 (10%)] (detection I), or by dipping into a $KMnO_4$ reagent (2.5 g/L $KMnO_4$ in H_2O) (detection II). Compounds were purified by flash chromatography on silica gel Merck 60 (230–400 mesh). Petroleum ether had a boiling range of 60–90°C. Solvents were dried and freshly distilled by common practice. For anhydrous reactions, flasks were dried at 150°C and flushed with dry argon just before use. Sulcatol (±)-**2** was purchased from Aldrich and *m*-chloroperbenzoic acid (70%) was purchased from Fluka. For the biotransformations, lyophilized bacterial cells were used. Bacteria were obtained from culture collections and SM strain numbers refer to the culture collection of the Institute of Biotechnology, Graz University of Technology. All strains were grown as previously described.[17] Lipase from *C. antarctica* B (SP 525, Batch: PPW 5328) was obtained from Novo (DK), and Ru-catalyst was kindly donated by J.-E. Bäckvall.

3.2. Synthesis of substrates and reference materials

3.2.1. Sulcatyl acetate (±)-3. Acetate (±)-**3** was synthesized according to a known method.[18] Spectroscopic data were in full agreement with those previously reported.[19]

3.2.2. Deracemization of (±)-2

3.2.2.1. (*R*)-Sulcatol 2 via in-situ inversion. Lipase from *C. antarctica* B (250 mg) was dispersed in heptane (50 mL), and after addition of (±)-**2** (1.0 g, 7.80 mmol) and vinyl acetate (2.0 g, 23.2 mmol) the mixture was agitated on an orbit shaker (rt, 120 rpm). The reaction was monitored by GC on a chiral stationary phase. After agitation of the mixture for 30 h the conversion reached ~50% and after filtration of the biocatalyst, the solution was concentrated in vacuo. The residue was dissolved in anhydrous THF (150 mL) and AcOH (2.5 g, 41.6 mmol), PPh_3 (9.0 g, 34.3 mmol), diisopropyl azidodicarboxylate (7.8 g, 29.7 mmol) were added. The solution was stirred at rt for 72 h to yield crude (*R*)-**3** (>98 e.e.). Without further isolation, the reaction mixture was diluted with dil. H_2SO_4 (2.5%, 200 mL) and heated to 80°C for 8 h. After neutralization with aqueous $NaHCO_3$ solution (satd, 300 mL), extraction with EtOAc (3×150 mL) and evaporation afforded (*R*)-**2** (820 mg, 82%) e.e. >98%. $[\alpha]_D^{20}$ −14.3 (*c* 1.685, EtOH); $[\alpha]_D^{20}$ −10.6 (*c* 0.98, $CHCl_3$).[8]

3.2.2.2. (*R*)-Sulcatyl acetate 2 via dynamic resolution. (±)-Sulcatol (14 mg, 0.11 mmol) was dissolved in anhydrous toluene (3 mL) and 4-chlorophenyl acetate (70 mg, 0.38 mmol) and Ru-cat.[14] (13 mg, 0.007 mmol) were added. The suspension was stirred at 70°C and *C. antarctica* B lipase (5 mg) was added. After 12 h the solution was filtered through a plug of Celite 545 and the filtrate was concentrated. Flash chromatography purification of the residue gave (*R*)-**3** as a colorless oil (15 mg, 89%) e.e. >98% (GC).

3.2.2.3. (*S*)-Sulcatol 2 via in-situ inversion. *C. antarctica* B lipase (260 mg) was dissolved in buffer-saturated heptane (50 mL) and (±)-**3** (1.0 g, 5.87 mmol) was added. The reaction was monitored by GC on a chiral stationary phase. After 35 h the conversion had reached ~50% and the solution was dried over Na_2SO_4 and concentrated in vacuo. The residue was treated with AcOH (0.6 g, 10 mmol), PPh_3 (2.6 g, 9.9 mmol) and, diisopropyl azidodicarboxylate (1.9 g, 9.4 mmol) in anhydrous THF (60 mL) was added as described above to yield (*S*)-**3** in >98 e.e. after 72 h. Acid-catalyzed hydrolysis gave (*S*)-**2** (604 mg, 80%) e.e. >98%. $[\alpha]_D^{20}$ +14.5 (*c* 1.685, EtOH); $[\alpha]_D^{20}$ +10.3 (*c* 1.68, $CHCl_3$).[8]

3.2.3. (*R*)-6-Bromo-2-methyl-2-heptene (*R*)-4. PPh_3 (1.66 g, 6.33 mmol) and CBr_4 (1.88 g, 5.67 mmol) were dissolved in anhydrous CH_2Cl_2 (20 mL) and cooled to 0°C and (*S*)-**2** (380 mg, 3.02 mmol, >98% e.e.) were added. After 30 min the solution was concentrated and pentane (20 mL) was added. The mixture was filtered and the filtrate was concentrated in vacuo. After flash chromatography (pentane), (*R*)-**4** was isolated as a colorless liquid (490 mg, 85%, >98% e.e., GC). R_f (petroleum ether/EtOAc 1:1) 0.90 (detection II). ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 2.06 (3H, s), 2.11 (3H, s), 2.14 (3H, d, $J=16$), 2.19 (1H, m), 2.28 (1H, m), 2.57 (2H, m), 4.54 (1H, m), 5.49 (1H, t, $J=7$); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 17.8, 25.7, 26.4, 29.7, 41.2, 51.5, 122.8, 132.8.

3.2.4. (*S*)-6-Bromo-2-methyl-2-heptene (*S*)-4. (*R*)-**2** (540 mg, 4.3 mmol, >98% e.e.) was treated with PPh_3 (2.39 g, 9.1 mmol) and CBr_4 (2.70 g, 8.14 mmol) in CH_2Cl_2 as described above to yield (*S*)-**4** (780 mg, 95%, >98% e.e., GC) as a colorless liquid. R_f (petroleum ether/EtOAc 1:1) 0.90 (detection II). NMR data matched those for (*R*)-**4**.

3.2.5. (3*RS*,6*R*)-6-Bromo-2-methyl-2-heptene oxide (*R*)-5. Bromoalkene (*R*)-**4** (490 mg, 2.59 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL), the solution was cooled to 0°C and K_2CO_3 (1.32 g, 9.55 mmol) and *m*-chloroperbenzoic acid (1.06 g, 4.28 mmol) were added. After 1 h the white suspension was filtered and the solution was washed with aq. $Na_2S_2O_5$ (30 mL, 10%) and satd $NaHCO_3$ solution (30 mL). The organic phase was dried (Na_2SO_4) and concentrated. After flash chromatography (pentane/ether 3/1) (*R*)-**5** (340 mg, 64%, 12% d.e.) was isolated as a colorless oil. R_f (petroleum ether/EtOAc 1:1) 0.72 (detection I). ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 1.29 (3H, s), 1.32 (3H, s), 1.70–2.17 (7H, m), 2.72–2.76 (1H, m), 4.13–4.24 (1H, m); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 18.8, 18.9, 24.8, 24.9, 26.4, 26.7, 26.8, 27.7, 37.8, 28.3, 50.6, 51.4, 58.4, 58.6, 63.3, 63.8.

3.2.6. (3*RS*,6*S*)-6-Bromo-2-methyl-2-hepten oxide (*S*)-5. Treatment of (*S*)-**4** (750 mg, 3.92 mmol) with *m*-CPBA (1.82 g, 7.3 mmol) and K_2CO_3 (1.65 g, 11.9 mmol) as described above gave (*S*)-**5** as a colorless oil (691 mg, 85%, 14% d.e.). R_f (petroleum ether/EtOAc 1:1) 0.73 (detection I). NMR data matched those of (3*RS*,6*R*)-**4**.

3.2.7. (2*R*,5*R*)-Pityol (2*R*,5*R*)-1. Lyophilized cells of *R. ruber* DSM 44540 (0.4 g) were rehydrated in tris buffer (20 mL, pH 8.0, 50 mM) for 1 h and (3*RS*,6*S*)-**5** (235 mg, 1.13 mmol) was added in one portion. After shaking the mixture at 30°C for 100 h, the reaction was complete and products were extracted with pentane (3×20 mL). The organic phase was dried (Na_2SO_4) and concentrated in vacuo to yield 150 mg of crude product (65% d.e.). After flash chromatography, pure (2*R*,5*R*)-**1** was isolated as a colorless oil (88 mg, 54%, >98 d.e., >98% e.e.). R_f (petroleum ether/EtOAc 1:1) 0.45 (detection I). $[\alpha]_D^{20}$ −10.8 (*c* 0.56, $CHCl_3$); Spectroscopic data were in full agreement with those previously reported.[9] (2*S*,5*R*)-**1** (20 mg, 12%, 80% d.e., >98% e.e.) was also isolated as the minor stereoisomer.

3.2.8. (2*R*,5*S*)-Pityol (2*R*,5*S*)-1. Incubation of *R. ruber* DSM 44540 cells (260 mg) in tris buffer (10 mL, pH 8.0, 50 mM) with (3*RS*,5*R*)-**5** (100 mg, 0.48 mmol) as described above gave crude product (60 mg, 65% d.e.), which furnished pure (2*R*,6*S*)-**1** (30 mg, 43%, >98% d.e., >98% e.e.) after flash chromatography. R_f (petroleum ether/EtOAc 1:1) 0.45 (detection I). $[\alpha]_D^{20}$

Table 2. Retention times on GC on a chiral stationary phase

Compound	Conditions	Column	Retention time [min] (configuration)
1	14 psi H_2, 90°C (iso)	A	2.38 (2*R*,5*R*), 2.51 (2*S*,5*S*), 2.75 (2*R*,5*S*), 2.98 (2*S*,5*R*)
2	14 psi H_2, 100°C (iso)	A	1.78 (2*S*), 1.88 (2*R*)
3	14 psi H_2, 100°C (iso)	A	1.95 (2*S*), 2.28 (2*R*)
4	12 psi H_2, 55°C (iso)	B	11.90 (6*R*), 12.46 (6*S*)

+17.4 (*c* 0.44, $CHCl_3$); Spectroscopic data were in full agreement with those previously reported.[8](2*S*,5*S*)-**1** (8 mg, 12%, 70% d.e., >98% e.e.) was also isolated as the minor stereoisomer.

3.3. General procedure for the screening for biocatalytic activity

Diastereomeric mixtures of epoxides **5** (5 μL) were hydrolyzed using rehydrated lyophilized cells (50 mg) in tris-buffer (1 mL, 0.05 M, pH 8.0) by shaking the mixture at 30°C with 130 rpm. The reactions were monitored by TLC and GC. After 47 h the cells were removed by centrifugation and products were extracted with EtOAc (2×1 mL). The combined organic layers were dried (Na_2SO_4) and analyzed.

3.4. Chiral analysis

Enantiomeric excesses were analyzed by GC on a chiral stationary phase (Table 2).

3.5. Determination of absolute configuration

The absolute configuration of Sulcatol **2** was proven by comparison of optical rotation data with literature values.[8] Acetate **3** was elucidated via co-injection on GC with independently synthesized material. The determination of all four stereoisomers of Pityol was performed as previously described.[11]

Acknowledgements

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