133. Synthesis and Absolute Configuration of the C_{12}-Terpenoid Dehydrogeosmin from the Flower Scents of *Rebutia marsoneri* and *Dolichothele sphaerica* (Cactaceae); a New Approach to Bis-Angularly Substituted *trans*-Decalins

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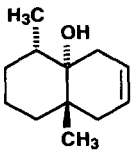
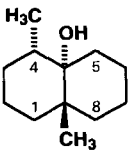
Optically pure (+)-(4*S*,4a*S*,8a*S*)-1,2,3,4,4a,5,8,8a-octahydro-4,8a-dimethylnaphthalen-4a-ol ((+)-**1**; dehydrogeosmin) is released from flower heads of the two cactaceae *Rebutia marsoneri* and *Dolichothele sphaerica*. The absolute configuration of (+)-**1** is identical with that of the known microbial metabolite geosmin (–)-**2**. The key reactions of the synthesis of **1** are the kinetically controlled transesterification of the primary alcohol **4** using a lipase from *Candida cyclindracea* and the stereo- and regiospecific angular alkylation of a *cis*-decalin skeleton by a *Lewis*-acid-assisted ring opening of the quaternary epoxy-alcohol **3** with MeMgBr/CuI. The sequence provides a new entry into the class of bis-angularly substituted *trans*-decalins.

Introduction. – In 1990, *Kaiser* and *Nussbaumer* described dehydrogeosmin **1** as the olfactorily dominant component of the flower scent of several cactaceae like for example *Rebutia marsoneri* WERD., *Dolichothele longimamma* (DC) BR. *et* R. and *Sulcorebutia kruegeri* (CARD.) RITT [1]. The odor of **1** exhibits a strong camphoraceous, earthy-musty tonality, which is reminiscent of freshly ploughed soil. Usually, this very marked odor quality is due to the microbial metabolite geosmin **2** which is produced by certain cyanobacteria, actinomycetes, and fungi that inhabit aquatic and soil environments [2]. The remarkable coincidence in the human odor sensation of **1** and **2** is reflected by their molecular structures. Both compounds possess a *trans*-decalin skeleton with the same substitution pattern and relative configuration [2]. Due its typical origin from aquatic sources or wet earth, certain insects may have learned to associate the odor of geosmin **2** with water or humidity, and, hence, the emission of dehydrogeosmin **1** from flower heads of cactaceae, which often inhabit hot and dry areas, might be considered as a signal for pollinators [1]. According to this interesting ecological background, we decided to synthesize both enantiomers of **1** for biological-activity tests and for the determination of the absolute configuration of natural **1** by GLC on chiral stationary phases [3]. Moreover, concerning the biosynthesis of **1** and **2** from farnesol [4] [5], it might be interesting to compare the absolute configurations of **1** and **2** [6] as products of bacterial- and plant metabolism, respectively.

The syntheses of both enantiomers of **1** and the successful GC determination of the configuration and optical purity of natural **1** are reported.



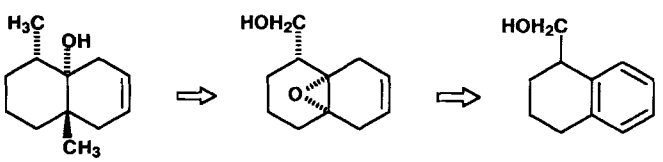
1, Dehydrogeosmin



2, (–)-Geosmin

Results and Discussion. – *Synthesis of (+)- and (−)-Dehydrogeosmin* **1**. The retrosynthetic analysis of the substitution pattern of the *trans*-decalin **1** suggests an alkylating ring-opening of the epoxy-alcohol **3** as a particularly interesting approach. As a matter of fact, the envisaged introduction of the Me group should proceed with inversion of the configuration at the attacked quaternary centre and should place all three substituents into the correct spatial position (*Scheme 1*). The successful realisation of such an approach could be of general synthetic value for the construction of chiral quaternary centres in decalin chemistry and even beyond.

Scheme 1



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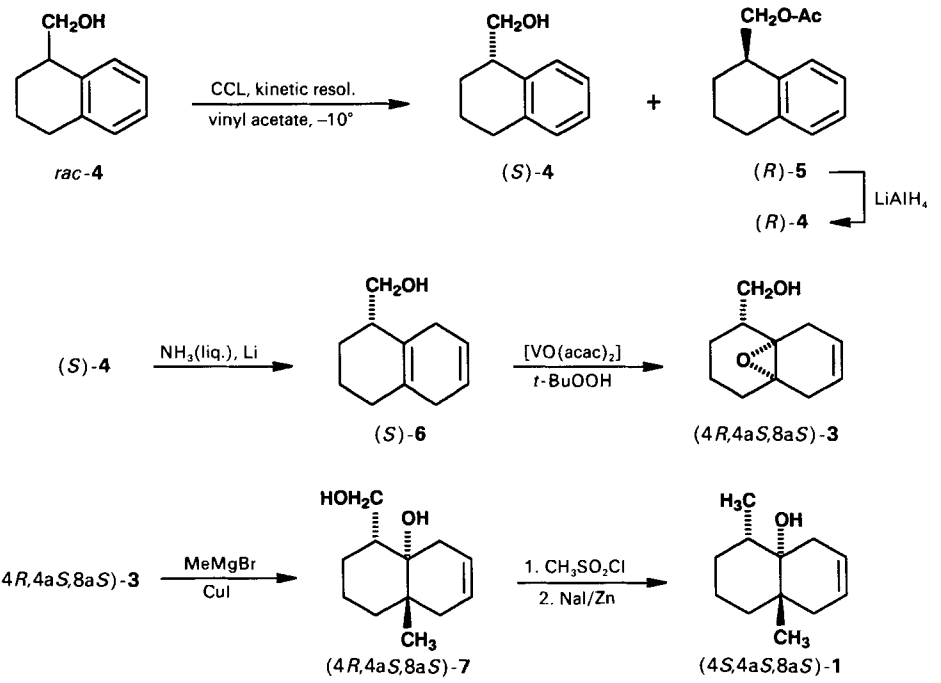
The required epoxy-alcohol **3** should be available from the aromatic precursor **4** [7] by *Birch* reduction followed by a transition-metal-catalyzed epoxidation of the central C=C bond. Moreover, the by now well established methods of enantioselective transesterification with lipases and esterases can be expected to provide both enantiomers of **4**.

Out of several lipolytic enzymes (*cf. Exper. Part*), a lipase from *Candida cyclindracea* (CCL) yielded acceptable results at low temperature (−10°) using vinyl acetate as the solvent and irreversible acyl donor. At high conversion rate (65%), the unreacted alcohol (4*S*)-**4** is obtained with 86% e.e. If the reaction is conducted at room temperature, a conversion rate of at least 80% is required to achieve the same result. The optical purity of **4** is determined by GLC on permethyl-α-cyclodextrin as the chiral stationary phase. While the alcohol **4** exhibits baseline separation, the corresponding acetate **5** fails to separate. At low conversion rate (28%) the enantiomeric alcohol (4*R*)-**5** is obtained with high e.e. (84%) after removal of the acetate. As expected, the alcohol **4** is smoothly reduced to the diene **6** upon treatment with Li in liquid NH_3 (*Birch* conditions; *Scheme 2*). The reaction is accompanied by the formation of *ca.* 10% of an uncharacterized tetrahydro product and *ca.* 2% of starting material which are not removed by chromatography.

Using the system [$VO(acac)_2$] and *t*-BuOOH [8], the O-atom is delivered exclusively to the central, tetra-substituted C=C bond. The direction of the attack is controlled by the CH_2OH substituent and the chelated transition metal leading to the *syn*-addition product **3** in high yield. Since the tetrahydro product does not react with V^{5+}/*t*-BuOOH the polar

Scheme 2



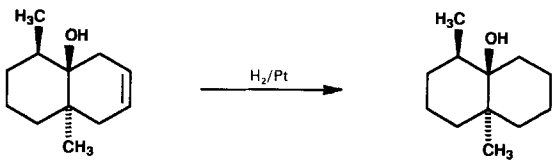
epoxy-alcohol **3** is readily purified by column chromatography on SiO_2. The crucial step of the synthesis is the alkylating ring opening of **3**. This attempt is not trivial because of two major reasons. First, highly substituted oxirans are generally difficult to alkylate, and this is particularly true for the concave *cis*-decalin epoxide **3**, where the two quaternary centres C(4a) and C(8a) are effectively shielded against a nucleophilic attack. The second problem is provided by the regioselectivity of the reaction which can principally occur at both quaternary C-atoms leading to two isomeric alcohols. However, both problems could be solved simultaneously, if an appropriate *Lewis* acid binds to the CH_2OH substituent and the epoxide O-atom, thus weakening the C–O bonds of the oxiran. This approach should favor the formation of a carbenium ion at C(8a), since in this case a six-membered metallacycle can be formed. The resulting carbenium ion is less shielded and should allow the entry of a Me nucleophile from the back side.

First experiments with $LiCuMe_2$ in the presence of $BF_3 \cdot Et_2O$ [9], $LiAlMe_4$ [10], or $MeTiCl_3$ [11] were not successful. However, treatment of **3** with MeMgBr and CuI furnished the desired alcohol **7** as a single diastereoisomer in 67% yield. Best yields are obtained using 30 equiv. of MeMgBr and stoichiometric amounts of CuI (with respect to the epoxide **3**) in refluxing Et_2O. The final reduction of the CH_2OH group is achieved according to the protocol of *Kaiser* and *Nussbaumer* [1]. As described, the primary OH group of **7** is first converted into the corresponding methanesulfonate which is directly reduced to the Me group by treatment with NaI/Zn in refluxing THF.

Determination of the Absolute Configuration and the Enantiomeric Excess of Natural **1**. Since the optical rotation and the absolute configuration of natural geosmin (–)-**2** are

known [6], the configuration of the enantiomers of (+)- and (−)-dehydrogeosmin **1** can be correlated with natural (−)-**2** after hydrogenation. As a matter of fact, hydrogenation of (−)-(4*R*,4a*R*,8a*R*)-**1** with PtO_2/H_2 in THF yields (+)-(4*R*,4a*R*,8a*S*)-**2** which is the non-natural enantiomer of **2** (*Scheme 3*).

Scheme 3



(4*R*,4a*R*,8a*R*)-**1** (4*R*,4a*R*,8a*S*)-**2**

The e.e. and absolute configuration of the dehydrogeosmin (+)-(4*S*,4a*S*,8a*S*)-**1**, scented from the flower heads of cactaceae, is readily determined by GLC using heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-*β*-cyclodextrin as the chiral stationary phase [12]. Compound (±)-**1** exhibits baseline separation ($\alpha = 1.074$, 50-m capillary at 125°). Due to these analyses (*Fig.*), the dehydrogeosmin (+)-**1** from flower heads of *Rebutia marsoneri* and *Dolichothele sphaerica* is optically pure and has the same absolute configuration as the microbial metabolite geosmin (−)-**2**.

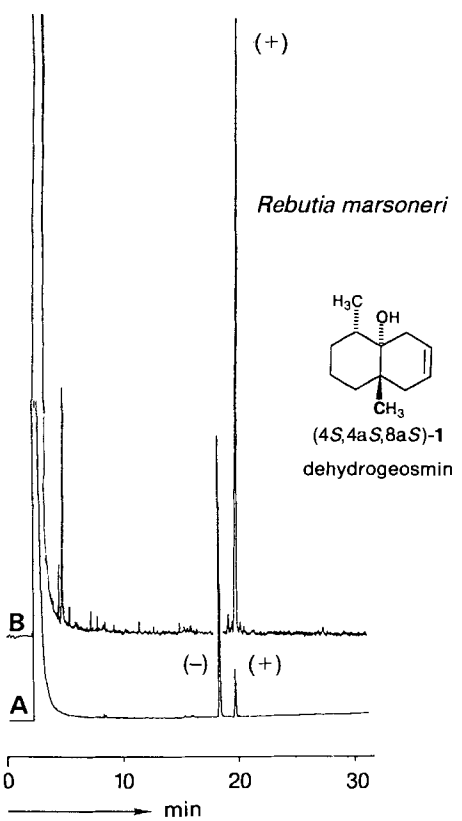


Figure. *GC Determination of the absolute configuration and e.e. of dehydrogeosmin* **1** *from* Rebutia marsoneri. Conditions: glass-capillary (50 m × 0.25 mm) coated with heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-*β*-cyclodextrin at 125°. H_2 at 1 bar as carrier gas. The elution order of the enantiomers of dehydrogeosmin **1** is determined using the synthetic references described in this work (*A*). (+)-(4*S*,4a*S*,8a*S*)-**1** is emitted as an enantiomerically pure compound from the flower heads of the cactaceae *Rebutia marsoneri* (*B*).

Both enantiomers of **1** elicit a comparable odor quality, but (+)-**1** exhibits a fresher and stronger camphoraceous tonality than (−)-**1**. Moreover, the threshold concentrations for the recognition of the two enantiomers of **1** are also different. According to *Kaiser* and *Etzweiler*, the nonnatural (−)-(4*R*,4a*R*,8a*R*)-**1** is perceived at 10 pg/l air, whereas *ca.* 140 pg/l are required for the recognition of the natural (+)-(4*S*,4a*S*,8a*S*)-**1**.

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Experimental Part

General. Reactions are performed under Ar. Solvents and reagents are purified and dried prior to use. Anh. Na_2SO_4 is used for drying operations. Solns. are usually concentrated by flash evaporation under reduced pressure. Anal. TLC: 20 × 20-cm TLC plates, SiO_2 *60* F_{254}, layer thickness 0.2 mm (*Macherey & Nagel*, D–5160 Düren). Anal. GLC: *Carlo Erba* gas chromatograph *HRGC 5300*, equipped with fused-silica capillaries coated with *SE 30* (10 m × 0.31 mm), permethyl-α-cyclodextrin (50 m × 0.25 mm); *K. Ziemer*, D–6800 Mannheim, or heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin (50 m × 0.25 mm, 0.125 μm film) [12]. H_2 at 30 cm/s served as carrier gas. Polarimetry: *Perkin-Elmer 241* polarimeter. IR [cm^{-1}]: *Perkin-Elmer 882* IR spectrophotometer. ^{1}H-NMR (250 MHz or 400 MHz, $CDCl_3$, TMS as internal standard): *Bruker Cryospec WM 250* and *Bruker WM 400*. MS [*m*/*z*]: *Finnigan MAT 90* and *Finnigan ITD 800* combined with a *Carlo Erba* gas chromatograph, model *Vega*; He at 30 cm/s as carrier gas.

Biocatalytical Resolution of (±)-1,2,3,4-Tetrahydronaphthalene-4-methanol (**4**). *General Procedure.* A suspension of (±)-**4** (10.0 g, 0.06 mol) and CCL (*Candida cylindraceae*, lipase; 1 g) in freshly distilled vinyl acetate (200 ml) is gently stirred at −10° until GLC indicates a conversion rate of *ca.* 28–30% (*ca.* 3–5 d). Following removal of the enzyme (filtration) and evaporation, the unreacted alcohol **4** and the acetate (*R*)-**5** (84% e.e.) are separated by CC on SiO_2. To enhance the enantiomeric excess of the alcohol, (*S*)-**4** is redissolved in vinyl acetate, and the CCL-catalyzed esterification is continued as described before (−10°), until a total conversion rate of 70% is reached. Following separation of the compounds by CC, the unreacted alcohol (*S*)-**4** is obtained with high e.e. Reductive removal of the acetate moiety from (*R*)-**5** using $LiAlH_4$ gives (*R*)-**4**. The lipases from *Pseudomonas fluorescens* (PFL), *Penicillium roquefortii*, and *Wheat germ* do not convert (±)-**4**. The lipases from *Porcine pancreas* (PPL) and *Aspergillus niger* (ANL) are able to acylate (±)-**4**, but the e.e. of the unreacted alcohol is low to almost zero.

(4S)-1,2,3,4-Tetrahydronaphthalene-4-methanol ((4*S*)-**4**). From 10.0 g of (±)-**4** in 25% yield (79% e.e.) as described above (at 70% conversion). $[\alpha]_D^{20} = -4.7$ (*c* = 15.73, CH_2Cl_2). IR (neat): 3345, 3059, 3016, 2933, 2866, 1487, 1447, 1430, 1080, 1033, 963, 938, 899, 758, 737. ^{1}H-NMR ($CDCl_3$): 7.32–7.04 (*m*, 4 arom. H); 3.80 (*t*, CH_2OH); 2.97 (*quint.*, H–C(4)); 2.76 (*t*, 2 H–C(1)); 2.02–1.68 (*m*, 2 H–C(2), 2 H–C(3)); 1.50 (*s*, OH). MS (70 eV): 162 (4, M^+), 145 (10), 144 (12), 132 (13), 131 (100), 130 (7), 129 (19), 128 (13), 116 (13), 115 (16), 91 (20), 39 (8).

(4R)-1,2,3,4-Tetrahydronaphthalene-4-methanol ((4*R*)-**4**). From 10.0 g of (±)-**4** in 23% overall yield (28% conversion). $[\alpha]_D^{20} = 6.8$ (*c* = 15.18, CH_2Cl_2, sample of 92% e.e. according to GLC). Spectroscopic data identical with those of (4*S*)-**4**.

(4S)-1,2,3,4,5,8-Hexahydronaphthalene-4-methanol ((4*S*)-**6**). A soln. of (4*S*)-**4** (2.5 g, 13.3 mmol) in THF (17 ml) is added to a well stirred, cold (−78°) soln. of granular Li in liq. NH_3 (*ca.* 110 ml). Stirring is continued for 5 h at this temp., followed by addition of MeOH (25 ml) to destroy excess of the metal. Most of the NH_3 is evaporated. Then, H_2O (80 ml) and solid NH_4Cl (27.2 g) are added while stirring. Extractive workup (Et_2O, 3 × 250 ml) affords (4*S*)-**6** along with *ca.* 11% of a tetrahydro by-product and *ca.* 2% of starting material which are not removed by CC on SiO_2. Yield: 1.8 g (71%). IR (neat): 3334, 3026, 2927, 2870, 1656, 1447, 1432, 1071, 1032, 663. ^{1}H-NMR ($CDCl_3$): 5.73 (br. *s*, H–C(6), H–C(7)); 3.67 (*m*, CH_2OH); 2.90–2.40 (*m*, 2 H–C(5), 2 H–C(8)); 2.21 (*s*, OH); 2.05–1.20 (*m*, 2 H–C(1), 2 H–C(2), 2 H–C(3)). MS (70 eV): 164 (33, M^+), 146 (12), 133 (67), 131 (48), 118 (21), 117 (26), 115 (11), 105 (30), 104 (55), 92 (17), 91 (100), 79 (14), 77 (11), 67 (13). HR-MS: 164.1176 ($C_{11}H_{16}O$, M^+; calc. 164.1201).

(4R)-1,2,3,4,5,8-Hexahydronaphthalene-4-methanol ((4*R*)-**6**). From (4*R*)-**4** (1.4 g, 8.6 mmol) as described above. Yield: 1.2 g (85%). Spectroscopic data identical with those of (4*S*)-**6**.

(4R,4aS,8aS)-4a,8a-Epoxy-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4-methanol ((4*R*,4a*S*,8a*S*)-**3**). A chilled soln. of crude (4*S*)-**6** (1.8 g, 11 mmol) in CH_2Cl_2 (110 ml) is treated with [VO(acac)$_2$] and *t*-BuOOH (5.3 ml, 3M soln. in isooctane). The soln. turns from green to dark red, and stirring is continued for 3 h at r.t. The mixture is hydrolyzed by addition of Na_2SO_3 (9.6 ml, 10% aq. soln.). Stirring is maintained for *ca.* 1 h, at which the mixture becomes green again. Extractive workup (Et_2O) and CC on SiO_2 yields pure (4*R*,4a*S*,8a*S*)-**3** (1.5 g, 76%). $[\alpha]_D^{20} = -19.6$ (*c* = 18.27, CH_2Cl_2). IR (neat): 3426, 3031, 2932, 1722, 1662, 1446, 1421, 1363, 1349, 1071, 1041, 1021, 889, 866, 837, 658, 625, 530, 482. ^{1}H-NMR ($CDCl_3$): 5.45 (*d*, H–C(6), H–C(7)); 3.84 (*d*, C*H*$_2$OH); 2.82–2.72 (*m*, H–C(5)); 2.54–2.42 (*m*, H–C(8)); 2.31 (*m*, H–C(5), H–C(8)); 2.20 (*s*, OH); 2.02–1.83 (*m*, 2 H–C(1)); 1.75–1.20 (*m*, 2 H–C(2), 2 H–C(3)). ^{13}C-NMR ($CDCl_3$): 122.5 (C(6)); 122.4 (C(7)); 64.2 (CH_2OH); 62.7 (C(4a)); 60.6 (C(8a)); 39.6 (C(4)); 31.6 (C(3)); 31.0 (C(5)); 30.4 (C(8)); 24.0 (C(1)); 18.3 (C(2)). MS (70 eV): 180 (8, M^+), 162 (29), 149 (87), 147 (18), 133 (28), 132 (100), 131 (53), 121 (22), 120 (38), 108 (38), 107 (68), 105 (19), 104 (35), 95 (18), 93 (27), 91 (64), 79 (54), 77 (30), 67 (22), 55 (20). HR-MS: 180.1140 ($C_{11}H_{16}O_2$, M^+; calc. 180.1150).

(4S,4aR,8aR)-4a,8a-Epoxy-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4-methanol ((4*S*,4a*R*,8a*R*)-**3**). From (4*R*)-**6** (1.2 g, 7.4 mmol) as described above. Yield: 0.58 g (44%). $[\alpha]_D^{20} = 14.3$ (*c* = 17.82, CH_2Cl_2). Spectroscopic data identical with those of (4*R*,4a*S*,8a*S*)-**3**.

(4R,4aS,8aS)-1,2,3,4,4a,5,8,8a-Octahydro-4-(hydroxymethyl)-8a-methylnaphthalen-4a-ol ((4*R*,4a*S*,8a*S*)-**7**). To a soln. of MeMgBr (41 mmol) in Et_2O (23 ml) is added CuI (0.265 g, 1.4 mmol) with stirring at r.t. Following 15 min of stirring, the epoxy-alcohol (4*R*,4a*S*,8a*S*)-**3** (250 mg, 1.4 mmol) in Et_2O (10 ml) is added slowly. The mixture is refluxed for 2 h prior to hydrolysis with ice/sat. NH_4Cl. The product is extracted with Et_2O (4 × 75 ml). The combined org. layers are successively washed with aq. solns. of $NaHSO_3$, $NaHCO_3$, and brine. CC on SiO_2 affords (4*R*,4a*S*,8a*S*)-**7** as a colorless solid (0.137 g, 30%). M.p. 116°. $[\alpha]_D^{20} = 12.2$ (*c* = 12.45, CH_2Cl_2). IR (KBr): 3407, 3027, 2975, 2937, 2908, 2859, 1460, 1444, 1421, 1401, 1370, 1326, 1311, 1297, 1241, 1117, 1064, 1036, 986, 914, 875, 661, 611. ^{1}H-NMR ($CDCl_3$): 5.69 (*m*, H–C(6), H–C(7)); 4.10 (*dd*, C*H*$_2$OH); 3.58 (*d*, H–C(4)); 2.44–2.29 (*m*, H–C(5), H–C(8)); 2.20–1.94 (*m*, H–C(5), H–C(8), 2 OH); 1.76–1.48 (*m*, H–C(1), H–C(2), H–C(3)); 0.97 (*s*, CH_3). ^{13}C-NMR ($CDCl_3$): 126.4 (C(6)); 123.3 (C(7)); 75.6 (C(4a)); 64.4 (CH_2OH); 40.5 (C(4)); 37.2 (C(5)); 36.4 (C(8a)); 35.2 (C(8)); 34.6 (C(3)); 25.2 (C(1)); 21.4 (CH_3); 21.0 (C(2)). MS (70 eV): 178 (12, $[M - H_2O]^{+\cdot}$), 147 (11), 145 (15), 142 (100), 118 (17), 111 (21), 110 (10), 105 (12), 81 (10), 67 (6), 55 (6). HR-MS: 178.1358 ($C_{12}H_{18}O$, $[M - H_2O]^{+\cdot}$; calc. 178.1341).

(4S,4aR,8aR)-1,2,3,4,4a,5,8,8a-Octahydro-4-(hydroxymethyl)-8a-methylnaphthalen-4a-ol ((4*S*,4a*R*,8a*R*)-7). From (4*S*,4a*R*,8a*R*)-**3** (0.25 g, 1.4 mmol) as described above. Yield: 0.167 g (67%). $[\alpha]_D^{20} = -18.9$ (*c* = 15.91, CH_2Cl_2). Spectroscopic data identical with those of (4*R*,4a*S*,8a*S*)-**7**.

(4S,4aS,8aS)-1,2,3,4,4a,5,8,8a-Octahydro-4,8a-dimethylnaphthalen-4a-ol (= dehydrogeosmin; (4*S*,4a*S*,8a*S*)-**1**). Diol (4*R*,4a*S*,8a*S*)-**7** (0.137 g, 0.76 mmol) is dissolved in CH_2Cl_2/pyridine (11 ml, 4:1, *v*/*v*) and CH_3SO_2Cl (0.314 g, 2.7 mmol) is added. Stirring is maintained for 24 h at r.t. The mixture is poured into chilled HCl (40 ml, 0.1N), and the product is extracted into AcOEt (4 × 75 ml). After drying and evaporation, the crude methanesulfonate is dissolved in THF (20 ml) and refluxed for 9 h together with NaI (1.05 g, 7 mmol) and Zn dust (1.05 g, 16.06 mmol). The solids are removed by filtration, H_2O is added, and the product is extracted with Et_2O (4 × 50 ml). CC on silica gel yields pure (4*S*,4a*S*,8a*S*)-**1** as a colorless liquid. Yield: 0.081 g (64%). $[\alpha]_D^{20} = 27.6$ (*c* = 7.36, CH_2Cl_2). IR (neat): 3463, 3024, 2928, 1723, 1456, 1422, 1373, 1286, 1209, 1164, 1125, 1045, 1000, 954, 881, 837. ^{1}H-NMR ($CDCl_3$): 5.77–5.63 (*m*, H–C(6)); 5.63–5.51 (*m*, H–C(7)); 2.18–1.98 (*m*, 2 H–C(5), H–C(8)); 1.80–1.38 (*m*, 2 H–C(1), 2 H–C(2), 2 H–C(3), H–C(8), OH); 1.13 (*m*, H–C(4)); 0.98 (*s*, CH_3–C(8a)); 0.89 (*d*, CH_3–C(4)). ^{13}C-NMR ($CDCl_3$, TMS): 126.3 (C(6)); 123.6 (C(7)); 73.3 (C(4a)); 38.0 (C(5)); 36.3 (C(8a)); 35.3 (C(8)); 34.8 (C(4)); 34.5 (C(3)); 30.7 (C(1)); 21.4 (CH_3–C(4)); 21.3 (C(2)); 14.8 (CH_3–C(8)). MS (70 eV): 180 (0.2, M^+), 162 (12), 126 (100), 111 (19), 109 (13), 106 (16), 105 (25), 97 (6), 95 (7), 92 (6), 91 (6), 84 (6), 81 (7), 55 (7). HR-MS: 180.1514 ($C_{12}H_{20}O$, M^+; calc. 180.1519).

(4R,4aR,8aR)-1,2,3,4,4a,5,8,8a-Octahydro-4,8a-dimethylnaphthalen-4a-ol (= dehydrogeosmin; (4*R*,4a*R*,8a*R*)-**1**). From (4*S*,4a*R*,8a*R*)-**7** (0.15 g, 0.8 mmol) as described above. Yield: 0.107 g (78%). $[\alpha]_D^{20} = -28.7$ (*c* = 9.73, CH_2Cl_2). Spectroscopic data identical with those of (4*S*,4a*S*,8a*S*)-**1**.

Determination of the Absolute Configuration of Dehydrogeosmin. A soln. of (4*R*,4a*R*,8a*R*)-**1** (0.17 g, 0.59 mmol) in THF (10 ml) is hydrogenated over PtO_2, until GLC indicates complete conversion. Removal of solvent *i.v.* and CC on SiO_2 affords (pentane/Et_2O 90:10) unnatural geosmin (4*R*,4a*R*,8a*S*)-**2** (0.077 g, 71%). $[\alpha]_D^{20} = 14.6$ (*c* = 7, EtOH), natural (4*S*,4a*S*,8a*R*)-**2**: $[\alpha]_D^{20} = -18.3$ (*c* = 15.3, EtOH, [6]).

GC Determination of the Absolute Configuration and e.e. of Dehydrogeosmin **1** *from Cactaceae.* Volatiles are collected from the head space of flourishing plants on a bed of activated carbon (1.5 mg) as described in [13] [14]. The carbon traps are eluted with CH_2Cl_2 (30 µl) and the compounds are separated on a column coated with heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin (50 m × 0.25 mm). Temp.: 125° isothermal. The identification of the natural enantiomer of **1** is achieved by co-injection with the synthetic references of (4*S*,4a*S*,8a*S*)-**1** and (4*R*,4a*R*,8a*R*)-**1**.

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