# Vanadium(V)-Catalyzed Oxidation of (3*R*)-Linalool – The Selective Formation of Furanoid Linalool Oxides and their Conversion into Isocyclocapitelline Derivatives

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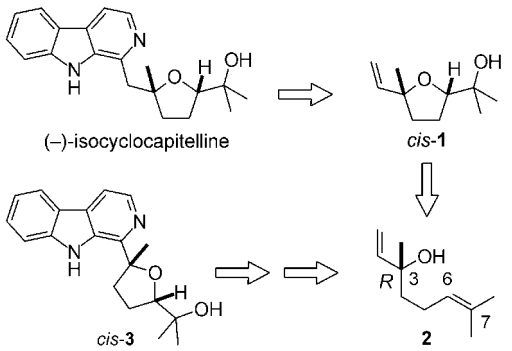
Dedicated to Professor Dr. Peter Welzel on the occasion of his 65th birthday.

**Abstract:** Oxidation of (3*R*)-linalool (**2**) with *tert*-butyl hydroperoxide (TBHP) occurs at the 6,7-position to selectively afford linalool oxide *cis*-**1**, if catalyzed by vanadium(V) Schiff base complexes **4**. Substituted tetrahydrofuran *cis*-**1** and its isomer *trans*-**1** served as starting materials for short concise syntheses of β-carbolines *cis*-**3** and *trans*-**3** which are lower homologues of alkaloids (–)-isocyclocapitelline and (+)-cyclocapitelline.

**Key words:** *tert*-butyl hydroperoxide, linalool oxide, oxidation, Schiff base complex, vanadium

(–)-Isocyclocapitelline (Scheme 1), (+)-cyclocapitelline, and (+)-chrysotricine are tetrahydrofuran-derived β-carboline alkaloids, which have been extracted from far eastern medicinal plants.[1,2] From a biosynthetic point of view it seems likely that linalool oxides **1** and therefore linalool **2** serve as precursors for the formation of these alkaloids.[1,3] In organic synthesis, however, the abovementioned β-carbolines are generally obtained in multistep transformations that use other precursors than terpenol **2** as starting material for the following reasons.[4] Conversion of substrate **2** into functionalized tetrahydrofurans **1** requires selective oxygenation at the 6,7-π-bond which is attainable by e.g. peracids[5] or the combination of $H_3CReO_3/H_2O_2$.[6] Unfortunately, the observed diastereoselectivities in these reactions are negligible. If oxidized with *tert*-butyl hydroperoxide in the presence of an early transition metal catalyst such as $VO(acac)_2$,[7] a selective conversion of linalool **1** into the corresponding 1,2-epoxyalcohol has been reported.[8,9] In view of the significance of linalool oxides **1** as versatile building blocks,[10] and the contemporary interest in tetrahydrofuran-derived β-carboline alkaloids,[1,2,4] we have developed a new stereoselective access to furanoid linalool oxide *cis*-**1** and disclose our latest results in this communication as a part of the synthesis of hitherto unknown β-carbolines *cis*-**3** and *trans*-**3**.

The selected strategy for diastereoselectively oxidizing substrate **2** at the 6,7-position is based on the use of TBHP as primary oxidant and vanadium(V) Schiff base complexes **4** as catalysts.[11] The latter reagents were chosen for this purpose, since vanadium compound **4a** does not catalyze the epoxidation of allylic alcohols[12] but efficiently mediates diastereoselective formation of functionalized tetrahydrofurans from bishomoallylic alcohols and TBHP.[11,13,14]




**Scheme 1** (3*R*)-Linalool (**2**) and derived linalool oxide *cis*-**1** as building block in synthesis.

In an initial experiment, terpenol **2** was treated with TBHP and 10 mol% of vanadium(V) catalyst **4a** in $CHCl_3$ at 20 °C for 12 hours. Previous optimization studies had shown that these conditions provide high selectivities for tetrahydrofuran formation in combination with a satisfactory peroxide efficiency.[14] Purification of the reaction mixture furnished furanoid linalool oxides **1** (62%, *cis*:*trans* = 61:39), 1,2-epoxylinalool oxides **5** (6%, *cis*:*trans* = 56:44), and pyranoid linalool oxides **6** (3%, *cis*:*trans* = 40:60) (Scheme 2).[15–17] No 1,2-epoxides of linalool were detected ($^1$H NMR, GC).[8,9] The relative configurations of major isomers of heterocycles **1**, **5**, and **6** were established by NMR experiments (NOE, HMBC, HMQC). In a second run, oxidation of substrate **2** with TBHP was repeated in the presence of (1*R*,2*S*)-aminoindanol-derived catalyst **4b**. The latter reagent had attracted attention in previous experiments since it generally provided higher diastereoselectivities for tetrahydrofuran formation compared to **4a**. This oxidation, however, only led to a minor increase in yield of target compound *cis*-**1** without improving its diastereoselectivity. A time dependent analysis of product formation in the latter run provided two important results. (i) Formation of epoxide **5** follows formation of linalool oxide **1**. This observation in combination with the fact that no linalool 1,2-epoxides were

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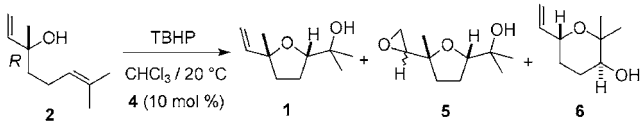
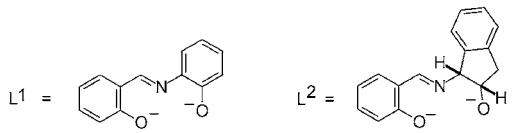
formed is indicative of tetrahydrofuran **1** as starting material for epoxide **5**. (ii) *Cis*/*trans*-ratios of tetrahydrofuran **1**, epoxide **5**, and tetrahydropyran **6** remained constant throughout the conversion of substrate **2**. These findings point to an absence of kinetic resolution in this experiment.[18] Therefore, the origin of the observed fair preference for formation of 2,5-*cis*-configured tetrahydrofuran *cis*-**1** in this work is not associated with a mismatched effect using a chiral auxiliary in **4b** and the substrate (3*R*)-linalool (**2**). This explanation is supported by the fact that approximately the same diastereoselectivities were obtained, if the oxidation of **2** was catalyzed by vanadium reagent **4a** with an achiral Schiff base auxiliary. Still, a *cis*/*trans*-ratio of 61:39 for formation of trisubstituted tetrahydrofuran **1** is slightly superior to results, which have been reported so far for other transition metal catalyzed oxidations of linalool **2**.[6,19–21]



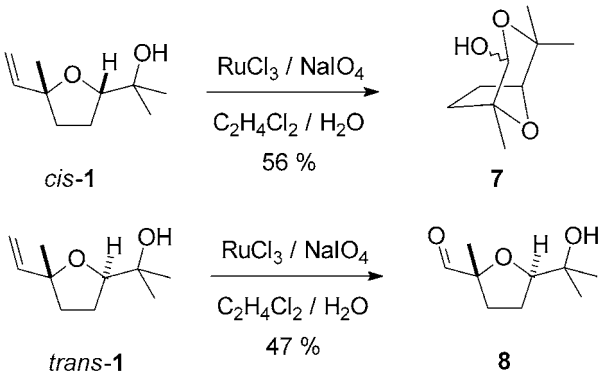

| 4 | | 1 [%] (*cis* : *trans*) | 5 [%] (*cis* : *trans*) [b] | 6 [%] (*cis* : *trans*) |
|---|---|---|---|---|
| VOL[1] (EtO)(EtOH) | (**4a**) | 62 (61 : 39) | 6 (56 : 44) | 3 (40 : 60) |
| VOL[2](EtO) | (**4b**) | 65 (61 : 39) | 7 (54 : 46) | 4 (38 : 62) |




**Scheme 2** Vanadium(V)-catalyzed regio- and stereoselective oxidation of (3*R*)-linalool (**2**).

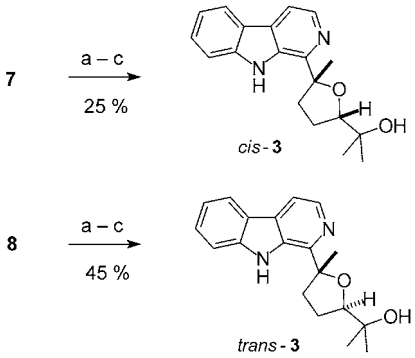
To continue the synthesis of tetrahydrofuran-derived β-carbolines **3**, linalool oxides, *cis*-**1** and *trans*-**1** were separated by column chromatography.[16] Conversion of vinyl-substituted tetrahydrofuran *cis*-**1** into bicyclic lactol **7**[22] was achieved by a $RuO_4$-catalyzed[23] oxidation. This reaction furnished after chromatographic purification 56% of analytically pure material (Scheme 3). Alternative reagents, such as $OsO_4/NaIO_4$ (in 1,4-dioxane/$H_2O$) or $KMnO_4$ (in acetone/$H_2O$), failed to provide compound **7**. Therefore, the reagent combination of $RuCl_3$ and $NaIO_4$ in $C_2H_4Cl_2/H_2O$ was also applied for the conversion of *trans*-configured tetrahydrofuran *trans*-**1** into aldehyde **8**[22] (47%, Scheme 3).

Finally, lactol **7** was treated with tryptamine in a Pictet–Spengler-type reaction.[4c] This transformation was performed in $CH_2Cl_2$ at room temperature and afforded an imine (not shown in Scheme 4), which was treated at –78 °C with $CF_3CO_2H$. The reaction time was limited to 1 hour since, according to TLC analysis, formation of additional products started, if this period was extended. Work up of the reaction mixture furnished a tetrahydro-β-carboline (27%),[24] which was treated with Pd on charcoal in




**Scheme 3** Ruthenium-catalyzed oxidation of linalool oxides *cis*-**1** and *trans*-**2** into lactol **7** and aldehyde **8**.

hot xylenes in order to provide target compound *cis*-**3** as colorless crystals[25] (90%, Scheme 4). In a similar sequence, formyl-substituted tetrahydrofuran **8** was treated at 20 °C with tryptamine and subsequently at –78 °C with $CF_3CO_2H$ to yield 88% of a tetrahydro-β-carboline[24] (not shown in Scheme 4) which upon dehydrogenation afforded target compound *trans*-**3**[25] in 51% yield (Scheme 4).




**Scheme 4** Preparation of β-carbolines *cis*-**3** and *trans*-**3** from lactol **7** and aldehyde **8**. *Reagents and conditions*: (a) Tryptamine, $CH_2Cl_2$, 20 °C; (b) $CF_3CO_2H$, $CH_2Cl_2$, –78 °C → 20 °C; (c) Pd/C, xylenes, reflux.

In summary, we have devised a new synthesis of linalool oxides **1** via a vanadium-catalyzed selective oxygenation of linalool **2** at the 6,7-position. This oxidation provides tetrahydrofuran *cis*-**1** as major product. Functionalized heterocycles **1** served as building blocks for the synthesis of hitherto unknown 1-substituted β-carbolines *cis*-**3** and *trans*-**3**, which will be subjected to pharmacological testing.

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(16) A solution of (3*R*)-linalool (**2**) (154 mg, 1.00 mmol) in $CHCl_3$ (5 mL) and vanadium(V) complex **4b** (36.3 mg, 0.10 mmol) was stirred for 5 min at 25 °C. Subsequently, TBHP (273 μL, 5.5 M in nonane, 1.50 mmol) was added and the deep red reaction mixture was stirred for additional 12 h at 25 °C. Afterwards, the solvent was removed at 250 mbar/ 40 °C to afford a dark brown residue which was filtered through a short pad of $Al_2O_3$ in order to remove the catalyst. The product was washed with $Et_2O$ (75 mL) from the column. Combined filtrate and eluate were concentrated in vacuo to provide an oil which was distilled under reduced pressure. The distillate was purified by column chromatography [$SiO_2$, petroleum ether–$Et_2O$–acetone, 5:2:1 (v/v/v); $R_f$ *cis*-**1** = 0.48; $R_f$ *trans*-**1** = 0.45] to provide 111 mg (65%) linalool oxide **1**: colourless liquid, bp 80 °C/ 10 mbar (Kugelrohr, Lit. 78 °C/13 Torr), *cis*:*trans* = 61:39. *cis*-**1**: $[\alpha]_D^{25}$ +29.1 (*c* 1.1, $CHCl_3$), ref.[17]: $[\alpha]_D^{25}$ +11.7 (*c* = 0.1, $CH_3OH$). $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.11 (s, 3 H), 1.20 (s, 3 H), 1.29 (s, 3 H), 1.75–1.89 (m, 4 H), 2.05 (s br, 1 H, OH), 3.84 (dd, *J* = 8, 7 Hz, 1 H), 4.97 (dd, *J* = 11, 2 Hz, 1 H), 5.17 (dd, *J* = 17, 2 Hz, 1 H), 5.96 (dd, *J* = 17, 11 Hz, 1 H). *trans*-**1**: $[\alpha]_D^{25}$ –13.1 ( *c* 1.0, $CHCl_3$), ref.[17]: $[\alpha]_D^{25}$ –10.1 (*c* 0.1, $CH_3OH$). $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.10 (s, 3 H), 1.21 (s, 3 H), 1.29 (s, 3 H), 1.66–1.74 ($m_c$, 1 H), 1.75–1.93 (m, 3 H), 2.05 (s, br., 1 H, OH), 3.78 (t, *J* = 7 Hz, 1 H), 4.98 (dd, *J* = 11, 2 Hz, 1 H), 5.18 (dd, *J* = 17, 2 Hz, 1 H), 5.85 (dd, *J* = 17, 11 Hz, 1 H).

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(24) *cis*-1-[5-(1-Hydroxy-1-methylethyl)-2-methyltetrahydrofuran-2-yl]-1,2,3,4-tetrahydro-9*H*-β-carboline: colorless crystals, mp 119 °C; $[\alpha]_D^{25}$ –22.9 (*c* 0.82, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.08 (s, 3 H), 1.24 (s, 3 H), 1.38 (s, 3 H), 1.80–2.16 (m, 4 H), 2.78 (ddd, *J* = 12.1, 7.9, 5.5 Hz, 2 H), 3.21 (ddd, *J* = 12.5, 9.8, 5.5 Hz, 2 H), 4.02 (t, *J* = 7.0 Hz, 1 H), 4.06 (s, 1 H), 7.00–7.19 (m, 2 H), 7.24–7.36 (m, 1 H), 7.49 ($m_c$, *J* = 7.0 Hz, 1 H), 8.75 (s, 1 H), 10.23 (s, 1 H). $^{13}$C NMR (63 MHz, $CDCl_3$): δ = 20.5, 22.6, 25.0, 25.8, 27.4, 36.0, 43.9, 61.2, 71.2, 83.0, 85.6, 110.9, 112.8, 118.0, 119.0, 121.4, 135.4, 156.7, 175.5. MS (EI, 70 eV,): *m/z* (%) = 314 (3) [$M^+$], 171 (100) [$C_{11}H_{11}N_2^+$], 143 (6) [$C_8H_{15}O_2^+$], 84 (11) [$C_5H_8O^+$], 43 (10) [$C_3H_6^+$]. UV/Vis (EtOH): $\lambda_{max}$ (lg ε): 232 nm (3.76), 282 (3.81), 373 (2.46). $C_{19}H_{26}N_2O_2$ (314.4): Calcd C, 72.58; H, 8.33; N, 8.91. Found: C, 67.25; H, 8.26; N, 7.99. *trans*-1-[5-(1-Hydroxy-1-methylethyl)-2-methyltetrahydrofuran-2-yl]-1,2,3,4-tetrahydro-9*H*-β-carboline: colorless solid, mp 113 °C. $[\alpha]_D^{25}$ –19.5 (*c* 0.63, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.08 (s, 3 H), 1.22 (s, 3 H), 1.40 (s, 3 H), 1.89–2.22 (m, 4 H), 2.68–2.90 (m, 2 H), 3.22 (ddd, *J* = 15.0, 9.8, 5.2 Hz, 2 H), 3.99 (dd, *J* = 8.2, 5.4 Hz, 1 H), 4.08–4.12 (m, 1 H), 7.05–7.20 (m, 2 H), 7.33 ($m_c$, 1 H), 7.50 ($m_c$, 1 H), 8.60 (s, 1 H). $^{13}$C NMR (63 MHz, $CDCl_3$): δ = 21.6, 22.6, 24.6, 26.1, 28.8, 36.8, 43.0, 60.6, 70.4, 77.0, 86.6, 110.1, 110.9, 118.0, 119.0, 121.5, 142.3, 153.4, 174.1. MS (EI, 70 eV): *m/z* (%) = 314(3) [$M^+$], 171(100) [$C_{11}H_{11}N_2^+$], 143(6) [$C_8H_{15}O_2^+$], 84(11) [$C_5H_8O^+$], 43(10) [$C_3H_6^+$]. UV/Vis (EtOH): $\lambda_{max}$ (lg ε): 242 nm (4.52), 282 (3.85), 371 (2.57). $C_{19}H_{22}N_2O_2$ (314.4): Calcd C, 72.58; H, 8.33; N, 8.91. Found: C, 67.94; H, 8.06; N, 7.78.

(25) *cis*-1-[5-(1-Hydroxy-1-methylethyl)-2-methyltetrahydrofuran-2-yl]-9*H*-β-carboline *cis*-**3**: colorless solid, mp 161 °C. $[\alpha]_D^{25}$ –32.9 (*c* 0.57, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.23 (s, 3 H), 1.45 (s, 3 H), 1.78 (s, 3 H), 1.75–3.08 (m, 4 H), 4.15 (t, *J* = 7.3 Hz, 1 H), 7.24 (ddd, *J* = 7.8, 6.1, 1.8 Hz, 1 H), 7.52 ($m_c$, 2 H), 7.86 (d, *J* = 5.5 Hz, 1 H), 8.13 (d, *J* = 7.9 Hz, 1 H), 8.39 (d, *J* = 5.5 Hz, 1 H), 9.53 (s, 1 H). $^{13}$C NMR (63 MHz, $CDCl_3$): δ = 24.2, 26.2, 27.6, 27.9, 37.3, 73.3, 88.4, 90.2, 111.5, 113.4, 119.7, 121.6, 121.7, 128.3, 133.2, 136.1, 138.0, 143.2, 148.0. MS (EI, 70 eV): *m/z* (%) = 310(17) [$M^+$], 151(24) [$C_{16}H_{15}N_2O^+$], 209 (100) [$C_{14}H_{12}N_2^+$], 182 (11) [$C_{10}H_{16}NO_2^+$], 43 (9) [$C_2H_4O^+$]. UV/ Vis (EtOH): $\lambda_{max}$ (lg ε): 242 nm (4.52), 288 (4.26), 348 (3.77). $C_{19}H_{22}N_2O_2$ (310.4): Calcd C, 73.52; H, 7.14; N,

9.03. Found: C, 72.86; H, 7.11; N, 8.68. *trans*-1-[5-(1-Hydroxy-1-methylethyl)-2-methyltetrahydrofuran-2-yl]-9*H*-β-carboline *trans*-**3**: colorless solid, mp 158 °C. $[\alpha]_D^{25}$ –50.5 (*c* 0.5, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.25 (s, 3 H), 1.38 (s, 3 H), 1.72 (s, 3 H), 1.75–2.10 (m, 4 H), 4.15 (t, *J* = 7.6 Hz, 1 H), 7.22 (ddd, *J* = 7.9, 6.4, 1.5 Hz, 1 H), 7.48 ($m_c$, 2 H), 7.86 (d, *J* = 5.2 Hz, 1 H), 8.11 (d, *J* = 7.5 Hz, 1 H), 8.36 (d, *J* = 5.2 Hz, 1 H), 10.48 (s, 1 H). $^{13}$C NMR (63 MHz, $CDCl_3$): δ = 26.2, 26.7, 26.8, 28.4, 38.6, 72.6, 86.0, 88.2, 111.9, 114.1, 119.7, 121.5, 121.9, 128.4, 132.6, 133.0, 137.7, 142.9, 148.9. MS (EI, 70 eV): *m*/*z* (%) = 310 (17) [$M^+$], 151 (24) [$C_{16}H_{15}N_2O^+$], 209 (100) [$C_{14}H_{12}N_2^+$], 182 (11) [$C_{10}H_{16}NO_2^+$], 43(9) [$C_2H_4O^+$]. UV/Vis (EtOH): $\lambda_{max}$ (lg ε): 227 nm (4.09), 289 (4.03), 340 (3.57). $C_{19}H_{22}N_2O_2$ (310.4): Calcd C, 73.52; H, 7.14; N, 9.03. Found: C, 72.86; H, 7.11; N, 8.68.