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メタデータ	言語: eng 出版者: 公開日: 2017-10-04 キーワード (Ja): キーワード (En): 作成者: メールアドレス: 所属:
URL	http://hdl.handle.net/2297/11563

A NOVEL REDUCTIVE AMINO-CYCLIZATION METHOD AND ITS APPLICATION FOR THE TOTAL SYNTHESSES OF (±)-AURANTIOCLAVINE AND (±)-LOPHOCERINE^{1a#}

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Abstract – A novel reductive amino-cyclization method for the synthesis of azacycloalkanes is developed. Its versatility is proved by the total syntheses of (±)-aurantioclavine (**1**), an ergot alkaloid, and (±)-lophocerine (**2**), a cactus alkaloid, as examples of azepane and piperidine skeletons, respectively.

In our project for developing biologically active compounds,² we needed a novel simple method for constructing azacycloalkanes under acidic conditions. Generally speaking, however, the formation of a C—N bond between nitrogen atom of amines and carbocation generated *in situ* by the action of an acid is impossible, because the basic nitrogen is protonated completely and eventually loses the nucleophilic ability.

To overcome the problem we have conceived the following idea as shown in general formula in Scheme 1. If the type **A** compound, having both nitro and unsaturated groups in a molecule, is subjected to an acidic reduction (in this case, $E^+ = H^+$), the nitrogen atoms of both the resulting intermediates, hydroxylamine (**B**) or oxime (**C**), would not be protonated completely due to the attached electron-attracting oxygen atom. So, in cases where a carbocation is generated in the neighborhood of the nitrogen atom, both carbon and nitrogen atoms can connect together resulting in the formation of a cyclic hydroxylamine or a cyclic nitrone (**D**). Simultaneous acidic reduction can provide the desired type **E** azacycloalkanes.

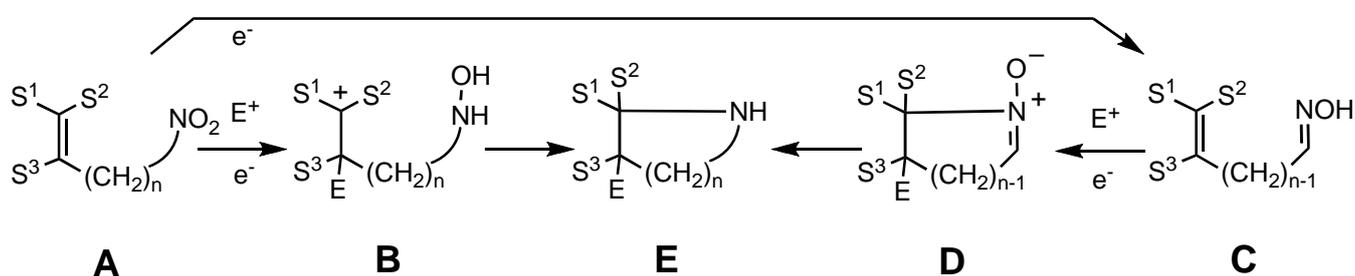
On the basis of the above idea, we have succeeded in creating a novel reductive amino-cyclization method.³ We wish to report its application for the total syntheses of (±)-aurantioclavine⁴ (**1**), a member of ergot alkaloid and (±)-lophocerine (**2**), a cactus alkaloid, as examples of azepane and a piperidine forma-

Dedicated to the 75th birthday of Prof. Dr. Eckelhard Winterfeldt.

tions, respectively (Scheme 2). Part of these works is reported as preliminary communications.^{3,6}

As for an example of pyrrolidine formation, we had already applied the method for the synthesis of 6,6a,7,8,9,9a-hexahydro-2*H*-isoindolo[4,5,6-*cd*]indole^{3,6} (**3**), a synthetic intermediate for α -cyclopiazonic acid (**4**). We had demonstrated as well that the process, **C** \rightarrow **D** in Scheme 1, actually worked.⁷ Thus, the compound (**5**) was successfully converted to a nitrone (**6**, in this case, $E^+ = Br^+$), an important intermediate for the synthesis of gibberellin A₁₅ (**7**).⁷

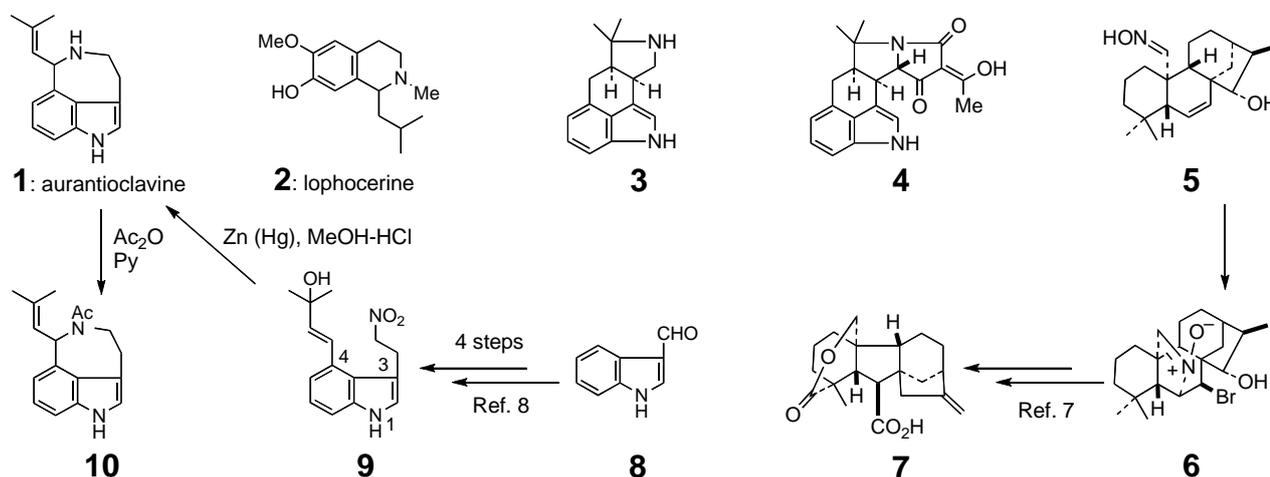
Scheme 1. S¹—S³: an appropriate substituent. E⁺: an electrophile.



An Efficient Total Synthesis of (\pm)-Aurantioclavine (**1**)

According to our synthetic procedures,^{6,8} we first prepared (*E*)-2-methyl-4-[3-(2-nitroethyl)indol-4-yl]-3-buten-2-ol (**9**, Scheme 2), our common synthetic intermediate for the ergot alkaloids,² in 46% overall yield from indole-3-carbaldehyde (**8**) in four steps.⁸ Since the compound (**9**) contains the type **A** structure, the desired allyl cation being a benzyl cation as well, can be generated on the side chain at the 4-position of **9** by an acid treatment. The carbocation is so stable that it would survive during the time when the acidic reduction of the nitro group on the side chain at the 3-position of **9** proceeds, and it would eventually have a chance to form a bond to the hydroxylamine nitrogen.

Scheme 2



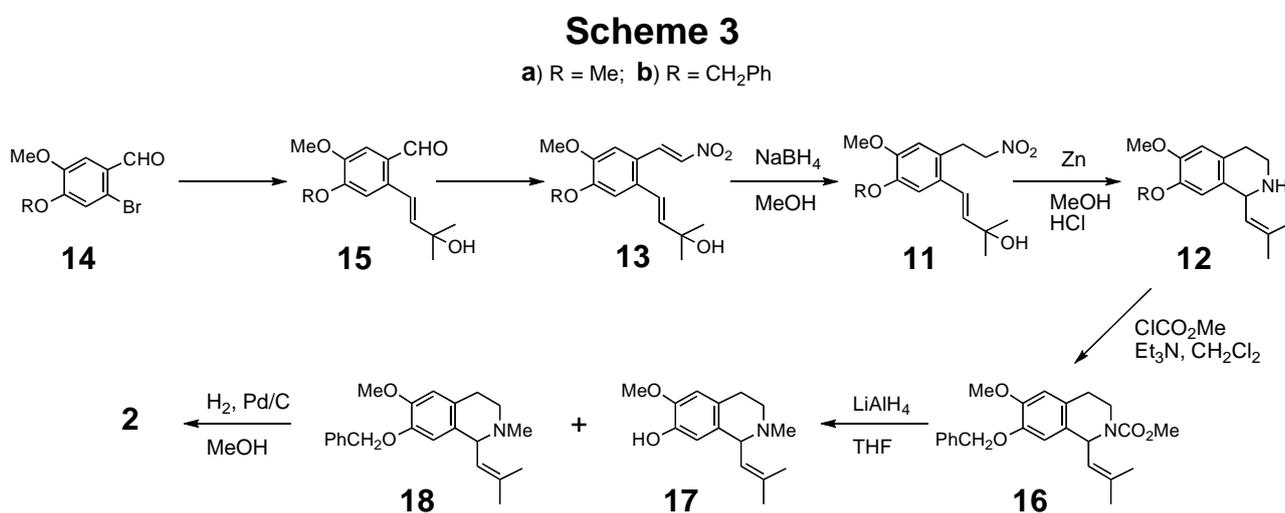
In fact, however, treatment of **9** with such reagent systems as SnCl₂/HCl/MeOH, TiCl₃/MeOH, Fe/AcOH, and Zn/AcOH ended in failure under various examined reaction conditions. Finally, we tried amalgamated zinc (Zn (Hg)) and found it a reagent of choice. Thus, treatment of **9** with Zn (Hg) in refluxing methanolic HCl gave (±)-aurantioclavine (**1**) in 72% yield. Further treatment of **1** with Ac₂O and pyridine afforded (±)-*N*-acetylaurantioclavine (**10**) in 93% yield. Spectral data of **1** were identical with those of aurantioclavine, reported in the literature.⁴

Thus, we accomplished the first total synthesis of (±)-aurantioclavine (**1**) in the simplest five steps with a 33% overall yield from **8** without using any protective groups. Hegedus' group⁹ achieved the total syntheses of (±)-**1** afterwards, too.¹⁰

Total Synthesis of (±)-Lophocerine (**2**)

In order to examine whether our amino-cyclization method works for the piperidine formation, we selected (±)-lophocerine (**2**)⁵ as a target molecule, which is known to exist as a racemate.⁵

For the synthesis of intermediates having 1-substituted isoquinoline skeletons (**12a,b**, Scheme 3), we chose 4-[4,5-dimethoxy- (11a) and 4-[5-benzyloxy-4-methoxy-2-(2-nitroethyl)phenyl]-2-methyl-3-buten-2-ol¹¹ (**11b**) as suitable substrates because they have the type **A** structure (Scheme 1) in the molecules.



Employing the reduction with NaBH₄ in MeOH, compounds (**11a,b**)¹¹ were easily prepared in 74 and 81% yields, respectively, from **13a** and **13b**.¹¹ They were prepared according to our procedures¹¹ from 6-bromoveratraldehyde (**14a**) and 6-bromo-4-benzyloxy-3-methoxybenzaldehyde (**14b**) in two steps through **15a** and **15b**.

The reductive amino-cyclization method, using zinc instead of Zn (Hg), was successfully applied for **11a** and **11b**. Thus, treatment of **11a** and **11b** with zinc in refluxing methanolic HCl provided 6,7-dimethoxy-

(**12a**) and 7-benzyloxy-1-(2-methoxy-1-(2-methyl-1-propen-1-yl)-1,2,3,4-tetrahydroisoquinoline (**12b**) in 67 and 77% yields, respectively.

Further treatment of **12b** with ClCO_2Me and Et_3N afforded 7-benzyloxy-6-methoxy-2-methoxycarbonyl-1-(2-methyl-1-propen-1-yl)-1,2,3,4-tetrahydroisoquinoline (**16**) in 99% yield. Subsequent reduction of **16** with LiAlH_4 in dry THF gave 7-benzyloxy-1-(2-methyl-1-propen-1-yl)-6-methoxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (**17**) in 86% yield together with an 11% yield of the debenzylated compound **18**. Catalytic hydrogenation of the double bond and debenylation of **17** over 10% Pd/C in MeOH produced (\pm)-lophocerine (**2**) in 39% yield. Our synthesized **2** and its picrate were identical with the samples prepared according to the procedure described in the literature.⁵

In conclusion, we have established a novel reductive amino-cyclization method for the synthesis of azacycloalkanes based on our idea shown in Scheme 1. Its versatility was proved by the total syntheses of (\pm)-aurantioclavine (**1**) and (\pm)-lophocerine (**2**) as examples of the azepane and piperidine skeletons, respectively.

EXPERIMENTAL

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were determined with a Shimadzu IR-420 spectrophotometer, and $^1\text{H-NMR}$ spectra with a JEOL JNM-PMX 60 or a JEOL FX-100 spectrometer, with tetramethylsilane as an internal standard. MS were recorded on a Hitachi M-80 spectrometer. Preparative thin-layer chromatography (p-TLC) was performed on Merck Kiesel-gel GF₂₄₅ (Type 60) (SiO_2). Column chromatography was performed on silica gel (SiO_2 , 100—200 mesh, from Kanto Chemical Co., Inc.) throughout the present study.

(\pm)-**Aurantioclavine (1)** from (*E*)-2-Methyl-4-[3-(2-nitroethyl)indol-4-yl]-3-buten-2-ol (**9**) — A solution of **9** (113.2 mg, 0.41 mmol) in MeOH (24 mL) and 3% HCl (8 mL) was added to Zn (Hg), prepared from Zn powder (1.386 g, 21.2 mmol) and HgCl_2 (229.0 mg, 0.84 mmol) in 3% HCl (8 mL), and the mixture was refluxed for 3.5 h with stirring. Unreacted Zn (Hg) was filtered off and the filtrate was evaporated under reduced pressure. The residue was made basic by adding 8% NaOH and the whole was extracted with CH_2Cl_2 -MeOH (95:5, v/v). The organic layer was washed with brine, dried over Na_2SO_4 , and evaporated under reduced pressure to leave an oil, which was subjected to p-TLC on SiO_2 with CHCl_3 -MeOH-28% aq. NH_3 (46:5:0.5, v/v) as a developing solvent. Extraction of the band having an *R_f* value of 0.29—0.58 with CHCl_3 -MeOH-28% aq. NH_3 (46:5:0.5, v/v) gave **1** (66.9 mg, 72%). **1**: mp 194—196°C (colorless leaves, recrystallized from CH_2Cl_2 -hexane). IR (KBr): 3290, 2915 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.71 (1H, br s, disappeared on addition of D_2O), 1.84 (6H, s), 2.83—3.24 (3H, m), 3.33—3.71 (1H, m), 4.86 (1H, d, $J=9.0$ Hz), 5.44 (1H, br d, $J=9.0$ Hz), 6.80 (1H, br d, $J=6.8$ Hz),

6.89—7.27 (2H, m), 6.94 (1H, br s), 8.17 (1H, br s, disappeared on addition of D₂O). MS *m/z*: 226 (M⁺). *Anal.* Calcd for C₁₅H₁₈N₂: C, 79.60; H, 8.02; N, 12.38. Found: C, 79.52; H, 8.10; N, 12.53.

(±)-*N*-Acetylaurotioclavine (10) from 1 — Ac₂O (1 mL) was added to a solution of **1** (53.1 mg, 0.24 mmol) in pyridine (2 mL) and the mixture was stirred at rt for 13 h. After evaporation of the solvent, saturated aqueous NaHCO₃ was added and the whole was extracted with CH₂Cl₂–MeOH (95:5, v/v). The organic layer was washed with brine, dried over Na₂SO₄, and evaporated under reduced pressure to leave a solid, which was recrystallized from MeOH to give **10** (58.5 mg, 93%) as colorless needles. **10**: mp 235—236°C. IR (KBr): 3200, 1664, 1593 cm⁻¹. ¹H-NMR (10% CD₃OD in CDCl₃) δ: 1.70 (3H, s), 1.80 (3H, s), 2.18 (3H, s), 2.64—4.54 (4H, m), 5.72 (1H, br d, *J*=7.5 Hz), 5.80 (1H, br d, *J*=7.5 Hz), 6.57—7.28 (4H, m). MS *m/z*: 268 (M⁺). *Anal.* Calcd for C₁₇H₂₀N₂O: C, 76.08; H, 7.51; N, 10.44. Found: C, 75.90; H, 7.59; N, 10.22.

(*E*)-4-[4,5-Dimethoxy-2-(2-nitroethyl)phenyl]-2-methyl-3-buten-2-ol (11a) from (*E,E*)-4-[4,5-Dimethoxy-2-(2-nitrovinyl)phenyl]-2-methyl-3-buten-2-ol (13a) — NaBH₄ (1.045g, 27.5 mmol) was added to a solution of **13a** (2.009g, 6.86 mmol) in MeOH (120 mL) and the mixture was stirred at rt for 30 min. Brine was added and the mixture was adjusted to pH 8 by adding 6% HCl. The whole was extracted with CH₂Cl₂–MeOH (95:5, v/v). The organic layer was washed with brine, dried over Na₂SO₄, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO₂ with Et₂O–hexane (3:1, v/v) to give **11a** (1.245 g, 62%). **11a**: mp 99—100°C (colorless prisms, recrystallized from CH₂Cl₂–hexane). IR (KBr): 3460, 1602, 1538, 1503, 1343, 1261 cm⁻¹. ¹H-NMR (CDCl₃) δ: 1.42 (6H, s), 1.83 (1H, br s, disappeared on addition of D₂O), 3.27 (2H, t, *J*=7.2 Hz), 3.78 (3H, s), 3.81 (3H, s), 4.43 (2H, t, *J*=7.2 Hz), 6.03 (1H, d, *J*=15.6 Hz), 6.52 (1H, s), 6.64 (1H, d, *J*=15.6 Hz), 6.82 (1H, s). MS *m/z*: 295 (M⁺). *Anal.* Calcd for C₁₅H₂₁NO₅·1/10H₂O: C, 60.63; H, 7.19; N, 4.71. Found: C, 60.61; H, 7.27; N, 4.79.

6,7-Dimethoxy-1-(2-methyl-1-propen-1-yl)-1,2,3,4-tetrahydroisoquinoline (12a) from 11a — A solution of **11a** (50.9 mg, 0.17 mmol) in MeOH (6 mL) was added to a mixture of Zn powder in 6% HCl (2 mL), and the mixture was refluxed for 3 h with stirring. Unreacted Zn was filtered off and the filtrate was evaporated under reduced pressure. The residue was made basic by adding 8% NaOH and the whole was extracted with CH₂Cl₂–MeOH (95:5, v/v). The organic layer was washed with brine, dried over Na₂SO₄, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on SiO₂ with CHCl₃–MeOH–28% aq. NH₃ (46:5:0.5, v/v) to give **12a** (28.7 mg, 67%). **12a**: mp 57—58°C (colorless needles, recrystallized from petroleum ether). IR (KBr): 3400, 2910, 2760, 1605, 1509, 1259 cm⁻¹. ¹H-NMR (CDCl₃) δ: 1.80 (3H, d, *J*=1.2 Hz), 1.84 (3H, d, *J*=1.2 Hz), 2.04 (1H, br s, disappeared on addition of D₂O), 2.44—3.40 (4H, m), 3.80 (3H, s), 3.84 (3H, s), 4.65 (1H, d, *J*=9.3 Hz), 5.28 (1H, br d,

$J=9.3$ Hz), 6.51 (1H, s), 6.57 (1H, s). MS m/z : 247 (M^+). Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.62; H, 8.66; N, 5.59.

7-Benzyloxy-6-methoxy-1-(2-methyl-1-propen-1-yl)-1,2,3,4-tetrahydroisoquinoline (12b) from 11b — A solution of **11b** (36.2 mg, 0.09 mmol) in MeOH (6 mL) was added to a mixture of Zn powder (332.1 mg, 5.08 mmol) in 6% HCl (2 mL) and the mixture was refluxed for 4 h with stirring. Unreacted Zn was filtered off and the filtrate was evaporated under reduced pressure. The residue was made basic by adding 20% NaOH and the whole was extracted with CH_2Cl_2 –MeOH (95:5, v/v). The organic layer was washed with brine, dried over Na_2SO_4 , and evaporated under reduced pressure to leave an oil, which was subjected to p-TLC on SiO_2 with $CHCl_3$ –MeOH–28% aq. NH_3 (46:5:0.5, v/v) as a developing solvent. Extraction of the band having an R_f value of 0.49–0.72 with $CHCl_3$ –MeOH–28% aq. NH_3 (46:5:0.5, v/v) gave **12b** (24.2 mg, 77%). **12b**: mp 114–116°C (colorless prisms, recrystallized from MeOH– H_2O). IR (KBr): 3230, 2900, 1604, 1502, 1359, 1258, 1245, 1215 cm^{-1} . 1H -NMR ($CDCl_3$) δ : 1.71 (6H, d, $J=2$ Hz), 1.89 (1H, br s, disappeared on addition of D_2O), 2.46–2.89 (2H, m), 2.89–3.33 (2H, m), 3.77 (3H, s), 4.46 (1H, d, $J=9$ Hz), 4.97 (2H, s), 5.07 (1H, br d, $J=9$ Hz), 6.36 (1H, s), 6.44 (1H, s), 7.02–7.45 (5H, m). MS m/z : 323 (M^+). Anal. Calcd for $C_{21}H_{25}NO_2$: C, 77.98; H, 7.79; N, 4.33. Found: C, 77.69; H, 7.83; N, 4.20.

7-Benzyloxy-6-methoxy-2-methoxycarbonyl-1-(2-methyl-1-propen-1-yl)-1,2,3,4-tetrahydroisoquinoline (16) from 12b — A solution of $ClCO_2Me$ (45.4 mg, 0.48 mmol) in CH_2Cl_2 (1 mL) and Et_3N (0.2 mL) were added to a solution of **12b** (82.4 mg, 0.26 mmol) in CH_2Cl_2 (4 mL) and the mixture was stirred at rt for 3 h. Saturated aqueous $NaHCO_3$ was added and the whole was extracted with CH_2Cl_2 –MeOH (95:5, v/v). The organic layer was washed with brine, dried over Na_2SO_4 , and evaporated under reduced pressure to leave an oil, which was subjected to p-TLC on SiO_2 with CH_2Cl_2 –MeOH (99:1, v/v) as a developing solvent. Extraction of the band having an R_f value of 0.34–0.68 with CH_2Cl_2 –MeOH (95:5, v/v) gave **16** (96.6 mg, 99%). **16**: Colorless oil. IR (film): 1697, 1608 cm^{-1} . 1H -NMR ($CDCl_3$) δ : 1.67 (3H, d, $J=1.2$ Hz), 1.83 (3H, d, $J=1.2$ Hz), 2.21–4.37 (4H, m), 3.61 (3H, s), 3.73 (3H, s), 4.91 (2H, s), 5.08 (1H, br d, $J=9.5$ Hz), 5.49 (1H, d, $J=9.5$ Hz), 6.31 (1H, s), 6.39 (1H, s), 7.01–7.42 (5H, m). High-resolution MS m/z : Calcd for $C_{23}H_{27}NO_4$: 381.1938. Found: 381.1956.

7-Benzyloxy- (17) and 7-Hydroxy-6-Methoxy-2-methyl-1-(2-methyl-1-propen-1-yl)-1,2,3,4-tetrahydroisoquinoline (18) from 16 — $LiAlH_4$ (109.2 mg, 0.29 mmol) was added to a solution of **16** (96.6 mg, 0.25 mmol) in anhydrous THF (6 mL) and the mixture was refluxed for 24 h. After the addition of MeOH and saturated aqueous Rochelle salt under ice cooling, the whole was extracted with CH_2Cl_2 –MeOH (95:5, v/v). The organic layer was washed with brine, dried over Na_2SO_4 , and evaporated under reduced pressure to leave an oil, which was subjected to p-TLC on SiO_2 with $CHCl_3$ –MeOH–28% aq. NH_3 (46:5:0.5, v/v) as a developing solvent. Extraction of the band having an R_f value of 0.37–0.69

with CHCl_3 -MeOH-28% aq. NH_3 (46:5:0.5, v/v) gave **17** (73.8 mg, 86%). **17**: Colorless oil. IR (film): 2930, 2780, 1610, 1507, 1252 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.67 (3H, d, $J=1.2$ Hz), 1.85 (3H, d, $J=1.5$ Hz), 2.15—3.28 (4H, m), 2.28 (3H, s), 3.72 (1H, d, $J=9.5$ Hz), 3.77 (3H, s), 4.93 (1H, d, $J=9.5$ Hz), 4.98 (2H, s), 6.35 (1H, s), 6.46 (1H, s), 7.02—7.38 (5H, m). High-resolution MS m/z : Calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_2$: 337.2040. Found: 337.2038. Extraction of the band having an R_f value of 0.20—0.29 with CHCl_3 -MeOH-28% aq. NH_3 (46:5:0.5, v/v) gave **18** (6.7 mg, 11%). **18**: mp 159—160°C (colorless prisms, recrystallized from MeOH- H_2O). IR (KBr): 2900, 1589, 1501, 1268 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.77 (6H, d, $J=1.2$ Hz), 2.17—3.17 (4H, m), 2.32 (3H, s), 3.74 (3H, s), 3.83 (1H, d, $J=9.6$ Hz), 4.77 (1H, br s, disappeared on addition of D_2O), 5.05 (1H, br d, $J=9.6$ Hz), 6.42 (2H, s). MS m/z : 247 (M^+). High-resolution MS m/z : Calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_2$: 247.1573. Found: 247.1569.

(\pm)-**Lophocerine (2) from 17** — A solution of **17** (30.9 mg, 0.09 mmol) in MeOH (7 mL) was hydrogenated in the presence of 10% Pd/C (33.7 mg) at rt and 1 atm for 7 h. Catalyst was filtered off and the filtrate was evaporated under reduced pressure to leave an oil, which was purified by p-TLC with CHCl_3 -MeOH-28% aq. NH_3 (46:5:0.5, v/v) as a developing solvent. Extraction of the band having an R_f value of 0.37—0.50 with CHCl_3 -MeOH-28% aq. NH_3 (46:5:0.5, v/v) gave **2** (8.8 mg, 39%). **2**: Colorless oil. IR (film): 2940, 1592, 1505, 1461, 1360, 1266, 1210, 1130, 1102, 1021, 869, 775 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 0.90 (3H, d, $J=6$ Hz), 0.95 (3H, d, $J=6$ Hz), 1.22—2.02 (3H, m), 2.17—3.57 (5H, m), 2.40 (3H, s), 3.80 (3H, s), 4.33 (1H, br s, disappeared on addition of D_2O), 6.43 (1H, s), 6.50 (1H, s). MS m/z : 249 (M^+). **2**-picrate: mp 194—196°C (lit.,⁵ mp 191.5—193°C, yellow prisms, recrystallized from benzene). IR (KBr): 3370, 2950, 1609, 1507, 1309, 1269 cm^{-1} .

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