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Synthesis of sedamine by tethered cyclofunctionalisation

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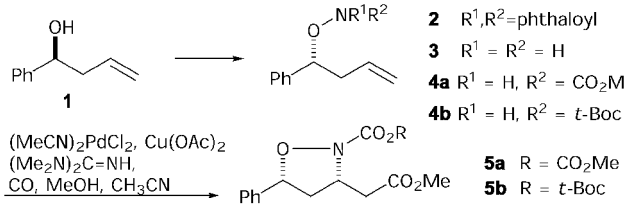
Received 5th October 2004, Accepted 15th November 2004
First published as an Advance Article on the web 6th January 2005

The piperidine alkaloid, (+)-sedamine has been synthesised starting from (*S*)-1-phenyl-3-butenol using a stereoselective, intramolecular palladium-catalysed cyclocarbonylation reaction of a substituted hydroxylamine.

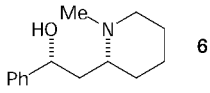
Introduction

We recently reported the palladium catalysed cyclisation of readily available O-homoallylic hydroxylamines **4** to give *cis*-disubstituted isoxazolidines **5**.[1] Given the ease with which the N–O bond may be reduced, this can be considered as a tethered cyclofunctionalisation (Scheme 1).



Scheme 1 Isoxazolidine synthesis.

We now wish to report the application of this reaction to the synthesis of the alkaloid sedamine, **6**. This compound is the best known of a large group of piperidine alkaloids that have been isolated from *Sedum* and other species. They may be of interest in the treatment of cognitive disorders.[2] While numerous syntheses of sedamine have been reported,[3] typically they result in mixtures of sedamine and its diastereoisomer, allosedamine. Isoxazolidine intermediates have been used, formed by 1,3-dipolar cycloadditions of nitrones with styrene.[4] However, these reactions lead to allosedamine, a diastereomer, as the major product. On the other hand, *cis*-isoxazolidines, such as **5**, have the appropriate stereochemistry to lead to **6**.



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Results and discussion

The isoxazolidines **5a,b** were prepared as reported previously,[1] with alcohol **1** of *ca.* 95% ee as the starting material. There are a number of ways to prepare alcohol **1** in an optically active form. For this work, the method of Maruoka was used, involving allylation of benzaldehyde in the presence of a chiral Lewis acid derived from chlorotitanium triisopropoxide, silver oxide and (*S*)-BINOL.[5] Using the isoxazolidines **5a,b** for the synthesis of sedamine **6** (Scheme 2) would require addition of a further two carbon atoms in order to construct the piperidine ring. The Wittig reaction with a stabilised ylide was selected for this transformation because of the mildness of the conditions. Attempts to selectively reduce the ester group of the methyl carbamate-protected isoxazolidine **5a**, in order to prepare for such a Wittig reaction, led to the aminal **8**, rather than the expected alcohol. The identity of the aminal was indicated by a pair of doublets in the ^{1}H NMR spectrum (4.60 and 5.04 ppm) with J = 12.6 Hz. It may be suggested that the intermediate alkoxide cyclises to carbamate **7** which then undergoes further reduction to the aminal. Aminal **8** appears to be resistant to further reduction (*e.g.* H^+, $NaCNBH_3$).

On the other hand, careful reduction of the corresponding *t*-Boc protected isoxazolidine **5b** led cleanly to the expected alcohol **9**. Careful temperature control of this reaction is essential. Oxidation to the corresponding aldehyde **10** with IBX,[6] followed by Wittig olefination allowed installation of the required pair of carbon atoms. A short cut is possible, as DIBAL reduction of the ester group of **5b**, followed by Wittig olefination in one pot leads to the same ester **11** in similar yield, although chromatographic removal of any unreacted starting material is difficult. After routine removal of the *t*-Boc group, hydrogenation of isoxazolidine **12** using palladium on carbon resulted in a tandem process; the alkene double bond and the O–N bond were cleaved, although, happily, no cleavage of the benzylic C–O bond was observed. It is known that amino groups can inhibit hydrogenolysis of benzylic bonds.[7] The resulting amino ester **13** cyclised on standing to lactam **14**. This could be easily converted to norsedamine **15** by $LiAlH_4$ reduction. The spectroscopic data (^{1}H NMR, ^{13}C NMR, IR) of our synthetic material were in good agreement with those reported by Pilli for the racemate.[8] Although a one step methylation of norsedamine **15** to sedamine **6** has been reported, we found that a more convenient method was to proceed *via* the known bicyclic oxazine **16** which, following the reported procedure, gave sedamine **6** on lithium aluminium hydride reduction, accompanied by a small amount of the aminal **17**. The spectroscopic data, melting point and optical rotation of the synthetic (+)-sedamine **6** were in agreement with those previously reported.[3b,9,10]

In conclusion, we have succeeded in preparing sedamine in a straightforward way, using 1,3-asymmetric induction to introduce the *N*-substituted chiral centre. The efficiency of the route rests on the rapid introduction of the required nitrogen, minimising the use of protecting groups, and the use of a tandem process to construct the piperidine ring. Application of this strategy to other targets is in hand.

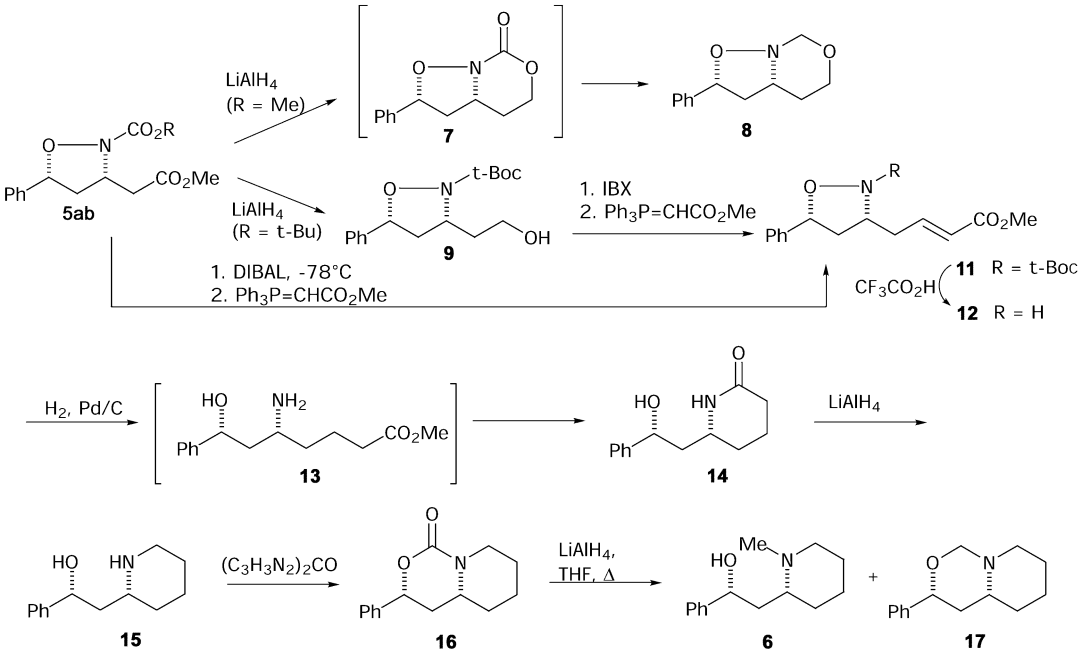
Support of this work by the Thailand Research Fund, the University of Exeter and Pfizer Global Research and Development is gratefully acknowledged. The part of this work carried out in Thailand was made possible by the generous provision of facilities by the Chulabhorn Research Institute.

Experimental

General

IBX and bis(acetonitrile)palladium(II) chloride were prepared by the reported methods. THF was distilled from sodium–benzophenone, acetonitrile and dichloromethane were distilled from calcium hydride and methanol was distilled from activated

DOI: 10.1039/b415297b



Scheme 2 Sedamine synthesis.

magnesium. Other reagents and solvents were commercial and used as received. Petrol refers to the fraction boiling between 40 and 60 °C.

IR spectra were recorded on a Nicolet Magna 550 spectrometer either neat or as nujol mulls using NaCl plates. ^{1}H NMR spectra were recorded on a Bruker AM300 or a Varian Gemini at 300 or 200 MHz with residual protic solvent as the reference. ^{13}C spectra were recorded at the corresponding frequencies on the same machines. Chemical shifts are in ppm and coupling constants, *J*, are in Hz. Mass spectra were recorded on a Finigan GCQ instrument at 70 eV and high resolution mass spectra on a Micromass GCT instrument. Specific rotations, $[\alpha]_D$, were recorded on an Optical Activity Ltd AA-1000 polarimeter and are given with units of 10^{-1} deg cm^2 g^{-1}. Elemental analysis was carried out at the University of Exeter.

(*R*)-2-(1-Phenylbut-3-en-1-yloxy)isoindole-1,3-dione (2)

This compound was prepared following the previously reported procedure and purified by flash chromatography on silica gel eluting with 5% ethyl acetate–petrol. mp 85–86 °C, $[\alpha]_D^{29}$ + 193 (c = 1.5, CH_2Cl_2). Found: C, 73.49; H, 5.12; N, 4.50. Calc. for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N 4.78; ν_{max}/cm^{-1} 2918, 2930, 2852 (CH), 1793,1728 (CO); δ_H (300 MHz; $CDCl_3$) 2.72 (1H, dtt, *J* 14.5, 7, 1.5, C*H*H), 2.95 (1H, dtt, *J* 14.5, 7, 1.5, C*H*H), 5.07 (1H, ddd, *J* 1.5, 2, 10, =CH), 5.15 (1H, ddd, *J* 1.5, 2, 17, =CH), 5.39 (1H, t, *J* 7, C*H*ON), 5.79 (1H, ddt, *J* 17, 10, 7, =CH), 7.32 (3H, m, Ar), 7.47 (2H, m, Ar), 7.70 (4H, m, Ar) δ_C (75 MHz; $CDCl_3$) 39.0, 88.1, 117.9, 123.1, 128.0, 128.1, 128.3, 128.6, 128.9, 133.4, 132.8, 137.3, 163.5.

N-*t*-Butoxycarbonyl-*O*-((*R*)-1-phenylbut-3-en-1-yl)hydroxylamine (4b)

This compound was prepared following the previously reported procedure. $[\alpha]_D^{29}$ + 131 (c = 4.9, CH_2Cl_2). Other data have been reported previously.

Methyl ((3*S*,5*R*)-2-*t*-butoxycarbonyl-5-phenylisoxazolidin-3-yl) acetate (5b)

This compound was prepared following the previously reported procedure. mp 47–49 °C; $[\alpha]_D^{29}$ −2.3 (c = 5.5, CH_2Cl_2). Found: C, 63.56; H, 7.36; N, 4.27. Calc. for $C_{18}H_{15}NO_3$: C, 63.54; H, 7.36; N 4.27. Other data have been reported previously.

2-((3*R*,5*R*)-2-*t*-butoxycarbonyl-5-phenylisoxazolidin-3-yl)ethanol (9)

A solution of the ester **5b** (500 mg, 1.6 mmol) in THF (6 ml) was cooled to −78 °C. $LiAlH_4$ (121 mg, 3.2 mmol) was gradually added to the cool solution from a solid addition tube. The mixture was stirred at −78 °C for 2 h and left to warm up to −20 °C. Water was added to the mixture and it was stirred until a white crystalline precipitate formed. The mixture was then filtered through celite, washing with EtOAc, and evaporated to give the alcohol **9** as a colourless oil (434 mg, 94%) $[\alpha]_D^{29}$ + 32 (c = 4.9, CH_2Cl_2). ν_{max}/cm^{-1} 3450, 2875, 2930, 2979, 1708; δ_H (200 MHz; $CDCl_3$) 1.50 (9H, s, *t*-Bu), 1.65–2.05 (3H, m, H4, CH_2), 2.87 (1H, ddd, J 6.6 8.8 12.5, H4), 2.97 (1H, brs, OH), 3.71 (1H, ddd, *J* 3.7 5.9 12.0, C*H*HOH), 3.81 (1H, ddd, *J* 4.4 9.5 11.7, C*H*HOH), 4.49 (1H, dddd, *J* 4.4 7.3 8.8 11.0, H3), 4.82 (1H, dd, *J* 10.3 5.9, H5), 7.3 (5H, m); δ_C (50 MHz; $CDCl_3$) 28.1, 38.8, 43.6, 57.9, 59.6, 82.5, 83.2, 126.6, 128.5, 136.9, 159.2; *m*/*z* 294 (28%, M + H$^+$), 293 (26, M$^+$), 238 (32, M + H$^+$–C_4H_8), 193 (36, M + H$^+$-Boc), 117 (100, M + H$^+$-Boc-Ph). *m*/*z* (FI) 293.1617 (M$^+$ $C_{16}H_{23}NO_4$ requires 263.1627).

2-((3*R*,5*R*)-2-*t*-Butoxycarbonyl-5-phenylisoxazolidin-3-yl)acetaldehyde (10)

IBX (229 mg, 0.68 mmol) was added to a solution of the alcohol **9** (229 mg, 0.8 mmol) in DMSO (1.7 ml). The solution was stirred for 5 h, then diluted with water. The precipitate was removed by filtration through celite, washing thoroughly with ethyl acetate. The layers were separated, and the aqueous layer was re-extracted with ethyl acetate. The combined organic layers were washed (brine), dried (Na_2SO_4) and evaporated to give the aldehyde as yellow oil (254 mg) which was used without purification. ν_{max}/cm^{-1} 2930, 2980, 1724; δ_H (200 MHz; $CDCl_3$) 1.50 (9H, s, *t*-Bu), 1.93 (1H, ddd, *J* 6.6 10.3 12.5, H4), 2.73 (1H, ddd, *J* 1.5 8.0 16.9, C*H*HCHO), 2.90 – 3.05 (2H, m, H4, C*H*HCHO), 4.75 (1H, ddd, *J* 6.6 8.0 13.2, H3), 4.89 (1H, dd, *J* 6.6 10.3, H5), 7.18 (5H, m, Ph), 9.82 (1H, t, *J* 1.5, CHO); δ_C (50 MHz; $CDCl_3$) 28.1, 43.3, 49.8, 56.0, 82.5, 82.8, 126.5, 128.5, 136.7, 157.5, 200.5; *m*/*z* 291 (10%, M$^+$), 236 (16, M + H$^+$–C_4H_8), 191 (19, M$^+$-Boc), 131 (100, $C_9H_{11}^+$).

Methyl 4-((3*R*,5*R*)-2-*t*-butoxycarbonyl-5-phenylisoxazolidin-3-yl)but-2-enoate (11)

From the isolated aldehyde: methyl (triphenylphosphoranylidene)acetate (97 mg, 0.27 mmol) was added to a solution of aldehyde **10** (40 mg, 0.14 mmol) in CH_2Cl_2 (1 ml). The mixture was stirred overnight, then pre-absorbed onto silica gel and purified by flash chromatography on silica gel (1.2 g) using 5–10% EtOAc–hexane as eluent to give the *Z* and *E* alkenes **11** (33 mg, 67%).

In situ generation of the aldehyde: DIBAL (357 µl of a 1M solution in hexane, 03.7 mmol) was added dropwise to a solution of the ester **5b** (100 mg, 0.31 mmol) in THF (2 ml) under N_2 at −55 °C. This was stirred for 2 h, then a solution of the ylide (221 mg, 0.62 mmol) in 1 : 1 THF : CH_2Cl_2 (2 ml) was transferred to the reaction flask by canula. The mixture was allowed to warm up to room temperature and stirred overnight. Water was added and the mixture was stirred for 30 min followed by addition of Na_2SO_4 until all of the white jelly-like precipitate turned crystalline. It was filtered, washed with EtOAc and the filtrate was evaporated. The residue was purified by flash chromatography on silica gel (3 g) using 5–10% EtOAc–hexane as eluent to give the *Z* alkene as an oil and the *E* alkene as a colourless solid (70 mg, 64%).

E isomer: mp 57–58 °C, $[a]_D^{29}$ + 10 (*c* = 4.7, CH_2Cl_2). Found: C, 65.61; H, 7.47; N, 3.95. Calc. for $C_{19}H_{25}NO_5$: C, 65.69; H, 7.25; N 4.03. ν_{max}/cm^{-1} 2981, 1724, 1660; δ_H (200 MHz; $CDCl_3$) 1.50 (9H, s, *t*-Bu), 1.94 (1H, ddd, *J* 6.0, 10.3, 12.0, H4), 2.45–2.90 (3H, m, H4, CH_2), 3.66 (3H, s, OMe), 4.44 (1H, app q, *J* 7.0, H3), 4.87 (1H, dd, *J* 6.6, 10.3, H5), 5.93 (1H, d, *J* 15.4, =CH), 6.98 (1H, dt, *J* 15.4, 7.3, =CH), 7.38 (5H, m, Ph); δ_C (50 MHz; $CDCl_3$) 28.0, 38.6, 42.6, 51.3, 59.3, 82.1, 82.8, 123.3, 126.4, 128.3, 128.4, 136.9, 144.6, 157.4, 166.4; *m*/*z* 292 (M + H$^+$–C_4H_8), 148 (M$^+$-Boc-$C_3H_4CO_2Me$), 130 (M$^+$-Boc-$C_3H_4CO_2Me$–H_2O), 105 ($PhC_2H_4^+$), 103 ($PhC_2H_2^+$), 77 (Ph^+).

Z isomer: δ_H (200 MHz; $CDCl_3$) 1.52 (9H, s, *t*-Bu), 1.98 (1H, ddd, *J* 6.6 10.3 12.5, H4), 2.81 (1H, ddd, *J* 6.6 8.0 12.5, H4), 3.00–3.15 (2H, m, CH_2), 3.50 (3H, s, OMe), 4.47 (1H, app tt, *J* 6.6 8.0, H3), 4.82 (1H, dd, *J* 6.6 10.3, H5), 5.92 (1H, td, *J* 2.0 11.7, =CH), 6.42 (1H, td, *J* 7.3 11.7, =CH), 7.35 (5H, m, Ph).

Methyl 4-((3*R*,5*R*)-5-phenylisoxazolidin-3-yl)but-2-enoate (12)

Trifluoroacetic acid (222 µl, 2.9 mmol) was added dropwise to the isoxazolidine **11** (100 mg, 0.29 mmol) at room temperature under nitrogen. The mixture was stirred for 1 h, then the volatiles were evaporated under reduced pressure. Saturated $NaHCO_3$ (aq) was added to the residue and the mixture was extracted with EtOAc (3 times). The combined organic layers were dried (Na_2SO_4) and evaporated to give the deprotected isoxazolidine **12** as a pale yellow oil (97 mg) which was used without purification. ν_{max}/cm^{-1} 3234 (NH), 2950, 1719, 1658; 1.85 (1H, ddd, *J* 5.5 8.1 12.5, H4), 2.38 (1H, dtd, *J* 1.5 7.3 13.9, CH_2), 2.60 (1H, dtd, *J* 1.5 7.3 13.9, CH_2), 2.82 (1H, ddd, *J* 7.3 8.1 12.5, H4), 3.60–3.75 (4H, m, H3, OMe), 4.68 (1H, brs, NH), 4.88 (1H, t, *J* 8.1, H5), 5.89 (1H, td, *J* 1.5, 16.0, =CH), 6.98 (1H, td, J 7.3 16.0, CH=), 7.30 (5H, m, Ph); δ_C (50 MHz; $CDCl_3$) 37.6, 43.8, 51.4, 59.9, 84.5, 123.0, 126.0, 127.8, 128.5, 139.4, 145.4, 166.6; *m*/*z* 248 (4%, M + H$^+$), 149 (10, M$^+$–$C_5H_7O_2$), 130 (100, M$^+$–$C_5H_7O_2$–H_2O), 103 (71, $PhC_2H_2^+$), 77 (32, Ph^+).

(6*R*)-6-((2*R*)-2-Hydroxy-2-phenylethyl)piperidin-2-one (14)

A solution of the alkene **12** (167 mg, 0.68 mmol) in MeOH (4 ml) containing Pd/C (17 mg, 10%) was stirred under H_2 (1 atm) for 7 h. The mixture was filtered through celite and the filtrate was evaporated. The residue was purified by flash chromatography on silica gel (3 g) eluting with 75% EtOAc–hexane to give lactam **14** as a colourless solid (148 mg, 100%) ν_{max}/cm^{-1} 3300, 3187, 2900, 2948, 1652; δ_H (300 MHz; $CDCl_3$) 1.3 (1H, m, CH), 1.5–1.8 (5H, m, CH_2), 2.22 (1H, ddd, *J* 18, 11, 6, CH), 2.35 (1H, ddt, *J*, 18, 5, 2, CH), 3.63 (1H, tt, *J* 8.8, 3, H3), 3.80 (1H, brs, OH), 4.85 (1H, dd, *J* 3.5 9.5, C*H*OH), 7.2 (5H, m, Ph), 7.72 (1H, s, NH); δ_C (50 MHz; $CDCl_3$) 19.9, 29.4, 30.5, 45.3, 53.8, 74.5, 125.3, 127.2, 128.3, 145.2, 172.2; *m*/*z* 220 (M + H$^+$), 201 (M$^+$–H_2O), 112 (MH$^+$–$PhCH_2OH$), 98 ($C_5H_8NO^+$), 77 (Ph^+); *m*/*z* 219.1248 (M$^+$ $C_{13}H_{17}NO_2$ requires 219.1259).

(+)-Norsedamine (15)

$LiAlH_4$ was added to a solution of the lactam **14** (1g, 4.6 mmol) in THF (20 ml) at 0 °C. This mixture was gradually allowed to warm up to room temperature and was then stirred for 1 h. H_2O was added dropwise until a white precipitate had completely formed. The mixture was filtered, washing with EtOAc and evaporated to give norsedamine as a colourless solid (926 mg, 98%) which was used without further purification. mp 57–60 °C $[a]_D^{29}$ + 1 (*c* = 1.7, CH_2Cl_2); ν_{max}/cm^{-1} 3298, 3087, 2820, 2933; δ_H (300 MHz; $CDCl_3$) 1.0–2.0 (8H, m, CH), 2.66 (1H, ddd, *J* 14, 11.6, 3, CH), 2.92 (1H, tt, *J* 10.5, 3, CH), 3.09 (1H, brd, *J* 14, CHN), 3.2 (2H, br, CH_2N), 4.94 (1H, dd, *J* 2.9 10.3, C*H*OH), 7.1 (5H, m, Ph); δ_C (50 MHz; $CDCl_3$) 24.2, 26.9, 33.8, 44.9, 45.8, 57.9, 75.1, 125.4, 126.8, 128.0, 145.1; *m*/*z* 206 (29%, M + H$^+$), 84 (100, $C_5H_{10}N^+$), 77 (50, Ph^+), 56 (35, $C_4H_8^+$).

(3*R*,5*R*)-3-Phenylhexahydro-3*H*-pyrido[1,2-*c*][1,3]oxazin-1-one (16)

Carbonyl diimidazole (101 mg, 0.62 mmol) was added to a solution of crude norsedamine **15** (106 mg, 0.52 mmol) in THF (2 mL). The solution was stirred at room temperature overnight, then diluted with ethyl acetate and washed with dilute hydrochloric acid. The aqueous layer was re-extracted with ethylacetate. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography on silica gel (3 g) eluting with 30% ethyl acetate–petrol to give the oxazine **16** (71 mg, 59%). mp 135–138 °C (lit.[9] 127–129 °C), $[a]_D^{32}$ + 61.5 (*c* = 0.55, $CHCl_3$), δ_H (300 MHz; $CDCl_3$) 1.0–1.9 (7H, m, CH), 2.25 (1H, ddd, *J* 13.9, 5.7, 2.0, CH), 2.67 (1H, dt, *J* 12.6, 2.8, CHN), 3.43 (1H, ddt, *J* 11.1, 5.5, 2.5, CHN), 4.54 (1H, brd, *J* 13.4, CHN), 5.17 (1H, dd, *J* 11.7, 2.0, CHO), 7.3 (5H, m, Ph), δ_C (75 MHz; $CDCl_3$) 23.4, 24.1, 24.8, 33.3, 38.1, 54.0, 76.3, 126.6, 128.1, 128.3, 138.8, 153.4.

(+)-Sedamine (6)

$LiAlH_4$ (23 mg, 0.6 mmol) was added to a solution of the oxazine **16** (70 mg, 0.3 mmol) in THF (2 mL) under nitrogen. The mixture was heated at reflux for 2 h, then cooled and quenched by the cautious addition of the minimum amount of water. The colourless, precipitated solids were removed by filtration through celite, washing thoroughly with ethyl acetate. The filtrate was evaporated and the residue was purified by flash chromatography on silica gel (2 g) eluting with 30% ethyl acetate–petrol to give the aminal **17** (5 mg, 8%) and 20% methanol–chloroform to give sedamine **6** (50 mg, 76%) as a viscous oil which solidified slowly on standing; mp (ether–petrol) 57–59 °C, (lit.,[3b,10] 54–56, 59–61); $[a]_D^{29}$ + 80 (*c* = 1.2, EtOH), (lit.[3b] $[a]_D^{20}$ + 87 (*c* = 1.1, EtOH)); δ_H (200 MHz; $CDCl_3$) 1.20–1.90 (7H, m, CH), 2.24 (1H, ddd, *J* 14.3, 10.5, 9.2, CH), 2.50 (3H, s, Me), 2.57 (1H, m, CHN), 2.86 (1H, m, CHN), 3.07 (1H, m, CHN), 4.89 (1H, dd, *J* 2.9 10.5, C*H*OH), 7.3 (5H, m, Ph); δ_C (75 MHz; $CDCl_3$) 20.5, 22.3, 25.8, 39.7, 39.9, 51.4, 60.8, 74.3, 125.5, 126.9, 128.2, 145.5; *m*/*z* 220 (25%, M + H$^+$), 98 (100, $C_6H_{12}N^+$), 77 (14, Ph^+), 70 (37, $C_5H_{10}^+$).

^{1}H NMR data for aminal **17** δ_H (200 MHz; $CDCl_3$) 1.3 (2H, m), 1.7 (5H, m), 2.04 (1H, m), 2.28 (1H, m), 2.83 (1H, brd, *J* 11.1), 3.94 (1H, d, *J* 8.1), 4.50 (1H, dd, *J* 9.6, 4.5), 4.58 (1H, d, *J* 8.1), 7.3 (5H, m).

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