Synthesis and reactions of *N*,*N*-bis[1-(trimethylsiloxy)alkyl]-formamides: preparation of (±)-argemonine and (±)-norargemonine

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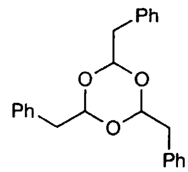
Symmetrical and unsymmetrical *N*,*N*-bis[1-(trimethylsiloxy)alkyl]formamides are prepared and their reactions investigated, including an application to the synthesis of the pavine alkaloids (±)-argemonine and (±)-norargemonine

Introduction

In the preceding two articles[1,2] we have described the synthesis and reactions of *N*-[1-(trimethylsiloxy)alkyl]amides [1-acylamino-1-(trimethylsiloxy)alkanes], showing how silylated amides can add to aldehydes to give stable (in most cases) adducts which are versatile precursors to acyl imine/iminium salts. In the course of this work we also encountered formation of *N*,*N*-bis-[1-(trimethylsiloxy)alkyl]formamides, which initially were undesired byproducts. These compounds are nevertheless interesting in their own right, and in this paper we describe the general synthesis of symmetrical and unsymmetrical *N*,*N*-bis[1-(trimethylsiloxy)alkyl]formamides. As well as reporting some reactions of these bis-adducts, we will describe their use in the preparation of the alkaloids (±)-argemonine and (±)-norargemonine.



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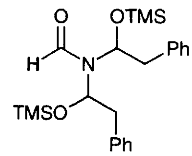

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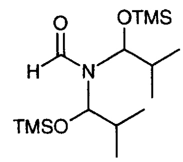

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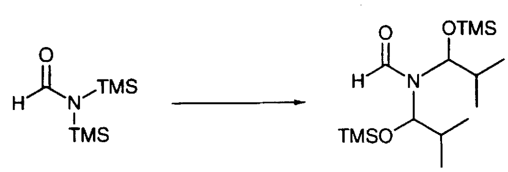
TMS = $SiMe_3$

Discussion

It was not anticipated that the preparation of bis(trimethylsilyl)formamide bis-aldehyde adducts, *e.g.* **2**, would pose any great problems as these species had been obtained as the major product when roughly equal quantities of bis(trimethylsilyl)formamide (BSF) and an aldehyde were mixed in the presence of trimethylsilyl (TMS) triflate. However, when two equivalents of isobutyraldehyde and one of BSF were mixed in the presence of TMS triflate, chromatography of the resulting mixture did not result in the isolation of any product. The order of addition was altered so that first TMS triflate and then BSF were added to phenylacetaldehyde, but subsequent work-up this time gave 2,4,6-tribenzyl-1,3,5-trioxane **1**,[3] which was presumably formed either before addition of BSF or in preference to formation of adduct. This product was not expected to react further with BSF as it had been noted previously[1] that acetals would not react with BSF under these conditions.

On re-investigation it was found that addition of two equivalents of phenylacetaldehyde to a mixture of one equivalent of BSF and a catalytic quantity of TMS triflate did give the BSF–bis-phenylacetaldehyde adduct **2**. The ^1H NMR spectrum of the reaction mixture revealed that it contained compound **2** and little else, but decomposition occurred on chromatographic work-up. When BSF–bis-aldehyde adducts were first isolated from reactions which were intended to give the corresponding mono-adducts, a small excess of BSF had been present at completion of the reaction. The presence of this excess of BSF appeared to be the only significant difference between reactions from which it was possible to isolate bis-adducts and those from which it proved impossible. Therefore, following preparation of the BSF–bis-phenylacetaldehyde adduct **2** *in situ*, a further portion of BSF was added and stirring was continued for 0.5 h. Subsequent chromatographic work-up gave a good yield of the adduct **2** (62%). Once isolated, compound **2** could be rechromatographed without decomposition, which suggested that in the absence of residual BSF the TMS triflate present at completion of the reaction was, in some way, responsible for decomposition of the adduct. Unfortunately, preparation of the BSF–bis-isobutyraldehyde adduct **3** by this method gave a poor yield (38%).

Bis(trimethylsilyl)acetamide (BSA) had been found to be unreactive towards aldehydes under these conditions[1] but we thought it was reasonable to assume that it might behave in a similar manner to BSF in preventing decomposition of the bis-adducts on work-up. This proved to be the case, as in the presence of BSA with an excess of aldehyde the bis-adduct **3** could be prepared in excellent yield (99%) (Scheme 1).



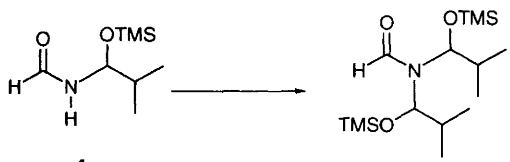
BSF 3

Scheme 1 *Reagents and conditions:* BSA (1 equiv.), room temp., then TMSOTf, CCl_4; and finally Pr^iCHO (4 equiv.), room temp., 3 h (99%)

Preparation of mixed BSF–bis-aldehyde adducts

In considering the application of these methods to natural product synthesis, in most cases it would be necessary to prepare *mixed* BSF–bis-aldehyde adducts; *i.e.* bis-adducts in which the two substituents on the formamide nitrogen originated from different aldehydes. It was expected that this would be possible *via* silylation of a mono-adduct, followed by reaction with another aldehyde. We thought that BSA could be conveniently used for this purpose (BSF[4] has been used as a silylating agent) as it is inert towards aldehydes under these conditions, and thus need not be removed on completion of silylation. In fact, the removal of BSA after silylation would be disadvantageous as its presence prevents decomposition of the bis-adduct on work-up.

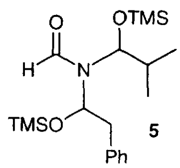
In order to establish that this methodology was viable, we aimed to make the known BSF–bis-isobutyraldehyde adduct **3**[1] from the BSF–isobutyraldehyde adduct **4**.[1] Following the procedure outlined in Scheme 2, adduct **4** was first N-silylated



4 **3**

Scheme 2 *Reagents and conditions:* BSA (3 equiv.), room temp., 4 h; then Pr^{i}CHO (2.9 equiv.), TMSOTf (cat.), room temp., 0.25 h (100%)

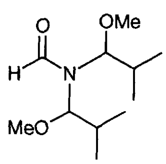
in situ with BSA, then addition of isobutyraldehyde and TMS triflate formed the bis-adduct **3**, which was isolated in 100% yield. In a similar manner, the mixed BSF–phenylacetaldehyde–isobutyraldehyde adduct **5** was prepared from the mono-adduct



4 in 61% yield. The yield of this reaction could be enhanced to 96% by the use of an excess of phenylacetaldehyde in the second stage of the reaction.

Reactions of BSF–bis-aldehyde adducts involving substitution of the trimethylsiloxy group

Formation of the bis-methoxy adduct **6** in methanol proceeded



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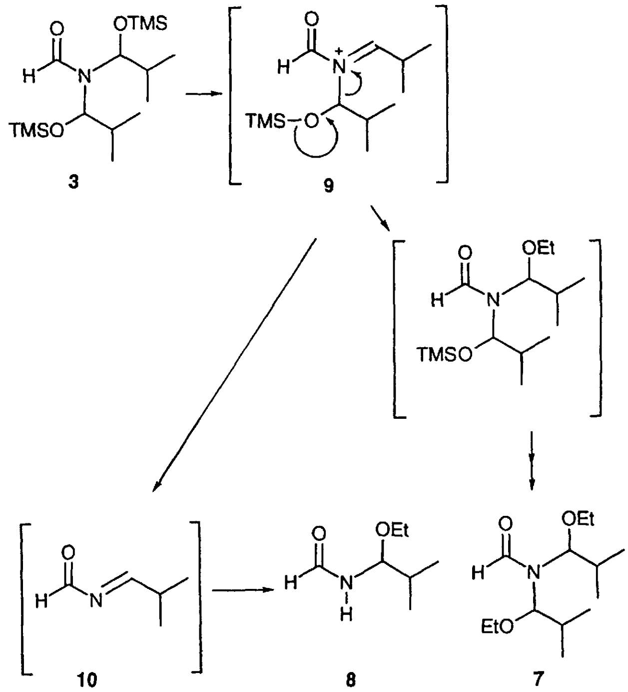
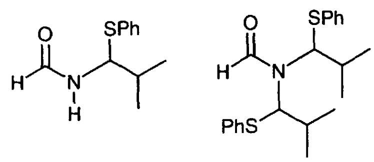
in only moderate yield (44%), using a method succesfully applied to the analogous transformation of mono-adduct **4**.[2] The corresponding reaction in ethanol gave both the bis-ethoxy adduct **7** (53%) and the mono-adduct **8** (31%). We supposed that the formation of the latter was due to the loss of propionaldehyde from the intermediate *N*-acyliminium ion intermediate **9** to give the *N*-acylimine **10**, which then added ethanol to give mono-adduct **8** (Scheme 3). Following this argument we reasoned that a more reactive nucleophile might trap the *N*-acyliminium ion **9** before such a fragmentation was possible. The importance of having an effective nucleophile was duly demonstrated by the addition of thiophenol to the BSF–bis-isobutyraldehyde adduct **3**. In the presence of a small amount of thiophenol (2.6 equiv.) only the mono-phenylsulfanyl adduct **11** (93%) was isolated. Increasing the quantity of thiophenol dramatically altered the course of this reaction, so that the use of thiophenol as solvent gave an excellent yield of the bis-phenylsulfanyl adduct **12** (90%). In the former case the concentration of thiophenol was not large enough to trap the *N*-acyliminium ion **9** before it decomposed



Scheme 3 *Reagents and conditions:* EtOH, TMSOTf (cat), room temp., 1 h

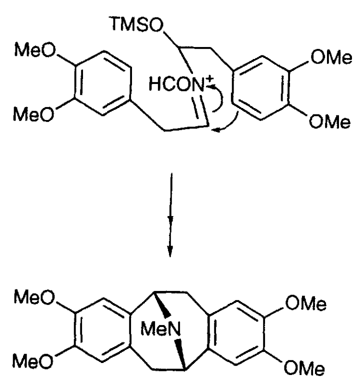


11 **12**

to aldehyde and the *N*-acylimine **10**. Thiophenol then presumably added to this *N*-acylimine to give the mono-phenylsulfanyl adduct **11** as the only isolable product. However, in the latter case the concentration of thiophenol was as large as is possible, and in this case it was able to trap iminium ion **9** before it had decomposed.

Synthesis of (±)-argemonine and (±)-norargemonine

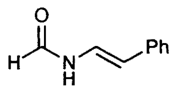
Argemonine **13** is a member of the pavine family of alkaloids,[5] and unusually it had been prepared, and named as *N*-methylpavine, before it was isolated from a natural source.[6] (−)-Argemonine is one of three related alkaloids isolated from the perennial plants *Argemone hispida* and *A. munita*[7] which are found in North and South America, and from *Berberis buxifolia*.[8] We envisaged that this alkaloid might be synthesized *via* double cyclisation of a suitable BSF–bis-phenylacetaldehyde derivative (Scheme 4).



Argemonine **13**

Scheme 4

In the first instance, cyclisation of the BSF–bis-phenylacetaldehyde adduct **2** was attempted in the presence of TMS triflate, but this resulted in formation of the mono-enamides **14** and **15**



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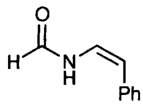

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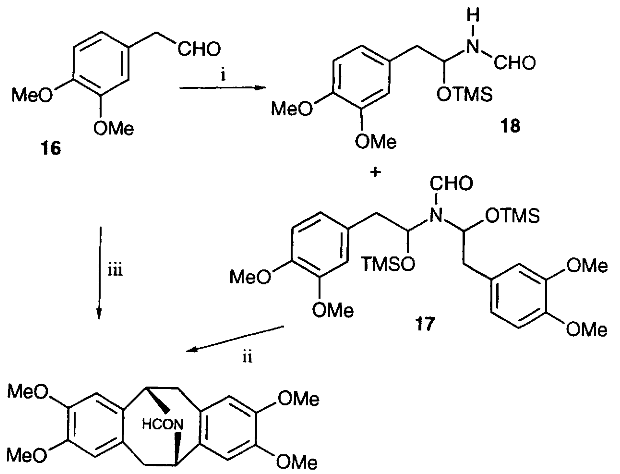
(49% combined) and phenylacetaldehyde. Treatment with refluxing acetic acid gave a similar result. Despite these failures we considered it worthwhile to attempt the analogous reaction with dioxygenated aromatic rings, as these are much more nucleophilic than the unsubstituted parent and so are more likely to give a cyclised product. 3,4-Dimethoxyphenylacetaldehyde **16** was prepared by Swern oxidation[9] of the corresponding alcohol, or by a Darzens-type homologation of 3,4-dimethoxybenzaldehyde.[10] Treatment of 3,4-dimethoxyphenylacetaldehyde with BSF in the presence of TMS triflate, gave the bis-adduct **17** (37%) along with mono-adduct **18** (15%). Subsequent cyclisation of adduct **17** in formic acid at room temperature gave an 82% yield of *N*-formylpavine **19**. Alternatively, it was possible to prepare *N*-formylpavine **19** directly from the aldehyde (Scheme 5). This reaction went

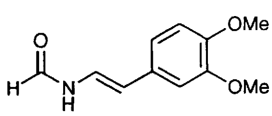


N-formylpavine **19**

Scheme 5 *Reagents and conditions:* i, BSF (0.55 equiv.), CCl_4, room temp., TMSOTf (cat.), 1.5 h; then BSF (0.5 equiv.), 22.5 h [**17** (37%) + **18** (15%)]; ii, HCO_2H, room temp., 5 h (82%); iii, BSF (0.58 equiv.), CCl_4, room temp., TMSOTf (cat.), 0.3 h; then addition of HCO_2H, room temp, 0.3 h [**19** (69%) + recovered **16** (19%)]

with an excellent conversion, and only a small amount of a compound which appeared, by proton NMR and IR spectroscopy, to be the enamide **20** (*cf.* **14**/**15**) was isolated along with some recovered aldehyde. Thus, from readily available precursors the argemonine skeleton was obtained in a two-step, one-pot process and in excellent yield (69% yield, 81% conversion).

(±)-Argemonine **13** was easily obtained from *N*-formylpavine **19** by reduction of the formyl group, but treatment with



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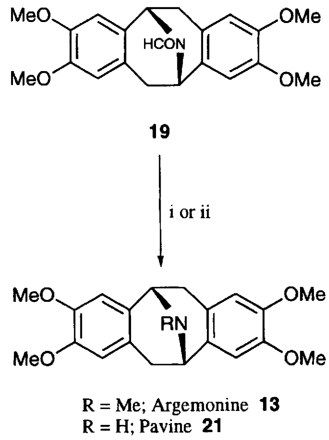
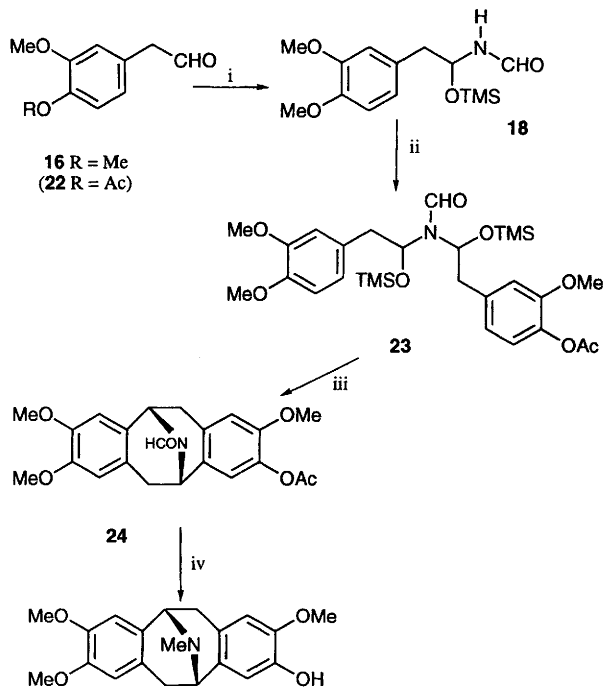
aluminium hydride in diethyl ether–1,2-dimethoxyethane (DME) at 0 °C gave a mixture of (±)-pavine **21** and (±)-argemonine **13** (~1 : 1, 50% combined yield). The problem of carbon–nitrogen bond cleavage in lithium aluminium hydride reductions of tertiary amides has been reported in the literature,[11] and so we then investigated the use of borane–tetrahydrofuran (THF) to effect the desired reduction. This was found to proceed cleanly, and treatment of *N*-formylpavine **19** with this reducing agent gave (±)-argemonine **13** alone in excellent yield (86%) (Scheme 6).



Scheme 6 *Reagents and conditions:* i, $LiAlH_4$, THF–DME, room temp., 7 h [**13** (26%) + **21** (24%)]; ii, BH_3–THF, reflux, 4 h [**13** only (86%)]

In a similar fashion the unsymmetrical pavine alkaloid (±)-*O*-norargemonine **25**[5,8,12] was prepared *via* a mixed bis-adduct **23**, as illustrated in Scheme 7. In this case the second aldehyde, 4-acetoxy-3-methoxyphenylacetaldehyde **22**, was simply prepared by ozonolysis of eugenol acetate with reductive work-up. Cyclisation (to the formamide **24**) was again achieved with formic acid, and borane–THF reduction reduced the formyl group and cleaved the O-acetyl protection to yield (±)-norargemonine **25**.



2-*O*-norargemonine **25**

Scheme 7 *Reagents and conditions:* i, $ArCH_2CHO$ **16**, BSF (4 equiv.), CCl_4, room temp., TMSOTf (cat.) (85%); ii, BSA (2 equiv.), CCl_4, room temp., 1 h; then TMSOTf (cat), $ArCH_2CHO$ **22**, room temp., 48 h. iii, HCO_2H, room temp., 3 h (70%); iv, BH_3–THF (3 equiv.), reflux 2 h (79%)

Conclusions

Symmetrical and unsymmetrical BSF–bis-aldehyde adducts can be prepared in excellent yield and will undergo substitution of both trimethylsiloxy groups in the presence of high concentrations of a good nucleophile, otherwise fragmentation is observed. The utility of these intermediates for synthetic strategies has been demonstrated by the preparation of the pavine alkaloids (±)-argemonine and (±)-norargemonine.

Experimental

Experimental protocols such as the drying and purification of reaction solvents, instrumentation and other such details are identical with those described elsewhere.[1]

2,4,6-Tribenzyl-1,3,5-trioxane 1

TMS triflate (0.15 cm^3 of a 0.26 mol dm^{-3} solution in dichloromethane (DCM) (0.04 mmol, 1 mol%) was added to a stirred solution of phenylacetaldehyde (0.44 cm^3, 3.8 mmol) in dry carbon tetrachloride (5 cm^3) at room temperature under nitrogen. BSF (0.4 cm^3, 1.9 mmol) was added and the mixture was stirred for 30 min. Solvent was removed under reduced pressure and purification of the residue by flash column chromatography [silica (50 g); (10:1) light petroleum–ether] gave the *title compound* **1** (308 mg, 68%) as prisms, mp 154–155 °C (from EtOAc) (lit.,[3] 155 °C) (Found: C, 79.85; H, 6.75%; M^+, 360.1724. Calc. for $C_{24}H_{24}O_3$: C, 79.97; H, 6.71%; M, 360.1725); R_f 0.59 [(4:1) light petroleum–ether]; ν_{max}(Nujol)/cm^{-1} 3040, 1500, 1130 and 700; δ ($CDCl_3$; 90 MHz) 7.3 (15 H, s, Ph), 5.05 (3 H, t, *J* 5, OCHO) and 3.10 (6 H, d, *J* 5, CH_2Ph); *m/z* 269 (4%, M^+ − benzyl), 241 (17, M − benzyl − CO), 121 (100, $PhCH_2CH{=}O^+H$), 103 (23) and 91 (69, $PhCH_2^+$).

N,N-Bis[2-phenyl-1-(trimethylsiloxy)ethyl]formamide 2

Phenylacetaldehyde (0.30 cm^3, 2.6 mmol) was added to a stirred solution of BSF (0.3 cm^3, 1.4 mmol, 0.54 equiv.) and TMS triflate (0.1 cm^3 of a 0.26 mol dm^{-3} solution in DCM, 0.026 mmol, 1 mol%) in dry carbon tetrachloride (6 cm^3) under nitrogen at room temperature. After 1 h further BSF (0.3 cm^3, 1.4 mmol, 0.54 equiv.) was added and after a further 30 min the solvent was removed under reduced pressure. Purification of the residue by flash column chromatography [silica (40 g); (10:1) light petroleum–ether] gave the *title compound* **2** (339 mg, 62%) as needles, mp 104–105 °C (from light petroleum) (Found: C, 64.3; H, 8.25; N, 3.2%; M^+, 429.2157. $C_{23}H_{35}NO_3Si_2$ requires C, 64.29; H, 8.22; N, 3.26%; M, 429.2155); R_f 0.72 (ether); ν_{max}(CCl_4)/cm^{-1} 3030, 1680 (C=O) and 1255; δ_H(CCl_4; 90 MHz) 8.55 and 8.4 (1 H, 2 s, CHO of each diastereoisomer), 7.3 (10 H, s, Ph), 6.05 (1 H, m, NC*H*OSiMe$_3$ deshielded by formyl), 5.3 (1 H, m, NC*H*OSiMe$_3$ shielded by formyl), 3.4–2.7 (4 H, m, C*H*$_2$Ph) and 0.05, 0.00, −0.05 and −0.1 (18 H, 4 s, SiMe$_3$); δ_H($CDCl_3$; 400 MHz) (spectrum of the one diastereoisomer obtained by recrystallisation) 8.58 (1 H, s, CHO), 7.36–7.20 (10 H, m, Ph), 5.97 (1 H, dd, *J* 3.2 and 9.3, NC*H*OSiMe$_3$ deshielded by formyl), 5.28 (1 H, dd, *J* 3.2 and 9.0, NC*H*OSiMe$_3$ shielded by formyl), 3.14 (1 H, dd, *J* 3.2 and 13.1, C*H*HPh deshielded by formyl), 2.96 (1 H, dd, *J* 9.0 and 13.1, CH*H*Ph deshielded by formyl), 2.93 (1 H, dd, *J* 9.3 and 12.9, C*H*HPh shielded by formyl), 2.86 (1 H, dd, *J* 3.2 and 12.9, CH*H*Ph shielded by formyl) and −0.11 and −0.20 (18 H, 2 s, SiMe$_3$ of each side-chain); *m/z* 338 (2%, M^+ − $PhCH_2$), 218 (19), 193 (20), 120 (24, $PhCH_2CHO$), 91 (100, $PhCH_2^+$) and 73 (28 $SiMe_3^+$).

N,N-Bis[2-methyl-1-(trimethylsiloxy)propyl]formamide 3

To a mixture of BSF (684 mg, 3.61 mmol), BSA (0.9 cm^3, 3.6 mmol, 1.0 equiv.) and TMS triflate (0.1 cm^3 of a 0.52 mol dm^{-3} solution in CCl_4, 0.05 mmol, 1 mol%), at room temperature under nitrogen, was added isobutyraldehyde (1.3 cm^3, 14.3 mmol, 4.0 equiv.) dropwise. After 3 h the solvent was removed under reduced pressure, and purification of the residue by flash column chromatography [silica (50 g); (9:1) light petroleum–ether] gave the *title compound* **3** (1.196 g, 99%) as plates, mp 77–78 °C (from cyclohexane) (Found: C, 53.9; H, 10.65; N, 4.25%; M^+, 333.2156. $C_{15}H_{35}NO_3Si_2$ requires C, 54.00; H, 10.57; N, 4.20%; M, 333.2155); R_f 0.9 (ether); ν_{max}(CCl_4)/cm^{-1} 2970, 1670 (C=O) and 1255; δ_H(CCl_4; 90 MHz) 8.45 and 8.35 (1 H, 2 s, CHO in each diastereoisomer), 5.55 and 5.50 (1 H, 2 d, *J* 10, O–CH–N deshielded by formyl), 4.95 and 4.95 (1 H, 2 d, *J* 4, O–CH–N shielded by formyl), 2.2–1.6 (2 H, m, C*H*Me$_2$), 1.0 (12 H, d, *J* 7, CH*Me*$_2$) and 0.2, 0.2, 0.15 and 0.1 (18 H, 4 s, SiMe$_3$ shielded and deshielded by formyl in each diastereoisomer); *m/z* 290 (3%, M^+ − Pr^i), 218 (87, M − Pr^i − Me_2CHCHO), 145 (94, $Me_2CHCH{=}O^+TMS$), 75 (44, $Me_2Si{=}O^+H$) and 73 (100, SiMe$_3$).

N,N-Bis[2-methyl-1-(trimethylsiloxy)propyl]formamide 3 from the BSF–isobutyraldehyde adduct 4

BSA (0.45 cm^3, 1.82 mmol, 3 equiv.) was added to *N*-[2-methyl-1-(trimethylsiloxy)propyl]formamide[1] **4** (115 mg, 0.607 mmol) at room temperature under nitrogen. After 4 h, isobutyraldehyde (0.16 cm^3, 1.76 mmol, 2.9 mol equiv.) and then TMS triflate (0.1 cm^3 of 0.26 mol dm^{-3} solution in carbon tetrachloride, 0.026 mmol, 4%) were added to the solution, and the mixture was stirred overnight. Purification of the residue by flash column chromatography [silica (10 g); (9:1) light petroleum–ether] gave the *title compound* **3** (203 mg, 100%) as crystals, identical with a previously characterised sample by TLC and ^{1}H NMR spectroscopy (see above).

N-[2-Methyl-1-(trimethylsiloxy)propyl)]-*N*-[2-phenyl-1-(trimethylsiloxy)ethyl]formamide 5

BSA (0.17 cm^3, 0.688 mmol, 2.1 equiv.) was added to compound **4**[1] (62 mg, 0.327 mmol) at room temperature under nitrogen. After the mixture had been stirred for 20 min phenylacetaldehyde (0.1 cm^3, 0.85 mmol, 2.6 equiv.) was added, followed by TMS triflate (0.06 cm^3 of a 0.26 mol dm^{-3} solution in carbon tetrachloride, 0.016 mmol, 4.8 mol%). After 1 h, chromatography on flash silica gel (15 g) with 5% ether in light petroleum as eluent gave the *title compound* **5** (120 mg, 96%) as an oil, R_f 0.38 [(4:1) light petroleum–ether]; ν_{max}(CCl_4)/cm^{-1} 3015, 1675 (NC=O), 1250 and 845; δ_H($CDCl_3$; 400 MHz) (as compound **5** is a mixture of diastereoisomers, each of which has two rotamers, a total of 4 'isomers' were observed) 8.64, 8.54, 8.43 and 8.31 (1 H, 4 s, CHO of each isomer), 7.35–7.18 (5 H, m, Ph), 6.01 (0.25 H, dd, *J* 3.5 and 9.5, NC*H*CH$_2$Ph of one isomer), 5.90 (0.25 H, dd, *J* 3 and 9.5, NC*H*CH$_2$Ph of one isomer), 5.49 and 5.46 (0.5 H, 2 d, *J* 9.5, NC*H*Pr^i of two isomers), 5.25 (0.25 H, t, *J* 6.5, NC*H*CH$_2$Ph of one isomer), 5.18 (0.25 H, dd, *J* 3 and 9.5, NC*H*CH$_2$Ph of one isomer), 4.90 (0.25 H, d, *J* 5, NC*H*Pr^i of one isomer), 4.80 (0.25 H, d, *J* 6.3, NC*H*Pr^i of one isomer), 3.16 (0.25 H, dd, *J* 3 and 13, C*H*HPh of one isomer), 3.07 (0.5 H, 2 d, *J* 6.5, C*H*$_2$Ph of one isomer), 3.02 (0.25 H, dd, *J* 3 and 13, C*H*HPh of one isomer), 2.99 (0.25 H, dd, *J* 3.5 and 13, C*H*HPh of one isomer), 2.91 (0.75 H, 3 dd, *J* 9.5 and 13, CH*H*Ph of three isomers), 2.19 (0.25 H, d heptet, *J* 6.3 and 6.75, C*H*Me$_2$ of one isomer), 2.06 (0.25 H, d heptet, *J* 5 and 6.7, C*H*Me$_2$ of one isomer), 1.87 and 1.82 (0.5 H, 2 d heptet, *J* 6.75 and 9.5, C*H*Me$_2$ of two isomers), 1.00, 0.95, 0.91, 0.90, 0.86 and 0.69 (6 H, 6 d, *J* 6.75, CH*Me*$_2$ of each diastereoisomer, two of which give two doublets due to being diastereotopic) and 0.160, 0.153, 0.149, 0.136, −0.109, −0.196, −0.201 and −0.231 (18 H, 8 s, all isomers of both SiMe$_3$ groups); δ_C($CDCl_3$; 100 MHz) 162.78, 162.68, 162.13 and 162.09 (CH, formyl), 137.73, 137.10, 137.06 and 136.92 (aromatic C), 129.92, 129.84, 129.82, 129.79, 129.78, 128.47, 128.45, 128.31, 128.25, 126.88, 126.67 and 126.53 (aromatic CH), 83.48, 80.68, 80.65, 80.45, 79.75, 77.25, 77.18 and 77.12 (N*C*HOSiMe$_3$), 47.68, 46.14, 43.37 and 42.51 (*C*H$_2$Ph), 34.94, 34.20, 33.12 and 32.74 (*C*HMe$_2$), 19.57, 19.34, 19.33, 19.30, 18.48, 18.04, 16.90 and 15.54 (diastereotopic Me_2CH) and 0.31, 0.24, 0.16, 0.11, 0.02, 0.00, −0.35 and −0.54 ($SiMe_3$); *m/z* 338 (2%, M^+ − Pr^i), 290 (5, M − benzyl), 218 (100, M − Pr^i − $PhCH_2CHO$), 193 (30, $PhCH_2CH{=}O^+TMS$), 145 (63, $Me_2CHCH{=}O^+TMS$), 91 (8, $PhCH_2^+$) and 73 (58, $SiMe_3$) (Found: M^+, 381.2149. $C_{19}H_{35}NO_3{}^{28}Si_2$ requires M, 381.2155).

N,N-Bis(1-methoxy-2-methylpropyl)formamide 6

To a solution of compound **3** (68 mg, 0.204 mmol) in dry methanol (3 cm^3) under nitrogen at room temperature was added TMS triflate (0.04 cm^3 of a 0.26 mol dm^{-3} solution in carbon tetrachloride, 0.01 mmol, 5 mol%). After 30 min the solvent was removed under reduced pressure, and purification of the residue by flash column chromatography [silica (5 g); (2:1) light petroleum–ether] gave the *title compound* **6** (19 mg, 44%) as an oil, R_f 0.38 [(2:1) light petroleum–ether]; $\nu_{max}(CCl_4)/cm^{-1}$ 1670, 1255, 1090 and 1070; $\delta_H(CDCl_3$; 90 MHz) 8.45 (1 H, s, CHO), 5.05 and 4.95 (1 H, 2 d, *J* 7, O–CH–N of one side-chain), 4.25 (1 H, d, *J* 6, O–CH–N of one side-chain), 3.4 and 3.35 [6 H, 2 s, OMe in major diastereoisomer (80%) and minor diastereoisomer (20%)], 2.1 (2 H, m, C*H*Me_2) and 1.1 and 0.9 (12 H, 2 d, *J* 6, CH*Me_2* in major and minor diastereoisomers); *m/z* 218 (< 0.5%, [M + 1]$^+$), 186 (1, M − OMe), 174 (11, M − Pr^i) and 87 (100, $Pr^iCH{=}O^+Me$) (Found: [M + 1]$^+$, 218.1762. $C_{11}H_{24}NO_3$ requires *m/z* 218.1756).

N,N-Bis(1-ethoxy-2-methylpropyl)formamide 7 and *N*-(1-ethoxy-2-methylpropyl)formamide 8

To a solution of **3** (47 mg, 0.14 mmol) in dry ethanol (2 cm^3) under nitrogen at room temperature, was added TMS triflate (0.02 cm^3 of a 0.26 mol dm^{-3} solution in carbon tetrachloride, 0.0052 mmol, 4 mol%). After 1 h the solvent was removed under reduced pressure and purification of the residue by flash column chromatography [silica (2.5 g); (3:1) light petroleum–ether] gave the *title compound* **7** (18 mg, 53%) as an oil, R_f 0.41 [(3:1) light petroleum–ether]; $\nu_{max}(CCl_4)/cm^{-1}$ 1670, 1255 and 1070; $\delta_H(CCl_4$; 90 MHz) 8.4 (1 H, s, CHO), 5.1 and 5.0 (1 H, 2 d, *J* 6, O–CH–N of one side-chain, in each diastereoisomer), 4.4 and 4.3 (1 H, 2 d, *J* 4, O–CH–N of one side-chain, in each diastereoisomer), 3.5 (4 H, m, OC*H_2*Me), 1.9 (2 H, m, C*H*Me_2), 1.2 (6 H, t, *J* 6, OCH_2*Me*) and 1.0 (12 H, d, *J* 6, CH*Me_2*); *m/z* 202 (9%, M^+ − Pr^i), 101 (100, $Pr^iCH{=}O^+Et$) and 73 (35, $Pr^iCH{=}O^+H$) (Found: M^+, 245.1985. $C_{13}H_{27}NO_3$ requires M, 245.1991); and *N*-(1-ethoxy-2-methylpropyl)formamide **8** (6.3 mg, 31%) as an oil, which was identical with a previously characterised sample[2] by TLC and ^1H NMR spectroscopy.

Formation of *N*-[2-methyl-1-(phenylsulfanyl)propyl]formamide 11 from compound 3

To a solution of compound **3** (75 mg, 0.225 mmol) and thiophenol (0.06 cm^3, 0.584 mmol, 2.6 equiv.) in dry carbon tetrachloride (2 cm^3) under nitrogen at room temperature was added TMS triflate (0.05 cm^3 of a 0.26 mol dm^{-3} solution in carbon tetrachloride, 0.01 mmol, 6 mol%). After 1 h the solvent was removed under reduced pressure and purification of the residue by flash column chromatography [silica (10 g); (1:1) light petroleum–ether] gave the *title compound* **11** (44 mg, 93%) as square plates, which was identical with a previously characterised sample[2] by TLC; IR and ^1H NMR spectroscopy.

N,N-Bis[2-methyl-1-(phenylsulfanyl)propyl]formamide 12 and *N*-[2-methyl-1-(phenylsulfanyl)propyl]formamide 11

To a solution of compound **3** (13 mg, 0.039 mmol) in thiophenol (1 cm^3) under nitrogen at room temperature was added TMS triflate (0.01 cm^3 of a 0.26 mol dm^{-3} solution in carbon tetrachloride, 0.0026 mmol, 7 mol%). After 10 min the solvent was removed under a stream of dry nitrogen and flash column chromatography [silica (1 g); (10:1) light petroleum–ether] gave the *title compound* **12** (13 mg, 90%) as an oil, R_f 0.22 [(4:1) light petroleum–ether]; $\nu_{max}(CCl_4)/cm^{-1}$ 3060, 1665 and 1390; $\delta_H(CCl_4$; 90 MHz) 8.50 and 8.35 (1 H, 2 s, CHO of both diastereoisomers), 7.6–6.9 (10 H, m, Ph), 5.75 and 5.60 (1 H, 2 d, *J* 10, SCHN of one side-chain in both diastereoisomers), 4.95 (0.5 H, d, *J* 4, SCHN of one side-chain in one diastereoisomer), 4.70 (0.5 H, d, *J* 6, SCHN of one side-chain in one diastereoisomer), 2.3–1.5 (2 H, m, C*H*Me_2) and 1.3–0.8 (12 H, m, CH*Me_2*); *m/z* (no peak found for M^+ at 373) 264 (12%, M^+ − SPh), 165 (100, $PhS^+{=}CHPr^i$), 126 (35), 110 (34) and 55 (43); and *N*-[2-methyl-1-(phenylsulfanyl)propyl]formamide **11** (0.8 mg, 10%), identical (TLC and ^1H NMR) with a previously characterised sample.[2]

N,N-Bis[2-(3,4-dimethoxyphenyl)-1-(trimethylsiloxy)ethyl]formamide 17 and *N*-[2-(3,4-dimethoxyphenyl)-1-(trimethylsiloxy)ethyl]formamide 18

To a stirred solution of 3,4-dimethoxyphenylacetaldehyde[10] **16** (121 mg, 0.674 mmol) and BSF (0.08 cm^3, 0.37 mmol, 0.55 equiv.), in dry chloroform (5 cm^3) at room temperature under nitrogen was added TMS triflate (0.1 cm^3 of a 0.26 mol dm^{-3} solution in carbon tetrachloride, 0.026 mmol, 4%). After 1.5 h further BSF (0.08 cm^3, 0.37 mmol, 0.55 mol equiv.) was added and then after a further 22.5 h the solution was evaporated to dryness. Chromatography of the residue on flash silica gel (20 g) with (1:1) light petroleum–ether as eluent gave the *title compound* **17** (69 mg, 37%) as an oil, R_f 0.55 (ether); $\nu_{max}(CCl_4)/cm^{-1}$ 2960, 1680 and 1160; $\delta_H(CCl_4$; 90 MHz) 8.50 and 8.35 (1 H, 2 s, CHO), 6.80 (6 H, m, ArH), 6.0 (1 H, m, NC*H*-$OSiMe_3$ of one side-chain), 5.25 (1 H, m, NC*H*$OSiMe_3$ of other side-chain), 3.9 (12 H, s, OMe), 2.85 (4 H, m, C*H_2*Ar) and 0.0, −0.05 and −0.1 (18 H, 3 s, $SiMe_3$); *m/z* 459 (2%, M^+ − $HOSiMe_3$), 398 (3, M − $ArCH_2$), 253 (31, $ArCH_2CH{=}O$ + $SiMe_3$), 218 (33, M − $HOSiMe_3$ − $HOSiMe_3$ − $ArCH_2$), 151 (26, $ArCH_2^+$) and 73 (100, $SiMe_3^+$) (Found: M^+, 549.2580. $C_{27}H_{43}NO_7{}^{28}Si_2$ requires M, 549.2578); and N-[2-(3,4-*dimethoxyphenyl*)*ethyl*]*formamide* **18** (31 mg, 15%) as an oil, R_f 0.29 (ether); $\nu_{max}(CCl_4)/cm^{-1}$ 3430, 1700 and 1515; $\delta_H(CCl_4$; 90 MHz) 7.9 (1 H, s, CHO), 6.9–6.5 (1 H, d, *J* 9, NH), 6.65 (3 H, s, ArH), 5.6 and 4.85 (1 H, 2 dt, *J* 5 and 9, NHC*H*$OSiMe_3$), 3.7 (6 H, s, OMe), 2.75 (2 H, d, *J* 5, C*H_2*Ar) and 0.0 and −0.05 (9 H, 2 s, $SiMe_3$); *m/z* 297 (1%, M^+), 282 (1, M − Me), 252 (3, M − $HCONH_2$), 207 (10 M − $HOSiMe_3$), 180 (31, M − $OSiMe_3$ − CO), 151 (100, $ArCH_2^+$), 146 (17, M − $ArCH_2^+$) and 73 (12, $SiMe_3^+$) (Found: M^+, 297.1391. $C_{14}H_{23}NO_4{}^{28}Si$ requires M, 297.1396).

N-[2-(3,4-Dimethoxyphenyl)ethyl]formamide 18

To a stirred solution of TMS triflate (0.06 cm^3, 0.313 mmol, 9 mol%) and BSF (3.0 cm^3, 14.1 mmol, 4 equiv.), in dry CCl_4 (2 cm^3) at room temperature under nitrogen was added 3,4-dimethoxyphenylacetaldehyde[10] **16** (0.635 mg, 3.52 mmol). After being stirred at room temperature overnight the mixture was evaporated under reduced pressure. Purification of the residue by flash column chromatography [silica (20 g); (2:1) light petroleum–ether] gave the *title compound* **18** (889 mg, 85%) as an oil. The ^1H NMR and IR spectra were identical with previously characterised sample (see above).

N-Formylpavine 19

N,N-Bis[2-(3,4-dimethoxyphenyl)-1-(trimethylsiloxy)ethyl]-formamide **17** (62 mg, 0.113 mmol) was dissolved in dry formic acid (5 cm^3). After 5 h at room temperature the solution was evaporated to dryness. Purification by flash column chromatography [silica (6 g); ethyl acetate] gave the *title compound* **19** (34 mg, 82%) as crystals, mp 146–149 °C (from ethyl acetate) (Found: C, 68.45; H, 6.4; N, 3.6%; M^+, 369.1572. $C_{21}H_{23}NO_5$ requires C, 68.28; H, 6.28; N, 3.79%; M, 369.1576); R_f 0.31 (ether); λ_{max}(MeOH)/nm 221 and 280 (ε 63 000 and 47 000); $\nu_{max}(CHCl_3)/cm^{-1}$ 1660 and 1510; $\delta_H(CDCl_3$; 400 MHz) (certain types of proton give rise to pairs of peaks due to the anisotropy of the formyl group) 8.27 (1 H, s, CHO), 6.67 and 6.65 (2 H, 2 s, ArH), 6.47 and 6.45 (2 H, 2 s, ArH), 5.73 (1 H, d, *J* 5.5, NC*H*CHH), 4.94 (1 H, d, *J* 5.4, NC*H*CHH), 3.87 and 3.86 (6 H, 2 s, OMe), 3.785 and 3.780 (6 H, 2 s, OMe), 3.40 (1 H, dd, *J* 5.5 and 16.0, NCHC*H*H), 3.39 (1 H, dd, *J* 5.4 and 15.4, NCHC*H*H), 2.90 (1 H, d, *J* 15.4, NCHCH*H*) and 2.77 (1 H, d, *J* 16.0, NCHCH*H*); *m/z* 369 (100%, M^+), 340 (26, M − CHO), 218 (76, M − CH_2Ar), 190 (67, M − CH_2Ar − CO) and 49 (28).

N-Formylpavine 19—synthesis in 'one pot' from the aldehyde

To a solution of 3,4-dimethoxyphenylacetaldehyde **16** (101 mg, 0.56 mmol) and BSF (0.07 cm^3, 0.33 mmol, 0.58 equiv.) in dry carbon tetrachloride (0.4 cm^3) at room temperature under nitrogen was added TMS triflate (0.05 cm^3 of a 0.26 mol dm^{-3} solution in carbon tetrachloride, 0.01 mmol, 2 mol%). After 20 min, dry formic acid (10 cm^3) was added and after a further 20 min the solution was evaporated to dryness. Purification of the residue by flash column chromatography [silica (20 g); ethyl acetate] gave recovered aldehyde **16** (19 mg, 19%, by NMR spectroscopy), a compound believed to be the monoenamide **20** (2 mg, 2%, by NMR and IR spectroscopy) and *N*-formylpavine **19** (72 mg, 69%). The ^1H NMR and IR spectra were identical to a previously characterised sample (see above).

(±)-Argemonine 13 (N-methylpavine) and (±)-pavine 21 from lithium aluminium hydride reduction of N-formylpavine

To a stirred stirred suspension of lithium aluminium hydride (10 mg, 0.26 mmol, 7.5 mol equiv.) in dry THF at 0 °C under nitrogen was slowly added a solution of *N*-formylpavine **19** (13 mg, 0.0352 mmol) in a mixture of THF (1 cm^3) and DME (1 cm^3). After 30 min the solution was allowed to warm to room temperature and after a further 7 h the solution was cooled to 0 °C. Water was added (0.1 cm^3) followed by sodium hydroxide (0.1 cm^3 of a 15% solution) and a further portion of water (0.1 cm^3). The solution was rinsed through a pad of Celite with excess of ethyl acetate and then the solvent removed under reduced pressure. Preparative TLC with ethyl acetate containing a trace of triethylamine as developer gave (±)-argemonine **13** (3.3 mg, 26%) as crystals, R_f 0.28 (3 developments with EtOAc containing a trace of NEt_3); $\nu_{max}(CCl_4)/cm^{-1}$ 3010, 1615, 1520 and 1250; $\delta_H(CDCl_3$; 90 MHz) 6.61 and 6.45 (4 H, 2 s, ArH), 4.02 (2 H, d, *J* 6, NC*H*CHH), 3.85 and 3.78 (12 H, 2 s, OMe), 3.42 (2 H, dd, *J* 6 and 17, NCHC*H*H), 2.59 (2 H, d, *J* 17, NCHCH*H*) and 2.54 (3 H, s, NMe); *m/z* 355 (22%, M^+), 340 (4, M − Me) and 204 (100, M − $ArCH_2$) (Found: M^+, 355.1777. $C_{21}H_{25}NO_4$ requires M; 355.1784); and (±)-pavine **21** (2.9 mg, 24%); R_f 0.14 (3 developments with EtOAc containing a trace of NEt_3); $\nu_{max}(CCl_4)/cm^{-1}$ 3010, 1615, 1520 and 1260; $\delta_H(CDCl_3$; 90 MHz) 6.62 and 6.45 (4 H, 2 s, ArH), 4.41 (2 H, d, *J* 5, NC*H*CHH), 3.85 and 3.78 (12 H, 2 s, OMe), 3.35 (2 H, dd, *J* 5 and 16, NCHC*H*H), 2.72 (2 H, d, *J* 16, NCHCH*H*) and 1.79 (1 H, s, NH); *m/z* 341 (51%, M^+), 326 (6, M − Me), 190 (100, M − $ArCH_2$) and 152 (8) (Found: M^+, 341.1624. $C_{20}H_{23}NO_4$ requires M, 341.1627).

(±)-Argemonine 13 (N-methylpavine) from borane reduction of N-formylpavine 19

N-Formylpavine **19** (26 mg, 0.0705 mmol) was added to BH_3·THF (0.12 cm^3 of a 1.0 mol dm^{-3} solution, 0.12 mmol, 1.7 equiv.) over a period of 15 min at 0 °C in dry THF (5 cm^3). The solution was heated at reflux for 2 h, then cooled, a further portion of BH_3·THF (0.1 cm^3 of a 1.0 mol dm^{-3} solution, 0.1 mmol, 1.4 equiv.) added, and the solution was heated at reflux for a further 2 h. The solution was allowed to cool and then hydrochloric acid was added (10 cm^3 of a 0.3 mol dm^{-3} solution). Solvent was removed by distillation, sodium hydroxide (0.2 g) and water (5 cm^3) were added, and the solution was extracted with ethyl acetate (3 × 10 cm^3). The extract was dried ($MgSO_4$), and evaporated to dryness. Chromatography on flash silica gel (1 g) with ethyl acetate (containing a trace of triethylamine) as eluent gave the title compound **13** (22 mg, 86%) as crystals, mp 109–110 °C (recrystallised as the hydrochloride salt from water and then treated with ammonia to liberate the free amine) (Found: C, 70.65; H, 7.05; N, 3.9. $C_{21}H_{25}NO_4$ requires C, 70.95; H, 7.09; N, 3.94%). The IR and ^1H NMR spectra were identical with those of the previously characterised sample (see above).

4-[2-{N-[2-(3,4-Dimethoxy phenyl)-1-(trimethylsiloxy)ethyl]-formamide}-2-(trimethylsiloxy)ethyl]-2-methoxyphenyl acetate 23

A solution of compound **18** (0.121 g, 0.407 mmol) and BSA (0.21 cm^3, 0.815 mmol, 2 equiv.) in CCl_4 (1 cm^3) was stirred at room temperature for 1 h, and then to this was added TMSOTf (0.01 cm^3, 0.02 mmol, 5 mol%) followed by 4-(formylmethyl)-2-methoxyphenyl acetate **22** (0.186 g, 0.896 mmol, 2.2 equiv.). After the mixture had been stirred at room temperature for 48 h the solvent was removed under reduced pressure, and purification of the residue by flash column chromatography [silica (20 g); ether] gave the *title compound* **23** (0.130 g, 80%) as an oil, $\delta_H(CDCl_3$; 400 MHz) [two diastereoisomers (1 : 1), and rotamers] 8.56 (33%), 8.51 (17%), 8.38 (33%) and 8.35 (17%) (1 H, 4 s, CHO, all isomers), 7.06–6.65 (6 H, m, 6 ArH), 6.08–6.02 (0.5 H, m, C*H*OSiMe$_3$), 5.99–5.96 (0.5 H, m, C*H*OSiMe$_3$), 5.26–5.23 (1 H, m, C*H*OSiMe$_3$), 3.90–3.82 (9 H, m, 3 × OMe), 3.14–2.59 (4 H, m, 2 × CH_2), 2.313, 2.311, 2.300 and 2.293 (3 H, 4 peaks, Ac) and 0.20 to −0.3) (18 H, m, 2 × $OSiMe_3$); *m/z* 488 (0.5%, M^+ − $OSiMe_3$), 487 (2), 281 (25), 253 (25), 252 (32), 218 (100), 151 (28), 146 (31), 73 (80) and 43 (14, $NCHO^+$) (Found: M^+, 577.2509. $C_{28}H_{43}NO_6{}^{28}Si_2$ requires M, 577.2527).

2-O-Acetyl-N-formyl-2-O-norpavine 24

To compound **23** (0.292 g, 0.518 mmol) was added formic acid (10 cm^3) and the resulting solution was stirred at room temperature for 3 h. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography [silica (20 g); ether] to yield the *title compound* **24** (0.141 g, 70%) as a solid, mp 164–167 °C [(1:1) ethyl acetate–ether] (Found: C, 66.5; H, 5.8; N, 3.45%; M^+, 397.1518. $C_{22}H_{23}NO_6$ requires C, 66.49; H, 5.83; N, 3.53%; M, 397.1525); $\delta_H(CDCl_3$; 400 MHz) 8.27–8.24 (1 H, m, CHO), 6.88–6.86, 6.65–6.64, 6.58–6.54 and 6.46–6.43 (4 H, 4 m, 4 × ArH), 5.74–5.73 (1 H, br d, *J* 5.4, C*H*NCHO, one rotamer), 4.96–4.95 (1 H, br d, *J* 5.4, C*H*NCHO, other rotamer), 3.87 and 3.86 (3 H, 2 s, OMe, two rotamers), 3.78 and 3.77 (3 H, 2 s, OMe, two rotamers), 3.74 and 3.73 (3 H, 2 s, OMe, two rotamers), 3.49–3.34 (2 H, m, C*H*H), 2.99–2.71 (2 H, m, CH*H*) and 2.303, 2.298, 2.296 and 2.292 (3 H, 4 peaks, Ac, both rotamers); $\nu_{max}(Nujol)/cm^{-1}$ 2920m, 2850m, 1790s and 1645s; *m/z* 397 (81%, M^+), 355 (89, M − NCHO), 326 (30), 218 (97), 204 (48), 190 (61), 176 (52) and 43 (100, $NCHO^+$).

(±)-2-O-Norargemonine 25

To a solution of compound **24** (0.054 g, 0.136 mmol) in dry THF (10 cm^3) was added dropwise BH_3·THF (0.1 mol dm^{-3}; 0.46 cm^3, 0.408 mmol, 3 equiv.), and then the mixture was heated at reflux for 2 h. After cooling, the solution was quenched with 0.1 mol dm^{-3} HCl (20 cm^3), and the solvent was removed under reduced pressure. Next, water (10 cm^3) was added along with KOH (0.2 g), and this mixture was extracted with ethyl acetate (3 × 10 cm^3). The combined extracts were dried ($MgSO_4$), filtered, and evaporated. Purification of the residue by flash column chromatography [silica (2 g); ethyl acetate with 0.1% Et_3N] gave the *title compound* **25**, (0.041 g, 79%) as a solid, mp 219–223 °C (from EtOH) (lit.,[12b] 222–223 °C); $\delta_H(CDCl_3$; 400 MHz) 6.67 (1 H, s, ArH), 6.60 (1 H, s, ArH), 6.43 (1 H, s, ArH), 6.42 (1 H, s, ArH), 3.99 (2 H, dd, *J* 7.0 and 6.8, C*H*HCHNMe), 3.85 (3 H, s, OMe), 3.78 (3 H, s, OMe), 3.77 (3 H, s, OMe), 2.58 (2 H, dd, *J* 16.0 and 6.8, CH*H*CHNMe), 3.43–3.35 (2 H, m, C*H*NMe), 2.53 (3 H, s, NMe) and 1.70 (1 H, br s, OH); ν_{max}(Nujol)/cm^{-1} 3450m, 3000–2880br, 1725w, 1600w, 1505s and 860s; *m/z* 341 (46%, M^+), 340 (32), 326 (9), 204 (99), 190 (100) and 42 (7).

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