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ALKALOIDS OF FORMOSAN *THALICTRUM SESSILE*

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Key Word Index—*Thalictrum sessile*; Ranunculaceae; roots; diterpenoid alkaloids; aporphinoid alkaloids.

Abstract—Separation of the basic fraction from the roots of *Thalictrum sessile* afforded two new alkaloids, thalicsessine and thalicsiline, together with the known alkaloids, spiradine A, spiredine, spirasine I, spirasine II, spirasine III, (+)-thalifarazine, magnoflorine and berberine.

INTRODUCTION

We reported recently the isolation of two cytotoxic aporphinoid alkaloids from the aerial part of *Thalictrum sessile* Hayata [1]. To date, although there are numerous references to the isolation and identification of various *Thalictrum* alkaloids [2–19], they have shown the presence of only isoquinoline alkaloids. A number of studies of the pharmacology and toxicology of the diterpenoid alkaloids have appeared recently [20–25]. Moreover, Kitagawa *et al.* have published studies on the anti-inflammatory and analgesic effects of several diterpenoid alkaloids [26]. We describe here the isolation and identification of seven C_{20}-diterpenoid alkaloids along with two aporphinoid alkaloids, (+)-thalifarazine (**9**) and magnoflorine (**10**), and one protoberberine alkaloid, berberine (**11**), from an extract of the roots of this plant. The seven C_{20}-diterpenoid alkaloids are spiradine A (**1**), spiredine (**2**), spirasine I (**3**), spirasine II (**4**), and spirasine III (**5**), as well as two new alkaloids thalicsessine (**6**) and thalicsiline (**8**). This is the first report of the presence of diterpenoid alkaloids in the genus *Thalictrum*.

RESULTS AND DISCUSSION

The plant material was collected in July, and the extraction and separation of the alkaloids were performed by a combination of the usual procedures and medium pressure liquid chromatography (MPLC). From the non-phenolic fractions, the two new alkaloids thalicsessine (**6**) and thalicsiline (**8**) were isolated, together with spiradine A (**1**), spiredine (**2**), spirasine I (**3**), spirasine II (**4**), spirasine III (**5**) and (+)-thalifarazine (**9**). Magnoflorine (**10**) and berberine (**11**) were also isolated from the quaternary base fraction as iodide salts. The latter eight known alkaloids were identified by direct comparison (mmp, UV, IR, ^{1}H NMR, ^{13}C NMR and MS) with authentic samples, respectively.

Thalicsessine (**6**), $C_{22}H_{27}NO_4$ [*m/z* 369 (M^+)]. The spectral data exhibits a hydroxyethyl group attach to nitrogen {ν_{max}^{Nujol} cm^{-1} 3350, ^{1}H NMR δ 2.85 (1H, *t*, *J* = 5.12 Hz, disappeared on addition of D_2O), 3.45 (1H, *ddd*, *J* = 14.16, 5.13, 3.41 Hz), 3.62 (1H, *ddd*, *J* = 14.16, 8.05, 3.41 Hz), 3.78 [1H, *m*, changed to *ddd* (*J* = 11.48, 5.13, 3.41 Hz) on addition of D_2O], 3.88 [1H, *m*, changed to *ddd* (*J* = 11.48, 8.05, 3.41 Hz) on addition of D_2O] and ^{13}C NMR δ 49.7 (*t*) and 60.9 (*t*)}, two carbonyl groups [ν_{max}^{Nujol} cm^{-1} 1710, ^{13}C NMR δ 207.6 (*s*) and 208.9 (*s*)], one lactam keto group [ν_{max}^{Nujol} cm^{-1} 1630 and ^{13}C NMR δ 177.1 (*s*)], one exocyclic methylene group [ν_{max}^{Nujol} cm^{-1} 1620 and 890, ^{1}H NMR δ 4.85 (1H, *d*, *J* = 2.40 Hz), 5.02 (1H, *d*, *J* = 2.40 Hz) and ^{13}C NMR δ 111.1 (*t*) and 141.9 (*s*)] and one methyl group [^{1}H NMR δ 1.50 (3H, *s*) and ^{13}C NMR δ 25.5 (*q*)]. Moreover, there is a close resemblance between thalicsessine (**6**) and the known diketone **6a** derived from spiradine A (**1**) in terms of ^{13}C NMR spectra. The structure of thalicsessine (**6**) is similar to that of **6a**, having a C_{20} spiradine-type skeleton [6], except for the hydroxyethyl and lactam ketone groups. In addition, treatment of **6** with NaOD in dioxane gave a deuterio compound (**6b**) [*m/z* 372 (M^+), $C_{20}H_{24}D_3NO_4$] which showed no signals corresponding to those at δ 51.5 (*t*) and 60.6 (*t*) in the ^{13}C NMR spectrum of **6**. Treatment of **6b** with sodium borohydride in THF followed by acetylation with acetic anhydride in pyridine gave an acetate (**7**) [*m/z* 458 (M^+), $C_{26}H_{30}D_3NO_6$] which showed a singlet at δ 4.18 as against a multiplet at δ 4.20 of H-6 in the ^{1}H NMR spectrum of **7a** derived from **6** by the same procedure. These results indicate that one of the two carbonyl groups is located at the C-6 position. Moreover, the other carbonyl group should be located at the C-11 position owing to the UV absorption maximum at 308 nm for the β,γ-unsaturated ketone and CD [a positive Cotton effect at 314 nm ($\Delta\varepsilon$ + 1.32) and a negative Cotton effect at 276 nm ($\Delta\varepsilon$ − 0.75)] spectra of thalicsessine (**6**). This behaviour is also common in the spirasine series [27–29]. From the above discussion, the structure of thalicsessine may be assigned as **6**.

Thalicsiline (**8**), $C_{24}H_{35}NO_5$ [*m/z* 417 (M^+)], showed IR ν_{max}^{Nujol} cm^{-1} 3540 (hydroxy), 1720 and 1240 (acetyl) and 1100 (ether). The presence of an ajaconine-type [C-7(C-20) carbinolamine ether linkage] skeleton in **8** was indicated by comparison of the ^{13}C NMR chemical shift values with literature data [30, 31]. The ^{1}H NMR spectrum of **8** is in accordance with the assigned structure.

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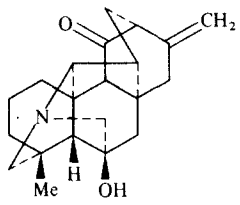

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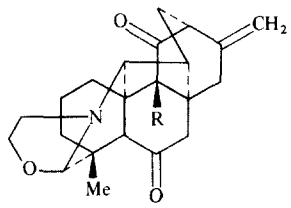

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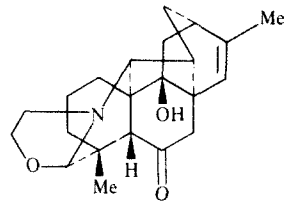

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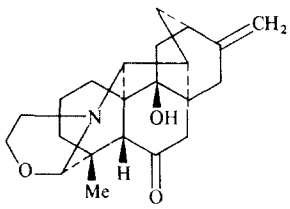

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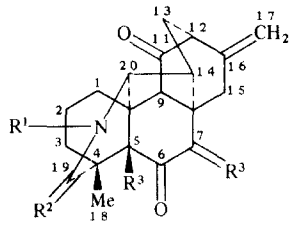
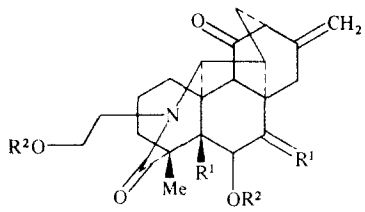
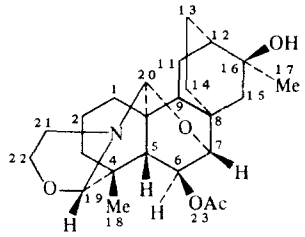


6 R^1 = CH_2CH_2OH, R^2 = O, R^3 = H
6a R^1 = Me, R^2 = H, R^3 = H
6b R^1 = CH_2CH_2OH, R^2 = O, R^3 = D



7 R^1 = D, R^2 = COMe
7a R^1 = H, R^2 = COMe



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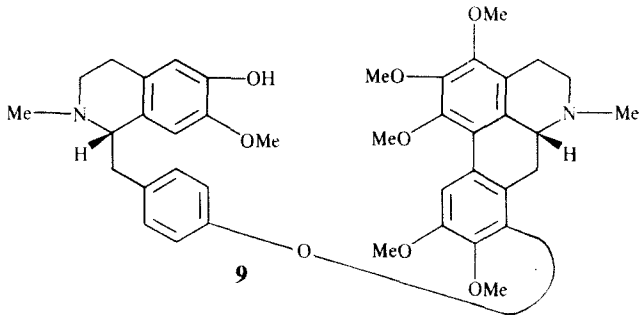

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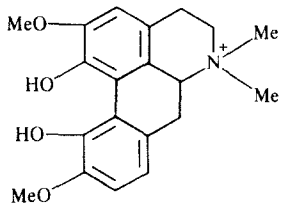

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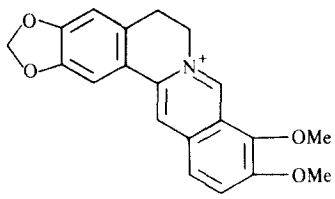

11

The presence of an oxazolidine ring system was revealed by a five-proton multiplet pattern between δ 3.00 and 4.10, in which the proton at C-19 occurs as a distinct epimeric pair of signals at δ 4.11 [(*S*)] and 3.86 [(*R*)] in a ratio of *ca* 1 : 3, a phenomenon which is also common in the spirasine series [27–29]. Other epimeric pairs, a doublet of doublets (J = 2.40 Hz) at δ 5.32 and 5.67 as well as singlets at δ 2.05 and 2.06, in approximately the same ratio of 1 : 3 for each, were assigned to H-6 and C-6-OOCMe, respectively. The rest of the characteristic pairs of signals (all *ca* 1 : 3) were assigned as follows: δ 4.82 and 4.58 (H-20), 1.31 and 1.30 (Me-16), and 0.94 and 1.11 (Me-4). Moreover, the complete structure and relative stereochemistry of **8** were defined unequivocally by a single-crystal X-ray analysis [32]. Thalicsiline (**8**) is the first ajaconine-type alkaloid bearing an oxazolidine ring and an oxygen function at C-6 and is the second ajaconine-type alkaloid in nature.

Spiradine A (**1**) was first isolated from the shrub *Spiraea japonica* L. fil. (Rosaceae) in 1964 [33]. However, the structure had not been unequivocally determined at that time. It was subsequently isolated from the same species some four years later and was named spiradine A [34]. Spiredine (**2**) was initially isolated from the same species of *S. japonica* in 1976 [35]. Both spiradine A and spiredine have not been isolated from any other plant to date. Spirasine I (**3**), spirasine II (**4**) and spirasine III (**5**) were isolated recently from the same species [27–28]. The present paper represents the second report of the isolation of these five C_{20}-diterpenoid alkaloids and the first

report of the presence of all seven C_{20}-diterpenoid alkaloids in the genus *Thalictrum*. (+)-Thalifarazine (**9**) was isolated from *T. cultratum* in 1986 [36] and is now reported for the second time. Magnoflorine (**10**) and berberine (**11**) have been isolated from over 30 *Thalictrum* species [37].

The antiinflammatory activity and other pharmacological activity of these seven diterpenoid alkaloids will be reported elsewhere.

EXPERIMENTAL

Mps: uncorr; ^{1}H NMR: 400 MHz, $CDCl_3$ with TMS as int. standard and chemical shifts were recorded in δ (ppm) units. NH_2-silica (Nomura Chemical) was used for medium pressure liquid chromatography. Silica gel (230-400 mesh) (Merck) were used for CC and silica gel Gf-254 for TLC.

Plant material used in this study was collected from Mt Yuh (Yuh-shan), Taiwan in July, 1976. A voucher specimen is kept in the school of Pharmacy, Kaohsiung Medical College, Taiwan, Republic of China.

Extraction and isolation. The fresh roots of *T. sessile* (5.8 kg) were extracted with 95% EtOH. The EtOH soln was concd under red. pres. to leave a dark brownish viscous residue. The bases in the EtOH extracts were extracted with 3% HOAc. The HOAc soln of the total bases were basified with NH_4OH and extracted with $CHCl_3$. The aq mother liquors were acidified with HCl. The 4° base chloride was obtained by the route reineckate——sulphate——chloride from the HCl soln. The $CHCl_3$ soln of the non-quaternary bases was extracted with 2% H_2SO_4. The H_2SO_4 solns were basified with NH_4OH and extracted with $CHCl_3$, then the $CHCl_3$ extracts was shaken with 2% NaOH to separate the phenolic base and the non-phenolic base.

Spiradine A (**1**). This non-phenolic base (28.3 g) crystallized in contact with Me_2CO as needles. The crystals were purified by neutral alumina CC (MeOH) and recrystallized from MeOH to yield spiradine A (**1**, 310 mg) as colourless needles, mp 271–273° (lit. 281–282°) [34], $[\alpha]_D^{24}$ +51.7° ($CHCl_3$; *c* 0.1), ^{1}H NMR and MS *m/z* 311 [M$^+$] as in ref [34]. Identification was by direct comparison with an authentic sample (mmp, TLC, IR and ^{1}H NMR) [34].

Spirasine III (**5**). The mother liquor of spiradine A (**1**) crystallized in contact with MeOH as needles which recrystallized from MeOH as colourless prisms (400 mg). These prisms were dissolved in $CHCl_3$ (3 ml) and chromatographed over silica gel (50 gm) (column X). Elution with $CHCl_3$–MeOH–NH_4OH (10000:50:1) afforded three (A, B and C) fractions which were collected (50 ml each) and combined according to TLC analysis. The former fraction A (500 ml) of the elution afforded an almost colourless oily base which on treatment with MeOH gave spirasine III (**5**, 155 mg) as colourless prisms, mp 218–220° (lit. 210–212°) [27]; $[\alpha]_D^{24}$ −11.7° (MeOH, *c* 0.1) (lit. −9.0°) [27]; UV λ_{max}^{MeOH} nm (log ε): 310 (1.68); CD (MeOH): $[\theta]_{317}$ +4.797 × 10^3, $[\theta]_{274}$ −1.033 × 10^3; ^{1}H NMR, ^{13}C NMR and MS *m/z* 369 [M]$^+$ as in ref. [27]. Identification was by direct comparison with an authentic sample (mmp, TLC, UV, CD, IR, ^{1}H NMR and ^{13}C NMR) [27].

Spirasine I (**3**). Fraction B (300 ml) of column X gave an oily base which after prep. TLC (silica gel, $CHCl_3$–MeOH–NH_4OH 10000:50:1) was recrystallized from MeOH to give colourless prisms of spirasine I (**3**, 124 mg), mp 250–251° (lit. 244–246°) [28]; CD (MeOH): $[\theta]_{290}$ −0.994 × 10^3; ^{1}H NMR, ^{13}C NMR and MS *m/z* 355 [M]$^+$ as in ref. [28]. Identification was by direct comparison with an authentic sample (mmp, TLC, IR, CD, ^{1}H NMR and ^{13}C NMR) [28].

Spirasine II (**4**). Fraction C (400 ml) of column X afforded an oily base which on treatment with MeOH gave spirasine II (**4**, 146 mg) as colourless prisms, mp 230–231° (lit. 208–209°) [28]; $[\alpha]_D^{24}$ −37.6° (MeOH, *c* 0.05); CD (MeOH): $[\theta]_{287}$ −1.640 × 10^3; ^{1}H NMR, ^{13}C NMR and MS *m/z* 355 [M]$^+$ as in refs [28]. Identical by direct comparison (TLC, IR, ^{1}H NMR and ^{13}C NMR) with an authentic sample [28].

Spiredine (**2**). The mother liquor obtained by separation of spirasine I (**3**), spirasine II (**4**) and spirasine III (**5**) was extracted with 2% HCl. The filtrate of the HCl soln was basified with NH_4OH and extracted with Et_2O. The Et_2O soln was dried (K_2CO_3) and evapd to leave a light orange viscous residue (16.09 g). The residue was placed on a silica gel column (500 g) (column Y) and eluted with $CHCl_3$ gradually enriched with MeOH. The residue (1.22 gm) of the fraction eluting with $CHCl_3$ was separated by MPLC × 5 [NH_2-silica column, 25 × 310 mm (column Z)]. Elution with *n*-C_6H_{14}–$CHCl_3$ (3:2) (Flow rate 0.5 ml/min) afforded three (D, E and F) fractions which were collected (5 ml each) and combined according to TLC analysis. The residue of the fraction D (No. 1–16) which after prep. TLC (silica gel *n*-C_6H_{14}–$CHCl_3$ = 3:2) was recrystallized from MeOH as colourless prisms of spiredine (**2**, 115 mg), mp 160–162° (lit. 163°) [27, 34]; $[\alpha]_D^{24}$ −21° ($CHCl_3$; *c* 0.2); UV λ_{max}^{MeOH} nm (log ε): 305 (1.64); CD (MeOH): $[\theta]_{312}$ +4.307 × 10^3, $[\theta]_{275}$ −2.330 × 10^3; MS *m/z* 353 [M]$^+$, ^{1}H NMR and ^{13}C NMR as in ref. [27]. Identical by direct comparison (mmp, TLC, UV, IR, ^{1}H NMR and ^{13}C NMR) with an authentic sample [27].

Thalicsiline (**8**). The residue of the fraction *E* (no. 17–25) of column Z subjected to prep. TLC (silica gel *n*-C_6H_{14}–$CHCl_3$ = 3:2) and recrystallized from MeOH as colourless prisms of thalicsiline (**8**, 83 mg), mp 183–186°; $[\alpha]_D^{24}$ −11.4° (MeOH; *c* 0.1); IR ν_{max}^{Nujol} cm^{-1}: 3540 (hydroxy), 1720 and 1240 (acetyl), and 1100 (ether); HRMS *m/z* 417.2481 (calc. for $C_{24}H_{35}NO_5$ 417.2511). Anal. calc. for $C_{24}H_{35}NO_5 \cdot 1/2\ H_2O$; C, 67.61; H, 8.51; N, 3.29; found: C, 67.89; H, 8.49; N, 3.29%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.11 and 3.86 (1H, *s*, H-19), 5.32 and 5.67 (1H, *d*, *J* = 2.40 Hz, H-6), 2.05 and 2.06 (3H, *s*, C-6 − OOCMe), 4.82 and 4.58 (1H, *s*, H-20), 1.31, 1.30 (3H, *s*, Me-16), 0.94 and 1.11 (3H, *s*, Me-4) and 3.00–4.10 (5H, *m*, H-19, 21 and 22). All signals in ratio of *ca* 1:3 for each pair. ^{13}C NMR (25.0 MHz, $CDCl_3$): δ 40.54 (*t*, C-1), 22.70 (*t*, C-2), 47.21 (*t*, C-3), 35.16 (*s*, C-4), 52.18 (*d*, C-5), 70.79 (*d*, C-6), 70.91 (*d*, C-7), 36.27 (*s*, C-8), 42.53 (*d*, C-9), 35.28 (*s*, C-10), 29.02 (*t*-C-11), 38.26 (*d*, C-12), 26.68 (*t*, C-13), 23.52 (*t*, C-14), 20.24 (*t*, C-15), 73.83 (*s*, C-16), 30.19 (*q*, C-17), 22.58 (*q*, C-18), 94.60 (*d*, C-19), 85.59 (*d*, C-20), 51.01 (*t*, C-21), 63.30 (*t*, C-22), 169.72 (*s*, C-23), 21.41 (*q*, C-24).

Thalicsessine (**6**). The residue (300 mg) of the fraction eluting with $CHCl_3$–MeOH–Et_2NH (2000:100:1) off column Y, after prep. TLC (silica gel, $CHCl_3$–MeOH–Et_2NH = 20:1:0.05), was recrystallized from MeOH as colourless prisms of thalicsessine (**6**, 125 mg), mp 213–216°; $[\alpha]_D^{25}$ +113° ($CHCl_3$, *c* 0.2); UV λ_{max}^{MeOH} nm (log ε): 308 (1.65); CD (MeOH): $[\theta]_{314}$ +4.305 × 10^3, $[\theta]_{277}$ −2.334 × 10^3; IR ν_{max}^{Nujol} cm^{-1}: 3350 (hydroxy), 1710 and 1630 (carbonyl) and 1620 (exocyclic methylene); Anal. calc. for $C_{22}H_{27}NO_4 \cdot H_2O$: C, 68.19; H, 7.54; N, 3.62; Found: C, 68.33, H, 7.71; N, 3.49%; MS *m/z* (%): 369 [M]$^+$ (23), 351 (14), 339 (100) and 325 (37). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (3H, *s*, Me-4), 2.85 (1H, *t*, *J* = 5.12 Hz, alcoholic H), 3.45 (1H, *ddd*, *J* = 14.16, 5.13, 3.41 Hz, H-21 ax), 3.62 (1H, *ddd*, *J* = 14.16, 8.05, 3.41 Hz, H-21 eq), 3.78 [1H, *m*, H-22 ax, changed to *ddd* (*J* = 11.48, 5.13, 3.41 Hz) on addition of D_2O], 3.88 [1H, *m*, H-22 eq, changed to *ddd* (*J* = 11.48, 8.05, 3.41 Hz) on addition of D_2O], 4.85 (1H, *d*, *J* = 2.40 Hz, H-17 ax) and 5.02 (1H, *d*, *J* = 2.40 Hz, H-17 eq).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ 39.8 (*t*, C-1), 20.6 (*t*, C-2), 34.2 (*t*, C-3), 46.5 (*s*, C-4), 60.0 (*d*, C-5), 207.6 (*s*, C-6 or C-11), 51.5 (*t*, C-7), 43.9 (*s*, C-8), 75.6 (*d*, C-9), 42.9 (*s*, C-10), 208.9 (*s*, C-11 or C-6), 63.7 (*d*, C-12), 33.3 (*t*, C-13), 47.0 (*d*, C-14), 35.1 (*t*, C-15), 141.9 (*s*, C-16), 111.1 (*t*, C-17), 25.5 (*q*, C-18), 177.1 (*s*, C-19), 53.9 (*d*, C-20), 49.7 (*t*, C-21) and 60.9 (*t*, C-22).

Treatment of thalicsessine (**6**) *with* NaOD. A soln of NaOD [from D_2O (0.1 ml) and Na (100 mg) in dioxane (2 ml)] was poured into a soln of thalicsessine (**6**) (6 mg) in dioxane (1 ml) and then refluxed under N_2 at 130–140° for 4 hr. Removal of the solvent under red. pres. gave a brown oil, which was treated with ion exchange resin (IRC_{50} cation) (MeOH) and then subjected to prep. TLC (silica gel, $CHCl_3$–MeOH–Et_2NH = 20:1:0.05). The deuterio base at R_f 0.75 obtained by prep. TLC was purified by neutral alumina CC ($CHCl_3$) to give an oily base (5 mg) of deuterio thalicsessine (**6b**). MS *m/z* 372 $[M]^+$ ($C_{22}H_{24}D_3NO_4$); ^{13}C NMR (25.0 MHz, $CDCl_3$): δ 39.7 (*t*, C-1), 20.6 (*t*, C-2), 34.2 (*t*, C-3), 46.6 (*s*, C-4), 207.8 (*s*, C-6 or C-11), 44.0 (*s*, C-8), 75.5 (*d*, C-9), 42.8 (*s*, C-10), 208.8 (*s*, C-11 or C-6), 63.7 (*d*, C-12), 33.5 (*t*, C-13), 47.1 (*d*, C-14), 35.1 (*t*, C-15), 142.0 (*s*, C-16), 111.2 (*t*, C-17), 25.6 (*q*, C-18), 177.1 (*s*, C-19), 53.9 (*d*, C-20), 49.8 (*t*, C-21) and 60.9 (*t*, C-22).

Reduction and acetylation of deuterio thalicsessine (**6b**). $NaBH_4$ (30 mg) was added slowly to a stirred soln of deuterio thalicsessine (**6b**) (3.0 mg) in THF (1 ml), and the stirring continued for 2 hr at room temp. The mixture was poured into Me_2CO (10 ml) and then the solvent was removed under red. pres.; a brown viscous residue resulted (2.5 mg). Treatment of this residue with Ac_2O (1.0 ml) and pyridine (0.5 ml) gave an acetate (**7**) (2.0 mg), MS *m/z* 458 $[M]^+$ ($C_{26}H_{30}D_3NO_6$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (3H, *s*), 2.01 (6H, *s*), 3.19 (1H, *ddd*, *J* = 13.92, 7.06, 5.86 Hz), 3.85 (1H, *ddd*, *J* = 13.92, 5.61, 5.37 Hz), 4.18 (1H, *s*), 4.26 (2H, *m*), 4.74 (1H, *s*) and 4.93 (1H, *s*).

Reduction and acetylation of thalicsessine (**6**). Thalicsessine (3.5 mg) was treated in the same way as (**6b**) to give an acetate (**7a**) (2.0 mg) with MS *m/z* 455 $[M]^+$ ($C_{26}H_{33}NO_6$), IR ν_{max}^{Nujol} cm^{-1}: 1710 and 1620 (carbonyl) and 1610 (exocyclic methylene) and ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (3H, *s*), 2.03 (6H, *s*), 3.20 (1H, *ddd*, *J* = 13.92, 7.08, 5.86 Hz), 3.86 (1H, *ddd*, *J* = 13.92, 5.61, 5.37 Hz), 4.20 (1H, *br m*), 4.28 (2H, *m*), 4.75 (1H, *s*) and 4.95 (1H, *s*).

Formation of N-*methyldiketon of spiradine A* (**6a**). A soln of spiradine A methiodide (30 mg) in MeOH (5 ml) was poured into a soln of Ag_2O (3 mg) in 50% aq. MeOH (30 ml). The mixture was refluxed for 3 hr and then treated in the usual manner to give a *N*-methyldiketone of spiradine A (**6a**) (20 mg) with MS *m/z* 325 $[M]^+$ ($C_{21}H_{27}NO_2$), IR ν_{max}^{Nujol} cm^{-1}: 2800, 1710, 1690 and 1650 and ^{13}C NMR (25.0 MHz, $CDCl_3$): δ 40.6 (*t*, C-1), 18.7 (*t*, C-2), 30.2 (*t*, C-3), 47.0 (*s*, C-4), 60.3 (*d*, C-5), 204.0 (*s*, C-6 or C-11), 50.7 (*t*, C-7), 43.0 (*s*, C-8), 38.1 (*s*, C-10), 211.1 (*s*, C-11 or C-6), 65.3 (*d*, C-12), 33.6 (*t*, C-13), 45.6 (*d*, C-14), 35.1 (*t*, C-15), 143.5 (*s*, C-16), 110.2 (*t*, C-17), 30.7 (*q*, C-18), 60.7 (*t*, C-19), 53.4 (*d*, C-20) and 43.1 (*q*, N-Me) was afforded.

(+)-*Thalifarazine* (**9**). Continuous elution with $CHCl_3$–MeOH–Et_2NH (2000:200:1) of column Y afforded a yellowish white amorphous solid (75 mg), $[\alpha]_D^{24}$ + 50° (MeOH; *c* 0.1). It was characterized by spectral analyses and comparison with an authentic sample (UV, IR, ^{1}H NMR and MS) isolated from the aerial part of the plant [1].

Berberine (**11**). The 4° base chlorides (27.7 gm) were dissolved in H_2O (380 ml) and satd with KI. The ppts of the iodides were filtered, dissolved in MeOH and concentrated under reduced pressure to yield crystalline berberine iodide as yellowish needles (3.10 gm), mp 266–267° (MeOH) which was identified (mmp, TLC, IR, ^{1}H NMR and MS) by comparison with an authentic sample available in our laboratory.

Magnoflorine (**10**). The residue of the mother liquor obtained by separation of berberine iodide crystallized in contact with Me_2CO as prisms which recrystallized from MeOH to yield magnoflorine iodide (3.40 mg) as colourless prisms, mp 250–252°; $[\alpha]_D^{24}$ + 158.3° (EtOH; *c* 0.4), identical (mmp, TLC, IR, ^{1}H NMR and MS) to an authentic sample available in our laboratory.

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