# Thienopyrrolizines: New Condensed Triheterocyclic Systems



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Cyclization of 3-(1-pyrrolyl)thiophene-2-carboxamide derivatives of methyl 3-(1-pyrrolyl)-2-thiophenecarboxylate afforded imminium salts and resulted in the formation of thieno[2,3-*b*]pyrrolizine derivatives.

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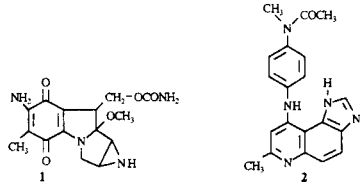
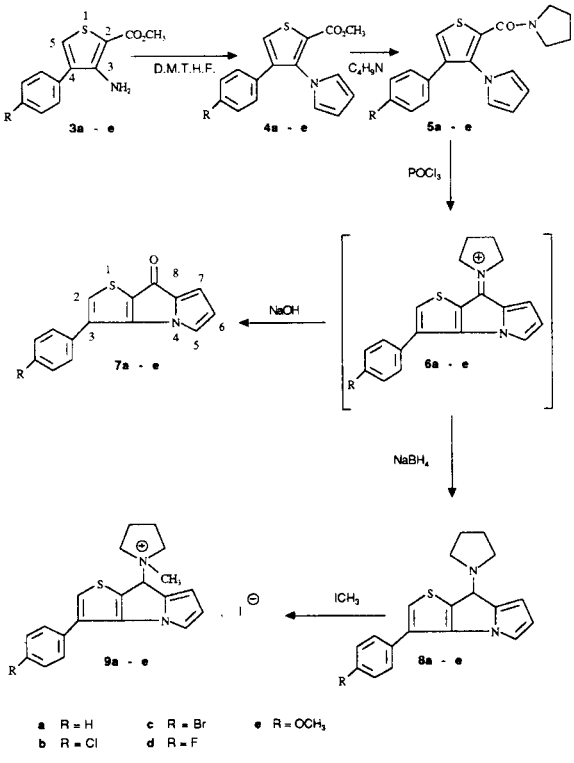
In previous work we reported the synthesis of new aminopyrroloindoles and aminomethylenedioxypyrroloindoles [1,2]. We wish to describe now the first application of this method to the preparation of new 8*H*-thieno[2,3-*b*]pyrrolizines and methyl iodides.

Scheme 1



Scheme 2




The presence of the pyrrolizine system makes thieno-[2,3-*b*]pyrrolizine derivatives interesting as potential antineoplasic agents. In fact, several natural substances belonging to the pyrrolizine class [3] as well as other related polycyclic compounds of pharmaceutical value, mitomycin C **1** and acodazole **2**, were found display useful anticancer activities.

The reaction of methyl 3-amino-4-substituted-2-thiophenecarboxylates **3** [4,5] with 2,5-dimethoxytetrahydrofuran in glacial acetic acid according to the Clauson-Kaas method [6] gave methyl 3-(1-pyrrolyl)-2-thiophenecarboxylates **4**. Compounds **4** in boiling pyrrolidine afford the pyrrolidinecarboxamides **5**. Cyclization of the latter compounds in boiling phosphorus oxychloride affords the imminium salts **6** which were hydrolyzed to the ketones **7** by the action of the aqueous sodium hydroxide. The reduction of imminium salts **6** with a large excess of sodium borohydride gives the 8-pyrrolidino-8*H*-thieno[2,3-*b*]pyrrolizines **8** which were converted into the quaternary salts **9** by treatment in acetone with methyl iodide in excess. The studies concerning biological investigation are in progress.

## EXPERIMENTAL

Melting points were determined on Kofler type WME apparatus and are uncorrected. The ir spectra were recorded on Philips P.U. spectrometer. The nmr spectra were recorded on a Varian E.M. 390 spectrometer at 90 MHz in hexadeuteriodimethyl sulfoxide with tetramethylsilane as an internal reference. Chemical shifts are expressed as $\delta$ (ppm) relative to TMS.

Methyl 3-(1-Pyrrolyl)-4-phenyl-2-thiophenecarboxylate (**4a**).

A solution of **3a** (20 g, 0.0858 mole) and 2,5-dimethoxytetrahydrofuran (11.32 g, 0.0858 mole) in glacial acetic acid (200 ml) was heated at reflux for 30 minutes, then the reaction mixture was cooled and evaporated *in vacuo*. The residue was diluted with water (200 ml) and extracted with ether (150 ml). The organic layer was washed with sodium bicarbonate, dried (sodium sulfate) and evaporated to yield a solid **4a** which was crystallized from ether-hexane (60/40) (18.5 g, 76%), mp 138°; ir (potassium bromide): $\nu$ CO 1720 $cm^{-1}$; $^1H$ nmr: $\delta$ 8.00 (s, 1H, $H_5$), 7.15-6.83 (2 m,

5H, $C_6H_4$), 6.56 (t, 2H, $H_{2',5'}$), 6.03 (t, 2H, $H_{3',4'}$), 3.63 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{16}H_{13}NO_2S$: C, 67.82; H, 4.62; N, 9.56; S, 11.31. Found: C, 67.80; H, 4.63; N, 9.60; S, 11.50.

Methyl 3-(1-Pyrrolyl)-4-*para*-chlorophenyl-2-thiophenecarboxylate (**4b**).

This compound was prepared as described for **4a**, yield 76%, yellow solid (ether-hexane), mp 178°; ir (potassium bromide): $\nu$ CO 1720 $cm^{-1}$; $^1H$ nmr: $\delta$ 8.06 (s, 1H, $H_5$), 7.25-6.85 (2 d, 4H, $C_6H_4$), 6.60 (t, 2H, $H_{2',5'}$), 6.06 (t, 2H, $H_{3',4'}$), 3.68 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{16}H_{12}ClNO_2S$: C, 60.46; H, 3.80; N, 4.40; S, 10.09. Found: C, 60.50; H, 3.76; N, 4.36; S, 10.10.

Methyl 3-(1-Pyrrolyl)-4-*para*-bromophenyl-2-thiophenecarboxylate (**4c**).

This compound was prepared as described for **4a**, yield 72%, brown solid (ether-hexane), mp 173°; ir (potassium bromide): $\nu$ CO 1720 $cm^{-1}$; $^1H$ nmr: $\delta$ 8.06 (s, 1H, $H_5$), 7.36-6.80 (2 d, 4H, $C_6H_4$), 6.55 (t, 2H, $H_{2',5'}$), 6.00 (t, 2H, $H_{3',4'}$), 3.63 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{16}H_{12}BrNO_2S$: C, 53.04; H, 3.34; N, 3.86; S, 8.85. Found: C, 53.12; H, 3.36; N, 3.90; S, 8.79.

Methyl 3-(1-Pyrrolyl)-4-*para*-fluorophenyl-2-thiophenecarboxylate (**4d**).

This compound was prepared as described for **4a**, yield 70%, yellow solid (ether-hexane), mp 140°; ir (potassium bromide): $\nu$ CO 1720 $cm^{-1}$; $^1H$ nmr: $\delta$ 8.00 (s, 1H, $H_5$), 6.93 (m, 4H, $C_6H_4$), 6.60 (t, 2H, $H_{2',5'}$), 6.06 (t, 2H, $H_{3',4'}$), 3.66 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{16}H_{12}FNO_2S$: C, 63.77; H, 4.01; N, 4.64; S, 10.64. Found: C, 63.82; H, 4.00; N, 4.72; S, 10.72.

Methyl 3-(1-Pyrrolyl)-4-*para*-methoxyphenyl-2-thiophenecarboxylate (**4e**).

This compound was prepared as described for **4a**, yield 70%, pale yellow solid (ether-hexane), mp 116°; ir (potassium bromide): $\nu$ CO 1690 $cm^{-1}$; $^1H$ nmr: $\delta$ 7.90 (s, 1H, $H_5$), 6.80 (m, 4H, $C_6H_4$), 6.60 (t, 2H, $H_{2',5'}$), 6.06 (t, 2H, $H_{3',4'}$), 3.70 ppm (s, 6H, $CO_2CH_3$, $OCH_3$).

*Anal.* Calcd. for $C_{17}H_{15}NO_3S$: C, 65.15; H, 4.82; N, 4.46; S, 10.23. Found: C, 65.22; H, 4.76; N, 4.50; S, 10.31.

4-Phenyl-3-(1-pyrrolyl)-2-thiophene-*N*-pyrrolidinocarboxamide (**5a**).

A stirred solution of **4a** 4 g (10 g, 0.035 mole) in pyrrolidine (40 ml) was refluxed for 8 hours. The mixture was stirred for 1 hour at room temperature, then was diluted with water (400 ml) and extracted with ether (2 x 150 ml). The organic extracts were collected, dried (sodium sulfate) and evaporated to afford 9.0 g (79%) of **5a**, mp 122° (ether); ir (potassium bromide): $\nu$ CO 1615 $cm^{-1}$; $^1H$ nmr: $\delta$ 7.80 (s, 1H, $H_5$), 7.26-7.03 (2 m, 5H, $C_6H_5$), 6.56 (t, 2H, $H_{2',5'}$), 6.13 (t, 2H, $H_{3',4'}$), 3.30-1.66 ppm (2 m, 8H, pyrrolidine).

*Anal.* Calcd. for $C_{19}H_{18}N_2OS$: C, 70.77; H, 5.62; N, 8.69; S, 9.94. Found: C, 70.92; H, 5.63; N, 8.70; S, 10.00.

4-*para*-Chlorophenyl-3-(1-pyrrolyl)-2-thiophene-*N*-pyrrolidinocarboxamide (**5b**).

This compound was prepared as described for **5a**, yield 60%, yellow solid (ether), mp 200°; ir (potassium bromide): $\nu$ CO 1620 $cm^{-1}$; $^1H$ nmr: $\delta$ 7.80 (s, 1H, $H_5$), 7.23-6.86 (2 d, 4H, $C_6H_4$), 6.46 (t, 2H, $H_{2',5'}$), 6.06 (t, 2H, $H_{3',4'}$), 3.26-1.56 ppm (2 m, 8H, pyrrolidine).

*Anal.* Calcd. for $C_{19}H_{17}ClN_2OS$: C, 63.94; H, 4.80; N, 7.85; S, 8.98. Found: C, 64.00; H, 4.82; N, 7.90; S, 9.00.

4-*para*-Bromophenyl-3-(1-pyrrolyl)-2-thiophene-*N*-pyrrolidinocarboxamide (**5c**).

This compound was prepared as described for **5a**, yield 65%, yellow solid (ether), mp 209°; ir (potassium bromide): $\nu$ CO 1610 $cm^{-1}$; $^1H$ nmr: $\delta$ 7.80 (s, 1H, $H_5$), 7.40-6.83 (2 d, 4H, $C_6H_4$), 6.53 (t, 2H, $H_{2',5'}$), 6.10 (t, 2H, $H_{3',4'}$), 3.30-1.66 ppm (2 m, 8H, pyrrolidine).

*Anal.* Calcd. for $C_{19}H_{17}BrN_2OS$: C, 56.86; H, 4.27; N, 6.98; S, 7.98. Found: C, 56.90; H, 4.30; N, 7.00; S, 7.92.

4-*para*-Fluorophenyl-3-(1-pyrrolyl)-2-thiophene-*N*-pyrrolidinocarboxamide (**5d**).

This compound was prepared as described for **5a**, yield 72%, yellow solid (ether), mp 122°; ir (potassium bromide): $\nu$ CO 1620 $cm^{-1}$; $^1H$ nmr: $\delta$ 7.80 (s, 1H, $H_5$), 7.03 (m, 4H, $C_6H_4$), 6.40 (t, 2H, $H_{2',5'}$), 6.10 (t, 2H, $H_{3',4'}$), 3.76-1.61 ppm (2 m, 8H, pyrrolidine).

*Anal.* Calcd. for $C_{19}H_{17}FN_2OS$: C, 67.03; H, 5.03; N, 8.23; S, 9.41. Found: C, 67.00; H, 5.09; N, 8.30; S, 9.52.

4-*para*-Methoxyphenyl-3-(1-pyrrolyl)-2-thiophene-*N*-pyrrolidinocarboxamide (**5e**).

This compound was prepared as described for **5a**, yield 59%, yellow solid (ether), mp 165°; ir (potassium bromide): $\nu$ CO 1630 $cm^{-1}$; $^1H$ nmr: $\delta$ 7.63 (s, 1H, $H_5$), 6.83 (m, 4H, $C_6H_4$), 6.50 (t, 2H, $H_{2',5'}$), 6.06 (t, 2H, $H_{3',4'}$), 3.30-1.66 ppm (2 m, 8H, pyrrolidine).

*Anal.* Calcd. for $C_{20}H_{20}N_2O_2S$: C, 68.15; H, 5.72; N, 7.95; S, 9.09. Found: C, 68.22; H, 5.80; N, 7.96; S, 9.10.

3-Phenyl-8*H*-thieno[2,3-*b*]pyrrolizin-8-one (**7a**).

A stirred solution of **5a** (4 g, 0.0124 mole) in phosphorus oxychloride (30 ml) was refluxed for 1 hour. After cooling the mixture was diluted with water (200 ml), made basic with 50% sodium hydroxide solution and extracted with ethyl acetate (2 x 100 ml). The organic layer, washed with brine (2 x 100 ml), was dried (sodium sulfate) and evaporated to give **7a** as a solid, which was crystallized from diethyl ether (2.20 g, 71%), mp 78°; ir (potassium bromide): $\nu$ CO 1680 $cm^{-1}$; $^1H$ nmr: $\delta$ 8.03 (s, 1H, $H_2$), 7.50 (m, 5H, $C_6H_5$), 7.60 (dd, 1H, $H_7$), 6.66 (dd, 1H, $H_5$), 6.03 ppm (dd, 1H, $H_6$).

*Anal.* Calcd. for $C_{15}H_9NOS$: C, 71.69; H, 3.61; N, 5.57; S, 12.75. Found: C, 71.72; H, 3.70; N, 5.49; S, 12.80.

1-*para*-Chlorophenyl-8*H*-thieno[2,3-*b*]pyrrolizin-8-one (**7b**).

This compound was prepared as described for **7a**, yield 60%, (acetonitrile), mp 186°; ir (potassium bromide): $\nu$ CO 1675 $cm^{-1}$; $^1H$ nmr: $\delta$ 8.13 (s, 1H, $H_2$), 7.60 (m, 4H, $C_6H_4$), 6.86 (dd, 1H, $H_7$), 6.73 (dd, 1H, $H_5$), 6.10 ppm (dd, 1H, $H_6$).

*Anal.* Calcd. for $C_{15}H_8ClNOS$: C, 63.04; H, 2.82; N, 4.90; S, 11.22. Found: C, 63.07; H, 2.90; N, 4.95; S, 11.20.

3-*para*-Bromophenyl-8*H*-thieno[2,3-*b*]pyrrolizin-8-one (**7c**).

This compound was prepared as described for **7a**, yield 71%, (acetonitrile), mp 164°; ir (potassium bromide): $\nu$ CO 1670 $cm^{-1}$; $^1H$ nmr: $\delta$ 8.06 (s, 1H, $H_2$), 7.73, 7.53 (2 d, 4H, $C_6H_4$), 6.86 (dd, 1H, $H_7$), 6.70 (dd, 1H, $H_5$), 6.03 ppm (dd, 1H, $H_6$).

*Anal.* Calcd. for $C_{15}H_8BrNOS$: C, 54.56; H, 2.44; N, 4.24; S, 9.71. Found: C, 54.60; H, 2.45; N, 4.30; S, 9.82.

3-*para*-Fluorophenyl-8*H*-thieno[2,3-*b*]pyrrolizin-8-one (**7d**).

This compound was prepared as described for **7a**, yield 8%,

(acetonitrile), mp 145°; ir (potassium bromide): ν CO 1680 $cm^{-1}$; $^1H$ nmr: δ 8.01 (s, 1H, $H_2$), 7.60-7.30 (m, 4H, $C_6H_4$), 6.80 (dd, 1H, $H_7$), 6.71 (dd, 1H, $H_5$), 6.08 ppm (dd, 1H, $H_6$).

*Anal.* Calcd. for $C_{15}H_8FNOS$: C, 66.90; H, 2.99; N, 5.20; S, 11.90. Found: C, 67.00; H, 3.02; N, 5.24; S, 11.96.

3-*para*-Methoxyphenyl-8*H*-thieno[2,3-*b*]pyrrolizin-8-one (**7e**).

This compound was prepared as described for **7a**, yield 72%, (acetonitrile), mp 182°; ir (potassium bromide): ν CO 1670 $cm^{-1}$; $^1H$ nmr: δ 7.93 (s, 1H, $H_2$), 7.46-7.00 (2 d, 4H, $C_6H_4$), 7.11 (dd, 1H, $H_7$), 6.66 (dd, 1H, $H_5$), 6.03 (dd, 1H, $H_6$), 3.76 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{16}H_{11}NO_2S$: C, 68.30; H, 3.94; N, 4.97; S, 11.39. Found: C, 68.42; H, 3.96; N, 4.92; S, 11.41.

3-Phenyl-8-pyrrolidino-8*H*-thieno[2,3-*b*]pyrrolizine (**8a**).

A stirred solution of **5a** (3 g, 0.0093 mole) in phosphorus oxychloride (20 ml) was refluxed for 25 minutes. The imminium salt precipitate which formed was filtered and washed with petroleum ether. The imminium salt was dissolved in methanol (150 ml), was added to a suspension of sodium borohydride in excess and refluxed for 2 hours. The solution was evaporated to dryness, taken-up with water and extracted with ethyl acetate. After workup, 1.70 g (60%) of **8a** as a viscous colorless oil was obtained; ir (potassium bromide): ν 2940, 2780, 1590, 1250, 1030, 840 and 720 $cm^{-1}$; $^1H$ nmr: δ 7.46 (m, 6H, $C_6H_5$, $H_2$), 6.63 (dd, 1H, $H_5$), 6.06 (m, 2H, $H_7$, $H_6$), 5.06 (s, 1H, $H_8$), 2.53-1.66 ppm (2 m, 8H, pyrrolidine).

*Anal.* Calcd. for $C_{19}H_{18}N_2S$: C, 74.47; H, 5.92; N, 9.14; S, 10.46. Found: C, 74.50; H, 5.87; N, 9.15; S, 10.52.

3-*para*-Chlorophenyl-8-pyrrolidino-8*H*-thieno[2,3-*b*]pyrrolizine (**8b**).

This compound was prepared ad described for **8a**, yield 58%, oil; ir (potassium bromide): ν 2940, 2860, 1490, 1080, 820 and 700 $cm^{-1}$; $^1H$ nmr: δ 7.55 (m, 5H, $C_6H_4$, $H_2$), 6.60 (dd, 1H, $H_5$), 6.03 (m, 2H, $H_7$, $H_6$), 5.00 (s, 1H, $H_8$), 2.43-1.56 ppm (2 m, 8H, pyrrolidine).

*Anal.* Calcd. for $C_{19}H_{17}ClN_2S$: C, 66.97; H, 2.93; N, 8.22; S, 9.40. Found: C, 67.00; H, 3.00; N, 8.31; S, 9.46.

3-*para*-Bromophenyl-8-pyrrolidino-8*H*-thieno[2,3-*b*]pyrrolizine (**8c**).

This compound was prepared as described for **8a**, yield 65°, (ether), mp 124°; ir (potassium bromide): ν 2980, 2840, 1510, 1130, 1020, 830 and 710 $cm^{-1}$; $^1H$ nmr: δ 7.60 (m, 5H, $C_6H_4$, $H_2$), 6.63 (dd, 1H, $H_5$), 6.06 (m, 2H, $H_7$, $H_6$), 5.00 (s, 1H, $H_8$), 2.46-1.60 ppm (2 m, 8H, pyrrolidine).

*Anal.* Calcd. for $C_{19}H_{17}BrN_2S$: C, 59.22; H, 4.44; N, 7.27; S, 8.32. Found: C, 59.33; H, 4.45; N, 7.30; S, 8.40.

3-*para*-Fluorophenyl-8-pyrrolidino-8*H*-thieno[3,2-*b*]pyrrolizine (**8d**).

This compound was prepared as described for **8a**, yield 71%, oil; ir (potassium bromide): ν 3940, 2800, 1600, 1220, 1030, 830 and 700 $cm^{-1}$; $^1H$ nmr: δ 7.56-7.30 (2 m, 5H, $C_6H_4$, $H_2$), 6.66 (dd, 1H, $H_5$), 6.13 (m, 2H, $H_7$, $H_6$), 5.13 (s, 1H, $H_8$), 2.60-1.76 (2 m, 8H, pyrrolidine).

*Anal.* Calcd. for $C_{19}H_{17}FN_2S$: C, 70.34; H, 5.28; N, 8.63; S, 9.88. Found: C, 70.36; H, 5.30; N, 8.72; S, 9.90.

3-*para*-Methoxyphenyl-8-pyrrolidino-8*H*-thieno[3,2-*b*]pyrrolizine (**8e**).

This compound was prepared as described for **8a**, yield 58%, oil; ir (potassium bromide): ν 2940, 2800, 1600, 1240, 1030, 820 and 700 $cm^{-1}$; $^1H$ nmr: δ 7.40 (m, 3H, $H_{3'}$, $H_{5'}$, $H_2$), 6.96 (d, 2H, $H_{2'}$, $H_{6'}$), 6.63 (dd, 1H, $H_5$), 6.03 (m, 2H, $H_7$, $H_6$), 5.00 (s, 1H, $H_8$), 3.73 (s, 3H, $OCH_3$), 2.46-1.60 ppm (2 m, 8H, pyrrolidine).

*Anal.* Calcd. for $C_{20}H_{20}N_2OS$: C, 71.39; H, 5.99; N, 8.32; S, 9.53. Found: C, 71.41; H, 6.00; N, 8.40; S, 9.62.

3-Phenyl-8-pyrrolidino-8*H*-thieno[2,3-*b*]pyrrolizine Methiodide (**9a**).

To a solution of compound **8a** (1 g, 0.0032 mole) in acetone (15 ml) was added methyl iodide (2 ml) in excess. The mixture was stirred at room temperature for 10 hours. The precipitate product was filtered and crystallized from ethanol to give **9a**, yield (1.20 g, 82%), mp 152°; ir (potassium bromide): ν 1500, 1220, 1040 and 700 $cm^{-1}$; $^1H$ nmr: δ 7.83 (s, 1H, $H_2$), 7.43 (m, 5H, $C_6H_5$), 6.76 (dd, 1H, $H_5$), 6.63 (dd, 1H, $H_7$), 6.16 (dd, 1H, $H_6$), 5.93 (s, 1H, $H_8$), 3.70-2.13 (2 m, 8H, pyrrolidine), 2.70 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{20}H_{21}IN_2S$: C, 53.57; H, 4.72; N, 6.24; S, 7.15. Found: C, 53.40; H, 4.76; N, 6.32; S, 7.20.

3-*para*-Chlorophenyl-8-pyrrolidino-8*H*-thieno[2,3-*b*]pyrrolizine Methiodide (**9b**).

This compound was prepared as described for **9a**, yield 63%, (acetonitrile), mp 159°; ir (potassium bromide): ν 1590, 1090, 810 and 715 $cm^{-1}$; $^1H$ nmr: δ 7.86 (s, 1H, $H_2$), 7.50 (m, 4H, $C_6H_4$), 6.83 (dd, 1H, $H_5$), 6.66 (dd, 1H, $H_7$), 6.20 (dd, 1H, $H_6$), 6.00 (s, 1H, $H_8$), 3.73, 2.23 (2 m, 8H, pyrrolidine), 2.76 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{20}H_{20}ClIN_2S$: C, 49.75; H, 4.17; N, 5.80; S, 6.64. Found: C, 49.82; H, 4.20; N, 5.85; S, 6.72.

3-*para*-Bromophenyl-8-pyrrolidino-8*H*-thieno[2,3-*b*]pyrrolizine Methiodide (**9c**).

This compound was prepared as described for **9a**, yield 70% (acetonitrile), mp 167°; ir (potassium bromide): ν 1470, 1380, 1010, 830 and 710 $cm^{-1}$; $^1H$ nmr: δ 7.90 (s, 1H, $H_2$); 7.53 (2 d, 4H, $C_6H_4$), 6.83 (dd, 1H, $H_5$), 6.63 (dd, 1H, $H_7$), 6.16 (dd, 1H, $H_6$), 6.00 (s, 1H, $H_8$), 3.73-2.16 (2 m, 8H, pyrrolidine), 2.76 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{20}H_{20}BrIN_2S$: 45.55; H, 3.82; N, 5.31; S, 6.08. Found: C, 45.65; H, 3.80; N, 5.36; S, 6.12.

3-*para*-Fluorophenyl-8-pyrrolidino-8*H*-thieno[3,2-*b*]pyrrolizine Methiodide (**9d**).

This compound was prepared as described for **9a**, yield 72% (ethanol), mp 136°; ir (potassium bromide): ν 1510, 1220, 1040, 830 and 720 $cm^{-1}$; $^1H$ nmr: δ 7.86 (s, 1H, $H_2$), 7.56 (q, 2H, $H_{3'}$, $H_{5'}$), 7.03 (t, 2H, $H_{2'}$, $H_{6'}$), 6.80 (dd, 1H, $H_5$), 6.63 (dd, 1H, $H_7$), 6.20 (dd, 1H, $H_6$), 6.03 (s, 1H, $H_8$), 3.76-2.16 (2 m, 8H, pyrrolidine), 2.76 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{20}H_{20}FIN_2S$: C, 51.50; H, 4.32; N, 6.00; S, 6.87. Found: C, 51.55; H, 4.40; N, 6.10; S, 6.90.

3-*para*-Methoxyphenyl-8-pyrrolidino-8*H*-thieno[2,3-*b*]pyrrolizine Methiodide (**9e**).

This compound was prepared as described for **9a**, yield 82%, (acetonitrile), mp 173°; ir (potassium bromide): ν $cm^{-1}$ 1520, 1250, 1040, 840 and 730 $cm^{-1}$; $^1H$ nmr: δ 7.76 (s, 1H, $H_2$), 7.43 7.00 (2 d, 4H, $C_6H_4$), 6.80 (dd, 1H, $H_5$), 6.60 (dd, 1H, $H_7$), 6.16 (dd, 1H, $H_6$), 5.93 (s, 1H, $H_8$), 3.66, 2.10 (2 m, 8H, pyrrolidine), 2.66 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{21}H_{23}IN_2OS$: C, 52.73; H, 4.84; N, 5.85; S, 6.70. Found: C, 52.30; H, 4.90; N, 5.85; S, 6.72.

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