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Syntheses of 13a-Substituted Dibenzo[*a*,*f*]quinolizines

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The reaction of a series of 1-halogenophenethyl-3,4-dihydroisoquinolines (**6**), (**10**), (**14**) and (**20**) with sodium methylsulfinylmethanide was investigated to yield 5,6,12,13,13a-pentahydro-13a-(methylsulfinyl)methyldibenzo[*a*,*f*]quinolizines (**7**), (**12**), (**18**) and (**23**) which were converted to the corresponding 13a-(methylthio)methyl derivatives (**8**), (**13**), (**17**) and (**24**), respectively. Desulfurization of **8** and **24** afforded the 13a-methyl derivatives (**9**) and (**25**), respectively.

The benzyne reaction of 1-halogenobenzyl-1,2,3,4-tetrahydroisoquinolines and 1-halogenophenethyl-1,2,3,4-tetrahydroisoquinoline (**1**) has been widely used for the syntheses of the tetrahydrodibenzo[*b*,*g*]indolizines[2,3] and the pentahydrodibenzo[*a*,*f*]quinolizine (**2**),[4] respectively, though, few work on the benzyne reaction of 3,4-dihydroisoquinolines have been investigated. Kametani reported the benzyne reaction of 1-(2-bromo-4,5-dimethoxybenzyl)-3,4-dihydro-6,7-dimethoxyisoquinoline (**3**) using sodium methylsulfinylmethanide as a base in dimethyl sulfoxide to yield the dihydrodibenzo[*b*,*g*]indolizine (**4**).[5] We examined the similar reaction of a series of 1-halogenophenethyl-3,4-dihydroisoquinolines. These results were described in this paper.

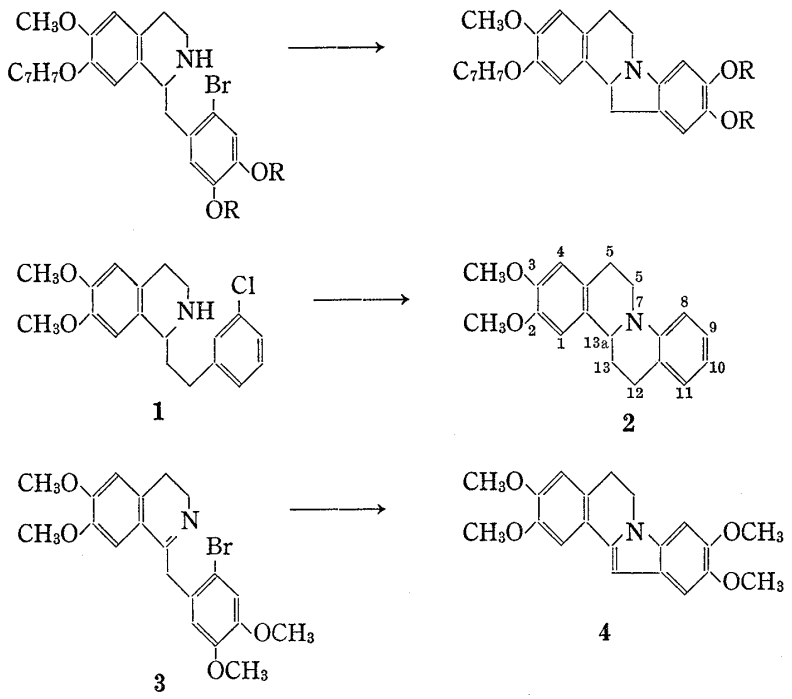
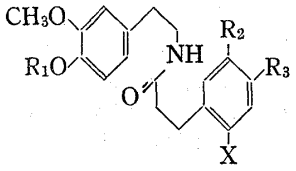


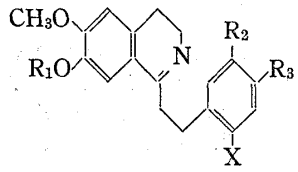
Chart 1

1) Location: *3-20-1, Kitashinjuku, Shinjuku-ku, Tokyo.*
2) T. Kametani and Ogasawara, *J. Chem. Soc.* (*C*), **1967**, 2287.
3) T. Kametani, A. Ujiie, K. Takahashi, T. Nakano, T. Suzuki and K. Fukumoto, *Chem. Pharm. Bull.* (Tokyo), **21**, 766 (1973) and references were cited therein.
4) T. Kametani, T. Terui and K. Fukumoto, *Yakugaku Zasshi*, **88**, 1388 (1968).
5) T. Kametani, S. Shibuya and S. Kano, *J. Chem. Soc.* (*C*), **1973**, 1212.

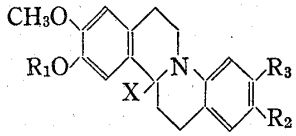
First, 1-(2-bromo-4,5-dimethoxyphenethyl)-3,4-dihydro-6,7-dimethoxyisoquinoline (**6**), prepared by cyclization of the amide (**5**), was treated with sodium methylsulfinylmethanide in dimethyl sulfoxide. The crude product, obtained by the usual work-up, was chromatographed on silica gel to give the 13a-(methylsulfinyl)methyldibenzo[*a*,*f*]quinolizine (**7**). The molecular formula, $C_{23}H_{29}O_5NS$, was confirmed by microanalysis and mass spectrum (M^+, *m/e* 431). Its nuclear magnetic resonance (NMR) ($CDCl_3$) spectrum showed that the product (**7**) would be a mixture of diastereoisomers and separation of each isomer was unsuccessful. The structural proof of **7** was based upon the following transformation. Reductive deoxygenation of **7** with amalgamated zinc in a mixture of 50% acetic acid and conc. hydrochloric acid afforded the 13a-(methylthio)methyldibenzo[*a*,*f*]quinolizine (**8**). The NMR ($CDCl_3$) spectrum showed a singlet due to CH_3S at 1.97 ppm. Microanalysis and mass spectrum (M^+, *m/e* 385) were also agreeable with the structure (**8**). Desulfurization of **8** with Raney Ni catalyst gave the 13a-methyldibenzo[*a*,*f*]quinolizine (**9**). The NMR ($CDCl_3$) spectrum of **9** showed a singlet at 1.63 ppm which was characteristic of 13a-CH_3 signal. Therefore the product obtained from **6** through the reaction with sodium methylfinylsulmethanide was assigned to be **7**.



5: $R_1=CH_3$, $R_2=R_3=OCH_3$, X=Br
15: $R_1=C_7H_7$, $R_2=R_3=-OCH_2O-$, X=Br
22: $R_1=C_7H_7$, $R_2=Br$, $R_3=OCH_3$, X=H



6: $R_1=CH_3$, $R_2=R_3=OCH_3$, X=Br
10: $R_1=H$, $R_2=R_3=OCH_3$, X=Br
11: $R_1=C_7H_7$, $R_2=R_3=OCH_3$, X=Br
14: $R_1=H$, $R_2=R_3=-OCH_2O-$, X=Br
16: $R_1=C_7H_7$, $R_2=R_3=-OCH_2O-$, X=Br
20: $R_1=X=H$, $R_2=Br$, $R_3=OCH_3$
21: $R_1=C_7H_7$, $R_2=Br$, $R_3=OCH_3$, X=H



7: $R_1=CH_3$, $R_2=R_3=OCH_3$, $X=CH_2SOCH_3$
8: $R_1=CH_3$, $R_2=R_3=OCH_3$, $X=CH_2SCH_3$
9: $R_1=X=CH_3$, $R_2=R_3=OCH_3$
12: $R_1=H$, $R_2=R_3=OCH_3$, $X=CH_2SOCH_3$
13: $R_1=H$, $R_2=R_3=OCH_3$, $X=CH_2SCH_3$
17: $R_1=H$, $R_2=R_3=-OCH_2O-$, $X=CH_2SOCH_3$
18: $R_1=H$, $R_2=R_3=-OCH_2O-$, $X=CH_2SCH_3$
23: $R_1=R_2=H$, $R_3=OCH_3$, $X=CH_2SOCH_3$
24: $R_1=R_2=H$, $R_3=OCH_3$, $X=CH_2SCH_3$
25: $R_1=R_2=H$, $R_3=OCH_3$, $X=CH_3$

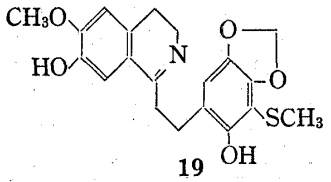


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Chart 2

Secondly, 1-(2-bromo-4,5-dimethoxyphenethyl)-3,4-dihydro-7-hydroxy-6-methoxyisoquinoline (**10**), obtained by hydrolysis of the 3,4-dihydroisoquinoline (**11**),[6] was treated with sodium methylsulfinylmethanide as in formation of **7** to yield the 13a-(methylsulfinyl)methyldibenzo[*a*,*f*]quinolizine (**12**). Reductive deoxygenation of **12** afforded the 13a-(methylthio)-methyldibenzo[*a*,*f*]quinolizine (**13**). The benzyne reaction of 1-(2-bromo-4,5-methylenedioxyphenethyl)-7-hydroxy-6-methoxyisoquinoline (**14**) also examined to give the similar results. The chromatographic separation of the crude product, obtained through the usual work-up, gave two products. The first one was assigned to be a diastereoisomeric mixture of 13a-(methylsulfinyl)methyldibenzo[*a*,*f*]quinolizine (**17**), which was converted to the 13a-(methyl-

6) T. Kametani, Y. Satoh, S. Shibuya, M. Koizumi and K. Fukumoto, *J. Org. Chem.* **36**, 3733 (1971).

thio)methyl derivative (**18**) by reductive deoxygenation with amalgamated zinc. The NMR ($CDCl_3$) spectrum of **18** was similar to those of **8** and **13**. The molecular formula of the second product (**19**), $C_{20}H_{21}O_5NS$, was established by microanalysis and mass spectrum (M^+, *m/e* 387). Its NMR ($CDCl_3$) spectrum showed a singlet due to CH_3S at 2.45 ppm and three aromatic protons resonated at 6.50, 6.60 and 7.07 ppm as singlets, respectively.

Finally, the benzyne reaction of 1-(3-bromo-4-methoxyphenethyl)-3,4-dihydro-7-hydroxy-6-methoxyisoquinoline (**20**) was investigated in order to examine whether any difference was observed between the position isomers according to the location of the bromine atom. The isoquinoline (**20**) was prepared by debenzylation of the 3,4-dihydroisoquinoline (**21**) which was obtained from the amide (**22**). The isoquinoline (**20**) also yielded the similar product (**23**) in moderate yields. Reductive deoxygenation of **23** gave the 13a-(methylthio)methyldibenzo[*a,f*]quinolizine (**24**). Desulfurization of **24** gave the 13-methyldibenzo[*a,f*]quinolizine (**25**).

Thus, as mentioned as above, the benzyne reaction of 1-halogenophenethyl-3,4-dihydroisoquinoline with sodium methylsulfinylmethanide was found to be an excellent method to yield 13a-substituted dibenzo[*a,f*]quinolizine.

Experimental[7]

N-(3,4-Dimethoxyphenethyl)-2-(2-bromo-4,5-dimethoxyphenyl)propionamide (**5**)——A mixture of 5.4 g of 3,4-dimethoxyphenethylamine and 8.7 g of 2-bromo-4,5-dimethoxyphenylpropionic acid was heated at 180° for 1.5 hr. After cooling, the mixture was recrystallized from benzene to give 9.8 g of **5** as colorless needles, mp 123—125°. *Anal.* Calcd. for $C_{21}H_{26}O_5NBr$: C, 55.74; H, 5.79; N, 3.12. Found: C, 55.83; H, 5.60; N, 3.25.

1-(2-Bromo-4,5-dimethoxyphenethyl)-3,4-dihydro-6,7-dimethoxyisoquinoline (**6**)——A mixture of 8 g of the amide (**5**) and 8 g of $POCl_3$ in 100 ml of dry benzene was refluxed for 2 hr. After the reaction, excess *n*-hexane was added to the reaction mixture. The supernatant liquid was decanted and the precipitate was made basic with 28% NH_4OH and extracted with $CHCl_3$. The extract was washed with H_2O and dried (Na_2SO_4). Evaporation of the solvent gave 7 g of the 3,4-dihydroisoquinoline (**6**), mp 95—96° (from MeOH). *Anal.* Calcd. for $C_{21}H_{24}O_4NBr$: C, 58.08; H, 5.05; N, 3.25. Found: C, 58.25; H, 5.21; N, 3.18.

The Reaction of 1-(2-Bromo-4,5-dimethoxyphenethyl)-3,4-dihydro-6,7-dimethoxyisoquinoline (6) with Sodium Methylsulfinylmethanide——A solution of 4 g of the isoquinoline (**6**) in 40 ml of dimethyl sulfoxide (DMSO) was added to a solution of sodium methylsulfinylmethanide (prepared from 2.0 g of NaH and 30 ml of DMSO) within 15 min under stirring at room temperature. After the stirring had been continued for 14 hr, the mixture was poured into 300 ml of H_2O and extracted with $CHCl_3$. The extract was washed with H_2O, dried (Na_2SO_4), and evaporated. The remaining residue was chromatographed on 25 g of silica gel. The eluant with $CHCl_3$ (200 ml) was discarded and the successive elution with 2% MeOH–$CHCl_3$ (100 ml) afforded the stereoisomeric mixture of the 13a-(methylsulfinyl)methyldibenzo[*a,f*]quinolizine (**7**). Recrystallization from MeOH–ether gave 1.1 g of colorless needles, mp 191—192°. Mass Spectrum *m/e*: 431 (M^+). *Anal.* Calcd. for $C_{23}H_{29}O_5NS$: C, 64.02; H, 6.77; N, 3.25. Found: C, 64.31; H, 6.90; N, 3.55.

5,6,12,13,13a-Pentahydro-2,3,9,10-tetramethoxy-13a-(methylthio) methyldibenzo[*a,f*]quinolizine (**8**)——A mixture of 0.4 g of **7** and Zn-Hg (prepared from 5 g of Zn and 0.5 g of $HgCl_2$) in 60 ml of a mixture of 50% AcOH and conc. HCl (1: 1) was heated on a water bath for 1 hr. Inorganic material was filtered and the filtrate was made basic with 28% NH_4OH and extracted with $CHCl_3$. The extract was washed with H_2O, dried over Na_2SO_4 and evaporated. Recrystallization of the remaining residue from MeOH–ether afforded 0.3 g of **8** as colorless needles, mp 168—170°, NMR ($CDCl_3$) δ: 1.97 (3H, s, SCH_3), 6.50 (1H, s, Ar-H), 6.60 (2H, s, Ar-H), 6.35 (1H, s, Ar-H). Mass Spectrum *m/e*: 415 (M^+). *Anal.* Calcd. for $C_{23}H_{29}O_4NS$: C, 66.49; H, 7.04; N, 3.37. Found: C, 66.65; H, 7.23; N, 3.18.

5,6,12,13,13a-Pentahydro-2,3,9,10-tetramethoxy-13a-methyldibenzo[*a,f*]quinolizine (**9**)——A solution of 200 mg of **8** in 70 ml of EtOH was refluxed in the presence of 1 ml of Raney Ni catalyst for 8 hr. After removal of the catalyst, the solvent was evaporated. The resulting solid was recrystallized from ether–*n*-hexane to give 150 mg of **9** as colorless needles, mp 125—126°. Mass Spectrum *m/e*: 369 (M^+), 354 (M^+–15). NMR ($CDCl_3$) δ: 1.63 (3H, s, 13a-CH_3), 6.60 (3H, broad s, Ar–H), 6.70 (1H, s, Ar–H). *Anal.* Calcd. for $C_{22}H_{27}O_4N$: C, 71.52; H, 7.37; N, 3.79. Found: C, 71.35; H, 7.58; N, 3.52.

1-(2-Bromo-4,5-dimethoxyphenethyl)-3,4-dihydro-7-hydroxy-6-methoxyisoquinoline (**10**)——A solution of 6.5 g of 7-benzyloxy-1-(2-bromo-4,5-dimethoxyphenethyl)-3,4-dihydro-6-methoxyisoquinoline (**11**)[6] in

7) All melting points were uncorrected. NMR spectra were taken with Varian T-60 spectrometer using tetramethylsilane (TMS) as an internal standard.

100 ml of EtOH–conc. HCl (1 : 1) was refluxed for 1.5 hr. After removal of the solvent, the resulting residue was basified with 28% NH_4OH and extracted with $CHCl_3$. The extract was washed with H_2O, dried (Na_2SO_4) and evaporated to leave 4.9 g of **10** as pale yellowish needles, mp 179.5—180.5° (from MeOH–ether). *Anal.* Calcd. for $C_{20}H_{22}ONBr_4$: C, 57.15; H, 5.28; N, 3.33. Found: C, 57.14; H, 5.27; N, 3.21.

5,6,12,13,13a-Pentahydro-2-hydroxy-3,9,10-trimethoxy-13a-(methylthio)methyldibenzo[*a*,*f*]quinolizine (13)——A solution of 3.5 g of the 3,4-dihydroisoquinoline (**10**) in 40 ml of DMSO was added to a solution of sodium methylsulfinylmethanide (prepared from 2 g of NaH and 30 ml of DMSO) under stirring at room temperature. After the stirring had been continued for 14 hr, the mixture was poured into 300 ml of H_2O containing excess NH_4Cl and extracted with $CHCl_3$. The extract was washed with H_2O, dried (Na_2SO_4) and evaporated. The resulting residue was chromatographed on 20 g of silica gel. After removal of the eluant with $CHCl_3$ (200 ml), the elution with 2% MeOH–$CHCl_3$ afforded 1.3 g of **12** as an oil, which was treated with Zn–Hg (prepared from 7 g of Zn and 0.7 g of $HgCl_2$) in 60 ml of a mixture of 50% of AcOH and conc. HCl (1 : 1) as in the case of **7**. The reaction mixture was worked up as usual to give 1 g of **13** as colorless needles, mp 136—138° (from MeOH). NMR ($CDCl_3$) δ: 1.98 (3H, s, SCH_3), 3.82 (3H, s, OCH_3), 3.90 (6H, s, $2\times OCH_3$), 6.5 (1H, s, Ar–H), 6.55 (2H, s, Ar–H), 6.60 (1H, s, Ar–H). Mass Spectrum *m/e*: 401 (M^+), 355. *Anal.* Calcd. for $C_{22}H_{27}O_4NS$: C, 65.81; H, 6.78; N, 3.49. Found: C, 65.99; H, 6.94; N, 3.31.

N-(4-Benzyloxy-3-methoxyphenethyl)-2-(2-bromo-4,5-methylenedioxyphenyl) propionamide (15)——A mixture of 7 g 4-benzyloxy-3-methoxyphenethylamine and 7 g of 2-bromo-4,5-methylenedioxyphenylpropionic acid was heated at 180° for 1.5 hr. After cooling, the mixture was recrystallized from benzene containing small portion of *n*-hexane to yield 10 g of the amide (**15**), mp 146—148°. *Anal.* Calcd. for $C_{26}H_{26}O_5NBr$: C, 60.95; H, 5.11; N, 2.73. Found: C, 61.18; H, 4.82; N, 2.83.

7-Benzyloxy-1-(2-bromo-4,5-methylenedioxyphenethyl)-3,4-dihydro-6-methoxyisoquinoline (16)——A mixture of 8 g of the amide (**14**), 8 g of $POCl_3$ and 100 ml of dry benzene was refluxed for 2 hr. To the reaction mixture was added 400 ml of *n*-hexane and allowed to stand for several hr. The supernatant liquid was removed by decantation and the precipitate was made basic with 28% NH_4OH, and extracted with $CHCl_3$. The extract was washed with H_2O, dried (Na_2SO_4). Evaporation of the solvent afforded 6.2 g of the isoquinoline (**16**), mp 148.5—149° (from benzene–*n*-hexane). *Anal.* Calcd. for $C_{26}H_{24}O_4NBr$: C, 63.17; H, 4.89; N, 2.83. Found: C, 63.44; H, 4.86; N, 2.92.

1-(2-Bromo-4,5-methylenedioxyphenethyl)-3,4-dihydro-7-hydroxy-6-methoxyisoquinoline (14)——A mixture of 5 g of the isoquinoline (**16**), 40 ml of conc. HCl and 55 ml of EtOH was refluxed for 1.5 hr. The solvent was evaporated and the residue was basified with 28% NH_4OH and extracted with $CHCl_3$. The extract was washed with H_2O, dried over Na_2SO_4 and evaporated to leave 3.2 g of the solid. Recrystallization from MeOH yielded colorless needles, mp 184—186°. *Anal.* Calcd. for $C_{19}H_{18}O_4NBr$: C, 56.45; H, 4.49; N, 3.47. Found: C, 56.20; H, 4.38; N, 3.02.

The Reaction of the Isoquinoline (14) with Sodium Methylsulfinylmethanide——A solution of 3 g of the isoquinoline (**14**) in 40 ml of DMSO was added to a solution of sodium methylsulfinylmethanide (prepared from 2 g of NaH and 35 ml of DMSO) under stirring at room temperature. After the stirring had been continued for 14 hr, the mixture was poured into 300 ml of H_2O containing excess NH_4Cl, and extracted with $CHCl_3$. The extract was washed with H_2O, dried (Na_2SO_4). The solvent was evaporated and the remaining residue was chromatographed on 25 g of silica gel. The eluant with $CHCl_3$ (150 ml) was discarded and the elution with 2% MeOH–$CHCl_3$ (100 ml) yielded 0.9 g of **17**, which was subjected to the following reaction without purification. The successive elution with the same eluant (100 ml) afforded 0.5 g of the 1-(2-hydroxy-3-methylthio-4,5-methylenedioxyphenethyl)isoquinoline (**19**). mp 162.5—163° (from MeOH–ether). Mass Spectrum *m/e*: 387 (M^+), NMR ($CDCl_3$) δ: 2.47 (3H, s, SCH_3), 3.93 (3H, s, OCH_3), 3.90 (2H, s, $-OCH_2O-$), 6.57, 6.65, 7.13 (3H, each s, Ar–H). *Anal.* Calcd. for $C_{20}H_{21}O_5NS$: C, 62.00; H, 5.46; N, 3.62. Found: C, 62.25; H, 5.21; N, 3.66.

5,6,12,13,13a-Pentahydro-2-hydroxy-3-methoxy-9,10-methylenedioxy-13a-(methylthio)methyldibenzo-[*a*,*f*]quinolizine (18)——A solution of 0.8 g of the preceding crude 13a-(methylsulfinyl)methyldibenzo[*a*,*f*]-quinolizine (**15**) in 60 ml of 50% AcOH–conc. HCl (1 : 1) was heated on a water bath in the presence of Zn–Hg (prepared from 5 g of Zn and 0.5 g of $HgCl_2$) for 1.5 hr. After removal of the inorganic material, the mixture was basified with 28% NH_4OH, and extracted with $CHCl_3$. The extract was washed with H_2O, dried (Na_2SO_4) and evaporated. The resulting solid was recrystallized from ether–*n*-hexane afforded 0.5 g of **18** as colorless needles, mp 175—176°. Mass Spectrum *m/e*: 385 (M^+), 324, NMR ($CDCl_3$) δ: 1.98 (3H, s, SCH_3), 3.85 (3H, s, OCH_3), 5.83 (2H, s, $-OCH_2O-$), 6.42, 6.53, 6.57, 6.83 (4H, each s, Ar–H). *Anal.* Calcd. for $C_{21}H_{23}O_4NS$: C, 65.43; H, 6.01; N, 3.63. Found: C, 65.08; H, 5.87; N, 3.91.

N-(4-Benzyloxy-3-methoxyphenethyl)-2-(3-bromo-4-methoxyphenyl)propionamide (22)——A mixture of 7 g of 4-benzyloxy-3-methoxyphenethylamine and 7 g of 3-bromo-4-methoxyphenylpropionic acid was heated at 180° for 1.5 hr. After cooling, the reaction mixture was recrystallized from benzene to yield 9.2 g of the amide (**22**), mp 114—116°. *Anal.* Calcd. for $C_{26}H_{28}O_4NBr$: C, 62.66; H, 5.66; N, 2.81. Found: C, 62.84; H, 5.73; N, 2.70.

7-Benzyloxy-1-(3-bromo-4-methoxyphenethyl)-3,4-dihydro-6-methoxyisoquinoline (21)——A mixture of 8 g of the amide (**22**), 8 g of $POCl_3$ and 100 ml of dry benzene was refluxed for 2 hr, and worked up as usual

to give 7.2 g of the 3,4-dihydroisoquinoline (**21**), mp 88—88.5° (from benzene–*n*-hexane). *Anal.* Calcd. for $C_{26}H_{26}O_3NBr$: C, 65.01; H, 5.46; N, 2.92. Found: C, 65.08; H, 5.48; N, 2.64.

1-(3-Bromo-4-methoxyphenethyl)-3,4-dihydro-7-hydroxy-6-methoxyisoquinoline (**20**)——A solution of 7 g of the 3,4-dihydroisoquinoline (**21**) in a mixture of 110 ml of EtOH–conc. HCl (1 : 1) was refluxed for 1.5 hr. The solvent was evaporated and the residue was basified with 28% NH_4OH and extracted with $CHCl_3$. The extract was washed with H_2O, dried (Na_2SO_4) and evaporated. The resulting residue was recrystallized from ether to give 4.2 g of the isoquinoline (**20**), mp 134—134.5°. *Anal.* Calcd. for $C_{19}H_{20}O_3NBr$: C, 58.47; H, 5.17; N, 3.59. Found: C, 58.31; H, 5.15; N, 3.64.

5,6,12,13,13a-Pentahydro-2-hydroxy-3,9-dimethoxy-13a-(methylthio)methyldibenzo[*a*,*f*]quinolizine (**24**)——A solution of 3 g of the isoquinoline (**20**) in 40 ml of DMSO was added to a solution of sodium methylsulfinylmethanide (prepared from 2 g of NaH and 30 ml of DMSO) under stirring at room temperature. After the stirring had been continued for 14 hr, the mixture was worked up as in the case of **10**, and the crude product was chromatographed on 25 g of silica gel. The eluant with $CHCl_3$ (150 ml) was discarded and the elution with 2% MeOH–$CHCl_3$ (200 ml) gave 1.2 g of **23** as pale brownish syrup; this was subjected to the following reaction.

A solution of **23** in 60 ml of 50% AcOH–conc. HCl (1 : 1) was heated on a water bath in the presence of Zn–Hg (prepared from 7 g of Zn and 0.7 g of $HgCl_2$) for 1.5 hr. After removal of the inorganic material, the mixture was made basic with 28% NH_4OH, and extracted with $CHCl_3$. The extract was washed with H_2O, dried (Na_2SO_4) and evaporated. The remaining solid was recrystallized from MeOH to give 0.8 g of **24** as colorless needles, mp 115—116°. Mass Spectrum *m/e*: 371 (M^+), 310, NMR ($CDCl_3$) δ: 1.97 (3H, s, SCH_3), 3.80, 3.87 (6H, each s, $2\times OCH_3$), 6.23 (1H, d,d, $J_{10,11}=7$ Hz, $J_{8,10}=2$ Hz, C_{10}–H), 6.50 (1H, d, $J_{8,10}=2$ Hz, C_8–H), 6.57 (1H, s, C_1–H or C_4–H), 6.87 (1H, d, $J_{10,11}=7$ Hz, C_{11}–H), 6.92 (1H, s, C_1–H or C_4–H). *Anal.* Calcd. for $C_{21}H_{25}O_3NS$: C, 67.89; H, 6.78; N, 3.77. Found: C, 68.19; H, 6.87; N, 3.64.

5,6,12,13,13a-Pentahydro-2-hydroxy-3,9-dimethoxy-13a-methyldibenzo[*a*,*f*]quinolizine (**25**)——A mixture of 0.4 g of **24** and 1.5 ml of Raney Ni catalyst in 70 ml of EtOH was refluxed for 8 hr. The residual solid was recrystallized from ether–*n*-hexane to give 250 mg of **24** as colorless needles, mp 66—67°. Mass Spectrum *m/e*: 325 (M^+), 310 (M^+–15), NMR ($CDCl_3$) δ: 1.47 (3H, s, 13a–CH_3), 3.78, 3.82 (6H, each s, $2\times OCH_3$), 6.20 (1H, d,d, $J_{10,11}=7$ Hz, $J_{8,10}=2$ Hz, C_{10}–H), 6.43 (1H, d, $J_{8,10}=2$ Hz, C_9–H), 6.52, 6.80 (2H, each s, Ar–H), 6.87 (1H, d, $J_{10,11}=7$ Hz, C_{11}–H). *Anal.* Calcd. for $C_{20}H_{23}O_3N$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.36; H, 7.17; N, 4.80.

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