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DIMERIC APORPHINOID ALKALOIDS, III[1]

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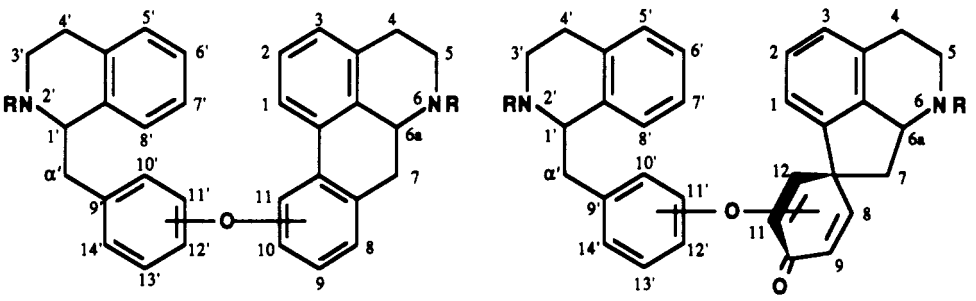
Substantial progress has been made during the past five years in the field of the dimeric aporphinoid alkaloids. This classically includes the aporphine-benzylisoquinoline dimers, the proaporphine-benzylisoquinoline dimers, the bisaporphines, and the hernandaline-type and coyhaiquine-type alkaloids, which are, respectively, oxidation products of aporphine-benzylisoquinolines and proaporphine-benzylisoquinolines. A number of the dimeric aporphinoids have been included in a recent review on the bisbenzylisoquinoline alkaloids (6).

The present review supplements our earlier ones (15,16) by including data published since 1984 along the following lines: additional data on previously reported dimeric aporphinoid alkaloids (structures **1–59**), a revised structure (Table 1), additional physical and spectral data (Table 2), and known dimeric aporphinoids reisolated from new sources (Table 3), and previously unreported dimeric aporphinoids (structures **60–109**, Table 4). For the new dimeric aporphinoids the following are included: thalicarpine type, structures **60**, **61**, **65**, **66**; fetidine type, structures **62–64**; istanbulamine type, structure **67**; thalifaberine type, structures **68–78**; pakistanine type, structures **79**, **80**; kalashine type, structure **81**; pakistanamine type, structure **82**; epivaldiberine type, structures **83**, **84**; hernandaline type, structures **85**, **86**; coyhaiquine type, structure **87**; 7-7′-bisaporphinoids, structures **88–109**.

The organization, intent, and content of the present review are essentially the same as those of the previous ones. Included in this listing are the oxygen-bonded aporphine-benzylisoquinolines, oxygen-bonded proaporphine-benzylisoquinolines, oxygen-bonded and oxidized aporphine-benzylisoquinolines and proaporphine-benzylisoquinolines, and carbon-bonded dimers (bisaporphinoids).

Within each section, the material has been arranged in an ascending order of substitution pattern. The numbering system is according to the accepted rules.

Unless stated otherwise, uv (nm, log ϵ) and cd ($\Delta\epsilon$, nm) spectra were obtained in EtOH or MeOH, ^{1}H-nmr spectra in $CDCl_3$; chemical shifts are in ppm on the δ scale, and the coupling constants are in Hz. Values with identical superscripts are interchangeable. In the case of a symmetrical bisaporphinoid structure, the nmr values have



[1]For Parts I and II, see Guinaudeau *et al.* (15,16).

only been reported around one half of the molecule. Ir frequencies are in cm^{-1}, and melting points are in degrees centigrade.

Owing to the cytotoxic and antitumor activities of thalicarpine [**10**] (= thaliblastine), several pharmacological studies on this alkaloid have been published (20,21,27,31). Cytotoxic activity has been also reported for the new thalifarazine [**72**] (35). A quantitative determination of thalicarpine [**10**] in drugs has been reported (10) and various syntheses have been reviewed (31). The biosyntheses of thalicarpine [**10**] (25), adiantifoline [**16**], and thalmelatidine [**18**] (30) in *Thalictrum minus* have been studied.

TABLE 1. Revised Structure of Previously Reported Dimeric Aporphinoids.

20. REVOLUTOPINE $C_{39}H_{44}N_2O_8$ 668.3097
Revised structure (17)

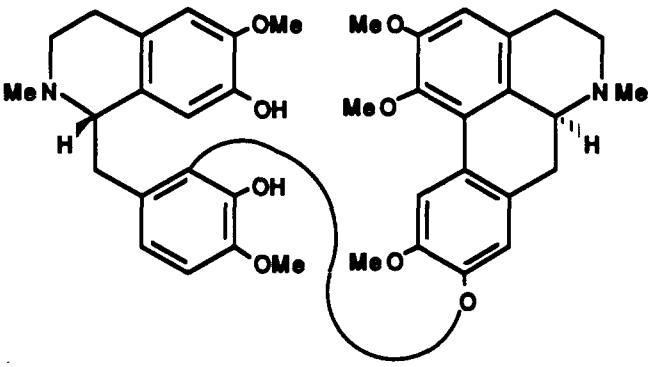
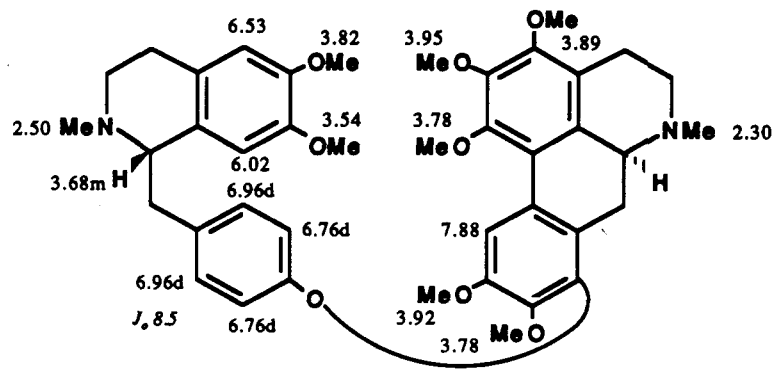


TABLE 2. Additional Physical and Spectral Data on Previously Reported Dimeric Aporphinoids.

35. THALIFABERINE $C_{41}H_{48}N_2O_8$ 696.3398
^{1}H NMR (400 MHz) (17,33)



36. THALIFABINE $C_{41}H_{46}N_2O_9$ 710.3191
^{1}H NMR (80 MHz) (33)

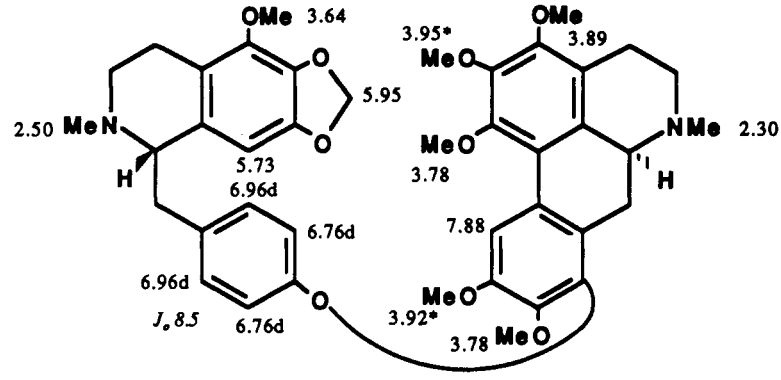


TABLE 3. Known Dimeric Aporphinoids Reisolated from New Sources.

Aporphine-Benzylisoquinoline Dimers

6. THALMELATINE $C_{40}H_{46}N_2O_8$ 682.3254
SOURCES: Hernandiaceae: *Hernandia peltata* (9)

7. DEHYDROTHALMELATINE $C_{40}H_{44}N_2O_8$ 680.3097
SOURCES: Hernandiaceae: *Hernandia peltata* (9)

10. THALICARPINE (Thaliblastine) $C_{41}H_{48}N_2O_8$ 696.3410
SOURCES: Hernandiaceae: *Hernandia peltata* (9), Synthesis (31)

13. THALILUTINE $C_{41}H_{48}N_2O_9$ 712.3360
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17)

14. *O*-DESMETHYLADIANTIFOLINE $C_{41}H_{48}N_2O_9$ 712.3360
SOURCES: Ranunculaceae: *Thalictrum minus* var. *majus* (29)

16. ADIANTIFOLINE $C_{42}H_{50}N_2O_9$ 726.3516
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17), *Thalictrum minus* var. *adiantifolium* (26)

17. THALMINELINE $C_{41}H_{50}N_2O_{10}$ 742.3465
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17)

18. THALMELATIDINE $C_{42}H_{48}N_2O_{10}$ 740.3309
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17), *Thalictrum minus* var. *majus* (4,29), *Thalictrum minus* var. *minus* (5)

19. FETIDINE (Foetidine) $C_{40}H_{46}N_2O_8$ 682.3254
SOURCES: Ranunculaceae: *Thalictrum foetidum* (28)

29. 2′-NORTHALICARPINE (Northalicarpine) $C_{40}H_{46}N_2O_8$ 682.3254
SOURCES: Hernandiaceae: *Hernandia peltata* (9)

33. HUANGSHANINE $C_{42}H_{50}N_2O_9$ 726.3503
SOURCES: Ranunculaceae: *Thalictrum faberi* (33)

35. THALIFABERINE $C_{41}H_{48}N_2O_8$ 696.3398
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17), *Thalictrum faberi* (33)

36. THALIFABINE $C_{41}H_{46}N_2O_9$ 710.3191
SOURCES: Ranunculaceae: *Thalictrum faberi* (33)

39. 1-*O*-METHYLCHITRALINE $C_{37}H_{40}N_2O_6$ 608.2886
SOURCES: Berberidaceae: *Berberis darwinii* (13)

Proaporphine-Benzylisoquinoline Dimers

26. PAKISTANAMINE $C_{38}H_{42}N_2O_6$ 622.3042
SOURCES: Berberidaceae: *Berberis actinacantha* (34), *Berberis hakeoides* (32)

44. BERBIVALDINE $C_{36}H_{38}N_2O_6$ 594.2728
SOURCES: Berberidaceae: *Berberis actinacantha* (34)

45. VALDIBERINE $C_{36}H_{38}N_2O_6$ 594.2728
SOURCES: Berberidaceae: *Berberis hakeoides* (32)

46. VALDIVIANINE $C_{37}H_{40}N_2O_6$ 608.2886
SOURCES: Berberidaceae: *Berberis hakeoides* (32)

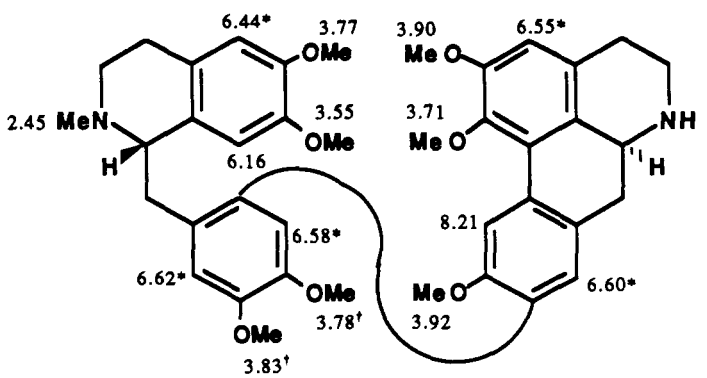
47. PATAGONINE $C_{37}H_{40}N_2O_6$ 608.2886
SOURCES: Berberidaceae: *Berberis actinacantha* (34), *Berberis hakeoides* (32)

Oxidized Proaporphine-Benzylisoquinoline Dimers

52. COYHAIQUINE $C_{26}H_{27}NO_5$ 433.1888
SOURCES: Berberidaceae: *Berberis empetrifolia* (11,12)

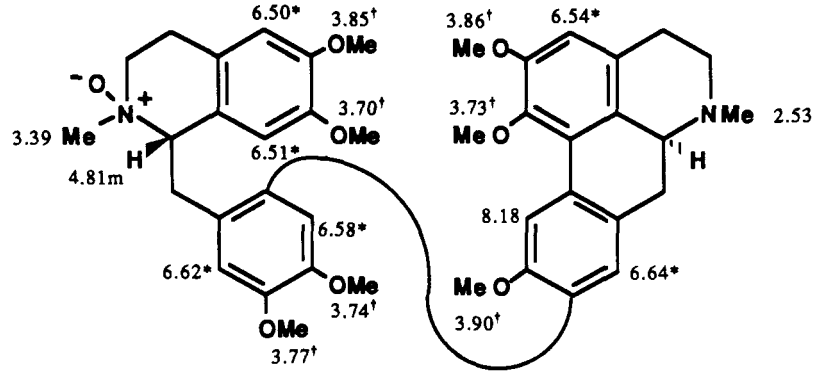
TABLE 4. Previously Unreported Dimeric Aporphinoids.[a]

60. 6-NORTHALICARPINE $C_{40}H_{46}N_2O_8$ 682.3254
^{1}H NMR: (240 MHz) (9)
MS: 680 (1), 490 (8), 324 (20), 322 (27), 206 (49), 192 (100) (9)
SOURCES: Hernandiaceae: *Hernandia peltata* (9)



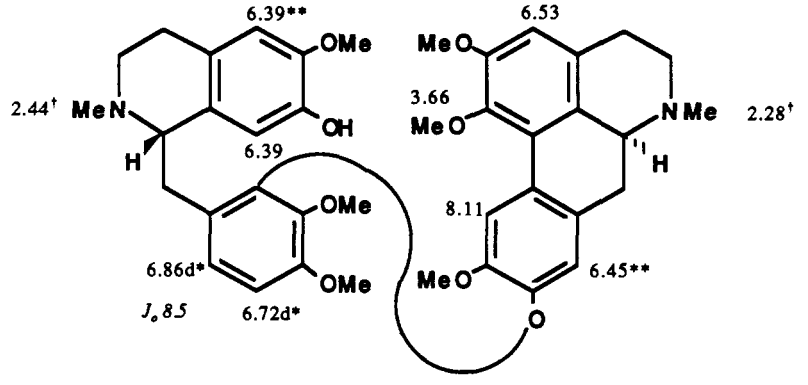
61. THALICARPINE 2′-*N*-OXIDE $C_{41}H_{48}N_2O_9$ 712.3360
$[\alpha]_D$: +15° (c = 0.14, $CHCl_3$) (9)
UV: (MeOH) 215 (4.36), 280 (3.98), 300 sh (3.86) (9)
^{1}H NMR: (200 MHz) (9)
MS: $[M]^+$ 712 (0.1), 696 (0.3), 695 (0.8), 505 (1.5), 490 (4), 340 (7), 206 (100) (9)
SOURCES: Hernandiaceae: *Hernandia peltata* (9)

[a]Not previously reported in "Dimeric Aporphinoid Alkaloids" I and II (15,16).



62. FABERIDINE $C_{40}H_{46}N_2O_8$ 682.3254

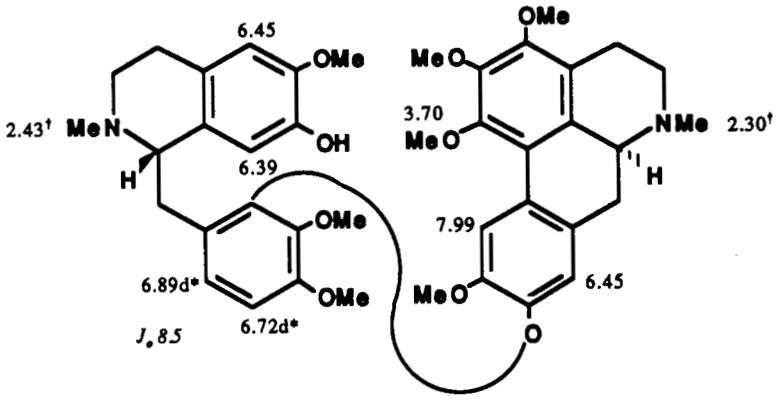
[α]D: +105° (*c* = 0.7, MeOH) (33)
UV: (MeOH) 281 (4.30), 302 (4.14), 313 sh (4.06) (33)
IR: ($CHCl_3$) 3540 (33)
^{1}H NMR: (80 MHz) (33)
MS: $[M]^+$ 682, 490, 489, 340, 324, 192 (100) (33)
CD: +3.7 (302), −6.3 (278), +45.8 (241), +7.8 (211), −44.1 (199) (33)
SOURCES: Ranunculaceae: *Thalictrum faberi* (33)



Five OMe at 3.78 (6H), 3.86, 3.88, 3.99

63. FABERONINE $C_{41}H_{48}N_2O_9$ 712.3360

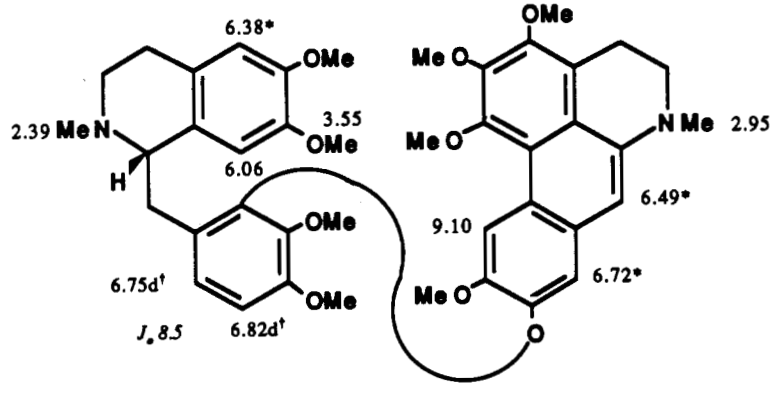
[α]D: +83° (*c* = 0.5, MeOH) (33)
UV: (MeOH) 281 (4.33), 301 (4.18), 312 sh (4.12) (33)
IR: ($CHCl_3$) 3540 (33)
^{1}H NMR: (80 MHz) (33)
MS: $[M]^+$ 712 (0.1), 520, 370, 354, 192 (100) (33)
CD: −4.9 (307), −5.8 (278), +47.0 (243), +6.2 (213), −39.0 (198) (33)
SOURCES: Ranunculaceae: *Thalictrum faberi* (33)



Six OMe at 3.78 (6H), 3.86, 3.88, 3.96, 4.01

64. DEHYDROHUANGSHANINE $C_{42}H_{48}N_2O_9$ 724.3347

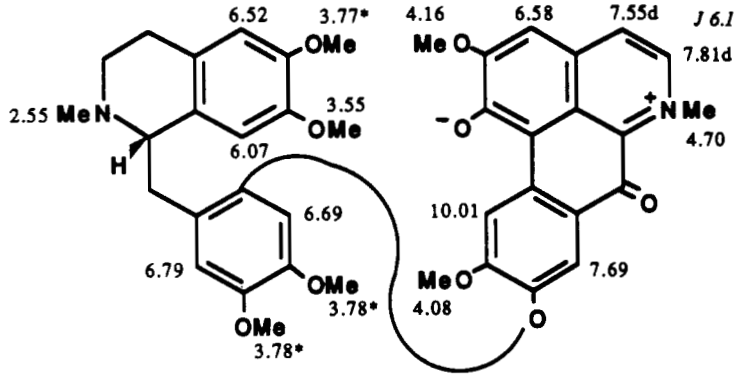
$[\alpha]_D$: +42° (c = 0.17, MeOH) (33)
UV: 257 (4.54), 267 sh (4.51), 275 sh (4.49), 332 (3.85) (33)
^{1}H NMR: (200 MHz) (33)
MS: $[M]^+$ 724 (0.2), 519 (4), 518 (2), 517 (4), 411 (6), 206 (100) (33)
CD: +1.6 (290), +7.0 (233), +18.4 (213), −21.3 (202) (33)
SOURCES: Ranunculaceae: *Thalictrum faberi* (33)



Seven OMe at 3.78, 3.79, 3.90, 3.93, 3.99, 4.06, 4.09

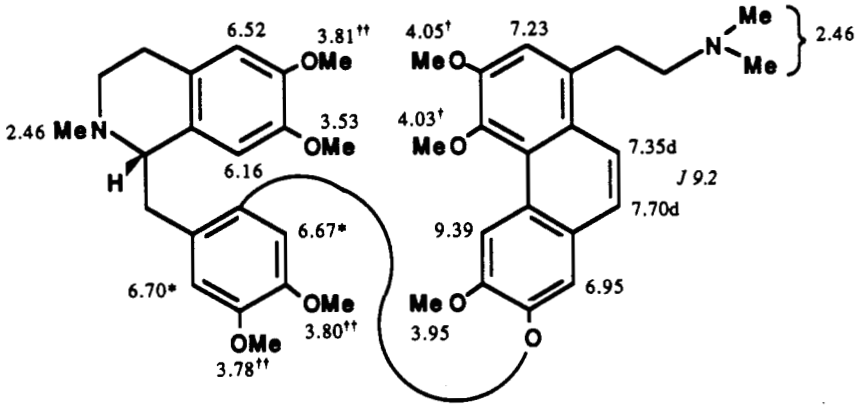
65. VILAPORTINE $C_{40}H_{40}N_2O_9$ 692.2723

UV: (MeOH) 227 sh (4.57), 257 sh (4.30), 320 (4.45), 392 (3.67) (9)
^{1}H NMR: (200 MHz) (9)
MS: $[M]^+$ 692 (10), 648 (20), 647 (40), 632 (12), 487 (6), 486 (4), 324 (13), 206 (100) (9)
CD: +0.25 (286), +2.0 (257 sh), +11.0 (246), 0 (220), positive tail below 220 (9)
SOURCES: Hernandiaceae: *Hernandia peltata* (9)



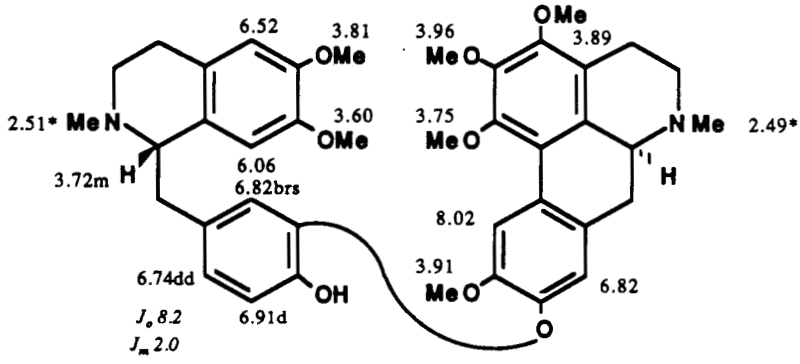
66. HEBRIDAMINE $C_{42}H_{50}N_2O_8$ 710.3554

[α]D: Positive value (9)
UV: (MeOH) 220, 260, 315 (9)
^{1}H NMR: (200 MHz) (9)
MS: $[M]^+$ 710 (0.2), 708 (0.8), 504 (0.1), 503 (0.2), 206 (100), 58 (65) (9)
SOURCES: Hernandiaceae: *Hernandia peltata* (9)



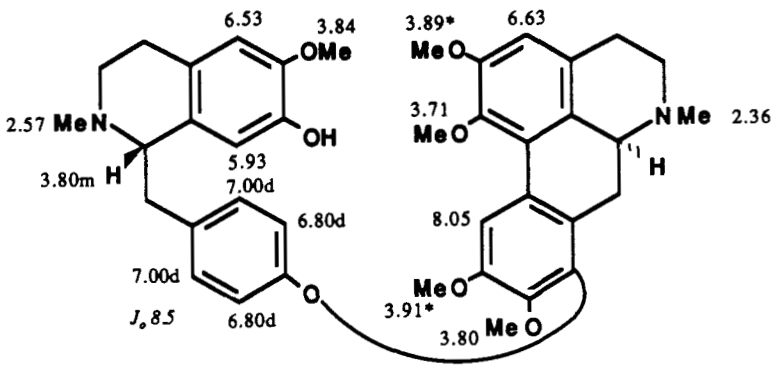
67. THALIBULAMINE $C_{40}H_{46}N_2O_8$ 682.3254

[α]D: +63° (c = 0.2, MeOH) (17)
UV: (MeOH) 225 (4.79), 270 sh (4.29), 281 (4.42), 301 (4.31), 314 (4.24) (17)
^{1}H NMR: (200 MHz) (17)
MS: $[M]^+$ 682 (0.07), 681 (0.2), 680 (0.3), 476 (1), 475 (2), 206 (100), 190 (4) (17)
CD: 0 (320), −5.6 (300), −8.0 (272), 0 (255), +80.0 (239), negative tail below 230 (17)
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17)



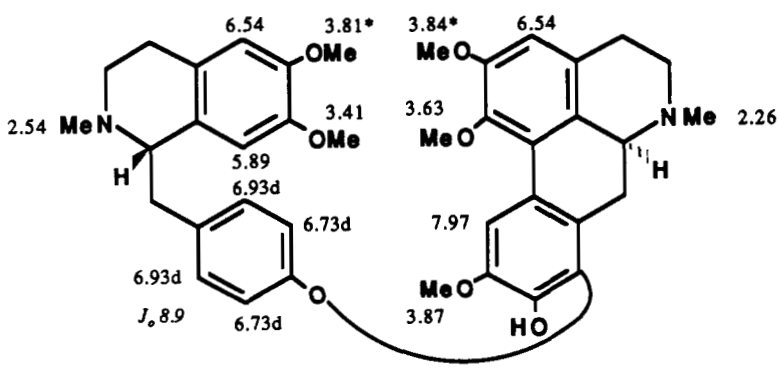
68. THALIFARAMINE $C_{39}H_{44}N_2O_7$ 652.3137

[α]D: +76° (*c* = 0.06, MeOH) (17)
UV: 228 (4.75), 270 sh (4.35), 280 (4.42), 308 (4.04) (17)
^{1}H NMR: (200 MHz) (17)
MS: $[M]^+$ 652 (0.8), 651 (1), 637 (0.4), 460 (2), 459 (3), 192 (100), 177 (8) (17)
CD: 0 (310), −4.0 (300), −8.0 (270), 0 (250), +87.0 (237), negative tail below 234 (17)
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17)



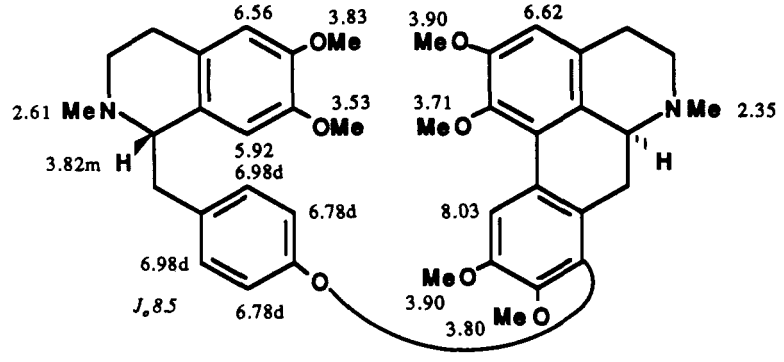
69. THALIFABORAMINE (Thalifabomine) $C_{39}H_{44}N_2O_7$ 652.3137

[α]D: +107° (*c* = 0.13, MeOH) (24)
UV: 283 (4.30), 313 sh (3.98) (24)
IR: ($CHCl_3$) 3530 (24)
^{1}H NMR: (400 MHz) (24)
MS: $[M]^+$ 652 (0.1), 446 (5), 206 (100) (24)
CD: −3.3 (305), −4.0 (276), +51.7 (243) (24)
SOURCES: Ranunculaceae: *Thalictrum faberi* (24,33)



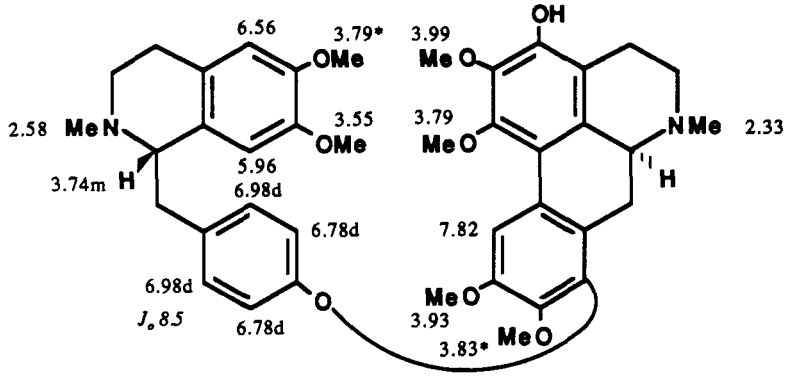
70. THALIFARONINE $C_{40}H_{46}N_2O_7$ 666.3293

[α]D: +68° (*c* = 0.1, MeOH) (17)
UV: 227 (4.75), 268 sh (4.30), 280 (4.38), 304 sh (4.08) (17)
^{1}H NMR: (360 MHz) (17)
MS: $[M]^+$ 666 (0.3), 665 (0.6), 664 (0.5), 460 (1), 459 (1), 206 (100), 190 (4) (17)
CD: 0 (310), −4.0 (297), −1.7 (287), −8.1 (270), 0 (255), +74.0 (236), negative tail below 232 (17)
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17)



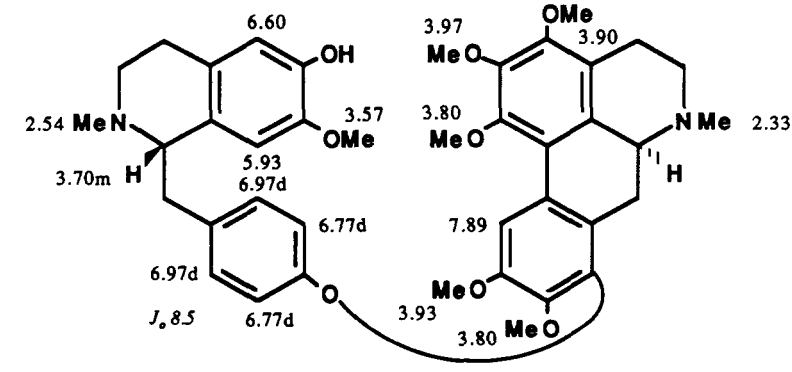
71. THALIFARAPINE (Thalifaroline) $C_{40}H_{46}N_2O_8$ 682.3254

[α]D: +99° (*c* = 0.42, MeOH) (33)
UV: 225 (4.69), 275 sh (4.28), 285 (4.37), 300 sh (4.24), 310 sh (4.16) (33)
^{1}H NMR: (200 MHz) (33)
MS: $[M]^+$ 682 (0.1), 681 (0.3), 478 (0.2), 477 (0.5), 476 (0.8), 206 (100), 190 (4) (33)
CD: 0 (315), −4.2 (305), −5.6 (272), 0 (257), +68.0 (241), negative tail below 237 (33)
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17), *Thalictrum faberi* (33)



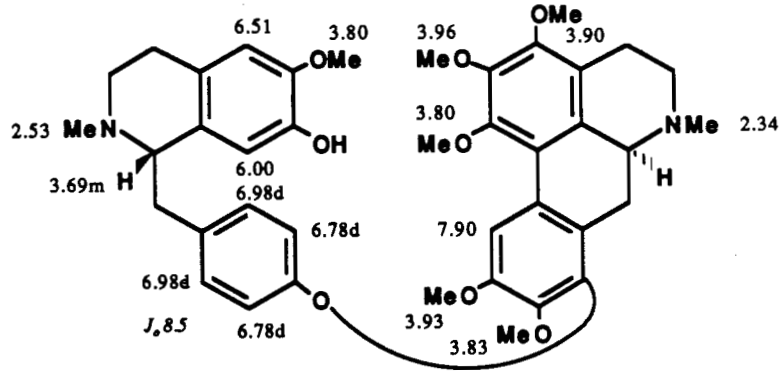
72. THALIFARAZINE $C_{40}H_{46}N_2O_8$ 682.3254

[α]D: +72° (*c* = 0.06, MeOH) (17)
UV: 228 (4.70), 270 sh (4.29), 283 (4.38), 297 sh (4.25), 310 sh (4.02) (16)
^{1}H NMR: (360 MHz) (17)
MS: $[M]^+$ 682 (0.2), 681 (0.4), 680 (0.4), 490 (2.2), 192 (100), 177 (7) (17)
CD: 0 (315), −4.7 (297), −9.4 (272), 0 (255), +80.0 (240), negative tail below 232 (17)
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17), *Thalictrum sessile* (35)



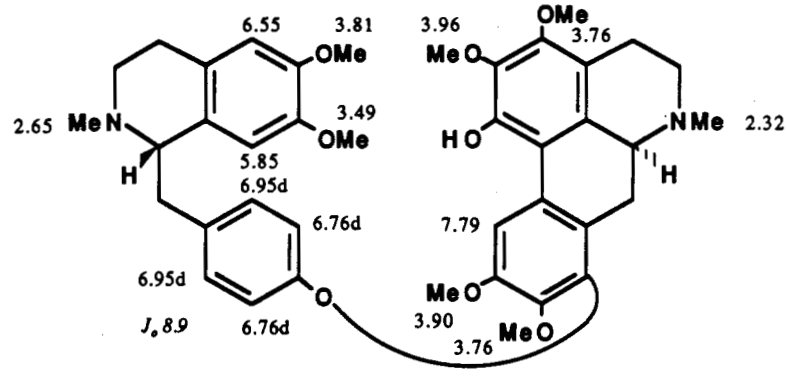
73. THALIFARETINE $C_{40}H_{46}N_2O_8$ 682.3254

[α]D: +61° (*c* = 0.1, MeOH) (17)
UV: 222 (4.76), 272 sh (4.24), 283 (4.39), 293 sh (4.27), 310 sh (4.04) (17)
^{1}H NMR: (360 MHz) (17)
MS: $[M]^+$ 682 (0.8), 490 (1.2), 192 (100), 177 (5) (17)
CD: 0 (314), −8.4 (300), −10.0 (273), 0 (255), +81.0 (239), negative tail below 230 (17)
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17)



74. THALIFALANDINE $C_{40}H_{46}N_2O_8$ 682.3254

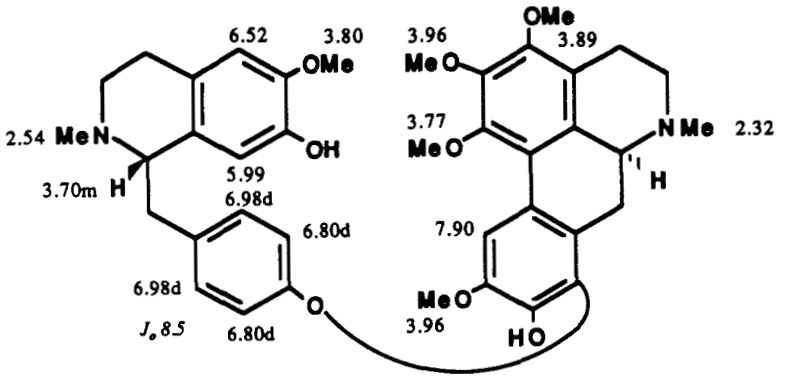
[α]D: +83° (*c* = 0.37, MeOH) (23)
UV: 205 (4.47), 225 sh (4.37), 285 (4.03), 308 sh (3.89) (23)
IR: ($CHCl_3$) 3530 (23)
^{1}H NMR: (400 MHz)[b] (23)
MS: $[M]^+$ 682 (0.1), 476 (5), 206 (100) (23)
CD: −7.5 (304), −8.8 (278), +75.0 (243) (23)
SOURCES: Ranunculaceae: *Thalictrum faberi* (23)



75. THALIFARICINE $C_{39}H_{44}N_2O_8$ 668.3097

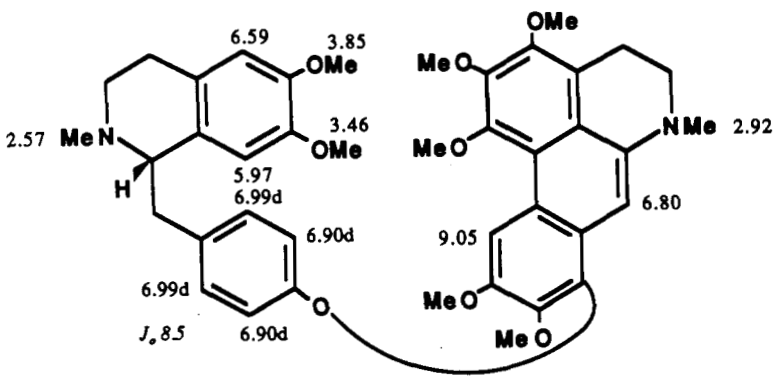
[α]D: +66° (*c* = 0.1, MeOH) (17)
UV: 224 (4.74), 274 sh (4.31), 283 (4.40), 295 sh (4.31), 310 sh (4.17) (17)
^{1}H NMR: (360 MHz) (17)
MS: $[M]^+$ 668 (0.1), 667 (0.2), 666 (0.2), 476 (2.2), 192 (100), 177 (8) (17)
CD: 0 (315), −5.2 (300), −2.0 (288), −6.6 (275), 0 (255), +73.0 (240), negative tail below 236 (17)
SOURCES: Ranunculaceae: *Thalictrum cultratum* (17)

[b]The nmr assignments for the two NMe have been reversed to be in agreement with those of thalifaronine [**70**] for which nOe studies have been carried out.



76. DEHYDROTHALIFABERINE $C_{41}H_{46}N_2O_8$ 694.3254

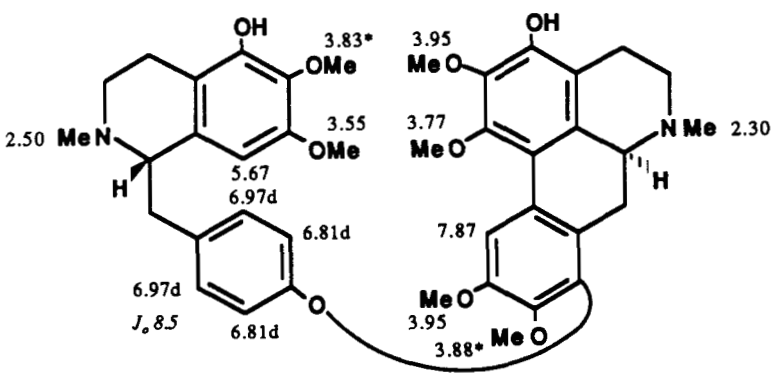
[α]D: +96° (*c* = 0.14, MeOH) (33)
UV: 256 (4.56), 272 (4.56), 332 (4.06) (33)
^{1}H NMR: (80 MHz) (33)
MS: $[M]^+$ 694 (0.2), 488, 487, 206 (100) (33)
CD: +0.2 (385), +0.8 (334), +4.7 (290), +13.0 (231), +12.7 (213), −26.0 (196) (33)
SOURCES: Ranunculaceae: *Thalictrum faberi* (33), Synthesis (33)



Five OMe at 3.94, 3.99, 4.04, 4.07, 4.11

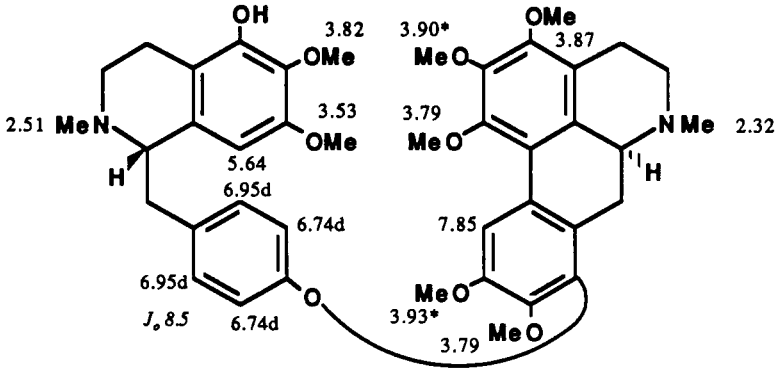
77. THALIFASINE $C_{40}H_{46}N_2O_9$ 698.3200

[α]D: +68° (*c* = 0.8, MeOH) (33)
UV: 282 (4.29), 310 sh (4.05) (33)
IR: ($CHCl_3$) 3528 (33)
^{1}H NMR: (80 MHz) (33)
MS: $[M]^+$ 698 (0.1), 476, 475, 222 (100) (33)
CD: −6.6 (298), −7.8 (285), +61.2 (243), −21.9 (216) (33)
SOURCES: Ranunculaceae: *Thalictrum faberi* (33)



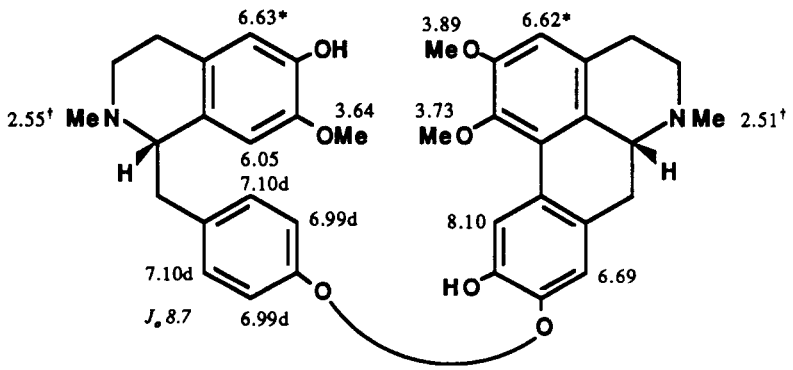
78. THALIFABATINE $C_{41}H_{48}N_2O_9$ 712.3360

[α]D: +61° (c = 0.15, MeOH) (33)
UV: 281 (4.26), 311 sh (3.93) (33)
IR: ($CHCl_3$) 3530 (33)
^{1}H NMR: (80 MHz) (33)
MS: $[M]^+$ 712 (0.1), 490, 489, 222 (100) (33)
CD: −6.0 (305), −11.0 (281), +51.8 (242), −24.3 (212) (33)
SOURCES: Ranunculaceae: *Thalictrum faberi* (33)



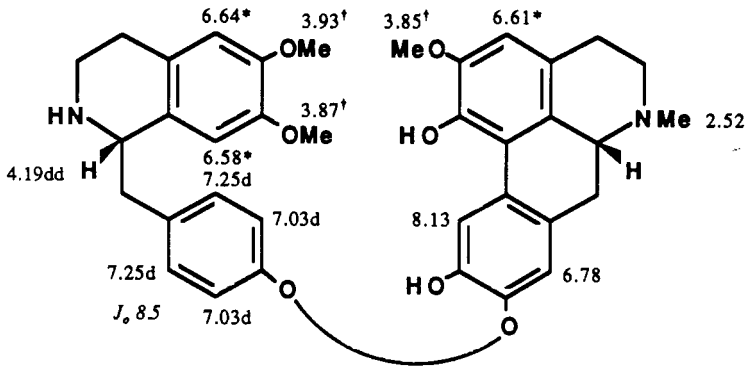
79. 1-*O*-METHYLPORVENIRAMINE $C_{37}H_{40}N_2O_6$ 608.2886

[α]D: +43° (c = 0.08, $CHCl_3$) (34)
UV: 229 sh (4.87), 277 (4.49), 302 (4.33) (34)
^{1}H NMR: (200 MHz) (34)
MS: $[M]^+$ 608 (0.2), 607 (0.3), 606 (0.2), 417 (4), 416 (6), 415 (3), 309 (1), 207 (3), 206 (9), 193 (14), 192 (100), 191 (6), 190 (8), 189 (3), 188 (3), 178 (2), 177 (9), 176 (1), 175 (1), 163 (1), 162 (2) (34)
SOURCES: Synthesis (34)



80. 2′-NORPAKISTANINE $C_{36}H_{38}N_2O_6$ 594.2728

MP: 148° (13)
[α]D: +9° (c = 0.05, MeOH) (13)
UV: 224 (4.66), 268 (4.16), 277 (4.26), 292 (4.05), 308 (4.12) (13)
^{1}H NMR: (360 MHz) (13)
MS: $[M]^+$ 594 (0.4), 593 (2), 592 (6), 591 (8), 590 (15), 588 (11), 575 (6), 207 (6), 206 (62), 192 (100) (13)
SOURCES: Berberidaceae: *Berberis valdiviana* (13)



81. 6′-*O*-DEMETHYLKALASHINE $C_{36}H_{38}N_2O_6$ 594.2728

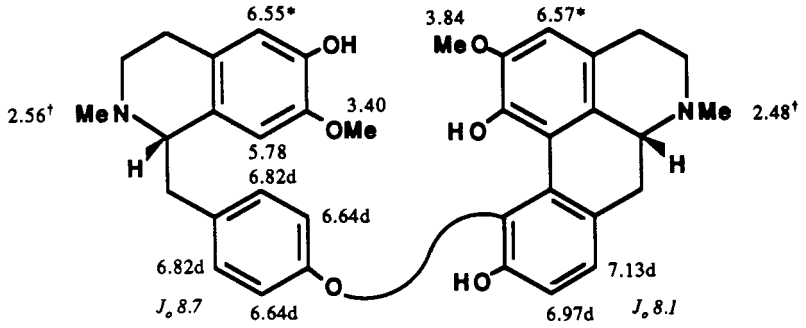
[α]D: −78° (*c* = 0.09, $CHCl_3$) (34)

UV: 222 sh (4.55), 273 (4.13), 295 sh (3.98), 309 sh (3.93) (34)

^{1}H NMR: (200 MHz) (34)

MS: $[M]^+$ 594 (0.1), 593 (0.2), 403 (3), 402 (1), 297 (4), 296 (7), 295 (9), 281 (2), 280 (4), 279 (2), 278 (3), 265 (3), 264 (3), 263 (2), 251 (2), 250 (2), 236 (2), 207 (2), 206 (2), 193 (14), 192 (100), 191 (11), 190 (14), 189 (6), 188 (6), 178 (3), 177 (15), 163 (2), 162 (4) (34)

SOURCES: Synthesis (34)



82. RUPANCAMINE $C_{37}H_{40}N_2O_6$ 608.2886

[α]D: +117° (*c* = 0.12, $CHCl_3$) (34)

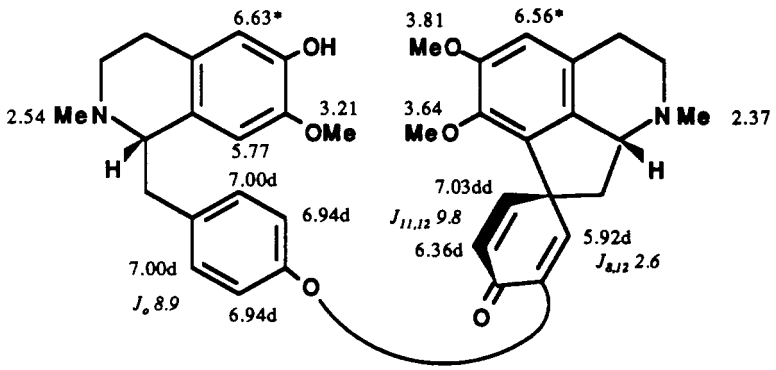
UV: 231 (4.27), 285 (3.49) (34)

IR: ($CHCl_3$) 3550, 1670, 1645 (34)

^{1}H NMR: (200 MHz) (34)

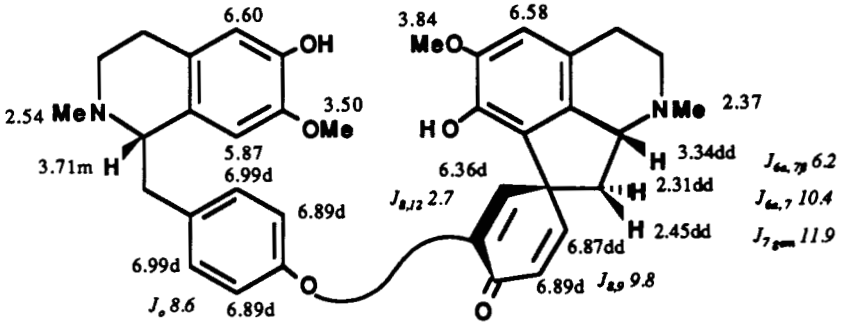
MS: $[M]^+$ 608 (6), 607 (5), 417 (2), 416 (3), 415 (3), 310 (1), 309 (1), 294 (1), 293 (1), 280 (1), 266 (1), 236 (1), 206 (2), 204 (1), 193 (14), 192 (100), 191 (4), 190 (7), 178 (2), 177 (12), 176 (2), 163 (2), 162 (2) (34)

SOURCES: Berberidaceae: *Berberis actinacantha* (34)



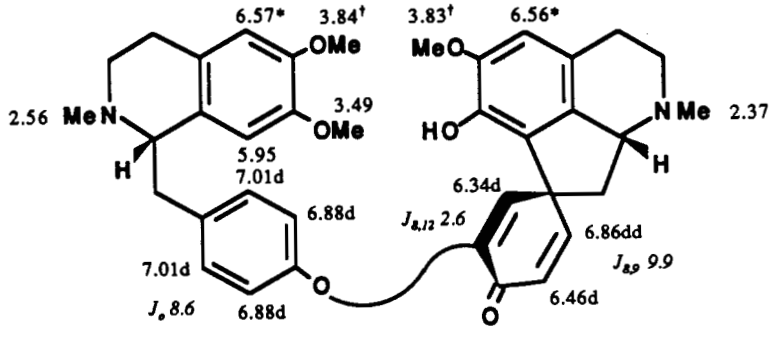
83. EPIBERBIVALDINE $C_{36}H_{38}N_2O_6$ 594.2728

[α]D: +46° (c = 0.12, $CHCl_3$) (34)
UV: 233 (4.47), 286 (3.98) (34)
IR: ($CHCl_3$) 3555, 1675, 1645 (34)
^{1}H NMR: (360 MHz) (34)
MS: $[M]^+$ 594 (19), 593 (15), 403 (3), 402 (3), 297 (2), 295 (3), 294 (3), 293 (2), 193 (13), 192 (100), 191 (36), 190 (14), 177 (11), 176 (7) (34)
SOURCES: Berberidaceae: *Berberis actinacantha* (34)



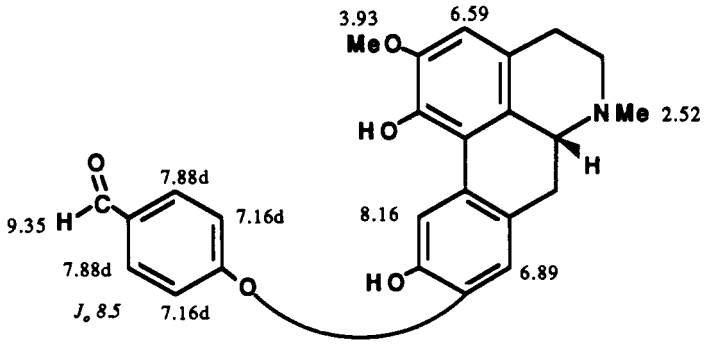
84. EPIVALDIVIANINE $C_{37}H_{40}N_2O_6$ 608.2886

[α]D: +69° (c = 0.1, MeOH) (13)
UV: 234 sh (4.50), 285 (3.93) (13)
IR: ($CHCl_3$) 3670, 1665, 1635 (13)
^{1}H NMR: (200 MHz) (13)
MS: $[M]^+$ 608 (0.02), 604 (0.3), 588 (0.1), 575 (0.1), 401 (0.6), 295 (8), 207 (14), 206 (100) (13)
SOURCES: Berberidaceae: *Berberis valdiviana* (13)

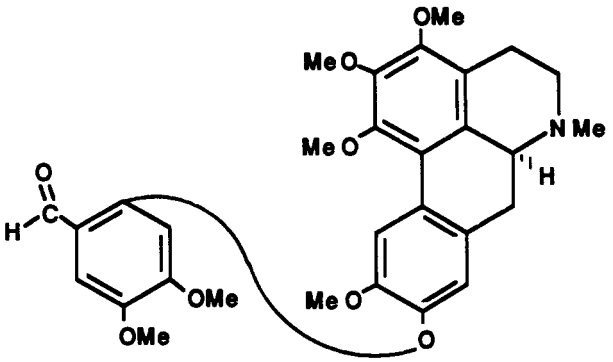


85. NATALININE $C_{25}H_{23}NO_5$ 417.1570

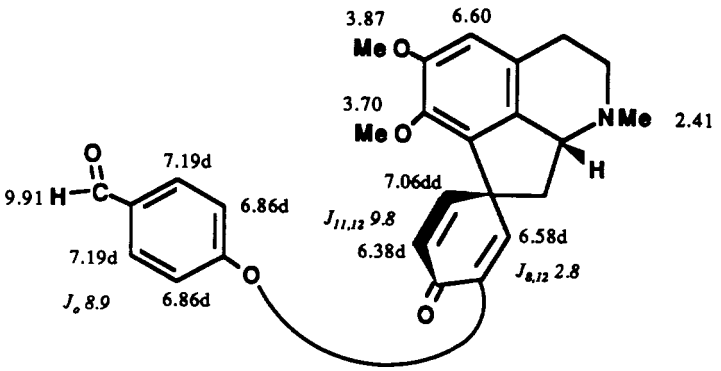
UV: 209 (4.41), 277 (4.03), 308 (3.87) (12)
^{1}H NMR: (200 MHz) (12)
MS: $[M]^+$ 417 (100), 402 (36), 312 (72), 297 (99), 296 (98) (12)
CD: +1.0 (310), +1.7 (273), −6.5 (243), +1.7 (213) (12)
SOURCES: Berberidaceae: *Berberis empetrifolia* (12)



86. THALIADINE[c] $C_{30}H_{33}NO_8$ 535.2610
SOURCES: Ranunculaceae: *Thalictrum minus* var. *majus* (29)

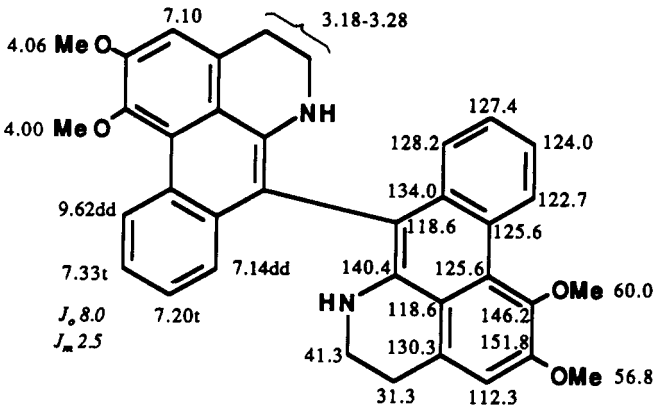


87. COYHAIQUININE $C_{26}H_{25}NO_5$ 431.1726
UV: 209 (4.54), 275 (4.17) (11)
^{1}H NMR: (200 MHz) (11)
MS: $[M-1]^+$ 430, 310 (3), 282 (20) (11)
SOURCES: Berberidaceae: *Berberis empetrifolia* (11)

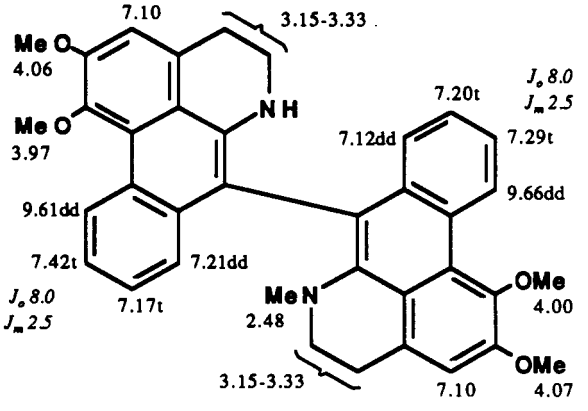


[c]Data have been already given in Aporphine Alkaloids II: see Guinaudeau *et al.* (15), structure **244**.

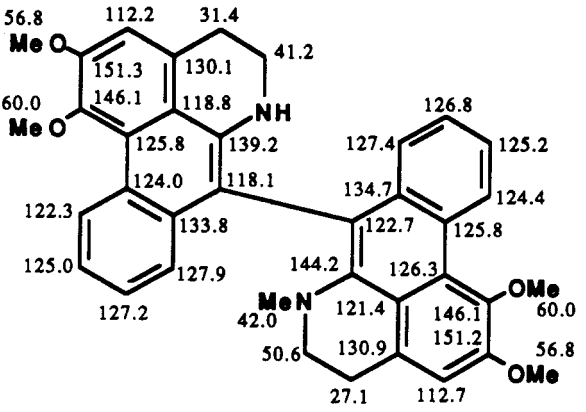
88. URABAINE (7,7′-Bisnordehydronuciferine) $C_{36}H_{32}N_2O_4$ 556.2354
MP: >280° (2)
UV: 212 (4.02), 256 sh (4.17), 263 (4.19), 328 (3.82) (2)
^{1}H NMR: (400 MHz) (2)
^{13}C NMR: (2,22)
MS: $[M]^+$ 556, 279 (2)
SOURCES: Annonaceae: *Oxandra xylopioides* (1,2), *Unonopsis spectabilis* (22), Synthesis (18)



89. *N*-METHYLURABAINE $C_{37}H_{34}N_2O_4$ 570.2510
MP: 262° (2)
UV: 210 (4.54), 235 sh (4.50), 256 sh (4.74), 260 (4.76), 330 (4.26) (2)
^{1}H NMR: (60 MHz) (2)
^{13}C NMR: (2,22)
MS: $[M]^+$ 570, 293, 279 (2)
SOURCES: Annonaceae: *Oxandra xylopioides* (1,2)

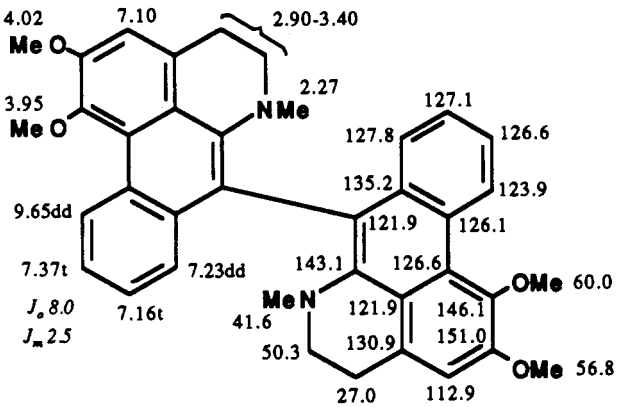


Each datum of one moiety is interchangeable with the corresponding value in the other half.

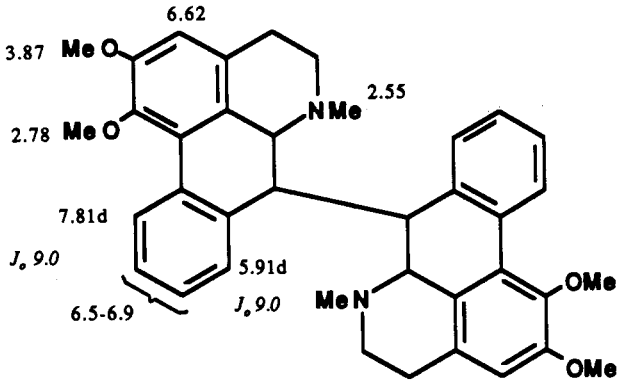


Each datum of one moiety is interchangeable with the corresponding value in the other half.

90. *N,N'*-DIMETHYLURABAINE (7,7'-Bisdehydronuciferine) $C_{38}H_{36}N_2O_4$ 584.2666
MP: 254° (2)
UV: 204 (4.52), 236 sh (4.36), 256 sh (4.60), 262 (4.63), 330 (4.08) (2)
^{1}H NMR: (400 MHz) (2)
^{13}C NMR: (2,22)
MS: $[M+1]^+$ 585 (34), 307 (99), 293 (100) (2)
SOURCES: Annonaceae: *Oxandra xylopioides* (1,2)

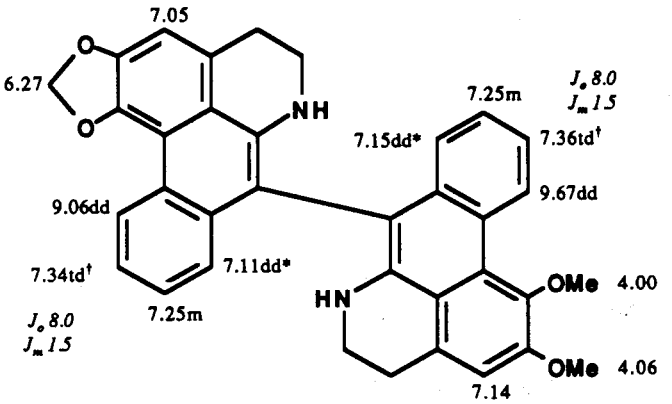


91. 7,7'-BISNUCIFERINE $C_{38}H_{40}N_2O_4$ 588.2978
MP: 262–264° (7)
UV: 212 (4.27), 232 sh (4.16), 264 (4.00), 314 sh (3.60) (2)
^{1}H NMR: (80 MHz) (7)
MS: $[M]^+$ 588 (15), 294 (40), 293 (100) (7)
SOURCES: Synthesis (2,7)



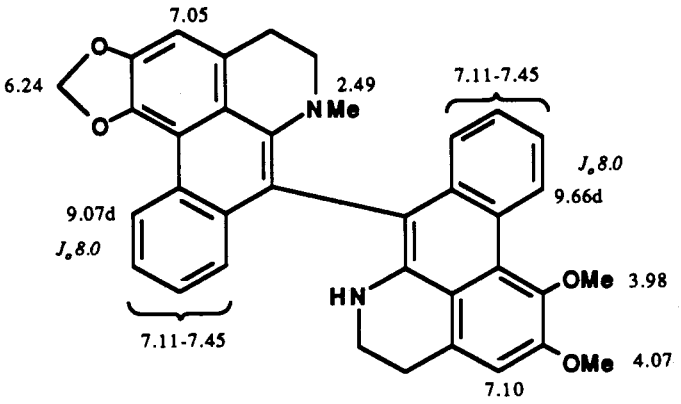
92. HETEROPSINE $C_{35}H_{28}N_2O_4$ 540.2042

UV: 256 sh (4.36), 263 (4.39), 329 (3.75) (22)
IR: (KBr) 3360, 2900, 2840, 1590, 1580, 1490, 1450, 1380, 1330, 1300, 1210, 1120, 1040, 1015, 760 (22)
^{1}H NMR: (250 MHz) (22)
MS: $[M]^+$ 540 (51), 270 (49), 263 (100), 232 (24) (22)
SOURCES: Annonaceae: *Unonopsis pacifica* (3), *Unonopsis spectabilis* (22)

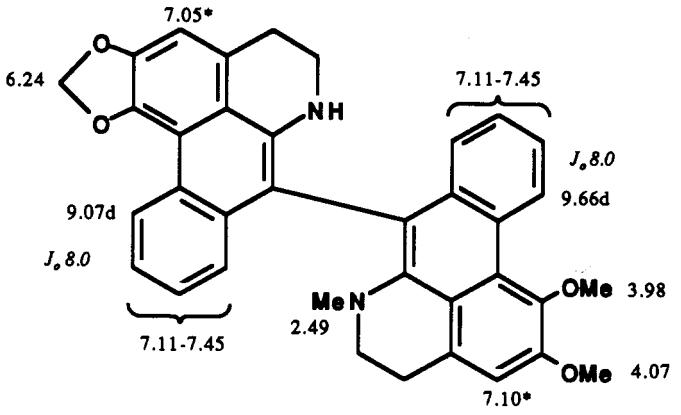


93. 6-*N*-METHYLHETEROPSINE $C_{36}H_{30}N_2O_4$ 554.2198

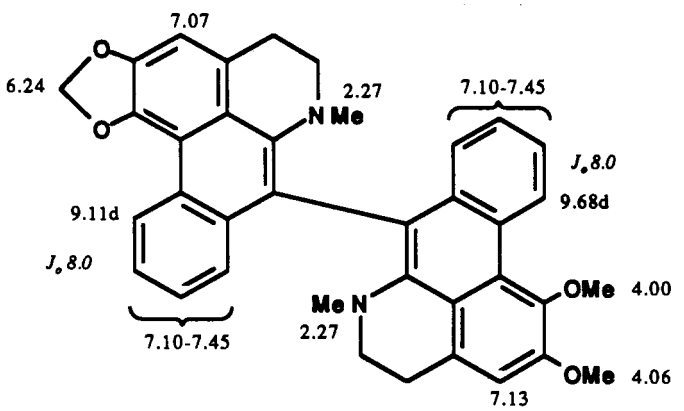
^{1}H NMR: (90 MHz) (22)
SOURCES: Synthesis (22)



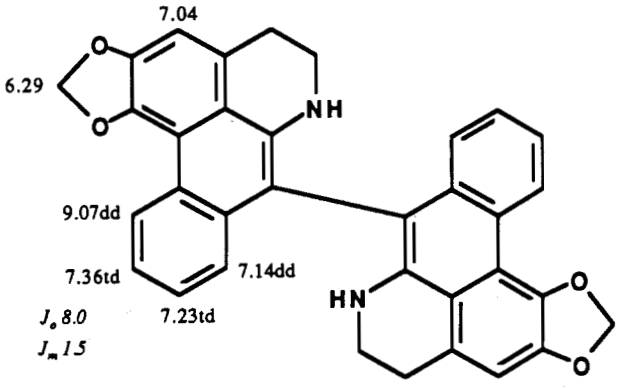
94. 6′-*N*-METHYLHETEROPSINE $C_{36}H_{30}N_2O_4$ 554.2198
^{1}H NMR: (90 MHz) (22)
SOURCES: Synthesis (22)



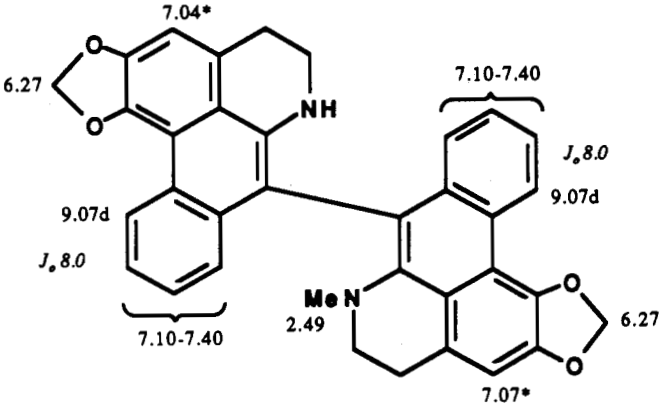
95. *N,N′*-DIMETHYLHETEROPSINE $C_{37}H_{32}N_2O_4$ 568.2354
UV: 242 (4.43), 248 sh (4.55), 254 (4.61), 259 (4.65), 265 (4.66), 285 sh (4.37), 331 (4.06) (22)
^{1}H NMR: (90 MHz) (22)
MS: $[M]^+$ 568 (68), 553 (11), 306 (72), 290 (100), 284 (28) (22)
SOURCES: Synthesis (22)



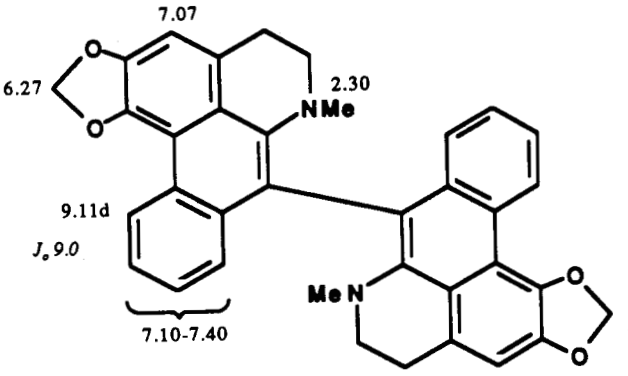
96. UNONOPSINE (7,7′-Bisdehydroanonaine) $C_{34}H_{24}N_2O_4$ 524.1730
UV: 214 (3.78), 252 sh (4.14), 260 (4.14), 328 (3.25), 380 (3.10) (18)
IR: (KBr) 3360, 2900, 2820, 1620, 1600, 1580, 1495, 1450, 1380, 1330, 1300, 1210, 1115, 1085, 950, 930 (22)
^{1}H NMR: (250 MHz) (22)
MS: $[M]^+$ 524 (100), 263 (46), 262 (46), 261 (41), 232 (22), 202 (11) (22)
SOURCES: Annonaceae: *Unonopsis pacifica* (3), *Unonopsis spectabilis* (22), Synthesis (18)



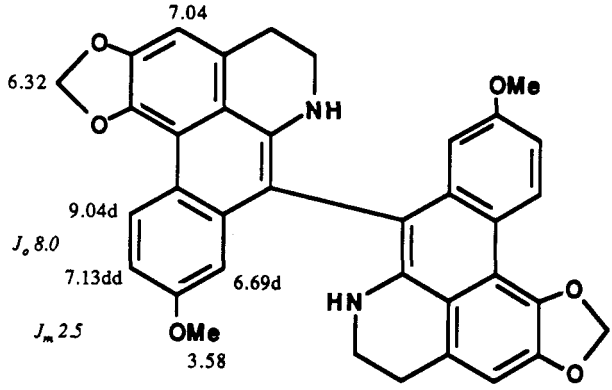
97. *N*-METHYLUNONOPSINE $C_{35}H_{26}N_2O_4$ 538.1886
UV: 235 sh (4.12), 249 sh (4.19), 255 (4.25), 261 (4.28), 267 (4.31), 284 sh (4.02), 335 (3.72), 400 (3.38) (22)
^{1}H NMR: (90 MHz) (22)
MS: $[M]^+$ 538 (100), 276 (34), 269 (17), 263 (22) (22)
SOURCES: Synthesis (22)



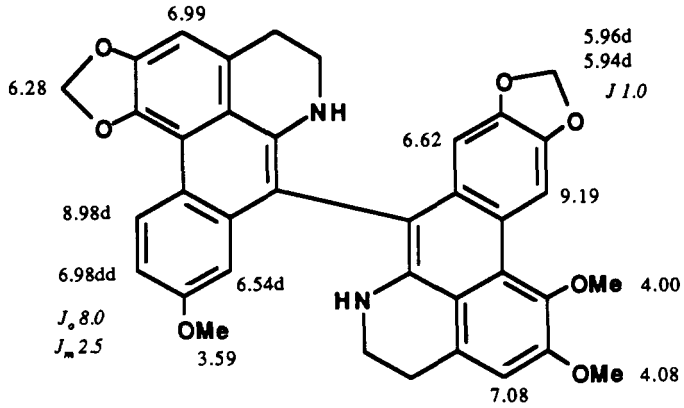
98. *N,N'*-DIMETHYLUNONOPSINE (7,7'-Bisdehydroroemerine) $C_{36}H_{28}N_2O_4$ 552.2042
UV: 235 (4.15), 256 sh (4.22), 261 (4.23), 276 sh (4.00), 336 (3.59) (22)
^{1}H NMR: (90 MHz) (22)
MS: $[M]^+$ 552 (33), 290 (100), 276 (21) (22)
SOURCES: Synthesis (22)



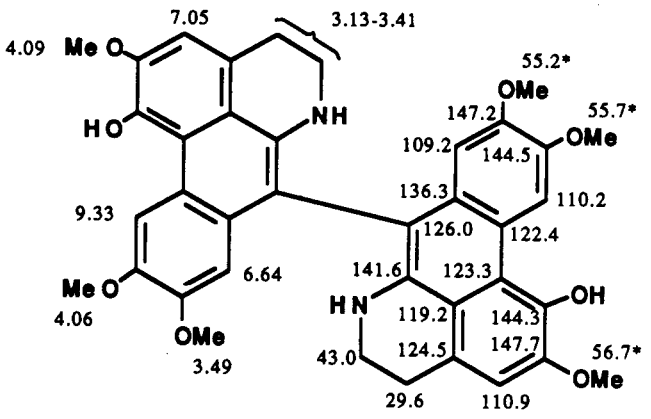
99. BISDEHYDROXYLOPINE $C_{36}H_{28}N_2O_6$ 584.1940
UV: 210 (4.16), 258 sh (4.19), 268 (4.21), 330 (3.75), 380 sh (3.29) (18)
^{1}H NMR: (250 MHz; $CDCl_3/CD_3OD$-5%) (18)
MS: (cims) $[M+1]^+$ 585 (100), 294 (10), 292 (10) (18)
SOURCES: Synthesis (18)



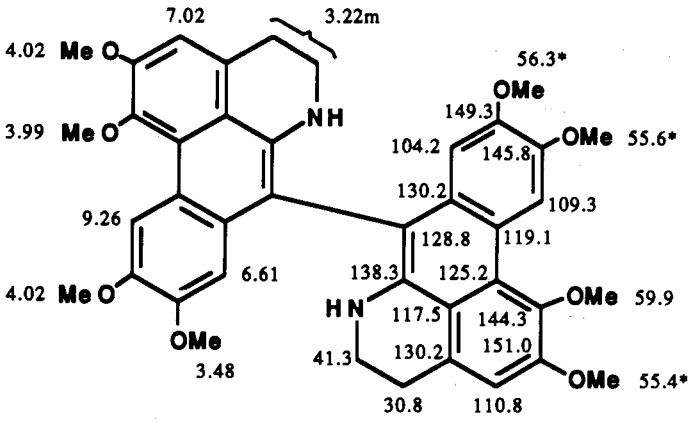
100. 7-DEHYDROXYLOPINYL-7′-DEHYDRONORNANTENINE $C_{37}H_{30}N_2O_7$ 614.2045
UV: 210 (4.13), 260 sh (4.15), 269 (4.16), 338 (3.27), 385 (3.15) (18)
^{1}H NMR: (250 MHz) (18)
MS: (cims) $[M+1]^+$ 615 (100), 324 (5), 322 (5), 294 (18), 292 (10) (18)
SOURCES: Synthesis (18)



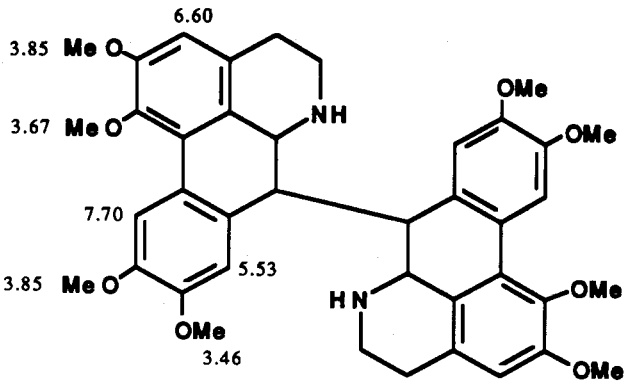
101. BIPOWINE (7,7′-Bisdehydrowilsonirine) $C_{38}H_{36}N_2O_8$ 648.2462
MP: 249–251° (19)
UV: 212 (4.14), 266 (4.51), 335 (3.87), 388 (3.66) (19)
^{1}H NMR: (500 MHz) (19)
^{13}C NMR: (19)
MS: $[M]^+$ 648 (100), 633 (28), 618 (6), 325 (40), 324 (50), 310 (28), 292 (17), 290 (21) (19)
SOURCES: Annonaceae: *Popowia pisocarpa* (19)



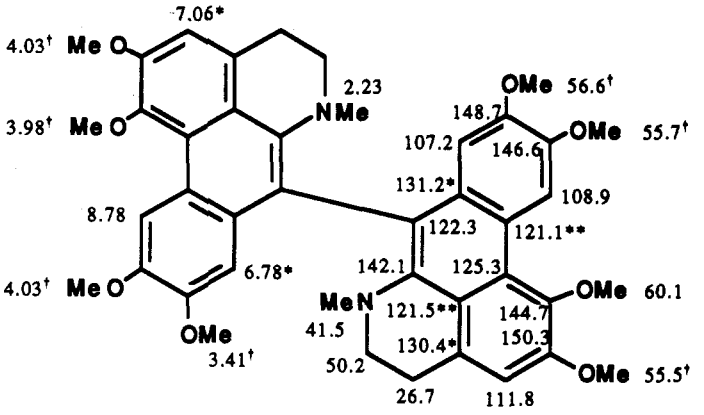
102. BISDEHYDRONORGLAUCINE (7,7′-Bisnordehydroglaucine) $C_{40}H_{40}N_2O_8$ 676.2774
MP: 251–252° (19)
UV: 208 sh (4.21), 215 (4.22), 265 (4.45), 273 (4.44), 340 (4.14), 390 sh (3.41) (19)
^{1}H NMR: (90 MHz) (19)
^{13}C NMR: (19)
MS: $[M]^+$ 676 (100), 662 (10), 661 (19), 338 (26), 322 (16) (19)
SOURCES: Synthesis (19)



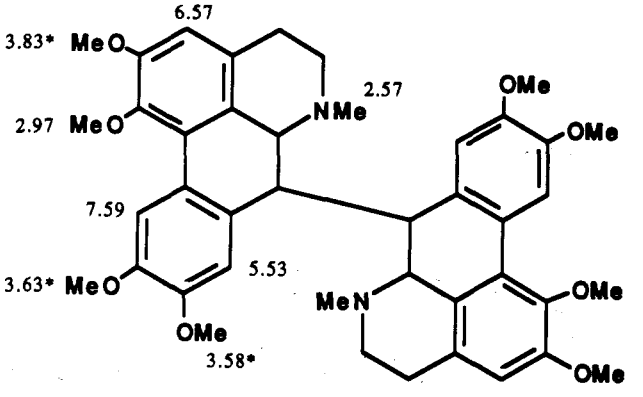
103. BISNORGLAUCINE $C_{40}H_{44}N_2O_8$ 680.3086
^{1}H NMR: (90 MHz) (19)
SOURCES: Synthesis (19)



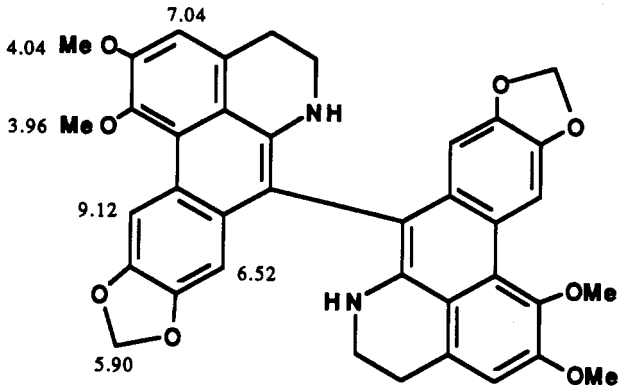
104. BISDEHYDROGLAUCINE $C_{42}H_{44}N_2O_8$ 704.3086
MP: 272–274° (7)
UV: 266 (4.91), 337 (4.27) (7)
^{1}H NMR: (80 MHz) (7)
^{13}C NMR: (8)
MS: $[M]^+$ 704 (58) (7)
SOURCES: Synthesis (7)



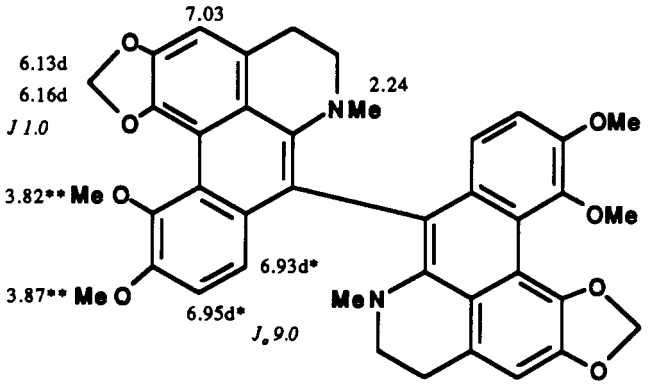
105. 7,7′-BISGLAUCINE $C_{42}H_{48}N_2O_8$ 708.3398
UV: 286 (4.26), 302 (4.24) (7)
^{1}H NMR: (80 MHz) (7)
MS: $[M]^+$ 708 (41), 354 (80), 353 (100) (7)
SOURCES: Synthesis (7)



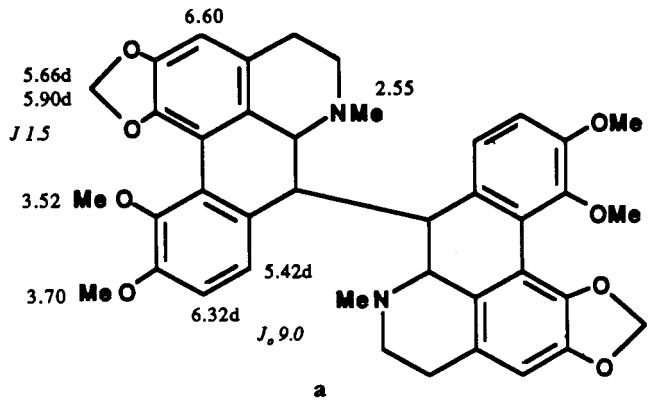
106. BISDEHYDRONORNANTENINE (7,7′-Bisnordehydronantenine) $C_{38}H_{32}N_2O_8$ 644.2150
MP: 285–290° (dec) (18)
UV: 212 (3.64), 257 (4.14), 280 sh (3.89), 336 sh (3.28), 395 (3.16) (18)
^{1}H NMR: (90 MHz) (18)
MS: (cims) $[M + 1]^+$ 645 (100), 324 (8), 322 (6) (18)
SOURCES: Synthesis (18)



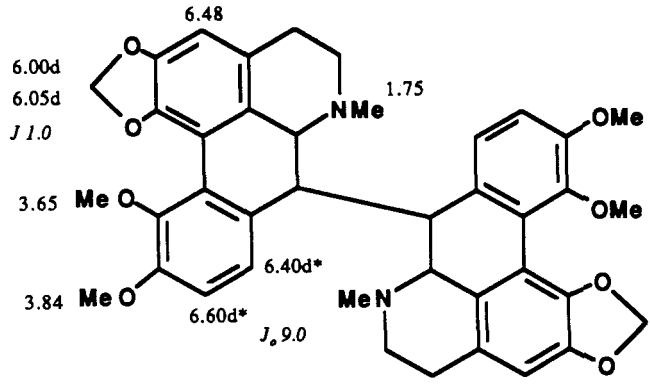
167. 7,7′-BISDEHYDRO-*O*-METHYLBULBOCAPNINE $C_{40}H_{36}N_2O_8$ 672.2462
MP: 187–194° (14)
UV: 253 (4.88), 263 (4.88), 344 (4.38), 400 sh (4.04) (14)
^{1}H NMR: (100 MHz) (14)
MS: $[M]^+$ 672, 657, 350 (14)
SOURCES: Synthesis (14)



168. 7,7′-BIS-*O*-METHYLBULBOCAPNINE $C_{40}H_{40}N_2O_8$ 676.2774
(Two isomers **a** and **b** with undetermined configuration)
UV: 226 (4.76), 280 (4.23), 310 (4.05) (14)
^{1}H NMR: **a** (100 MHz) (14)
b (90 MHz) (14)
MS: $[M]^+$ 676, 661, 338, 322, 279 (14)
SOURCES: Synthesis (14)



a



b

109. BIPOWINONE (7,7′-Bispancoridine) $C_{38}H_{28}N_2O_8$ 640.1838
UV: 237 (4.56), 248 sh (4.49), 278 sh (4.24), 290 (4.18), 300 sh (4.11), 410 (3.97), 474 (3.92), 506 sh (3.93); [(H^+) 209, 249, 265 sh, 285 sh, 300 sh, 410 sh, 433, 496] (19)
IR: (KBr) 1625 (19)
^{1}H NMR: (500 MHz) (19)
^{13}C NMR: (19)
MS: $[M]^+$ 640 (50), 625 (29), 609 (19), 321 (73), 320 (20), 307 (42), 290 (100) (19)
SOURCES: Annonaceae: *Popowia pisocarpa* (19)

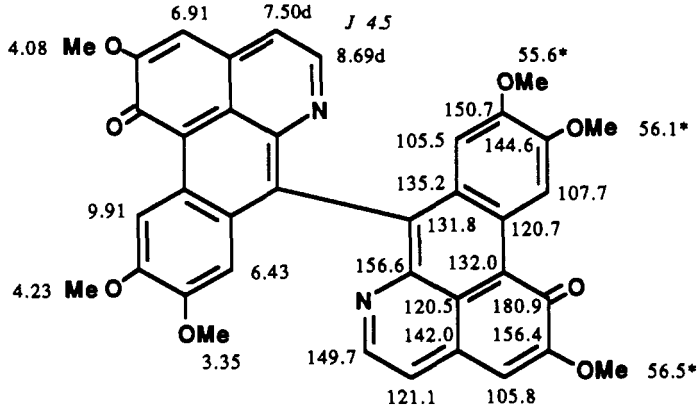


TABLE 5. Calculated Molecular Weights of New Dimeric Aporphinoids.

417.1570 Natalinine **85**	$C_{25}H_{23}NO_5$	540.2042 Heteropsine **92**	$C_{35}H_{28}N_2O_4$
431.1726 Coyhaiquinine **87**	$C_{26}H_{25}NO_5$	552.2042 *N,N′*-Dimethylunonopsine **98**	$C_{36}H_{28}N_2O_4$
524.1730 Unonopsine **96**	$C_{34}H_{24}N_2O_4$	554.2198 6-*N*-Methylheteropsine **93** 6′-*N*-Methylheteropsine **94**	$C_{36}H_{30}N_2O_4$
535.2610 Thaliadine **86**	$C_{30}H_{33}NO_8$	556.2354 Urabaine **88**	$C_{36}H_{32}N_2O_4$
538.1886 *N*-Methylunonopsine **97**	$C_{35}H_{26}N_2O_4$		

568.2354 $C_{37}H_{32}N_2O_4$
N,N'-Dimethylheteropsine **95**

570.2510 $C_{37}H_{34}N_2O_4$
N-Methylurabaine **89**

584.1940 $C_{36}H_{28}N_2O_6$
Bisdehydroxylopine **99**

584.2666 $C_{38}H_{36}N_2O_4$
N,N'-Dimethylurabaine **90**

588.2978 $C_{38}H_{40}N_2O_4$
7,7'-Bisnuciferine **91**

594.2728 $C_{36}H_{38}N_2O_6$
6'-*O*-Demethylkalashine **81**
Epiberbivaldine **83**
2'-Norpakistanine **80**

608.2886 $C_{37}H_{40}N_2O_6$
Epivaldivianine **84**
1-*O*-Methylporveniramine **79**
Rupancamine **82**

614.2045 $C_{37}H_{30}N_2O_7$
7-Dehydroxylopinyl-7'-dehydronornantenine **100**

640.1838 $C_{38}H_{28}N_2O_8$
Bipowinone **109**

644.2150 $C_{38}H_{32}N_2O_8$
Bisdehydronornantenine **106**

648.2462 $C_{38}H_{36}N_2O_8$
Bipowine **101**

652.3137 $C_{39}H_{44}N_2O_7$
Thalifaboramine **69**
Thalifaramine **68**

666.3293 $C_{40}H_{46}N_2O_7$
Thalifaronine **70**

668.3097 $C_{39}H_{44}N_2O_8$
Thalifaricine **75**

672.2462 $C_{40}H_{36}N_2O_8$
7,7'-Bisdehydro-*O*-methylbulbocapnine **107**

676.2774 $C_{40}H_{40}N_2O_8$
Bisdehydronorglaucine **102**
7,7'-Bis-*O*-methylbulbocapnine **108**

680.3086 $C_{40}H_{44}N_2O_8$
Bisnorglaucine **103**

682.3254 $C_{40}H_{46}N_2O_8$
Faberidine **62**
6-Northalicarpine **60**
Thalibulamine **67**
Thalifalandine **74**
Thalifarapine **71**
Thalifarazine **72**
Thalifaretine **73**

692.2723 $C_{40}H_{40}N_2O_9$
Vilaportine **65**

694.3254 $C_{41}H_{46}N_2O_8$
Dehydrothalifaberine **76**

698.3200 $C_{40}H_{46}N_2O_9$
Thalifasine **77**

704.3086 $C_{42}H_{44}N_2O_8$
Bisdehydroglaucine **104**

708.3398 $C_{42}H_{48}N_2O_8$
7,7'-Bisglaucine **105**

710.3554 $C_{42}H_{50}N_2O_8$
Hebridamine **66**

712.3360 $C_{41}H_{48}N_2O_9$
Faberonine **63**
Thalicarpine 2'-*N*-oxide **61**
Thalifabatine **78**

724.3347 $C_{42}H_{48}N_2O_9$
Dehydrohuangshanine **64**

TABLE 6. Botanical Sources of Natural Dimeric Aporphinoids.[a]

ANNONACEAE

Oxandra xylopioides
N,N'-Dimethylurabaine **90**
N-Methylurabaine **89**
Urabaine **88**

Polyalthia cauliflora var. *beccarii*
Beccapoline **57**
Beccapolinium **58**
Beccapolydione **59**
Polybeccarine **56**

Popowia pisocarpa
Bipowine **101**
Bipowinone **109**

Unonopsis pacifica
Heteropsine **92**
Unonopsine **96**

Unonopsis spectabilis
Heteropsine **92**
Unonopsine **96**
Urabaine **88**

BERBERIDACEAE

Berberis actinacantha
Berbivaldine **44**
Epiberbivaldine **83**
Pakistanamine **26**
Patagonine **47**
Rupancamine **82**

[a]Including those previously tabulated in "Dimeric Aporphinoid Alkaloids" I and II (15,16).

Berberis baluchistanica
Pakistanamine **26**
Pakistanine **23**

Berberis calliobotrys
Chitraline **38**
Kalashine **41**
Khyberine **40**

Berberis darwinii
1-*O*-Methylchitraline **39**

Berberis empetrifolia
Chitraline **38**
Coyhaiquine **52**
Coyhaiquinine **87**
Natalinine **85**
Patagonine **47**
Porveniramine **37**
Valdivianine **46**

Berberis hakeoides
Pakistanamine **26**
Patagonine **47**
Valdiberine **45**
Valdivianine **46**

Berberis orthobotrys
Chitraline **38**
Kalashine **41**

Berberis valdiviana
Berbivaldine **44**
Chitraline **38**
Epivaldiberine **48**
Epivaldivianine **84**
2′-Norpakistanine **80**
Patagonine **47**
Valdiberine **45**
Valdivianine **46**

Berberis zabeliana
Chitraline **38**

HERNANDIACEAE

Hernandia peltata
Dehydrothalmelatine **7**
Hebridamine **66**
2′-Northalicarpine **29**
6-Northalicarpine **60**
Thalicarpine **10**
Thalicarpine 2′-*N*-oxide **61**
Thalmelatine **6**
Vilaportine **65**

Hernandia ovigera
Dehydrothalicarpine **12**
Oxothalicarpine **11**
Thalicarpine **10**

RANUNCULACEAE

Thalictrum cultratum
Adiantifoline **16**
Thalibulamine **67**
Thalifaberine **35**
Thalifaramine **68**
Thalifarapine **71**
Thalifarazine **72**
Thalifaretine **73**
Thalifaricine **75**
Thalifaronine **70**
Thalilutine **13**
Thalmelatidine **18**
Thalmineline **17**

Thalictrum dasycarpum
Dehydrothalicarpine **12**
Thalicarpine **10**

Thalictrum dioicum
Pennsylvanine **9**
Thalicarpine **10**
Thalictrogamine **1**
Thalictropine **3**
Thalidoxine **8**
Thalmelatine **6**

Thalictrum faberi
Dehydrohuangshanine **64**
Dehydrothalifaberine **76**
Faberidine **62**
Faberonine **63**
Huangshanine **33**
Thalifabatine **78**
Thalifaberine **35**
Thalifabine **36**
Thalifaboramine **69**
Thalifalandine **74**
Thalifarapine **71**
Thalifasine **77**

Thalictrum fendleri
Thalicarpine **10**

Thalictrum flavum
Thalicarpine **10**

Thalictrum foetidum
Fetidine **19**
Thalicarpine **10**

Thalictrum minus
Adiantifoline **16**
O-Desmethyladiantifoline **14**
Thalicarpine **10**
Thalmelatidine **18**

Thalictrum minus race B
Adiantifoline **16**
O-Desmethyladiantifoline **14**
Thaliadanine **15**
Thalicarpine **10**

Thalictrum minus var. *adiantifolium*
Adiantifoline **16**

Thalictrum minus var. *majus*[b]

[b]*Thalictrum minus* var. *majus* is also known as *Thalictrum minus* var. *elatum*.

Dehydrothalicarpine **12**
O-Desmethyladiantifoline **14**
Thaliadine **86**
Thalicarpine **10**
Thalmelatidine **18**
Thalmelatine **6**
Thalmineline **17**

Thalictrum minus var. *microphyllum*
Bursanine **30**
Istanbulamine **34**
Iznikine **32**
2′-Noradiantifoline **31**
Uskudaramine **53**

Thalictrum minus var. *minus*
Thalmelatidine **18**

Thalictrum polygamum
Pennsylpavine **27**
Pennsylpavoline **28**
Pennsylvanamine **2**
Pennsylvanine **9**
Thalicarpine **10**
Thalictrogamine **1**
Thalictropine **3**
Thalipine **5**

Thalictrum revolutum
2′-Northalicarpine **29**
Pennsylvanine **9**
Revolutopine **20**
Thalicarpine **10**
Thalictrogamine **1**
Thalilutidine **4**
Thalilutine **13**
Thalipine **5**
Thalirevoline **21**
Thalirevolutine **22**
Thalmelatine **6**

Thalictrum sessile
Thalifarazine **72**

TABLE 7. Names and Synonyms of Dimeric Aporphinoids Cited in this Review.[a]

Adiantifoline **16** *ia*
Berbivaldine **44** *ia*
Bipowine **101** *na*
Bipowinone **109** *na*
7,7′-Bisdehydroanonaine **96** *na*
Bisdehydroglaucine **104** *na*
7,7′-Bisdehydro-*O*-methylbulbocapnine **107** *na*
Bisdehydronorglaucine **102** *na*
Bisdehydronornantenine **106** *na*
7,7′-Bisdehydronuciferine **90** *na*
7,7′-Bisdehydroroemerine **98** *na*
7,7′-Bisdehydrowilsonirine **101** *na*
Bisdehydroxylopine **99** *na*
7,7′-Bisglaucine **105** *na*
7,7′-Bis-*O*-methylbulbocapnine **108** *na*
7,7′-Bisnordehydroglaucine **102** *na*
7,7′-Bisnordehydronantenine **106** *na*
7,7′-Bisnordehydronuciferine **88** *na*
Bisnorglaucine **103** *na*
7,7′-Bisnuciferine **91** *na*
7,7′-Bispancoridine **109** *na*
Coyhaiquine **52** *ia*
Coyhaiquinine **87** *na*
Dehydrohuangshanine **64** *na*
Dehydrothalifaberine **76** *na*
Dehydrothalmelatine **7** *ia*
7-Dehydroxylopinyl-7′-dehydronornantenine **100** *na*
6′-*O*-Demethylkalashine **81** *na*
O-Desmethyladiantifoline **14** *ia*
N,N′-Dimethylheteropsine **95** *na*
N,N′-Dimethylunonopsine **98** *na*
N,N′-Dimethylurabaine **90** *na*
Epiberbivaldine **83** *na*
Epivaldivianine **84** *na*
Faberidine **62** *na*
Faberonine **63** *na*
Fetidine **19** *ia*
Foetidine **19** *ia*
Hebridamine **66** *na*
Heteropsine **92** *na*
Huangshanine **33** *ia*
1-*O*-Methylchitraline **39** *ia*
6-*N*-Methylheteropsine **93** *na*
6′-*N*-Methylheteropsine **94** *na*
1-*O*-Methylporveniramine **79** *na*
N-Methylunonopsine **97** *na*
N-Methylurabaine **89** *na*
Natalinine **85** *na*
2′-Norpakistanine **80** *na*
2′-Northalicarpine **29** *ia*
6-Northalicarpine **60** *na*
Pakistanamine **26** *ia*
Patagonine **47** *ia*
Revolutopine **20** *rs*
Rupancamine **82** *na*
Thaliadine **86** *na*
Thaliblastine **10** *ia*
Thalibulamine **67** *na*
Thalicarpine **10** *ia*
Thalicarpine 2′-*N*-oxide **61** *na*

[a]*rs*: revised structure; *sd*: additional physical and spectral data; *ia*: known dimeric aporphinoid isolated again; *na*: new dimeric aporphinoid.

Thalifabatine **78** *na*
Thalifaberine **35** *ia,sd*
Thalifabine **36** *ia,sd*
Thalifabomine **69** *na*
Thalifaboramine **69** *na*
Thalifalandine **74** *na*
Thalifaramine **68** *na*
Thalifarapine **71** *na*
Thalifarazine **72** *na*
Thalifaretine **73** *na*
Thalifaricine **75** *na*
Thalifaroline **71** *na*
Thalifaronine **70** *na*
Thalifasine **77** *na*
Thalilutine **13** *ia*
Thalmelatidine **18** *ia*
Thalmelatine **6** *ia*
Thalmineline **17** *ia*
Unonopsine **96** *na*
Urabaine **88** *na*
Valdiberine **45** *ia*
Valdivianine **46** *ia*
Vilaportine **65** *na*

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