

## DIMERIC APORPHINOID ALKALOIDS, II<sup>1</sup>

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Substantial progress has been registered during the past five years in the realm of the dimeric aporphinoid alkaloids. These classically include the aporphine-benzylisoquinoline dimers, the proaporphine-benzylisoquinoline dimers, and the hernandaline-type alkaloids which are oxidation products of the aporphine-benzylisoquinolines. To this listing must now be added novel structural types of dimeric aporphinoids, such as uskudaramine, which is an aporphine-benzylisoquinoline dimer bonded through carbon-to-carbon linkage, and the bisaporphines, which are dimeric aporphinoids also connected through carbon-to-carbon bonding.

The present review supplements an earlier one that appeared in 1979.<sup>1</sup> Twenty-eight dimers were known at that time; however, additional physical and spectral data have become available for some of these compounds since that time, and this information is included in the present review. Furthermore, some 30 new dimers have been described since 1979 and have been duly included here.

It is important to note that all of the known, naturally occurring dimeric aporphinoids have been found in only four plant genera: *Berberis* (Berberidaceae), *Hernandia* (Hernandiaceae), *Polyalthia* (Annonaceae), and *Thalictrum* (Ranunculaceae).

The present review has been organized along the following lines:

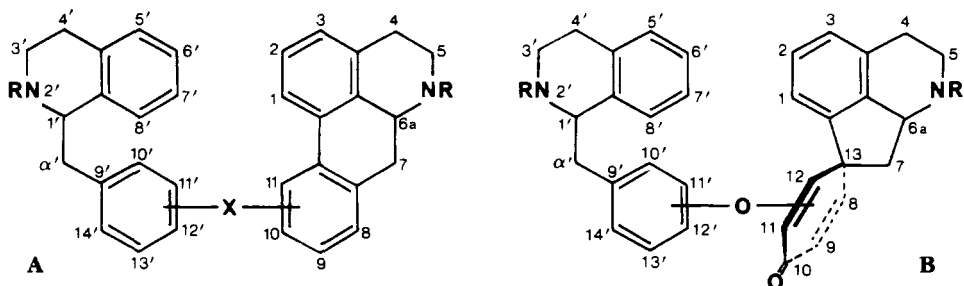
1. Additional data on previously reported dimeric aporphinoids (structures **1-28**)
  - a. physical and spectral data
  - b. new botanical sources
2. New dimeric aporphinoids<sup>2</sup> (structures **29-59**)
  - a. oxygen-bonded aporphine-benzylisoquinolines
    - i. reticuline-reticuline dimers (thalicarpine type **29-31**, foetidine type **32-33**)
    - ii. reticuline-coclaurine dimers (istanbulamine **34**, thalifaberine-type **35-36**)
    - iii. coclaurine-coclaurine dimers (pakistanine type **37-39**, kalashine type **40-42**, lumipakistanine **43**).
  - b. oxygen-bonded proaporphine-benzylisoquinolines (pakistanamine type **44-47**, epivaldiberine **48**)
  - c. oxygen-bonded and oxidized aporphine-benzylisoquinolines (**49-51**),<sup>3</sup> and proaporphine-benzylisoquinolines (**52**)
  - d. carbon-bonded dimers
    - i. aporphine-benzylisoquinoline dimer (**53**)
    - ii. bisaporphines (**54-59**)

<sup>1</sup>H. Guinaudeau, M. Leboeuf and A. Cavé, "Dimeric Aporphine-benzylisoquinoline and Aporphine-pavine Alkaloids," *J. Nat. Prod.*, **42**, 133 (1979).

<sup>2</sup>Synthetically derived proaporphine-aporphines and bisaporphines with unlikely biogenetic linkages (*viz.* reference 5, 11, 27, and 41) have not been taken into account in the present review.

<sup>3</sup>The known oxidized aporphine-benzylisoquinoline dimers hernandaline, hernandalinol, thaliadine, and dehydrothaliadine have been reported in "Aporphine Alkaloids," *Lloydia*, **38**, 275 (1975), and *J. Nat. Prod.*, **42**, 325 (1979).

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  $\epsilon$ ) and cd ( $\Delta\epsilon$  nm) spectra were obtained in EtOH or MeOH. Nmr spectra are in  $\text{CDCl}_3$ , chemical shifts are in ppm on the  $\delta$  scale, and the coupling constants are in Hz. Values with identical superscripts are interchangeable. Ir frequencies are in  $\text{cm}^{-1}$ . Melting points are in degrees centigrade and are uncorrected.

TABLE 1. Additional Physical and Spectral Data on Previously Reported Dimeric Aporphinoids

23	Pakistanine	$\text{C}_{37}\text{H}_{40}\text{N}_2\text{O}_6$	608.2886
	cd: +17.6 (310), +32.0 (274), -52.9 (244), +80.1 (212)	(17)	
24	1-O-Methylpakistanine	$\text{C}_{38}\text{H}_{42}\text{N}_2\text{O}_6$	622.3043
	cd: +12.8 (290), -61.2 (241), +24.7 (220)	(18)	
25	1,10-Di-O-Methylpakistanine	$\text{C}_{39}\text{H}_{44}\text{N}_2\text{O}_6$	636.3199
	cd: +14.5 (277), -76.1 (240), +66.6 (212)	(18)	
26	Pakistanamine <sup>a</sup>	$\text{C}_{38}\text{H}_{42}\text{N}_2\text{O}_6$	622.3043
	mp: 93-94°	(19)	
	$[\alpha]_D$ : +135° (c=0.5, MeOH)	(19)	
	cd: +7.7 (278), +4.8 (248), +15.0 (232), +6.6 (218)	(19)	

<sup>a</sup>The decoupling experiments and NOEDS studies of the 6a-H and 7-H were given. The stereochemistry at the C-13 proaporphine spiro-centre is the same as in berbivaldine 44.

TABLE 2. Known Natural Dimeric Aporphinoids Reisolated from New Sources

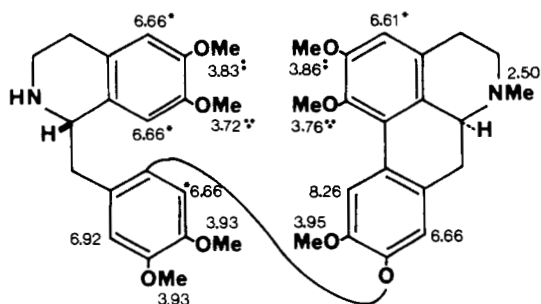
5	Thalipine	$\text{C}_{39}\text{H}_{44}\text{N}_2\text{O}_8$	668.3097
	Sources: <i>Thalictrum minus</i> (6) <i>Thalictrum revolutum</i> (46)		
6	Thalmelatine	$\text{C}_{40}\text{H}_{46}\text{N}_2\text{O}_8$	682.3254
	Sources: <i>Thalictrum minus</i> (6) <i>Thalictrum revolutum</i> (46)		
10	Thalicarpine (Thaliblastine) <sup>a</sup>	$\text{C}_{41}\text{H}_{48}\text{N}_2\text{O}_8$	696.3410
	Sources: <i>Thalictrum alpinum</i> (48) <i>Thalictrum foliosum</i> (4) <i>Thalictrum minus</i> (6,25,31,37) <i>Thalictrum revolutum</i> (46)		
15	Thaliadanine	$\text{C}_{41}\text{H}_{48}\text{N}_2\text{O}_9$	712.3359
	Sources: <i>Thalictrum minus</i> var. <i>microphyllum</i> (2)		
16	Adiantifoline	$\text{C}_{42}\text{H}_{50}\text{N}_2\text{O}_9$	726.3516
	Sources: <i>Thalictrum minus</i> var. <i>microphyllum</i> (2)		
18	Thalmelatidine	$\text{C}_{42}\text{H}_{48}\text{N}_2\text{O}_{10}$	740.3309
	Sources: <i>Thalictrum minus</i> var. <i>microphyllum</i> (2)		
21	Thalirevoline	$\text{C}_{40}\text{H}_{46}\text{N}_2\text{O}_8$	682.3254
	Sources: <i>Thalictrum revolutum</i> (46)		

<b>23</b>	Pakistanine Sources: <i>Berberis calliobotrys</i> (20) <i>Berberis empetrifolia</i> (7,9,10) <i>Berberis orthobotrys</i> (16-18)	$C_{37}H_{40}N_2O_6$	608.2886
<b>24</b>	1-O-methylpakistanine Sources: <i>Berberis calliobotrys</i> (20) <i>Berberis orthobotrys</i> (16,17) Synthesis (18)	$C_{38}H_{42}N_2O_6$	622.3043
<b>25</b>	1,10-Di-O-methylpakistanine Sources: Synthesis (18)	$C_{39}H_{44}N_2O_6$	636.3199
<b>26</b>	Pakistanamine Sources: <i>Berberis calliobotrys</i> (20) <i>Berberis empetrifolia</i> (12) <i>Berberis julianae</i> (26) <i>Berberis orthobotrys</i> (16-18) <i>Berberis valdiviana</i> (12)	$C_{38}H_{42}N_2O_6$	622.3042

<sup>a</sup>The biosynthesis of thalicarpine has been extensively studied (3,31,37). Owing to its cytotoxic and antitumor activities (thalicarpine=thaliblastine), a number of pharmacological (1,21,22,28,30,32,34,35,39,40,42-44) and toxicological (21,22,33,36,45) studies have been published. An hplc method for the determination of thalicarpine and derivatives has been reported (38).

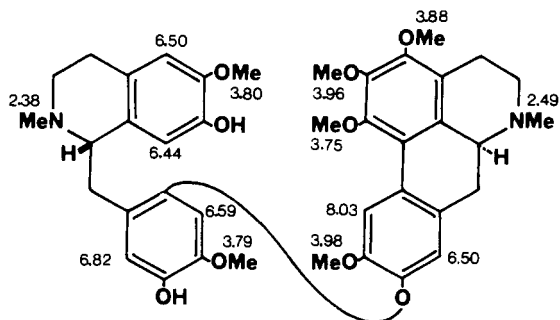
TABLE 3. Completely New Dimeric Aporphinoids<sup>a</sup>

<b>29</b>	Northalicarpine [ $\alpha$ ]D: +108° (c=0.25, MeOH) (47) UV: 282 (4.21), 303sh (4.08), 314sh (3.97) (47) IR: (CHCl <sub>3</sub> ) 3002, 2940, 2860, 2840, 2800, 1620, 1602, 1580, 1500, 1465, 1400, 1380, 1360, 1325, 1270, 1170, 1150, 1085, 1005, 880, 850 (47) PMR: (60 MHz) (47) MASS: 682 (M <sup>+</sup> , 0.4), 490 (4), 341 (11), 340 (2), 325 (2), 324 (1), 206 (69), 192 (100), 177 (3), 176 (10), 148 (5) (47) Sources: <i>Thalictrum revolutum</i> (47)	$C_{40}H_{46}N_2O_8$	682.3254
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<b>30</b>	Bursanine [ $\alpha$ ]D: +117° (c=0.17, MeOH) (13) UV: 209 (4.81), 221sh (4.75), 283 (4.34), 304sh (4.24), 314 (4.19) (13) PMR: (200 MHz) (13) MASS: 698 (M <sup>+</sup> , 0.1), 696 (0.7), 506 (7), 476 (4), 369 (1), 192 (100) (13) CD: -5.2 (306), -2.6 (290), -4.9 (275), +49.0 (241), -11.0 (214) (13) Sources: <i>Thalictrum minus</i> var. <i>microphyllum</i> (13)	$C_{40}H_{46}N_2O_9$	698.3200
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<sup>a</sup>Not previously reported in "Dimeric aporphine-benzylisoquinoline and aporphine-pavine alkaloids," *J. Nat. Prod.*, **42**, 133 (1979).

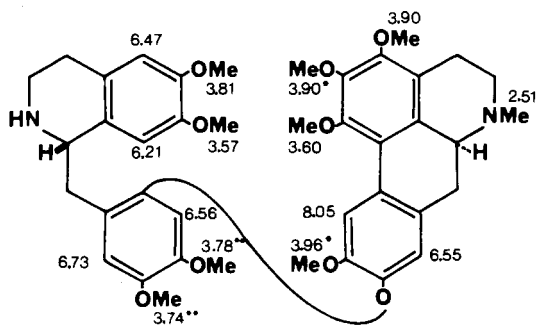
**31** 2'-NoradiantifolineC<sub>41</sub>H<sub>48</sub>N<sub>2</sub>O<sub>9</sub> 712.3359[α]<sub>D</sub>: +39° (c=0.08, MeOH) (15)

UV: 208 (4.77), 220sh (4.69), 280 (4.31), 296sh (4.24), 302sh (4.17), 314 (4.10) (15)

PMR: (200 MHz) (15)

MASS: 712 (M<sup>+</sup>, 0.3), 710 (0.8), 681 (0.6), 520 (6), 519 (7), 490 (3), 369 (1), 192 (100), 177 (8) (15)

CD: -5.3 (304), -4.0 (287), -5.9 (272), +38.0 (246), -16.0 (213) (15)

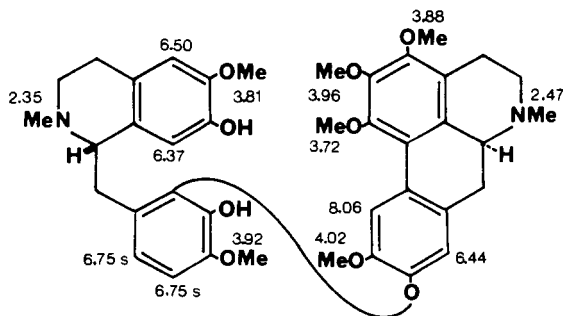
Sources: *Thalictrum minus* var. *microphyllum* (15)**32** IznikineC<sub>40</sub>H<sub>46</sub>N<sub>2</sub>O<sub>9</sub> 698.3200[α]<sub>D</sub>: +76° (c=0.07, MeOH) (13)

UV: 208 (4.68), 222sh (4.54), 281 (4.17), 301sh (4.03), 312 (3.98) (13)

PMR: (200 MHz) (13)

MASS: 697 (0.3), 608 (0.8), 506 (1.7), 367 (0.8), 192 (100) (13)

CD: -6.6 (305), -1.3 (285), -5.3 (273), +27.5 (241), -3.4 (220) (13)

Sources: *Thalictrum minus* var. *microphyllum* (13)**33** HuangshanineC<sub>42</sub>H<sub>50</sub>N<sub>2</sub>O<sub>9</sub> 726.3503[α]<sub>D</sub>: +121° (c=0.4, MeOH) (29)

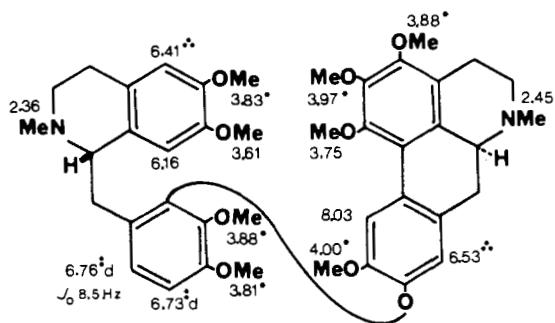
UV: 281 (4.41), 302 (4.20), 312 (4.13) (29)

PMR: (200 MHz) (29)

MASS: 725, 520, 370, 354, 206 (100) (29)

CD: -4.8 (301), -4.9 (277), +29.2 (243) (29)

Sources: *Thalictrum faberi* (29)



**34** Istanbulamine

$C_{39}H_{44}N_2O_8$  668.3097

$[\alpha]_D$ : +60° ( $c=0.09$ , MeOH) (13)

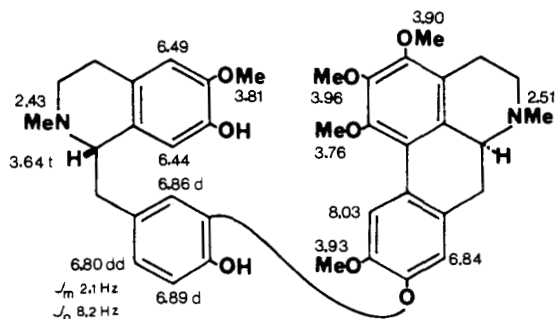
UV: 205 (4.87), 225sh (4.75), 270sh (4.20), 282 (4.34), 304sh (4.15), 313 (4.12) (13)

PMR: (200 MHz) (13)

MASS: 668 ( $M^+$ , 0.2), 666 (1), 638 (0.6), 608 (0.3), 476 (4), 475 (6), 369 (0.4), 354 (1), 192 (100) (13)

CD: -15.3 (306), -8.7 (284), -10.9 (275), +61.2 (243), -16.0 (210) (13)

Sources: *Thalictrum minus* var. *microphyllum* (13)



**35** Thalifaberine

$C_{41}H_{48}N_2O_8$  696.3398

$[\alpha]_D$ : +95° ( $c=0.4$ , MeOH) (29)

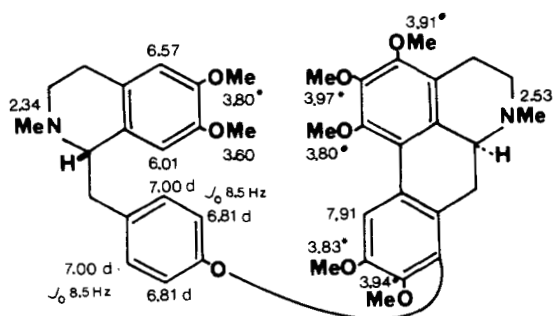
UV: 282 (4.36), 310sh (3.98) (29)

PMR: (60 MHz) (29)

MASS: 696 ( $M^+$ , <0.1), 490, 206 (100) (29)

CD: -2.5 (299), -3.2 (278), +29.9 (241) (29)

Sources: *Thalictrum faberi* (29)



**36** THALIFABINE

$C_{41}H_{46}N_2O_9$  710.3191

$[\alpha]_D$ : +78° ( $c=0.5$ , MeOH) (29)

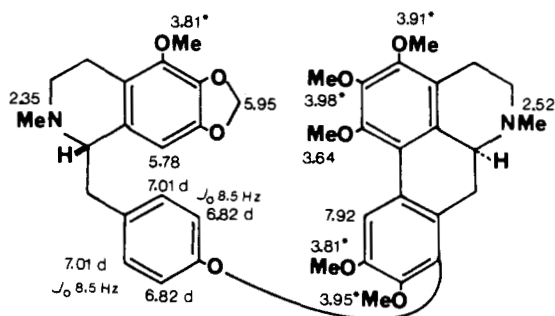
UV: 282 (4.30), 310sh (4.03) (29)

PMR: (29)

MASS: 710 ( $M^+$ ), 490, 220 (100) (29)

CD: -8.4 (295), -11.3 (280), +87.9 (242) (29)

Sources: *Thalictrum faberi* (29)

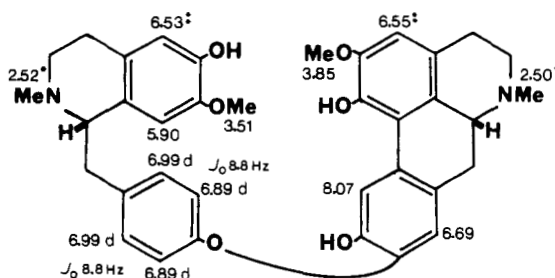
**37 PORVENIRAMINE** $C_{36}H_{38}N_2O_6$  594.2728[ $\alpha$ ]<sub>D</sub>: +40° (c=0.1, MeOH) (12)

UV: 225 (4.66), 267sh (4.19), 277 (4.26), 307 (3.90) (12)

PMR: (360 MHz) (12)

MASS: 594 ( $M^+$ , 0.2), 402 (7), 295 (2), 192 (100) (12)

CD: +5.4 (305), +8.2 (274), -24.0 (244), +22.0 (212) (12)

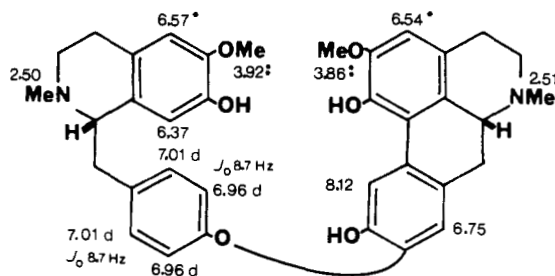
Sources: *Berberis empetrifolia* (12)**38 CHITRALINE** $C_{36}H_{38}N_2O_6$  594.2728[ $\alpha$ ]<sub>D</sub>: +136° (c=0.17, MeOH) (12)

UV: 220sh (4.51), 268sh (4.03), 278 (4.10), 292sh (3.94), 304 (3.96) (17)

PMR: (200 MHz) (17)

MASS: 593, 401, 192 (100), 177 (17)

CD: +12.3 (310), +14.0 (272), -52.7 (244), +35.1 (215) (17)

Sources: *Berberis calliobotrys* (20), *B. empetrifolia* (12), *B. orthobotrys* (17), *B. valdiviana* (12), *B. zabeliana* (20)**39 NO NAME (1-O-METHYLCHITRALINE)** $C_{37}H_{40}N_2O_6$  608.2886[ $\alpha$ ]<sub>D</sub>: +29° (c=0.4, MeOH) (12)

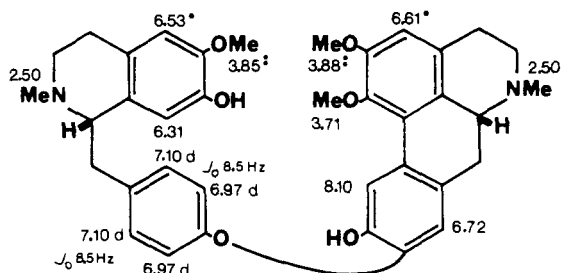
UV: 210 (4.60), 224 (4.54), 267sh (4.04), 278 (4.17), 304 (3.97) (12)

PMR: (360 MHz) (12)

MASS: 608 ( $M^+$ , 0.2), 416 (4), 206 (10), 192 (100) (12)

CD: +2.6 (304), +7.2 (275), -33.0 (239), +27.0 (210) (12)

Sources: Synthesis (12)

**40 KHYBERINE** $C_{36}H_{38}N_2O_6$  594.2728

MP: 145-147° (20)

[ $\alpha$ ]<sub>D</sub>: -47° (c=0.06, MeOH) (12)

UV: 220sh (4.53), 264sh (3.97), 272 (4.02), 292sh (3.80), 304 (3.70) (20)

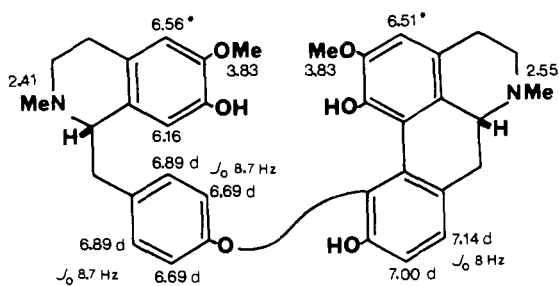
PMR: (200 MHz) (20)

MASS: 593, 403, 402, 296, 192 (100), 107 (20)

CD: +3.2 (308), +3.1 (292), +3.4 (275), -54.0 (234), +36.0 (214) (20)

Sources: *Berberis calliobotrys* (20)

Synthesis (12)

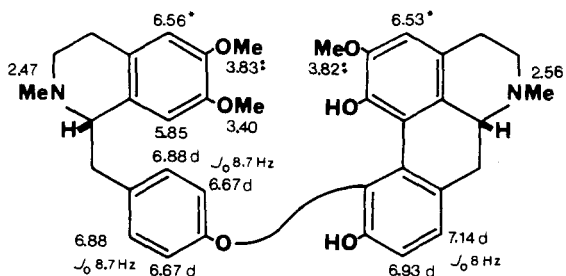
**41 KALASHINE** $C_{37}H_{40}N_2O_6$  608.2886

UV: 220 (4.54), 272 (4.04), 290sh (3.74), 304 (3.70) (18)

PMR: (200 MHz) (18)

MASS: 607, 403, 311, 296, 206 (100), 107 (18)

CD: +9.5 (280), -50.6 (236), +41.0 (214) (18)

Sources: *Berberis calliobotrys* (20), *B. orthobotrys* (16,18)**42 1-O-METHYLKALASHINE** $C_{38}H_{42}N_2O_6$  622.3043

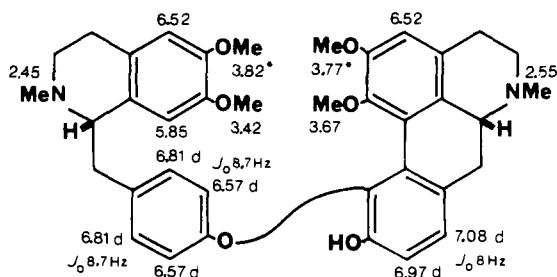
UV: 222 (4.51), 272 (4.00), 302 (3.68) (18)

PMR: (200 MHz) (18)

MASS: 620, 417, 310, 206 (100), 190 (18)

CD: +6.6 (285), -5.5 (260), -60.8 (236), +37.2 (212) (18)

Sources: Synthesis (16,18)

**43 LUMIPASKISTANINE** $C_{38}H_{42}N_2O_6$  622.3043

MP: 112-114° (19)

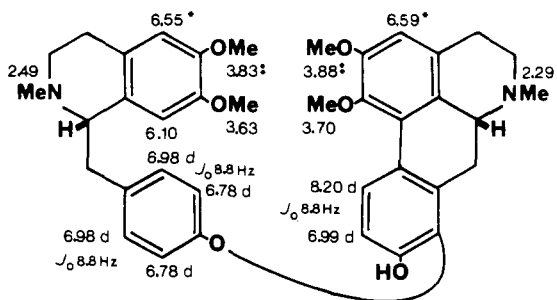
[ $\alpha$ ]<sub>D</sub>: +117° (c=0.5, EtOH) (19)

UV: 220sh (4.87), 282 (4.55) (19)

PMR: (200 MHz) (19)

MASS: 621, 416, 310, 206 (100), 190 (19)

Sources: Synthesis (19)

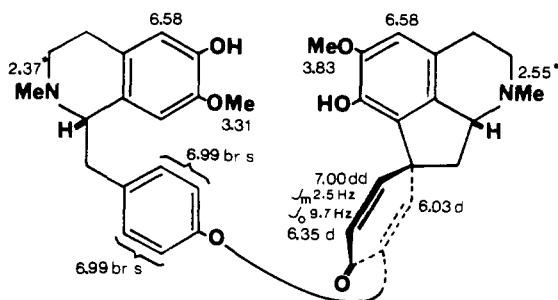
**44 BERBIVALDINE** $C_{36}H_{38}N_2O_6$  594.2728[ $\alpha$ ]<sub>D</sub>: +140° (c=0.4, MeOH) (12)

UV: 214 (4.72), 231sh (4.63), 284 (4.03) (12)

PMR: (360 MHz) (12)

MASS: 594 ( $M^+$ , 4), 593 (5), 402 (4), 192 (100), 177 (17) (12)

CD: -0.5 (302), +6.4 (278), +2.4 (242), +12 (212) (12)

Sources: *Berberis valdiviana* (12)**45 VALDIBERINE** $C_{36}H_{38}N_2O_6$  594.2728[ $\alpha$ ]<sub>D</sub>: +91° (c=0.4, MeOH) (12)

UV: 212 (4.71), 231sh (4.57), 284 (4.02) (12)

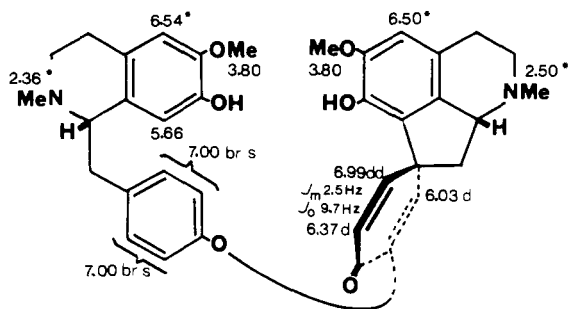
PMR: (360 MHz) (12)

MASS: 594 ( $M^+$ , 0.2), 402 (3), 192 (100), 177 (34) (12)

CD: -0.6 (300), +10 (277), +5.1 (239), +14 (230) (12)

Sources: *Berberis valdiviana* (12)





## 46 VALDIVIANINE

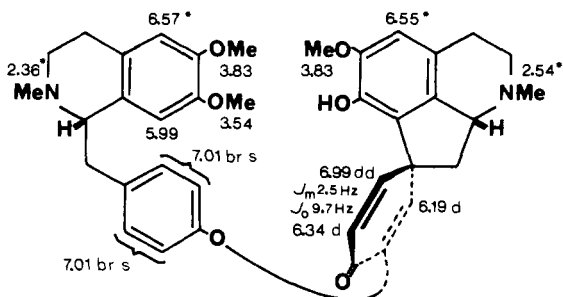
C<sub>37</sub>H<sub>40</sub>N<sub>2</sub>O<sub>6</sub> 608.2886[α]<sub>D</sub>: +120° (c=0.2, MeOH) (12)

UV: 214 (4.74), 232sh (4.72), 282 (4.12) (12)

PMR: (360 MHz) (12)

MASS: 608 (M<sup>+</sup>, 0.1), 402 (4), 206 (100), 204 (14) (12)

CD: -0.7 (300), +8.0 (278), +3.8 (235), +17.0 (211) (12)

Sources: *Berberis empetrifolia* (12), *B. valdiviana* (12)

## 47 PATAGONINE

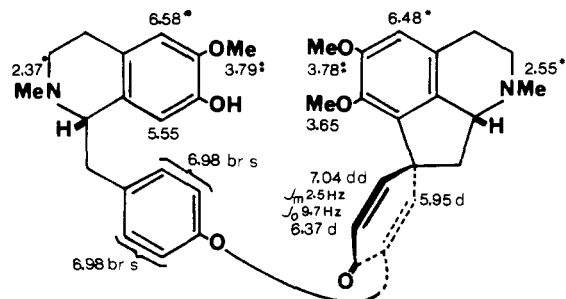
C<sub>37</sub>H<sub>40</sub>N<sub>2</sub>O<sub>6</sub> 608.2886[α]<sub>D</sub>: +192° (c=0.2, MeOH) (12)

UV: 204 (4.70), 231sh (4.50), 283 (4.01) (12)

PMR: (360 MHz) (12)

MASS: 608 (M<sup>+</sup>, 0.2), 416 (5), 398 (4), 294 (4), 192 (100), 177 (24) (12)

CD: +8.8 (279), +5.5 (248), +32.0 (230) (12)

Sources: *Berberis empetrifolia* (12), *B. valdiviana* (12)

## 48 EPIVALDIBERINE

C<sub>36</sub>H<sub>38</sub>N<sub>2</sub>O<sub>6</sub> 594.2728[α]<sub>D</sub>: +31° (c=0.1, MeOH) (12)

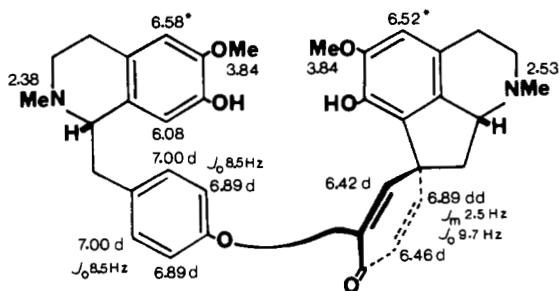
UV: 210 (4.65), 232sh (4.47), 284 (3.86) (12)

PMR: (360 MHz) (12)

MASS: 593 (0.1), 402 (5), 192 (100) (12)

CD: +2.3 (300), +3.7 (277), -5.2 (246), +8.7 (212) (12)

Sources: *Berberis valdiviana* (12)



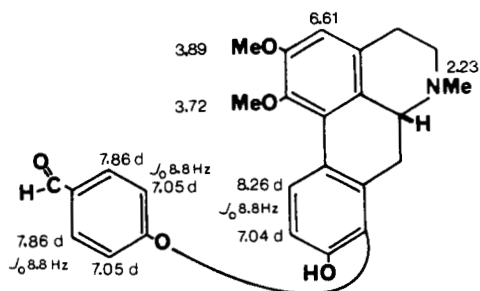
## 49 NEOLUMIPAKISTANINE

C<sub>26</sub>H<sub>25</sub>NO<sub>5</sub> 431.1726

PMR: (200 MHz) (19)

MASS: 431 (M<sup>+</sup>), 416, 400 (100), 388, 357, 312 (19)

Sources: Synthesis (19)



## 50 NO NAME

C<sub>26</sub>H<sub>27</sub>NO<sub>5</sub> 433.1888[α]<sub>D</sub>: -29° (c=0.04, MeOH) (8)

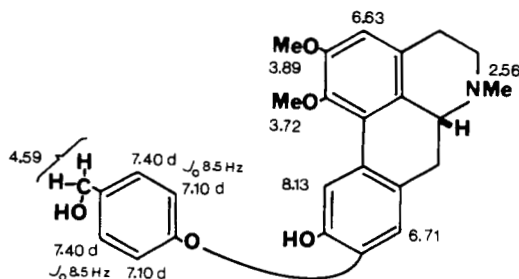
UV: 217 (4.36), 227 (3.99), 304 (3.84) (8)

PMR: (200 MHz) (8)

MASS: 433 (M<sup>+</sup>, 21), 416 (16), 310 (4), 204 (100) (8)

CD: +1.9 (300), +4.2 (274), -23 (239), positive tail at 210 (8)

Sources: Synthesis (8)



## 51 NO NAME

C<sub>29</sub>H<sub>29</sub>NO<sub>7</sub> 503.1936

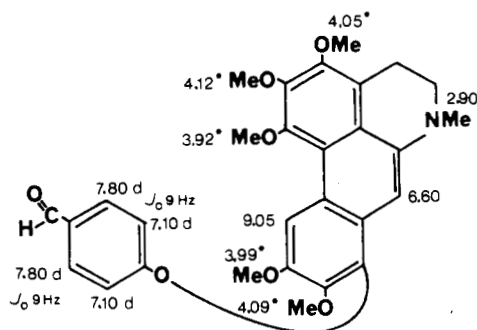
UV: 257 (5.13), 270 (5.13), 335 (4.49) (29)

PMR: (29)

MASS: 501 (M<sup>+</sup>)\* (29)

Sources: Synthesis (29)

\*This value was inadvertently given instead of the more exact 503 (29).

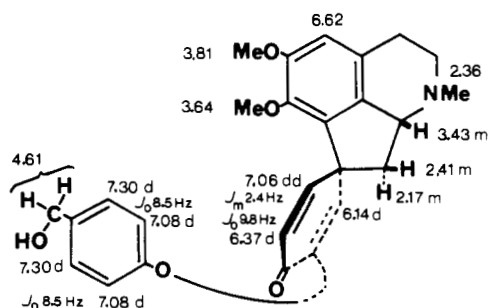
**52 COYHAIQUINE** $C_{26}H_{27}NO_5$  433.1888[ $\alpha$ ]<sub>D</sub>: +28° (c=0.02, MeOH) (8)

UV: 210 (4.44), 231sh (4.24), 283 (3.63) (8)

PMR: (360 MHz) (8)

MASS: 433 ( $M^+$ , 100), 432 (85), 416 (30), 404 (58), 310 (32) (8)

CD: +5.2 (270), +1.3 (246), +6.5 (229) (8)

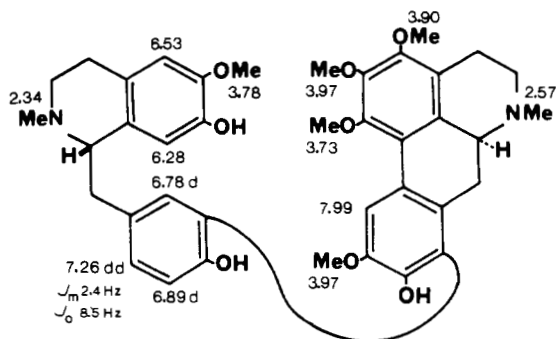
Sources: *Berberis empetrifolia* (8)**53 USKUDARAMINE** $C_{39}H_{44}N_2O_8$  668.3097[ $\alpha$ ]<sub>D</sub>: +84° (c=0.15, MeOH) (14)

UV: 209 (4.78), 221sh (4.73), 286 (4.35), 300sh (4.18), 312sh (4.06) (14)

PMR: (360 MHz) (14)

MASS: 668 ( $M^+$ , 0.1), 667 (0.1), 608 (0.3), 476 (3.3), 461 (1.2), 460 (2.6), 446 (1.8), 416 (0.7), 192 (100), 177 (13) (14)

CD: -4.8 (297), -3.9 (280), +48 (244), -32 (212) (14)

Sources: *Thalictrum minus* var. *microphyllum* (14)**54 DESOXYDECAHYDROBECCAPOLINE** $C_{37}H_{34}N_2O_6$  602.2415

MP: 178-182° (23)

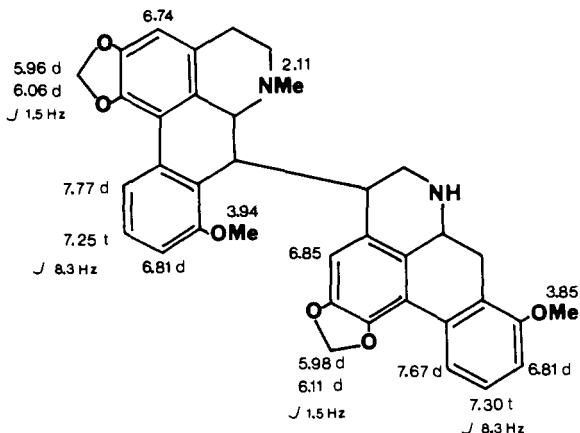
[ $\alpha$ ]<sub>D</sub>: 0 (23)

UV: 225 (4.59), 244sh (4.35), 276 (4.35), 304sh (3.98), 328sh (3.76) (24)

PMR: (90 MHz) (24)

MASS: 602 ( $M^+$ , 1), 601 (12), 598 (5), 309 (10), 308 (41), 307 (38), 305 (14), 294 (16), 292 (100), 290 (16), 278 (10), 277 (16), 276 (26), 266 (16) (24)

Sources: Synthesis (23) (24)

**55 BISTEPHANINE** $C_{38}H_{36}N_2O_6$  616.2511

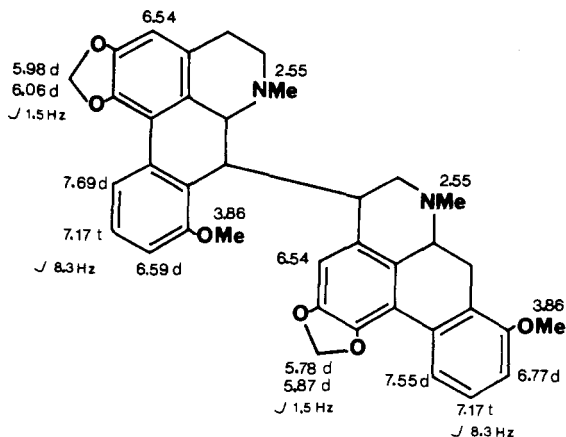
MP: 136-140° (23)

[ $\alpha$ ]<sub>D</sub>: 0 (23)

UV: 225 (4.61), 244sh (4.34), 278 (4.32), 306sh (3.94), 330 (3.67) (24)

PMR: (90 MHz) (24); also in  $C_6D_6$  (23)MASS: 616 ( $M^+$ , 1), 615 (3), 614 (6), 308 (36), 307 (100), 306 (37), 305 (74), 293 (13), 292 (40), 291 (11), 290 (42), 266 (9) (24)

Sources: Synthesis (23) (24)

**56 POLYBECCARINE** $C_{36}H_{22}N_2O_6$  578.1476

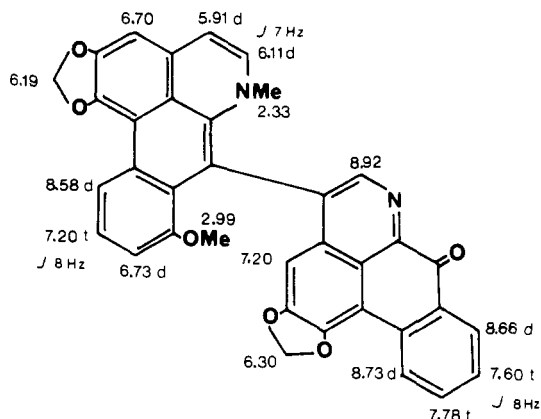
MP: &gt;280° (24)

UV: 216 (4.66), 234 (4.70), 248sh (4.68), 273 (4.55), 308 (4.17), 334 (4.05), 406 (4.24), 425 (4.23); [(HCl) 216, 234sh, 266, 280sh, 340, 396, 470] (24)

IR: (KBr) 1650 (24)

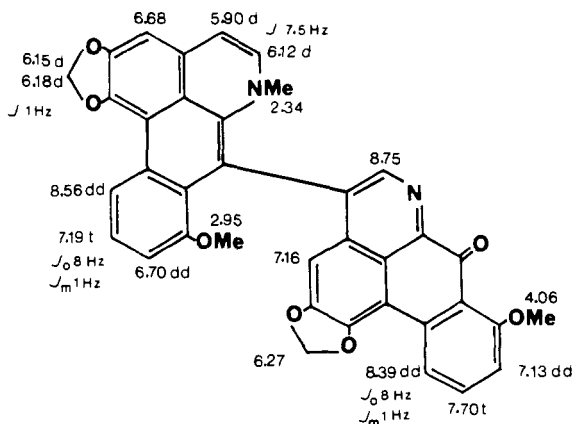
PMR: (250 MHz) (24)

MASS: 579 (40), 578 ( $M^+$ , 100), 563 (15), 548 (11), 532 (11), 305 (5), 291 (12), 290 (18), 276 (9), 275 (5) (24)Sources: *Polyalthia cauliflora* var. *beccarii* (24)

**57 BECCAPOLINE** $C_{37}H_{24}N_2O_7$  608.1582MP:  $>280^\circ$  (23)

UV: 218sh (4.52), 231 (4.63), 250sh (4.53), 279 (4.40), 310 (4.01), 366sh (4.07), 428 (4.22), 440 (4.21); [(HCl) 223sh, 234, 265, 279, 339, 384, 486] (23)

IR: (KBr) 1650 (23)

PMR: (CDCl<sub>3</sub>/CD<sub>3</sub>OD, 250 MHz) (23); also in TFA (24)MASS: 609 (40), 608 (M<sup>+</sup>, 100), 594 (17), 578 (7), 562 (7), 305 (3), 304 (3), 291 (4), 290 (13), 276 (2), 260 (2) (24)Sources: *Polyalthia cauliflora* var. *beccarii* (23) (24)**58 BECCAPOLINIUM** $C_{38}H_{27}N_2O_7$  623.1816MP:  $250^\circ$  (dec) (24)

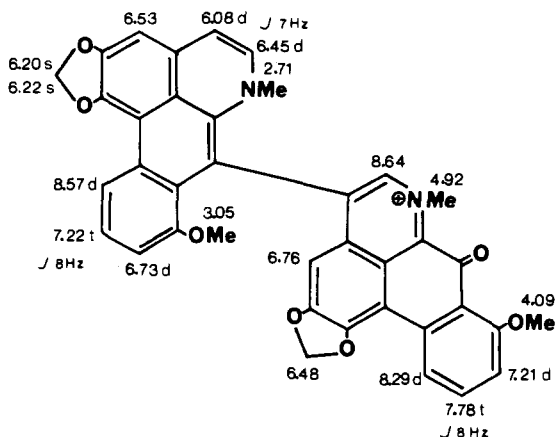
UV: 218 (4.71), 235sh (4.67), 262 (4.57), 280sh (4.50), 338sh (3.97), 384 (4.18), 440sh (4.05), 480sh (3.90) (23)

IR: (KBr) 1650 (23)

PMR: (400 MHz) (23)

MASS: 625 (75), 612 (26), 611 (100), 597 (16), 582 (15), 316 (30), 308 (11), 302 (20), 301 (23), 286 (20) (24)

Sources: *Polyalthia cauliflora* var. *beccarii* (23) (24)

**59 BECCAPOLYDIONE** $C_{37}H_{22}N_2O_9$  638.1324MP:  $>280^\circ$  (24)

UV: 218sh (4.53), 224 (4.70), 250 (4.67), 276 (4.47), 314 (4.19), 325sh (4.19), 370sh (4.02), 438 (4.29); [(HCl) 220, 245, 257sh, 290, 325, 384, 464] (24)

IR: (KBr) 1665, 1650 (24)

PMR: (250 MHz) (24)

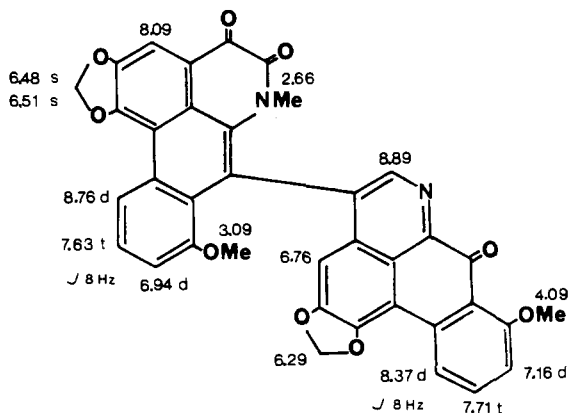
MASS: 639 (43), 638 ( $M^+$ , 100), 624 (36), 597 (18), 337 (32), 335 (32), 308 (30), 307 (21), 305 (29), 290 (25) (24)Sources: *Polyalthia cauliflora* var. *beccarii* (24)

TABLE 4. Calculated Molecular Weights of New Dimeric Aporphinoids

431.1726	$C_{26}H_{25}NO_5$	594.2728	$C_{36}H_{38}N_2O_6$
Neolumipakistanine	<b>49</b>	Porveniramine	<b>37</b>
		Chitraline	<b>38</b>
433.1888	$C_{26}H_{27}NO_5$	Khyberine	<b>40</b>
No name	<b>50</b>	Berbivaldine	<b>44</b>
Coyhaiquine	<b>52</b>	Valdiberine	<b>45</b>
		Epivaldiberine	<b>48</b>
503.1936	$C_{29}H_{29}NO_7$	602.2415	$C_{37}H_{34}N_2O_6$
No name	<b>51</b>	Desoxydecahydrobeccapoline	<b>54</b>
578.1476	$C_{36}H_{22}N_2O_6$	608.1582	$C_{37}H_{24}N_2O_7$
Polybeccarine	<b>56</b>	Beccapoline	<b>57</b>

TABLE 4. *Continued*

608.2886	$C_{37}H_{40}N_2O_6$	682.3254	$C_{40}H_{46}N_2O_8$
1-O-Methylchitraline	<b>39</b>	Northalicarpine	<b>29</b>
Kalashine	<b>41</b>		
Valdivianine	<b>46</b>		
Patagonine	<b>47</b>	696.3398	$C_{41}H_{48}N_2O_8$
		Thalifaberine	<b>35</b>
616.2571	$C_{38}H_{36}N_2O_6$		
Bistephanine	<b>55</b>	698.3200	$C_{40}H_{46}N_2O_9$
		Bursanine	<b>30</b>
622.3043	$C_{38}H_{42}N_2O_6$	Iznikine	<b>32</b>
1-O-Methylkalashine	<b>42</b>		
Lumipakistanine	<b>43</b>		
623.1816	$C_{38}H_{27}N_2O_7$	710.3191	$C_{41}H_{46}N_2O_9$
Beccapolinium	<b>58</b>	Thalifabine	<b>36</b>
638.1324	$C_{37}H_{22}N_2O_9$	712.3359	$C_{41}H_{48}N_2O_9$
Beccapolydione	<b>59</b>	2'-Noradiantifoline	<b>31</b>
668.3097	$C_{39}H_{44}N_2O_8$	726.3503	$C_{42}H_{50}N_2O_9$
Istanbulamine	<b>34</b>	Huangshanine	<b>33</b>
Uskudaramine	<b>53</b>		

TABLE 5. Names and Synonyms of Dimeric Aporphinoids Cited in This Review

Adiantifoline	<b>16</b> <i>ia</i>	Neolumipakistanine	<b>49</b> <i>na</i>
Beccapoline	<b>57</b> <i>na</i>	2'-Noradiantifoline	<b>31</b> <i>na</i>
Beccapolinium	<b>58</b> <i>na</i>	Northalicarpine	<b>29</b> <i>na</i>
Beccapolydione	<b>59</b> <i>na</i>	Pakistanamine	<b>26</b> <i>sd, ia</i>
Berbivaldine	<b>44</b> <i>na</i>	Pakistanine	<b>23</b> <i>sd, ia</i>
Bistephanine	<b>55</b> <i>na</i>	Patagonine	<b>47</b> <i>na</i>
Bursanine	<b>30</b> <i>na</i>	Polybeccarine	<b>56</b> <i>na</i>
Chitraline	<b>38</b> <i>na</i>	Porveniramine	<b>37</b> <i>na</i>
Coyhaiquine	<b>52</b> <i>na</i>	Thaliadanine	<b>15</b> <i>ia</i>
Desoxydecahydrobeccapoline	<b>54</b> <i>na</i>	Thaliblastine	<b>10</b> <i>ia</i>
1,10-Di-O-methylpakistanine	<b>25</b> <i>sd</i>	Thalicarpine	<b>10</b> <i>ia</i>
Epivaldiberine	<b>48</b> <i>na</i>	Thalifaberine	<b>35</b> <i>na</i>
Huangshanine	<b>33</b> <i>na</i>	Thalifabine	<b>36</b> <i>na</i>
Istanbulamine	<b>34</b> <i>na</i>	Thalipine	<b>5</b> <i>ia</i>
Iznikine	<b>32</b> <i>na</i>	Thalirevoline	<b>21</b> <i>ia</i>
Kalashine	<b>41</b> <i>na</i>	Thalmelatidine	<b>18</b> <i>ia</i>
Khyberine	<b>40</b> <i>na</i>	Thalmelatine	<b>6</b> <i>ia</i>
Lumipakistanine	<b>43</b> <i>na</i>	Uskudaramine	<b>53</b> <i>na</i>
1-O-Methylchitraline	<b>39</b> <i>na</i>	Valdiberine	<b>45</b> <i>na</i>
1-O-Methylkalashine	<b>42</b> <i>na</i>	Valdivianine	<b>46</b> <i>na</i>
1-O-Methylpakistanine	<b>24</b> <i>sd, ia</i>		

*ia* = known dimeric aporphinoid isolated again*na* = new dimeric aporphinoid alkaloid*sd* = additional physical and spectral data

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