

THE HOMOAPORPHINE ALKALOIDS

EMILIA TOJO

Departamento de Química Orgánica, Universidad de Santiago de Compostela, Spain

ABSTRACT.—A list of naturally occurring and synthetic homoaporphines is presented. Spectral and optical data are provided, together with botanical sources.

The homoaporphines are alkaloids derived from phenethylisoquinoline precursors by direct intramolecular oxidative coupling (1). They incorporate nucleus **A** and are always penta-oxygenated at C-1, -2, -10, -11, and -12. The nitrogen function in ring B is usually *N*-methylated, but it may also be secondary.

Seventeen naturally occurring homoaporphines are presently known. They have been obtained from seven genera of higher plants, namely *Androcymbium*, *Colchicum*, *Kreysigia*, *Bulbocodium*, *Iphigenia*, *Merendera*, and *Gloriosa*, all belonging to the botanical family Liliaceae (Table 1). All homoaporphines originating from the genus *Androcymbium* have so far proven to be dextrorotatory and thus incorporate the C-6a *S* configuration. On the other hand, alkaloids from *Colchicum* may be either dextrorotatory or levorotatory.

The alkaloids are here arranged in an ascending order of substitution, and some purely synthetic but relevant compounds have also been included. Because most synthetic

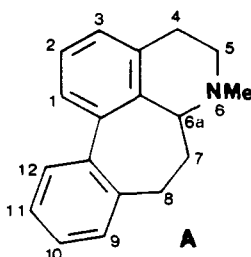


TABLE 1. Botanical Sources of Homoaporphinoid Alkaloids.

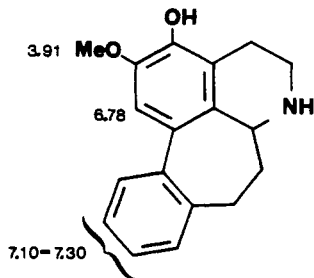
Liliaceae	(+)-Szovitsamine [36]
	(+)-Szovitsine [46]
	Szovitsinine [28]
<i>Androcymbium</i>	
(+)-Androbine [27]	
(+)-Androcimine [34]	
(+)-Androcine [33]	
(+)-Kreysigine [30]	
(+)- <i>O</i> -Methylkreysigine [38]	
(+)-Norandrobine [26]	
(+)-Nor- <i>O</i> -methylkreysigine [37]	
(+)-Szovitsamine [36]	
<i>Bulbocodium</i>	
(-)-Kreysigine [31]	
<i>Colchicum</i>	
(-)-1, 12-Dihydroxy-2, 10, 11-trimethoxy-homoaporphine [25]	
(+)-Floramultine [20]	
(-)-Kreysigine [31]	
(+)- <i>O</i> -Methylkreysigine [38]	
	(+)-Szovitsamine [36]
	(+)-Szovitsine [46]
	Szovitsinine [28]
	<i>Gloriosa</i>
	(-)-1, 12-Dihydroxy-2, 10, 11-trimethoxy-homoaporphine [25]
	(+)-Floramultine [20]
	<i>Iphigenia</i>
	(+)-Floramultine [20]
	(-)-Multifloramine [23]
	<i>Kreysigia</i>
	(-)-Floramultine [21]
	(±)-Kreysigine [32]
	(-)-Multiflorine [23]
	<i>Merendera</i>
	(+)-Baytopine [29]
	(+)-Floramultine [20]

homoaporphines are less highly oxygenated than the natural products, they appear at the beginning of the present listing.

^1H -nmr chemical shifts (δ values) are quoted for CDCl_3 solutions unless specified otherwise; coupling constants are in Hz. Values with identical superscripts are interchangeable. It is worth pointing out that in the nmr spectra of naturally occurring (and pentasubstituted) homoaporphines, the H-8 signal appears at higher field than H-3. This order, however, is reversed with the synthetic tetraoxygenated homoaporphines where it is the H-3 signal that is further upfield.

If more than one reference is cited, it is the first reference only that is actually quoted in this review. Uv wavelengths are in nm, and $\log \epsilon$ values are given in parentheses. Only values for λ max are quoted. Ir values are in cm^{-1} . Melting points are in degrees centigrade and are uncorrected. Circular dichroism data refer to $\Delta\epsilon$ values.

1. (\pm)-3-HYDROXY-2-METHOXY-NORHOMOAPORPHINE



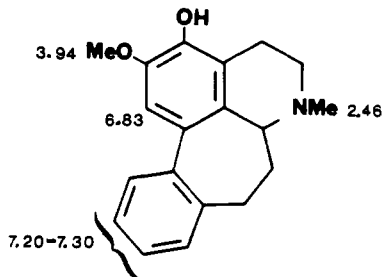
$\text{C}_{18}\text{H}_{19}\text{O}_2\text{N}$: 281.1416

MP: 198–199.5° (dec.) (2)

^1H NMR: ($\text{CDCl}_3/\text{CD}_3\text{OD}$; 100 MHz) (2)

SOURCES: Synthesis (2)

2. (\pm)-3-HYDROXY-2-METHOXY-HOMOAPORPHINE



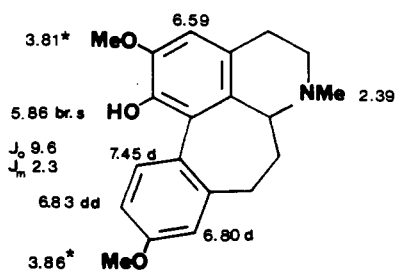
$\text{C}_{19}\text{H}_{21}\text{O}_2\text{N}$: 295.1572

MP: 200.5–201.5° (dec.) (2)

^1H NMR: (100 MHz) (2)

SOURCES: Synthesis (2)

3. (\pm)-1-HYDROXY-2,10-DIMETHOXY-HOMOAPORPHINE



$\text{C}_{20}\text{H}_{23}\text{O}_3\text{N}$: 325.1678

MP: 72–73° (3)

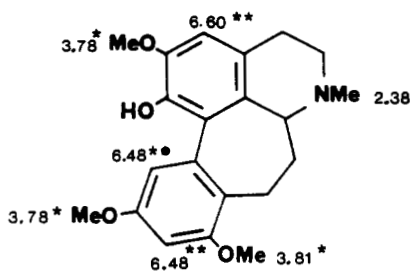
UV: (MeOH) 260 (4.17), 290 (3.77) (3)

IR: (CHCl_3) 3505 (3)

^1H NMR: (60 MHz) (3)

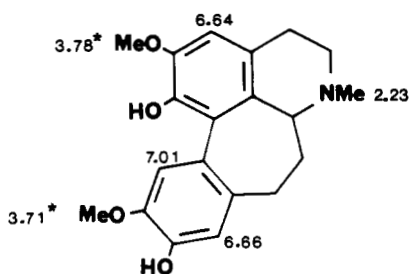
SOURCES: Synthesis (3)

4. (±)-1-HYDROXY-2,9,11-TRI-METHOXYHOMOAPORPHINE



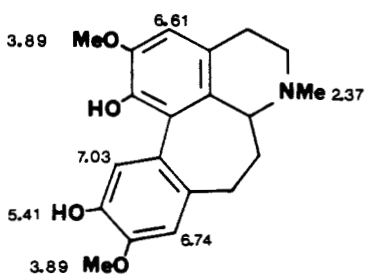
$C_{21}H_{25}O_4N$: 355.1783
 MP: 190–191° (4)
 UV: (MeOH) 260 (4.23), 293 (4.03) (4)
 IR: (CHCl₃) 3500 (4)
¹H NMR: (60 MHz) (4)
 MS: 355 [M]⁺ (4)
 SOURCES: Synthesis (4)

5. (±)-1,10-DIHYDROXY-2,11-DI-METHOXYHOMOAPORPHINE



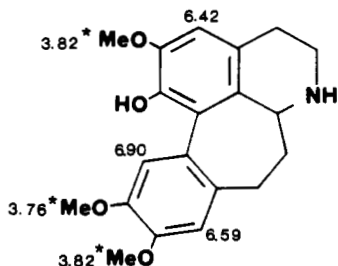
$C_{20}H_{23}O_4N$: 341.1627
 MP: 241–242° (3)
 UV: (MeOH) 264 (4.13), 293 (4.04) (3)
 IR: (CHCl₃) 3475 (3)
¹H NMR: [(CD₃)₂SO, 100 MHz] (5)
 SOURCES: Synthesis (3, 5–7)

6. (±)-1,11-DIHYDROXY-2,10-DI-METHOXYHOMOAPORPHINE



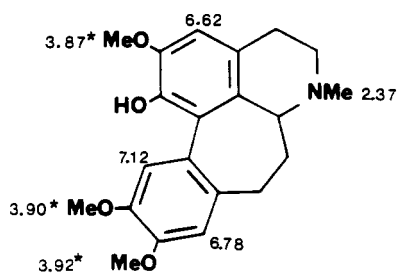
$C_{20}H_{23}O_4N$: 341.1627
 MP: 185–187° (3)
 UV: (MeOH) 264 (4.14), 291 (4.11) (3)
¹H NMR: (100 MHz) (8), also in (CD₃)₂SO (3) and CF₃CO₂H (3)
 SOURCES: Synthesis (3, 5, 8, 9)

7. (±)-1-HYDROXY-2,10,11-TRI-METHOXYNORHOMOAPORPHINE



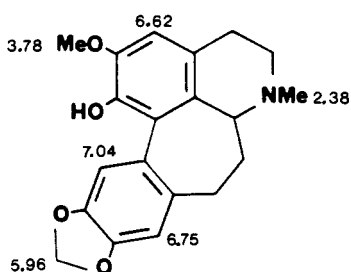
$C_{20}H_{23}O_4N$: 341.1627
¹H NMR: (60 MHz) (2)
 SOURCES: Synthesis (2)

8. (±)-1-HYDROXY-2,10,11-TRI-METHOXYHOMOAPORPHINE



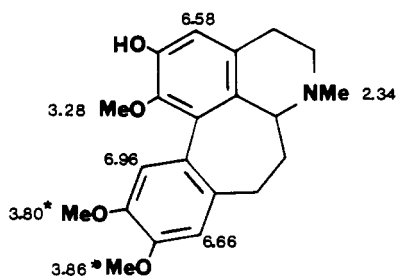
$C_{21}H_{25}O_4N$: 355.1783
 MP: 195–196° (10)
 IR: (CHCl₃) 3540 (5)
¹H NMR: (100 MHz) (5)
 MS: [M]⁺ 355 (10)
 SOURCES: Synthesis (2, 5, 10, 11)

9. (±)-1-HYDROXY-2-METHOXY-10,11-METHYLENEDIOXYHOMOAPORPHINE



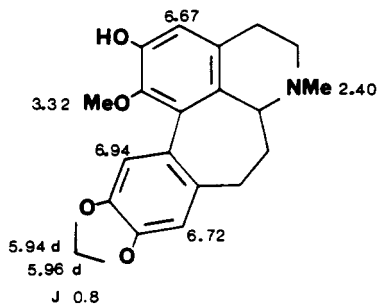
$C_{20}H_{21}O_4N$: 339.1470
 MP: 139–141° (12)
 IR: (CHCl₃) 3540 (12)
¹H NMR: (100 MHz) (12)
 SOURCES: Synthesis (12, 13)

10. (±)-2-HYDROXY-1,10,11-TRI-METHOXYHOMOAPORPHINE



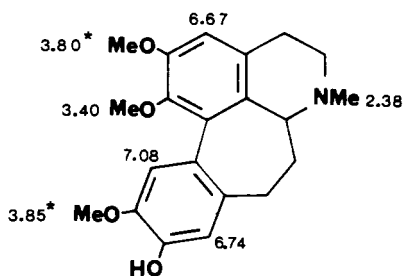
$C_{21}H_{25}O_4N$: 355.1783
 MP: 170–171° (14)
 IR: (CHCl₃) 3550 (14)
¹H NMR: (100 MHz) (14)
 SOURCES: Synthesis (14)

11. (±)-2-HYDROXY-1-METHOXY-10,11-METHYLENEDIOXYHOMOAPORPHINE



$C_{20}H_{21}O_4N$: 339.1470
 MP: 178–181° (14)
 IR: (CHCl₃) 3520 (14)
¹H NMR: (100 MHz) (14)
 SOURCES: Synthesis (14)

12. (±)-10-HYDROXY-1,2,11-TRI-METHOXYHOMOAPORPHINE



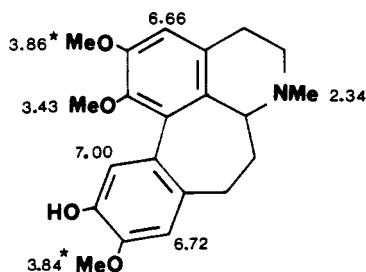
$C_{21}H_{25}O_4N$: 355.1783

IR: 3530 (5)

1H NMR: (100 MHz) (5)

SOURCES: Synthesis (5)

13. (±)-11-HYDROXY-1,2,10-TRI-METHOXYHOMOAPORPHINE



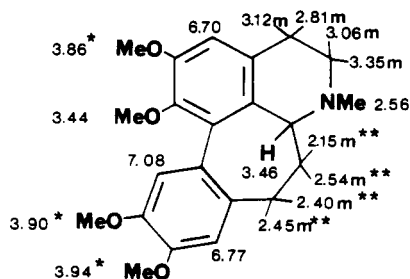
$C_{21}H_{25}O_4N$: 355.1783

IR: 3530 (5)

1H NMR: (100 MHz) (5)

SOURCES: Synthesis (5)

14. (±)-HOMOGLAUCINE



$C_{22}H_{27}O_4N$: 369.1940

MP: 234–236° (MeI) (15), 239–242° (HCl) (16)

IR: (CHCl₃) 1599 (16)

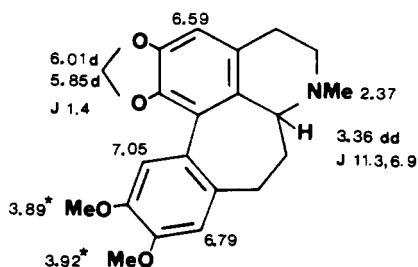
1H NMR: (500 MHz) (16)

^{13}C NMR: (62.83 MHz) (15)

MS: $[M]^+$ 369 (28), 368 (13), 354 (18), 338 (100), 33.6 (5), 322 (10), 232 (9) (15)

SOURCES: Synthesis (8, 14–16)

15. (±)-HOMODICENTRINE



$C_{21}H_{23}O_4N$: 353.1627

MP: 257–259° (MeI) (15)

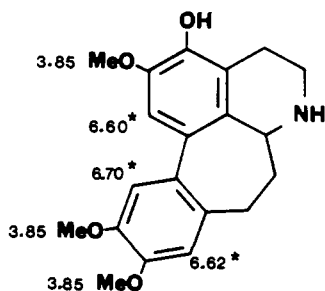
1H NMR: (250 MHz) (15)

^{13}C NMR: (62.83 MHz) (15)

MS: $[M]^+$ 353 (45), 352 (26), 338 (13), 323 (61), 322 (100), 310 (24), 308 (27), 306 (11), 294 (8), 280 (10), 216 (27), 190 (37) (15)

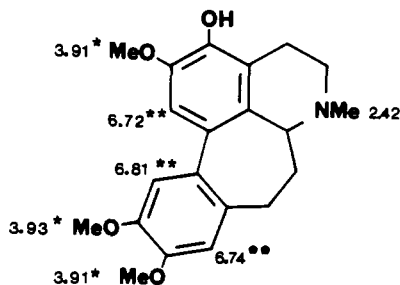
SOURCES: Synthesis (15)

16. (±)-3-HYDROXY-2,10,11-TRI-METHOXYNORHOMOAPORPHINE



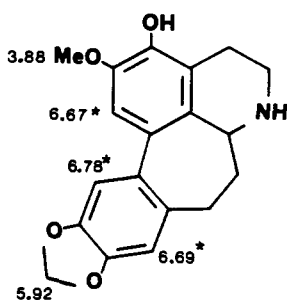
$C_{20}H_{23}O_4N$: 341.1627
 MP: 215–217° (2)
 1H NMR: (100 MHz) (2)
 SOURCES: Synthesis (2)

17. (±)-3-HYDROXY-2,10,11-TRI-METHOXYHOMOAPORPHINE



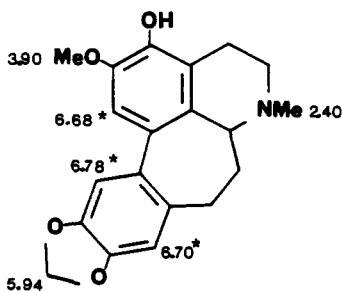
$C_{21}H_{25}O_4N$: 355.1783
 MP: 199–200° (17)
 1H NMR: (100 MHz) (17)
 SOURCES: Synthesis (2, 17)

18. (±)-3-HYDROXY-2-METHOXY-10,11-METHYLENEDIOXYNORHOMOAPORPHINE



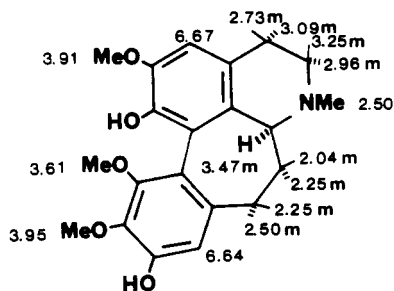
$C_{19}H_{19}O_4N$: 325.1314
 MP: 216–218° (dec.) (2)
 1H NMR: (100 MHz) (2)
 SOURCES: Synthesis (2)

19. (±)-3-HYDROXY-2-METHOXY-10,11-METHYLENEDIOXYHOMOAPORPHINE



$C_{20}H_{21}O_4N$: 339.1470
 MP: 181–183° (2)
 1H NMR: (100 MHz) (2)
 SOURCES: Synthesis (2, 17)

20. (+)-FLORAMULTINE (BECHUANINE)
(MERENDERINE)

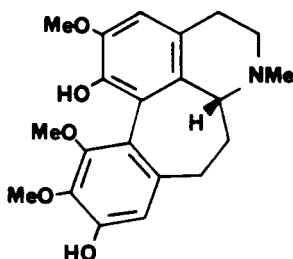


$C_{21}H_{25}O_5N$: 371.1733
 MP: 232–235° (dec.) (18)
 $[\alpha]_D$: +76° ($c=0.788$, $CHCl_3$) (18)
 UV: (EtOH) 218 (4.60), 260 (4.11), 291 (3.71) (18)

1H NMR: (250 MHz)¹
 CD: (EtOH) -0.46 (294 sh), -16.50 (257), +27 (210) (18)

SOURCES: Liliaceae: *Iphigenia bechuanica*, *Iphigenia indica*, *Iphigenia pallida* (18), *Merendera raddeana* (19), *Gloriosa superba* (20), *Iphigenia stellata* (21), *Colchicum szovitsii*¹

21. (-)-FLORAMULTINE



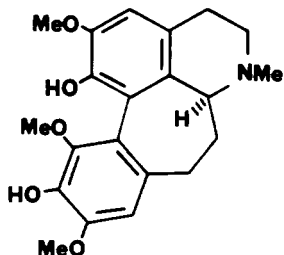
$C_{21}H_{25}O_5N$: 371.1733
 MP: 230–231° (22)
 $[\alpha]_D$: -77° ($c=1.19$, $CHCl_3$); -97° (EtOH) (18)

UV: (EtOH) 218 (4.60), 260 (4.10), 291 (3.71) (18)

IR: ($CHCl_3$) 3550, 3400, 1600, 1120 (22)

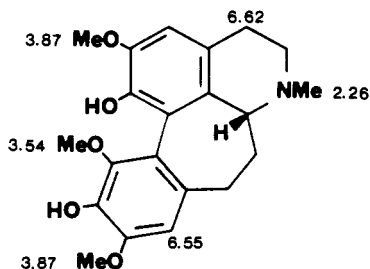
1H NMR: (22)
 MS: $[M]^+$ 371 (56), 356 (33), 354 (100) (22)
 SOURCES: Liliaceae: *Kreysigia multiflora* (22)

22. (+)-MULTIFLORAMINE



$C_{21}H_{25}O_5N$: 371.1733
 MP: 189–190° (23)
 $[\alpha]_D$: +112° (23)
 CD: (23)
 SOURCES: Synthesis (23)

23. (-)-MULTIFLORAMINE



$C_{21}H_{25}O_5N$: 371.1733
 MP: 209–212° (22)
 $[\alpha]_D$: -108° ($CHCl_3$) (22)
 UV: 221 (4.34), 261 (3.72), 295 (3.56) (22)
 IR: (CCl_4) 3560, 1618, 1488, 1124 (22)
 1H NMR: (22)
 MS: $[M]^+$ 371 (50), 354 (100) (22)
 CD: (23)
 SOURCES: Liliaceae: *K. multiflora* (22), *I. stellata* (21), synthesis (23)

¹Unpublished results, E. Tojo and M. Shamma.

24. (±)-MULTIFLORAMINE

C₂₁H₂₅O₃N: 371.1733

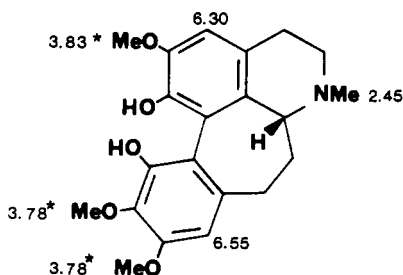
MP: 190° (24)

UV: (MeOH) 261 (4.25), 291 (4.02) (24)

IR: (CHCl₃) 3450 (24)¹H NMR: (24)

SOURCES: Synthesis (24–26)

25. (–)-1,12-DIHYDROXY-2,10,11-TRI-METHOXYHOMOAPORPHINE

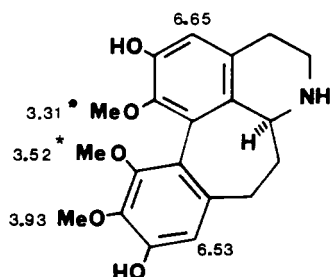
C₂₁H₂₅O₃N: 371.1733[α]_D: (–) (27)

MP: 223–225° (28)

UV: (MeOH) 221 (4.45), 258 (4.12), 289 (3.84), 298 (3.76) (28)

IR: (CHCl₃) 3500 (28)¹H NMR: (60 MHz) (28)MS: [M]⁺ 371, 354 (100) (28)SOURCES: Liliaceae: *Colchicum cornigerum* (27), *G. superba* (20). Specific rotation and absolute configuration for the *G. superba* alkaloid were not indicated. Synthesis of racemate (28)

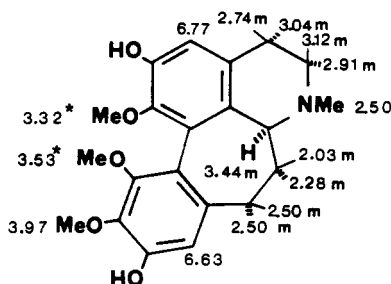
26. (+)-NORANDROBINE

C₂₀H₂₃O₃N: 357.1576[α]_D: +20° (c = 0.10, MeOH) (29)UV: (MeOH) 218 (3.89), 258 (3.42), 291 sh (3.10); (OH[–]) 313 (3.40) (29)IR: (CHCl₃) 3680, 3000, 1595, 1460 (29)¹H NMR: (200 MHz) (29)MS: [M]⁺ 357 (27), 342 (26), 326 (100), 310 (23) (29)

CD: (MeOH) –1.5 (254) (29)

SOURCES: Liliaceae: *Androcymbium palaestinum* (29)

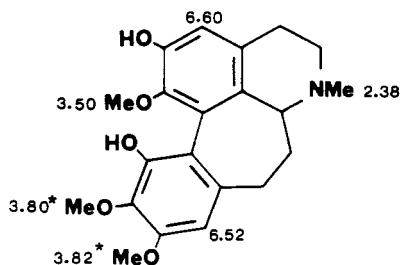
27. (+)-ANDROBINE

C₂₁H₂₅O₃N: 371.1733[α]_D: +39° (c = 0.12, MeOH) (29)UV: (MeOH) 215 (4.44), 262 (3.98), 289 sh (3.65), (OH[–]) 295 (3.95) (29)IR: (CHCl₃) 3520, 2930, 1590, 1460 (29)¹H NMR: (360 MHz) (29)MS: [M]⁺ 371 (22), 356 (13), 340 (100) (29)

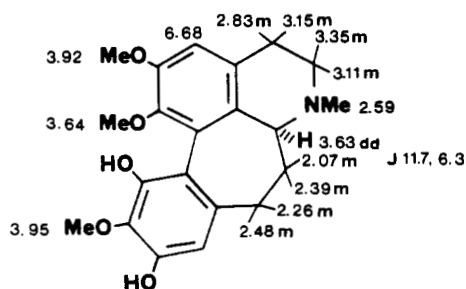
CD: (MeOH) –2.5 (254) (29)

SOURCES: Liliaceae: *A. palaestinum* (29)

28. SZOVITSININE

C₂₁H₂₅O₃N: 371.1733¹H NMR: (30)MS: [M]⁺ 371, 340, 328 (30)SOURCES: Liliaceae: *C. szovitsii* (30)

29. (+)-BAYTOPINE

 $C_{21}H_{25}O_5N$: 371.1733[α]_D: +74° ($c = 0.28$, $CHCl_3$) (31)UV: (EtOH) 215 (4.55), 257 (4.02), 287 sh (3.67), 296 sh (3.62), (OH⁻) 217 (4.39), 287 (4.00), 296 sh (3.97) (31)

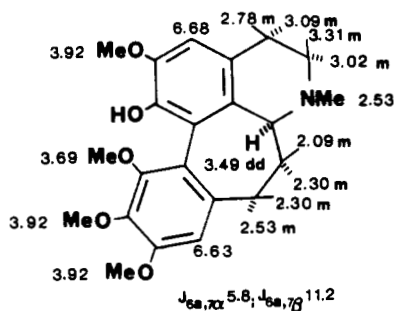
IR: 3400–3500 (31)

¹H NMR: (400 MHz) (31)¹³C NMR: (100 MHz) (31)MS: [M]⁺ 371, 354 (100) (31)

CD: (EtOH) +20.09 (209), -11.20 (258) (31)

SOURCES: Liliaceae: *Merendera kurdica* (31)

30. (+)-KREYSIGINE

 $C_{22}H_{27}O_5N$: 385.1889[α]_D: +64° ($c = 0.11$, MeOH) (29)

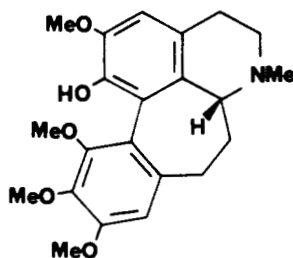
UV: (MeOH) 216 (3.94), 257 (3.49), 287 sh (3.24) (29)

IR: ($CHCl_3$) 3520, 3000, 1595, 1460 (29)¹H NMR: (360 MHz) (29)MS: [M]⁺ 385 (40), 368 (100), 354 (18) (29)

CD: (MeOH) -1.95 (254) (29)

SOURCES: Liliaceae: *A. palaestinum* (29), synthesis (32)

31. (-)-KREYSIGINE

 $C_{22}H_{27}O_5N$: 385.1889

MP: 122–124° (33)

[α]_D: -65.4 ($c = 0.31$, $CHCl_3$) (33)

UV: (EtOH) 218 (4.62), 257 (4.10), 293 (3.67) (34)

MS: [M]⁺ 385 (34)

CD: (EtOH) +1.77 (295), +15.59 (258), -21.1 (210) (33)

SOURCES: Liliaceae: *Bulbocodium vernum* (33), *C. cornigerum* (34), synthesis (32)

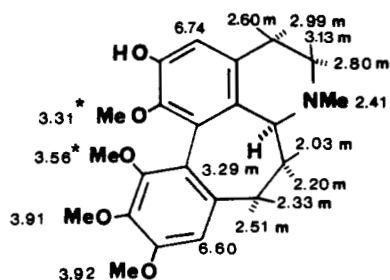
32. (±)-KREYSIGINE

 $C_{22}H_{27}O_5N$: 385.1889

MP: 188° (35)

SOURCES: Liliaceae: *K. multiflora* produces kreysigine with essentially zero specific rotation (35), synthesis (5, 10, 11, 13, 26, 36)

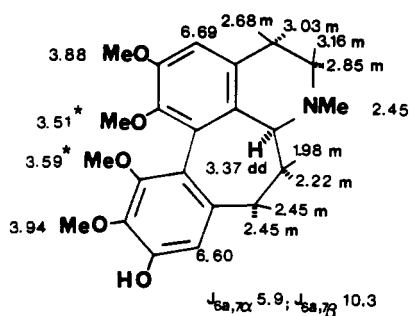
33. (+)-ANDROCINE

 $C_{22}H_{27}O_5N$: 385.1889[α]_D: +39° ($c = 0.10$, MeOH) (29)UV: (MeOH) 217 (4.47), 260 (3.99), 292 sh (3.93); (OH⁻) 313 (3.79) (29)IR: ($CHCl_3$) 3520, 2920, 1590, 1460 (29)¹H NMR: (360 MHz) (29)MS: [M]⁺ 385 (17), 370 (12), 354 (100) (29)

CD: (MeOH) -2.9 (254) (29)

SOURCES: Liliaceae: *A. palaestinum* (29)

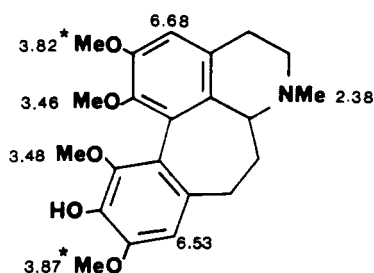
34. (+)-ANDROCIMINE

C₂₂H₂₇O₅N: 385.1889[α]_D: +51° (c = 0.11, MeOH) (29)UV: (MeOH) 218 (4.47), 260 (3.94), 291 sh (3.60); (OH⁻) 212 (4.47), 262 (3.83), 291, (3.82) (29)IR: (CHCl₃) 3520, 2930, 1590, 1460 (29)¹H NMR: (360 MHz) (29)MS: [M]⁺ 385 (24), 370 (18), 354 (100) (29)

CD: (MeOH) -0.79 (254) (29)

SOURCES: Liliaceae: *A. palaestinum* (29)

35. (±)-11-HYDROXY-1,2,10,12-TETRAMETHOXYHOMOAPORPHINE

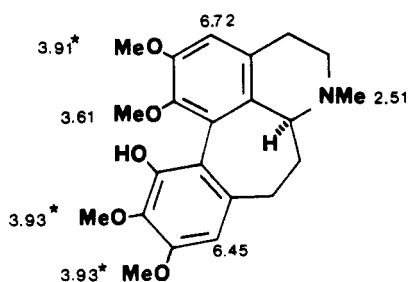
C₂₂H₂₇O₅N: 385.1889

MP: 168–169° (5)

IR: (CHCl₃) 3520 (5)¹H NMR: (100 MHz) (5)

SOURCES: Synthesis (5)

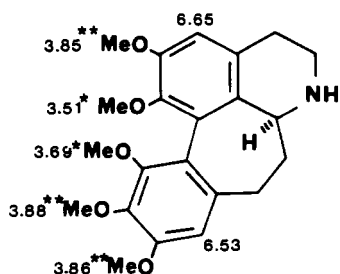
36. (+)-SZOVITSAMINE

C₂₂H₂₇O₅N: 385.1889[α]_D: +55° (c = 0.10, MeOH) (29)UV: (MeOH) 218 (4.29), 260 (3.78), 286 sh (3.50); (OH⁻) 290 (3.37), 314 (3.18) (29)IR: (CHCl₃) 3500, 2950, 1590, 1455 (29)¹H NMR: (200 MHz) (29)MS: [M]⁺ 385 (19), 370 (17), 354 (100), 338 (21) (29)

CD: (MeOH) -1.2 (254) (29)

SOURCES: Liliaceae: *A. palaestinum* (28), *C. szovitsii* (37)

37. (+)-NOR-O-METHYLKREYSIGINE

C₂₂H₂₇O₅N: 385.1889[α]_D: +27° (c = 0.07, MeOH) (29)

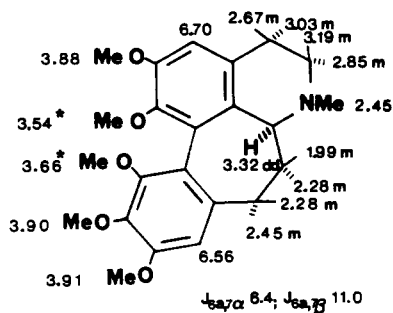
UV: (MeOH) 218 (4.37), 259 (3.88), 292 sh (3.38) (29)

IR: (CHCl₃) 3000, 1590, 1410 (29)¹H NMR: (200 MHz) (29)MS: [M]⁺ 385 (33), 370 (25), 354 (100), 338 (14) (29)

CD: (MeOH) -1.8 (254) (29)

SOURCES: Liliaceae: *A. palaestinum* (29)

38. (+)-O-METHYLKREYSIGINE

C₂₃H₂₉O₅N: 399.2046[α]_D: +68° (c = 0.10, MeOH) (29)

UV: (MeOH) 220 (4.44), 260 (3.95), 289 (3.46) (29)

IR: (CHCl₃) 2920, 1700, 1590, 1455 (29)¹H NMR: (360 MHz) (29)MS: [M]⁺ 399 (21), 384 (18), 368 (100) (29)

CD: (MeOH) -2.2 (254) (29)

SOURCES: Liliaceae: *A. palaestinum* (29), *C. szovitsii* (38), synthesis (39)

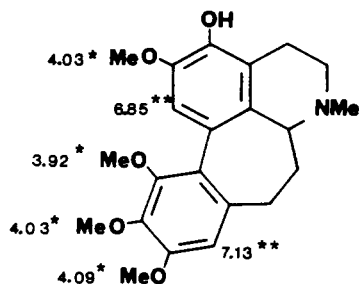
39. (±)-O-METHYLKREYSIGINE

C₂₃H₂₉O₅N: 399.2046

MP: 152.3° (MeI) (25)

SOURCES: Synthesis (25)

40. (±)-3-DIHYDROXY-2,10,11,12-TETRAMETHOXYHOMOAPORPHINE

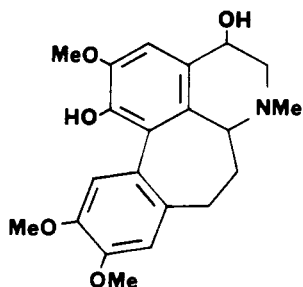
C₂₂H₂₇O₅N: 385.1889

MP: 240–245° (17)

¹H NMR: (CF₃CO₂D; 100 MHz) (17)MS: [M]⁺ 385 (17)

SOURCES: Synthesis (17)

42. (±)-1,4β-DIHYDROXY-2-METHOXY-10,11-METHYLENEDIOXYHOMOAPORPHINE

C₂₀H₂₁O₅N: 355.1420

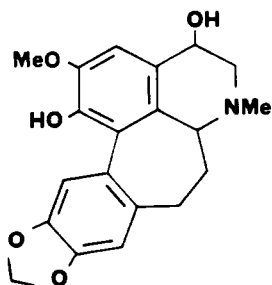
MP: 199–200° (diacetate) (40)

IR: 1720, 1760 (diacetate) (40)

¹H NMR: (diacetate) (40)

SOURCES: Synthesis (40)

41. (±)-1,4β-DIHYDROXY-2,10,11-TRIMETHOXYHOMOAPORPHINE

C₂₁H₂₅O₅N: 371.1733

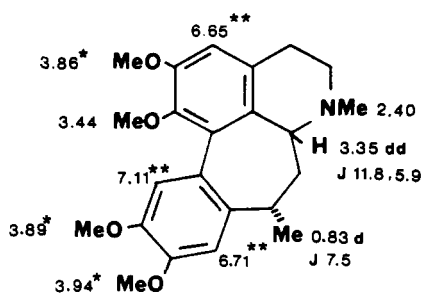
MP: (methiodide of diacetate) 235–237° (40)

IR: 1720, 1755 (diacetate) (40)

¹H NMR: (diacetate) (40)

SOURCES: Synthesis (40)

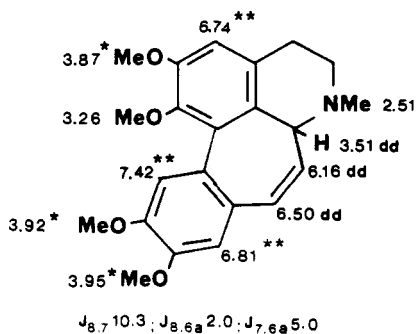
43. (±)-8-METHYLHOMOGLAUCINE

C₂₃H₂₉O₄N: 383.2096

MP: 196–198° (MeI) (15)

¹H NMR: (250 MHz) (15)¹³C NMR: (62.83 MHz) (15)MS: [M]⁺ 383 (22), 382 (12), 268 (24), 352 (100), 340 (12), 336 (8), 246 (22) (15)

SOURCES: Synthesis (15)

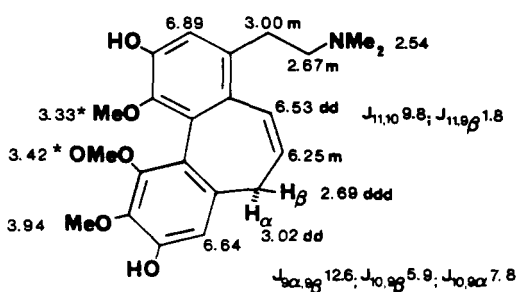
44. (±)-7-DEHYDROHOMOGLAUCINE
(7,8-DIDEHYDROHOMOGLAUCINE)C₂₂H₂₅O₄N: 367.1783

MP: 246–248° (MeI) (15)

¹H NMR: (250 MHz) (15)¹³C NMR: (62.83 MHz) (15)MS: [M]⁺ 367 (100), 366 (74), 352 (33), 337 (17), 336 (26), 324 (21), 322 (11), 320 (9), 309 (36), 294 (10), 278 (10), 266 (11), 250 (9) (15)

SOURCES: Synthesis (15)

45. (+)-ANDROBINEMETHINE

C₂₂H₂₇O₅N: 385.1889[α]_D: +242 (c = 0.21, MeOH) (29)

UV: (MeOH) 251 (4.33), 285 sh (3.72);

(OH⁻) 272 (4.27), 301 sh (4.00) (29)IR: (CHCl₃) 3510, 2990, 1590, 1445 (29)¹H NMR: (360 MHz) (29)MS: [M]⁺ 385 (2), 327 (0.4), 58 (100) (29)

CD: (MeOH) +3.4 (258) (29)

SOURCES: Hemisynthesis (29)

46. (+)-SZOVITSINE²C₄₂H₅₀O₁₀N₂: 742.3465

MP: 139–141° (41)

[α]_D: +72° (c = 1.52, CHCl₃) (41)

UV: 260 (4.22), 290 (3.94) (41)

¹H NMR: (41)MS: [M]⁺ 742 (50), 741 (9), 727 (20), 725 (100), 723 (5), 713 (12), 711 (60), 709 (11), 699 (5), 697 (4), 695 (9), 204 (12) (30)SOURCES: Liliaceae: *C. szovitsii* (41)

LITERATURE CITED

1. A. R. Battersby, P. Böhler, M. H. G. Munro, and R. Ramage, *J. Chem. Soc., Perkin Trans. 1*, 1399 (1974).

²Structure assignment is doubtful.

2. O. Hoshino, H. Ogasawara, A. Takahashi, and B. Umezawa, *Heterocycles*, **25**, 155 (1987).
3. T. Kametani, F. Satoh, H. Yagi, and K. Fukumoto, *J. Chem. Soc. C*, 1003 (1968).
4. T. Kametani, F. Satoh, H. Yagi, and K. Fukumoto, *J. Chem. Soc. C*, 382 (1970).
5. H. Hara, O. Hoshino, B. Umezawa, and Y. Iitaka, *J. Chem. Soc., Perkin Trans. 1*, 2657 (1979).
6. T. Kametani, K. Fukumoto, F. Satoh, K. Kigasawa, and H. Sugi, *J. Pharm. Soc. Jpn.*, **13**, 29 (1976).
7. T. Kametani, M. Ihara, M. Takemura, and F. Satoh, *Heterocycles*, **14**, 817 (1980).
8. S.M. Kupchan, O.P. Dhingra, C.-K. Kim, and V. Kameswaran, *J. Org. Chem.*, **43**, 2521 (1978).
9. S.M. Kupchan, O.P. Dhingra, and C.-K. Kim, *J. Org. Chem.*, **43**, 4076 (1978).
10. T. Kametani, Y. Satoh, M. Koizumi, and K. Fukumoto, *J. Org. Chem.*, **36**, 3733 (1971).
11. O. Hoshino, T. Toshioka, K. Ohyama, and B. Umezawa, *Chem. Pharm. Bull.*, **22**, 1307 (1974).
12. O. Hoshino, M. Hara, N. Serizawa, and B. Umezawa, *Chem. Pharm. Bull.*, **23**, 2048 (1975).
13. B. Umezawa and O. Hoshino, *Heterocycles*, **3**, 1005 (1975).
14. O. Hoshino, K. Kikuchi, H. Ogose, B. Umezawa, and Y. Iitaka, *Chem. Pharm. Bull.*, **35**, 3666 (1987).
15. J.L. Castro, L. Castedo, and R. Riguera, *J. Org. Chem.*, **52**, 3579 (1987).
16. J. Landais, D. Rambault, and J.P. Robin, *Tetrahedron Lett.*, **28**, 543 (1987).
17. H. Mara, H. Shinoki, T. Komatsu, O. Moshino, and B. Umezawa, *Chem. Pharm. Bull.*, **34**, 1924 (1986).
18. F. Šantavý and L. Hruban, *Collect. Czech. Chem. Commun.*, **38**, 1712 (1973).
19. A.A. Trozyan, M.K. Yusupov, and Kh. A. Aslanov, *Khim. Prir. Soedin.*, 527 (1975); *Chem. Nat. Compd. (Engl. Transl.)*, 557 (1975).
20. S. Dvořáčková, P. Sedmera, H. Potěšilová, F. Šantavý, and V. Šimánek, *Collect. Czech. Chem. Commun.*, **49**, 1536 (1984).
21. H. Potěšilová, S. Dvořáčková, V. Preininger, and V. Šimánek, *Planta Med.*, 72 (1985).
22. A.R. Battersby, R.B. Bradbury, R.B. Herbert, M.H.G. Munro, and R. Ramage, *J. Chem. Soc., Perkin Trans. 1*, 1394 (1974).
23. A. Brossi, J. O'Brien, and S. Teitel, *Helv. Chim. Acta*, **52**, 678 (1969).
24. T. Kametani and M. Koizumi, *J. Chem. Soc. C*, 3976 (1971).
25. E.C. Taylor, J.G. Andrade, G.J.H. Rall, and A. McKillop, *J. Am. Chem. Soc.*, **102**, 6513 (1980).
26. S.M. Kupchan, O.P. Dhingra, and C.-K. Kim, *J. Org. Chem.*, **41**, 4049 (1976).
27. A.R. Battersby, R. Ramage, A.F. Cameron, C. Hannaway, and F. Šantavý, *J. Chem. Soc. C*, 3514 (1971).
28. T. Kametani, Y. Satoh, and K. Fukumoto, *Tetrahedron*, **29**, 2027 (1973).
29. E. Tojo, M.H. Abu Zarga, S.S. Sabri, A.J. Freyer, and M. Shamma, *J. Nat. Prod.*, **52**, 1055 (1989).
30. A.K. Kasimov, E.Kh. Timbekov, M.K. Yusupov, and Kh.A. Aslanov, *Khim. Prir. Soedin.*, 230 (1977); *Chem. Nat. Compd. (Engl. Transl.)*, 197 (1977).
31. A. Husek, N. Sütlüpinar, P. Sedmera, and V. Šimánek, *Heterocycles*, **2**, 79 (1989).
32. T. Kametani, Y. Satoh, and K. Fukumoto, *J. Chem. Soc., Perkin Trans. 1*, 2160 (1972).
33. F. Šantavý, P. Sedmera, G. Snatzke, and T. Reichstein, *Helv. Chim. Acta*, **54**, 1084 (1971).
34. H. Potěšilová, J. Šantavý, A. El-Hamidi, and F. Šantavý, *Collect. Czech. Chem. Commun.*, **34**, 3540 (1969).
35. G.M. Badger and R.B. Bradbury, *J. Chem. Soc. C*, 445 (1960).
36. T. Kametani, M. Koizumi, K. Shishido, and K. Fukumoto, *J. Chem. Soc. C*, 1923 (1971).
37. M.K. Yusupov, D. Ngo, Kh.A. Aslanov, and A.S. Sadykov, *Khim. Prir. Soedin.*, 109 (1975); *Chem. Nat. Compd. (Engl. Transl.)*, 127 (1975).
38. M.K. Yusupov, D.B. Ngo, and Kh. A. Aslanov, *Khim. Prir. Soedin.*, 526 (1975); *Chem. Nat. Compd. (Engl. Transl.)*, 555 (1975).
39. Z. Czarnocki, D.B. Maclean, and W.A. Szarek, *Can. J. Chem.*, **65**, 2356 (1987).
40. H. Hara, O. Hoshino, and B. Umezawa, *Nippon Kagaku Kaishi*, 813 (1981); *Chem. Abstr.*, **95**, 150967w.
41. M.K. Yusupov, Kh.A. Aslanov and D.B. Ngo, *Khim. Prir. Soedin.*, 431 (1975); *Chem. Nat. Compd. (Engl. Transl.)*, 448 (1975).