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CULARINE, CANCENTRINE, AND QUETTAMINE ALKALOIDS

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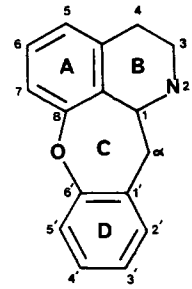
The culanines are isoquinoline alkaloids with a tetracyclic nucleus incorporating a central dihydrooxepine or oxepine system. Most culanines have been found among plants of the Fumariaceae, where they are formed by intramolecular oxidative coupling of 7,8,3′,4′-tetraoxygenated tetrahydrobenzylisoquinolines.

Lately, however, the culanine base gouregine (**31**) has been isolated from a member of the Annonaceae, and its biogenesis probably proceeds by oxidation of an aporphine precursor (54). Even more recently, the culanines linaresine (**36**) and dihydrolinaresine (**37**) have been encountered in a barberry bush (Berberidaceae), and their biogenetic origin may possibly derive from initial oxidation of a protoberberinium salt (70).

Over the years, different numbering systems for the culanines have been used, but the more systematic one is given below and is based on analogy with the numbering system for the benzylisoquinolines.

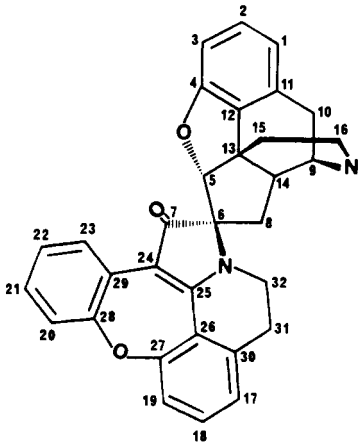


Culanine alkaloids obtained from the Fumariaceae are generally strongly dextrorotatory. (+)-Culanine (**7**) itself was assigned the S configuration at C-1 based on chemical (15) as well as X-ray evidence (31, 32).

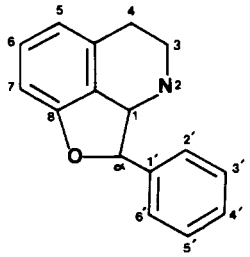
Culanine and aporphine alkaloids exhibit an interesting parallelism. Oxoculanines (*e.g.*, **20**) are found in nature and should be compared with the numerous oxoaporphines known. The 4-hydroxylated culanines limousamine (**14**) and 4-hydroxysarcocapnine (**27**) have their counterparts among the 4-hydroxylated aporphines. Additionally, a 3,4-dioxoculanine such as yagonine (**39**) is the analog of the 4,5-dioxoaporphines pontevedrine and cepharadione-B. The aptly named aristoyagonine (**40**) bears a distinct structural analogy to the aristolactams. Finally, quaternary N-methoculanines may undergo Hofmann β-elimination to afford secoculanines (*e.g.*, **42**) as a counterpart to the formation of β-dimethylaminoethylphenanthrenes from aporphines.

Cancentrine-type alkaloids are dimers involving a culanine unit linked to a morphinan unit through a spiro-bridge. They were found in a *Dicentra* species, and they have been included in the present listing. The numbering system is as indicated below.

Whereas classical-type culanine alkaloids of the Fumariaceae are biogenetically derived from intramolecular oxidative coupling of tetraoxygenated tetrahydrobenzylisoquinoline precursors, the quettamines are obtained from in vivo intramolecular

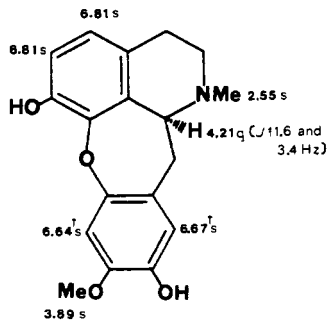


oxidation of a trioxygenated tetrahydrobenzyisoquinoline. So far, only three naturally occurring quettamines are known; all found in *Berberis baluchistancia* Ahrendt (Berberidaceae) (62). The numbering system is shown below.



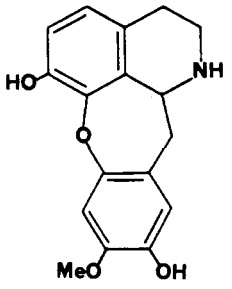
Uv wavelengths are in nm and log ϵ values are given in parentheses. These are λ max values unless otherwise specified. The solvent is given whenever it has been indicated in the relevant literature. Ir frequencies are in cm^{-1}. The pmr chemical shifts are given as δ values. Some were obtained at 60 MHz, and TMS is the internal standard unless specifically indicated. Chemical shifts possessing identical superscripts are interchangeable. Mass spectral mass numbers are followed in parentheses by relative abundance of ions, when these have been reported in the original literature.

1. (+)-CULACORINE
(Breoganine)



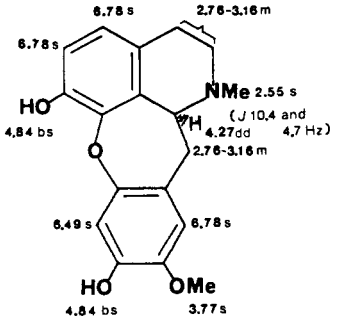
$C_{18}H_{19}NO_4$: 313.1314
MP: 249-250° (EtOH) (65)
$[\alpha]^{25}D$: +188° (c=0.08, MeOH) (2)
+278° (=0.057, MeOH) (65)
UV: (MeOH) 209 (4.50, 225 sh (4.19), 285 (3.80), 296 sh (3.64) (2)
IR: (KBr) 3300, 1510, 1300 (65)
PMR: 200 MHz ($CDCl_3$) (2)
MS: 313 (M^+, 100), 312 (7), 298 (75), 296 (42), 270 (16), 161 (4) (2)
CD: (MeOH) $\Delta\epsilon_{nm}$ $+0.45_{290}$, -1.9_{274}, -3_{232}, 0_{228}, positive tail at 217 (2)
Sources:
Fumariaceae: *Corydalis claviculata* (L.) DC. (2)
Sarcocapnos crassifolia DC. (65)
Partial synthesis from (+)-cularine (65). See also (3, 4).

2. NORCULACORINE



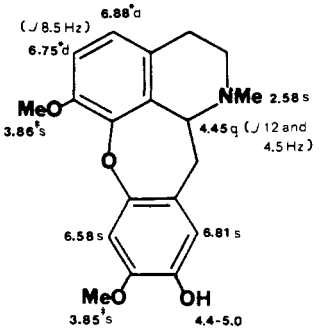
$C_{17}H_{17}NO_4$: 299.1157
MP: 103-104° (hexane-EtOAc) (3)
PMR: (TFA) 3.96 (3H, s, OCH_3) (3)
MS: (3)
Sources:
Synthetic (3, 4)

3. (+)-CELTISINE



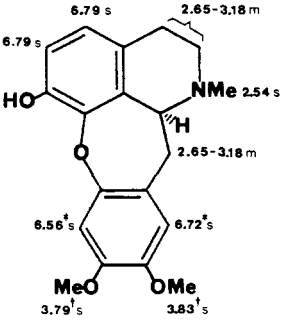
$C_{18}H_{19}NO_4$: 313.1314
MP: 158-160° (EtOH) (65)
$[\alpha]_D$: +212° (c=0.025, MeOH) (65)
UV: (MeOH) 225 (4.10), 283 (3.85); (EtOH-OH^-) 225 (4.50), 294 (3.91) (65)
IR: (KBr) 3400, 1510, 1305 (65)
PMR: 80 MHz ($CDCl_3$) (65)
MS: 313 (M^+, 54), 298 (100), 296 (12), 270 (9), 161 (5) (65)
Sources:
Fumariaceae: *Sarcocapnos enneaphylla* DC. (65)
Partial synthesis from cularine (65)

4. 3′-O-DEMETHYLCULARINE



$C_{19}H_{21}NO_4$: 327.1470
MP: 126-127° (5, 6)
IR: ($CHCl_3$) 3560 (7)
PMR: ($CDCl_3$) (7)
See also (5)
MS: 327 (M^+, 100) (7)
See also (5,8)
Sources:
Synthetic (5-10)

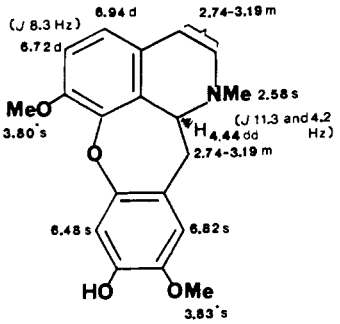
5. (+)-CULARIDINE
(O-Desmethylcularine)
(F10)



$C_{19}H_{21}NO_4$: 327.1470
MP: 156° (MeOH) (11, 18a)
157° (Et_2O-MeOH) (4, 12, 16)
($HClO_4$) 297° (MeOH) (11)
$[\alpha^{22}]_D$: +292° (c=0.99, $CHCl_3$) (11, 18a)
UV: 284 (3.85) (18a)
IR: 3550, 3015, 2930, 2905, 2840, 2800, 1618, 1516, 1497, 1462, 1452, 1443, 1402, 1374, 1352, 1340, 1326, 1304, 1292, 1260, 1169, 1134, 1112, 1068, 1060, 1048, 1021, 1004, 976, 938, 882, 859, 840, 820, 811 (18a)
PMR: ($CDCl_3$ (17)
MS: 327 (43), 312 (100), 161 (8) (17)
CD: $\Delta\epsilon_{nm}$ 0_{297}, $+0.3_{292}$, -2.9_{274}, -3.5_{233}, 0_{227}, positive tail at 222 nm (19)

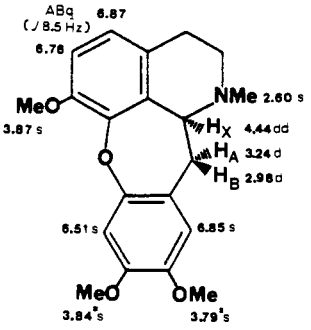
Sources:
Fumariaceae: *Corydalis claviculata* (L.) DC. (11, 13)
Dicentra cucullaria (L.) Bernh. (12, 16)
For structure elucidation, see (12,14)
For absolute configuration, see (15)
For synthesis, see (20, 4, 21).

6. (+)-CELTINE

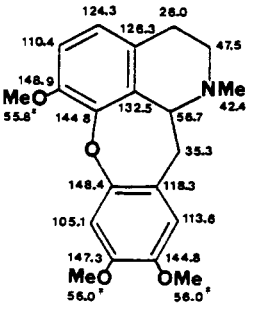


$C_{19}H_{21}NO_4$: 327.1470
MP: 94-96° (EtOH) (65)
$[\alpha]_D$: +181° (c=0.08, MeOH) (65)
UV: (EtOH) 216 (4.11), 228 sh (3.95), 282 (3.58); (EtOH-OH^-) 216 (4.59), 298 (3.60) (65)
IR: (KBr) 3350, 1510, 1280 (65)
PMR: 80 MHz ($CDCl_3$) (65)
MS: 327 (M^+, 45), 312 (100), 284 (9), 253 (8), 174 (10), (65)
Sources:
Fumariaceae: *Sarcocapnos enneaphylla* DC. (65)
Partial synthesis from cularine (65)

7. (+)-CULARINE (F9)



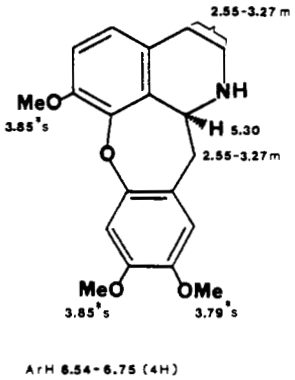
J_{AX} 4 Hz; J_{BX} 12 Hz; J_{AB} 16 Hz



$C_{20}H_{23}NO_4$: 341.1627
MP: 113-114.5° (Et_2O) (22)
115° (Et_2O) (12, 13, 16)
(HCl) 207° (EtOAc-MeOH) (13)
(oxalate) 244-245° (dec) (MeOH) (22, 24)
(methiodide) 205° (MeOH) (23)
See also (11, 18b, 23)
$[\alpha]_D$: +284° (c=0.92, MeOH) (22, 24)
$[\alpha]^{25}D$: +285° (c=0.8, MeOH) (12, 22, 24, 25)
See also (16, 18b)
UV: (EtOH) 206 sh (5.21), 229 sh (4.12), 274 (3.63), 283 (3.79), 295 sh (3.48) λ_{min} 256 (3.13) (25)
See also (18b, 26)
IR: 3010, 2940, 2910, 2840, 2810, 1621, 1518, 1506, 1470, 1447, 1406, 1376, 1345, 1330, 1283, 1263, 1195, 1175, 1166, 1115, 1090, 1066, 1045, 1022, 1000, 969, 928, 860, 845, 815, 805 (18b)
See also (22, 24)
PMR: 100 MHz ($CDCl_3$) (25)
See also (17)
CMR: (27)
See also (28)
MS: 341 (M^+), 326 (100), 310 (29, 30)
See also (17)
ORD: (c=0.075, EtOH) $[\alpha]_{333}$ +1276°, $[\alpha]_{297}$ +1844° pk, $[\alpha]_{283}$ +36.9° tr, $[\alpha]_{213}$ +41,500° pk, $[\alpha]_{200}$ −92,400° (25)
X-RAY: (methiodide) (31, 32)
Sources:
Fumariaceae: *Corydalis claviculata* (L.) DC. (12, 13, 16)
Dicentra cucullaria (L.) Bernh. (12, 16)
Dicentra eximia Torr. (12, 16)
Dicentra formosa Walp. (12, 16)
Dicentra oregana Eastw. (12, 16)
Partial synthesis from (+)-cularicine (11)
Partial synthesis from (±)-cularimine (22, 24)
Partial synthesis from (+)-culacorine (2)

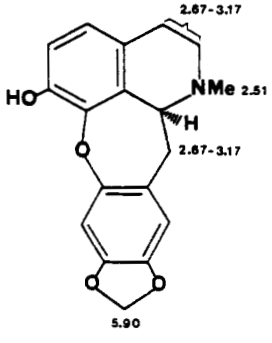
Other syntheses (5-7, 9, 22, 33-41)
For absolute configuration, see (15, 25, 31, 32)
For conformation, see (25, 27, 32)
For (+)-cularine methiodide, see (23)

8. (+)-CULARIMINE
(N-Desmethylcularine)
(F30)



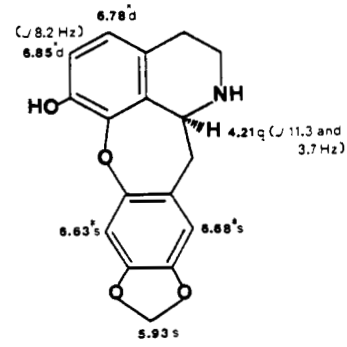
$C_{19}H_{21}NO_4$: 327.1470
MP: 100-101° (Et_2O) (22, 24)
See also (12, 16, 43)
$[\alpha]_D$: +259.5° (c=0.94, MeOH) (22, 24)
$[\alpha]_D$: +261.0° (c=0.9, MeOH) (43)
PMR: ($CDCl_3$) (43, 17)
MS: 327 (M^+, 51), 312 (100), 161 (19) (17)
Sources:
Fumariaceae: *Dicentra eximia* Torr. (12, 16)
Also obtained through optical resolution of (±)-cularimine (22, 24, 43)
Syntheses (26, 33-35, 38, 43)
For structure elucidation, see (23)
For absolute configuration, see (15)

9. (+)-CULARICINE



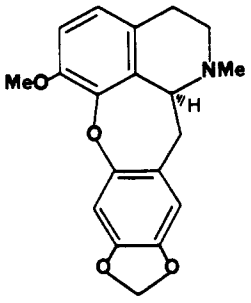
$C_{18}H_{17}NO_4$: 311.1157
MP: 185° (MeOH) (11, 18c)
$[\alpha]^{22}_D$: +295° (c=0.96, $CHCl_3$) (11)
See also (18c)
UV: 288 (3.79) (18c)
IR: 1620, 1580, 1543, 1500, 1342, 1332, 1311, 1300, 1290, 1246, 1229, 1204, 1174, 1160, 1143, 1130, 1076, 1059, 1038, 992, 974, 941, 870, 850, 813, 798, 783, 775, 740 (18c)
PMR: ($CDCl_3$) (17)
MS: 311 (25), 296 (20), 161 (8) (17)
Sources:
Fumariaceae: *Corydalis claviculata* (L.) DC. (11)
Partial synthesis from (+)-norcularicine (2)
Other syntheses (44, 45)
For absolute configuration, see (15)
For structure elucidation, see (11).

10. (+)-NORCULARICINE



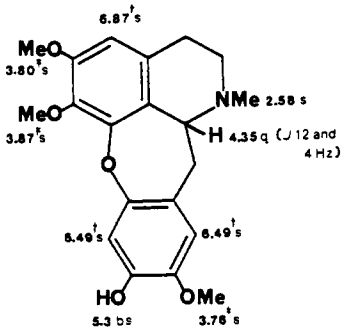
$C_{17}H_{15}NO_4$: 297.1001
$[\alpha]^{25}_D$: 216° (c=0.06, MeOH) (2)
UV: (MeOH) 206 (4.57), 224 sh (4.23), 287 (3.79) (2)
PMR: 200 MHz ($CDCl_3$) (2)
MS: 297 (M^+, 100), 296 (62), 280 (51), 267 (20), 147 (23) (2)
CD: (MeOH) $\Delta\epsilon_{nm}$ -0.7_{273}, -0.5_{232}, 0_{228}, positive tail at 215 (2)
Sources:
Fumariaceae: *Corydalis claviculata* (L.) DC. (2)
Synthesis (44)

11. O-METHYLCULARICINE



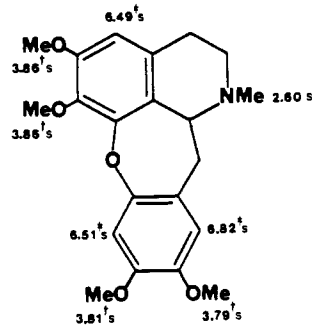
$C_{19}H_{19}NO_4$: 325.1314
MP: (HCl) 267° (MeOH) (11)
Sources:
Semisynthetic: O-Methylation of (+)-cularicine (11)

12. (±)-6-METHOXYCELTINE



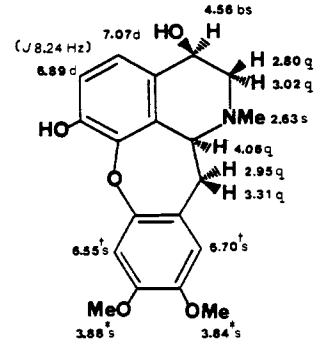
$C_{20}H_{23}NO_5$: 357.1576
MP: 145-147° (Et_2O) (47)
(H_2O) 188-189° (Et_2O) (48)
See also (46)
IR: ($CHCl_3$) 3500 (46, 48)
See also (47)
PMR: ($CDCl_3$) (47)
See also (46, 48)
Sources:
Synthetic (46, 47, 48)

13. (±)-6-METHOXYCULARINE



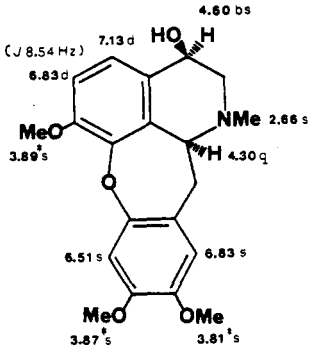
$C_{21}H_{25}NO_5$: 371.1732
MP: 113-115° (Et_2O) (47, 49)
PMR: 100 MHz ($CDCl_3$) (49)
MS: 371.356 (49)
Sources:
Synthetic (47, 49)

14. (+)-LIMOUSAMINE



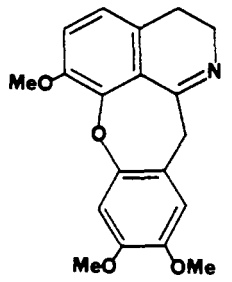
$C_{19}H_{21}NO_5$: 343.1419
$[\alpha]^{25}D$: +185° (c=0.074, MeOH) (19)
UV: (MeOH) 210 (4.54), 230 sh (4.14), 283 (3.82), 292 sh (3.69); (MeOH-OH^-) 211 (4.60), 251 sh (4.06), 291 (3.92) (19)
PMR: 200 MHz ($CDCl_3$) (19)
MS: 343, 328 (100), 310, 177, 159 (19)
CD: (MeOH) $\Delta\epsilon_{nm}$ 0_{296}, $+0.6_{291}$, -3.1_{273}, -2.7_{237}, 0_{231}, positive tail at 217 (19)
Sources:
Fumariaceae: *Corydalis claviculata* (L.) DC. (19)

15. (+)-O-METHYLLIMOUSAMINE



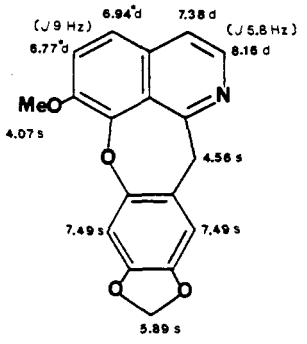
$C_{20}H_{23}NO_5$: 357.1576
PMR: 360 MHz ($CDCl_3$) (19)
MS: 357 (M^+, 31), 342 (100), 324 (47), 172 (6) (19)
Sources:
Semisynthetic: O-Methylation of limousamine (19)

16. 1,2-DEHYDROCULARIMINE



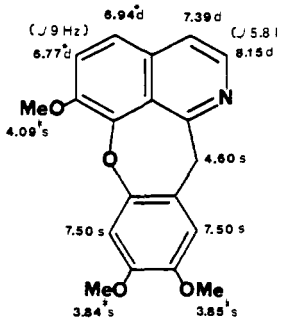
$C_{19}H_{19}NO_4$: 325.1314
MP: 134-135° (26)
(picrate) 193-194° (50)
UV: (EtOH) 284 (3.88), 351 (3.61); (EtOH-0.1 N HCl) 226 (4.34), 285 (3.95), 368 (3.53), 394 (3.49) (26)
IR: (KBr) 1620 (26)
See also (50)
Sources:
Synthetic (26, 50)

17. 1,2,3,4-TETRADEHYDRO-O-METHYLNORCULARICINE



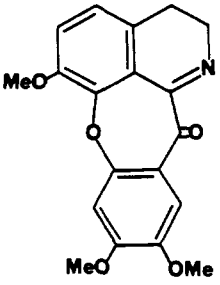
$C_{18}H_{13}NO_4$: 307.0844
MP: 154-156° (petroleum ether-$CHCl_3$ (51)
UV: (EtOH) 215, 230, 285, 350; (EtOH-HCl) 218, 250, 295, 394 (51)
IR: (KBr) 1600, 1490 (51)
PMR: ($CDCl_3$) (51)
MS: 307 (M^+, 100), 292 (20), 264 (17), 262 (24) (51)
Sources:
Synthetic (51)

18. 1,2,3,4-TETRADEHYDRO-CULARIMINE



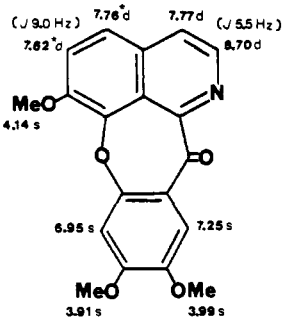
$C_{19}H_{17}NO_4$: 323.1157
MP: 133° (light petroleum-Et_2O) (33)
(picrate) 222° (Me_2CO) (33)
See also (26, 37)
UV: (EtOH) 228 (4.61), 284 (3.92), 348 (3.74; (EtOH-0.1 N HCl) 251 (4.51), 284 (3.76), 396 (3.73) (26)
See also (33)
IR: (KBr) 1620, 1403 (33)
PMR: 80 MHz ($CDCl_3$ (51)
MS: 323 (M^+, 100), 308 (28) (51)
Sources:
Synthetic (26, 33, 37, 51)

19. 3,4-DIHYDROOXOCULARINE



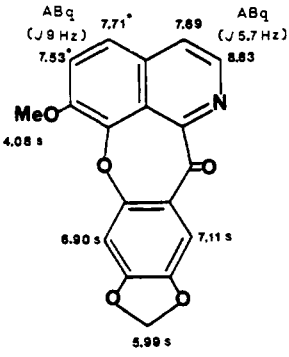
$C_{19}H_{19}NO_5$: 341.1263
MP: 193-194° (hexane-Et_2O) (50)
IR: (KBr) 1730 (50)
Sources:
Synthetic (50)

20. OXOCULARINE



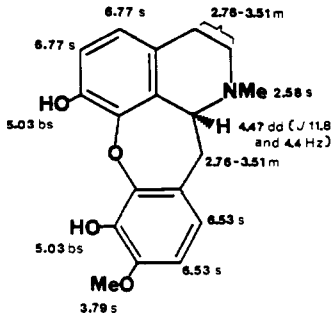
$C_{19}H_{15}NO_5$: 337.0950
MP: 191-193° (26)
(½ H_2O) 194-195° (26)
198-199° (EtOH) (51)
UV: (MeOH) 214 (4.53), 254 (4.40), 302 sh (3.62), 402 (3.71); (MeOH-H^+) 224 (4.47), 267 (4.37), 331 sh (3.70), 345 sh (3.60), 486 (3.61) (2)
See also (26)
IR: ($CHCl_3$) 1665 (2)
See also (26)
PMR: 200 MHz ($CDCl_3$) (2)
See also (51)
MS: 337 (M^+, 100), 294 (54), 279 (8) (2)
See also (51)
Sources:
Fumariaceae: *Corydalis claviculata* (L.) DC. (2, 51)
Total synthesis (26, 51)
Partial synthesis from natural cularine (2)

21. OXOCOMPOSTELLINE



$C_{18}H_{11}NO_5$: 321.0637
MP: 295° (EtOH) (51)
UV: (EtOH) 208 (4.67), 254 (4.41), 292 sh, 397 (3.61); (EtOH-HCl) 208 (4.67), 261 (4.34), 410 (3.47), 4.60 (3.23) (51)
IR: (KBr) 1670 (51)
PMR: 80 MHz ($CDCl_3$) (51)
MS: 321 (M^+, 72), 306 (5), 293 (5), 278 (100) (51)
Sources:
Fumariaceae: *Sarcocapnos enneaphylla* DC. (51)
Total synthesis (51)

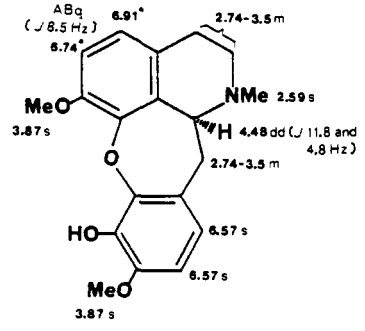
22. (+)-CLAVICULINE



$C_{18}H_{19}NO_4$: 313.1314
MP: 112-113° (EtOH) (10)
$[\alpha]_D$: +443° (c=0.41, MeOH) (10)
UV: (EtOH) 218 (4.59), 276 (4.10); (EtOH-OH^-) 240 (5.66), 292 (4.55) (10)
IR: 3420 (10)
PMR: ($CDCl_3$) (10)
CMR: (DMSO-d_6+D_2O) (only nonoxygenated carbons) 109.48 d, 115.33 d, 121. 62 d, 121.97 s, 126.34 d,, 126.50 s, 131.87 s; (DMSO-d_6+NaOD) 109.50 d, 117.85 d, 113.62 d, 123.04 s, 125.15 d, 119.69 s, 131.04 s, (10)
MS: 313.1323 (M^+, 100), 298 (43), 296 (34), 270 (13), 161 (9), 148 (11), 132 (16) (10)

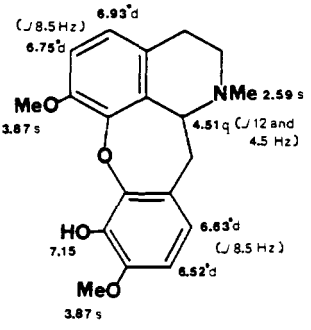
Sources:
Fumariaceae: *Sarcocapnos crassifolia* DC. (10)

23. (+)-SARCOCAPNIDINE



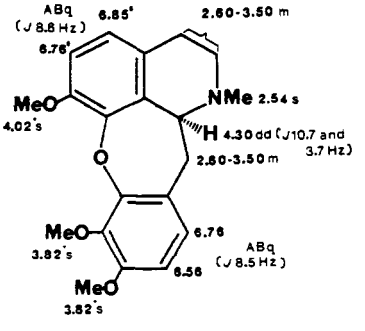
$C_{19}H_{21}NO_4$: 327,1470
MP: 126-127° (EtOH) (10)
$[\alpha]_D$: +385.4° (c=0.0696) (10)
UV: (EtOH) 238 (3.8), 281 (3.5); (EtOH-OH^-) 250 (3.73), 294 (3.62) (10)
IR: 3460 (10)
PMR: ($CDCl_3$) (10)
CMR: (DMSO-d_6; dioxane as internal standard) (only nonoxygenated carbons) 109.08 d, 111.12 d, 120.69 d, 121.00 s, 125.57 d, 127.32 s, 132.10 s; (DMSO-d_6+NaOD) 109.05 d, 110.92 d, 114.31 d, 120.92 s, 125.03 d, 126.66 s, 133.00 s (10)
MS: 327.1456 (M^+, 100), 312 (51), 310 (29), 296 (20), 284 (24), 281 (36), 174 (40), 148 (14) (10)
Sources:
Fumariaceae; *Sarcocapnos crassifolia* DC. (10)
Partial synthesis from crassifoline (10)

24. (±)-5′-O-DEMETHYLISO-CULARINE



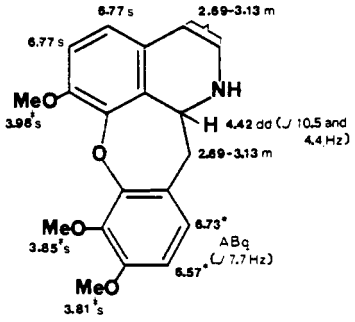
$C_{19}H_{21}NO_4$: 327.1470
MP: 127-129° (Et_2O) (52)
See also (7)
UV: (EtOH) 276 sh (3.77), 283 (3.78) (7)
IR: ($CHCl_3$) 3480 (7, 9)
PMR: ($CDCl_3$) (7, 9)
MS: 327 (M^+, 100) (7, 9)
Sources:
Synthetic (7, 9, 52)

25. (+)-SARCOCAPNINE
(Isocularine)



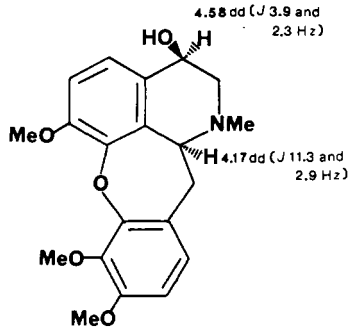
$C_{20}H_{23}NO_4$: 341.1627
MP: (HCl) 213-215° (Et_2O-EtOH) (53)
$[\alpha]^{25}_D$: +218° (c=0.3, EtOH) (53)
UV: (MeOH) 232 (4.12), 283 (3.14) (53)
PMR: 80 MHz ($CDCl_3$) (53)
MS: 341 (M^+, 100), 326 (66), 298 (40) (53)
Sources:
Fumariaceae: *Sarcocapnos enneaphylla* DC. (53)
Synthesis (7, 9, 52)

26. (±)-NORSARCOCAPNINE (Norisocularine)



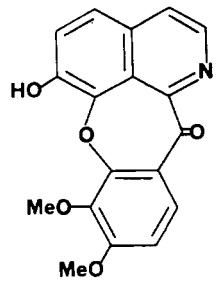
$C_{19}H_{21}NO_4$: 327.1470
UV: (EtOH) 229 sh, 274, 283, 295 (53)
PMR: ($CDCl_3$) (53)
MS: 327 (M^+, 100), 312 (32), 294 (20), 162 (47), 86 (34), 84 (56) (53)
Sources:
Semisynthetic: Reduction of natural oxosarcocapnine (53)

27. (+)-4-HYDROXYSARCOCAPNINE



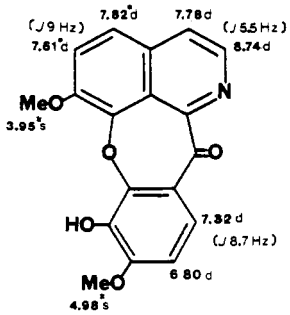
$C_{20}H_{23}NO_5$: 357.1576
PMR: (68)
Sources:
Fumariaceae: *Sarcocapnos enneaphylla* DC. (68)
Total synthesis (68)
The 4-epi isomer is also known synthetically, H-1 appearing at δ 4.60 (68).

28. OXOSARCOPHYLLINE



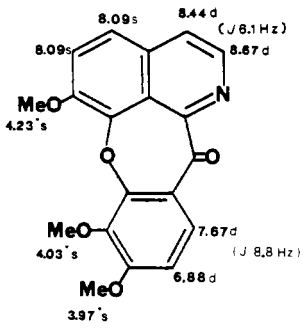
$C_{18}H_{13}NO_5$: 323.0793
Sources:
Fumariaceae: *Sarcocapnos enneaphylla* DC. (67)

29. OXOSARCOCAPNIDINE



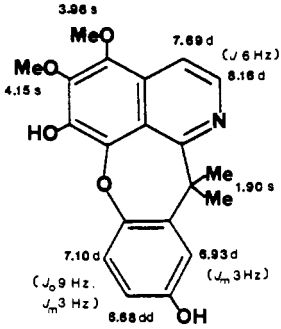
$C_{18}H_{13}NO_5$: 323.0793
MP: 231-232° (MeOH) (10)
UV: (EtOH) 252 (4.26), 432 (3.34), 396 (3.59); (EtOH-OH^-) 243 (4.26), 340 (3.34), 400 (3.57); (EtOH-H^+) 217 (4.28), 265 (4.05), 458 (3.55) (10)
IR: 3400, 1670 (10)
PMR: ($CDCl_3$) (10)
MS: 323 (M^+, 100), 308 (8), 306 (14), 295 (13), 280 (50), 265 (11), 237 (16), 209 (11) (10)
Sources:
Fumariaceae: *Sarcocapnos crassifolia* DC. (10)
Partial synthesis from sarcocapnidine (10)

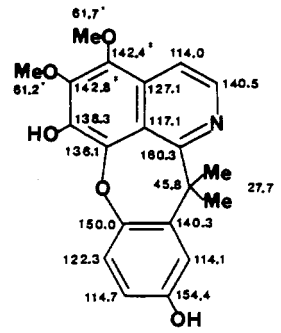
30. OXOSARCOCAPNINE



$C_{19}H_{15}NO_5$: 337.0950
MP: 202-203° (EtOH) (53)
UV: (EtOH) 254 (4.19), 330 (3.16), 400 (3.53); (EtOH-HCl) 266, 398, 462 (53)
IR: (KBr) 1675 (53)
PMR: ($CDCl_3$+TFAA-*d*) (53)
MS: 337 (M^+, 100), 294 (60) (53)
Sources:
Fumariaceae: Sarcocapnos enneaphylla ADC. (53)
Partial synthesis (53)

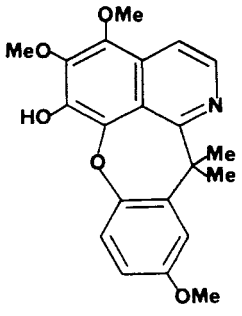
31. GOUREGINE





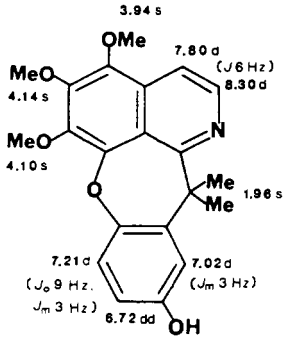
$C_{20}H_{19}NO_5$: 353.1263
MP: 112-114° (MeOH) (54)
UV: (EtOH) 229 (4.28), 247 (4.25), 291 (3.50), 348 (3.45); (EtOH-OH^-) 260 (4.47), 307 (4.15), 379 (3.98); (EtOH-H^+) 231 (4.22), 274 (4.27), 304 (3.35), 404 (3.35) (54)
PMR: ($CDCl_3$) (54)
CMR: 15.08 MHz ($CDCl_3$) (54)
MS: 354 (20), 353.1265 (M^+, 100), 352 (8), 329 (21), 338 (85), 323 (5), 322 (6), 308 (7) (54)
X-RAY: (Diacetylgouregine) (54)
Sources:
Annonaceae: *Guatteria ouregou* Dunal (54)
Partial synthesis from melosmine (54)

32. 3′-O-METHYLGOUREGINE



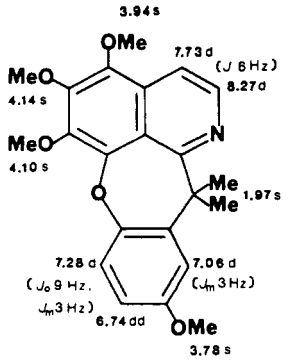
$C_{21}H_{21}NO_5$: 367.1419
Sources:
Semisynthetic: O-Methylation of gouregine (71)

33. 7-O-METHYLGOUREGINE



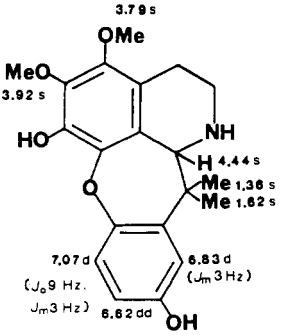
$C_{21}H_{21}NO_5$: 367.1419
PMR: 250 MHz ($CDCl_3$) (71)
Sources:
Semisynthetic: O-Methylation of gouregine (71)

34. O,O-DIMETHYLGOUREGINE



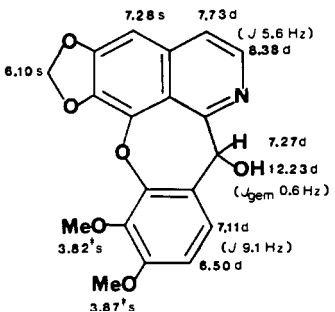
$C_{22}H_{23}NO_5$: 381.1576
UV: (EtOH) 225 (4.09), 237 sh (4.03) (71)
IR: (KBr) 2980, 2925, 2840, 1600, 1580, 1545, 1485, 1455, 1405, 1380, 1370, 1315, 1295, 1265, 1190, 1170, 1135, 1110, 1070, 1020, 995, 950, 915, 865, 825, 800 (71)
PMR: 400 MHz ($CDCl_3$) (54, 71)
MS: 381 (M^+, 93), 366 (100), 356 (7), 336 (17) (54, 71)
Sources:
Semisynthetic: O-Methylation of gouregine (54, 71)

35. (±)-TETRAHYDROGOUREGINE



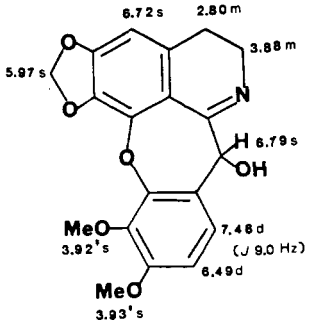
$C_{20}H_{23}NO_5$: 357.1576
UV: (EtOH) 208 (4.44), 279 (3.97); (EtOH+NaOH) 216 (4.78), 241 sh (4.31), 290 (4.09) (71)
IR: (KBr) 3400, 3300, 2890, 2810, 1600, 1465, 1380, 1330, 1290, 1190, 1100, 1050, 965 (71)
PMR: 250 MHz ($CDCl_3$) (71)
MS: 357 (M^+, 100), 342 (15), 340 (100), 326 (36), 310 (25), 235 (33), 207 (37) (71)
Sources:
Semisynthetic: Reduction of gouregine (71)

36. (±)-LINARESINE



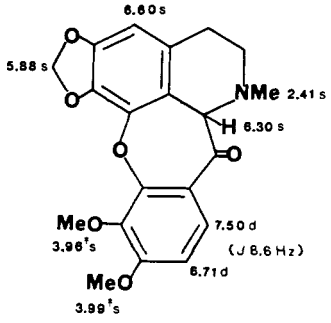
$C_{19}H_{15}NO_6$: 353.0899
MP: 215° (C_6H_6-Et_2O-MeOH) (70)
UV: (MeOH) 236 (4.71), 298 (4.27), 334 (4.09); (MeOH-H^+) 245 (4.61), 312 (4.23), 346 (4.11) (70)
IR: ($CDCl_3$) 3680, 3000 (70)
PMR: 360 MHz (CD_3CN) (70)
NOEDS: (70)
MS: 353 (M^+, 85), 336 (5), 324 (16), 310 (11), 294 (100), 279 (14), 211 (3), 181 (14), 172 (78) (70)
Sources:
Berberidaceae: *Berberis valdiviana* Phil. (70)

37. (±)-DIHYDROLINARESINE



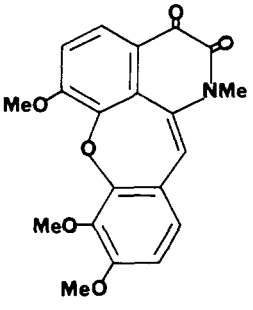
$C_{19}H_{17}NO_6$: 355.1055
MP: 170° (C_6H_6-Et_2O-MeOH) (70)
UV: (MeOH) 230 (4.37), 299 (4.23), 325 (4.07); (MeOH-H^+) 238 (4.22), 250 (4.22), 260 (4.06), 307 (4.14), 381 (3.86) (70)
IR: ($CHCl_3$) 3660, 3000 (70)
PMR: 360 MHz ($CDCl_3$) (70)
MS: 355 (M^+, 52), 338 (4), 326 (18), 312 (5), 296 (100), 280 (9), 181 (13), 176 (12) (70)
Sources:
Berberidaceae: *Berberis valdiviana* Phil. (70)

38. (±)-N-METHYLDIHYDRO-LINARESINONE



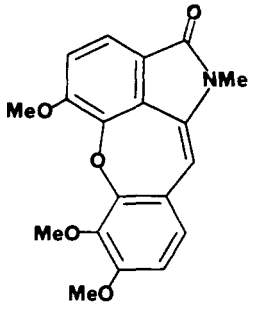
$C_{20}H_{19}NO_6$: 369.1212
MP: 84° (MeOH) (70)
UV: (MeOH) 235 (4.09), 295 (4.11), 337 (3.36); (MeOH-H^+) 238 (4.09), 253 (4.10), 309 (4.08), 369 (3.72) (70)
IR: ($CHCl_3$) 1710 (70)
PMR: 360 MHz ($CDCl_3$) (70)
MS: 369 (M^+, 54), 368 (5), 354 (17), 341 (22), 340 (100), 338 (7) (70)
Sources:
Semisynthetic: N-methylation of natural dihydro-linaresine (70)

39. YAGONINE



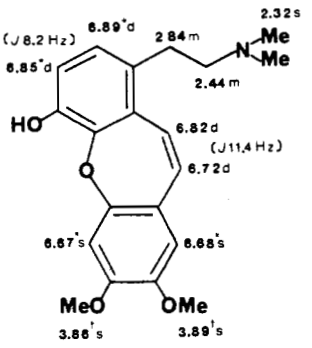
$C_{20}H_{17}NO_6$: 367.1056
Sources:
Fumariaceae: *Sarcocapnos enneaphylla* DC. (67)
Partial synthesis from (+)-4-hydroxy sarcocapnine (67)

40. ARISTOYAGONINE



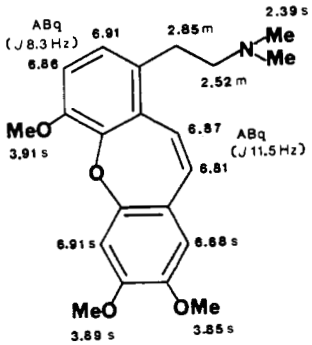
$C_{19}H_{19}NO_4$: 325.1314
Sources:
Fumariaceae: *Sarcocapnos enneaphylla* DC. (67)

41. SECOCULARIDINE



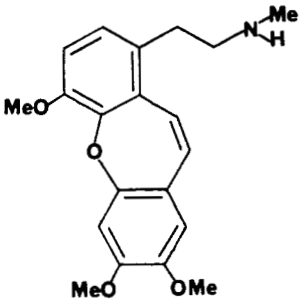
$C_{20}H_{23}NO_4$: 341.1627
MP: 189-190° (MeOH) (69)
UV: (EtOH) 216 (3.88), 236 sh (3.83), 296 sh (3.41), 320 (3.51); (EtOH-OH^-) 216 (4.13), 330 (3.57) (69)
IR: (KBr) 1604, 1565, 1512 (69)
PMR: 250 MHz ($CDCl_3$) (69)
MS: 341 (M^+, 2), 284 (1), 283 (1), 165 (1), 152 (2), 139 (2), 115 (2), 58 (100) (69)
Sources:
Fumariaceae: *Corydalis claviculata* (L.) DC. (69)
Partial synthesis from cularidine (69)

42. SECOCULARINE



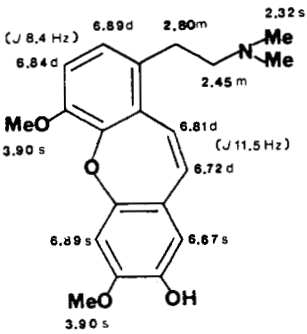
$C_{21}H_{25}NO_4$: 355.1783
MP: ($HClO_4$) 194-196° (69)
UV: (EtOH) 220 (4.32), 235 sh (4.25), 296 sh (3.78), 320 (3.88) (69)
IR: (KBr) 1604, 1562, 1510 (69)
PMR: 250 MHz ($CDCl_3$) (69)
NOEDS: (69)
MS: 355 (M^+, 6), 297 (2), 165 (1), 152 (1), 139 (1), 58 (100) (69)
Sources:
Fumariaceae: *Sarcocapnos crassifolia* DC. (69)
Partial synthesis from cularine methiodide (69)
Partial synthesis from norsecocularine (69)
Partial synthesis from secocularidine (69)

43. NORSECOCULARINE



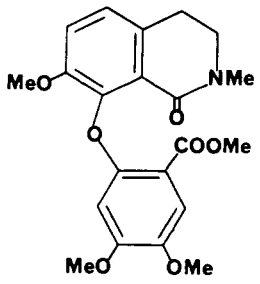
$C_{20}H_{23}NO_4$: 341.1627
Sources:
Fumariaceae: *Corydalis claviculata* (L.) DC. (66)

44. 3′-O-DEMETHYLSECOCULARINE



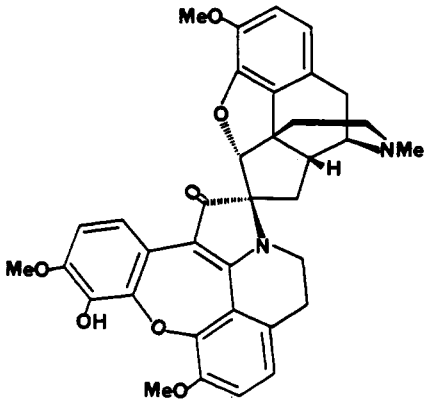
$C_{20}H_{23}NO_4$: 341.1627
UV: (EtOH) 226 (3.95), 298 sh (3.45), 320 (3.50); (EtOH-OH^-) 220 (4.19), 274 (3.91), 302 (3.65), 350 (3.42) (69)
PMR: 250 MHz ($CDCl_3$) (69)
NOEDS: (69)
MS: 341 (0.6), 287 (0.6), 283 (0.4), 165 (0.4), 152 (0.5), 139 (0.6), 115 (0.5), 59 (3), 58 (100) (69)
Sources:
Semisynthetic: Hofmann degradation of 3′-O-demethylcularine methiodide (69)

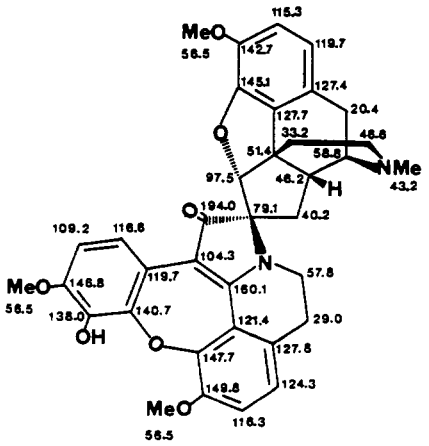
45. NOYAINE



$C_{21}H_{23}NO_7$: 401.1474
Sources:
Fumariaceae: *Corydalis claviculata* (L.) DC. (66)

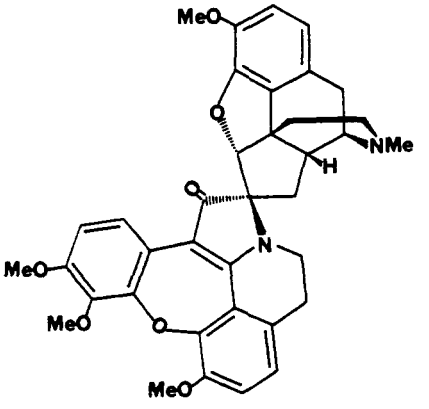
46. CANCENTRINE
(F-22)





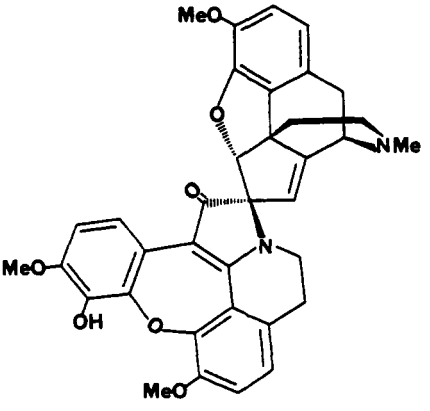
$C_{36}H_{34}N_2O_7$: 606.2365
MP: 237-238° ($CHCl_3$-MeOH) (55)
(HCl) 286° ($CHCl_3$-MeOH) (12)
See also (56)
UV: (EtOH) 213 (4.80), 230 sh (4.63), 268 (4.32), 291 sh (4.22), 330 sh (3.62), 435 (3.82) (56, 57)
IR: ($CHCl_3$) 3450, 1665 (56, 57)
PMR: 100 MHz ($CDCl_3$)
δ 1.6-3.8 (14H, aliphatic protons, partially assigned), 2.51 (3H, s, NCH_3), 3.86, 3.95 and 4.00 (9H, 3s, 3 OCH_3), 4.88 (1H, s, H-5), 6.5-7.2 (5H, m, ArH′ s), 7.51 (1H, d, H-23) (57)
See also (56)
NOE: δ3.91 OCH_3 irr., δ 6.83 ArH (25%), 3.76 OCH_3 irr., 6.68 ArH (25%), 3.83 OCH_3 irr., 6.98 ArH (24%) (56)
See also (57)
CMR: (58)
MS: 606 (75), 363 (25), 350 (20), 303 (M^{2+}), 256 (12), 243 (40), 185 (100) (57)
See also (56)
X-RAY: (Dihydromethine-O-methylether hydrobromide) (56, 57)
Sources:
Fumariaceae: *Dicentra canadensis* (Goldie) Walp. (12, 55)
For structure elucidation, see (56, 57)
For synthesis of spiro moiety, see (59)
For acetolysis products and derivatives, see (60)

47. CANCENTRINE O-METHYL ETHER



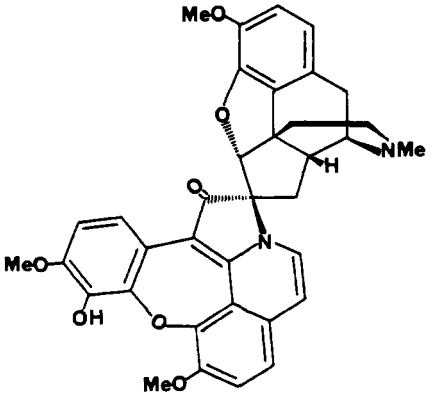
$C_{37}H_{36}N_2O_7$: 620.2522
MP: 269° (cyclohexane-MeOH) (57)
UV: (EtOH) 210 (4.83), 230 sh (4.66), 269 (4.22), 330 sh (3.56), 433 (3.71) (57)
IR: ($CHCl_3$) 1660 (57)
See also (56)
PMR: 100 MHz ($CDCl_3$)
δ 1.5-3.8 (14H, aliphatic protons), 2.52 (3H, s, NCH_3), 3.84, 3.94, 3.96 and 4.01 (12H, 4s, 4 OCH_3), 4.88 (1H, s, H-5), 6.5-7.2 (5H, m, ArH' s), 7.70 (1H, d, H-23) (57)
MS: 620.253, 377, 364, 256, 243 (57)
Sources:
Semisynthetic: O-Methylation of natural cancentrine (56, 57)

48. DEHYDROCANCENTRINE A



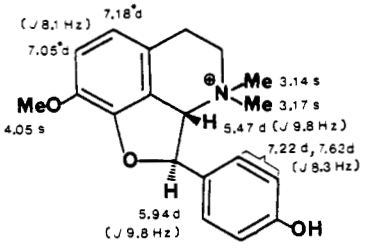
$C_{36}H_{32}N_2O_7$: 604.2209
MP: 194° (MeOH) (61)
UV: (EtOH) 216 (4.77), 269 (4.36), 296 sh (4.29), 445 (3.87) (61)
IR: 3440, 1660, 1620 (61)
PMR: 100 MHz ($CDCl_3$)
δ 2.53 (3H, s, NCH_3), 3.80 (6H, s, 2 OCH_3), 3.93 (3H, s, OCH_3), 5.04 (2H, s) (61)
MS: 604 (M^+, 35), 546 (100) (61)
Sources:
Fumariaceae: *Dicentra canadensis* (Goldie) Walp. (61)
For structure elucidation, see (61)

49. DEHYDROCANCENTRINE B



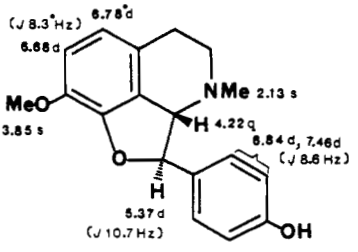
$C_{36}H_{32}N_2O_7$: 604.2209
MP: 206° (MeOH) (61)
UV: (EtOH) 216 sh (4.86), 242 (4.78), 270 sh (4.23), 310 sh (4.16), 370 (3.90), 446 (4.00), 492 (3.95), 525 sh (3.85) (61)
IR: 3450, 1660, 1630 (61)
PMR: 100 MHz ($CDCl_3$)
δ 2.50 (3H, s, NCH_3), 3.84, 3.90 and 3.99 (9H, 3s, 3 OCH_3), 4.84 (1H, s, 5β) (61)
MS: 604 (100), 361 (11), 348 (6), 256 (2), 243 (12), 185 (21) (61)
Sources:
Fumariaceae: *Dicentra canadensis* (Goldie) Walp. (61)
For structure elucidation, see (61)

50. (±)-QUETTAMINE



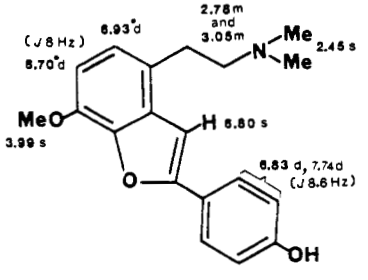
$C_{19}H_{22}NO_3^+$: 312.1599
UV: (Cl^-) (MeOH) 223 sh (3.89), 280 (3.16); (MeOH-OH^-) 248 (3.83), 283 (3.32) (62)
PMR: (Cl^-) 200 MHz (TFA-*d*) (62)
MS: 311 (0.9), 253 (0.7), 238 (0.5), 204 (0.9), 181 (0.4), 174 (1.6), 145 (0.7), 107 (0.4), 91 (0.5), 73 (2.3), 72 (1.3), 60 (1), 59 (3.6), 58 (100) (62)
Sources:
Berberidaceae: *Berberis baluchistanica* Ahrendt (62)
Total synthesis (63)

51. (±)-N-DEMETHYLQUETTAMINE



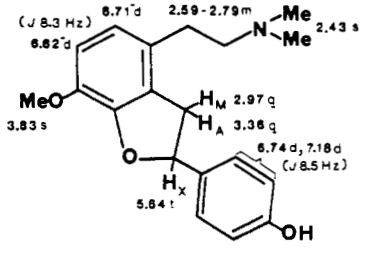
$C_{18}H_{19}NO_3$: 297.1365
MP: 187-189° (dec) (MeOH) (63)
UV: (MeOH) 208 (4.49), 231 (4.26), 275 (4.04) (63)
PMR: 360 MHz ($CDCl_3$) (63)
MS: 297 (M^+, 76), 174 (100) (63)
Sources:
Synthetic (63)

52. SECOQUETTAMINE



$C_{19}H_{21}NO_3$: 311.1521
MP: 171-172° (MeOH) (62)
[α]D: 0° (62)
UV: (MeOH) 205 (4.19), 250 (3.75), 300 (4.12), 308 (4.11), 323 sh (3.85); (MeOH-OH^-) 220 (4.08), 250 (3.50), 324 (4.17) (62)
PMR: 200 MHz ($CDCl_3$) (62)
MS: 311 (M^+, 2.2), 253 (1.9), 238 (1.4), 181 (1.2), 165 (0.8), 84 (4.8), 58 (100), 42 (2.3) (62)
Sources:
Berberidaceae: *Berberis baluchistanica* Ahrendt (62)
Total synthesis (63, 64)
Partial synthesis from natural quettamine (62)

53. (±)-DIHYDROSECOQUETTAMINE



J_{AM} 15.3 Hz; J_{AX} 9.1 Hz; J_{MX} 9.2 Hz

$C_{19}H_{23}NO_3$: 313.1678
UV: (MeOH) 275 (3.51), 300 sh (2.72) (62)
PMR: 200 MHz ($CDCl_3$) (62)
MS: 313 (M^+, 3.2), 255 (0.1), 107 (0.6), 58 (100) (62)
Sources:
Berberidaceae: *Berberis baluchistanica* Ahrendt (62)
Total synthesis (63)
Partial synthesis from natural quettamine (62)

Alphabetical List of the Cularine Alkaloids

Aristoyagonine (**40**)
(+)-Celtine (**6**)
(+)-Celtisine (**3**)
(+)-Claviculine (**22**)
(+)-Culacorine (**1**)
(+)-Cularicine (**9**)
(+)-Cularidine (**5**)
(+)-Cularimine (**8**)
(+)-Cularine (**7**)
(±)-Dihydrolinaresine (**37**)
Gouregine (**31**)
(+)-4-Hydroxysarcocapnine (**27**)
(+)-Limousamine (**14**)
(±)-Linaresine (**36**)
(+)-Norcularicine (**10**)
Norsecocularine (**43**)
Noyaine (**45**)
Oxocompostelline (**21**)
Oxocularine (**20**)
Oxosarcocapnidine (**29**)
Oxosarcocapnine (**30**)
Oxosarcophylline (**28**)
(+)-Sarcocapnidine (**23**)
(+)-Sarcocapnine (**25**)
Secocularidine (**41**)
Secocularine (**42**)
Yagonine (**39**)

Alphabetical List of the Cancentrine Alkaloids and the Quettamines

Cancentrine Alkaloids	Quettamines
Cancentrine (**46**)	(±)-Dihydrosecoquettamine (**53**)
Dehydrocancentrine A (**48**)	(±)-Quettamine (**50**)
Dehydrocancentrine B (**49**)	Secoquettamine (**52**)

Bŏtanical Distribution of the Cularine Alkaloids

Aristoyagonine (**40**)
Fumariaceae:
Sarcocapnos enneaphylla DC. (67)
(+)-Celtine (**6**)
Fumariaceae:
Sarcocapnos enneaphylla DC. (65)
(+)-Celtisine (**3**)
Fumariaceae:
Sarcacapnos enneaphylla DC. (65)
(+)-Claviculine (**22**)
Fumariaceae:
Sarcocapnos crassifolia DC. (10)
(+)-Culacorine (**1**)
Fumariaceae:
Corydalis claviculata (L.) DC. (2)
Sarcocapnos crassifolia DC. (65)
(+)-Cularicine (**9**)
Fumariaceae:
Corydalis claviculata (L.) DC. (11)
(+)-Cularidine (**5**)
Fumariaceae:
Corydalis claviculata (L.) DC. (11, 13)
Dicentra cucullaria (L.) Bern. (12, 16)
(+)-Cularimine (**8**)
Fumariaceae:
Dicentra eximia Torr. (12, 16)
(+)-Cularine (**7**)
Fumariaceae:
Corydalis claviculata (L.) DC. (12, 13, 16)
Dicentra cucullaria (L.) Bernh. (12, 16)
Dicentra eximia Torr. (12, 16)
Dicentra formosa Walp. (12, 16)
Dicentra oregana Eastw. (12, 16)
(±)-Dihydrolinaresine (**37**)
Berberis valdiviana Phil. (70)
Gouregine (**31**)
Annonaceae:
Guatteria ouregou Dunal (54)
(+)-4-Hydroxysarcocapnine (**27**)
Fumariaceae:
Sarcocapnos enneaphylla DC. (68)
(+)-Limousamine (**14**)
Fumariaceae:
Corydalis claviculata (L.) DC. (19)
(±)-Linaresine (**36**)
Berberidaceae:
Berberis valdiviana Phil. (70)
(+)-Norcularicine (**10**)
Fumariaceae:
Corydalis claviculata (L.) DC. (2)
Norsecocularine (**43**)
Fumariaceae:
Corydalis claviculata (L.) DC. (66)
Noyaine (**45**)
Fumariaceae:
Corydalis claviculata (L.) DC. (66)
Oxocompostelline (**21**)
Fumariaceae:
Sarcocapnos enneaphylla DC. (51)
Oxocularine (**20**)
Fumariaceae:
Corydalis claviculata (L.) DC. (2, 51)
Oxosarcocapnidine (**29**)
Fumariaceae:
Sarcocapnos crassifolia DC. (10)
Oxosarcocapnine (**30**)

Fumariaceae:
Sarcocapnos enneaphylla DC. (53)
Oxosarcophylline (**28**)
Fumariaceae:
Sarcocapnos enneaphylla DC. (67)
(+)-Sarcocapnidine (**23**)
Fumariaceae:
Sarcocapnos crassifolia DC. (10)
(+)-Sarcocapnine (**25**)
Fumariaceae:
Sarcocapnos enneaphylla DC. (53)
Secocularidine (**41**)
Fumariaceae:
Corydalis claviculata (L.) DC. (69)
Secocularine (**42**)
Fumariaceae:
Sarcocapnos crassifolia DC. (69)
Yagonine (**39**)
Fumariaceae:
Sarcocapnos enneaphylla DC. (67)

Botanical Distribution of the Cancentrine Alkaloids and the Quettamines

Cancentrine Alkaloids	Quettamines
1. Cancentrine (**46**) Fumariaceae: *Dicentra canadensis* (Goldie) Walp. (12, 55)	1. (±)-Dihydrosecoquettamine (**53**) Berberidaceae: *Berberis baluchistanica* Ahrendt (62)
2. Dehydrocancentrine A (**48**) Fumariaceae: *Dicentra canadensis* (Goldie) Walp. (61)	2. (±)-Quettamine (**50**) Berberidaceae: *Berberis baluchistanica* Ahrendt (62)
3. Dehydrocancentrine B (**49**) Fumariaceae: *Dicentra canadensis* (Goldie) Walp. (61)	3. Secoquettamine (**52**) Berberidacea: *Berberis baluchistanica* Ahrendt (62)

Occurrence of the Cularine, Cancentrine, and Quettamine Alkaloids by Plant Sources

Annonaceae
Guatteria ouregou Dunal
Gouregine (**31**)
Berberidaceae
Berberis baluchistanica Ahrendt
(±)-Dihydrosecoquettamine (**53**)
(±)-Quettamine (**50**)
Secoquettamine (**52**)
Berberis valdiviana Phil.
(±)-Dihydrolinaresine (**37**)
(±)-Linaresine (**36**)
Fumariaceae
Corydalis claviculata (L.) DC.
(+)-Culacorine (**1**)
(+)-Cularicine (**9**)
(+)-Cularidine (**5**)
(+)-Cularine (**7**)
(+)-Limousamine (**14**)
(+)-Norcularicine (**10**)
Norsecocularine (**43**)
Noyaine (**45**)
Oxocularine (**20**)
Secocularidine (**41**)
Dicentra canadensis (Goldie) Walp.
Cancentrine (**46**)
Dehydrocancentrine A (**48**)
Dehydrocancentrine B (**49**)
Dicentra cucullaria (L.). Bernh.
(+)-Cularidine (**5**)
(+)-Cularine (**7**)
Dicentra eximia Torr.
(+)-Cularine (**7**)
Dicentra formosa Walp.
(+)-Cularine (**7**)
Dicentra oregana Eastw.
(+)-Cularine (**7**)
Sarcocapnos crassifolia DC.
(+)-Claviculine (**22**)
(+)-Culacorine (**1**)
Oxosarcocapnidine (**29**)
(+)-Sarcocapnidine (**23**)
Secocularine (**42**)
Sarcocapnos enneaphylla DC.
Aristoyagonine (**40**)
(+)-Celtine (**6**)
(+)-Celtisine (**3**)
(+)-4-Hydroxysarcocapnine (**27**)
Oxocompostelline (**21**)
Oxosarcocapnine (**30**)
Oxosarcophylline (**28**)
(+)-Sarcocapnine (**25**)
Yagonine (**39**)

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Sunil K. Talapatra, Milan K. Pal, Asok K. Mallik, and Bani Talapatra, "Structure and Synthesis of (−)-Anabellamide. A New Phenylalanine Derived Ester Amide from *Anaphalis subumbellata:* Occurrence of 4′-Hydroxydehydrokawain," *J. Nat. Prod.*, **46**, 140 (1983): It has been brought to the editor's attention that the structure represented for (−)-anabellamide is identical with that for asperphenamate, a metabolite of *Aspergillus flavipes* and *Penicillium canadense* [*Lloydia* **40**, 146 (1977); *Phytochemistry* **17**, 552 (1977); *Tetrahedron* **34**, 2791 (1978)]. The physical data reported for (−)-anabellamide is nearly identical to that of asperphenamate which, therefore, has priority as the trivial name.