

THE PAVINE AND ISOPAVINE ALKALOIDS

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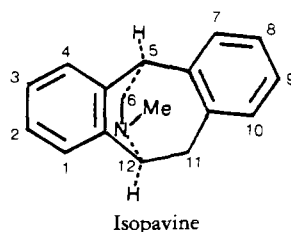
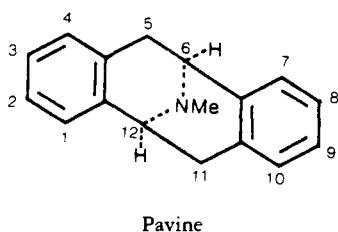
Twenty pavine and ten isopavine alkaloids are presently known, and their chemistry has been amply summarized. They are all derived biogenetically from benzylisoquinolines functionalized in ring B (1a-g).

Pavines are found in four plant families, namely the Papaveraceae, the Berberidaceae, the Lauraceae, and the Ranunculaceae. Within the ambit of the Papaveraceae, it is the genera *Argemone* and *Eschscholtzia* in which the pavines are known to occur. In the Berberidaceae, it is again two genera, *Berberis* and *Leontice*, which produce pavines. Only the genus *Cryptocarya* among the Lauraceae is known to possess pavines; and similarly within the Ranunculaceae, it is solely the genus *Thalictrum* that possesses pavines.

Interestingly enough, the genus *Thalictrum* also produces a wide variety of isopavines. It is, thus, a significant fact that only the genus *Thalictrum* (Ranunculaceae) generates both pavines and isopavines. Isopavines are also found in *Papaver* and *Roemeria* species (Papaveraceae).

The giant meadow Rue, *Thalictrum polygamum* Muhl., is presently the sole known source for the dimeric aporphine-pavine alkaloids pennsylvavine and pennsylvavoline. Because these two alkaloids have already been listed among the aporphine dimers, they are not included in the present review (1g).

Several of the pavines and isopavines are probably derived biogenetically from the tetrahydrobenzylisoquinoline (+)-reticuline, or a close analog thereof. They possess the corresponding stereochemistry, as indicated in the two structural expressions below (1d).



The absolute configuration of the pavines was first established by degradation of *N*-benzyl-(−)-argemonine chloride to (−)-*N,N*-dimethyldi-*n*-propyl aspartate of known absolute configuration. That of the isopavines was settled by a study of the circular dichroism curve of (−)-amurensine, and application of the aromatic chirality rule (1d). An X-ray study has confirmed the absolute configuration of the pavines (23).

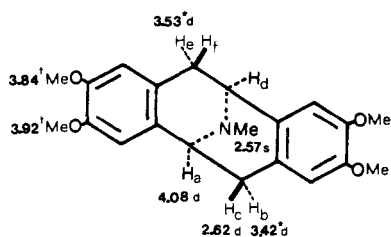
It will be noted that nearly all pavines and isopavines are levorotatory. The exceptions are the pavines argemonine and eschscholtzidine, which have also been reported in their dextrorotatory forms, and caryachine, which has been isolated in the levo as well as the racemic forms.

All uv data are in nm, with log ϵ values quoted in parentheses; ir frequencies are in cm^{-1} . ¹H-nmr chemical shift values are on the δ scale, and were measured at 60 MHz. Values with identical superscripts are interchangeable.

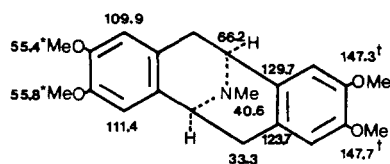
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It is important to note that the data quoted below are as cited in the original literature. In particular, we have refrained from reinterpreting some of the nmr spectral information.

1. (-)-ARGEMONINE
(-)-N-Methylpavine



ArH δ 6.59 s(2H), and 6.76 s(2H)
 J_{ab} 6 Hz, J_{ac} 0 Hz, J_{bc} 17 Hz



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

MP: 147-148° (2)

152-154° (MeOH) (3)

152.5-153° (MeOH) (4)

153.5-155° (5)

155-156° (Et₂O) (6)

155.5-156.6° (EtOH) (7)

(hydrate) 125-135° (8)

$[\alpha]^{24}_D$: -187.93° (c=1.01, CHCl₃) (4)

$[\alpha]_D$: -202° (CHCl₃) (3)

$[\alpha]^{25}_D$: -203° (c=3.31, CHCl₃) (5)

$[\alpha]^{21}_D$: -208° ± 3° (c=0.5, CHCl₃) (9)

$[\alpha]^{27}_D$: -209° (c=0.5, CHCl₃) (8)

$[\alpha]^{24}_D$: -214.22° (c=1.01, EtOH) (4, 10)

$[\alpha]^{20}_D$: -226° (c=0.1, CHCl₃) (7)

UV: 205 sh (4.94), 230 sh (4.15), 276 sh (3.79), 282 (3.91), 287 (3.93), 292 (3.89) (9, 10, 11, 12, 13a)

IR: (CHCl₃) 3010, 2960, 2940, 2910, 2860, 2835, 1618, 1519, 1510, 1470, 1458, 1410, 1373, 1358, 1343, 1311, 1290, 1258, 1178, 1130, 1113, 1100, 1018, 998, 973, 950, 920, 860, 826 (13a, 9, 14)

¹H-NMR: (CDCl₃) (11, 3, 6, 8, 15)

¹³C-NMR: (CDCl₃) (16)

MS: 355, 354, 204 (100) (17)

ORD: (c=0.12, EtOH) $[\alpha]_{370}$ -779°, $[\alpha]_{294}$ -1,353° tr, $[\alpha]_{287}$ -123° pk, $[\alpha]_{273}$ -5,600° sh, $[\alpha]_{241}$ -18,360° tr, $[\alpha]_{228}$ +3,280° pk, $[\alpha]_{212}$ -29,100° tr, $[\alpha]_{207}$ -7,787° (10, 7)

CD: (EtOH) $[\theta]_{298}$ 0, $[\theta]_{292.5}$ -1,344, $[\theta]_{291}$ 0, $[\theta]_{278}$ +12,680, $[\theta]_{251}$ 0, $[\theta]_{236}$ -74,890, $[\theta]_{223}$ 0, $[\theta]_{206}$ -415,000 (10, 18, 19, 20)

Absolute Configuration: (18, 20, 21, 22)

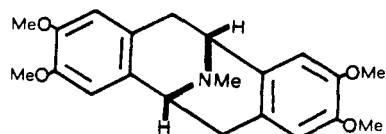
X-RAY: Methiodide (23)

SOURCES: PAPAVERACEAE: *Argemone gracilentia* Greene (5), *A. hispida* Gray (4, 8, 14), *A. munita* Dur. and Hilg. (24), *A. munita* Dur. and Hilg. var. *Rotundata* (Rydb.) G. B. Ownb. (4, 14, 25, 26), *A. munita* Dur. and Hilg. var. *argentea* G. B. Ownb. (27), *A. platyceras* Link and Otto (9), *A. sanguinea* Greene (28)

BERBERIDACEAE: *Berberis buxifolia* Lam. (3)

RANUNCULACEAE: *Thalictrum revolutum* DC (6, 29, 30), *T. strictum* Ledeb. (2)

2. (+)-ARGEMONINE



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

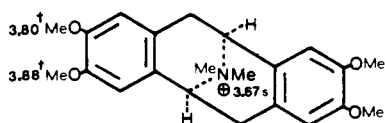
MP: 152-153° (CHCl₃) (31, 32)

$[\alpha]_D$: +218° (c=2.11, EtOH) (31, 32)

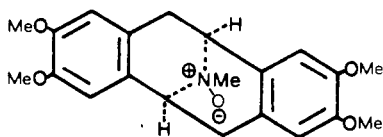
Remaining physical properties resemble those of (-)-argemonine.

SOURCE: BERBERIDACEAE: *Leontice smirnovii* Trautv. (31, 32)

3. (-)-ARGEMONINE N-METHO SALT

ArH δ 6.53 s(2H), and 6.82 s(2H)Aliph. CH δ 3.1-5.5 (6H) $C_{22}H_{28}O_4N^+$: 370.2018MP: (Cl^-) 170-172° (EtOH) (29)(I^-) 272-273° (dec.) (MeOH) (29)(ClO_4^-) 274-275° (MeOH) (33)[α] $^{25}_D$: (OH^-) -170° (c=2.81, $CHCl_3$) (5)[α] $^{25}_D$: (I^-) -200° \pm 6° (c=0.14, MeOH) (33)UV: (Cl^-) (MeOH) 286 (3.86) (29)(I^-) (MeOH) 230 sh (4.42), 285 (3.90) (29)IR: (OH^-) ($CHCl_3$) 2950, 1616, 1466, 1370, 1253, 1159, 1122, 1110, 1031, 1010, 998, 949, 861 (5) 1H -NMR: (OH^-) ($CDCl_3$) (5, 29)MS: (Cl^-) 370 (0.4), 356 (10), 355 (41), 354 (26), 340 (5), 205 (15), 204 (100) (29)(OH^-) 355 (54), 354 (36), 340 (6), 324 (5), 205 (22), 204 (100), 190 (6) (5)CD: (c=5.7 $\times 10^{-3}$ M, MeOH) [θ] $_{277} + 7,490$, [θ] $_{239} - 82,400$ (29)SOURCES: PAPAVERACEAE: *Argemone gracilentia* Greene (5), *A. platyceras* Link and Otto (33, 34)RANUNCULACEAE: *Thalictrum revolutum* DC (29)

4. (-)-ARGEMONINE N-OXIDE

 $C_{21}H_{25}O_5N$: 371.1732

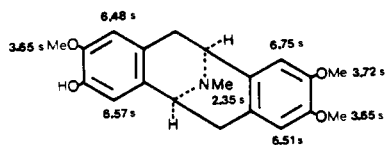
MP: 140-160° (effervescence) (5)

[α] $^{25}_D$: -185° (c=2.81, $CHCl_3$) (5)IR: ($CHCl_3$) 2959, 1618, 1511, 1466, 1366, 1344, 1159, 1131, 1110, 1072, 1012, 971, 951, 926, 911, 893 (5) 1H -NMR: ($CDCl_3$) 2.58-4.65 (m, 6H, saturated ring H), 3.35 (s, 3H, NCH_3), 3.78 (s, 6H, OCH_3), 3.82 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.50 (s, 1H, ArH), 6.54 (s, 1H, ArH), 6.65 (s, 2H, ArH) (5, 15)

MS: 371 (1), 369 (3), 355 (45), 354 (18), 205 (10), 204 (100), 190 (8) (5)

SOURCE: PAPAVERACEAE: *Argemone gracilentia* Greene (5)

5. (-)-NORARGEMONINE

 $C_{20}H_{23}O_4N$: 341.1627MP: 241-242° ($CHCl_3$ -MeOH) (9)242-244° (C_6H_6 - $CHCl_3$) (3)

244-250° (MeOH) (8)

255-256° (dec.) ($CHCl_3$) (35)[α] $^{20}_D$: -147° (c=1.64, $CHCl_3$) (35)[α] $^{25}_D$: -150° (c=0.34, $CHCl_3$) (36)[α] $^{27}_D$: -151° (c=0.5, $CHCl_3$) (8)[α] $^{21}_D$: -153° \pm 3° (c=0.30, $CHCl_3$) (37)[α] $^{27}_D$: -153.69° (c=2.786, $CHCl_3$) (14)[α] $_D$: -154° (c=2.79, $CHCl_3$) (10)[α] $^{20}_D$: -154° \pm 4° ($CHCl_3$) (3)

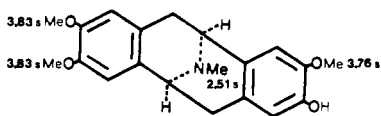
UV: (EtOH) 205 sh (4.94), 230 sh (4.12), 278 sh (3.81), 283 (3.92), 287 (3.93), 293 (3.92) (10, 3, 9, 13b, 37)

IR: (Nujol) 1612, 1537, 1519, 1507, 1482, 1313, 1293, 1258, 1245, 1232, 1214, 1190, 1172, 1136, 1110, 1053, 1030, 1020, 1002, 974, 950, 922, 874, 858, 843, 831, 819, 790, 764, 738 (13b, 9, 14, 37, 38)

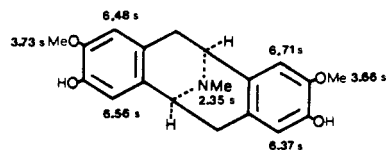
 1H -NMR: ($DMSO-d_6$) (39, 3, 8, 38)

MS: 341 (61), 340 (38), 204 (100), 190 (79) (40, 3)

6. (-)-ISONORARGEMONINE



ArH δ 6.45 bs(2H), and 6.58 bs(2H)

7. (-)-BISNORARGEMONINE
(-)-Rotundine

ORD: ($c=0.10$, EtOH) $[\alpha]_{360} -750$, $[\alpha]_{289} +450^\circ$, $[\alpha]_{273} -6,000^\circ$ sh, $[\alpha]_{241} -16,800^\circ$ tr, $[\alpha]_{288} -750^\circ$ pk, $[\alpha]_{212} -32,000^\circ$ tr, $[\alpha]_{205} +30,000$ (10)

CD: (EtOH) $[\theta]_{298} 0$, $[\theta]_{280} +14,630$, $[\theta]_{250} 0$, $[\theta]_{235} -58,520$, $[\theta]_{220} -22,510$, $[\theta]_{206} -225,000$ (10)

SOURCES: PAPAVERACEAE: *Argemone brevicornuta* G. B. Ownb. (41), *A. hispida* Gray (4, 8, 14), *A. platyceras* Link and Otto (9, 36), *A. munita* Dur. and Hilg. var. *rotundata* (Rydb.) G. B. Ownb. (14, 25, 26, 29), *Eschscholtzia californica* Cham. (37), *E. glauca* Greene (37), *E. douglasii* (Hook. and Arn.) Walp. (37)

BERBERIDACEAE: *Berberis buxifolia* Lam. (3)

RANUNCULACEAE: *Thalictrum dasycarpum* Fisch. and Lall. (42)

LAURACEAE: *Cryptocarya longifolia* Kostermans (35)

$C_{20}H_{23}O_4N$: 341.1627

MP: 219-221° (MeOH) (5)

$[\alpha]^{25}_D$: -202° ($c=3.31$, $CHCl_3$) (5)

UV: (MeOH) 287 (3.96) (30)

1H -NMR: ($CDCl_3$) (8, 30, 39)

CD: (MeOH) $[\theta]_{293} -1,930$, $[\alpha]_{275} +9,370$, $[\theta]_{232} -26,700$ (30)

SOURCES: PAPAVERACEAE: *Argemone gracilentia* Greene (5), *A. munita* Dur. and Hilg. var. *argentea* G. B. Ownb. (27)

RANUNCULACEAE: *Thalictrum revolutum* DC (30)

$C_{19}H_{21}O_4N$: 327.1470

MP: 243-246° (EtOH) (8)

254-255° (MeOH) (37)

$[\alpha]^{20}_D$: -134° ($c=0.4$, EtOH) (35)

$[\alpha]^{27}_D$: -222° ($c=0.3$, $CHCl_3$) (8)

$[\alpha]^{20}_D$: $-244^\circ \pm 3^\circ$ ($c=0.32$, MeOH) (37)

$[\alpha]^{20}_D$: $-244^\circ \pm 3^\circ$ ($c=0.19$, $CHCl_3$) (37)

$[\alpha]^{25}_D$: -265.8° ($c=0.158$, MeOH) (10, 25)

UV: (EtOH) 230 sh (4.07), 279 sh (3.83), 285 (3.92), 288 (3.93), 294 (3.89) (10, 13a, 37)

IR: (Nujol) 3480, 1610, 1540, 1517, 1508, 1320, 1287, 1264, 1248, 1223, 1214, 1175, 1143, 1125, 1108, 1025, 1011, 971, 950, 928, 871, 863, 836, 818, 783, 779, 738, 729 (13c, 37)

1H -NMR: ($DMSO-d_6$) (39, 8)

MS: 328 (15), 327 (70), 326 (57), 312 (11), 311 (9), 191 (37), 190 (100), 177 (7), 176 (6), 175 (15), 162 (7), 137 (6) (39, 8)

ORD: ($c=0.10$, EtOH) $[\alpha]_{260} -800^\circ$, $[\alpha]_{296} -1,225^\circ$ tr, $[\alpha]_{288} +250^\circ$ pk, $[\alpha]_{270} -6,800^\circ$ sh, $[\alpha]_{240} -16,400^\circ$ tr, $[\alpha]_{227} -5,000^\circ$ pk, $[\alpha]_{212} -37,000^\circ$ tr, $[\alpha]_{208} -11,500^\circ$ (10)

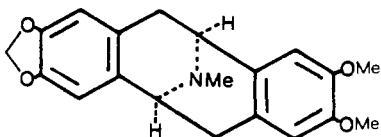
CD: (EtOH) $[\theta]_{300} 0$, $[\theta]_{294} -1,295$, $[\theta]_{280} +13,810$, $[\theta]_{250} 0$, $[\theta]_{235} -47,470$, $[\theta]_{224} -23,740$, $[\theta]_{206} -287,500$ (10)

SOURCES: PAPAVERACEAE: *Argemone hispida* Gray (8), *A. munita* Dur. and Hilg. var. *rotundata* (Rydb.) G. B. Ownb. (8, 25, 43), *Eschscholtzia californica* Cham. (37, 44), *E. douglasii* (Hook and Arn.) Walp. (37), *E. glauca* Greene (37)

RANUNCULACEAE: *Thalictrum dasycarpum* Fisch. and Lall. (42)

LAURACEAE: *Cryptocarya longifolia* Kostermans (35)

8. (-)-ESCHSCHOLTZIDINE
((-)-O-Methylcaryachine)



$C_{20}H_{21}O_4N$: 339.1470

MP: Amorphous

$[\alpha]^{24}_D$: -194.2° ($c=1.56$, MeOH) (10, 46)

UV: (EtOH) 235 sh (4.01), 282 sh (3.88), 290 (3.97), 303 (3.72) (10)

1H -NMR: (CDCl₃) 2.50 (s, 3H, NCH₃), 3.76 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 3.91 (s, 1H, CH), 4.01 (s, 1H, CH), 5.79 and 5.81 (ABq, $J=1$ Hz, 2H, OCH₂O), 6.41 (s, 2H, ArH), 6.58 (s, 2H, ArH) (6, 15, 45)

MS: 339, 338, 204, 188 (100) (17)

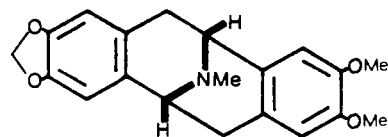
ORD: ($c=0.10$, EtOH) $[\alpha]_{360} -750^\circ$, $[\alpha]_{292} +150^\circ$ pk, $[\alpha]_{275} -5,200^\circ$ sh, $[\alpha]_{244} -10,400^\circ$ tr, $[\alpha]_{232} -5,500^\circ$ pk, $[\alpha]_{212} -33,500^\circ$ tr, $[\alpha]_{199} +75,000^\circ$ pk, $[\alpha]_{195} +56,250^\circ$ (10)

CD: (EtOH) $[\theta]_{305} 0$, $[\theta]_{301} -335$, $[\theta]_{299} 0$, $[\theta]_{285} +11,600$, $[\theta]_{251} 0$, $[\theta]_{240} -22,400$, $[\theta]_{225} 0$, $[\theta]_{207} -245,000$, $[\theta]_{198} 0$ (10)

SOURCES: PAPAVERACEAE: *Eschscholtzia californica* Cham. (46)

RANUNCULACEAE: *Thalictrum revolutum* DC (6, 29)

9. (+)-ESCHSCHOLTZIDINE
((+)-O-Methylcaryachine)



$C_{20}H_{21}O_4N$: 339.1470

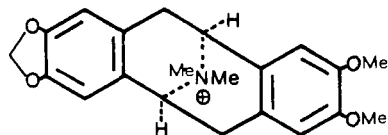
MP: (Cl⁻) 178-180° (H₂O) (47)

$[\alpha]^{25}_D$: $+195.1^\circ$ ($c=1.00$, EtOH) (47)

Remaining physical properties resemble those of (-)-eschscholtzidine

SOURCE: LAURACEAE: *Cryptocarya chinensis* Hemsl. (47)

10. (-)-ESCHSCHOLTZIDINE N-METHO
SALT



$C_{21}H_{24}O_4N^+$: 354.1705

MP: N.A.

$[\alpha]^{20}_D$: (Cl⁻) -170° ($c=0.26$, MeOH) (29)

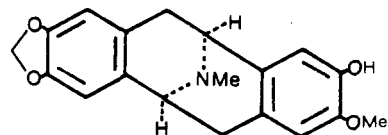
UV: (Cl⁻) (MeOH) 289 (3.74), 257 (3.46), 230 sh (3.91) (29)

1H -NMR: (Cl⁻) (CDCl₃) 3.68 (bs, 6H, N(CH₃)₂), 3.79 (s, 3H, OCH₃), 3.86 (s, 3H, OCH₃), 5.57 (bd, 2H, CH), 5.89 (bs, 2H, OCH₂O), 6.48 (s, 1H, ArH), 6.55 (s, 1H, ArH), 6.80 (s, 1H, ArH), 6.85 (s, 1H, ArH) (29)

CD: (Cl⁻) ($c=3.2 \times 10^{-3}$, MeOH) $[\theta]_{282} +6,440$, $[\theta]_{241} -40,600$ (29)

SOURCES: RANUNCULACEAE: *Thalictrum revolutum* DC (29)

11. (-)-CARYACHINE



$C_{19}H_{19}O_4N$: 325.1314

MP: 170° (Et₂O) (19)

174-175° (48)

$[\alpha]^{21}_D$: -269.6° ($c=1.00$, EtOH) (48)

$[\alpha]^{20}_D$: -251° ($c=0.43$, EtOH) (19)

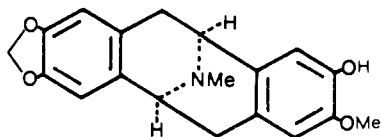
UV: (EtOH) 291.5 (4.02) (48)

(EtOH) 294 (3.95) (19)

(hexane) 303, 295, 290, 285, 278 (19)

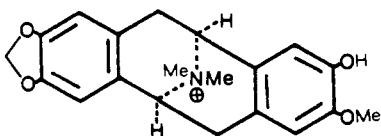
$^1\text{H-NMR}$: (CDCl_3) 2.49 (s, 3H, NCH_3), 2.49 and 2.54 (2 x d, $J=16.2$ Hz, 2H, CH_2), 3.41 (2 x q, $J=5.4$ Hz, $J=16.2$ Hz, 2H, CH_2), 3.79 (s, 3H, OCH_3), 3.96 (2 x d, $J=5.4$ Hz, 2H, 2CH), 5.78 and 5.84 (q, $J=1.2$ Hz, 2H, OCH_2O), 6.38 and 6.42 (2 x s, 2H, ArH), 6.54 (s, 2H, ArH) (48, 19)
 MS: 326 (15), 325 (50), 324 (34), 282 (3), 190 (100), 188 (100) (19)
 CD: (19)
 SOURCE: LAURACEAE: *Cryptocarya chinensis* Hemsl. (47, 48)

12. (+)-CARYACHINE

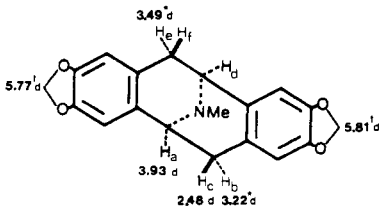


$\text{C}_{19}\text{H}_{19}\text{O}_4\text{N}$: 325.1314
 MP: 241-242° (EtOH) (48)
 $[\alpha]^{28}_{\text{D}}$: 0° ($c=0.27$, EtOH) (48)
 UV: (EtOH) 291.5 (3.97) (48)
 $^1\text{H-NMR}$: (CDCl_3) 2.54 (s, 3H, NCH_3), 3.86 (s, 3H, OCH_3), 5.83 and 5.88 (q, $J=1.8$ Hz, 2H, OCH_2O), 6.40 and 6.48 (2 x s, 2H, ArH), 6.59 (s, 2H, ArH) (48)
 SOURCE: LAURACEAE: *Cryptocarya chinensis* Hemsl. (47, 48)

13. (-)-CARYACHINE N-METHO SALT



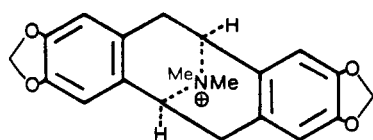
$\text{C}_{20}\text{H}_{22}\text{O}_4\text{N}^+$: 340.1549
 MP: (ClO_4^-) 211-212° (H_2O) (15)
 (I^-) 174-175° (MeOH) (15)
 $[\alpha]^{25}_{\text{D}}$: (ClO_4^-) -224° ($c=0.13$, MeOH) (15)
 $[\alpha]^{24}_{\text{D}}$: (I^-) -160° ($c=0.12$, MeOH) (15)
 UV: (ClO_4^-) (MeOH) 291.5 (3.95), 225 sh (4.07) (15)
 IR: (ClO_4^-) (KBr) 3400, 1628, 1600, 1506, 1485, 1447, 1392, 1355, 1303, 1270, 1246, 1112, 1036, 950, 930, 908, 879, 625 (15)
 $^1\text{H-NMR}$: (ClO_4^-) (CD_3OD) 3.30 (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.92 (s, 3H, OCH_3), 5.95 (ABq, $J=1$ Hz, 2H, OCH_2O), 6.60 (s, 2H, ArH), 6.82 (s, 1H, ArH), 6.95 (s, 1H, ArH) (15)
 MS: (I^-) 339 (10), 338 (7), 326 (11), 325 (48), 324 (35), 311 (6), 310 (11), 309 (8), 204 (12), 191 (10), 190 (67), 189 (16), 188 (100), 176 (8), 175 (11), 142 (43), 127 (18) (15)
 CD: (ClO_4^-) (MeOH) $\{\theta\}_{297} -39,400$, $\{\theta\}_{279} +82,000$, $\{\theta\}_{238} -380,400$ (15)
 SOURCE: LAURACEAE: *Cryptocarya chinensis* Hemsl. (15)

14. (-)-ESCHSCHOLTZINE
 ((-)-Crychine, (-)-Californine)

ArH δ 6.40 s(2H), and 6.58 s(2H)
 J_{ab} 6 Hz, J_{ac} 0 Hz, J_{bc} 17 Hz

$\text{C}_{19}\text{H}_{17}\text{O}_4\text{N}$: 323.1157
 MP: 128° (MeOH) (44)
 127-128° (Et₂O) (49)
 $[\alpha]^{20}_{\text{D}}$: -184.5° ($c=2.20$, CHCl_3) (48)
 $[\alpha]^{20}_{\text{D}}$: -202° ($c=1.00$, MeOH) (10, 44)
 $[\alpha]^{15}_{\text{D}}$: -220.2° ($c=1.00$, EtOH) (48)
 $[\alpha]^{19}_{\text{D}}$: -240° ± 3° ($c=0.50$, MeOH) (49)
 UV: (EtOH) 235 sh (3.80), 275 sh (3.93), 281 (4.03), 296 (4.04), 307 sh (3.96) (10, 12, 13d, 44, 48, 49)
 IR: (CHCl_3) 3010, 2960, 2890, 2770, 1624, 1503, 1482, 1438, 1380, 1370, 1339, 1311, 1283, 1270, 1168, 1130, 1119, 1070, 1041, 1019, 973, 952, 939, 866, 838 (13d, 48)
 $^1\text{H-NMR}$: (CDCl_3) (12, 48)

15. (-)-CALIFORNIDINE
(-)-Eschscholtzine N-metho salt)



MS: 323, 188 (12, 17)

ORD: ($c=0.10$, EtOH) $[\alpha]_{360} -900^\circ$, $[\alpha]_{301} -1,250^\circ$ tr, $[\alpha]_{292} +850^\circ$ pk, $[\alpha]_{275} -7,200^\circ$ sh, $[\alpha]_{245} -15,600^\circ$ tr, $[\alpha]_{232} -4,000^\circ$ pk, $[\alpha]_{215} -36,000^\circ$ (10, 7)

CD: (EtOH) $[\theta]_{306} 0$, $[\theta]_{300} -2,395$, $[\theta]_{297} 0$, $[\theta]_{286} +18,650$, $[\theta]_{254} 0$, $[\theta]_{240} -37,310$, $[\theta]_{227} +17,050$, $[\theta]_{205} -255,000$ (10)

SOURCES: PAPAVERACEAE: *Eschscholtzia californica* Cham. (44, 50), *E. douglasii* (Hook. and Arn.) Walp. (49), *E. glauca* Greene (49)

LAURACEAE: *Cryptocarya chinensis* Hemsl. (47, 48)

$C_{20}H_{20}O_4N^+$: 338.1392

MP: (I^-) 285-286° (MeOH) (49)

(ClO_4^-) 324-326° (H₂O) (49)

(ClO_4^-) 327-329° (MeOH) (51)

$[\alpha]^{18}D$: (I^-) $-212 \pm 3^\circ$ ($c=0.5$, MeOH) (49)

$[\alpha]^{19}D$: (ClO_4^-) -217° ($c=0.2$, EtOH) (49)

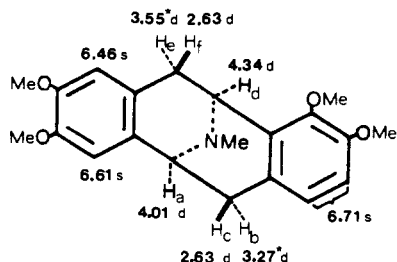
$[\alpha]^{23}D$: (ClO_4^-) $-219 \pm 10^\circ$ ($c=0.10$, MeOH) (51)

UV: (I^-) (MeOH) 292 (4.02) (49, 13e)

IR: (Nujol) 1510, 1494, 1483, 1342, 1239, 1225, 1210, 1178, 1153, 1131, 1074, 1038, 1019, 1010, 983, 950, 924, 908, 900, 860, 850, 839, 742 (13e)

SOURCES: PAPAVERACEAE: *Eschscholtzia californica* Cham. (52), *E. douglasii* (Hook. and Arn.) Walp. (49), *E. glauca* Greene (49), *E. oregana* Greene (51)

16. (-)-O-METHYLPLATYCERINE
(-)-O,O-Dimethylmunitagine)



Four OCH_3 δ 3.77, 3.80, 3.85 and 3.94.

$J_{ab=de}$ 6 Hz, $J_{ac=df}$ 0 Hz, $J_{bc=ef}$ 17 Hz

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

MP: 124-125.5° (Et₂O + Skellysolve A) (8)

$[\alpha]^{27}D$: -292° ($c=0.35$, $CHCl_3$) (8)

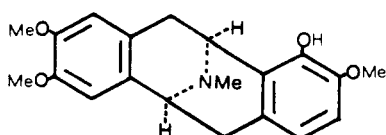
$[\alpha]^{20}D$: -202° ($c=0.14$, $CHCl_3$) (9)

IR: (KBr) 2950, 2860, 1610, 1510 d, 1450, 1430, 1370, 1350, 1280, 1250 d, 1220, 1135, 1110, 1080, 1040, 1015 d, 990, 978, 873, 863, 847, 820, 785, 770, 732 (8)

1H -NMR: ($CDCl_3$) (8)

SOURCE: Semisynthetic (8, 9; See also 53)

17. PLATYCERINE



$C_{20}H_{23}O_4N$: 341.1627

MP: 130-132° (Et₂O) (9)

$[\alpha]^{21}D$: $-267 \pm 3^\circ$ ($c=0.24$, $CHCl_3$) (9)

$[\alpha]^{28}D$: -305° ($c=0.2$, MeOH) (30)

UV: (MeOH) 282 (3.85), 315 sh (3.38) (30, 9, 13f)

IR: ($CHCl_3$) 3550, 3010, 2965, 2940, 2910, 2850, 2840, 2810, 2775, 1616, 1594, 1518, 1500, 1467, 1446, 1372, 1358, 1330, 1313, 1281, 1244, 1173, 1156, 1129, 1108, 1083, 1058, 1036, 1019, 1004, 985, 951, 931, 867, 858, 823 (13f, 9)

1H -NMR: ($CDCl_3$) 2.51 (s, 3H, NCH_3), 3.72 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.95 (d, $J=6$ Hz, 1H, CH), 4.36 (d,

$J=6$ Hz, 1H, CH), 6.47 and 6.72 (ABq, $J=8.5$ Hz, 2H, ArH), 6.46 (s, 1H, ArH), 6.55 (s, 1H, ArH) (30, 5).

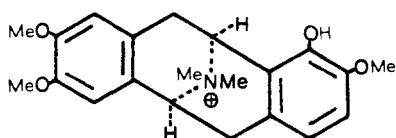
MS: 341 (33), 340 (22), 204 (100), 190 (30), 170.5 (3) (5)

CD: (MeOH) $[\theta]_{275} -15,800$, $[\theta]_{240} +32,400$ (30)

SOURCES: PAPAVERACEAE: *Argemone gracilentia* Greene (5), *A. platyceras* Link and Otto (9)

RANUNCULACEAE: *Thalictrum revolutum* DC (29, 30)

18. (-)-PLATYCERINE N-METHO
SALT



$C_{21}H_{26}O_4N^+$: 356.1862

MP: (ClO_4^-) 160-164° (MeOH) (34)

(ClO_4^-) 152-175° (MeOH-Et₂O) (33)

$[\alpha]^{22}_D$: $(ClO_4^-) -257^\circ \pm 3^\circ$ ($c=0.26$, MeOH) (33)

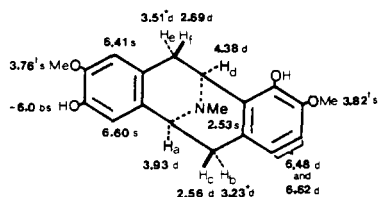
UV: (ClO_4^-) (MeOH) 227 (4.12), 234 (4.14), 260 (3.27), 284 (3.77) (33)

IR: (ClO_4^-) (Nujol) 3380, 3370 (33)

MS: (I⁻) 341, 340, 204, 190, 142, 127 (33)

SOURCE: PAPAVERACEAE: *Argemone platyceras* Link and Otto (33, 34)

19. (-)-MUNITAGINE



$J_{ab=de}$ 6 Hz, $J_{ac=df}$ 0 Hz, $J_{bc=ef}$ 17 Hz,
 $J_{9,10}$ 8 Hz

$C_{19}H_{21}O_4N$: 327.1470

MP: 167-169° (MeOH-Et₂O) (8)

$[\alpha]^{27}_D$: -239° ($c=0.5$, CHCl₃) (8)

UV: (EtOH) 283 (3.63) (54)

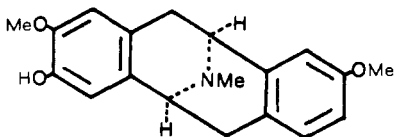
IR: (KBr) 3580, 3470, 2950, 2870, 1620, 1500, 1455, 1370, 1335, 1285, 1250, 1135, 1123, 1080, 1020, 990, 960, 870, 828, 804, 783, 768, 730 (8)

¹H-NMR: (CDCl₃) (8)

MS: 328 (7), 327 (30), 326 (25), 312 (7), 192 (16), 191 (17), 190 (100), 177 (6), 175 (7), 156 (7), 147 (12), 145 (6) (8)

SOURCES: PAPAVERACEAE: *Argemone gracilentia* Greene (5), *A. munita* Dur. and Hilg. var. *rotundata* (Rydb.) G. B. Ownb. (8, 43)

20. (-)-2-HYDROXY-3,8-
DIMETHOXYPAVINANE
((-)-2,9-Dimethoxy-3-
hydroxypavinane)



$C_{19}H_{21}O_3N$: 311.1521

MP: 197-198° (MeOH) (43)

$[\alpha]^{27}_D$: -254° ($c=1.59$, MeOH) (43)

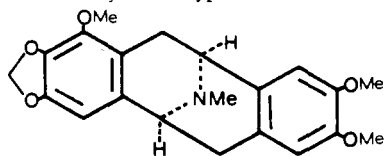
IR: (KBr) 2920, 1625, 1530, 1505, 1460, 1430, 1330, 1260, 1120, 1020, 875 (43)

¹H-NMR: 2.46 (s, 3H, NCH₃), 3.73 (s, 6H, OCH₃), 2.35-4.06 (m, 2 ABX, 6H, saturated ring H), 6.45-6.80 (m, 5H, ArH) (43)

MS: 311 (55), 190 (100), 174 (63) (43)

SOURCE: PAPAVERACEAE: *Argemone munita* Dur. and Hilg. var. *rotundata* (Rydb.) G. B. Ownb. (43)

21. (-)-2,3-METHYLENEDIOMOXY-
4,8,9-TRIMETHOXYPAVINANE
((-)-2,3,7-Trimethoxy-8,9-
methylenedioxy-pavinane)



$C_{21}H_{23}O_5N$: 369.1576

MP: 144-145° (Et₂O) (55)

$[\alpha]^{22}_D$: -174° ($c=0.977$, MeOH) (55)

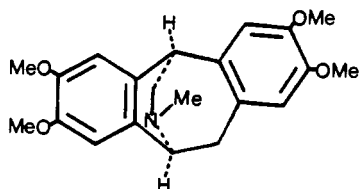
UV: (EtOH) 287 (3.84) (55)

¹H-NMR: (CDCl₃) 2.46 (s, 3H, NCH₃), 3.72 (s, 3H, OCH₃), 3.80 (s, 6H, OCH₃), 2.40-4.05 (m, 6H, saturated ring H), 5.75 and 5.80 (2 x d, $J=1.5$ Hz, 2H, OCH₂O), 6.23 (s, 1H, ArH), 6.36 (s, 1H, ArH), 6.54 (s, 1H, ArH) (55)

MS: 369, 368, 354, 204 (100), 218 (70) (55)

SOURCE: RANUNCULACEAE: *Thalictrum strictum* Ledeb. (55)

22. (-)-O-METHYLTHALISOPAVINE

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

MP: For synthetic racemate:

163-165° (MeOH-H₂O) (56)

165-166° (MeOH) (57)

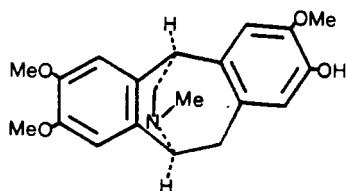
164-166.5° (MeOH) (55)

IR: (CHCl₃) 1605 (42)¹H-NMR: (CDCl₃) 2.46 (s, 3H, NCH₃), 3.75 (s, 3H, OCH₃), 3.84 (s, 9H, OCH₃), 2.60-4.00 (m, 6H, saturated ring H), 6.51 (s, 1H, ArH), 6.64 (s, 1H, ArH), 6.75 (s, 2H, ArH) (57, 42, 59)

MS: 355 (22), 354 (18), 312 (36), 281 (7), 269 (14), 204 (100) (59, 42, 56)

SOURCE: PAPAVERACEAE: *Papaver radicum* Rottb. (= *P. nudicaule* L. var. *radicum* Rottb.) (59)

23. (-)-THALISOPAVINE

 $C_{20}H_{23}O_4N$: 341.1627

MP: 211-212° (EtOH) (42)

[α]²⁵_D: -210° (c=0.21, CHCl₃) (42)

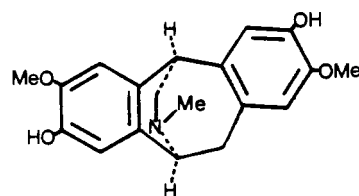
UV: (EtOH) 289(4.06) (42)

IR: (CHCl₃) 3571, 1610, 1600 (42)¹H-NMR: 2.48 (s, 3H, NCH₃), 3.86 (s, 9H, OCH₃), 4.90 (bs, 1H, OH), 6.54 (s, 1H, ArH), 6.61 (s, 1H, ArH), 6.75 (s, 2H, ArH) (42)

MS: 341, 204 (100) (42)

SOURCE: RANUNCULACEAE: *Thalictrum dasycarpum* Fisch. and Lall. (42)

24. (-)-THALIDICINE

 $C_{19}H_{21}O_4N$: 327.1470MP: 200° (EtOH-Et₂O) (60)

UV: (EtOH) 221(4.38), 290(3.96) (60)

IR: (KBr) 3420, 2940, 1595, 1510, 1450, 1260, 1140, 1030, 760 (60)

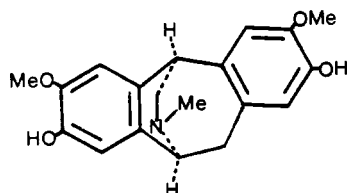
¹H-NMR: (DMSO-*d*₆) 2.26 (s, 3H, NCH₃), 3.06-3.6 (m, 7H, saturated ring H and 1 OH), 3.70 (s, 6H, OCH₃), 6.36 (s, 1H, ArH), 6.60 (s, 1H, ArH), 6.66 (s, 1H, ArH), 6.73 (s, 1H, ArH), 8.58 (s, 1H, OH) (60)

MS: 327 (12), 326 (17), 284 (34), 241 (14), 190 (100) (60)

SOURCE: RANUNCULACEAE: *Thalictrum dioicum* L. (60)

Structural determination is incomplete. Alkaloid may be identical with (-)-thalidine.

25. (-)-THALIDINE

 $C_{19}H_{21}O_4N$: 327.1470

MP: 205-207° (MeOH) (61)

[α]²⁵_D: -172° (c=0.7, MeOH) (61)

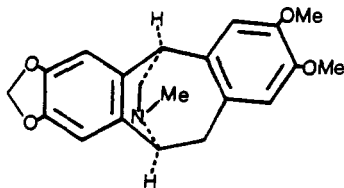
UV: (EtOH) 250 sh(4.08), 291(4.30) (61)

¹H-NMR: (TFA-*d*) 3.00 (s, 3H, NCH₃), 3.99 (s, 6H, OCH₃), 6.70 (s, 1H, ArH), 6.83 (s, 1H, ArH), 7.00 (s, 1H, ArH), 7.12 (s, 1H, ArH) (61)

MS: 327, 284, 190 (100) (61)

CD: (MeOH) [θ]₂₅₅ -2,753, [θ]₂₅₀ -8,261, [θ]₂₄₅ -26,848, [θ]₂₄₀ -33,043, [θ]₂₃₅ -30,290, [θ]₂₃₀ -22,373, [θ]₂₂₅ -13,768, [θ]₂₂₀ -4,130, [θ]₂₁₅ 0, [θ]₂₁₀ 0 (62)SOURCE: RANUNCULACEAE: *Thalictrum dioicum* L. (61)

26. (-)-AMURENSININE

C₂₀H₂₁O₄N: 339.1470MP: 136°-138° (Et₂O) (65)

144-146° (MeOH) (66)

143-144° (Et₂O) (64)

162-164° (63)

[α]²²_D: -102°±4° (c=0.14, MeOH) (66)[α]²¹_D: -108°±10° (c=0.14, MeOH) (64)[α]²²_D: -42.6°±3° (c=0.16, CHCl₃) (66)[α]²²_D: -142°±5° (c=0.10, MeOH) (65)[α]²²_D: -162°±4° (c=0.80, CHCl₃) (63)[α]²²_D: -175°±4° (c=0.750, MeOH) (63)

UV: (EtOH) 230 (4.07), 250 sh (3.67), 294 (3.95) (63-66)

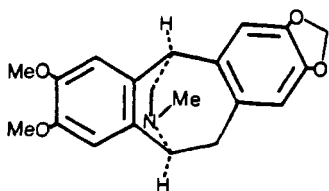
IR: (CHCl₃) 1606 (63)

¹H-NMR: (CDCl₃) 2.50 (s, 3H, NCH₃), 3.14 (m, 4H, 2 x CH₂), 3.78 (s, 3H, OCH₃), 3.86 (s, 3H, OCH₃), 3.84, 3.93 and 4.02 (t, 2H, CH), 5.83, 5.85, 5.90 and 5.93 (ABq, 2H, OCH₂O), 6.53 (d, 1H, ArH), 6.63 (d, 1H, ArH), 6.73 (s, 2H, ArH) (63, 66, 67)

MS: 339 (20), 338 (19), 312 (4), 296 (27), 188 (100) (68, 40, 64-66)

SOURCES: PAPAVERACEAE: *Papaver tauricola* Boiss. (68), *P. anomalum* Fedde (66), *P. pseudocanescens* M. Pop. (65), *P. pyrenaicum* L. (Kerner) (69), *P. pyrenaicum* L. (Kerner) var. *rhoeaticum* (Ler.) Fedde (64), *P. alpinum* L. (69), *P. alpinum* L. var. *burseri* (64), *P. alpinum* L. var. *kernerii* (64), *P. alpinum* L. var. *taticum* Nyár. (64, 69), *P. nudicaule* L. var. *xanthopetalum* (Trautv.) Fedde (69), *P. nudicaule* L. var. *leiocarpum* (Turz.) (69), *P. nudicaule* L. var. *rubroaurantiacum* DC (69), *P. radicum* Rottb. (= *P. nudicaule* L. var. *radicum* Rottb.) (59), *P. suaveolens* Lap. (69)

27. (-)-REFRAMINE

C₂₀H₂₁O₄N: 339.1470

MP: Amorphous

[α]²⁴_D: -146°±3° (c=0.50, MeOH) (70)

UV: (MeOH) 235 sh (4.00), 248 sh (3.75), 292 (3.83) (70)

IR: (CHCl₃) 1610-1460, 1145-945, 875, 865 (70)

¹H-NMR: (CDCl₃) 2.58 (s, 3H, NCH₃), 3.90 (s, 6H, OCH₃), 5.87 (q, J=2 Hz, 2H, OCH₂O), 6.55 (s, 1H, ArH), 6.70 (s, 1H, ArH), 6.83 (s, 1H, ArH), 6.90 (s, 1H, ArH) (57)

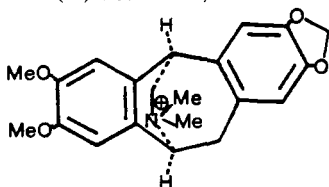
MS: 339, 338, 296, 253, 204 (100) (71)

SOURCE: PAPAVERACEAE: *Roemeria refracta* (Stev.) DC (= *R. rhoeadiflora* Boiss.) (70)

28. (-)-REMREFINE

((-)-Reframine N-metho salt,

(-)-Roemrefine)

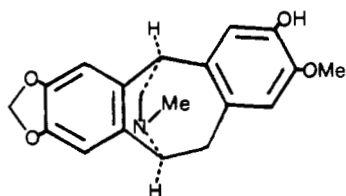
C₂₁H₂₄O₄N⁺: 354.1704MP: (Cl⁻) 241-242° (EtOH-acetone) (72)(I⁻) 244-245° (H₂O-MeOH) (72)(C⁻) 258-259° (MeOH) (70)(I⁻) 265-266° (MeOH) (70)[α]²¹_D: (Cl⁻) -147° (c=1.039, H₂O) (72)[α]²¹_D: (Cl⁻) -188°±3° (c=0.33, H₂O) (70)UV: (Cl⁻) (MeOH) 234 (4.11), 250 sh (3.75), 291 (3.88) (70, 72)

¹H-NMR: (D₂O) 2.9 and 3.38 (2s, 6H, N(CH₃)₂), 3.83 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 5.72 and 5.84 (2s, 2H, OCH₂O), 6.28 (s, 1H, ArH),

6.67 (s, 1H, ArH), 7.05 (s, 1H, ArH), 7.17 (s, 1H, ArH) (72, 73)

SOURCE: PAPAVERACEAE: *Roemeria refracta* (Stev.) DC (= *R. rhoeadiflora* Boiss.) (70)

29. (-)-AMURENSINE
(-)-Xanthopetaline



$C_{19}H_{19}O_4N$: 325.1314

MP: 206-208° (MeOH-Et₂O-hexane) (65)

213° (acetone) (74)

216-217° (acetone) (64)

221-223° (63)

$[\alpha]^{22}_D$: $-178 \pm 4^\circ$ ($c=0.819$, MeOH) (63)

$[\alpha]^{22}_D$: -194° ($c=0.25$, CHCl₃) (74)

UV: (EtOH) 230 (4.07), 250 sh (3.67), 294 (3.95) (63, 13g, 64-66, 75)

IR: (Nujol) 3580, 1596, 1530, 1501, 1339, 1308, 1290, 1256, 1243, 1225, 1200, 1172, 1150, 1136, 1119, 1104, 1073, 1051, 1034, 990, 969, 929, 882, 871, 861, 843, 819, 773, 764, 729, 716, 703 (13g, 63)

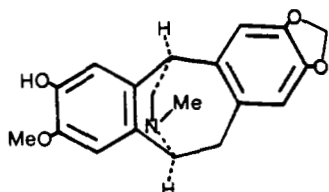
¹H-NMR: (CDCl₃) 2.50 (s, 3H, NCH₃), 2.69-3.63 (m, 4H, CH₂), 3.74, 3.81 and 3.88 (t, 2H, CH), 3.83 (s, 3H, OCH₃), 5.83, 5.85, 5.90 and 5.93 (ABq, 2H, OCH₂O), 6.53 (s, 1H, ArH), 6.58 (s, 1H, ArH), 6.70 (s, 2H, ArH) (63)

MS: 325, 309, 282, 239, 188 (100) (40)

CD: (EtOH) $\Delta\epsilon_{nm}$ -5.84_{295} , $+2.1_{275}$, -3.74_{245} , $+8.2_{230}$, -8.2_{215} (75, 19)

SOURCES: PAPAVERACEAE: *Papaver alpinum* L. (69), *P. alpinum* L. var. *tatricum* Nyár. (64), *P. alpinum* L. var. *burseri* (64), *P. alpinum* L. var. *kernereri* (Hay.) Fedde (64), *P. pseudocanescens* M. Pop. (65, 66), *P. nudicaule* L. var. *amurense* Hort. (74), *P. nudicaule* L. var. *xanthopetalum* (Trautv.) Fedde (69, 76), *P. nudicaule* L. var. *leiocarpum* (Turz.) (69), *P. nudicaule* L. var. *rubroaurantiacum* DC (69), *P. pyrenaicum* L. (Kernereri) (69), *P. tatricum* Nyár. (69), *P. suaveolens* Lap. (69), *P. anomalum* Fedde (76)

30. (-)-REFRAMOLINE



$C_{19}H_{19}O_4N$: 325.1314

MP: 160° (Et₂O), (19)

$[\alpha]^{20}_D$: -144° ($c=0.37$, EtOH) (19)

$[\alpha]^{20}_D$: $-140 \pm 5^\circ$ ($c=0.13$, MeOH) (70)

UV: (MeOH) 230 sh (4.00), 248 (2.43), 290 (3.92) (70, 19)

IR: (CHCl₃) 3540, 1605-1450, 1140-940, 875, 865 (70)

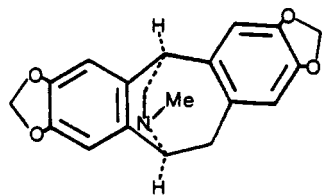
¹H-NMR: (CHCl₃) 2.55 (s, 3H, NCH₃), 2.8-3.8 (m, 6H, saturated ring H), 3.85 (s, 3H, OCH₃), 5.83 and 5.86 (2s, 2H, OCH₂O), 6.2 (bs, 1H, OH), 6.49 (s, 1H, ArH), 6.62 (s, 1H, ArH), 6.73 (s, 1H, ArH), 6.78 (s, 1H, ArH) (19)

MS: 326 (7), 325 (32), 324 (35), 282 (38), 190 (100), 188 (4) (19)

CD: (19)

SOURCE: PAPAVERACEAE: *Roemeria refracta* (Stev.) DC (= *R. rhoeadiflora* Boiss.) (70)

31. (-)-REFRAMIDINE

C₁₉H₁₇O₄N: 323.1157

MP: Amorphous (70)

[α]²³_D: -123° ± 3° (c=0.4, MeOH) (70)

UV: (MeOH) 235 sh (4.00), 248 sh (3.72), 294 (3.93) (70)

IR: (CHCl₃) 1505-1485, 1155-945, 870 (70)¹H-NMR: (CDCl₃) 2.45 (s, 3H, NCH₃), 2.60-3.92 (m, 6H, saturated ring H), 5.90 (m, 4H, OCH₂O), 6.55 (s, 1H, ArH), 6.65 (s, 1H, ArH), 6.75 (s, 2H, ArH) (57)

MS: 323, 322, 280, 237, 188 (100) (71, 57, 66)

SOURCES: PAPAVERACEAE: *Papaver anomalum* Fedde (66), *Roemeria refracta* (Stev.) DC (= *R. rhoeadiflora* Boiss.) (70)

Botanical Distribution of Pavine and Isopavine Alkaloids

(-)-argemonine

Berberidaceae:

Berberis buxifolia Lam. (3).

Papaveraceae:

Argemone gracilentia Greene (5), *A. hispida* Gray (4, 8, 14), *A. munita* Dur. and Hilg. (24), *A. munita* Dur. and Hilg. var. *argentea* G. B. Ownb. (27), *A. munita* Dur. and Hilg. var. *rotundata* (Rydb.) G. B. Ownb. (4, 14, 25, 26), *A. platyceras* Link and Otto (90), *A. sanguinea* Greene (28).

Ranunculaceae:

Thalictrum revolutum DC (6, 29, 30), *T. strictum* Ledeb. (2).

(+) - argemonine

Berberidaceae:

Leontice smirnovii Trautv. (31, 32).

(-) - argemonine N-metho salt

Papaveraceae:

Argemone gracilentia Greene (5), *A. platyceras* Link and Otto (33, 34)

Ranunculaceae:

Thalictrum revolutum DC (29).

(-) - argemonine N-oxide

Papaveraceae:

Argemone gracilentia Greene (5).

(-) - norargemonine

Berberidaceae:

Berberis buxifolia Lam. (3).

Papaveraceae:

Argemone brevicornuta G. B. Ownb. (41), *A. hispida* Gray (4, 8, 14), *A. munita* Dur. and Hilg. var. *rotundata* (Rydb.) G. B. Ownb. (14, 25, 26, 29), *A. platyceras* Link and Otto (9, 36), *Eschscholtzia californica* Cham. (37), *E. douglasii* (Hook. and Arn.) Walp. (37), *E. glauca* Greene (37).

Ranunculaceae:

Thalictrum dasycarpum Fisch. and Lall. (42).

Lauraceae:

Cryptocarya longifolia Kostermans (35).

(-) - isonorargemonine

Papaveraceae:

Argemone gracilentia Greene (5), *A. munita* Dur. and Hilg. var. *argentea* G. B. Ownb. (27).

Ranunculaceae:

Thalictrum revolutum DC (30).

(-) - bisnorargemonine

Papaveraceae:

Argemone hispida Gray (8), *A. munita* Dur. and Hilg. var. *rotundata* (Rydb.) G. B. Ownb. (8, 25, 43), *Eschscholtzia californica* Cham. (37, 44), *E. douglasii* (Hook. and Arn.) Walp. (37), *E. glauca* Greene (37).

Ranunculaceae:

Thalictrum dasycarpum Fisch. and Lall. (42).

Lauraceae:

Cryptocarya longifolia Kostermans (35).

(-) - eschscholtzidine

Papaveraceae:

Eschscholtzia californica Cham. (46).

Ranunculaceae:

Thalictrum revolutum DC (6, 29).

(+) - eschscholtzidine

Lauraceae:

Cryptocarya chinensis Hemsl. (47).

- (-)-eschscholtzidine N-metho salt
Ranunculaceae: *Thalictrum revolutum* DC (29).
- (-)-caryachine
Lauraceae: *Cryptocarya chinensis* Hemsl. (47, 48).
- (±)-caryachine
Lauraceae: *Cryptocarya chinensis* Hemsl. (47, 48).
- (-)-caryachine N-metho salt
Lauraceae: *Cryptocarya chinensis* Hemsl. (15)
- (-)-eschscholtzine
Papaveraceae: *Eschscholtzia californica* Cham. (44, 50), *E. douglasii* (Hook. and Arn.) Walp. (49), *E. glauca* Greene (49).
Lauraceae: *Cryptocarya chinensis* Hemsl. (47, 48).
- (-)-californidine
Papaveraceae: *Eschscholtzia californica* Cham. (52), *E. douglasii* (Hook. and Arn.) Walp. (49), *E. glauca* Greene (49), *E. oregana* Greene (51).
- (-)-platycerine
Papaveraceae: *Argemone gracilentia* Greene (5), *A. platyceras* Link and Otto (9).
Ranunculaceae: *Thalictrum revolutum* DC (29, 30).
- (-)-platycerine N-metho salt
Papaveraceae: *Argemone platyceras* Link and Otto (33, 34).
- (-)-munitagine
Papaveraceae: *Argemone gracilentia* Greene (5), *A. munita* Dur. and Hilg. var. *rotundata* (Rydb.) G. B. Ownb. (8, 43).
- (-)-2-hydroxy-3,8-dimethoxypavinane
Papaveraceae: *Argemone munita* Dur. and Hilg. var. *rotundata* (Rydb.) G. B. Ownb. (43)
- (-)-2,3-methylenedioxy-4,8,9-trimethoxypavinane
Ranunculaceae: *Thalictrum strictum* Ledeb. (55)
- (-)-O-methylthalisopavine
Papaveraceae: *Papaver radicum* Rottb. (= *P. nudicaule* L. var. *radicum* Rottb.) (59).
- (-)-thalisopavine
Ranunculaceae: *Thalictrum dasycarpum* Fisch. and Lall. (42)
- (-)-thalidicine
Ranunculaceae: *Thalictrum dioicum* L. (60).
- (-)-thalidine
Ranunculaceae: *Thalictrum dioicum* L. (61)
- (-)-amurensinine
Papaveraceae: *Papaver tauricola* Boiss. (68), *P. anomalum* Fedde (66), *P. pseudocanescens* M. Pop. (65), *P. pyrenaicum* L. (Kerner) (69), *P. pyrenaicum* L. (Kerner) var. *rheaticum* (Ler.) Fedde (64), *P. alpinum* L. (69), *P. alpinum* L. var. *burseri* (64), *P. alpinum* L. var. *kernerii* (64), *P. alpinum* L. var. *tatricum* Nyár (64, 69), *P. nudicaule* L. var. *xanthopetalum* (Trautv.) Fedde (69), *P. nudicaule* L. var. *leiocarpum* (Turz.) (69), *P. nudicaule* L. var. *rubroaurantiacum* DC (69), *P. radicum* Rottb. (= *P. nudicaule* L. var. *radicum* Rottb.) (59), *P. suaveolens* Lap. (69).
- (-)-reframine
Papaveraceae: *Roemeria refracta* (Stev.) DC (= *R. rhoeadiflora* Boiss.) (70).
- (-)-remrefine
Papaveraceae: *Roemeria refracta* (Stev.) DC (= *R. rhoeadiflora* Boiss.) (70).
- (-)-amurensine
Papaveraceae: *Papaver alpinum* L. (69), *P. alpinum* L. var. *tatricum* Nyár (64), *P. alpinum* L. var. *burseri* (64), *P. alpinum* L. var. *kernerii* (Hay.) Fedde (64), *P. pseudocanescens* M. Pop. (65),

- (-)-reframoline
Papaveraceae: *Roemeria refracta* (Stev.) DC (= *R. rhoeadiflora* Boiss. (70))
- (-)-reframidine
Papaveraceae: *Papaver anomalum* Fedde (66), *Roemeria refracta* (Stev.) DC (= *R. rhoeadiflora* Boiss.) (70).

Occurrence of Pavines and Isopavines by Plant Sources

Family Berberidaceae

Genus *Berberis**B. buxifolia* Lam. (-)-argemonine, (-)-norargemonineGenus *Leontice**L. smirnovii* Trautv. (+)-argemonine

Family Lauraceae

Genus *Cryptocarya**C. chinensis* Hemsl. (+)-caryachine, (-)-caryachine, (-)-caryachine N-metho salt, (+)-eschscholtzidine, (-)-eschscholtzine*C. longifolia* Kostermans (-)-bisnorargemonine, (-)-norargemonine

Family Papaveraceae

Genus *Argemone**A. brevicornuta* G. B. Ownb. (-)-norargemonine*A. gracilentia* Greene (-)-argemonine, (-)-argemonine N-metho salt, (-)-argemonine N-oxide, (-)-isonorargemonine, (-)-munitagine, (-)-platycerine*S. hispida* Gray (-)-argemonine, (-)-bisnorargemonine, (-)-norargemonine*A. munita* Dur. and Hilg. (-)-argemoninevar. *argentea* G. B. Ownb. (-)-argemonine, (-)-isonorargemoninevar. *rotundata* (Rydb.) G. B. Ownb. (-)-argemonine, (-)-bisnorargemonine, (-)-2-hydroxy-3,8-dimethoxypavinane, (-)-munitagine, (-)-norargemonine*A. platyceras* Link and Otto (-)-argemonine, (-)-argemonine N-metho salt, (-)-norargemonine, (-)-platycerine, (-)-platycerine N-metho salt*A. sanguinea* Greene (-)-argemonineGenus *Eschscholtzia**E. californica* Cham. (-)-bisnorargemonine, (-)-californidine, (-)-eschscholtzidine, (-)-eschscholtzine, (-)-norargemonine*E. douglasii* Hook. and Arn. (-)-bisnorargemonine, (-)-californidine, (-)-eschscholtzine, (-)-norargemonine*E. glauca* Greene (-)-bisnorargemonine, (-)-californidine, (-)-eschscholtzine, (-)-norargemonine*E. oregana* Greene (-)-californidineGenus *Papaver**P. alpinum* L. (-)-amurensine, (-)-amurensinine*P. anomalum* Fedde (-)-amurensine, (-)-amurensinine, (-)-reframidine*P. nudicaule* L.var. *amurense* Hort. (-)-amurensinevar. *leiocarpum* (Turz.) (-)-amurensine, (-)-amurensininevar. *rubro-aurantiacum* DC (-)-amurensine, (-)-amurensininevar. *xanthopetalum* (Trautv.) Fedde (-)-amurensine, (-)-amurensinine*P. pyrenaicum* L. (Kerner) (-)-amurensine, (-)-amurensininevar. *rhoeticum* (Ler.) Fedde (-)-amurensinine*P. radicum* Rottb. (-)-amurensinine, (-)-O-methylthalisopavine(=*P. nudicaule* L. var. *radicum* Rottb.)

<i>P. suaveolens</i> Lap.	(-)-amurensine, (-)-amurensinine
<i>P. tatricum</i> Nyár	(-)-amurensine
<i>P. tauricola</i> Boiss.	(-)-amurensinine
<i>P. alpinum</i> L.	
var. <i>tatricum</i> Nyár	(-)-amurensine, (-)-amurensinine
var. <i>burseri</i>	(-)-amurensine, (-)-amurensinine
var. <i>kernerii</i> (Hay.) Fedde	(-)-amurensine, (-)-amurensinine
<i>P. pseudocanescens</i> M. Pop.	(-)-amurensine, (-)-amurensinine
Genus <i>Roemeria</i>	
<i>R. refracta</i> (Stev.) DC (= <i>R. rhoeadiflora</i> Boiss.)	(-)-reframidine, (-)-reframine, (-)-reframoline, (-)-remrefine
Family Ranunculaceae	
Genus <i>Thalictrum</i>	
<i>T. dasycarpum</i> Fisch. and Lall.	(-)-bisorargemonine, (-)-norargemonine, (-)-thalisopavine
<i>T. dioicum</i> L.	(-)-thalidicine, (-)-thalidine
<i>T. revolutum</i> DC	(-)-argemonine, (-)-argemonine N-metho salt, (-)-eschscholtzidine, (-)-eschscholtzidine N-metho salt, (-)-isonorargemonine, (-)-platycerine
<i>T. strictum</i> Ledeb.	(-)-argemonine, (-)-2,3-methylenedioxy-4,8,9-trimethoxypavinane

Alphabetical List of Pavine Alkaloids

(-)-Argemonine (1)	(-)-Eschscholtzidine N-metho salt (10)
(+)-Argemonine (2)	(-)-Eschscholtzine (14)
(-)-Argemonine N-metho salt (3)	(-)-2-Hydroxy-3,8-dimethoxypavinane (20)
(-)-Argemonine N-oxide (4)	(-)-Isonorargemonine (6)
(-)-Bisorargemonine (7)	(-)-2,3-Methylenedioxy-4,8,9-trimethoxypavinane (21)
(-)-Californidine (15)	(-)-Munitagine (19)
(-)-Caryachine (11)	(-)-O-Methylplatycerine (16)
(±)-Caryachine (12)	(-)-Norargemonine (5)
(-)-Caryachine N-metho salt (13)	(-)-Platycerine (17)
(-)-Eschscholtzidine (8)	(-)-Platycerine N-metho salt (18)
(+)-Eschscholtzidine (9)	

Alphabetical List of Isopavine Alkaloids

(-)-Amurensine (29)	(-)-Reframoline (30)
(-)-Amurensinine (26)	(-)-Remrefine (28)
(-)-O-Methylthalisopavine (22)	(-)-Thalidicine (24)
(-)-Reframidine (31)	(-)-Thalidine (25)
(-)-Reframine (27)	(-)-Thalisopavine (23)

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