THE SPIROBENZYLISOQUINOLINE ALKALOIDS

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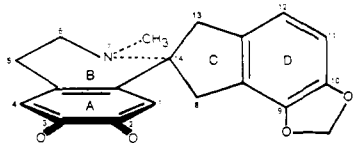
1. INTRODUCTION.—Twenty-nine spirobenzylisoquinoline alkaloids are presently known. They all possess the spirobenzylisoquinoline nucleus represented in expression I. A methylenedioxy group is always present at C–9, 10; C–2 and 3 are inevitably oxygenated, bearing hydroxyl, methoxyl or methylenedioxy substituents. No norspirobenzylisoquinolines are known to occur naturally; rather, the nitrogen atom is tertiary and bonded to a methyl group.

Spirobenzylisoquinoline alkaloids have been found only within the plant family Fumariaceae. More specifically, they occur with one exception, within the genera *Fumaria* and *Corydalis*. There is a report of the isolation of ochotensine from *Dicentra cucullaria* Bernh. which also belongs to the Fumariaceae (2).

2. RELATIONSHIP BETWEEN PLANT SOURCE AND SUBSTITUTION PATTERN OF RING C.—A direct relationship obtains between the plant source and the oxygenation pattern of ring C. The genus *Fumaria* yields spirobenzylisoquinolines bearing only one oxygenated substituent in ring C in the form of an alcohol, an acetate, a methoxy ether, or a ketone located at C–8. On the other hand, those bases originating from *Corydalis* species possess two oxygenated substituents in ring C, usually in the form of two alcohols or an alcohol plus a ketone. In those cases where an alcohol and a ketone are present, the alcohol is positioned at C–8 while the ketone is at C–13. The alkaloid fumarofine (**26**) is unusual in that it is found in *Fumaria* species, yet it incorporates a ketone at C–8 and an alcohol at C–13. Fumarostelline, isolated from *F. rostellata* Knaf (29), is almost certainly identical with fumarofine (**26**) so it has not been given, here, a separate identity.

There is also a small group of spirobenzylisoquinolines, consisting so far of ochotensine (**27**), ochotensimine (**28**), and raddeanamine (**29**), found mostly in *Corydalis* species, which possess an exocyclic methylene or a methyl plus an alcohol at C–13. In this instance, no oxygenated substituent is found at C–8.

3. ABSOLUTE CONFIGURATION AND RACEMIZATION.—The absolute configuration of the spirobenzylisoquinoline alkaloids was first considered within the context of the aromatic chirality rule. (+)-Ochotensine (**27**), (+)-ochotensimine (**28**), (+)-ochrobirine (**18**), and dihydrofumariline (**11**) and, by extension, (+)-fumariline (**10**) were thus shown to possess the absolute configuration denoted in expression I above (3a, b). These conclusions were further supported by a complete x-ray study of ochrobirine methanolate (4).



I

For the sake of simplicity, all the spirobenzylisoquinolines have been drawn here in an absolute configuration corresponding to expression I. It must be borne in mind, however, that this could eventually prove not to be the case.

Spirobenzylisoquinolines possessing both a ketone and an alcohol in ring C can undergo racemization through a series of base-catalyzed retro aldol condensations followed by recyclization. Such racemization has been shown to occur *in vitro* in the conversion of sibiricine (**21**) into corydaine (**25**) (6a, b). It must also account for the fact that raddeanone (**20**) is known only as a racemate, while yenhusomidine occurs either as the levorotatory isomer (**23**) or as the racemate (**24**). The alkaloid raddeanine possesses two alcoholic functions in ring C and is found both in the dextrorotatory (**13**) and the racemic (**14**) forms. It is likely that its precursor, raddeanone (**20**), must have undergone epimerization by a retro aldol cleavage, followed by aldol recyclization and reduction to yield a racemate.

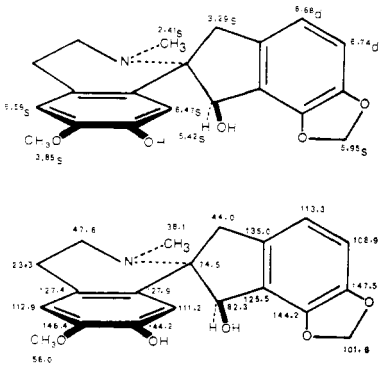
4. BIOGENESIS.—Depending upon the substitution pattern in ring C, somewhat different pathways for the biogenesis of the spirobenzylisoquinolines may be postulated.

If an exocyclic methylene is present at C–13, the precursor is likely to be a C–13 methylated dihydroprotoberberine *N*-metho salt. Such a salt can rearrange to a spiro structure via the intermediacy of a quinone methide, if phenolic groups are present in ring D (7); or by a photo-induced process, if no phenolic groups are available (8).

Those spirobenzylisoquinoline alkaloids possessing one or two oxygenated functions in ring C must originate from a protoberberine salt oxygenated or, at least, unsaturated in ring C, although the essential details of such a rearrangement still remain to be established (9a,b; 6a,b). They definitely are not formed through the intermediacy of a spirobenzylisoquinoline precursor possessing an exocyclic methylene group in ring C.

5. GENERAL REMARKS CONCERNING THE TABULATION.—All uv data are in nm, and log ϵ values are quoted between parentheses. Ir frequencies are in cm^{-1}. In several cases, the interpretation of a pmr spectrum has been slightly modified from that given in the original paper. Whenever two or more references are cited for a pmr spectrum, the first one is the one actually shown in the accompanying diagram. The coupling constant between H–11 and 12 is not quoted since it is consistently in the order of 8 Hz. If some other coupling value is not given, it is usually because this information is lacking in the original literature. Applications of the nuclear Overhauser effect to the spirobenzylisoquinolines have been discussed in detail in the literature (10). Cmr chemical shifts with identical superscripts are interchangeable.

1. FUMARITINE

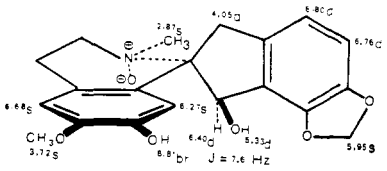


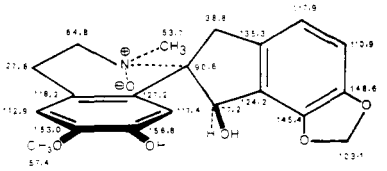
$C_{20}H_{21}O_5N$: 355.1419

MP: 157° (dry ether) (11); 157–159° (12)
$[\alpha]D$: N.A.
UV: (EtOH) 287 (3.83) (13a)
IR: ($CHCl_3$) 1100, 1275, 1590, 2880, 3550 (14); ($CHCl_3$) 3540 (15). See also (13a).
^1H NMR: ($CDCl_3$) (16, 14, 1a, 17, 15); (CF_3COOH) (17)
^{13}C NMR: ($CDCl_3$) (14)
MS: 355 (M^+), 340, 324, 206, 192 (18, 16)
CD: $\Delta\epsilon_{nm}$ $+8.96_{294}$, -2.68_{277}, $+3.58_{236}$ (63).
SOURCES: *Fumaria officinalis* L. (11)
Fumaria schleicheri Soyer-Willem (12)

2. FUMARITINE *N*-OXIDE

$C_{20}H_{21}O_6N$: 371.1369

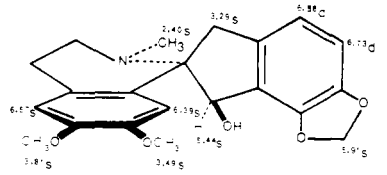




MP: 204° (10% MeOH in C_6H_6) (14)
$[\alpha]_D$: N.A.
UV: N.A.
IR: 2500–3500 (14)
^1H NMR: (DMSO) (14)
^{13}C NMR: (D_2O+2 drops 40% NaOD) (14)
MS: 371 (M^+), 192 (100) (14)
SOURCES: *Fumaria kralikii* Jord. (14, 19)

3. FUMARICINE

$C_{21}H_{23}O_5$: 369.1576

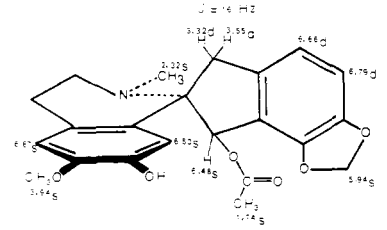


MP: 177° (MeOH) (20)
$[\alpha]_D$: −31° (c=0.97 $CHCl_3$) (21)
UV: (EtOH) 207 (4.74), 235 (3.94), 288 (3.74) (21, 16); (EtOH) 286 (3.81) (13b)
IR: (CS_2) 3560 (21, 16, 22); 3600 (23). See also (13b).
^1H NMR: ($CDCl_3$) (1a, 22)
MS: 369 (M^+), 354, 338, 220, 206 ,140 (18, 16)
SOURCES: *Fumaria officinalis* L. (20)

This alkaloid is probably identical with *O*-methylfumarophycinol found in Herba Fumariae Officinalis (36).

4. FUMAROPHYCINE

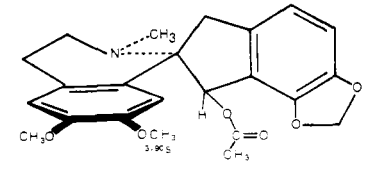
$C_{22}H_{23}O_6N$: 397.1525



MP: 107–109° (MeOH) (24)
$[\alpha]^{20}_D$: −67.5° (c=1% $CHCl_3$) (24)
UV: 290 (3.88) (24)
IR: 1730, 3500 (24)
^1H NMR: ($CDCl_3$) (25, 24)
MS: 397 (M^+) (25), 355 (26), 354 (100), 337 (48), 322 (23), 192 (6) (25, 18)
SOURCES: *Fumaria officinalis* L. (24, 26)

5. *O*-METHYLFUMAROPHYCINE

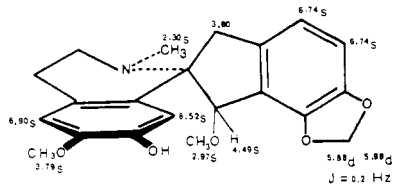
$C_{23}H_{25}O_6N$: 411.1682



MP: 124–126° (24); 124–127° (ether-MeOH) (36)
$[\alpha]^{22}_D$: −51° (c=27% $CHCl_3$) (36)
SOURCES: *Fumaria officinalis* L. (24, 27, 36)

The reported concentration of 27% ($CHCl_3$) for the measurement of the specific rotation is suspect.

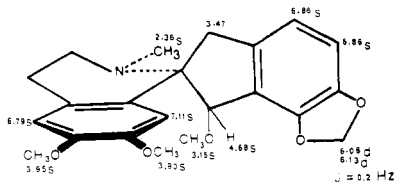
6. FUMARITRIDINE



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

MP: 198–200° (EtOH) (28, 29)
$[\alpha]^{22}D$: +18° (c=1% $CHCl_3$) (28, 29)
UV: ($CHCl_3$) 215 (3.73), 230 (3.70), 285 (3.48) (28)
IR: N.A.
^1H NMR: (28)
MS: 354 (M^+) (100), 338, 337, 192 (28)
SOURCES: *Fumaria rostellata* Knaf. (28, 29)

7. FUMARITRINE

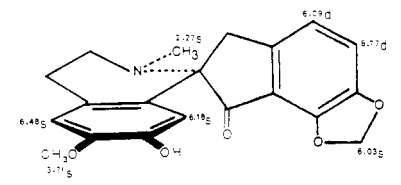


$C_{22}H_{25}O_5N$: 383.1732

MP: 153–155° (EtOH) (28, 36)
$[\alpha]D$: N.A.
IR: N.A.
^1H NMR: (28)
MS: N.A.
SOURCES: *Fumaria rostellata* Knaf. (29)
Fumaria officinalis L. (38, 36)

The presence of an aromatic singlet proton as far downfield as δ7.11 is unusual.

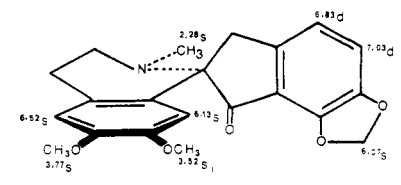
8. PARFUMINE



$C_{20}H_{19}O_5N$: 353.1263

MP: 111–112° (EtOH) (30); 118–119° (MeOH) (31); 118–120° (EtOH) (62); 118–120° ($CHCl_3$) (29)
$[\alpha]^{23}D$: +18°±1° (c=1.1 $CHCl_3$) (30)
UV: (EtOH) 235 (4.42), 260 (4.10), 290 sh, 358 (3.42) (30)
IR: 920, 1030, 1505, 1610, 1710, 3100, 3420 (30); ($CHCl_3$) 1710, 3545 (62)
^1H NMR: ($CDCl_3$) (30 (30a)
MS: 353 (M^+), 338, 324, 308 (30)
CD: $\Delta\epsilon_{nm}$ $+1.41_{355}$, -1.76_{295}, -6.36_{259}, $+1.18_{239}$ (63).
SOURCES: *Fumaria kralikii* Jord. (19)
Fumaria parviflora Lam. (30, 31)
Fumaria rostellata Knaf. (29)
Fumaria vaillantii Lois. (62)

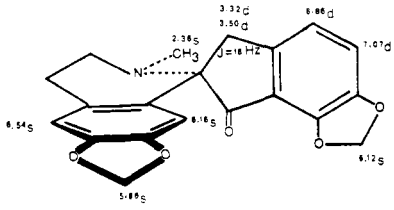
9. PARFUMIDINE



$C_{21}H_{21}O_5N$: 367.1419

MP: 170–171° (MeOH) (32); 171–172° (EtOH) (62); 169–171° (MeOH) (31); 165–168° (ether) (36)
$[\alpha]^{22}D$: −33.3° (c=0.5 $CHCl_3$) (32)
UV: 235 (4.46), 263 (4.14), 290 sh, 360 (3.40) (32). See also (62).
IR: 915, 1020, 1520, 1620, 1720, (32); ($CHCl_3$) 1705 (62)
^1H NMR: ($CDCl_3$) (32) (32a)
SOURCES: *Fumaria parviflora* Lam. (32, 31)
Fumaria officinalis L. (36)
Fumaria vaillantii Lois. (62)

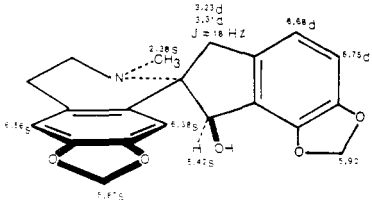
10. FUMARILINE



$C_{20}H_{17}O_5N$: 351.1106

MP: oil (33); 138° (MeOH) (11); 74–76° (MeOH) (29); 144° ($CHCl_3$-MeOH) (34); 141°–143° (EtOH) (36)
$[\alpha]_D$: +138° (c=1.05 $CHCl_3$) (21); +96° (c=1.0 $CHCl_3$) (34)
$[\alpha]^{24}_D$: +67° (c=1.58 $CHCl_3$) (33)
$[\alpha]^{17}_D$: +82.5° (c=0.6% $CHCl_3$) (36)
UV: (EtOH) 203 (4.60), 237 (4.31), 263 (4.05), 294 (3.66), 355 (3.51) (16, 21); (EtOH) 236 (4.38), 262 (4.07), 293 (3.68), 352 (3.51) (13c). See also (34, 33).
IR: ($CHCl_3$) 1709 (16, 21); 1710 (36); (Nujol) 1638, 1705, 1730, 3390 (33). See also (13c).
^{1}H NMR: ($CDCl_3$) (16, 21, 30, 33, 34, 1a)
MS: 351 (M^-) (34), 336 (10), 322 (100), 308 (3)) 293 (7), 264 (7), 175 (7), 135 (9, (34). See also (16, 18). 351 (M^+) (84), 323 (25), 322 (base), 293 (10), 279 (7), 264 (13), 175 (10), 149 (27), 135 (13), 69 (12), 57 (23) (33)
SOURCES: *Fumaria indica* (Haussk) Pugsley (33, 34)
Fumaria officinalis L. (11, 36)
Fumaria rostellata Knaf. (29)

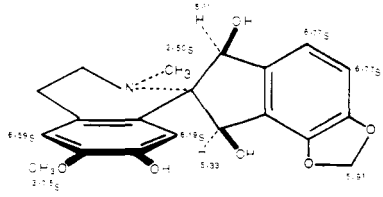
11. DIHYDROFUMARILINE



$C_{20}H_{19}O_5N$: 353.1263

MP: 129–133° (ether) (16)
$[\alpha]_D$: N.A.
UV: N.A.
IR: N.A.
^{1}H NMR: ($CDCl_3$) (16)
MS: 353 (M^+), 338, 190 (16)
SOURCES: Not a natural product, but obtained from $LiAlH_4$ reduction of naturally occurring fumariline.

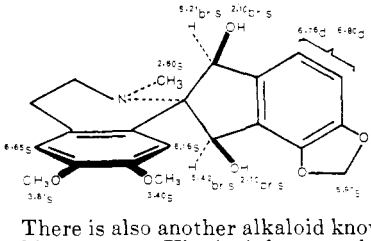
12. LEDEBORIDINE
(Ledebouridine)



$C_{20}H_{21}O_6N$: 371.1369
MP: 140–141° (35)

$[\alpha]_D$: +114° (c=0.28 MeOH) (35)
UV: N.A.
IR: 920, 1030, 1500, 1600, 3430, 3540 (35)
^{1}H NMR: ($CDCl_3$) (35)
MS: 371 (M^-), 353, 338, 324, 308, 294, 192, 190, 177 (35)
SOURCES: *Corydalis ledebouriana* K. et K. (35)

13. (+)-RADDEANINE

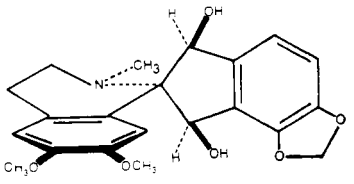


$C_{21}H_{23}O_6N$: 385.1525

MP: 200–202° (acetone) (36, 37); 204–205° (acetone) (35)
$[\alpha]^{22}_D$: +79.4° (c=0.11 MeOH) (26, 37)
$[\alpha]_D$: +107° (c=0.18 MeOH) (35)
UV: N.A.
IR: 920, 930, 1040, 1515, 3520, 3540 (35); ($CHCl_3$) 3590 (26, 37)
^{1}H NMR: ($CDCl_3$) (26, 35, 37, 17); (CF_3COOH) (17)
MS: 385 (M^+), 370, 367, 352, 338, 324, 308, 206 (26, 35, 37)
SOURCES: *Corydalis ochotensis* Turcz. var. *raddeana* (Regel) Nakai (26, 37)

There is also another alkaloid known by this name, see Kh. A. Aslanov and A. S. Sadykov, *J. Gen. Chem. USSR, 26*, 579 (1956).

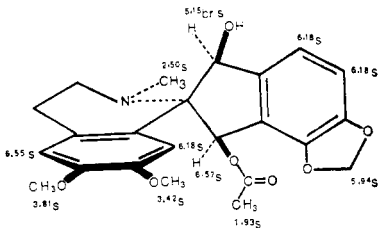
14. (±)-RADDEANINE



$C_{21}H_{23}O_6N$: 385.1525

MP: 219–220° (MeOH–$CHCl_3$) (35)
$[\alpha]_D$: 0° (35)
Remaining physical properties resemble those for (+)-raddeanine.
SOURCES: *Corydalis ledebouriana* K. et K. (35)

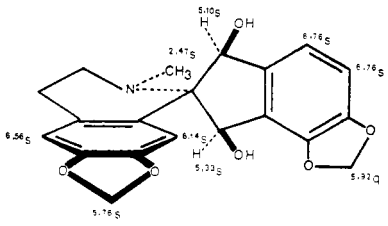
15. RADDEANIDINE



$C_{23}H_{23}O_7$:N 427.1630

MP: Oil (26)
$[\alpha]^{20}_D$: +82.7° (c=0.52 MeOH) (26, 37)
UV: N.A.
IR: ($CHCl_3$) 1740, 3580 (26, 37)
^{1}H NMR: ($CDCl_3$) (26, 37)
MS: 427 (M^+), 384, 367, 352, 338, 324, 322, 308, 206 (26)
SOURCES: *Corydalis ochotensis* Turcz. var. *raddeana* (Regel) Nakai (26, 37)

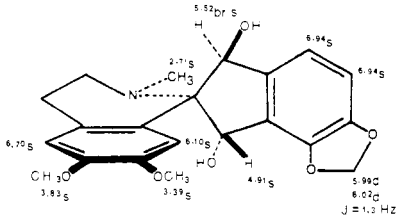
16. SEVERZINE
(Sewercinine)

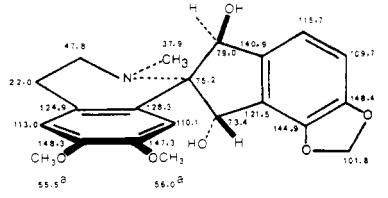


$C_{20}H_{19}O_6N$: 369.1212
MP: 90–91° (EtOH) (38)

$[\alpha]_D$: +109° (c=1.2 $CHCl_3$) (38)
UV: (EtOH) 290 (4.04) (38)
IR: 930, 1050, 1490, 1510, 3400 (38)
^{1}H NMR: (38)
MS: 369 (M^+), 336, 322 (100), 292, 190 (38)
SOURCES: *Corydalis sewerzowi* Regel (38)

17. YENHUSOMINE

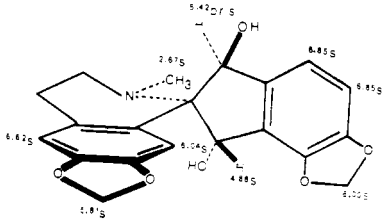


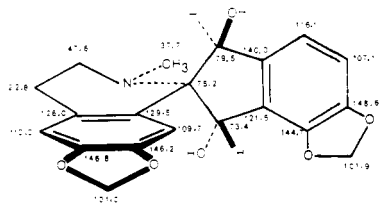


$C_{21}H_{23}O_6N$: 385.1525

MP: 127–128° (decomp.) (MeOH) (39, 40)
$[\alpha]^{19}_D$: +48° (c=1.0 MeOH) (39, 40)
UV: (EtOH) 241 (4.11), 288 (3.85) (38, 40); min: 236 (4.10), 261 (3.08) (40)
IR: (Nujol) 935, 1030, 3300, 3480 (39, 40)
^{1}H NMR: ($CDCl_3$) (39, 40)
^{13}C NMR: (41)
MS: 385 (M^+) (39)
SOURCES: *Corydalis ochotensis* Turcz. (39, 40)

18. OCHROBIRINE

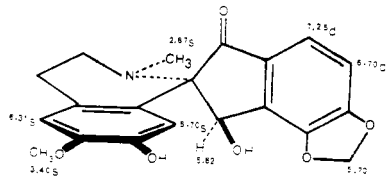




$C_{20}H_{19}O_6N$: 369.1212

MP: 198° (solvent free) (42, 43); 204° (EtOH) (44); Diacetate 179° (44); Methanolate 138–139° (42, 43)
$[\alpha]^{21}D$: +35.9° (c=0.4 $CHCl_3$) (42)
$[\alpha]^{20}D$: +36° (c=1.8 $CHCl_3$) (42)
UV: (MeOH) 205 (4.80), 240 (3.94), 291 (3.91) (45); (EtOH) 201 (4.21), 239 (3.91), 291 (3.87) (46); (EtOH) 205 (4.81), 240 (3.94), 250 (3.91) (44); (EtOH) 228 sh (4.36), 291 (3.87) (3a). See also (13d).
IR: (CCl_4) (45); $CHCl_3$) (23) 3300, 3585; (paraffin oil) 3450, 3530 (44). See also (13d).
^1H NMR: ($CDCl_3$) (45, 44)
^{13}C NMR: ($CDCl_3$) (41)
MS: 369 (M^+), 354, 351, 336, 322, 293, 265, 204, 190 (18); 369 (M^-), 206, 192, 190 (44)
X-Ray: Ochrobirine methanolate (4)
SOURCES: *Corydalis lutea* (L.) DC. (42)
Corydalis ochroleuca Koch (43)
Corydalis sibirica (L.) Pers. (47)
Corydalis vaginans Royle (44)

19. LEDEBORINE
(Lederbourine, ledebourine)

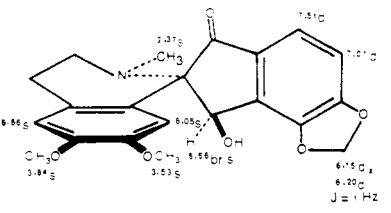


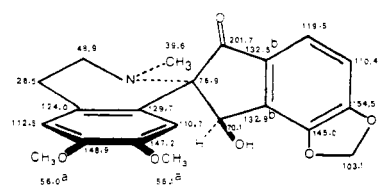
Structural assignment may be in error. For an alternate structure, see F. Šantavý in R. H. F. Manske's *The Alkaloids*, Vol. XVII, p. 502 (1979).

$C_{20}H_{19}O_6N$: 371.1369
MP: 184–185° ($CHCl_3$-MeOH) (17)

$[\alpha]D$: N.A.
UV: (MeOH) 238 (4.38), 293 (3.98), 3.16 (3.90) (17)
IR: 920, 1040, 1600, 1705, 3450 (17)
^1H NMR: (CF_3COOH) (17)
MS: 369 (M^-) (100), 354, 338, 206, 192, 177 (17)
SOURCES: *Corydalis ledebouriana* K. et K. (17)

20. RADDEANONE

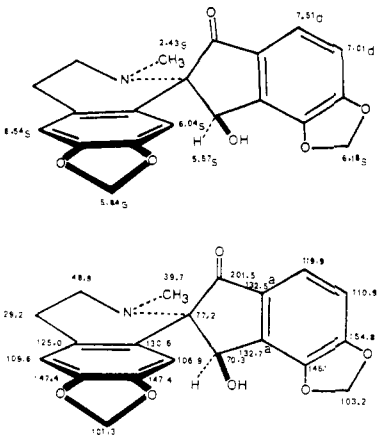




$C_{21}H_{21}O_6N$: 383.1369

MP: 168–170° (acetone) (37); 132–133° (acetone) (26)
$[\alpha]^{20}D$: 0° (c=0.085 MeOH) (26, 37)
UV: (EtOH) 238 (4.58), 289 (4.12), 313 (4.06) (26, 37)
IR: ($CHCl_3$) 1720, 3570 (26, 37)
^1H NMR: ($CDCl_3$) (26, 37)
^{13}C NMR: ($CDCl_3$) (41)
MS: 383 (M^+), 368, 352, 338, 324, 208, 206 (26, 37)
SOURCES: *Corydalis ochotensis* Turcz. var. *raddeana* (Regel) Nakai (26, 37)

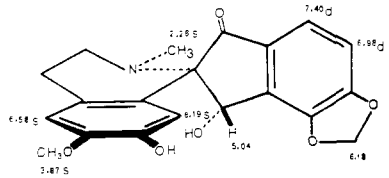
21. SIBIRICINE



$C_{20}H_{17}O_6N$: 367.1055

MP: 225° ($CHCl_3$-MeOH) (48)
$[\alpha]_D$: N.A.
UV: 205 (4.80), 240 (3.94), 291 (3.91), 313 sh (3.99) (48, 49)
IR: ($CHCl_3$) 1710, 3560 (48, 23); (KBr) 1700 (48)
^1H NMR: ($CDCl_3$) (48, 17)
^{13}C NMR: ($CDCl_3$) (41)
MS: 367 (M^+) (100), 352, 338, 322, 295, 266, 206, 190 (18)
X-Ray: (5)
SOURCES: *Corydalis ledebouriana* K. et K. (5)
Corydalis sibirica (L.) Pers. (48)

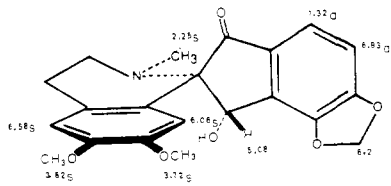
22. CORPAINE



$C_{20}H_{19}O_6N$: 369.1212

MP: 204° (EtOH) (50)
$[\alpha]_D$: N.A.
UV: (EtOH) 242 (3.4), 298 (3.3), 315 (3.4) (50)
IR: ($CHCl_3$) 1516, 1601, 1633, 1707, 3260, 3560 (50)
^1H NMR: ($CDCl_3$) (37, 50)
MS: 192 (50)
SOURCES: *Corydalis paczoskii* N. Busch (50)

23. (−)-YENHUSOMIDINE
(1-*O*-Methylcorpaine)

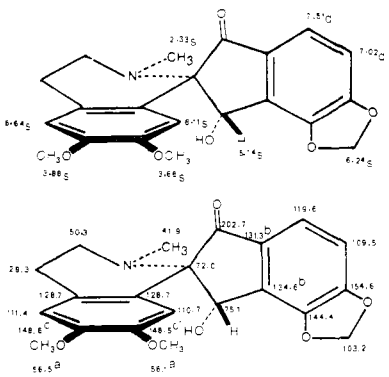


$C_{21}H_{21}O_6N$: 383.1369
MP: 220–221° (MeOH) (51)

$[\alpha]^{22}_D$: −36.7° (c=0.44 $CHCl_3$) (51)
UV: (EtOH) 204 (4.80), 240 (3.94), 291 (3.91), 313 (3.99) (51)
IR: ($CHCl_3$) 1700, 3260 (51)
^1H NMR: ($CDCl_3$) (51)
MS: 383 (M^+) (100), 368, 338, 206, 191.5 (M^{++}), 190, 177 (51)
SOURCES: *Corydalis vaginans* Royle (51)

This alkaloid was originally labeled 1-*O*-methylcorpaine. It is simply the levorotatory isomer of (±)-yenhusomidine which had been described previously in the literature.

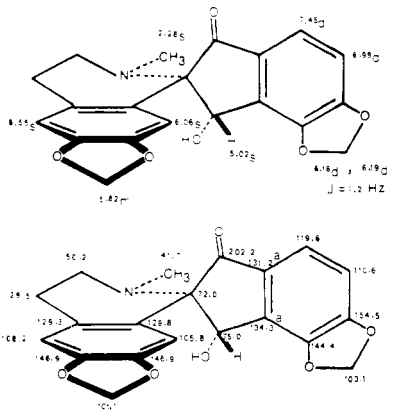
24. (±)-YENHUSOMIDINE



$C_{21}H_{21}O_6N$: 383.1369

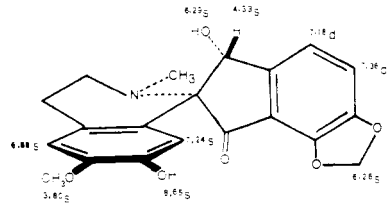
MP: 240–241° (acetone) (39, 40); picrate 214–215° (decomp.) (39, 40)
$[\alpha]^{29}_D$: 0° (c=0.41 $CHCl_3$) (39, 40)
UV: (EtOH) 207 (4.40), 238 (4.21), 290 (3.74), 314 (3.72) (39, 40); min: 222 (4.01), 258 (3.20), 303 (3.64) (40)
IR: (Nujol) 931, 1041, 1706, 3275 (39, 40)
^1H NMR: ($CDCl_3$) (39, 40)
^{13}C NMR: ($CDCl_3$) (41)
SOURCES: *Corydalis ochotensis* Turcz. (39, 40)

25. CORYDAINE



$C_{20}H_{17}O_6N$: 367.1056
MP: 184° (EtOH) (23); 189–189.5° (ether) (51)
$[\alpha]^{22}D$: +145° (c=1.3 $CHCl_3$) (51)
UV: (EtOH) 236 (4.49), 290 (4.04), 314 (4.03) (23)
IR: (Paraffin oil) 1610, 1638, 1710, 3050, 3200 (23); ($CHCl_3$) 3265 (23)
^1H NMR: ($CDCl_3$) (23)
^{13}C NMR: ($CDCl_3$) (41)
MS: 367 (M^+), 352, 338, 322, 190 (23)
SOURCES: *Corydalis paczoskii* N. Busch (23)

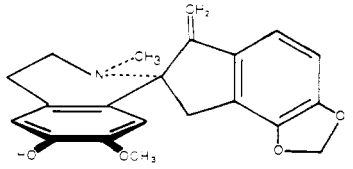
26. FUMAROFINE



$C_{20}H_{19}O_6N$: 369.1212
MP: 255° (MeOH–$CHCl_3$) (20); 256° (decomp.) (MeOH–dioxane) (darkening at 240–245°) (20); 256° (MeOH) (20)
$[\alpha]D$: N.A.
UV: (EtOH) for O-methylfumarofine 208 (4.45), 235 (4.35), 259 (3.96), 286 (3.37), 350 (3.40) (49)
IR: 1700, 3450 (49)
^1H NMR: (DMSO-d_6) (49)
MS: 369 (M^+) (100), 354, 341, 326, 324, 298, 284, 204, 192 (49)
SOURCES: *Fumaria kralikii* Jord. (14)
Fumaria officinalis L. (20)

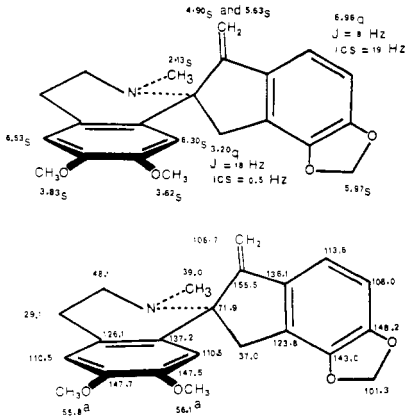
The oxygenation pattern of this alkaloid in ring C is unique. The alkaloid fumarostelline, found in *F. rostellata* Knaf., was originally assigned a structure corresponding to either corpaine or ledeborine (29). Its physical constants, however, indicate it to be identical with fumarofine.

27. OCHOTENSINE



$C_{21}H_{21}O_4N$: 351.1470
MP: 247–250° ($CHCl_3$) (52); 250–251° ($CHCl_3$) (37); 252° ($CHCl_3$) (53); 248° (MeOH) (47) or (NH_4OH) (53)
$[\alpha]^{20}D$: +51.0° (c=0.098 $CHCl_3$) (37)
$[\alpha]^{24}D$: +51.7° (c=0.2 $CHCl_3$) (53)
$[\alpha]^{28}D$: +63.9° (c=2.0 0.1 N HCl) (53)
UV: (EtOH-dioxane) 284 (4.04) (3a, 37); (MeOH) 290 (4.26) (54); (EtOH) 226 (4.41), 287 (4.20) (55); (EtOH) 226 (4.49), 285 (4.18) (13d)
IR: (KBr) 1605, 1645 (54, 55) 1650 sh (54). See also (13d).
^1H NMR: N.A.
MS: 352 (24), 251 (M^+) (100), 350 (50), 349 (48), 348 (22), 336 (24), 334 (16), 323 (10), 322 (24), 321 (12), 320 (26), 308 (10), 306 (14), 305 (14), 191 (16), 190 (18), 189 (16), 176 (16), 148 (34), 103 (16), 102 (16), 99 (16), 94 (22), 83 (14), 78 (14), 77 (16), 76 (14), 65 (12), 63 (14) (54)
X-Ray: Ochotensine methiodide (56, 57)
SOURCES: *Corydalis ochotensis* Turcz. (53)
Corydalis ochotenis Turcz. var. *raddeana* (Regel) Nakai (37)
Corydalis sibirica (L.) Pers. (47)
Corydalis solida (L.) Swartz (52, 58)
Dicentra cucullaria Bernh. (2)

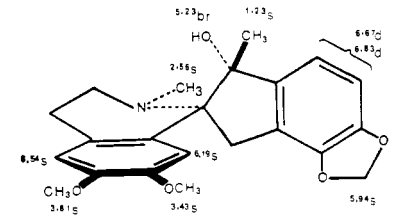
28. OCHOTENSIMINE



$C_{22}H_{23}O_4N$: 365.1627

MP: Oil (52, 59); Hydroiodide 190° (54); 189–190° (decomp.) (40); methiodide 225° (decomp.) (ether-MeOH) (53); perchlorate 172° (54)
$[\alpha]^{22}D$: +49.2° (c=0.2 MeOH) (53)
$[\alpha]^{20}D$: +46.3° (c=0.54 MeOH) (37)
UV: (MeOH) 220 (61); 226 (4.41), 287 (4.12) (54)
IR: 1613, 1629 (54)
^1H NMR: ($CDCl_3$) (1a, 61, 54, 60)
^{13}C NMR: ($CDCl_3$) (41)
MS: 366 (24), 365 (M^-) (100), 364 (40), 363 (14), 350 (18), 337 (10), 336 (18), 334 (10), 205 (10), 148 (16), 85 (50), 83 (24) (54, 60)
SOURCES: *Corydalis ochotensis* Turcz. (53, 47, 39, 40)
Corydalis ochotensis Turcz. var. *raddeana* (Regel) Nakai (53, 26, 37)
Corydalis solida (L.) Swartz (52)

29. RADDEANAMINE



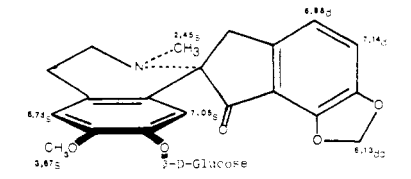
$C_{22}H_{25}O_5N$: 383.1732

MP: Oil (26, 37)
$[\alpha]^{20}D$: +166° (c=0.68 MeOH) (26, 37)
UV: N.A.
IR: ($CHCl_3$) 3240 (26, 37)
^1H NMR: ($CDCl_3$) (26, 37)
MS: 383 (M^+), 368, 365, 206 (26, 37)
SOURCES: *Corydalis ochotensis* Turcz. var. *raddeana* (Regel) Nakai (26, 37)

NOTE ADDED TO PROOF.—A recent reinvestigation of *Fumaria parviflora* Lam., which is now believed to be identical with *F. indica* (Haussk) Pugsley, has yielded parviflorine (**30**), the first glycosidic spirobenzylisoquinoline alkaloid (63). Acid hydrolysis of **30** yields (+)-parfumine (**8**). The sodium borohydride reduction product of **8** corresponds in all respect to fumaritine (**1**). The cd curve of fumaritine (**1**) shows a positive Davydov split between 277 and 294 nm so that the absolute configuration of this alkaloid is as indicated in expression **1**. It follows that (+)-parfumine (**8**) and the chemically related (+)-parfumidine (**9**) also possess the absolute configuration indicated in expressions **8** and **9** (63).

The recorded cd values in methanol are as follows

30. PARVIFLORINE



$C_{26}H_{29}NO_{10}$: 515.1784

MP: 230–232° (MeOH) (63)
$[\alpha]D$: +1° (c 0.0124 MeOH)
UV: (MeOH) 233 (4.50), 260 (4.18), 288 sh (3.70), 352 (3.66).
IR: (KBr) 1700, 3390.
^1H NMR: (Pyridine-d_5).
MS: 515 (M^-), 353, 338, 325, 324.
CD: $\Delta\epsilon_{nm}$ $+1.94_{355}$, -4.62_{293}, -18.25_{261}, $+4.62_{240}$. -4.38_{229}.
SOURCES: *Fumaria parviflora* Lam. (63)

Anomeric proton doublet at δ5.35 (J=7.3 Hz)

Occurrence of Spirobenzylisoquinolines by Plant Sources

(1) *Genus Corydalis*

C. ledebouriana K. et K.
Ledeboridine (**12**)
Ledeborine (**19**)
(±)-Raddeanine (**14**)
Sibiricine (**21**)

C. lutea (L.) DC.
Ochrobirine (**18**)

C. ochotensis Turcz.	Ochotensimine (**28**) Ochotensine (**27**) (±)-Yenhusomidine (**24**) Yenhusomine (**17**)
C. ochotensis Turcz. var. *raddeana* (Regel) Nakai	Ochotensimine (**28**) Ochotensine (**27**) Raddeanamine (**29**) Raddeanidine (**15**) (+)-Raddeanine (**13**) Raddeanone (**20**)
C. ochroleuca Koch	Ochrobirine (**18**)
C. paczoskii N. Busch	Corpaine (**22**) Corydaine (**25**)
C. sewerzowi Regel	Severzinine (**16**)
C. sibirica (L.) Pers.	Ochotensine (**27**) Ochrobirine (**18**) Sibiricine (**21**)
C. solida (L.) Swartz	Ochotensimine (**28**) Ochotensine (**27**)
C. vaginans Royle	Ochrobirine (**18**) (−)-Yenhusomidine (**23**)
(2) *Genus Dicentra*	
D. cucullaria Bernh.	Ochotensine (**27**)
(3) *Genus Fumaria*	
F. indica (Haussk) Pugsley	Fumariline (**10**)
F. kralikii Jord.	Fumaritine *N*-oxide (**2**) Fumarofine (**26**) Parfumine (**8**)
F. officinalis L.	Fumaricine (**3**) Fumariline (**10**) Fumaritine (**1**) Fumaritrine (**7**) Fumarofine (**26**) Fumarophycine (**4**) *O*-Methylfumarophycine (**5**) Parfumidine (**9**)
F. parviflora Lam.	Parfumidine (**9**) Parfumine (**8**) Fumaritine (**1**) Parviflorine (**30**)
F. rostellata Knaf.	Fumariline (**10**) Fumaritridine (**6**) Fumaritrine (**7**) Fumarofine (**26**) Parfumine (**8**)
F. schleicheri Soyer-Willem	Fumaritine (**1**)
F. vaillantii Lois.	Parfumidine (**9**) Parfumine (**8**)

Botanical Distribution of Spirobenzylisoquinoline Alkaloids

Corpaine (**22**):	*C. paczoskii* N. Busch
Corydaine (**25**):	*C. paczoskii* N. Busch
Fumaricine (**3**):	*F. officinalis* L.
Fumariline (**10**):	*F. indica* (Haussk) Pugsley *F. officinalis* L. *F. rostellata* Knaf.
Fumaritine (**1**):	*F. schleicheri* Soyer-Willem *F. parviflora* Lam.
Fumaritine *N*-oxide (**2**):	*F. kralikii* Jord.
Fumaritridine (**6**):	*F. rostellata* Knaf.
Fumaritrine (**7**):	*F. officinalis* L. *F. rostellata* Knaf.
Fumarofine (**26**):	*F. kralikii* Jord. *F. officinalis* L. *F. rostellata* Knaf.
Fumarophycine (**4**):	*F. officinalis* L.
Ledeboridine (**12**):	*C. ledebouriana* K. et K.

Ledeborine (**19**):	*C. ledebouriana* K. et K.
O-Melthylfumarophycine (**5**):	*F. officinalis* L.
Ochotensimine (**28**):	*C. ochotensis* Turcz.
	C. ochotensis Turcz. var. *raddeana* (Regel) Nakai
	C. solida (L.) Swartz
Ochotensine (**27**):	*C. ochotensis* Turcz.
	C. ochotensis Turcz. var. *raddeana* (Regel) Nakai
	C. sibirica (L.) Pers.
	C. solida (L.) Swartz
	D. cucullaria Bernh.
Ochrobirine (**18**):	*C. lutea* (L.) DC.
	C. ochroleuca Koch
	C. sibirica (L.) Pers.
	C. vaginans Royle
Parfumidine (**9**):	*F. officinalis* L.
	F. parviflora Lam.
	F. vaillantii Lois.
Parfumine (**8**):	*F. kralikii* Jord.
	F. parviflora Lam.
	F. rostellata Knaf.
	F. vaillantii Lois.
Parviflorine (**30**)	*F. parviflora* Lam.
Raddeanamine (**29**):	*C. ochotensis* Turcz. var. *raddeana* (Regel) Nakai
Raddeanidine (**15**):	*C. ochotensis* Turcz. var. *raddeana* (Regel) Nakai
(+)-Raddeanine (**13**):	*C. ochotensis* Turcz. var. *raddeana* (Regel) Nakai
(±)-Raddeanine (**14**):	*C. ledebouriana* K. et K.
Raddeanone (**20**):	*C. ochotensis* Turcz. var. *raddeana* (Regel) Nakai
Serverzinine (**16**):	*C. sewerzowi* Regel
Sibiricine (**21**):	*C. ledebouriana* K. et K.
	C. sibirica (L.) Pers.
(−)-Yenhusomidine (**23**):	*C. vaginans* Royle
(±)-Yenhusomidine (**24**):	*C. ochotensis* Turcz.
Yenhusomine (**17**):	*C. ochotensis* Turcz.

Alphabetical List of Spirobenzylisoquinoline Alkaloids

Corpaine (**22**)	Ledeboridine (**12**)	Raddeanidine (**15**)
Corydaine (**25**)	Ledeborine (**19**)	(+)-Raddeanine (**13**)
Fumaricine (**3**)	*O*-Methylfumarophycine (**5**)	(±)-Raddeanine (**14**)
Fumariline (**10**)	Ochotensimine (**28**)	Raddeanone (**20**)
Fumaritine (**1**)	Ochotensine (**27**)	Severzinine (**16**)
Fumaritine *N*-oxide (**2**)	Ochrobirine (**18**)	Sibiricine (**21**)
Fumaritridine (**6**)	Parfumidine (**9**)	(−)-Yenhusomidine (**23**)
Fumaritrine (**7**)	Parfumine (**8**)	(±)-Yenhusomidine (**24**)
Fumarofine (**26**)	Parviflorine (**30**)	Yenhusomine (**17**)
Fumarophycine (**4**)	Raddeanamine (**29**)	

ACKNOWLEDGMENT

This compilation was carried out in conjunction with research supported by grant No. CA-11450 awarded by the National Cancer Institute, DHEW.

Received 25 October 1979.

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