Some phytochemical studies of the genera *Aconitum,* L. *Delphinium* L. and *Consolida* (DC.) S.F. Gray

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Resum

FUENTE, G. DE LA & M. REINA (1990). Alguns estudis fitoquímics dels generes *Aconitum* L., *Delphinium* L., i Consolida (DC.) S.F. Gray. Collect. Bot. (Barcelona) 19: 129-140

Es revisen els alcaloides diterpènics obtinguts d'*Aconitum napellus* L. subsp. *castellanum* Molero & Blanché, *A. burnatii* Gayer, *A. compactum* Reichenb., *Delphinium gracile* DC., *D. pentagynum* Lam., *D. verdunense* Balbis (= *D. cardiopetalum* DC.), *D. requienii* DC., *Consolida orientalis* (Gay) Schröd. subsp. *orientallis* and *C. pubescens* (DC.) Soó, distribuïts a la Península Ibèrica, així com d'*A. napellus* L. s. str. (d'Anglaterra), *D. montanum* DC. (de França), *D. nanum* DC. subsp. *elongatum* (Boiss) Blanché & al. (= *D. peregrinum* L. var. *elongatum* Boiss.) (del Marroc) i *D. pictum* Willd. (de Mallorca).

El contingut en alcaloides, llurs tipus structurals i models d'oxigenació són discutits en relació a d'altres espècies afins.

Mots clau: Alcaloides diterpènics, *Aconitum*, *Delphinium*, *Consolida*.

Abstract

FUENTE, G. DE LA & M. REINA (1990), Some phytochemichal studies of the genera *Aconitum*, L. *Delphinium* L. and *Consolida* (DC.) S.F. Gray. Collect. Bot. (Barcelona) 19: 129-140

The diterpenoid alkaloids from *Aconitum napellus* L. subsp. *castellanum* Molero & Blanché, *A. burnatii* Gayer, *A. compactum* Reichenb., *Delphinium gracile* DC., *D. pentagynum* Lam., *D. verdunense* Balbis (= *D. cardiopetalum* DC), *D. requienii* DC., *Consolida orientalis* (Gay) Schröd. subsp. *orientalis* and *C. pubescens* (DC.) Soó, distributed in the Iberian Peninsula, and *A. napellus* L. s. str. (from England), *D. montanum* DC. (from France), *D. nanum* DC. subsp. *elongatum* (Boiss.) Blanché & al. (= *D. peregrinum* L. var. *elongatum* Boiss.) (from Morocco) and *D. pictum* Willd. (from Majorca) are reviewed.

The alkaloid content, structural types, and oxygenation patterns are discussed with respect to related species.

Keywords: Diterpenoid alkaloids, *Aconitum, Delphinium, Consolida.*

The genera *Aconitum, Delphinium* and *Consolida* are distributed almost exclusively in temperate and cold regions of the Northern Hemisphere, though some species of *Delphinium* from the high mountains of Southeast Africa (Zimbabwe, Kenya, Zaïre) have been described.

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Some fourteen species of *Aconitum,* twenty-six of *Delphinium* and *twelve* of *Consolida* are known in Europe (TUTIN, 1964; PAWLOWSKI, 1964 and CHATER, 1964). In the Iberian Peninsula the *Aconitum* species generally grow in moist meadows and on the banks of streams in the alpine and subalpine areas of the high mountains, while the *Delphinium* and *Consolida* species grow in temperate zones, on the roadsides and in fields of cereal crops. Five species of *Aconitum,* ten of *Delphinium* and four of *Consolida* have been reported from the *Flora Iberica* area, *Aconitum napellus* subsp. *castellanum* Molero & C. Blanché and *Delphinium bolosii* C. Blanché & Molero being endemic (BLANCHÉ & MOLERO, 1986; MOLERO & BLANCHÉ, 1986).

The great majority of the phytochemical studies carried out on the *Aconitum, Delphinium* and *Consolida* genera have dealth with diterpenoid alkaloids because these species are one of the main sources of such compunds, which continue to interest organic chemists owing to their complex structures (PELLETIER & PAGE, 1986) and pharmacological properties (BENN & JACYNO, 1983).

In this report we wish to review our work on diterpenoid alkaloids from the main *Aconitum, Delphinium* and *Consolida* species found, in the Iberian Peninsula.

Aconitum Species

From the above-ground parts of plants of *Aconitum napellus* L. subsp. *castellanum* J. Molero & C. Blanché, collected in wet soils in Laguna del Marquesado (Cuenca, Spain) five Aconitine-type alkaloids were isolated, aconitine (1), as the major constituent, 3-acetylaconitine (2), chasmanine (7), neoline (11), and 1,14-diacetylneoline (13); two lycoctonine-type alkaloids, delcosine (28) and delsoline (31); and three veatchine-type alkaloids, songoramine (69), 12-epidehydronapelline (70), and 13-epiacetyldehydronapelline (71) (DE LA FUENTE & AL., 1988a).

From the aerial parts of *A. burnatii* Gayer (*Aconitum nevadense* Vechtr., syn. *A. divergens* subsp. *burnatii* (Gayer) W. Seitz), collected in Sierra Nevada (Granada) we isolated ten aconitine-type alkaloids, 8-O-ethyl-14-benzoylaconine (5) and neoline (11), as major constituents, isotalatizidine (15), columbianine (16), chasmanine (7), 8-O-ethylchasmanine (18), senbusine A (17), aconine (3), 8-O-ethylaconine (14), and nevadenine (47); one lycoctonine-type alkaloid, nevadensine (49); and one veatchine-type alkaloid, songoramine (69) (DE LA FUENTE & AL., 1985a). It has been suggested that the 8-O-ethyl derivatives are artifacts formed from the corresponding base having a good leaving group at C-8, during the treatment of the vegetable material with ethanol (PELLETIER & AL., 1987).

Preliminary studies of plants of *Aconitum compactum* Reicheng, collected in Valle de Pineta (Huesca), led to the isolation of neoline (11) and 8-O-ethyl-14-benzoylaconine (5), as major constituents, in addition to aconitine (1) (DE LA FUENTE & AL., 1985b).

From plants of *Aconitum napellus* L. s. str. (syn. *A. anglicum* Stapt) from the Botanical Gardens, University of Cambridge (England), we were able to isolate one acontine-type alkaloid, 8-O-ethyl-14-benzoylaconine (5), as the major constituent; three atisine-type hetisine subtype alkaloids, 15-acetyl-13-dehydrocardiopetamine (60), 15-acetylcardiopetamine (59), and cardiopetamine (58); and two veatchine-type alkaloids, songoramine (69) and songorine (72) (DE LA FUENTE & AL., 1989a).

A. napellus L. subsp. *castellanum* and *A. burnatii* are characterized by having aconitine- and lycoctonine-type diterpenoid alkaloids as well as veatchine-type alkaloids, something which as occurs only with *A. monticola* Steinb. (AMETOVA & AL., 1977, 1981, and 1982) and *A. karakolicum* Rapaics (SULTANKHODZHAEV, 1980, 1986, 1987a, 1987b), this last species being the most similar to *A. napellus* L. subsp. *castellanum* and *A. burnatii* with regard to the number and distribution of the oxygenated functions. However, from *A. karakolicum,* C-19 diterpenoid alkaloids functionalized at C-9 and C-4 (18-seco) were isolated, which is not the case with *A. napellus* L. subsp. *castellanum* and *A. burnatii.*

From *A. napellus* L. s. str., alkaloids of the aconitine, hetesine, and veatchine types were isolated as occurred in the case of *A. carmichaeli* Debx. (PELLETIER & PAGE, 1983, 1984 and 1986), *A. yesoense* Nakai (PELLETIER & PAGE, 1981 and 1983), and *A. mitakense* Nakai (PELLETIER & PAGE, 1981).

If it is considered that 8-ethyl-14-benzoylaconine (11) is produced by solvolysis of the acetate group at C-8 of the alkaloid aconitine (1) during the process of extraction of the vegetable material with hot ethanol, aconitine would be the major component in *A. napellus* L. subsp. *castellanum, A. burnatii, A. compactum* and *A. napellus* s. str., and this fact would situate them among the Type-I *Aconitum* species, in accordance with the classification proposed by KATZ & STAELIN (1979).

***Delphinium* Species**

From *D. gracile* DC (Cádiz and Sardón del Duero, Valladolid, Spain), we were able to isolate five lycoctonine-type alkaloids, graciline (50), gracinine (32), gadesine (51), dihydrogadesine (33), and nudicaulidine (36); and four atisine-type hetisine subtype alkaloids, hetisinone (61), 13-acetylhetisinone (62), cardiopetamine (58), and 11-acetylcardionine (66) (GONZÁLEZ & AL., 1984a and 1986a; DE LA FUENTE & AL., 1990a).

The same types and subtypes of diterpenoid alkaloids isolated from *D. gracile* DC were found in *D. cardinale* Hook (BENN, 1966), *D. geyeri* Greene (GRINA & AL., 1986), *D. nudicaule* Torr. and Gray (KULANTHAIVEL & BENN, 1985) and *D. occidentale* S. Wats. (KULANTHAIVEL & AL., 1988). However, from *D. gracile* alkaloids were isolated that were relatively little functionalized even at C-16, e.g. graciline (50), and with functionalization at C-12, which is unusual in a lycoctonine-type skeleton, e.g. gracinine (32), and in a skeleton of the hetisine subtype, e.g. 11-acetylcardionine (66).

From *D. pentagynum* Lam. (Sembrado de Veger, Cádiz, Spain) we isolated seven lycoctonine-type alkaloids, gadesine (51), dihydrogadesine (33), 14-acetyldihydrogadesine (34), pentagydine (56), gadenine (39), 14-acetylgadesine (52), and gadeline (57); and four aconitine-type alkaloids, pentagynine (48), dihydropentagynine (19), pentagyline (20), and karakoline (21) (GONZÁLEZ & AL., 1979, 1982, 1983a, 1984b, and 1986b).

Analysis of *D. verdunense* Balb. (syn *D cardiopetalum* DC.) (Leon and Jaca, Huesca, Spain) led to the isolation of eight lycocotonine-type alkaloids, cardiopetalidine (40), dihydrogadesine (33), 14-benzoyldihydrogadesine (35), 14-acetyldihydrogadesine (34), 14-benzoylgadesine (53), nudicaulidine (36), 14-acetylnudicaulidine (37), and 14-benzoylnudicaulidine (38); two aconitine-type alkaloids, cardiopetaline (22) and karakoline (21), one atisine-type alkaloid, atisinium chloride (68); and seven hetisine subtype alkaloids, hetisinone (61), 13-acetylhetisinone (62), hetisine (63), cardionine (65), cardiopetamine (58), 15-acetylcardiopetamine (59), 13-acetylhetisine (64), and sanyonamine (67) (GONZÁLEZ & AL., 1980, 1981a, 1983b, and 1986b, and DE LA FUENTE & AL., 1990a).

The epigeal parts of plants of *D. montanum* DC (Vall d'Eina, Cerdanya, France) yielded seven lycoctonine-type diterpenoid alkaloids, nudicaulidine (36), gigactonine (41), delcosine (28), 1,14-diacetyldelcosine (30), gadesine (51), 14-benzoylgadesine (53), and methyllycaconitine (42); seven aconitine-type alkaloids, neoline (11), 14-acetylneoline (12), 1,14-diacetylneoline (13), senbusine A (17), karakoline (21), 1,6,14-tribenzoylsenbusine A (18), 8-O-ethyl-14-benzoyulaconine (5), and 8-O-ethyl-3,14,15-benzoylaconine (6); and two atisine-type hetisine subtype alkaloids, cardiopetamine (58), and 15-acetylcardiopetamine (59) (DE LA FUENTE & AL., 1990b).

Study of *D. nanum* DC. subsp. *elongatum* (Boiss.) Blanché, Molero & Simon (syn. *D. peregrinum* var. *elongatum* Boiss.) (Playa de Médiyah, Rabat, Morocco) led to the isolation of two lycoctonine-type alkaloids, dihydrogadesine (33) and nudicaulidine (36); two aconitine-type alkaloids, peregrinine (23) and bicoloridine (24); and one atisine-type hetisine subtype alkaloid, 13-acetylhetisinone (62) (DE LA FUENTE & AL., 1988b).

D. pentagynum, D. verdunense, D. montanum and *D. nanum* subsp. *elongatum* can be considered to belong to the group of species of *Delphinium* that contain lycoctonine- and aconitine-type alkaloids. It is noteworthy that only *D. pentagynum* did not afford either atisine-type or hetisine subtype alkaloids.

Diterpenoid alkaloids with a lycoctonine- or aconitine-type skeleton have also been isolated from *D. nuttallianum* Pritz (BAI & BENN, 1989), *D. bicolor* Nutt, (KULANTHAIVEL & BENN, 1986), *D. cashmirianum* Royle (SHAMMA & AL., 1979), *D. confusum* M. Popov (VAISOV & YUNUSOV, 1986), and *D. speciosum* M. Bieb. (BESHITAISHVILI & AL., 1984), but in these cases only *D. nuttallianum* afforded a hetisine subtype alkaloid, 13-acetylhetisine (64).

As far as we know, *D. montanum* DC is the first species from which C-19 diterpenoids as functionalized as the aconines have been obtained.

In general, the oxygen function at C-6 on a lycoctonine skeleton is in β configuration and that of aconitine is in α, but in certain cases, such as *D. peregrinum, D. speciosun, D. nuttallianum,* and *D. bicolor,* aconitine-type alkaloids with a C-6β oxygen function are isolated.

It should also be pointed out that *D. verdunense* and *D. gracile* are the only species of *Delphinium* to afford C-19 diterpenoid alkaloids without a C-16 functionality.

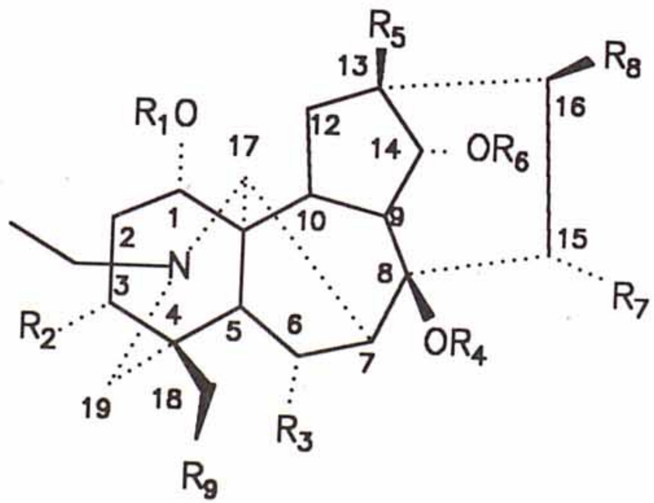
From *D. pictum* Willd. subsp. *pictum* (Majorca, Spain) we have isolated seven aconitine-type diterpenoid alkaloids, neoline (11), 14-acetylneoline (12), delphisine (8,14-diacetylneoline) (14), chasmaconitine (9), chasmanthinine (10), delphinine (25), and pictumine (26) (DE LA FUENTE & AL., 1989b). Preliminary work on *D. requienii* DC (Jardí Botànic "Mar i Murtra", Blanes, Girona, Spain) permitted the isolation of three aconitine-type alkaloids, neoline (11), delphinine (25), and 8-O-ethyl-14-benzoyldelphonine (27), which may be an artifact produced by solvolysis of delphinine during the treatment of the vegetable material with ethanol, and atisinium chloride (68) (DE LA FUENTE & AL., 1984).

D. pictum and *D. requienii,* the latter with reservations since only four alkaloids have been identified, can be considered to belong to the group of *Delphinium* species in which C-19 diterpenoid alkaloids possess only the aconitine-type skeleton, this also being a characteristic of *D. denudatum* Wall (PELLETIER & AL., 1967, and WANG, 1981), and of *D. staphisagria* L. (PELLETIER & AL., 1988, ROSS & PELLETIER, 1988, and PELLETIER & MODY, 1976).

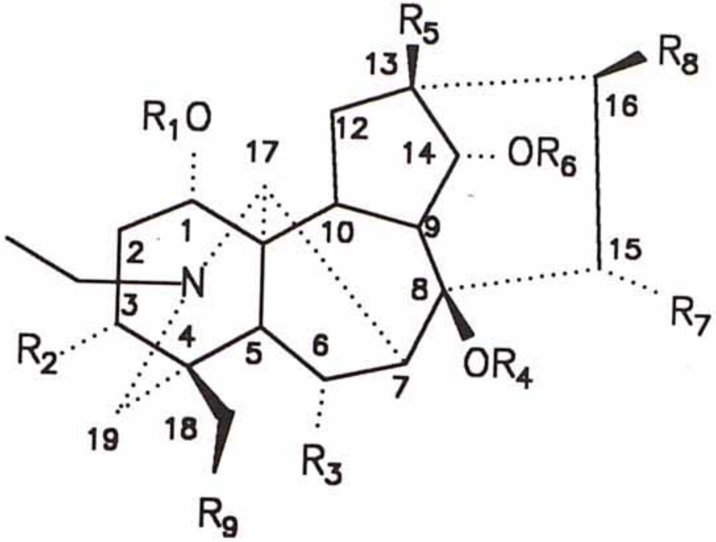
Consolida Species

From *C. orientalis* Gay subsp. *orientalis* (Cuenca, Spain) we isolated five lycoctonine-type diterpenoid alkaloids, delsoline (31), delcosine (28), gigactonine (41), 18-methoxygadesine (54), and 18-hydroxy-14-O-methoxygadesine (55) (GONZÁLEZ & AL., 1981b, and 1983c); and from *C. pubescens* (DC) Soó (Zaragoza, Spain) we isolated five lycoctonine-type diterpenoid alkaloids, browniine (43), 14-acetylbrowniine (44), delbonine (45), 14-acetyldelcosine (29), and pubescenine (46) (DE LA FUENTE & AL., 1988c). Pubescenine (46) was isolated as a major constituent of the alkaloid mixture, and is the first lycoctonine-type C-19 diterpenoid alkaloid bearing a C-6α functionality.

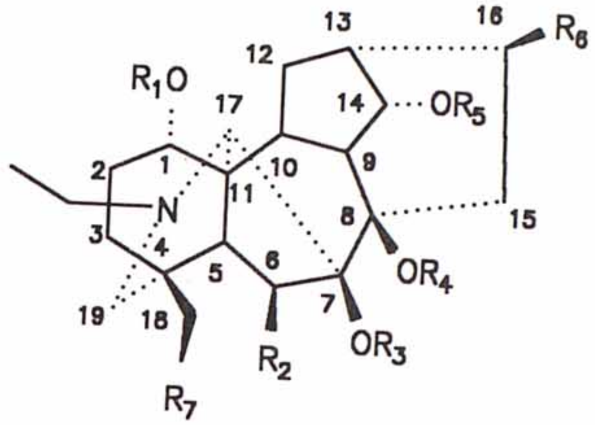
Fewer studies and publications have so far been devoted to the genus *Consolida* than to *Delphinium* and *Aconitum*. Moreover, data on diterpenoid alkaloids have been yielded why by *C. ambigua* (L.) P.W. Ball & V.H. Heywood (KULANTHAIVEL, 1989), *C. glandulosa* (SENER & AL., 1988a), and *C. regalis* subsp. *paniculata* var. *paniculata* (SENER & AL., 1988b).



		R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
Aconitine	(1)	Me	OH	OMe	Ac	OH	Bz	OH	OMe	OMe
3-Acetylaconitine	(2)	Me	OAc	OMe	Ac	OH	Bz	OH	OMe	OMe
Aconine	(3)	Me	OH	OMe	H	OH	H	OH	OMe	OMe
8-O-Ethylaconine	(4)	Me	OH	OMe	Et	OH	H	OH	OMe	OMe
8-O-Ethyl-14-benzoylaconine	(5)	Me	OH	OMe	Et	OH	Bz	OH	OMe	OMe
8-O-Ethyl-3,14,15-benzoylaconine	(6)	Me	OBz	OMe	Et	OH	Bz	OBz	OMe	OMe
Chasmanine	(7)	Me	H	OMe	H	H	H	H	OMe	OMe
8-O-Ethylchasmanine	(8)	Me	H	OMe	Et	H	H	H	OMe	OMe
Chasmaconitine	(9)	Me	H	OMe	Ac	OH	Bz	H	OMe	OMe
Chasmanthinine	(10)	Me	H	OMe	Ac	OH	Cn	H	OMe	OMe
Neoline	(11)	H	H	OMe	H	H	H	H	OMe	OMe
14-Acetylneoline	(12)	H	H	OMe	H	H	Ac	H	OMe	OMe
1,14-Diacetylneoline	(13)	Ac	H	OMe	H	H	Ac	H	OMe	OMe
8,14-Diacetylneoline	(14)	H	H	OMe	Ac	H	Ac	H	OMe	OMe
Isotalatizidine	(15)	H	H	H	H	H	H	H	OMe	OMe



Columbianine	(16)	H	H	H	H	H	H	H	OMe	OH
Senbusine A	(17)	H	H	OH	H	H	H	H	OMe	OMe
1,6-14-Tribenzoylsenbusine A	(18)	Bz	H	OBz	H	H	Bz	H	OMe	OMe
Dihydropentagynine	(19)	H	H	OMe	H	H	H	H	OMe	H
Pentagyline	(20)	H	H	OMe	H	H	Bz	H	OMe	H
		and C-10 ßOH								
Karakoline	(21)	H	H	H	H	H	H	H	OMe	H
Cardiopetaline	(22)	H	H	H	H	H	H	H	H	H
Peregrinine	(23)	Me	H	OAc	Me	H	H	H	OMe	H
Bicoloridine	(24)	Me	H	ßOAc	Me	H	H	H	OMe	H
Delphinine	(25)	Me	H	OMe	Ac	OH	Bz	H	OMe	OMe
		and N-Me								
Pictumine	(26)	H	H	OMe	Ac	H	Ac	H	OMe	OMe
		and N-Me								
8-O-Ethyl-14-benzoyldelphonine	(27)	Me	H	OMe	Et	OH	Bz	H	OMe	OMe
		and N-Me								



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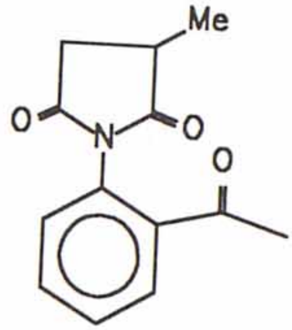
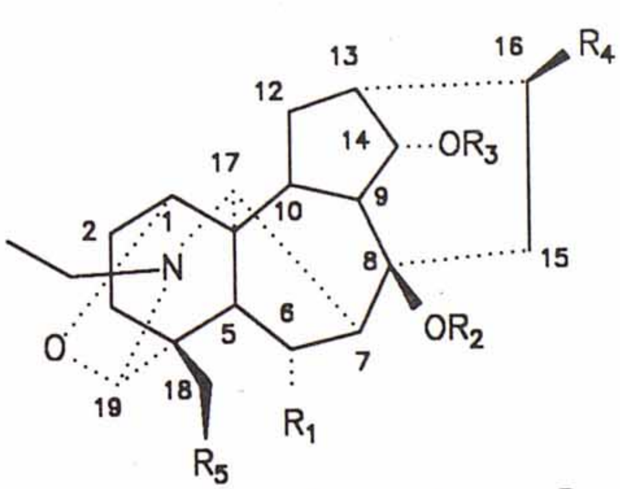
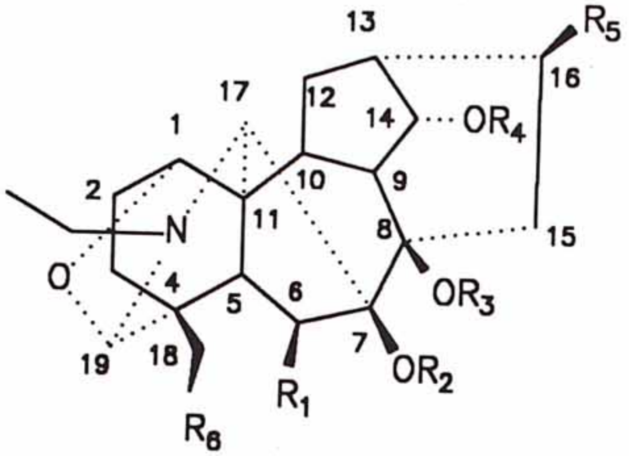


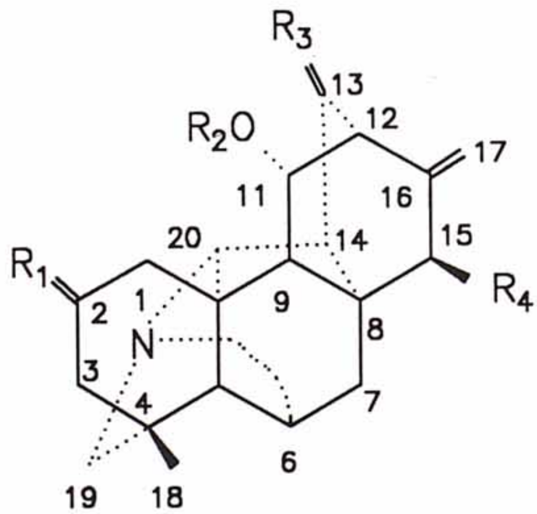
		R1	R2	R3	R4	R5	R6	R7
Delcosine	(28)	H	OMe	H	H	H	OMe	OMe
14-Acetyldelcosine	(29)	H	OMe	H	H	Ac	OMe	OMe
1,14-Diacetyldelcosine	(30)	Ac	OMe	H	H	Ac	OMe	OMe
Delsoline	(31)	H	OMe	H	H	OMe	OMe	OMe
Gracinine	(32)	H	OMe	H	H	Bz	OMe	H
		and C-12 ßOH						
Dihydrogadesine	(33)	H	OMe	H	H	H	OMe	H
14-Acetyldihydrogadesine	(34)	H	OMe	H	H	Ac	OMe	H
14-Benzoyldihydrogadesine	(35)	H	OMe	H	H	Bz	OMe	H
Nudicaulidine	(36)	Me	OMe	H	H	H	OMe	H
14-Acetylnudicaulidine	(37)	Me	OMe	H	H	Ac	OMe	H
14-Benzoylnudicaulidine	(38)	Me	OMe	H	H	Bz	OMe	H
Gadenine	(39)	H	OMe	H	H	Bz	OMe	H
		and C-10 ßOH						
Cardiopetalidine	(40)	H	H	H	H	H	H	
Gigactonine	(41)	H	OMe	H	H	Me	OMe	OH
Methyllicaconitine	(42)	Me	OMe	H	H	Me	OMe	Z
Browniine	(43)	Me	OMe	H	H	H	OMe	OMe
14-Acetylbrowniine	(44)	Me	OMe	H	H	Ac	OMe	OMe
Delbonine	(45)	H	OMe	H	Me	Ac	OMe	OMe
Pubescenine	(46)	H	γOH	H	Me	Ac	OMe	OMe



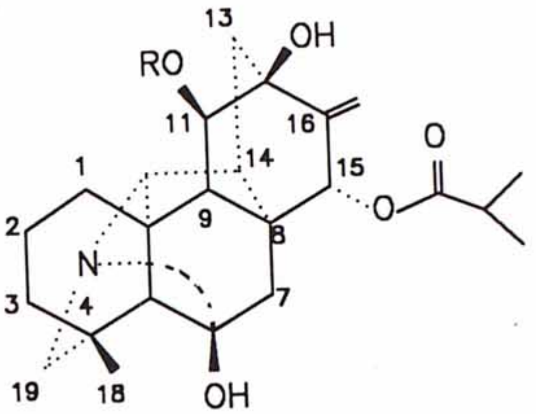
		R1	R2	R3	R4	R5
Nevadenine	(47)	H	H	H	OMe	OMe
Pentagynine	(48)	OMe	H	H	OMe	OMe



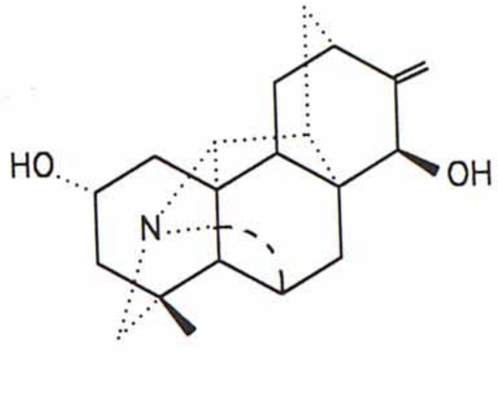
		R_1	R_2	R_3	R_4	R_5	R_6
Nevadensine	(49)	H	H	H	H	OMe	OMe
Graciline	(50)	H	H	H	H	H	H
Gadesine	(51)	OMe	H	H	H	OMe	H
14-Acetylgadesine	(52)	OMe	H	H	Ac	OMe	H
14-Benzoylgadesine	(53)	OMe	H	H	Bz	OMe	H
18-Methoxygadesine	(54)	OMe	H	H	H	OMe	OMe
18-Hydroxy-14-0-methoxygadesine	(55)	OMe	H	H	Me	OMe	OH
Pentagydine	(56)	H	H	H	H	OMe	H
Gadeline	(57)	OMe and C-10 ßOH	H	H	Bz	OMe	H



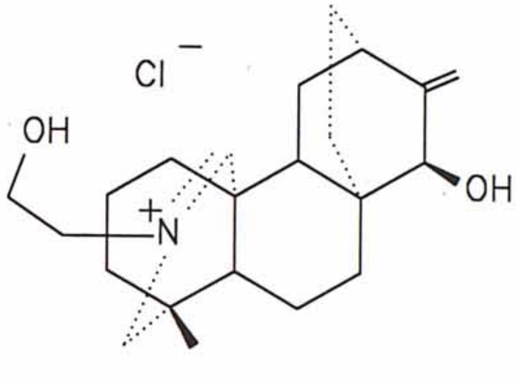
		R_1	R_2	R_3	R_4
Cardipetamine	(58)	O	Bz	H,ßOH	OH
15-Acetylcardiopetamine	(59)	O	Bz	H,ßOH	OAc
15-Acetyl-13-dehydro-cardiopetamine	(60)	O	Bz	O	OAc
Hetisinone	(61)	O	H	H,ßOH	H
13-Acetylhetisinone	(62)	O	H	H,ßOAc	H
Hetisine	(63)	H,nOH	H	H,ßOH	H
13-Acetylhetisine	(64)	H,γOH	H	H,ßOAc	H



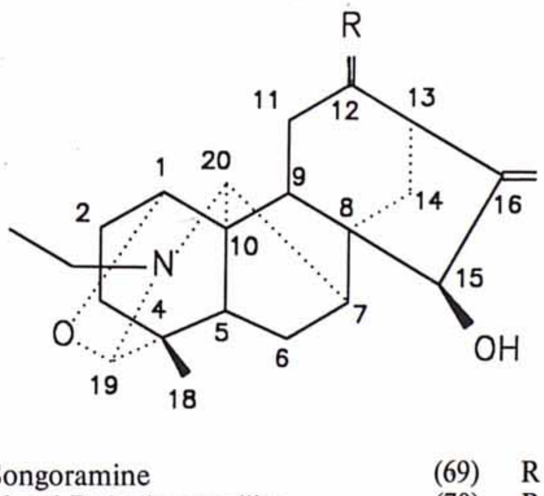
Cardionine (65) R = H
11-Acetylcardionine (66) R = Ac



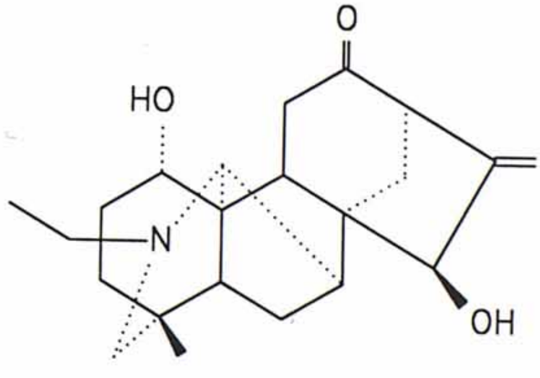
Sanyonamine (67)



Atisinium chloride (68)



Songoramine (69) R = O
12-epi-Dehydronapelline (70) R = H,ßOH
12-epi-Acetyldehydronapelline (71) R = H,ßOAc



Songorine (72)

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