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STEROID ALKALOIDS OF THE PLANT AND ANIMAL KINGDOMS

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This review, which covers the literature for 1988—1996, gives new information on the occurrence of steroid alkaloids in Nature and discusses ecological and biogenetic aspects of their study.

The field of science at the meeting point of ecology (studying the interrelationships of organisms with one another and with the environment), chemistry, and biochemistry, is sometimes called chemical (or biochemical) ecology.

The substances that are the subject of attention of biochemical ecology are, as a rule, present in organisms or are secreted in considerably smaller amounts than the substances used by the organisms primarily as bearers of energy or as structural material. Many of these classes of substances have long been objects of the study of biochemistry from the point of view of their structure and metabolism, the majority of them belonging to the so-called secondary metabolites [1, 2]. This relates above all to such large groups of compounds as alkaloids, flavonoids, terpenoids, etc., playing an important role in the complex interaction of natural systems: animal—animal, animal—plant, or plant—plant [3].

Steroid alkaloids form a group of compounds found in the plant and (though far more rarely) animal kingdoms (Table 1).

Plants of the Apocynaceae, Buxaceae, Liliaceae, and Solanaceae families have long been traditional natural "suppliers" of steroid alkaloids [4—6], certain alkaloids as a rule being characteristic for definite botanical families. Likewise, representatives of one systematic order of plants elaborate alkaloids of similar chemical structure, which makes it desirable to use alkaloid compositions for the solution of taxonomic problems within a genus or species. Some simple lower alkaloids may also be detected in remote plant families, but for complex highly specific alkaloids this is only exceptional. All this points to a considerable species specificity of the secondary metabolism, while in plants the primary metabolism is largely universal [7, 8].

One of the ecological aspects of the study of steroid alkaloids is the question of their role in the vital activity of organisms; i.e., structural investigations are, in essence, a component part of this problem and are called upon to answer the following questions: with what aim and in what way are steroid alkaloids synthesized in the organism.

In the study of the secretion of the skin glands of caudate amphibia (salamanders) and anural amphibia (neotropical frogs) it was established that the highly toxic steroid alkaloids isolated fulfilled a protective function [7, 8].

In relation to plant objects, the situation is somewhat more complicated. According to numerous experimental facts, the synthesis of alkaloids in plants is connected with the activity of the formative tissue — the meristem, which is particularly active in young plants [71, 72].

Experiments conducted on suspension cultures of isolated cells of alkaloid-bearing plants have shown that the accumulation of alkaloids coincides with the peak of mitotic activity of the cells, when the majority of them are present in the DNA-synthesizing period and the post-synthetic period preceding mitosis (G_2) [73, 74]. Cells present in the G_2 period of the cell cycle become resistant to extreme conditions of the environment (low temperatures, deficient supply of water, etc.). Because of this, after passing out of the conditions of stress they multiply actively and give an adapted progeny. The hypothesis has been made that one of the factors of adaptation may be the synthesis of alkaloids as a response to the neutralization of cell-toxic nitrogen compounds arising under the extreme conditions [75].

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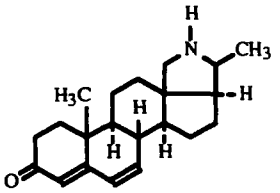
TABLE 1. Steroid Alkaloids of the Plant and Animal Kingdoms (results of investigations in 1988—1996)*

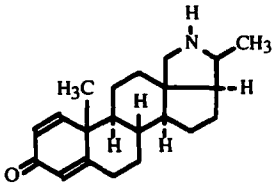
PLANTS

Fam. *Apocynaceae*



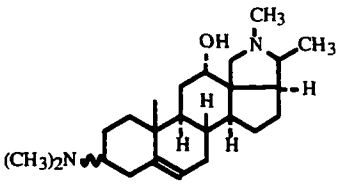
PUBESCINE

Holarrhena pubescens [9]



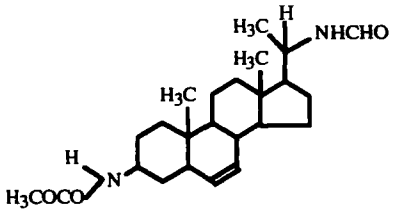
NORHOLADIENE

Holarrhena pubescens [9]



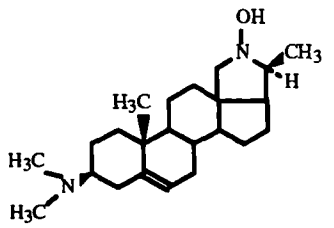
PUBESCIMINE

Holarrhena pubescens [9]



HOLARRHIFINE

Holarrhena antidysenterica [10]



REHOLARRHENINE D

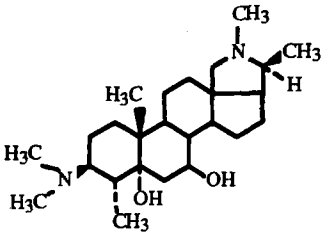
Holarrhena antidysenterica [11]
$C_{23}H_{38}N_2O$: 358
mp: 255-257°
IR (KBr): 3460, 3180, 2940, 2795, 1650, 1460, 1375, 1040, 980
Mass: 341(M-173$^+$, 60); 326(18), 85(99.8), 84(100); 57(95), 28(60)

^{1}H NMR: 5.36(s, 1H, C-6); 4.80(s, 1H, N-OH); 2.90(d, 2H, J=8, C-3α and C-20αH); 2.67(m, 2H, C-18); 2.34(s, 6H, NMe_2); 1.34(d, 3H, J=7, C-21); 0.96(s, 3H, C-19)

*Symbols used in the review: s — singlet; d — doublet; m — multiplet; t — triplet; q — quartet.

^{13}C NMR($CDCl_3$):

C-1	38.3	C-9	49.8	C-17	53.1
2	24.9	10	37.8	18	64.8
3	64.8	11	21.9	19	56.5
4	35.3	12	26.7	20	56.5
5	141.8	13	50.5	21	14.8
6	120.3	14	55.3	22	41.6
7	31.8	15	22.5	23	41.6
8	33.7	16	36.5		



REHOLARRHENINE E

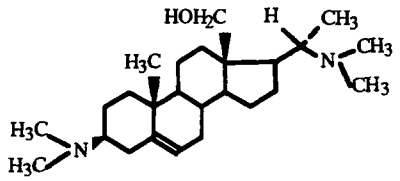
Holarrhena antidysenterica [11]
$C_{25}H_{44}N_2O_2$: 404
mp: 285-287°
IR (KBr): 3520, 3150, 2900, 1450, 1420, 1360, 1200, 1160, 1010
Mass: 404(M^+, < 0.1%); 389([M-15]$^+$, 5); 387([M-17]$^+$, 38); 374(70), 372(22), 264(18), 253(35), 252(25), 209(65), 142(45), 108(25), 98(65), 84(90), 71(99), 32(100), 28(98)

^1H NMR: 4.45(s, 1H); 3.52(1H, $W_{1/2}$=5.5; C-7βH); 3.45(1H); 3.07(dd, 2H, J=12.4, C-3α and C-20αH); 2,90(d, 1H, J=10, 4β-H axial); 2.32(s, 6H, NMe_2); 2.25(s, 3H, NMe); 1.29(d, J=10, C-25); 1.09(s, 3H, C-19); 1.03(d, 3H, J=6, C-21)

^{13}C NMR ($CDCl_3$):

C-1	38.5	C-10	37.5	C-19	16.0
2	26.5	11	21.5	20	63.0
3	63.8	12	26.5	21	13.5
4	34.0	13	50.6	22	40.0
5	74.5	14	54.5	23	40.0
6	26.5	15	22.2	24	40.8
7	75.0	16	44.5	25	23.5
8	33.0	17	53.5		
9	58.5	18	63.8		

REHOLARRHENINE F



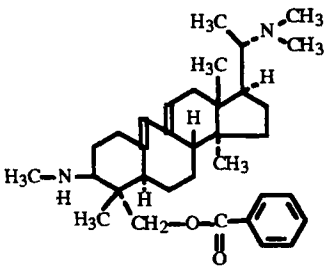
Holarrhena antidysenterica [11]
$C_{25}H_{44}N_2O$: 388
mp: 210-212°
IR (KBr): 3400, 2920, 1460, 1030
Mass: 388(M^+, < 1%); 373(1); 342(1); 316(2.34), 289(2), 84(63), 72(100), 58(10.7), 44(10), 28(90)

^1H NMR: 5.38(1H, C-6H); 3.46(s, 2H, C-18); 2.92(m, 2H, $W_{1/2}$=22; C-3α, C-20βH); 2.32(s, 6H, NMe_2); 2.30(s, 6H, NMe_2); 2.16(s, 1H); 1.08(d, 3H, J=12, C-21); 1.06(s, 3H, C-19)

^{13}C NMR ($CDCl_3$):

C-1	38.5	C-10	37.0	C-19	16.0
2	25.0	11	20.5	20	59.0
3	65.0	12	32.0	21	11.5
4	35.2	13	47.0	22	41.6
5	141.0	14	56.2	23	41.6
6	120.0	15	23.8	24	42.0
7	32.0	16	35.2	25	42.0
8	38.5	17	55.5		
9	51.0	18	59.0		

Fam. *Buxaceae*

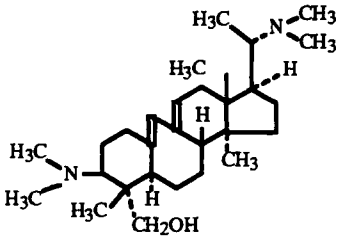


30-(O)-BENZOYL-16-DEOXYBUXIDIENINE-C

Buxus hildebrandtii [12]
$C_{34}H_{50}N_2O_2$: 518.3872
mp: resin
$[\alpha]_D$-75° ($CHCl_3$)
UV: 225(4.49), 238(4.53), 248(4.49), 254(4.23)
IR: 3400(NH), 2900, 1710(C=O), 1600(C=C)

Mass: 518(M^+); 497, 447, 396, 369, 367, 354, 326, 268, 211, 185, 183, 171, 119, 105, 84, 73, 72
^1H NMR: 2.24(1H, m, H-1β); 2.28(1H, m, H-1α); 1.42(1H, m, H-2β); 2.17(1H, m, H-2α); 2.54(1H, dd, $J_{3\alpha/2\alpha}$=11.8, $J_{3\alpha/2\alpha}$=4.2, H-3α); 1.84(1H, m, H-5α); 1.28(1H, m, H-6β); 1.54(1H, m, H-6α); 1.56(1H, m, H-7β); 1.89(1H, m, H-1α); 2.13(1H, m, H-8β); 5.52(1H, m, H-11); 2.00(1H, m, H-12β); 2.09(1H, m, H-12α); 1.27(1H, m, H-15β); 1.39(1H, m, H-15α); 1.45(1H, m, H-16β); 2.05(1H, m, H-16α); 2.47(1H, m, H-17α); 0.72(3H, s, Me-18); 6.00(1H, H-19); 2.49(1H, m, H-20); 0.85(3H, d, $J_{20/21}$=6.7, Me-21); 4.11(1H, d, J=11.4, H-30); 4.56(1H, d, J=11.4, H-30); 0.69(3H, s, Me-31); 0.67(3H, s, Me-32); 2.37(3H, s, N(a)-Me); 2.19(6H, s, N(b)-Me); 8.03(2H, m, H-2', 16'); 7.43(2H, m, H-3', 15'); 7.54(1H, m, H-4')
^{13}C NMR ($CDCl_3$):

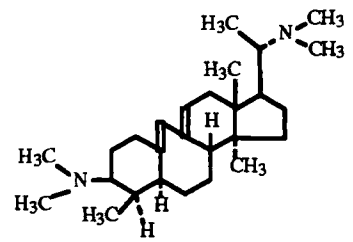
C-1	40.3	C-12	38.5	C-31	11.3
2	29.6	13	48.6	32	17.1
3	61.6	14	44.3	N(a)-CH_3	35.6
4	42.9	15	33.0	N(b)-CH_3	39.9
5	49.1	16	28.8	1'	130.5
6	25.4	17	45.7	2'	128.4
7	27.0	18	15.8	3'	129.5
8	49.7	19	130.1	4'	132.8
9	138.3	20	61.7	5'	129.5128.4
10	134.9	21	9.7	6'	166.2
11	129.5	30	65.9	C=O	



30-HYDROXYBUXAMINE A

Buxus hildebrandtii [12]
$C_{28}H_{48}N_2O$: 428.3767
mp: amorph.
$[\alpha]_D$ +61° ($CHCl_3$)
UV: 225, 238, 248, 254
IR: 3345(OH)
Mass: 428(M^+); 413.3551($C_{27}H_{45}N_2O$), 369, 357, 344, 342, 314, 282, 183, 157, 143, 91, 73, 72.0814($C_4H_{10}N$, 100)
^{1}H NMR: 2.16(1H,m, H-1β); 2.28(1H,m, H-1α);1.59 (1H, m, H-2β),1.73(1H, m, H-2α)2.62(1H, dd, J=3.7, 12.5, H-3α);5.52(1H, m, H-11); 2.00(1H, m, H-12β); 2.10(1H, m, H-12α); 2.56(1H, m, H-20β); 0.89 (3H, d, $J_{21/20}$=6.4, Me-21); 3.60(1H, d, J=10.4,H-30); 3.71 (1H, d, J=10.4, H-30); 0.74(3H, s, Me); 1.00(3H, s, Me); 0.68(3H, s, Me); 2.25 (6H, s, N(a)-Me_2); 2.30(6H, s, N(b)-Me_2)
^{13}C NMR($CDCl_3$):

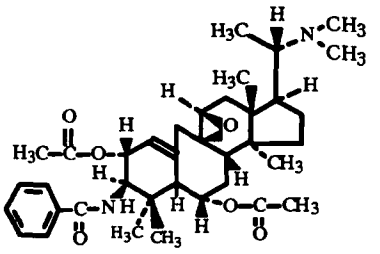
C-1	40.8	C-10	134.1	C-19	129.7
2	29.1	11	129.4	20	57.1
3	73.5	12	38.5	21	9.99
4	43.0	13	48.6	30	73.2
5	49.5	14	43.8	31	11.1
6	21.2	15	33.0	32	17.1
7	25.3	16	27.0	N(a)-CH_3	39.8
8	49.5	17	48.0	N(b)-CH_3	39.8
9	138.3	18	15.8		



30-NORBUXAMINE A

Buxus hildebrandtii [12]
$C_{27}H_{46}N_2$: 398.3666
mp: amorph.
$[\alpha]_D$ -13° ($CHCl_3$)
UV: 238, 246, 228, 254
IR: 1596(C=C)
Mass: 398(M^+); 383.3405 ($C_{27}H_{43}N_2$)369, 356, 308, 279,239,225, 183,169, 167, 157,129,119, 91,83, 72.0813 ($C_4H_{10}N$)
^{1}H NMR: 2.52(1H,m, H-2α); 5.54(1H, m, H-11); 5.88 (1H, H-19),2.40 (1H, m, H-20); 0.87(3H, d,$J_{21/20}$=6.4, Me-21); 0.72(3H, s, Me); 0.75(3H, s, Me); 1.02(3H, d, J=6.4); 2.23(6H, s, N(a)-Me_2);2.21(6H, s, N(b)-Me_2)
^{13}C NMR($CDCl_3$):

C-1	40.8	C-10	134.1	C-19	129.7
2	29.6	11	129.4	20	57.1
3	73.5	12	38.5	21	9.9
4	43.0	13	43.6	31	11.1
5	49.2	14	48.6	32	17.1
6	21.2	15	33.0	N(a)-CH_3	39.8
7	25.3	16	27.0	N(b)-CH_3	39.8
8	49.5	17	48.0		
9	138.3	18	15.8		

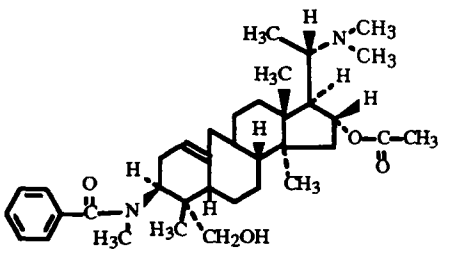


BUXAPAPILININE

Buxus papilosa [13]
$C_{37}H_{52}N_2O_6$: 620.3833
mp: amorph.
$[\alpha]_D$ -28° ($CHCl_3$)
UV (MeOH): 228
IR(KBr): 2950(NH), 1730(C=O), 1670(N-C=O), 1240(C-O-C)

Mass: 620.3862(M^+, 18); 605.3602(M-CH_3, 16); 489.2876($C_{27}H_{41}N_2O_6$, 40), 105.0810 (C_8H_9O, 50); 175.1012 ($C_{11}H_{13}NO$, 36);72.0824 ($C_4H_{10}N$, 100)
^{1}H NMR: 5.54(CH, H-1); 5.52(CH, H-2β); 4.12(CH, H-3α); 2.65(CH, H-5β); 4.79(CH, H-6β); 2.03(CH_2, H-7β); 1.63 (CH_2, H-7); 2.15(CH , H-8α); 3.01(CH, H-11α);1.77(CH_2, H-12β); 1.99(CH_2 H-12); 1.40 (CH_2, H-15β); 1.25 (CH_2 , H-15), 1.83(CH_2 H-16β); 1.54 (CH_2 , H-16), 1.80 (CH, H-17α); 0.84 (CH_3-18); 1.80(CH_2,H-19β); 2.79(CH_2, H-19α); 2.41(CH, H-20); 0.82 (CH_3-21);1.92 (CH_3, $OCOCH_3$); 2.04(CH_3, $OCOCH_3$);7.42(CH, 2-O, Ar); 7.73(CH, 2-m, Ar); 7.49 (CH, p, Ar); 2.16(CH_3); 1.18(CH_3-30); 0.84(CH_3-32)
^{13}C NMR($CDCl_3$):

C-1	129.44	C-12	35.21	$OCOCH_3$	21.85
2	70.03	13	42.83	$OCOCH_3$	169.73
3	59.33	14	49.16	$OCOCH_3$	171.85
4	39.01	15	27.01	=C-N	167.89
5	53.51	16	32.50	2-OArC	128.69
6	77.86	17	50.41	2-m,ArC	126.82
7	35.57	18	17.52	2-m,ArC	126.82
8	41.16	19	44.52	p,ArC	131.57
9	62.09	20	61.14	CH_3	39.94
10	134.42	21	9.61	Ar 10	134.2
11	63.47	$OCOCH_3$	21.04	C-30	27.31
				C-32	17.52

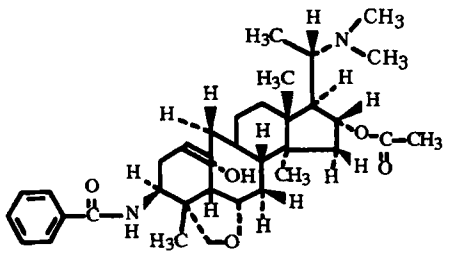


(+)-BUXABENZACINE

Buxus papilosa [14]
$C_{36}H_{54}N_2O_4$: 578.3987
$[\alpha]_D$ +48°
UV (MeOH): 224
IR($CHCl_3$): 3400(OH), 1722(OAc), 1626(C=C-CO), 1617(C=C)
Mass:578.4083(0.5); 563.3476($C_{35}H_{51}N_2O_4$, 2), 171.1170 ($C_9H_{17}NO_2$, 7), 157.1099($C_8H_{15}NO_2$, 5), 105.0337(C_7H_5O, 42); 72.0812($C_4H_{10}N$, 100)
^{1}H NMR ($CDCl_3$+CD_3OD): 0.80(3H,s, Me); 0.82(3H,s, Me);0.82 (3H, d, $J_{21,20}$=6.0, Me-21); 0.85(3H, s, Me); 1.12(3H, s, Me); 2.00(3H, s, OAc); 2.12(6H, s, N(b)-Me_2); 2.38(1H, m, H-20); 2.44 (2H, m, H-2); 2.74(2H, m, H_2-19); 2.75(3H, s, N(a)-Me); 3.84(1H, d, $J_{31\alpha,31\beta}$=9.3, H-31α), 3.99(1H, d, $J_{31\beta,31\alpha}$=9.3, H-31β); 4.73 (1H, m, H-16); 5.62(1H, H-1); 7.38-7.74(5H, m, Ar)

^{13}C NMR($CDCl_3$):

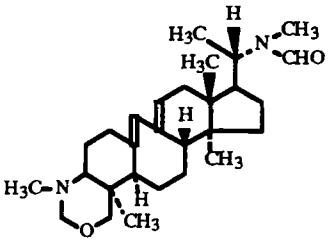
C-1	131.95	C-13	44.51	N(b)$(CH_3)_2$	39.78
2	35.58	14	49.05	N-CO	169.50
3	50.18	15	44.52	N(a)-CH_3	27.37
4	41.18	16	78.02	O<u>C</u>OCH_3	170.00
5	53.47	17	61.31	OCO<u>C</u>H_3	21.79
6	26.91	18	17.15	1′	134.48
7	30.35	19	35.13	2′	127.07
8	39.79	20	53.45	3′	128.52
9	38.72	21	9.63	4′	131.95
10	134.14	30	16.78	5′	128.52
11	32.44	31	67.78	6′	127.07
12	35.13	32	17.43		



(+)-BUXAFURANAMIDE

Buxus papilosa [14]
$C_{35}H_{48}N_2O_5$: 576.3587
$[\alpha]_D$ +190°
UV (MeOH): 228
IR($CHCl_3$): 3650(NH), 3410(OH), 1716(OAc), 1651(N-C=O), 1595(C=C), 1210(C-O)

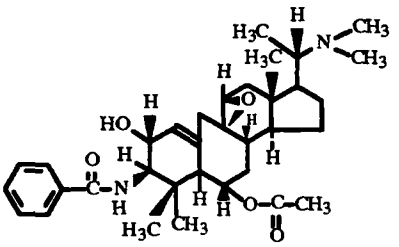
Mass: 576.4097(M^+,75); 561(85), 516(25), 171(12), 157(5), 105(40), 85(36), 72(100)
^1H NMR: ($CDCl_3$+CD_3OD): 0.74(3H, s, Me); 0.92(3H, s, Me); 1.15(3H, s, Me); 1.16(3H, d, $J_{21,20}$=6.0, 21-Me); 1.52-1.85 (2H, m, H-7α, H-7β); 1.56-1.60(2H, m, H-15α, H-15β); 1.96 (2H, m, H_2-12); 1.99(2H, m. H-5α); 1.95(3H, s, OAc); 2.05(1H, m, H-17α); 2.57(6H, NMe_2); 2.62(1H, m, H-20); 2.72(2H, s, H-19); 3.64(1H, d, $J_{21\alpha,31\beta}$=8.6, H-31α); 3.71(1H, d, $J_{31\beta,31\alpha}$=8.6, H-31β); 4.51(1H, m, H-6); 4.88 (1H, dd, $J_{3\alpha,NH}$=9.8, $J_{3\alpha,2}$=3.1, H-3α); 4.91(1H, m, H-16); 5.47 (1H, H-11); 5.86(1H, d, $J_{1,2}$=10.3, H-1); 5.88(1H, dd,$J_{2,1}$=10.3,$J_{2,3\alpha}$=3.1, H-2); 6.63(1H, d, $J_{NH,3\alpha}$=9.8, NH); 7.46-7.85(5H, m, Ar)



(+)-N-FORMYLHARAPPAMINE

Buxus papilosa [15]
$C_{28}H_{44}N_2O_2$: 440
mp: amorph.
$[\alpha]_D$ +40°($CHCl_3$)
UV (MeOH): 225, 238, 245, 254, (3.96, 4.04, 4.03, 3.90)
IR ($CHCl_3$):1653, 1624

Mass: 440(M^+, 70); 425(30), 411(10), 127(35), 86(100), 71(40), 58(90), 44(40), 28(38)
^1H NMR: ($CDCl_3$): 0.70(3H, s, Me); 1.09(3H, s, Me); 1.20(3H, s, Me); 0.83(3H, d, Me);2.20(3H, s, N(a)-CH_3); 2.74(3H, s, N(b)-CH_3); 3.60(d, J=7.6, CH_2); 4.48(d, J-7.6, CH_2); 3.25(d, J=10.8, 30-CH_2); 3.84(d, J=10.8, 30-CH_2); 5.98(s, H-19); 5.56(dd, H-11); 8.11(s, NCHO); 7.98(s, NCHO).



(-)-BUXOXYBENZAMINE

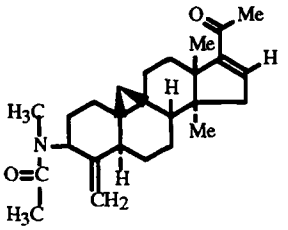
Buxus papilosa [16]
$C_{35}H_{50}N_2O_5$: 578.3729
mp: amorph.
$[\alpha]_D$ -22°($MeOH_3$)
UV (MeOH): 224
IR (KBr): 3400(NH and OH), 1730(C=O), 1640(N-C=O), 1540(C=C)
Mass: 578.3712($[M]^+$, 2); 563.3480 ($C_{34}H_{47}N_2O_5$, 4), 175.1167 ($C_{11}H_{13}NO$, 6), 119.1013(C_7H_6NO, 5); 105.0331(C_7H_5O, 10); 72.0813($C_4H_{10}N$, 100)

^{1}H NMR: ($CDCl_3$+CD_3OD): 0.78(3H, s, Me); 0.81(3H, s, Me); 0.82(3H, d, $J_{21,20}$=8.1, 21-Me); 0.83(3H, s, Me); 1.01(3H, s, Me); 1.98(3H, s, OAcMe); 1.65(1H, d, $J_{19\beta,19\alpha}$=13.88, H-19β); 1.75 (1H, m, H-12α); 1.72(1H, m, H-17); 1.99(1H, m, H-12β); 2.13(6H, s, NMe_2); 2.44(1H, dd, $J_{20,21}$=8.1, $J_{20,17}$=10.13, H-20); 2.50(1H, d, $J_{5\alpha,6\beta}$=11.0, $J_{5\alpha,3\alpha}$=9.5, H-5); 2.70(1H, d, $J_{16\alpha,19\beta}$=13.85, H-19α); 2.96(1H, d, $J_{11\alpha,12\beta}$=2.0, C-11); 3.82(1H, brs, $J_{3\alpha,2\beta}$ =8.7, C-3α); 3.98(1H, d, $J_{2\beta,3\alpha}$=8.7, C-2β); 4.70(1H, m, H-6β); 5.56(1H, brs, H-1); 6.28(1H, d, $J_{nH,3\alpha}$=9.5, NH); 7.34-7.71(5H, m, Ar).

^{13}C NMR($CDCl_3$):

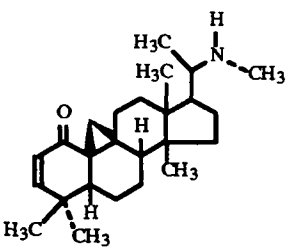
C-1	134.09	C-13	42.94	1′	134.41
2	67.48	14	38.65	2′	128.33
3	61.13	15	36.80	3′	126.95
4	38.52	16	32.41	4′	131.42
5	53.35	17	49.91	5′	126.95
6	77.89	18	16.63	6′	128.33
7	35.54	19	44.41	N-$(CH_3)_2$	39.56
8	41.07	20	61.51	O-C-$\underline{C}H_3$	21.61
9	62.48	21	9.70	6-CH_3-CO-Ar	169.76
10	131.78	30	17.29	3-NH-CO-Ar	169.76
11	63.36	31	27.22		
12	35.11	32	17.01		

(+)-N-ACETYL-N-DEMETHYLCYCLOMICROBUXEINE



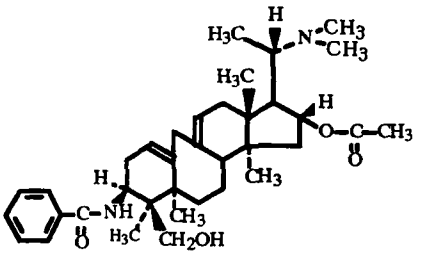
Buxus papilosa [17]
$C_{26}H_{37}NO_2$: 395.2910
mp: amorph.
$[\alpha]_D$ +36°($CHCl_3$)
UV: 237,245
IR :1645, 1595
Mass: 395(M^+,18); 380(12), 322(40), 74(100), 57(90)

^{1}H NMR: 0.11, 0.14(1H, d, J=4.2, H-19α); 0.38, 0.41(1H, d, J=4.2, H-19β); 0.99(3H, s, Me); 1.19(3H, s); 2.05, 2.14(3H, s, N-C-Me); 2.26(3H, s, C-Me); 2.88, 2.91 (3H, s, N-Me); 4.37, 4.58(1H, s, =C-H); 4.43, 4.70(1H, s, =C-H); 6.65(1H, dd, J_1=3.4, J_2=2.1, H-16).



CYCLOBUXOVIRAMINE

Buxus papilosa [18]

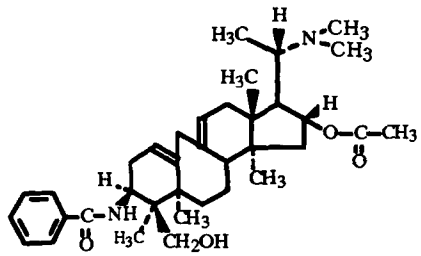


(-)-O-ACETYL-N-BENZOYLBUXIDIENINE

Buxus sempervirens [19]
$C_{34}H_{50}N_2O_4$: 562.3738
mp: amorph.
$[\alpha]_D$ -5°($CHCl_3$)
UV(MeOH): 232, 245, 255
IR ($CHCl_3$):3400(OH), 3350(NH), 1720(C=O), 1660(N-C=O), 1610(C=C)

Mass: 562.3736(M^+, 50); 547.3531[(M-Me)$^+$, 25]; 503.3610[(M-OAc)$^+$, 20]; 105.0340 (C_7H_5O, 30); 72.0812($C_4H_{10}N$, 100)
^{1}H NMR($CDCl_3$): 0.75(3H, s, Me-32); 0.91(3H, s, Me-18); 1.24(3H, s, Me-30); 0.93(3H, d, $J_{20,21}$=6.5, Me-21); 2.09(3H, s, OAc); 2.26(6H, s, NMe_2); 3.82 (1H, d, $J_{31\alpha,31\beta}$=11.2, H-31α); 4.00(1H, d, $J_{31\alpha,31\beta}$=11.2, H-31β); 4.11(1H, m, H-3α); 4.47(1H, m, H-16β); 5.53(1H, m, H-11); 5.74(1H, d, $J_{3\alpha NH}$=9.6NH); 6.01(1H, s, H-19); 7.37-7.72(5H, m, Ar)
^{13}C NMR($CDCl_3$):

C-1	38.01	C-13	39.76	N-$(CH_3)_2$	45.34
2	29.77	14	47.29	CH_3COO	40.15
3	49.34	15	43.07	CH_3COO	170.25
4	43.50	16	75.68	CONH	167.11
5	50.68	17	70.56	1′	138.24
6	25.34	18	11.63	2′	128.59
7	29.53	19	126.78	3′	128.79
8	55.80	20	60.50	4′	131.34
9	135.50	21	18.05	5′	130.43
10	138.25	30	21.02	6′	128.59
11	126.78	31	65.03		
12	30.22	32	16.64		



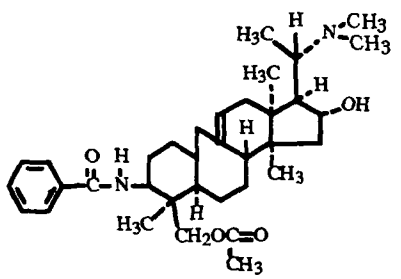
(+)-NOR-16α-ACETOXYBUXABENZAMIDIENINE

Buxus sempervirens [19]
$C_{34}H_{48}N_2O_3$: 532.3664
mp: amorph.
$[\alpha]_D$ +17.5°($CHCl_3$)
UV(MeOH): 230, 245, 254
IR ($CHCl_3$): 3350(NH), 1725(C=O), 1660(N-C=O), 1605(C=C)

Mass: 532.3665(M^+, 10); 501.3243[(M-$MeNH_2$)$^+$, 10]; 105.0340 (C_7H_5O, 45); 72.1311($C_4H_{10}N$, 100); 58.0579 (C_3H_8N, 50)
^{1}H NMR($CDCl_3$): 0.67(3H, s, Me-32); 0.75(3H, s, Me-31) 0.86(3H, s, Me-18); 0.99(3H, s, Me-30); 1.26(3H, d, $J_{21,20}$=6.5 Me-21); 1.76(3H, s, OAc); 2.43(3H, s, NMe); 4.36(1H, m, H-3α); 5.08(1H, m, H-16β); 5.57(1H, m, H-11); 5.93(1H, s, H-19); 6.34(1H, d, $J_{3\alpha,NH}$=8.52, NH); 7.40-7.70(5H, m, Ar)

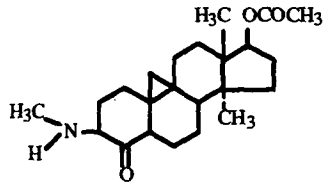
^{13}C NMR($CDCl_3$):

C-1	37.58	C-13	37.68	$NHCH_3$	45.40
2	29.73	14	47.72	CH_3COO	46.80
3	50.97	15	39.99	CH_3COO	170.30
4	40.50	16	79.53	CONH	167.14
5	51.44	17	68.32	1′	143.91
6	25.61	18	11.64	2′	127.95
7	29.20	19	126.83	3′	128.63
8	55.86	20	62.58	4′	131.33
9	135.20	21	24.08	5′	130.74
10	138.33	30	21.01	6′	128.55
11	126.70	31	17.70		
12	30.10	32	16.57		



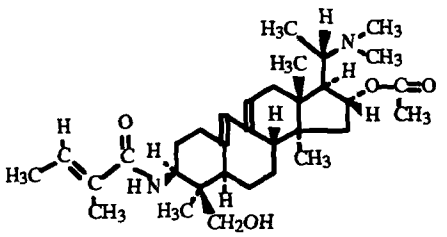
(+)31-ACETYLBUXANOLDINE

Buxus sempervirens [20]



(+)-CYCLOMICROBUXAMINE

Buxus sempervirens [20]

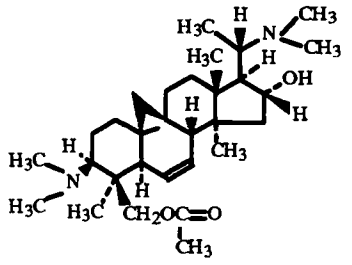


(+)-SEMPERVIRINE

Buxus sempervirens [21]
$C_{33}H_{52}N_2O_4$: 540.3927
mp: amorph.
$[\alpha]_D^{20}$ +2°($CHCl_3$)
UV(MeOH): 242
IR ($CHCl_3$): 3350(OH), 1720(C=O), 1660(C=O), 1600(C=C)
Mass: 540.3937(M^+, 50%); 525.3738[$(M\text{-}Me)^+$, 38]; 481.3791[$[Me\text{-}MeCO_2]^+$, 20); 171.1155 ($C_9H_{17}NO_2$, 35); 157.1005 ($C_8H_{15}NO_2$, 25); 72.0812($C_4H_{10}N$, 100)
^1H NMR($CDCl_3$): 0.68(3H, s, Me); 0.75(3H, s, Me); 0.91(3H, s, Me); 1.03(3H, d, J=6.5, Me-21); 1.71(3H, d, J=6.8, Me-4"); 1.79(3H, s, 2"-Me); 1.80(3H, s, Me-CO); 2.68(6H, s, NMe_2); 3.72(1H, d, J_{AB}=11.5, H-31α); 3.89(1H, d, J_{AB}=11.6, H-31β); 4.29(1H, m, H-16); 4.35(1H, m, H-3); 5.35(1H, d, J=9.2, NH); 5.51 (1H, s, H-11); 5.98(1H, s, H-19); 6.29(1, dd, J=6.9, H-3").

^{13}C NMR($CDCl_3$):

C-1	38.11	C-12	30.15	C-31	65.22
2	29.71	13	39.75	32	16.66
3	49.27	14	44.05	$NaCH_3$	29.27
4	44.00	15	44.04	CH_3COO	25.31
5	50.02	16	64.75	CH_3COO	171.36
6	25.28	17	68.50	1″	169.10
7	29.49	18	11.52	2″	132.66
8	55.87	19	129.93	2″-CH_3	45.00
9	134.93	20	62.00	3″	128.36
10	138.32	21	17.90	4″	45.21
11	130.19	30	21.02		

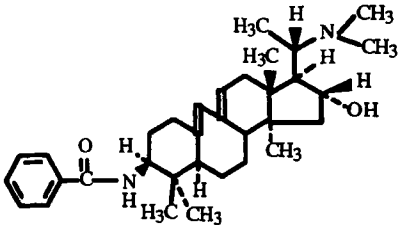


(-)-31-ACETYLCYCLOMICROPHYLLINE A

Buxus sempervirens [21]
$C_{30}H_{50}N_2O_3$: 486.3822
mp: amorph.
$[\alpha]_D^{20}$ -40°($CHCl_3$)
IR($CHCl_3$): 3350(OH), 1715(C=O), 1660(N-C=O), 1600(C=C)
Mass: 486.3821(20), 443.3637([M-Ac]$^+$, 50); 371.2029($C_{24}H_{37}NO$, 52); 72.0812($C_4H_{10}N$, 100)

^{1}H NMR ($CDCl_3$): 0.18(1H, d, $J_{19\alpha,\,19\beta}$=4.2, H-19α); 0.78(1H, $J_{19\alpha,19\beta}$=4.2, H-19β); 0.90(3H, s, Me); 0.91(3H, s, Me); 1.08(3H, s, Me); 0.96(3H, d, $J_{20,21}$=6.5, Me-21); 1.97(3H, s, Ac); 2.31(12H, 2NMe_2); 3.52(1H, d, $J_{31\alpha,\,31\beta}$=10.4, H-31α); 3.82(1H, d, $J_{31\beta,\,31\alpha}$=10.4, H-31β); 4.14(1H, m, H-16β); 5.51(2H, m, H-6, H-7)
^{13}C NMR($CDCl_3$):

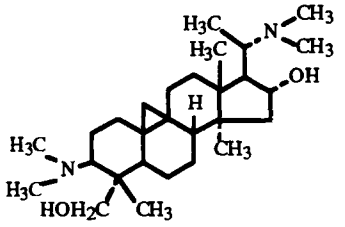
C-1	31.91	C-11	24.74	C-21	10.29
2	18.46	12	30.83	30	12.10
3	73.32	13	45.35	31	73.60
4	42.24	14	49.64	32	15.42
5	47.95	15	41.85	N(a)$(CH_3)_2$	45.11
6	129.39	16	78.21	N(a)$(CH_3)_2$	43.10
7	125.70	17	62.89	CH_3COO	18.28
8	44.10	18	15.43	CH_3COO	177.16
9	20.63	19	18.46		
10	27.87	20	56.68		



(-)-BENZOYLBUXIDIENINE

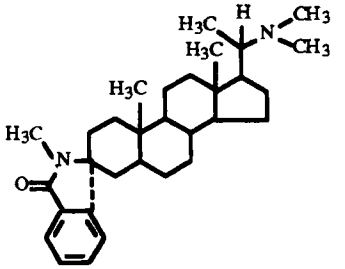
Buxus sempervirens [21]
$C_{33}H_{48}N_2O_2$: 504.3715
mp: amorph.
$[\alpha]_D^{20}$ -7°($CHCl_3$)
UV(MeOH): 242
IR($CHCl_3$): 3680(NH), 3350(OH), 1652(C=O), 1600(C=C)

Mass: 504.3715([M]$^+$, 50), 489.3481([M-Me]$^+$, 40); 105.0339(C_7H_5O, 60); 71.0812($C_4H_{10}N$, 100)
^{1}H NMR ($CDCl_3$): 0.76(3H, s, Me); 0.78(3H, s, Me); 0.93(3H, s, Me); 1.00(3H, s, Me); 1.05(3H, d, J=6.4, Me-21); 2.49(6H, NMe_2); 4.10(1H, m, H-16β); 4.36(1H, m, H-3α); 5.50(1H, s, H-11); 5.88(1H, d, J=9.46, NH); 5.95(1H, s, H-19); 7.45-7.71(5H, m, Ar)



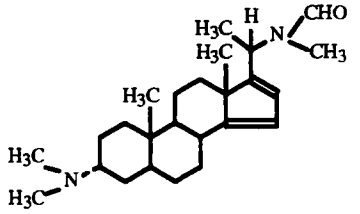
ISODIHYDROCYCLOMICROPHYLLINE A

Buxus sempervirens [22]
$C_{28}H_{50}N_2O_2$: 406
mp: 215-217°(ethanol)
$[\alpha]_D$ -64.27°($CHCl_3$)
IR: 3368, 3047, 1452
Mass: 446(M^+), 424, 383, 342, 98, 84, 72, (100%), 71, 70, 58
^{1}H NMR: 0.92(s, CH_3); 1.06(s, CH_3); 1.15(s, CH_3); 2.18(s, NMe_2); 2.32(s, NMe_2); 0.97(3H, d, J=7.52, CH_3); 4.09(1H, m, -CH-OH); 3.02(2H, q, -CH_2-OH); 3.52(2H, q, -CH_2-OH)



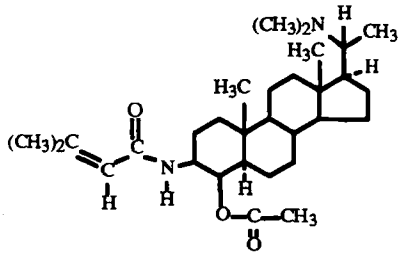
ISOSPIROPACHYSINE

Pachysandra axillaris [23]



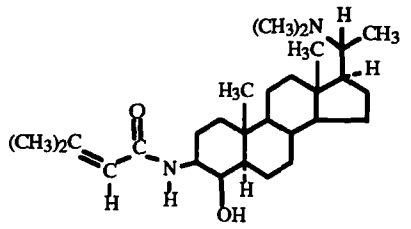
SARCORUCININE A

Sarcococca ruscifolia [24]



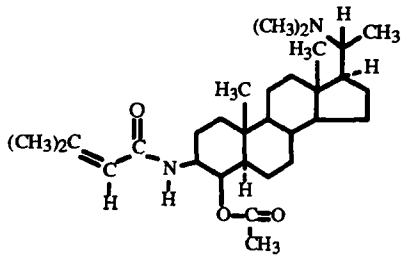
VAGANINE A

Sarcococca vagans [25]



VAGANINE B

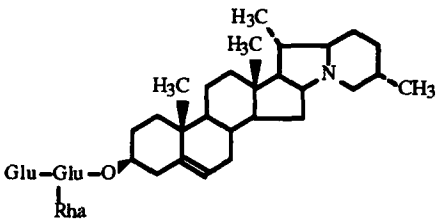
Sarcococca vagans [25]



VAGANINE C

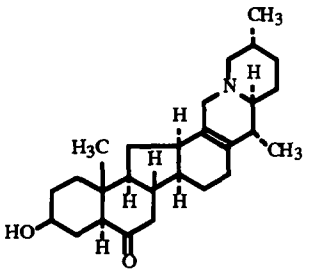
Sarcococca vagans [25]

Fam. *Liliaceae*



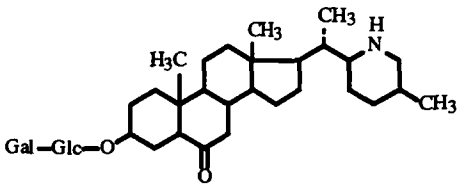
SOLANIDINE 3-O-{[α-*L*-RHAMNOPYRANOSYL(1→2)][β-*D*-GLUCOPYRANOSYL(1→4)]-β-*D*-GLUCOPYRANOSIDE}

Fritillaria camtschatcensis [26]
$C_{45}H_{43}NO_5$: 867
mp: >250°(decomp.), (MeOH)
Mass: 867(M^+)



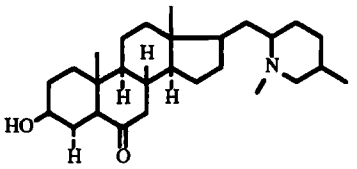
EBEIENONE

Fritillaria camtschatcensis [27]



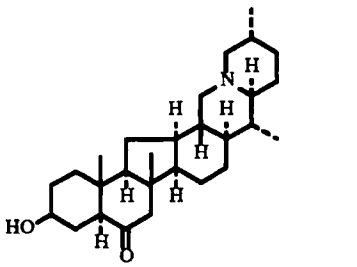
YIBEINOSIDE C

Fritillaria pallidiflora [28]



PUQIETINONE

Fritillaria puqiensis [29]
$C_{28}H_{47}NO_2$: 429.3609
mp: 240-245°(ac.)
$[\alpha]_D$ +29.4°($CHCl_3$)
XSA

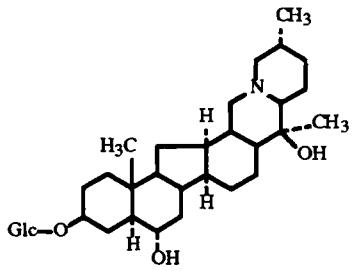


PUQIEDINONE

Fritillaria puqiensis [30]
$C_{27}H_{43}NO_2$: 413.3281
mp: 205-208°(ac.)
$[\alpha]_D$ -62.3°($CHCl_3$)
IR: 3525, 3280, 2750, 1690
Mass: 413(M^+, 36), 398(8), 112(35), 111(100), 98(9)

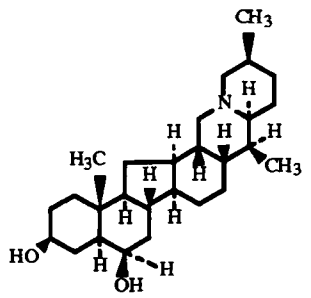
^{1}H NMR: 0.63(1H, m, H-17αa); 0.73(3H, s, Me-10); 0.84(3H, d, J=9.2; Me-20); 0.86(3H, d, J=9.2; Me-25); 2.15(1H, dd, J=2.4; 10.0; H-5αa); 2.49(1H, dd, J=4.0; 10.0; H-7βe); 2.76(2H, m, H_2-26); 2.78(2H, m, H_2-18); 3.57(1H, m, $W_{1/2}$=21, H-3αa)
^{13}C NMR:

C-1	36.9	C-10	38.4	C-19	12.8
2	30.4	11	30.1	20	44.8
3	70.9	12	41.2	21	14.8
4	30.2	13	40.9	22	68.3
5	56.7	14	44.3	23	33.4
6	211.3	15	25.3	24	28.8
7	46.0	16	24.5	25	30.7
8	40.1	17	46.4	26	61.2
9	56.7	18	64.6	27	19.6



ZHEBEININOSIDE

Fritillaria thunbergii [31]

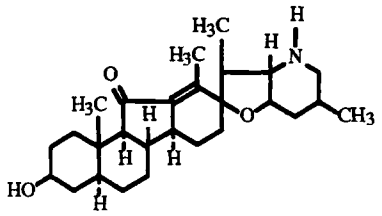


TORTIFOLINE

Fritillaria thunbergii [32]
$C_{27}H_{45}NO_2$: 415.344981
mp: 206-208°(MeOH)
$[\alpha]_D$ -41.4°($CHCl_3$)
IR($CHCl_3$): 3400(OH), 2720(trans-quinolizidine)

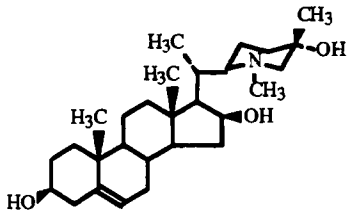
Mass: 415(M^+), 400(M^+, CH_3), 358, 164, 111, 98
^{1}H NMR ($CDCl_3$): 0.80(3H, d, J=5.1, 21-H); 0.82(3H, d, J=6.2, 27-H); 0.98(3H, s, 19-H); 3.66 (1H, m, $W_{1/2}$=22, 3α-H); 3.87(1H, m, $W_{1/2}$=8, 6α-H)
^{13}C NMR($CDCl_3$):

C-1	39.0	C-10	35.4	C-19	15.1
2	31.4	11	30.1	20	37.2
3	72.0	12	39.5	21	14.9
4	34.9	13	34.7	22	68.8
5	48.2	14	40.6	23	30.9
6	73.0	15	26.2	24	33.6
7	39.3	16	21.4	25	30.7
8	36.6	17	44.3	26	59.3
9	57.6	18	65.4	27	19.8



SONGBEISINE

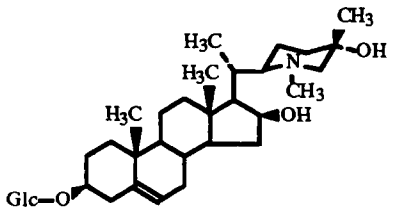
Fritillaria unibracteata [33]



PINGBEININE

Fritillaria ussuriensis [34]
$C_{28}H_{47}NO_3$: 445
mp: 223-235°(MeOH)
$[\alpha]_D$ -32.8°(MeOH)
IR(KBr): 3348, 2960, 2855, 2790, 1456, 1380, 1189, 1130, 1052, 950, 932, 920
Mass: 444.3444(M-1)$^+$, 128.1064($C_7H_{14}NO$)
^{1}H NMR ($CDCl_3$+CD_3OD): 0.95(3H, s, H-18); 1.03(3H, s, H-19); 1.10(3H, s, H-19); 1.10(3H, d, J=7.3, H-21); 1.31(3H, s, H-27); 1.72(1H, m, H_{ax}-23); 1.78(1H, m, H_{eq}-26); 2.05(1H, d, J=11.0, H_{ax}-26); 2.35(3H, s, NMe); 2.48(1H, m, H-20); 2.73(1H, d, J=11.0, H_{eq}-26); 3.45(1H, m, H-3); 4.50(1H, m, $W_{1/2}$=17.7, H-16); 5.34(1H, m, H-6)
^{13}C NMR:

C-1	37.7	C-10	36.9	C-19	19.6
2	31.5	11	21.4	20	30.3
3	71.6	12	41.0	21	21.3
4	42.2	13	43.4	22	73.0
5	141.4	14	54.5	23	23.7
6	121.6	15	35.7	24	38.0
7	32.2	16	72.4	25	68.5
8	32.0	17	60.6	26	68.5
9	50.5	18	13.7	27	25.0
				NCH_3	44.6

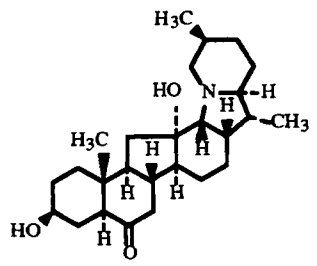


PINGBEININOSINE

Fritillaria ussuriensis [34]
$C_{34}H_{57}NO_8$: 609.445
mp: 224-246°(MeOH)
$[\alpha]_D$ -4.57°(MeOH)
IR(KBr): 3357, 2930, 1635, 1450, 1347, 1063, 930, 890

Mass: 609.445(M^+),430, 427, 172, 170, 170, 163, 156, 128, 127, 112, 110, 85, 84, 73, 70, 57
^{1}H NMR (C_5D_5N): 0.93(3H, s, H-18); 1.08(3H, s, H-19); 1.09(3H, d, J=6.4, H-21); 1.30(3H, s, H-27); 2.63(3H, s, NMe); 5.08(1H, d, J=7.5, H-1′); 5.56(1H, m, H-6)
^{13}C NMR ($CDCl_3$+CD_3OD):

C-1	37.7	C-13	43.5	C-25	68.4
2	29.1	14	54.6	26	68.5
3	78.0	15	35.8	27	24.9
4	38.1	16	72.4	NCH_3	44.6
5	141.4	17	60.7	1′	102.5
6	121.6	18	13.7	2′	75.2
7	32.3	19	19.6	3′	78.2
8	32.1	20	30.2	4′	71.6
9	50.5	21	21.3	5′	78.4
10	36.9	22	73.0	6′	62.7
11	21.4	23	23.7		
12	41.0	24	38.1		

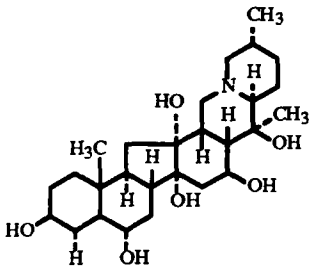


PINGBEINONE

Fritillaria ussuriensis [35]
$C_{26}H_{41}NO_3$:415.3076
mp: 200-202°
$[\alpha]_D$-22° ($CHCl_3$)
IR($CHCl_3$): 3500(OH), 2800(trans-quinolizidine), 1730(CO)
^{1}H NMR ($CDCl_3$): 0.70(3H, s, H-19); 0.86(3H, d, J=7.0, H-21); 0.92(3H, d, J=6.8, H-27); 3.60(1H, m, $W_{1/2}$=23, H-3α)

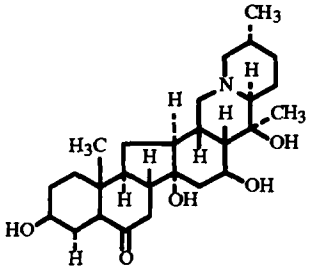
^{13}C NMR ($CDCl_3$):

C-1	37.2	C-10	38.3	C-19	12.6
2	30.4	11	44.5	20	36.1
3	70.3	12	77.5	21	13.5
4	30.3	13	73.1	22	63.5
5	56.4	14	52.3	23	23.8
6	211.2	15	26.9	24	28.4
7	46.4	16	21.4	25	30.6
8	47.9	17	42.0	26	58.4
9	52.5	18	16.0	27	20.0



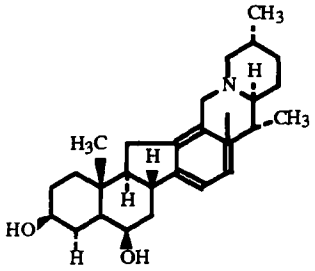
PINGBEIMINE B

Fritillaria ussuriensis [36]



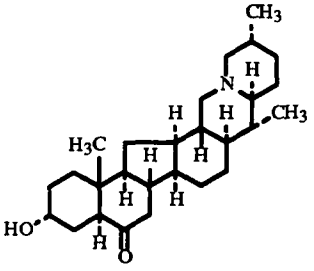
PINGBEIMINE C

Fritillaria ussuriensis [37]



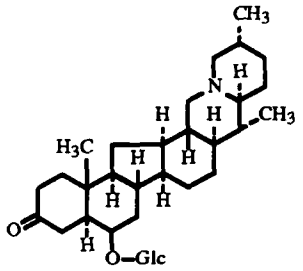
HEILONINE

Fritillaria ussuriensis [38]
$C_{27}H_{39}NO_2$: 409.2984
mp: 284-286° (MeOH)
UV(MeOH): 280(490), 271(520)
Mass: 409(M^+), 394, 312, 294, 170



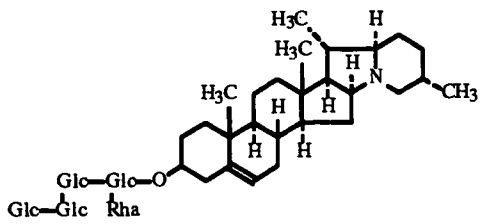
YUBEININE

Fritillaria yuminensis [39]



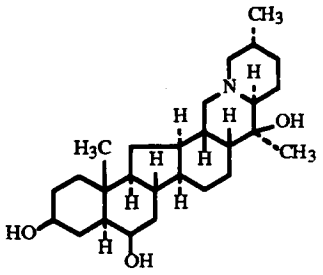
YUBEISIDE

Fritillaria yuminensis [39]



NEOHYACYNTHOSIDE

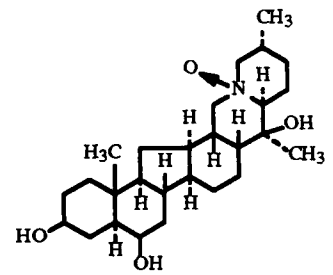
Notholiron hyacinthinum [40]



PETINE

Petilium eduardi [41]
$C_{27}H_{45}NO_3$
mp: 145-147°(hex. -ac.)
IR: 3445, 2940-2860, 2780
Mass: 413$(M)^+$,432, 429, 388, 380, 364, 358, 236, 180, 164, 162, 156, 155, 154, 150, 140, 125, 124, 113, 112(100), 98

PMR: 0.77(3H, d, J=7, CH_3-27); 0.94(3H, s, CH_3-19); 1.01(3H, s, CH_3-21); 3.56(1H, m, $W_{1/2}$=24, H-3); 3.76(1H, m, $W_{1/2}$=8, H-6)

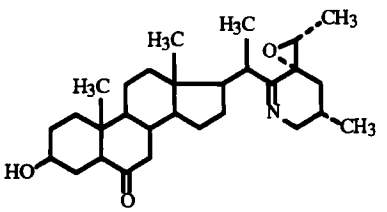


PETINE N-OXIDE

Petilium eduardi [41]

$C_{27}H_{45}NO_4$
mp: 240-243°(ac.)
IR: 3410, 2950-2860,1460, 970, 937, 930
Mass: 447(M^+), 431, 429, 413, 415, 388, 386, 374, 358, 236, 180, 164, 162, 156, 155, 154, 150, 140, 125, 124, 113, 112(100), 98

PMR: 0.85(3H, d, J=7, CH_3-27); 0.93(3H, s, CH_3-19); 1.01(3H, s, CH_3-21); 3.60(1H, m, $W_{1/2}$=24, H-3); 3.80(1H, m, $W_{1/2}$=8, H-6)

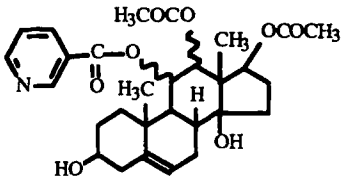


RADPETINE

Petilium raddeana [42]
$C_{29}H_{45}NO_3$: 455
mp: 229-231°
IR: 3380, 1712, 1645
Mass: 455(M^+), 440, 437, 424, 412, 398, 384, 206, 192, 178, 167(100), 152, 112

PMR: 0.65(3H, s, 18-CH_3); 0.71(3H, s, 19-CH_3); 0.95(3H, d, J=6, 27-CH_3); 1.01(3H, d, J=6, 21-CH_3); 1.29(3H, d, J=6, CH_3-CH-O-); 3.52(1H, m, H-C-OH)

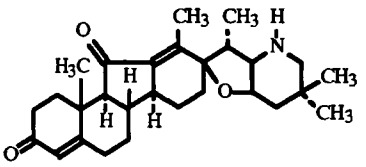
Fam. *Malvaceae*



TINCTORAMINE

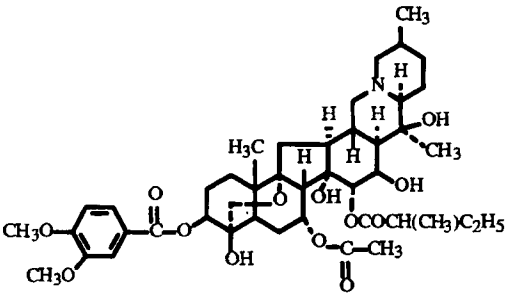
Marsdenia tinctoria [43, 44]

Fam. *Malanthiaceae*



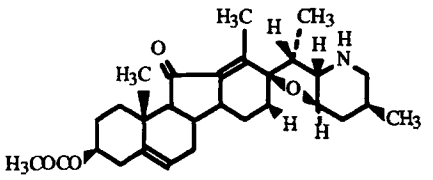
(+)-JERVINONE

Veratrum album [45]



(+)-VERABENZOAMINE

Veratrum album [45]



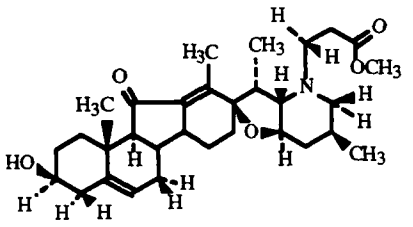
O-ACETYLJERVINE

Veratrum album [46]
$C_{29}H_{41}NO_4$:467.3035
mp: 240°
$[\alpha]_D$-120° (MeOH)
UV(MeOH): 250

IR: 3687(NH), 1716(CO), 1635(C=C)
Mass: 467.3085(M^+, 17), 438(10), 407(12), 125(50), 110(100)
^{1}H NMR ($CDCl_3$): 0.95(3H, d, J=6.6, Me-27); 0.99(3H, d, J=7.5, Me-21); 1.02(3H, s, Me-19); 2.17(3H, d, J=2.2, Me-18); 2.56(1H, m, H-20); 2.78(1H, m, H-22); 3.37(1H, m, H-23); 4.59(1H, m, H-3); 5.39(1H, m, H-6)

^{13}C NMR ($CDCl_3$):

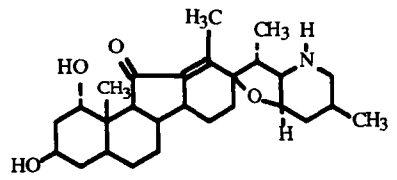
C-1	37.38	C-11	206.70	C-21	11.15
2	29.71	12	132.50	22	65.99
3	73.72	13	144.20	23	75.42
4	37.10	14	72.80	24	39.00
5	141.30	15	24.33	25	30.43
6	121.94	16	30.24	26	53.88
7	36.60	17	85.85	27	18.67
8	39.85	18	12.25	$COCH_3$	21.40
9	62.47	19	18.40	CO	170.56
10	38.52	20	37.89		



METHYL 3-(JERVIN-N-YL)PROPANOATE

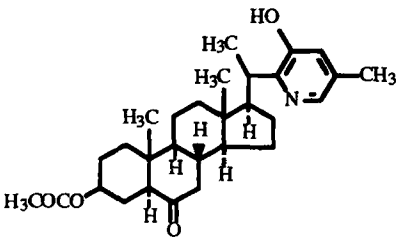
Veratrum album [46]
$C_{31}H_{45}NO_5$: 511.3297
mp: 234°
$[\alpha]_D$-76° (MeOH)
UV(MeOH): 250
IR: 3500(NH), 1730(CO), 1620(C=C)
Mass: 511.3282(M^+, 7), 438(2), 313(2), 198(100), 126(20)
^1H NMR ($CDCl_3$): 0.95(3H, d, J=6.6, Me-27); 1.00(3H, d, J=7.5, Me-21); 1.08(3H, s, Me-19); 2.19(3H, d, J=2.2, Me-18); 2.48(1H, m, H-20); 2.98(1H, m, H-22); 3.32(2H, m, CH_2-4); 3.45 (1H, m, H-3); 3.52 (1H, m, H-23); 3.67 (3H, s, MeO); 5.37(1H, m, H-6)
^{13}C NMR ($CDCl_3$):

C-1	36.86	C-12	137.03	C-23	74.82
2	30.75	13	142.31	24	41.49
3	71.96	14	29.35	25	38.02
4	37.88	15	24.36	26	51.12
5	146.57	16	32.05	27	19.14
6	120.96	17	84.96	1′	61.40
7	31.24	18	12.27	2′	31.72
8	44.82	19	18.53	3′	172.69
9	62.67	20	40.66	4′	51.63
10	37.09	21	10.50		
11	206.08	22	71.73		



1-HYDROXY-5,6-DIHYDROJERVINE

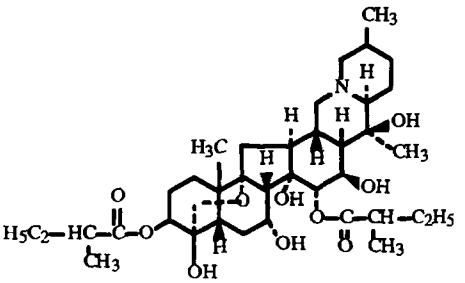
Veratrum album [47]



VERDININE

Veratrum lobelianum [48]
$C_{29}H_{41}NO_4$: 467
mp: 256-267°(ac.)
IR: 3515, 3045, 2970, 2865, 1740-1715, 1610, 1585, 1265, 750
Mass: 467(M^+, 25), 452(4), 451(8), 450(17), 425(8), 424(21), 407(42), 393(21), 392(63), 271(12), 175(17), 174(24), 160(24), 136(63), 137(100), 123(24), 119(8), 111(8), 110(8), 97(12).

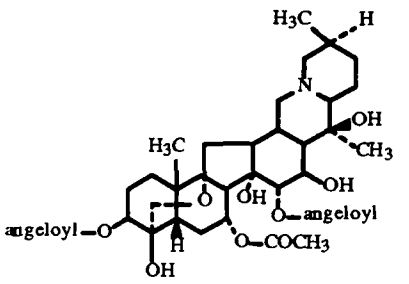
PMR(chlf-met): 0.66(s, 18-CH_3); 0.80(s, 19-CH_3); 1.11(d, J=7, 21-CH_3); 2.00(3H, s, Ac); 2.20(s, Ar-CH_3); 6.94(2H, s, H-Ac).



3,15-DI-O-(2-METHYLBUTYROYL)GERMINE

Veratrum lobelianum [48]
$C_{37}H_{59}NO_{10}$: 677.41358
mp: 214-216°(bz)
$[\alpha]_D$-25.15°(Py)
IR: 3490-3290, 2960-2900, 2830-2790, 1735, 1190
Mass: 677(M^+, 2), 593(37), 576(9), 575(8), 558(3), 557(3), 550(4), 548(2), 535(5), 509(2), 492(7), 491(6), 473(8), 471(4), 456(3), 454(2), 448(2), 182(2), 180(2), 164(2), 162(2), 154(4), 150(2), 138(3), 136(2), 125(2), 112(100), 111(37), 98(29)

PMR: 0.84(6H, t, J=7, 4′-CH_3, 4″-CH_3); 0.88(3H, s, 19-CH_3); 1.01(3H, d, J=7, 27-CH_3); 1.07(6H, d, J=7, 5′-CH_3, 5″-CH_3); 1.13(3H, s, 21-CH_3); 3.70-4.60(OH, gem H-OH); 5.03(1H, $W_{1/2}$=8, H-3); 5.27(1H, d, J=3, H-15); 6.26(1H, s, 4-OH)



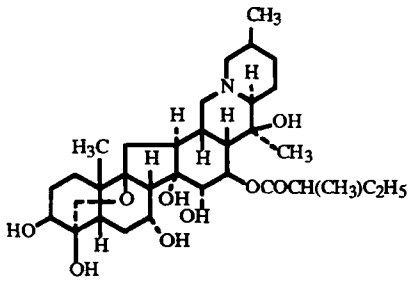
MAACKININE

Veratrum maackii [49]
$C_{39}H_{59}NO_{11}$: 717.4073
mp: 218-221°
$[\alpha]_D$+3.85 ($CHCl_3$)
UV: 218(4.18)
IR: 3520, 2870, 2820, 2790, 2780, 1750, 1715, 1235, 1165
Mass: 717.4087(M^+), 716(M^+-1, 13), 576(9), 601(49), 569(37), 463(35), 353(9), 297(17), 112(100)

^1H NMR: 1.72(m, 1-Hα); 1.62(td. 13.5, 6.0, 1-Hβ); 2.17(7dd, 14, 6.5, 4, 2-Hα); 1.72(m, 2-Hβ); 5.09(brd, 4, 3-Hα); 2.28(brs, 6-Hβ, 5-Hβ); 2.30(dd, 17, 5.5, 6-Hα); 2.04(dd, 17, 4, 6-Hβ); 5.83(brt, 5.5, 7-Hβ); 2.93(d, 5.5, 8-Hβ); 1.66(d, 15, 2, 11-Hα); 2.32(dd, 15, 8.5, 11-Hβ); 1.79(ddd, 11.5, 8.5, 2, 12-Hα); 1.56(qd, 11.5, 4, 13-Hβ); 5.28(d, 3.5, 15-Hβ); 4.31(dd, 3.5, 2, 16-Hα); 1.30(dd, 12, 2, 17-Hα); 1.71(t, 11.5, 4, 18-Hα); 2.72(dd, 11.5, 4, 18-Hβ); 1.72(m, 22-Hα); 1.49(m, 23-H_2); 1.50(m, 23-H_2); 1.50(m, 24-H_2); 1.62(m, 24-H_2); 1.62(m, 24-H_2); 1.90(m, 25-Hα); 2.28(dd, 11.5, 4, 26-Hα); 2.66(dt, 11.5, 26-Hβ); 1.01(s, 19-H_3); 1.19(s, 21-H_3); 1.08(d, 7, 27-H_3); 3.94(s, 4-OH); 3.82(s, 14-OH); 4.20(s, 16-OH); 3.28(s, 20-OH); 6.07(qq, 7, 1.5, 3′-H); 1.99(dq, 7, 1.5, 4′-H_3); 1.90(quintet, 1.5, 5″-H_3); 2.13(s, 7-Ac); 5.97(qq, 7, 1.5, 3″-H); 1.93(dq, 7, 1.5, 4″-H_3); 1.87(quintet, 1.5, 5″-H_3)

^{13}C NMR ($CDCl_3$):

C-1	32.7	C-14	80.0	C-27	17.1
2	26.5	15	69.7	1′	167.2
3	74.2	16	69.4	2′	127.9
4	105.0	17	45.8	3′	138.2
5	46.2	18	61.6	4′	15.7
6	27.8	19	19.4	5′	20.7
7	67.9	20	72.9	$\underline{C}OCH_3$	169.4
8	47.9	21	19.9	$CO\underline{C}H_3$	21.6
9	92.5	22	69.8	1″	166.8
10	45.8	23	18.4	2″	128.4
11	32.9	24	29.0	3″	136.3
12	46.8	25	27.4	4″	15.9
13	33.3	26	61.4	5″	20.7

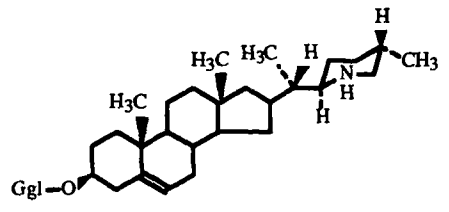


VERUSSURININE

Veratrum nigrum [50]
$C_{32}H_{51}NO_9$: 593.3563
mp: amorph.
$[\alpha]_D$ 28.40°(Py)
IR: 3230, 2880, 2820, 2760, 1740,
Mass: 593(M^+, 100), 575(M^+-H_2O), 550(15), 492(32), 474(15), 331(8), 154(17), 112(100), 98(61)
NMR (Py-d_5) 1.90(m, 1-H); 1.62(dd. 13, 6.5, 1-H); 2.39(m, 2-H); 1.90(m, 2-H); 4.47(br. d, 4, 3-H); 2.87(t, 3, 5-H); 2.44(dd, 15, 3, 6-H); 2.22(ddd, 15, 5.3, 6-H); 4.67(br. t, 5, 7-H); 2.67(d, 5, 8-H); 2.59(dd, 15, 9, 11-H); 1.84(t, 15, 11-H); 2.16(m, 12-H); 1.92(m, 13-H); 4.34(d, 3.5, 15-H); 6.27(ud, 3.5, 16-H); 1.92(m, 17-H); 3.04(dd, 11, 3, 18-H); 1.70(t, 11, 18-H); 1.55(dd, 11, 3, 22-H); 1.82(m, 23-H); 1.43(m, 23-H, 24-H); 1.76(s, 25-H); 2.74(d, 11, 26-H); 2.18(dd, 11.3, 26-H); 0.77(s, 19-H_3); 1.33(s, 21-H_3); 1.01(d, 7, 27-H_3); 6.71(us, 4-OH); 5.97(us, 15-OH); 3.92(s, 20-OH); 2.42(sextet, 7, 2′-H(H_3); 1.81(dkd, 14, 7, 7, 3′-H); 1.44(dkd, 14, 7, 7, 3′-H); 0.88(t, 7, 4′-H_3); 1.30(d, 7, 5′-H_3)

^{13}C NMR (Py-d_5) :

C-1	33.0(t)	C-12	47.6(d)	C-23	19.0(t)
2	30.2(t)	13	34.7(d)	24	29.6(t)
3	73.2(d)	14	82.5(s)	25	28.0(d)
4	107.4(s)	15	70.2(d)	26	61.9(t)
5	45.5(d)	16	70.7(d)	27	17.4(k)
6	30.3(t)	17	44.7(d)	1′	175.3(s)
7	67.8(d)	18	63.1(t)	2′	42.1(d)
8	48.0(d)	19	19.2(k)	3′	26.9(t)
9	93.0(s)	20	73.2(s)	4′	12.0(k)
10	47.0(s)	21	21.3(k)	5′	16.7(k)
11	34.3(m)	22	71.2(d)		

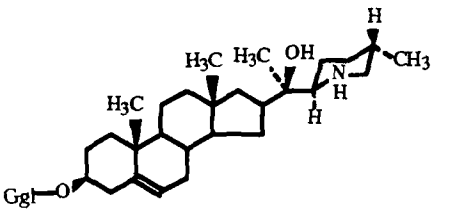


VERAMILINE 3-O-β-*D*-GLUCOPYRANOSIDE

Veratrum taliense [51]
$C_{33}H_{55}NO_6$: 516
mp: 303-305°
$[\alpha]_D$ -41.9°(MeOH)
IR(KBr): 3462, 1562, 1371, 1070, 1057, 1014
Mass:561(M^+, 1.1), 382(21), 126(0.3), 125(0.5), 112(20), 111(14), 99(64), 98(100), 96(12)

^{1}H NMR ($CDCl_3$+CD_3OD): 0.76(3H, s, 18-Me); 1.03(3H, s, 19-Me); 1.00(3H, d, J=6, 21-Me); 1.06(3H, d, J=7, 27-Me); 3.60(1H, m, $W_{1/2}$=22, 3α-H); 5.38(1H, m, 6-H)
^{13}C NMR (C_5D_5N):

C-1	37.7	C-12	39.3	C-23	27.0
2	29.1	13	43.2	24	30.9
3	78.5	14	56.3	25	36.8
4	38.2	15	23.7	26	51.0
5	140.0	16	28.4	27	20.6
6	121.1	17	51.9	1′	101.0
7	31.5	18	17.8	2′	75.6
8	31.8	19	18.7	3′	76.1
9	49.6	20	42.2	4′	73.2
10	36.2	21	17.4	5′	76.6
11	21.6	22	49.1	6′	61.3

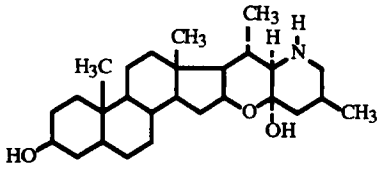


STENOPHYLLINE B 3-O-β-*D*-GLUCOPYRANOSIDE

Veratrum taliense [51]
$C_{33}H_{55}NO_7$: 577
mp: 286-288° (MeOH)
$[\alpha]_D$ -42.5° (MeOH)
IR(KBr):3500, 3326, 1380, 1362, 1076, 1055
Mass: 577(M^+, 1.9), 560(10.9), 381(13.9), 142(35.4), 125(21.1), 112(21.1), 111(30.2), 99(98), 98(100), 97(13.2)

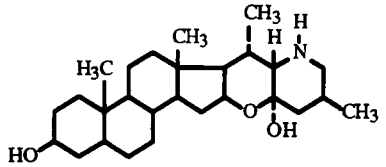
^{1}H NMR ($CDCl_3$): 0.94(3H, s, 18-Me); 1.03(3H, s, 19-Me); 1.35(3H, d, 21-Me); 1.01(3H, d, J=7, 27-Me); 3.60(1H, m, $W_{1/2}$=22, 3α-H); 5.38(1H, m, 6-H)
^{13}C NMR (C_5D_5N):

C-1	37.6	C-12	39.8	C-23	20.3
2	38.9	13	42.5	24	30.7
3	78.0	14	56.4	25	36.1
4	38.0	15	23.9	26	49.5
5	140.0	16	28.2	27	19.9
6	121.1	17	49.8	1′	101.0
7	31.1	18	17.4	2′	75.7
8	30.7	19	17.4	3′	76.1
9	51.0	20	73.6	4′	73.1
10	36.1	21	30.9	5′	76.6
11	21.1	22	54.4	6′	61.3



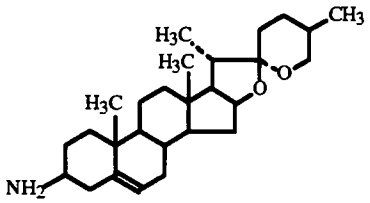
PIMPIFOLIDINE

Lycopersicon pimpinellifolium [52]



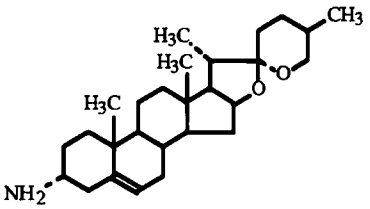
22-ISOPIMPIFOLIDINE

Lycopersicon pimpinellifolium [52]



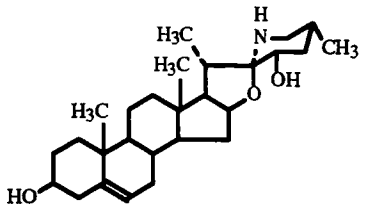
ANTILLARIDINE

Solanum antillarum [53]



ANTILLIDINE

Solanum antillarum [53]

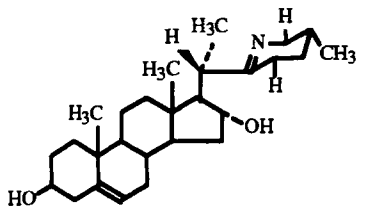


(23S)-HYDROXYSOLASODINE

Solanum fraxinifolium, Solanum canense [54]
$C_{27}H_{43}NO_3$: 429.3243
mp: 190-195°(decomp.)
$[\alpha]_D$ -93.2° ($CHCl_3$)
Mass: 492.3243(M^+, 23), 401[$(M\text{-}CO)^+$, 5], 385.2981($C_{25}H_{39}NO_2$, 100), 285(3), 217(5), 253(4), 154.1232($C_9H_{16}NO$, 15), 152(21)
^1H NMR ($CDCl_3$, TMS): 0.86(3H, s, H_3-18); 0.86(3H,d, J=6.3, H_3-27); 0.92(3H, d, J=7.1, H_3-21); 1.03(3H, s, H_3-19);

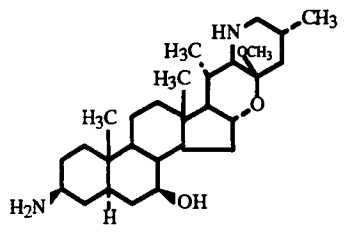
3.51(1H, m, H-3); 3.45(1H, m, H-23); 4.36(1H, m, H-16); 5.35(1H, brd, J=5.1, H-6)
^{13}C NMR ($CDCl_3$):

C-1	37.3	C-10	36.7	C-19	19.4
2	31.7	11	20.9	20	34.4
3	71.7	12	40.2	21	14.8
4	42.3	13	41.0	22	100.2
5	140.9	14	56.5	23	68.6
6	121.3	15	32.1	24	40.2
7	32.1	16	79.2	25	31.3
8	31.4	17	62.2	26	46.6
9	50.1	18	16.5	27	18.8



ISOETIOLINE

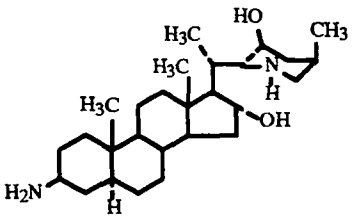
Solanum fraxinifolium, Solanum canense [55]
$C_{27}H_{45}NO_2$: 413
mp: 141-143°
$[\alpha]_D$ -73.6° ($CHCl_3$)
IR(KBr): 1654 (C=N)
Mass: 413(M^+, 10), 398[$(M-Me)^+$, 4], 395[$(M-H_2O)^+$, 12], 138(97), 125($C_8H_{15}N$, 100), 98(94)
^{1}H NMR ($CDCl_3$): 3.52(m, H-3α); 5.36(m, H-6); 3.83(m, H-16β); 0.74(s, H_3-18); 1.00(s, H_3-19); 1.14(d, J=6.9, H_3-21); 3.08(dd, J=17, 10, H-26α); 3.68(dd, J=17, 5, H-26e); 0.93(d, J=6.5, H_3-27)



7β-HYDROXY-O-METHYLSOLANOCAPSIN

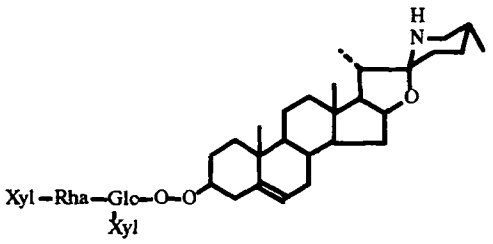
Solanum capsicastrum [56]
$C_{28}H_{48}N_2O_3$: 460.6976
mp: amorph.
$[\alpha]_D$ +65.2° ($CHCl_3$)
IR: 3340-3410 (br)
Mass: 460(M^+, 0.5), 445(1), 428(36), 424(15), 171(31), 139(72), 111(96), 98(25), 56(100)
PMR: 0.76(3H, s, 10-Me); 0.81(3H, s, 13-Me); 0.83(3H, d, J=6, 25-Me); 0.98(3H, d, J=6, 20-Me); 2.6(1H, br, 3-H); 3.04(1H, dd, J=12, 4, 26-H_{eq}); 3.13(3H, s, OMe); 3.32(1H, m, 7-H_{ax}); 4.08(1H, ddd, J=10, 10, 5, 16-H)
^{13}C NMR ($CDCl_3$):

C-1	37.3	C-11	20.4	C-20	33.0
2	32.4	12	39.1	21	15.3
3	50.9	13	42.4	22	68.8
4	38.8	14	54.1	23	98.4
5	42.7	15	30.6	24	30.6
6	38.8	16	74.1	25	30.6
7	75.0	17	60.6	26	54.8
8	43.0	18	13.5	27	18.6
9	52.8	19	12.4	OCH_3	46.3
10	35.1				



ISOSOLACAPINE

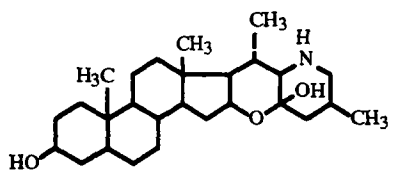
Solanum capsicastrum [57]



INCANUMINE

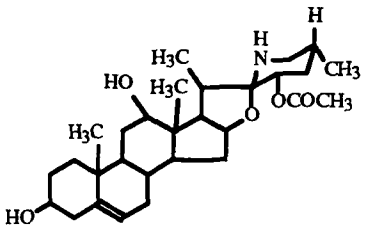
Solanum incanum [58]
$C_{49}H_{79}NO_{19}$: 985
mp: >300°
$[\alpha]_D$ +78° (MeOH)
IR: 3400
Mass: 986(11), 940(11), 904)61), 882(87), 742(17), 736(6), 720(29), 576(3), 442(7), 397(9); 165(100); 139(75); 114(14)
^{1}H NMR ($CDCl_3$+CD_3OD): 0.81(3H, s, 18-Me); 0.86(3H, d, J=6, 27-Me); 1.01(3H, s, 19-Me); 1.19(3H, d, J=7.5, Rha); 4.45(1H, d, J=7.5, anomeric H); 4.63(1H, d, J==7.5, H); 4.70(1H, brs, anomeric H); 5.19(1H, brs, anomeric H); 5.38(1H, m, 6H)
^{13}C NMR ($CDCl_3$+CD_3OD):

C-1	37.0	C-18	16.8	2''	74.3
2	30.5	19	19.3	3''	75.1
3	78.2	20	41.3	4''	70.5
4	39.0	21	15.1	5''	69.2
5	141.3	22	18.0	1'''	101.5
6	121.3	23	32.6	2'''	72.2
7	32.5	24	30.5	3'''	73.3
8	31.5	25	30.6	4'''	83.3
9	51.2	26	47.5	5'''	71.1
10	37.3	27	19.3	6'''	18.0
11	21.3	1'	10.1	1''''	104.8
12	41.2	2'	74.1	2''''	76.6
13	41.3	3'	85.3	3''''	77.5
14	57.1	4'	78.2	4''''	71.3
15	32.5	5'	76.5	5''''	69.3
16	78.9	6'	61.5		
17	63.4	1''	104.6		



SOLANOCARDINOL

Solanum neocardenasii [59]
$C_{26}H_{43}NO_3$: 417
Mass: 431[M^+, 50], 413[$(M-18)^+$, 4], 161(7), 157(22), 156(11), 142(100), 130(29), 125(40), 112(13), 84(13), 70(53)

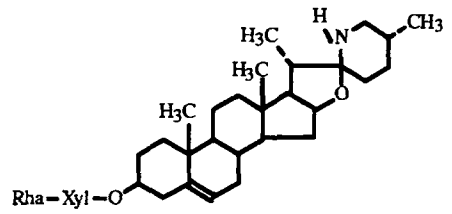


23-O-ACETYL-12β-HYDROXYSOLASODINE

Solanum nigrum [60]
$C_{29}H_{45}NO_5$: 487
mp: 145°
IR(KBr): 760, 790, 850, 955, 1060, 1170, 1460, 1725, 2940
Mass: 487(M^+),196, 172, 171

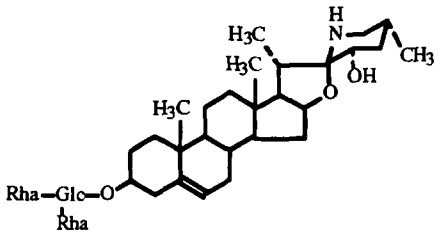
^{1}H NMR ($CDCl_3$): 0.72(3H, s, 18-CH_3); 0.93(3H, s, 19-CH_3); 1.14(3H, d, J=3.5, 27-CH_3); 1.61(3H, d, J=4.1, 21-CH_3); 1.63(1H, m, NH); 2.21 (2H, m, 26 CH_2); 1.92(s, CH_3COOH); 3.40(m, 1H, H-3); 4.18(1H, m, H-16); 5.24(1H, m, H-6)
^{13}C NMR ($CDCl_3$):

C-1	37.3	C-10	36.7	C-19	19.3
2	31.8	11	24.5	20	41.8
3	71.6	12	79.0	21	15.2
4	42.2	13	40.8	22	97.6
5	140.8	14	55.2	23	30.6
6	121.3	15	33.2	24	30.5
7	32.1	16	79.7	25	30.1
8	31.6	17	62.5	26	46.0
9	50.2	18	14.4	27	17.2



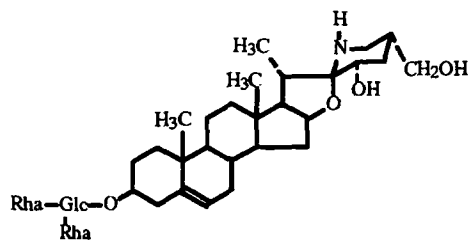
RAVIFOLINE

Solanum platanifolium [61]



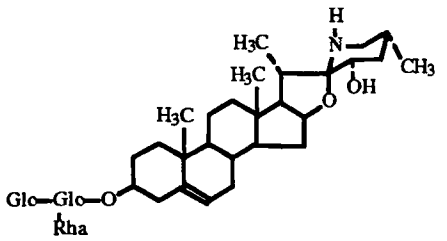
SOLAVERINE I

Solanum toxicarium, Solanum verbascifolium [62]



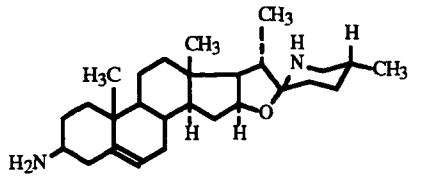
SOLAVERINE II

Solanum toxicarium, Solanum verbascifolium [62]



SOLAVERINE III

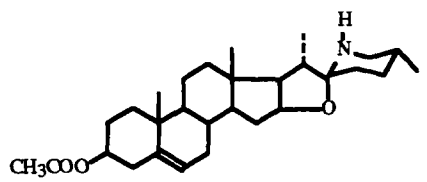
Solanum toxicarium, Solanum verbascifolium [62]



(22R,25R)-3β-AMINO-5-SPIROSOLENE

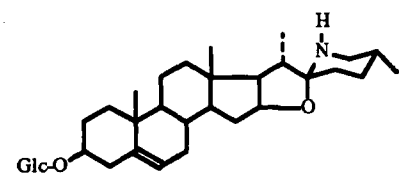
Solanum triste [63]
$C_{27}H_{44}N_2O$: 412.3461
mp: 165-167°(CH_3OH-$CHCl_3$-H_2O)
$[\alpha]_D$-52° (CH_3OH)
IR: 3250, 1550
Mass: 412.3461(M^+, 17), 283.2415(28), 138.1278($C_9H_{16}N$, 100), 114.0925($C_9H_{12}NO$, 41), 113.0847(18), 56.0521(41)
^{1}H NMR($CDCl_3$): 1.08(1-H); 1.82(1-H); 1.70(2-H); 1.32(2-H); 2.60(H-3); 2.16(H-4); 2.05(H-4); 5.32(H-6); 1.53(H-7); 2.00(H-7); 1.63(H-8); 0.97(H-9); 1.53(H-11); 1.45(H-11); 1.16(H-12); 1.74(H-12); 1.09(H-14); 1.32(H-15); 2.00(H-15); 4.29(H-16); 1.70(H-17); 0.81(H-18); 1.01(H-19); 1.88(H-20); 0.94(H-21); 1.63(H-23); 1.42(H-24); 1.60(H-24); 1.53(H-25); 2.60(H-26); 2.65(H-26); 0.84(H-27)
^{13}C NMR ($CDCl_3$):

C-1	38.15	C-10	36.69	C-19	19.45
2	32.57	11	20.82	20	41.21
3	51.95	12	39.98	21	16.27
4	43.66	13	40.50	22	98.23
5	141.84	14	56.54	23	34.05
6	120.34	15	32.16	24	30.30
7	32.05	16	78.73	25	31.45
8	31.56	17	62.79	26	47.66
9	50.18	18	16.41	27	19.29



O-ACETYLSOLASODINE

Solanum umbelliferum [64]
$C_{29}H_{45}NO_3$: 455.6782
mp: 192-194°(ac.)
$[\alpha]_D$-95.5°($CHCl_3$)



SOLASODINE 3-O-β-GLUCOPYRANOSIDE

Solanum umbelliferum [64]
$C_{33}H_{53}NO_7$: 575.7814
mp: 246-248°(ac.)
$[\alpha]_D$ -91.1° (MeOH)

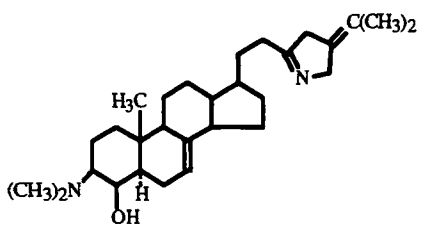
PMR: 0.83(3H, s, Me-18); 0.85(3H, d, J=6.2, Me-27); 0.97(3H, d, J=7.2, Me-21); 1.04(3H, s, Me-19); 2.57(2H, m, H-26), 3.58(1H, m, H-3), 4.34(1H, m, H-16), 4.37(1H, d, J=7.8, H-1), 5.37(1H, d, J=5.3, H-6)

^{13}C NMR:

C-1	38.5	C-12	39.7	C-23	34.8
2	31.0	13	41.6	24	30.7
3	80.5	14	57.7	25	31.5
4	40.9	15	33.0	26	48.2
5	142.0	16	79.7	27	19.7
6	142.0	17	63.9	1′	102.4
7	33.2	18	16.8	2′	75.1
8	32.7	19	19.8	3′	78.0
9	51.7	20	42.7	4′	71.6
10	38.0	21	15.4	5′	77.8
11	22.0	22	99.4	6′	62.7

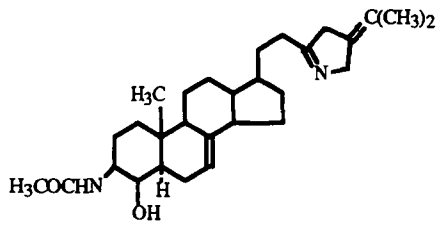
Animals

Sponge type (Spongie)



N,N-DIMETHYL-4β-HYDROXY-3-EPIPLAKINAMINE A

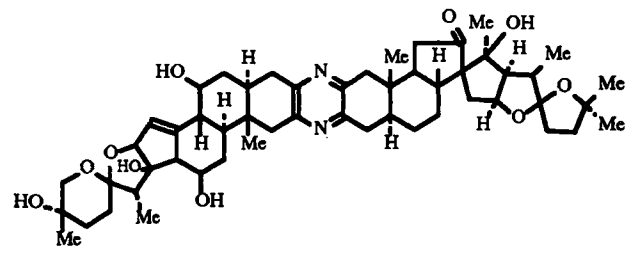
Corticium sp. [65]



N-ACETYL-4β-HYDROXY-3-EPIPLAKINAMINE A

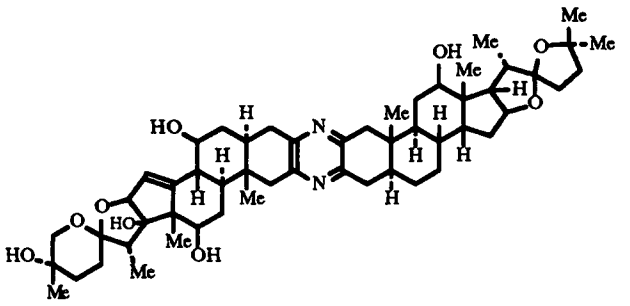
Corticium sp. [65]

Tunicate type (Tunicata)



RITTERAZINE A

Ritterella tokioka [66]



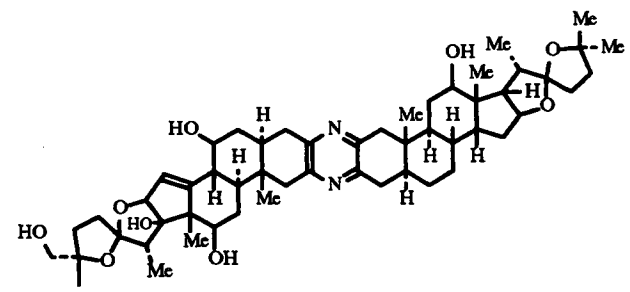
RITTERAZINE B

Ritterella tokioka [67]
$C_{54}H_{79}N_2O_9$: 899
$[\alpha]_D$ +43.0° (MeOH)
UV: 288(68.80), 308
IR: 3480, 2960, 2920, 2870, 2850, 1680, 1610, 1460, 1400, 1140, 1120, 1060, 1040, 1000, 980, 940, 880, 850
PMR (Py-d_5): 2.68(d, J=18.3, H-1′α); 3.15(d, 18.3, H-1′β); 2.98(dd, 17.7, 5.2, H-4′α); 2.77(dd, 17.7, 12.5, H-4′β); 1.84(m, H-5′); 2.18(dd, 12.4, 4.4, H-6′α); 1.76(ddd, 12.4, 12.3, 10.5, H-6′β); 4.06(dddd, 10.6, 10.5, 4.4, 2.2, H-7′); 241(dd, 10.6, 10.0, H-8′); 1.16(m, H-9′); 2.17(m, H-11′α); 1.88(m, H-11′β); 4.20(ddd, 11.2, 4.6, 2.0, H-12′); 6.13(d, 2.0, H-15′); 5.25(d, 2.0; 16′); 1.33(s, 18′); 0.85(s, 19′); 2.21(d, 6.9, 20′); 1.26(k, 6.9, 21′); 2.50(ddd, 13.4, 13.4, 4.8, 23′α); 1.49(m, 23′β); 1.87(m, 24′α); 2.16(m, 24′β); 3.61(dd, 11.6, 2.7, 26′α); 4.02(d, 11.6, 26′β); 1.22(s, 27′); 3.63(d, 2.2, 7-OH); 4.67(d, 2.0, 12′-OH); 5.00(s, 17′-OH); 3.69(us, 25′- OH); 2.71(d, 18.0, 1α); 3.17(d, 18.0, 1β); 2.94(dd, 17.5, 5.2, 4α); 2.68(dd, 17.5, 13.1, 4β); 1.57(m, 5), 1.48(m, 6α); 1.28(m, 6β); 1.10(m, 7α); 1.49(m, 7β); 1.68(m, 8); 1.36(m, 9); 2.04(m, 11α); 1.67(m, 11β); 3.64(dd, 11.7, 3.7, 12); 2.08(m, 14); 1.80(dd, 15.1, 13.8, 15α); 1.83(dd, 15.1, 7.0, 15β); 4.78(dd, 9.7, 7.0, 16); 3.15(dd, 9.7, 9.6, 17); 1.26(s, 18); 0.75(s, 19); 2.01(dk, 9.6, 6.7, 20); 1.18(d, 6.7, 21); 1.85(m, 23α); 2.12(m, 23β); 1.68(m, 24α); 2.04(m, 24β); 1.18(s, 26); 1.43(s, 27); 5.80(us, 12-OH)
^{13}C NMR (Py-d_5):

C-1′	45.9	C-19′	11.5	C-10	35.9
2′	148.6	20′	48.2	11	30.7
3′	148.1	21′	8.1	12	71.8
4′	35.6	22′	107.9	13	48.6
5′	40.0	23′	27.5	14	47.8
6′	38.4	24′	33.2	15	32.8
7′	69.4	25′	65.8	16	80.0
8′	42.8	26′	70.2	17	57.5
9′	51.2	27′	27.0	18	13.7
10′	35.9	1	46.3	19	11.9
11′	29.2	2	149.3	20	42.0
12′	75.6	3	149.0	21	14.9
13′	56.1	4	35.9	22	117.0
14′	151.6	5	41.5	23	33.2
15′	121.1	6	29.0	24	37.3
16′	94.0	7	31.7	25	81.4
17′	93.3	8	32.6	26	28.8
18′	12.5	9	45.5	27	30.3

Pharm.: A potential cytotoxic activity against P 388 leukemic cells has been shown.

RITTERAZINE C



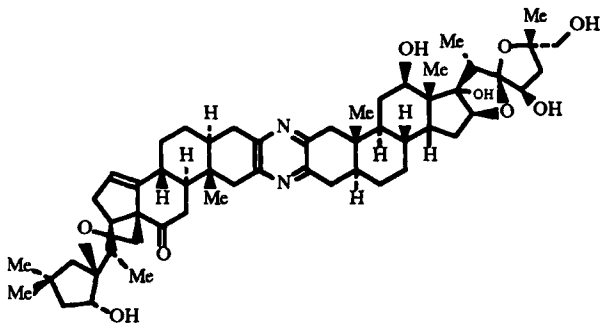
Ritterella tokioka [67]
$C_{54}H_{79}N_2O_9$: 899
$[\alpha]_D$ +72.0° (MeOH)
UV(MeOH): 285(8720), 303
IR(MeOH): 3400, 2970, 2940, 2880, 1780, 1680, 1610, 1510, 1460, 1380, 1200-1140, 1030, 1000, 980, 950, 870, 800, 720,700
Mass: 899.5861

PMR (Py-d_5): 2.64(d, 1'α); 3.11(d, 17.1, 1'β); 2.96(dd, 17.7, 5.2, 4'α); 2.75(dd, 17.7, 12.1, 4'β); 1.81(m, 5'); 2.17(m, 6'α); 1.72(m, 6'β); 4.00(ddd, 10.6, 10.1, 4.6, 7'); 2.40(dd, 10.6, 10.2, H-8'); 1.15(m, 9'); 2.16(m, 11'α); 1.87(m, 11'β); 4.16(dd, 11.3, 4.8, 12'); 5.98(dd, 1.7,1.6, 15'); 5.25(d, 1.7; 16'); 1.35(s, 18'); 0.83(s, 19'); 2.34(m, 20'); 1.19(d, 7.0, 21'); 2.36(m, 23'α); 1.65(m, 23'β); 2.02(m, 24'α); 1.67(m, 24'β); 3.80(d, 10.8, 26'α); 3.76(d, 10.8, 26'β); 1.29(s, 27'); 3.62(ds, 7'-OH); 2.72(d, 16.6, 1α); 3.16(d, 16.6 1β); 2.95(dd, 18.1,3.6, 4α); 2.66(dd, 18.1, 12.9 4β); 1.56(m, 5); 1.47(m, 6α); 1.29(m, 6β); 1.11(m, 7α); 1.49(m, 7β); 1.65(m, 8); 1.36(m, 9); 2.04(m, 11α); 1.68(m, 11β); 3.64(dd, 9.5,4.4, 12); 2.08(m, 14); 1.80(m, 15α); 1.84(m, 15β); 4.77(dd, 7.0, 7.0,16); 3.15(m, 17); 1.26(s,18); 0.75(s,19); 2.03(m, 20);1.17(d,6.6, 21); 1.70(m, 23α); 2.12(m, 23β); 1.67(m, 24α); 2.02(m, 24β); 1.19(c, 26); 1.43 (c, 27); 3.63 (us, 12-OH)
^{13}C NMR (Py-d_5):

C-1 '	45.8	C-19 '	11.8	C-10	35.8
2 '	148.6	20 '	45.0	11	30.8
3 '	148.3	21 '	8.2	12	71.8
4 '	35.6	22 '	118.1	13	48.6
5 '	40.0	23 '	32.1	14	47.8
6 '	38.4	24 '	33.5	15	32.8
7 '	69.4	25 '	86.1	16	80.0
8 '	42.7	26 '	69.7	17	57.5
9 '	51.3	27 '	23.7	18	13.7
10 '	35.8	1	46.3	19	11.9
11 '	29.4	2	149.4	20	42.0
12 '	75.7	3	148.8	21	14.7
13 '	55.9	4	35.8	22	117.0
14 '	151.5	5	41.5	23	33.2
15 '	131.1	6	29.0	24	37.3
16 '	93.4	7	31.8	25	81.4
17 '	92.9	8	32.6	26	28.8
18 '	12.6	9	45.5	27	30.3

Pharm.: A potential cytotoxic activity against P 388 leukemic cells has been shown.

Black Sea Hemichordate type (Hemichordata)



CEPHALOSTATINE I

Cephalodiscus gilchristi [68, 69]
$C_{54}H_{74}N_2O_{10}$: 911.5423
mp: 326°(MeOH)
$[\alpha]_D$ +102° (decomp. e.a.-met.)
UV(C_2H_5OH): 289, 309
IR(KBr): 3430, 3050, 2970, 2930, 2880, 2860, 1708, 1650-1615 br, 1445, 1400, 1152, 1115, 1090. 1045, 950, 892
Macc: 911.5442 $[M+H]^+$

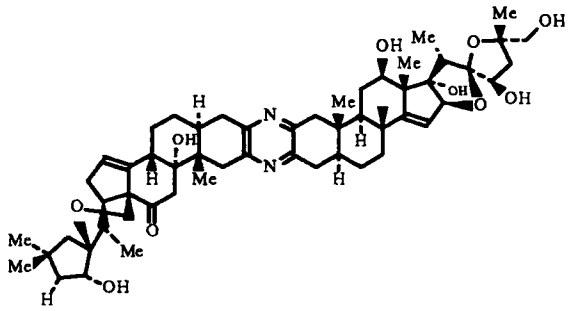
^{1}H NMR (C_5D_5N): 0.72(3H, s, H-19'); 0.75(3H, s, H-19); 0.88(dt, 4.5, 13.8, H-9); 1.26(m, H-9'); 1.28(m, H-8b'); 1.30(m, H-7b'); 1.33(3H, s, H-18); 1.34(m, H-6b); 1.35(m, H-7b) 1.35(3H, d, 7.0, H-21); 1.39(3H, s, H-27'); 1.47(3H, d, 7.0, H-21'); 1.47(3H, s, H-26'); 1.53(m, H-6a'); 1.59(m, H-6a'); 1.60(m, H-5); 1.61(m, H-5); 1.65(3H, s, H-27); 1.69(m, H-7a); 1.77(dt, 10.0, 14.0, H-11b); 1.95(d, 6.2, 12.0, H-24b'); 1.99(m, H-7a'); 2.04(m, H-11a); 2.07(m, H-8); 2.13(m, H-8'); 2.33(m, H-16b'); 2.35(m, H-24a'); 2.36(m, H-24b); 2.56(d, 17.0, H-1b'); 2.61(dd, 14.0, 3.2 H-11b'); 2.64(d, 17.0, H-1b); 2.65(2H, dd, 18.0, 12.5, H-4b and H-4b'); 2.72(dd, 12.0, 7.0, H-17'); 2.77(dd, 10.5, 7.9, H-24a); 2.78(t, 14.0, H-11a'); 2.86(q, 7.0, H-20); 2.87(dt, 4.0, 11.8, H-16a'); 2.91(dd, 17.9, 5.5, H-4'); 2.93(dd, 17.9, 5.5, H-4a); 3.04(d, 17.0, H-1a');

3.07(d, 17.0, H-1a); 3.17(dq, 7.0, 7.0, H-20'); 3.72(d, 11.2, H-26a); 3.78(d, 11.2, H-26b); 4.02(, 12.2, H-18a'); 4.05(m, H-12); 4.06(12.2, H-18b'); 4.05(m, H-12); 4.06(d, 12.2, H-18b'); 4.70(s. 12-OH); 4.80(2H, m, H-23, H-23'); 5.24(s, H-16); 5.44(s, H-15'); 5.64(s, H-15); 6.23(s, 17-OH); 6.54(brs, 26-OH); 7.19(brs, 23'-OH); 8.06(brs, 23-OH)

^{13}C NMR (C_5D_5N):

C-1 '	45.82	C-19 '	11.31	C-10	36.32
2 '	148.66	20 '	32.88	11	28.94
3 '	149.01	21 '	15.49	12	75.59
4 '	35.78	22 '	110.96	13	55.39
5 '	41.20	23 '	81.52	14	152.71
6 '	28.23	24 '	47.32	15	122.28
7 '	29.50	25 '	81.52	16	93.15
8 '	35.56	26 '	29.44	17	91.66
9 '	52.20	27 '	29.75	18	12.58
10 '	36.28	1	45.98	19	11.72
11 '	38.81	2	148.38	20	44.50
12 '	211.80	3	148.44	21	9.01
13 '	61.82	4	35.72	22	117.16
14 '	149.46	5	41.78	23	71.51
15 '	123.18	6	27.94	24	39.51
16 '	32.36	7	28.69	25	82.81
17 '	44.21	8	33.79	26	69.28
18 '	69.19	9	53.20	27	26.42

CEPHALOSTATINE 2



Cephalodiscus gilchristi [69]

$C_{54}H_{75}N_2O_{11}$: 927.5372

mp: >350°

$[\alpha]_D$ +111° (MeOH)

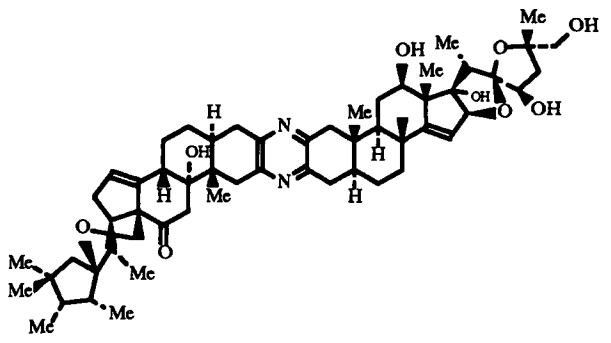
UV(C_2H_5OH): 290(13700), 308sh

IR(KBr): 3430, 3055, 2975, 2930, 2880, 1710, 1655-1625 br, 1448, 1402, 1385, 1092, 1045, 950

Macc: 927.5230 $(M+H)^+$

^{13}C NMR:

C-1	45.98	C-19	11.76	C-10'	41.23
2	148.56	20	44.52	11'	45.60
3	148.56	21	9.03	12'	211.0
4	35.77	22	117.18	13'	61.57
5	41.82	23	71.53	14'	148.28
6	28.16	24	39.51	15'	124.48
7	28.70	25	82.83	16'	32.56
8	33.80	26	69.30	17'	44.20
9	53.22	27	26.45	18'	64.06
10	36.35	1'	39.52	19'	16.06
11	28.96	2'	148.69	20'	32.89
12	75.61	3'	148.51	21'	15.49
13	55.41	4'	36.20	22'	110.95
14	152.74	5'	34.19	23'	81.60
15	122.28	6'	28.25	24'	47.35
16	93.17	7'	24.58	25'	81.14
17	91.68	8'	38.98	26'	29.81
18	12.60	9'	78.74	27'	29.53

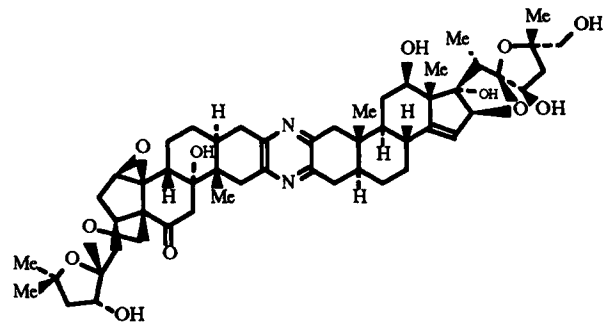


CEPHALOSTATINE 3

Cephalodiscus gilchristi [69]
$C_{55}H_{77}N_2O_{11}$: 941.5528
mp: >350°
$[\alpha]_D$ +99° (MeOH)
UV(C_2H_5OH): 290(12900), 308 sh
IR(KBr): 3430, 3050, 2967, 2928, 2872, 1707, 1645-1615 br, 1448, 1402, 1383, 1040, 977, 952, 935
Macc: 941.5546 $(M+H)^+$

^{13}C NMR:

C-1	45.98	C-20	44.51	C-12′	211.14
2	148.67	21	9.01	13′	61.25
3	148.67	22	117.18	14′	148.51
4	35.77	23	71.52	15′	124.51
5	41.80	24	39.52	16′	32.42
6	28.16	25	82.82	17′	43.92
7	28.68	26	69.28	18′	64.97
8	33.79	27	26.43	19′	15.03
9	53.20	1′	39.52	20′	32.58
10	36.33	2′	148.67	21′	15.20
11	28.95	3′	148.51	22′	109.06
12	75.59	4′	36.20	23′	87.17
13	55.40	5′	34.19	24′	51.65
14	152.73	6′	28.25	25′	81.32
15	122.27	7′	24.60	26′	28.02
16	93.16	8′	39.03	27′	23.33
17	91.67	9′	78.73	28′	12.71
18	12.59	10	41.22		
19	11.74	11	45.46		

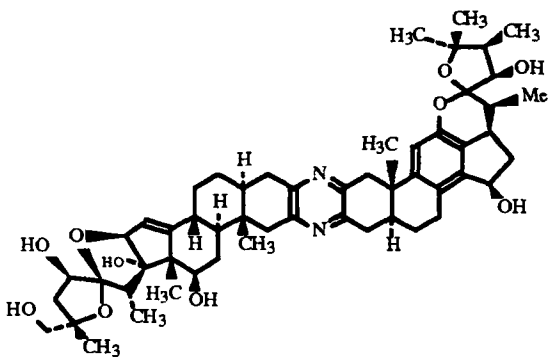


CEPHALOSTATINE 4

Cephalodiscus gilchristi [69]
$C_{54}H_{75}N_2O_{12}$: 943.5343
mp: >350°
$[\alpha]_D$ +89° (MeOH)
UV(C_2H_5OH): 290(10500), 308 sh
IR(KBr): 3430, 2970, 2928, 2875, 1711, 1660-1600 br, 1447, 1383, 1089, 1042, 948, 904
Macc: 941.5546 $(M+H)^+$

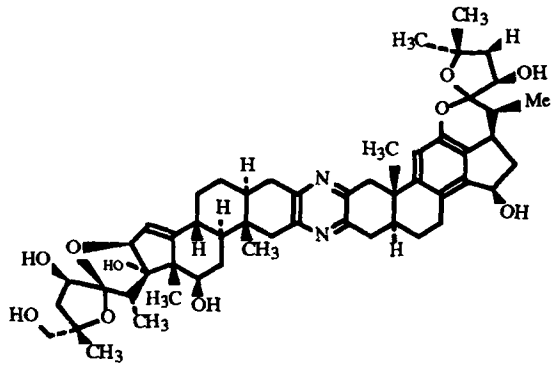
^{13}C NMR:

C-1	45.99	C-19	11.74	C-10	41.54
2	148.68	20	44.50	11	45.55
3	148.60	21	9.00	12′	209.36
4	35.77	22	117.16	13′	56.33
5	41.78	23	71.52	14′	72.83
6	28.21	24	39.52	15′	54.10
7	28.65	25	82.81	16′	27.70
8	33.78	26	69.28	17′	33.15
9	53.18	27	26.42	18′	62.42
10	36.32	1′	39.03	19′	14.87
11	28.94	2′	149.20	20′	31.99
12	75.58	3′	148.14	21′	15.06
13	55.38	4′	36.07	22′	110.25
14	152.71	5′	33.85	23′	81.48
15	122.26	6′	27.56	24′	47.31
16	93.15	7′	20.64	25′	81.10
17	91.65	8′	34.62	26′	29.65
18	12.57	9′	80.97	27′	29.32



CEPHALOSTATINE 5

Cephalodiscus gilchristi [70]
$C_{54}H_{72}N_2O_{10}$: 908.5187
mp: 350°
$[\alpha]_D$ +100° (MeOH)
UV(CH_3OH): 290(9500), 310 sh
Macc: 908.5164 (M^+)



CEPHALOSTATINE 6

Cephalodiscus gilchristi [70]
$C_{53}H_{70}N_2O_{10}$: 894.5031
mp: >350°
$[\alpha]_D$ +100° (CH_3OH)
UV(CH_3OH): 289(10000), 310 sh
Macc: 894.4985 (M^+)
^{1}HNMR(C_5D_5N): 3.08(d, 17.0, H-1); 2.63(d, 16.8, H-1); 2.90(H-4); 2.65(d, 16.8, H-4); 1.57(H-5); 1.49(H-6); 1.31(H-6); 1.69(H-7); 1.24(H-7); 2.05(H-8); 0.87(m, H-9); 2.05(-11); 4.05(ddd, 12.4, 4.9, 1.1, H-12); 5.63(s, H-15); 5.24(s, H-16); 1.34(s, 3H, H-18); 0.71(s, 3H, H-19); 2.86(H-20); 1.35(d, 7.1, 3H, H-21); 4.80(H-23); 2.73(dd, 11.2, 8.0, H-24); 2.35(t, 11.1, H-24); 3.81(dd, 10.9, 5.3, H-26); 3.71(dd, 10.9, 4.6, H-26); 1.64(s, 3H, H-27);

4.70(d, 1.1, 12-OH); 6.23(s, 17-OH); 8.08(d, 7.4, 23-OH); 6.55(26-OH); 3.56(d, 16.9, H-1′); 2.96(H-1′); 2.96(H-4′); 2.80(H-4′); 1.95(m, H-5′); 1.71(2H, H-6′); 3.09(brt, 2H, H-7′); 6.93(s, H-11′); 5.55(t, H-15′); 2.38(dd, 12.5, 6.0, H-16′); 2.18(ddd, 12.5, 10.5, 10.5, 5.5, H-16′); 4.44(dt, 10.0, 6.0, H-17′); 1.09(s, 3H, H-19′); 2.27(quint, 7.0, H-20′); 1.07(d, 7.1, 3H, H-21); 4.56(q, 8.7, H-23′); 2.58(t, 11.2, H-24′); 2.46(dd, 11.7, 8.0, H-24′); 1.27(s, 3H. H-26′); 1.43(s, 3H, H-27′); 6.54(15′-OH); 6.51(23′-OH)

^{13}C NMR (C_5D_5N):

C-1	45.95	C-19	11.67	C-10	37.12
2	149.63	20	44.50	11	111.46
3	149.32	21	8.99	12′	149.55
4	35.77	22	117.12	13′	127.88
5	41.73	23	71.50	14′	144.30
6	28.19	24	39.51	15′	74.54
7	28.66	25	82.80	16′	39.83
8	33.77	26	69.67	17′	36.90
9	53.20	27	29.41	18′	64.0
10	36.27	1′	47.24	19′	22.59
11	30.00	2′	149.54	20′	37.00
12	75.56	3′	148.94	21′	8.72
13	55.36	4′	35.77	22′	107.35
14	152.70	5′	39.07	23′	77.18
15	122.24	6′	25.29	24′	46.22
16	93.15	7′	26.35	25′	78.48
17	91.64	8′	124.58	26′	30.12
18	12.57	9′	146.21	27′	31.29

Note. Steroid alkaloids possessing pronounced physiological activity have also been detected previously in a representative of the class of amphibia — the European spotted salamander (fam. Salamandridae): samandarine, samandarone, cycloneosamandarone, etc. [7]. However, no reports of these compounds have been found in recent years. An analogous pattern is observed in relation to the neurotoxic alkaloids of the venom of neotropical frogs (fam. Dendrobatidae) which, from the structure of their main skeleton and functional features, may also be assigned to the steroid alkaloids [7].

During the G_2 period there is active formation of the enzymes of the nitrogen metabolism (nitrate reductase, phenylalanine-ammonia lyase) that are required for the passage of the cells into the following phase and for the synthesis of the nitrogen heterocycles that are precursors of the alkaloids. It must be mentioned that since the sources of nitrogen for the alkaloid precursors are the same amino acids as for proteins (for example, arginine in the biosynthesis of solanidine in *Veratrum grandiflorum*) the synthesis of alkaloids proceeds actively in those periods in which the synthesis of proteins is retarded [76, 77].

On the whole, in both animal and plant organisms the synthesis of steroid compounds takes place by a single route: from acetylcoenzyme A via the main intermediate compounds — mevalonic acid, isopentenyl pyrophosphate, farnesyl pyrophosphate, and, finally, squalene, which is transformed into various triterpenes according to the type of "bending" of the molecule, cyclization, and subsequent changes. This type of triterpenes includes a number of tetracycles with a perhydrocyclopentenophenathrene skeleton — for example, lanosterol and the pentacyclic cycloartenol. Since cycloartenol is widely distributed in the vegetable kingdom, it is assumed that it is precisely this compound which is the main triterpene intermediate in the biosynthesis of steroids in higher plants [78].

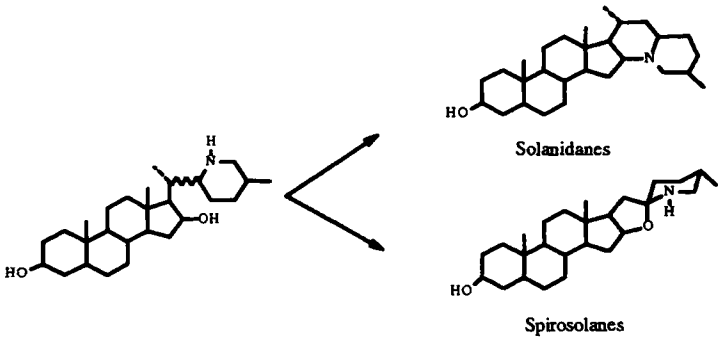
In the following stage, branching of the common biosynthetic pathway is observed.

Cholesterol is formed from cycloartenol via a compound called lophenol. The following step in biosynthesis is the hydroxylation of one of the terminal methyl groups of cholesterol [79]. The identification of dormantinone and dormantinol in *Veratrum grandiflorum* [80] shows the subsequent introduction of a hydroxy group at C-22, while the detection of alkaloids

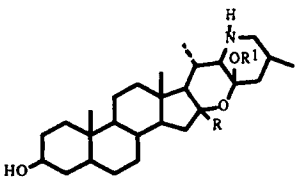
of the type of verazine in plants [79] shows replacement of the hydroxy group at C-26 by an amino group, followed by the construction of ring *F*. Only after this is the hydroxy group at C-16 introduced, the formation of the steroid alkaloids taking place in fact through the 16-hydroxy, and not the 16-oxo, derivative, as has been shown by experiments with labeled atoms in which tritium introduced into cholesterol was retained in the furan ring of tomatidine, only changing its orientation from α- to β- [81].

Precisely this order of the formation of the molecular skeleton has been confirmed by investigations of the plant *Solanum laciniatum*, in which it was revealed that the precursor in the biosynthesis of solasodine is (25R)-26-aminocholesterol, and not (25R)-26-aminocholest-5-ene-3β,16β-diol [82].

In a study of the plant *Solanum neocardenasii* an aglycon, solanocardinol, was isolated the spectral characteristics and chemical transformations of which showed that the spirosolanes and solanidanes, which are common alkamine ring systems in alkaloids of tuber-bearing species of *Solanum* genetically closely related to *Solanum tuberosum*, originate from a common intermediate with a β-oriented hydroxy group at C-16 [83].



On the other hand, the alkamines of *Solanum aculeum* — 3β-hydroxy-3-deaminosolanocapsine and aculeamine [84, 85] are cyclization products of a 16α-OH intermediate:



3-Deaminosolanocapsin-3β-ol R = αH, R^1 = H
Aculeamine R = αH, R^1 = Me
23-Ethoxy derivative R = αH, $R^1 = C_2H_5$
Solanocardinol R = βH, R^1 = H
23-Methoxy derivative R = βH, R^1 = Me
23-Ethoxy derivative R = βH, $R^1 = C_2H_5$

Up to the present, the following question has remained open: are the solidanes formed only through 16β-OH derivatives (which, for example, applies to the case of spiroaminoacetals) or also through the 16-αOH- derivatives (as was assumed previously), since solanidanes are isolated from plants containing both the α- and the β- forms of the precursors [78, 79, 86, 87].

Summarizing all that has been said above, it may be assumed that the biosynthesis of steroid alkaloids takes place by the route shown in the scheme.

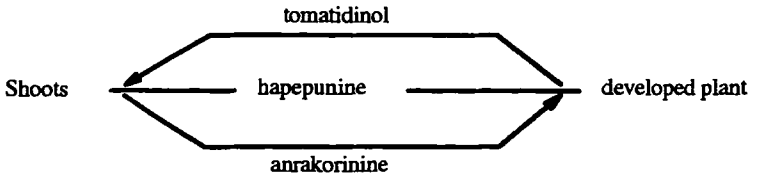
The chemotaxonomic closeness of plants of the genera *Solanum*, *Veratrum*, *Petilium*, *Fritillaria*, and *Korolkowia* enables general conclusions to be drawn on the biosynthesis of the steroid alkaloids as a whole, although individual points in the formation of the intermediates can be interpreted with various degrees of probability in each of these genera. Thus, for example, a hypothesis of the presence in *Solanum* plants of compounds with a β-oriented hydroxy group at C-16 [88] — possible precursors in the synthesis of solanidanes and spirosolanes — has found confirmation in the isolation of such compounds — pingbeinine (**39**) and pingbeininosine (**40**) (Table 1) — from the plant *Fritillaria ussuriensis* [34] and, previously, of hapepunine from *Fritillaria camtschatcensis* [86]. Both these genera, like *Solanum* are sources of solanidanes.

Thus, in the formation of typical steroid alkaloids, rings *A*, *B*, *C*, and *D* are introduced into the structure from cholesterol, then ring *F* is constructed, and, finally, ring *E* is formed (whether this leads to solanidanes, spirosolanes, or compounds with an epiminocyclohemiketal moiety such as, for example, solanocapsine or solanocardinol).

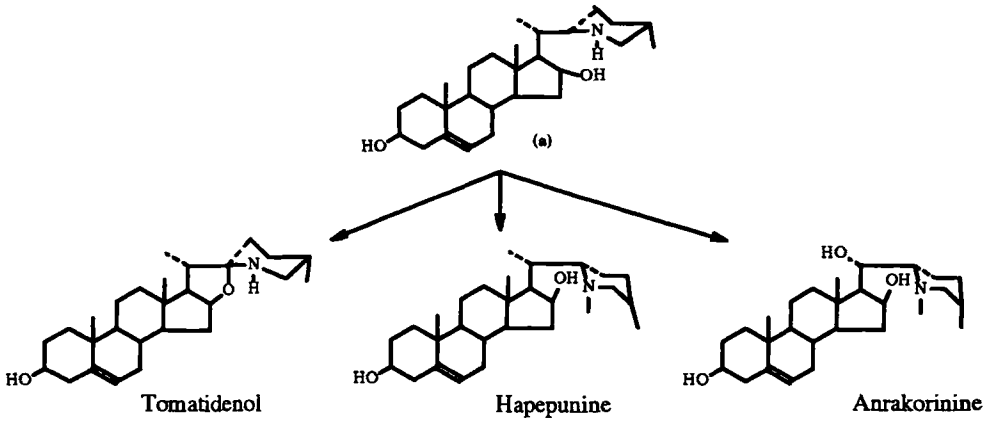
It must be mentioned that (25R)- and (25S)-spirosolanes are formed from the corresponding 26-amino compounds; i.e., apparently, epimerization at the C-25 asymmetric center begins as early as the stage of the formation of cholesterol and, thus,

solasodine is formed from (25R)-cholesterol and tomatidine from (25S)-cholesterol (Scheme).

In a study of the plant *Fritillaria camtschatcensis* it was found that, as the plant develops, there is, first, an accumulation of tomatidenol, after which its amount gradually decreases and that of anrakorinine — (22S,25S)-N-methyl-22,26-epiminocholest-5-ene-3β,16β,18β-triol — increases. During this process the amount of hapepunine — (22S,25S)-N-methyl-22,26-epiminocholest-5-ene-3β,16β-diol — remained unchanged:



On this basis the conclusion was drawn that the alkaloids anrakorinine and hapepunine are synthesized from tomatidenol on its degradation [86]. However, in the light of new results, the synthesis of hapepunine and anrakorinine not from tomatidenol but from its precursor (a) seems more probable.



With such an alternative route of biosynthesis, a decrease in the amount of tomatidenol will again be observed, since part of its precursor will be consumed in the synthesis of N-methyl derivatives as the plant develops. In other words, if the scheme of biosynthesis in which the spirosolanes are formed through the intermediate compound (a) is true and in view of the existence of natural compounds with a 16β-OH but without a N-methyl group [4], it is more logical (also in the light of energy consumption) to assume the involvement in biosynthesis of link (1) and not chain (2).

(a) → spirosolanes	(a) → spirosolanes → N-methyl compounds
↓	
N-methyl compounds	
(1)	(2)

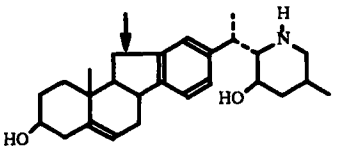
Alkaloids of *Veratrum* plants (for example, rubijervine, differing from solanidine only by the presence of a hydroxy group at C-12) are now synthesized not by the common route through etioline but by the chain: verazine → hakurirodine → baikeine → rubijervine (Scheme). That is, obviously, hydroxylation take place first at C-12 and then at C-16.

So far as concerns the 3-amino derivatives of steroid alkaloids (for example soladunalinidine in the spirosolane group, or solanocapsine in the spiroaminoacetal group), their simultaneous presence with the corresponding β-hydroxy compounds (in the plants *Solanum callium* and *Solanum dunalianum*) permits the latter to be considered as precursors [89].

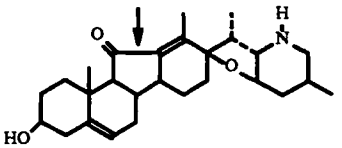
Modified or C-nor,D-homosteroid alkaloids are synthesized in plants from intermediate C-27 compounds with a normal steroid skeleton.

Experiments with the introduction of labeled atoms into the plant *Veratrum grandiflorum* have shown that common intermediate compounds are obviously involved in the biosynthesis of alkaloids of the jervine and veratramine types. It has been established that 11-deoxyjervine is a possible precursor for jervine (but not for veratramine); i.e., in all probability the

introduction of a carbonyl group in the C-11 position takes place after the splitting of the common biosynthetic route into two branches — the synthesis of veratramines and the synthesis of jervines:

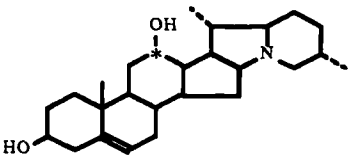


Veratramine



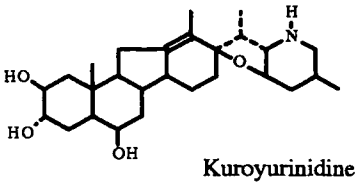
Jervine

The hypothesis has been expressed that the initial C-27 compound with a normal steroid skeleton could be a solanidine derivative with an equatorial hydroxy group at C-12 — a possible point of initiation for a C-nor,D-homo rearrangement:



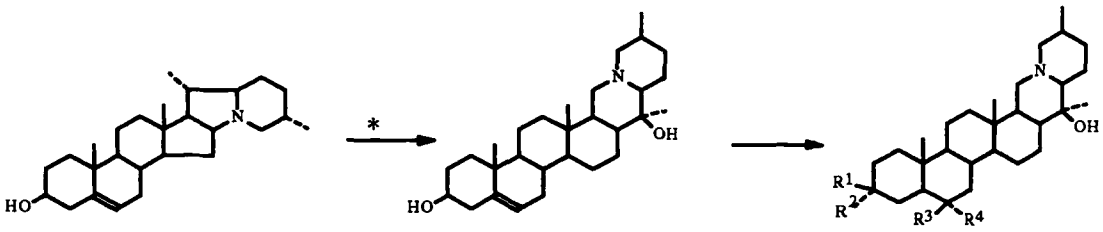
The basis for this hypothesis was provided by experiments in which, as a radioactive solanidine glycoside disappeared in illuminated *Veratrum grandiflorum* plants, radioactive jervine and radioactive veratramine appeared [90].

The plant *Fritillaria camtschatcensis* has also yielded an alkaloid of the jervine type — kuroyurininide, which, like jervine, can be formed from a solanidine derivative, since alkaloids of the solanidine type (solanidine, camtschatcanidine) were also detected in this plant [91]:



Kuroyurinidine

The isolation from plants of the *Fritillaria* genus of a large number of epimers (with respect to the C-3 and C-6 positions) [92, 93] gave grounds for the assumption that all these alkaloids are formed by a common biosynthetic route from a solanidine derivative activated at C-12, and then via veraflorizine.



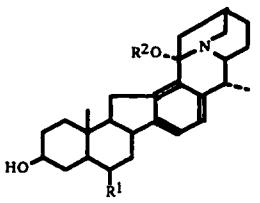
Solanidine

Veraflorizine

Verticine $R^1 = R^4 = OH$, $R^2 = R^3 = H$
Verticinone $R^1 = OH$, $R^2 = H$, R^3, $R^4 = O$
Baimonidine $R^1 = R^4 = H$, $R^2 = R^3 = OH$
Isoverticine $R^1 = R^3 = OH$, $R^2 = R^4 = H$
Isobaimonidine $R^1 = R^3 = H$, $R^2 = R^4 = OH$

The C-3α-OH epimers were detected mainly in the epigeal parts and the C-3β-OH epimers in the tubers. However, it is still early to speak of any common relationship whatever in relation to this question: this is obviously only a special case since, for example, both α- and β- isomers at C-3 and C-6 have been detected in equal degree in the epigeal part of the plant *Korolkowia sewerzowii*, chemotaxonomically related to *Fritillaria* [94].

Four alkaloids possessing an unusual seven-membered ring skeleton have been isolated from the plant *Fritillaria ussuriensis* Maxim. [95]:

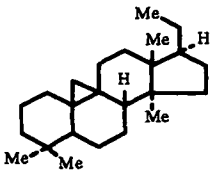


Ussurienine R^1 = βOH, R^2 = Me
Ussurienone R^1 = O, R^2 = Me
Ussuriedine R^1 = βOH, R^2 = H
Ussuriedinone R^1 = O, R^2 = H

That is, in addition to the cevanine skeleton, a carbon—carbon bond between C-18 and C-27 forms ring *G*. Thus, rings *E*, *F*, and *G* are combined into a tricyclo[4.4.0.$1^{4,7}$]-6-azaundecane partial structure. The formation of the tricyclic ring system requires that rings *E* and *F* should have a *cis*-quinolizidine structure in which the unshared pair of electrons of the nitrogen atom and H-22 are in the α-orientation. According to results on the biosynthesis of the cevane alkaloids, the C-18 and C-27 carbon atoms are inactive participants and are positioned remotely from one another. Consequently, the C-18—C-27 bond is a unique example in the biosynthesis of modified steroid alkaloids.

The alkaloid heilonine (**44**, Table 1) isolated from the same plant possesses a structure close to that of ussuriedine but without the C18—C-27 bond, while the unshared electron pair of the nitrogen is in the opposite orientation to H-22. Obviously, therefore, heilonine cannot be considered as an intermediate compound in the biosynthesis of alkaloids of the ussuriedine type, but it must undoubtedly be a key compound in this biosynthesis.

Buxus plants produce an unusual class of steroid alkaloids, unique in this genus. About 200 bases have been isolated from various species of the genus. Systematic comparative studies of the *Buxus* alkaloids known at the present time have shown that they all possess a fundamental skeleton known as buxane and can be characterized as derivatives of this system [21]:

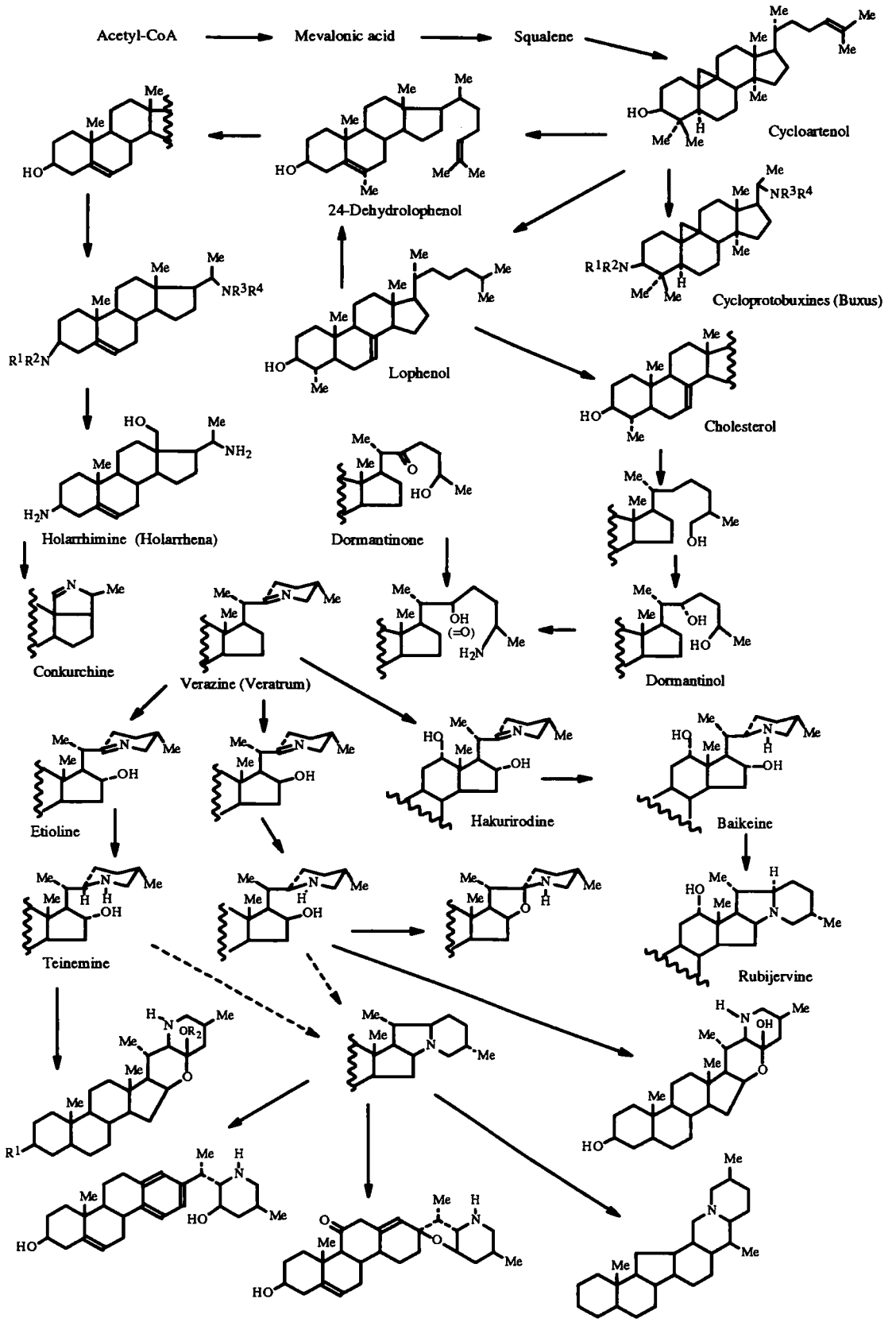


The biosynthesis of steroid alkaloids in plants of the Apocynaceae family and of some Buxaceae genera (*Sarcocca* and *Pachysandra*) is apparently connected with the biogenesis of steroid derivatives of pregnanes — in particular, pregnenolone. Progesterone and pregnenolone have also been isolated from the leaves of *Holarrhena floribunda*, and it has been shown that pregnenolone is a precursor of holaphyllamine (β-aminopregn-5-en-20-one) and of holamine (α-aminopregn-5-en-20-one) just as it is of conessine [96].

The *Buxus* alkaloids are obviously derivatives of 4,4,14α-trimethyl-9β,19-cyclo-5α-pregnanes. Since, in plants, cycloartenol apparently plays a role equivalent to that of lanosterol in animal tissues, it is quite logical to assume that the *Buxus* alkaloids take their origin directly from cycloartenol via cycloprotobuxines (scheme).

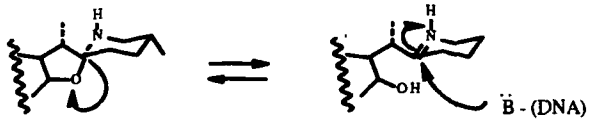
Thus the scheme shows with an adequate degree of probability the pattern of the biosynthesis of steroid alkaloids of plants of the families Apocynaceae, Buxaceae, Malvaceae, Melanthiaceae, Liliaceae, and Solanaceae that has been drawn up at the present time on the basis of experimental facts and theoretical conclusions. Thereby a taxonomic link has also been revealed between the plants of these families.

So far as concerns the steroid alkaloids of the animal kingdom, the biogenesis of the salamander alkaloids has already been discussed in the literature [96, 97], while the more complex dimeric steroid alkaloids of marine organisms are still under study.



Scheme of the Biosynthesis of Steroid Alkaloids in Plants

The biological activity of steroid alkaloids has been studied for a long time and successfully [94—99]. In recent years, in the course of investigations of the alkaloids of *Solanum umbelliferum* it was found that the alkaloids solasodine and O-acetylsolasodine possess DNA-damaging activity in relation to yeast cells, and the hypothesis has been expressed that this may be due to the presence of an spiro-aminoacetal function in the steroid moiety. This group my be opened up, forming an electrophilic radical capable of alkylating DNA [64]:



At the same time, solasodine 3-O-β-*D*-glucopyranoside does not possess this property, which is obviously connected with the fact that such molecules are incapable of passing through the yeast cell wall.

And, finally, it must be mentioned that in recent years investigations of steroid alkaloids have been conducted to an increasing extent by the screening method, namely: voluminous chemical studies are conducted in parallel with biochemical and biological investigations and they are all linked up into a single system which is the object of the study of chemical ecology.

REFERENCES

1. M. M. Telitchenko and S. A. Ostroumov, *Introduction to Problems of Biochemical Ecology* [in Russian], Nauka, Moscow (1990).
2. *BSÉ* [*Great Soviet Encyclopaedia*] [in Russian], Vol. **29** (1978), p. 597.
3. J. B. Harborne, *An Introduction to Ecological Biochemistry*, Academic Press, London (1977) [Russian translation, Mir, Moscow (1985, p. 312].
4. Atta-ur-Rahman and A. Muzaffar, in: *The Alkaloids* (ed. A. Brossi), Academic Press, San Diego, Vol. **32** (1988), p. 79.
5. D. M. Harrison, *Nat. Prod. Rep.*, **27**, 139 (1990);
6. R. Schakirov [Shakirov] and M. S.Yunusov, *Nat. Prod. Rep.*, **27**, 557 (1990).
7. B. N. Orlov, D. B. Gelashvili, and A. K. Ibragimov, *Poisonous Animals and Plants of the USSR* [in Russian], Vysshaya Shkola, Moscow (1990), p. 272.
8. S. M. Shuraeva and L. M. Safronova, Byul. Glav. Botan. Sada, **168**, 101 (1993).
9. S. Begum, S. B. Usmani, B. S. Siddiqi, and S. Siddiqi, *Phytochemistry*, **36**, 1537 (1994).
10. S. Siddiqi and B. A. Shamsuttdin, *J. Sci. Ind. Res.*, **32**, 1 (1989).
11. K. K. Bhutane, R. M. Vaid, M. Ali, R. Rapoor, S. R. Soodan, and D. Kumar, *Phytochemistry*, **29**, 969 (1990).
12. Atta-ur-Rahman, M. Alam, H. Nasir, and E. Y. A. Dagne, *Phytochemistry*, **29**, 1293 (1990).
13. Atta-ur-Rahman, Z. Igbal, M. I. Choudhary, and F. Talat, *Heterocycles*, **31**, 493 (1990).
14. Atta-ur-Rahman, Z. Igbal, and M. I. Choudhary, *J. Nat. Prod.*, **53**, 319 (1990).
15. M. I. Choudhary, Atta-ur-Rahman, and M. Shamma, *Phytochemistry*, **27**, 1561 (1988).
16. Atta-ur-Rahman, Z. Igbal, M. Alam, M. I. Choudhary, N. H. Igbal, and F. Talat, *Phytochemistry*, **29**, 683 (1990).
17. Atta-ur-Rahman, M. Alam, and M. I. Choudhary, *Phytochemistry*, **27**, 3342 (1988).
18. Atta-ur-Rahman, *Pure and Appl. Chem.*, **61**, 453 (1989).
19. Atta-ur-Rahman, A. Serfan, D. Ahmed, S. Bilge, and T. Sogul, *J. Nat. Prod.*, **52**, 1319 (1989).
20. Atta-ur-Rahman, D. Ahmed, M. Choudhary, B. Sener, and S. Turkoz, *Fitoterapia*, **26**, 439 (1989).
21. Atta-ur-Rahman, D. Ahmed, E. Asif, S. A. Gamal, M. I. Choudhary, B. Sener, and S. Turkoz, *Phytochemistry*, **30**, 1295 (1991).
22. B. U. Khodzhaev, M. R. Khodzhaeva, and Kh. Ubaev, *Khim. Prir. Soedin.*, 907 (1993).
23. M. Qui, R. Nie, Z. Li, and J. Zhou, *Acta Bot. Sin.*, **32**, 626 (1990).
24. M. Qui, C. He, R. Nie, and Q. Zheng, *Zhou Jun, Yunnan Zhiwu Yanjiu*, **12**, 111 (1990); *Chem. Abstr.*, **113**, 148873j (1990).
25. M. Qui, Z. Li, D. Cao, and R. Nie, *Zhiwu Xuebao*, **35**, 885 (1993); *Chem. Abstr.*, **121**, 78257a (1994).
26. Y. Mimaki and Y. Sashida, *Chem. Pharm. Bull.*, **38**, 1090 (1990).

27. Atta-ur-Rahman, A. Faroog, M. I. Choudhary, A. H. Gilani, F. Shaheen, R. A. Ali, F. Noor-e-ain, and B. Sener, *Planta Med.*, **60**, 377 (1994); *Chem. Abstr.*, **121**, 226438c (1994).
28. Y. J. Xu, D. M. Xu, D. B. Cui, J. S. Gao, E. X. Huang, S. Y. Liu, and D. Q. Yu, *Yaoxue Xuebao*, **29**, 200 (1994).
29. P. Li, X. G. Li, G. J. Xu, and K. Kaneko, *J. China Pharm. Univ.*, **21**, 198 (1990).
30. G. Lin, J.-P Ho, P. Li, and X. G. Li, *J. Nat. Prod.*, **58**, 1662 (1995).
31. J. Zhang, A. Lao, and R. Xu, *Zhiwu Xuebao*, **35**, 238 (1993); *Chem. Abstr.*, **120**, 129485n (1994).
32. Y. Kitamura, K. Kaneko, M. Shiro, Yuh-Pan Chen, Hong-Yen Hsu, Ping Lee, and Guo-Jun Xu, *Chem. Pharm. Bull.*, **37**, 1514 (1989).
33. Shichun Yu and Peigen Xiao, *Zhongcaoyao*, **21** 2 (1990); *Chem. Abstr.*, **113**, 112481r (1990).
34. D. M. Xu, M. L. Xu, S. Q. Wang, E. X. Hung, X. G. Wen, S. Arihara, and N. Shoji, *J. Nat. Prod.* , **53**, 549 (1990).
35. Y. Kitamura, M. Nishizawa, and K. Kaneko, *Tetrahedron Lett.*, **30**, 37, 4891 (1989).
36. D. M. Xu, C. H. He, S. Q. Wang, E. X. Huang, M. L. Xu, Y. X. Zhang, and X. G. Wen, *Yaoxue Xuebao*, **23**, 902 (1988).
37. D. M. Xu, C. H. He, S. Q. Wang, E. X. Huang, M. L. Xu, and X. Y. Wen, *Yaoxue Xuebao*, **25**, 127 (1990).
38. Y. Kitamura, M. Nishizawa, K. Kaneko, M. Shiro, Yuh-Pan Chen, and Hong-Yen Hsu, *Tetrahedron*, **45**, 7281 (1989).
39. Jian-Xing Zhang, Ai-na Lao, and Rensheng Xu, *Zhiwu Xuebao*, **35**, 963 (1993).
40. W. H. Xu and Z. Xue, *Yaoxue Xuebao*, **23**, 61 (1988).
41. U. T. Shakirova and R. Shakirov, *Khim. Prir. Soedin.*, 524 (1994).
42. B. Tashkhodzhaev, S. Nasirov, A. Nabiev, R. Shakirov, K. Samikov, and M. R. Yagudaev, *Khim. Prir. Soedin.*, 384 (1991).
43. A. K. Choudhary, B. C. Sen, M. F. Hashim, and M. Ahmed, *Pharmazie*, **48**, 628 (1993).
44. V. E. Sokolov, *Madagascar* [in Russian], Progress, Moscow (1990).
45. A. Charkravarty, B. Das, and S. J. Mekhopadhyay, *J. Nat. Prod.*, **55**, 965 (1992).
46. M. I. Choudhary, B. Sener, and S. Turkoz, *Phytochemistry*, **30**, 368 (1991).
47. Atta-ur-Rahman, Rahat Azhar Ali, G. Anwar-l-Hassan, M. I. Choudhary, K. Aftab, B. Sener, and S. Turkoz, *Planta Med.*, **59**, 969 (1993).
48. R. Shakirov, V. V. Kul'kova, and I. Nakhatov, *Khim. Prir. Soedin.*, 100 (1995).
49. W. Zhao, Y. Tezuka, T. Kikuchi, J. Chen, and Y. Guo, *Chem. Pharm. Bull.*, **37**, 2920 (1989).
50. W. Zhao, Y. Tezuka, T. Kikuchi, J. Chen, and Y. Guo, *Chem. Pharm. Bull.*, **39**, 549 (1991).
51. M. Mizuno, Ren-Xiang Tan, Pei Zhen, Zhi-Da Min, M. Iinuma, and T. Tanaka, *Phytochemistry*, **29**, 359 (1990).
52. H. Ripperger and A. Porzel, *Phytochemistry*, **35**, 813 (1994).
53. P. F. Coll, M. I. Rodriguez, C. Perez, and G. Adam, *Rev. Cubana Quim.*, **6**, 66 (1992).
54, H. Ripperger and A. Porzel, *Phytochemistry*, **30**, 1299 (1991).
55. H. Ripperger, *Phytochemistry*, **29**, 3375 (1990).
56. A. K. Chakravarty and S. C. Pakrashi, *Phytochemistry*, **27**, 956 (1988).
57. A. K. Chakravarty and S. C. Pakrashi, *Indian J. Chem., B*, **27**, 311 (1988).
58. G.-N. Lin, C.-M. Lu, M.-K. Cheng, and K.-H. Gan, *J. Nat. Prod.*, **53**, 513 (1990).
59. S. F. Osman, S. L. Sinden, P. Irwin, K. Deahl, and W. M. Tingey, *Phytochemistry*, **30**, 3161 (1991).
60. W. Dopke, S. Duday, and N. Matos, *Z. Chem.*, **28**, 185 (1988).
61. R. Puri, T. C. Wong, and R. K. Puri, *J. Nat. Prod.*, **57**, 587 (1994).
62. Y. Tomoyuki, F. Nobuyo, Y. Shoji, N. Toshiro, K. Syuji, and F. Kunimitsu, *Chem. Pharm. Bull.*, **38**, 827 (1990).
63. A. Maxwell, M. Seepersoud, R. Pingal, D. R. Mootoo, and W. F. Reynolds, **58**, 625 (1995).
64. J. C. Kim, Q. M. Che, A. A. Z. Gunatilaka, and D. G. I. Kingston, *J. Nat. Prod.*, **59**, 283 (1996).
65. J. Jurek, P. J. Scheuer, and M. Kelly-Borges, *J. Nat. Prod.* , **57**, 1004 (1994).
66. S. Fukuzawa, S. Matsunaga, and N. Fusetani, *J. Org. Chem.*, **59**, 6164 (1994).
67. S. Fukuzawa, S. Matsunaga, and N. Fusetani, *J. Org. Chem.*, **60**, 608 (1995).
68. G. R. Pettit, M. Inoue, Y. Kamano, D. L. Herald, C. Arm, C. Dufresne, N. D. Christie, J. M. Schmidt, D. L. Doubek, and T. S. Krupa, *J. Am. Chem. Soc.*, **110**, 2006 (1988).

69. G. R. Pettit, M. Inoue, Y. Kamano, C. Dufresne, N. Christie, M. L. Niven, and D. L. Herald, *J. Chem. Soc., Chem. Commun.*, 865 (1988).
70. G. R. Pettit, Y. Kamano, C. Dufresne, M. Inoue, N. Christie, J. M. Schmidt, and D. L. Doubek, *Can. J. Chem.*, **67**, 1509 (1989).
71. E. Novacki, M. Jurrysta, and P. A. Gorski, *Biochem. Physiol. Plants*, **169**, 1030 (1976).
72. K. G. Ramaval, M. Rideau, and J. Chenieux, *Phytochemistry*, **24**, 441 (1988).
73. L. N. Bereznegovskaya, *Rastit. Resurs.*, **19**, 370 (1983).
74. O. A. Gorelova and V. Rzherzhabek, *Dokl. Akad. Nauk SSSR*, **279**, 253 (1984).
75. P. M. Frischknecht and T. W. Baumann, *Phytochemistry*, **25**, 2255, (1985).
76. H. Ripperger and K. Schreiber, in: *The Alkaloids* (ed. R. H. F. Manske and R. G. A. Rodrigo), Academic Press, New York, Vol. **XIX** (1981), p. 81.
77. L. N. Bereznegovskaya, *Biologicheskie Nauki*, 17 (1988).
78. K. Schreiber in: *The Alkaloids* (ed. R. H. F. Manske), Academic Press, New York, Vol, **X** (1968), p. 117.
79. R. B. Herbert, in: *The Alkaloids* (ed. M. F. Grundon), Royal Society of Chemistry, London , Vol. **9** (1979), p. 27.
80. K. Kaneko, M. W. Tanaka, and H. Mitsuhashi, *Phytochemistry*, **16**, 1247 (1977).
81. L. Canonica, F. Ronchetti, G. Russo, and G. Sportoletti, *J. Chem. Soc., Chem. Commun.*, 286 (1977).
82. R. Tschesche and H. R. Brennecke, *Phytochemistry*, **19**, 1449 (1980).
83. S. F. Osman, S. L. Sinden, P. Irwin, K. Deahl, and W. M. Tingey, *Phytochemistry*, **30**, 3161 (1991).
84. F. Coll, A. Preiss, M. Bastereschea, J. L. Mola, and G. Adam, *Phytochemistry*, **22**. 2099 (1983).
85. F. Coll, A. Preiss, M. Bastereschea, L. Kutschabsky, J. L. Mola, K. Schreiber, and G. Adam, *Phytochemistry*, **23**, 883 (1984).
86. K. Kaneko, U. Nakaoka, M. Tanaka, H. Yoshida, and N. Mitsuhashi, *Phytochemistry*, **20**, 157 (1981).
87. K. Kaneko, M. Tanaka, U. Makaoka, Y. Tahaka, N. Yoshida, and H. Mitsuhashi, *Phytochemistry*, **20**, 327 (1981).
88. S. F. Osman, in: *Isoprenoids in Plants* (ed. W. D. Nes, G. Fuller, and L.-S Tsoi), Marcel Dekker, New York (1984), p. 519.
89. G. J. Bird, D. J. Collins, F. W. Eastwood, and J. M. Swan, *Aust. J. Chem.*, **32**, 611 (1979).
90. K. Kaneko, M. Watanabe, S. Taira, and H. Mitsuhashi, *Phytochemistry*, **11**, 3199 (1972).
91. Y. Sashida, Y. Mimaki, and S. Shimomura, *Chem. Lett.*, 897 (1989).
92. K. Kaneko, M. Tanaka, K. Haruki, N. Naruse, and H. Mitsuhashi, *Tetrahedron Lett.* , 3737 (1979).
93. K. Kaneko, N. Naruse, R. Haruki, and H. Mitsuhashi, *Chem. Pharm. Bull.*, **28**, 1345 (1980).
94. V. V. Kul'kova, *Author's Abtract of Dissertation ... Candidate of Chemical Science* [in Russian], Tashkent (1995).
95. Y. Kitamura, M. Nishizawa, and K. Kaneko, *Tetrahedron*, **45**, 5755 (1989).
96. R. Goutarel, in *The Alkaloids* (ed. J. E. Saxton), The Chemical Society, Burlington House, London, Vol. **1** (1971), p. 382.
97. G. Habermehl, in: *The Alkaloids* (ed. R. H. F. Manske), Academic Press, New York, Vol. **IX** (1967), p. 436.
98. T. P. Anatsulova and S. M. Nikolaev, *Rastit. Resurs.*, **27**, 75 (1991).
99. Yu. R. Mirzaev, K. Samikov, R. Shakirov, V. V. Kul'kova, D. U. Abdullaeva, and F. N. Dzhakhangirov, *Kimë va Farmatsiya*, No. 4, 62 (1996).