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金丝矮陀陀植物中甾体生物碱的分离与化学结构

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Isolation and Chemical Structures of Steroidal Alkaloids from Pachysandra Axillaris FRANCH

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Abstract: The chemical structures of steroidal alkaloids isolated from Bachysandra terminalis have been studied by Professor Kikuchi at Kyoto University, these alkaloids were called Pachysandra alkaloids.[1] Recently, we have studied the steroidalalkaloids from *pachysandra axillaris* collected in Yunnan of CHINA.

By means of systematic isolation, 22 steroidal alkaloids were isolated in crystalline form from the 95% EtOH extracts of *P. axillaris*. The basic characteristics of these compounds are listed in Tab 1. Their chemical structures were elucidated based on IR, UV, NMR MS, spectra and chemical evideces, and are shown in Tab 1. All the compounds belong to steroidal alkaloids of pregnane type, 17 of which, i.e. *iso*-spiropachysine (**2**), spiropachysine B (**3**), pachyaximine A, B (**17**, **18**), axillarine A-F (**21**, **20**, **13**, **14**, **10**, **15**), pachysamine H, G(**5**, **7**), pachysanaximine A (**12**), axillaridine A (**16**), pachyaxioside A, B (**11**, **19**) and *epi*-pachysamine B (**8**), are natural products reported for the first time. The detail of the isolation and characterization of these new compounds shall be reported elsewhere.

Descriptor: steroidal alkaloid, natural products, chemical structure

最近，我们研究了云南产的金丝矮陀陀植物中的甾体生物碱。对植物样品的乙醇提取物作了系统分离，从中得到22个甾体生物碱，其基本物理性质列于表1。这些化合物经IR、UV、NMR和MS等光谱分析，并通过一些化学转化确定了它们的化学结构(见图)。在这些化合物中，异螺旋富贵草碱(**2**)，螺旋富贵草碱B(**3**)，矮陀陀胺碱A，B(**17**，**18**)，矮陀陀碱A-F(**21**，**20**，**13**，**14**，**10**，**15**)，富贵草碱H，G(**5**，**7**)，矮陀陀酯碱A(**12**)，矮陀陀酰胺碱A(**16**)，矮陀陀甙A，B(**11**，**19**)为首次报道的新天然产物。表富贵草碱B(**8**)为^{13}C NMR检出的新成分。本文先报道它们的化学结构，推证及光谱数据以后将另行报道。

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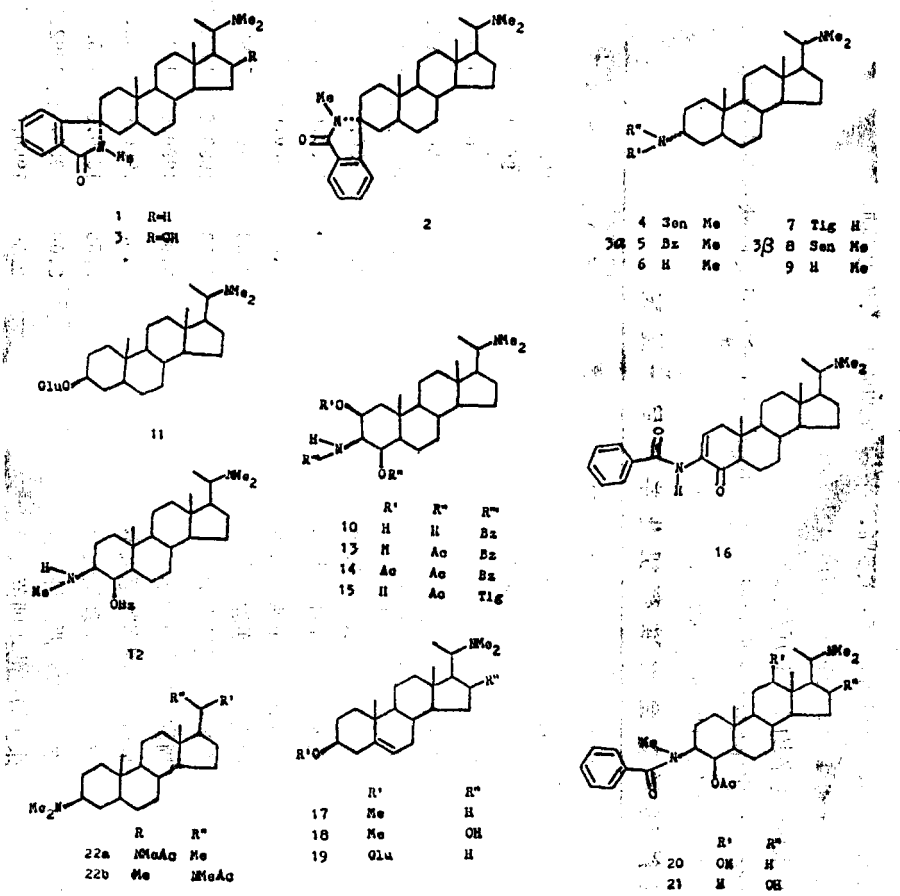
Tab 1. Properties and Yields of Steroidal Alkaloids 1～22 b

Compds.	Formula	m.p.(℃)	$(\alpha)_D$ (°, $CHCl_3$)	Yield(%)	^1H NMR characteristic signals (δ, ppm) 18,	19,	21-Me(J Hz)	other protons
spiropachysine(1)	$C_{31}H_{46}ON_2$	278～280	+34.9	0.10	0.678,	1.079,	0.878(6.4),	3.380(NMe)
iso-spiropachysine(2)	$C_{31}H_{46}ON_2$	297～298	+39.7	0.00045	0.696,	0.974,	0.900(6.4),	3.045(NMe)
spiropachysine B(3)	$C_{31}H_{46}O_2N_2$	294～296	+31.5	0.00027	0.909,	1.018,	0.955(6.4),	3.376(NMe), 4.332(16-H)
pachyaximine A(17)	$C_{24}H_{41}NO$	139～141	−45.5	0.011	0.691,	1.00,	0.989(6.5),	3.35(OMe), 3.08(3-H)
pachyaximine B(18)	$C_{24}H_{41}NO_2$	184～186	−48.2	0.00067	0.892,	1.014,	0.950(6.4),	3.357(OMe), 3.072(3-H)
axillarine E(10)	$C_{30}H_{46}N_2O_3$	285～290		0.00067				
axillarine C (13)	$C_{32}H_{46}N_2O_4$	272～274	+22.4	0.0029	0.654,	1.257,	0.867(6.2),	5.434(4-H),4.140(2-H), 4.254(3-H)
axillarine D(14)	$C_{34}H_{50}N_2O_5$	223～225	+11.6	0.00018	0.646,	1.168,	0.916(6.3),	5.342(4-H),5.260(2-H), 4.452(3-H)
axillarine F (15)	$C_{30}H_{50}N_2O_4$	241～244	+29.5	0.00011	0.644,	1.224,	0.865(6.2),	5.340(4-H), 4.045(2-H), 4.101(3-H)
axillarine B(20)	$C_{33}H_{50}N_2O_4$	233～234	+65.2	0.00011	0.708,	0.708,	1.126(7.1),	5.370(4-H, 2.921(NMe), 3.229(12-H)
axillarine A (21)	$C_{33}H_{50}N_2O_4$	256～258	+77.7	0.016	0.862,	0.862,	0.932(6.4),	5.378(4-H),2.926(NMe), 4.303(16-H)
pachysamine B(4)	$C_{29}H_{50}N_2O$	171～173	+67.2	0.0014	0.651,	0.809,	0.866(6.3),	1.863, 1.821(C=CMe$_2$), 5.784(C=C—H)
pachysamine H(5)	$C_{31}H_{48}N_2O$	159～153	+57.4	0.00016	0.642,	0.734,	0.872(6.3),	3.087(OMe)
pachysamine G (7)	$C_{28}H_{48}N_2O$	205～206	+11.4	0.0058	0.642,	0.795,	0.870(6.3),	6.389(=C—H,)5.689(NH)
pachysanaximine A (12)	$C_{31}H_{48}N_2O_2$	195～196	+27.9	0.00033	0.643,	0.933,	0.853(6.4),	5.331(4-H), 4.053(NH)
axillaridine A (16)	$C_{30}H_{42}N_2O_2$	223～224	+51.3	0.016	0.648,	0.901,	0.872(6.4),	8.646(NH), 7.805(2-H)
epi-pachysamine A (22a)	$C_{26}H_{46}N_2O$	203～204	−11.7	0.00056	0.726,	0.769,	1.153(6.7),	2.032(NCH_3O),2.778(NMe)
(22b)	$C_{26}H_{46}N_2O$				0.779,	0.758,	1.072(6.6),	2.105(NCH_3O),2.732(NMe)
epi-pachysamine B (8)	$C_{29}H_{50}N_2O$				0.643,	0.708,	0.870(6.3),	5.557(C=C—H)
pachysamine A (9)	$C_{24}H_{44}N_2$	148～153	+15.6	0.0010	0.636,	0.792,	0.854(6.4),	2.710(NH, 2.384(NMe)
pachysamine I (6)	$C_{24}H_{44}N_2$	200	+25.0	0.00027	0.651,	0.804,	0.928(6.3),	3.153(NH), 2.613(NMe)
pachyaxioside A (11)	$C_{29}H_{51}NO_6$	258～261	+14.8	0.00036	0.607,	0.696,	0.854(6.1),	5.101(1′-H)
pachyaxioside B (19)	$C_{29}H_{49}NO_6$	245～248	−43.5	0.00024	0.624,	0.936,	0.861(6.2),	5.101(1′-H)



Bz = benzoyl　Tig = tiglyl　Sen = senecioyl　Glu = β-D-glucopyranosyl

叙词： 甾体生物碱，天然产物，化学结构

参 考 文 献

[1] Saxton J. E., Battersby A. R., *"The Alkaloids (A Specialist Periodical Report)"*, Burlington House, London, 1971, Vol. 1, p. 428.

上图更正

	R′	R″
22a	$N(CH_3)COCH_3$	Me
22b	$N(CH_3)COCH_3$	Me