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滇重楼地上部分的两个微量皂甙

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摘要 从滇重楼(*Paris polyphylla* var. *yunnanensis*)地上部分中分离出两个新的微量的甾体皂甙 polyphylloside Ⅲ和Ⅳ, 根据化学降解和光谱分析, 它们的化学结构分别为 27-羟基-偏诺皂甙元-3-O-[α-L-鼠李吡喃糖基(1→2)][α-L-鼠李吡喃糖基(1→4)-α-L 鼠李吡喃糖基(1→4)]-β-D-葡萄吡喃糖甙(polyphylloside Ⅲ), 23β,27-二羟基-偏诺皂甙元-3-O-[α-鼠李吡喃糖(1→2)][α-L-鼠李吡喃糖基(1→4)-α-L-鼠李吡喃糖基(1→4)]-β-D-葡萄吡喃葡萄糖甙(polyphylloside Ⅳ).

关键词 滇重楼, 延龄草科, 甾体皂甙

皂甙, 化学成分, 百合科

TWO MINOR STEROIDAL SAPONINS FROM THE AERIAL PARTS OF PARIS POLYPHYLLA VAR. YUNNANENSIS

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Abstract Two new minor steroidal saponins polyphylloside Ⅲ and Ⅳ were isolated from the aerial parts of *Paris polyphylla* var. *yunnanensis*. On the basis of chemical and spectroscopic analysis, their structures were established as 27-hydroxyl-pennogenin 3-O-[α-L-rhamnopyranosyl (1→2)][α-L-rhamnopyranosyl (1→4)-α-L-rhamnopyranosyl (1→4)]-β-D-glucopyranoside and 23β, 27-dihydroxyl-pennogenin 3-O-[α-L-rhamnopyranosyl(1→2)][α-L-rhamnopyranosyl(1→4)-α-L-rhamnopyranosyl (1→4)]-β-D-glucopyranoside, respectively.

Key words *Paris polphylla* var. *yunnanensis*, Triliaceae, Steroidal saponins

"Chonglou"as a famous folk medicinal herb in the south of China have been used not only as an antibiotic and anti-inflammatory drug but also to treat injuries from falls, fractures, parotitis, mastitis and snake bite as well as to stop bleeding. There are several species of the genus *Paris* (Triliaceae) were used as original materials of "Chonglou". In the previous paper [1—8], we reported the isolation and structure elucidation of new steroidal saponins from several plants of *Paris* and found that some of them with interesting hemostatic and antitumor activity. As the part of systmatic study on the chemotaxonomy of this genus, we now report the structures of two new minor steroidal saponins from the aerial

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part of *P polyphylla* Smith var. *yunnanensis* (Fr) Hand.-Mazt.

RESULTS AND DISCUSSION

The crude saponins were subjected to column chromatography on silica gel, reversed phase RP-18 and highly porous polymer resin MCI gel HP-20P, yielded polyphylloside Ⅲ (1) and Ⅳ (2), both of which were predicted to be spirostanol glycosides by the usual colour test and IR spectra.

Table 1 ^{13}C NMR Chemical shifts of aglycons compounds 1-8 (δ,ppm, Py-d_5)

C	1	3	5	2	4	6	7	8
1	37 6	37.9	36.9	37.5	37.1	37 0	37.4	37 5
2	30.2	32.6	32.0	30.1	32.9	31.9	32.4	30.2
3	78 3	71.4	72.8	78.1	71.3	73.8	71.2	78.2
4	39.0	43.5	38.4	38.7	43.5	38.1	43.4	38.7
5	140.9	142.1	140 2	140.7	142.0	139.7	142.0	140.8
6	121.8	121 1	121.9	121.7	121.0	122.2	121.0	121.8
7	32.1	31.8	31.6	32 4	32.4	31.4	32.2	32.5
8	32.4	32.5	31.2	32.4	32.5	31.7	32.4	32.6
9	50.3	50.5	49.7	50.2	50.4	49.5	50.4	50.3
10	37.2	37.1	37.1	37.1	37.1	37.2	37.0	37.2
11	21.0	21.1	20 9	20.9	21.1	20.5	21.0	20.9
12	32.5	32.5	29.5	32.3	32.5	28.1	32.4	32.2
13	45.1	45.4	43.9	45.8	45.8	44.5	44.8	44.9
14	53.1	53 2	52.8	53.1	53.3	52 6	53.2	52.7
15	31.8	31.8	31.5	31.7	31.9	31.1	31.8	32.4
16	90.2	90 2	91.0	90.8	91.0	90.8	90.0	90.1
17	90.2	90.1	90.1	90.0	90.1	90.8	90.0	90.0
18	17 1	17.2	17.1	17.3	17 5	16.6	17.2	17.2
19	19.4	19 7	19.3	19.3	19.6	19.3	19 6	19.4
20	44.9	45.2	44.5	40.2	40.5	38.9	45.2	45.1
21	9.6	9 6	8.1	9.1	9.3	7.7	9.5	9.5
22	110.3	110.4	110.2	112.5	112.7	109.3	109.2	109.9
23	32.1	32.2	32.2	67.9	68.1	67.9	32.6	31.9
24	23 6	23.6	22.6	32.9	33.2	27.7	29.3	29.7
25	39.0	39.1	34 9	38.9	38.9	35.4	30.6	30.3
26	64 0	64.0	61.6	63.1	63.2	61.9	66.7	66.7
27	64 4	64.4	65.8	63.9	64.0	64.7	17.3	17.4
			170.5			170.9		
$COOCH_3$			170.2			170.5		
						170.3		
			20.5			21.1		
$COOCH_3$			20.4			20.8		
						20.5		

(5 and 6, δ, $CDCl_3$)

On hydrolysis with hydrochloric acid, saponin 1 yield an aglycone (3) and sugar constituents were identified by TLC and PC as D-glucose and L-rhamnose in a ratio of 1:3. Compound 3 has the molecular formula $C_{27}H_{42}O_5$ by EI-MS spectrum. The ^1H NMR spectrum of 3 was very similar to that of pennogenin (7), but the singlet due to the C_{27}-CH_3 was missing signals corresponding to a primary

hydroxylgroup. The ^{13}C NMR spectrum of 3 (Table 1) confirmed this by the presence of signal at δ 65.8(t) which corresponded to the primary hydroxyl carbon and the signals ascribable to C−24, C−25 and C−26 were shifted by −6.7, +4.3, −5.1ppm respectively. ^1H NMR of diacetata (5) of 3 showed δ3.74(1H, dd, J=5.2, 11.0Hz, H−26α), 3.91(1H, t, J=11.2Hz, H−26β) which were assignable H−25 to be axial conformation, the C−25 is D−configuration. On the basis of these data, 3 was concluded to 25D−spirost−5−ene−3β, 17α, 27−triol.

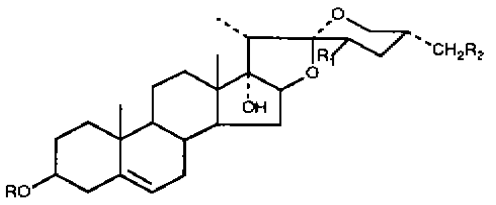
The positive ion FAB mass spectrum of 1 showed a quasi molecular ion peak at m/z 1047$[M+H]^+$ and fragment ions at m/z 899$[M-hexose]^+$, and 752$[M-2\ hexose]^+$. The EI−mass spectrum of acetate of 1 showed a fragment ion peak at m/z 273$[rhamnose\ (OAc)_3]^+$. The ^{13}C NMR spectrum of 1 exhibited four anomeric carbon signals at δ100.4, 102.1, 102.3 and 103.2 and the all of chemical shifts for sugar moieties were fully super overlapped with those of saponin Ⅷ(8)[2]. The glycosylation shift effect lead to the C−3 position of aglycone was downfield shifed from δ71.4 to δ78.3. Based on the above evidence, the structure of 1 was elucidated as 27−hydroxyl−pennogenin−3−O−[α−L−rhamnopyranosyl(1→ 2] [α−L−rhamnopyranosyl (1→ 4)α−L−rhamnopyranosyl (1→ 4)] −β−D−glucopyranoside.

Table 2 ^{13}C NMR chemical shifts of sugar moieties (in pyridine−d_5, δ, ppm)

Sugar−C		1	2	8	Sugar−C		1	2	8
Glc.					Rha.				
(inner)	1	100.4	100.3	100.3	(inner)	1	102.3	102.1	102.4
	2	80.4	80.2	80.4		2	73.2	73.0	73.3
	3	76.9	76.8	76.8		3	72.8	72.7	73.1
	4	78.3	78.1	78.2		4	78.1	78.0	78.1
	5	77.7	77.6	77.9		5	68.4	68.3	68.4
	6	61.4	61.2	61.4		6	18.7	18.5	18.7
Rha.					Rha.				
(terminal)	1	102.1	102.1	102.1	(terminal)	1	103.2	103.1	103.5
	2	72.8	72.7	72.8		2	72.8	72.7	73.0
	3	72.4	72.3	72.7		3	72.6	72.4	72.8
	4	74.1	74.0	74.1		4	74.0	73.8	73.7
	5	69.5	69.4	69.4		5	70.3	70.2	69.7
	6	18.4	18.3	18.6		6	18.8	18.7	18.9

Saponin 2 gave a aglycone (4) and D−glucose and L−rhamnose in a ration of 1:3 as sugar components under mineral acid hydrolysis. The molecular ion of compound 4 was at m/z 462$[M(C_{27}H_{42}O_6]^+$by EI−MS spectrum. It suggested that 4 had one more hydroxy group than that of 3. 4 afforded a triacetate (6) when acetylated with usually method. ^1H NMR spectrum of 6 is similary with that of 5. The difference of chemical shift only on the F ring. In the case of 6, a triplet at δ3.55 (J=11.2Hz, H−26α) and a double doublet at δ3.65(J=3.6Hz, 11.0Hz H−26β) were assignable and vicinal to 25β(axial)−H. Double doublets at δ4.88 was ascribable to a proton germinal to the acetoxy group. Its coupling constants J=5.0 and 11.8Hz) were understandable that this proton should be located at C−23 with α(axial) configuration. The ^{13}C NMR chemical shifts showed a downfield shift (+2.4ppm) for C−22 and an upfield shift for the C−20 (−4.7ppm) due to the γ−gauche effect which conforming the −CH−OH should attach to C−23. On the basis of above the structure of 4 was concluded to be 25D−23β, 27−dihydroxyl−pennogenin. Since the ^{13}C NMR signals of sugar moieties almost identical with those of 1 in the sugar residue, the structure of 2 was

elucidated as 23β, 27-dihydroxyl-pennogenin-3-O-[α-L-rhamnopyranosyl (1 → 2)][α-L-rhamnopyranosyl (1 →4)-α-L-rhamnopyranosyl (1→4)]-β-D-glucopyranoside.



	R	R_1	R_2
1	S	-H	-OH
2	S	-OH	-OH
3	-H	-H	-OH
4	-H	-OH	-OH
5	-OAc	-H	-OAc
6	-OAc	-OAc	-OAc
7	-H	-H	-H
8	S	-H	-H

S= -glc(2—1) rha
(4—1) rha (4—1) rha

glc: β-D-glucopyranosyl; rha: α-L-rhamnopyranosyl

EXPERIMENTAL

Mps: uncorr. NMR spectra were measured in pyridine d_5 and $CDCl_3$ and recorded at 400MHz for ^1H NMR and ^{13}C NMR (DEPT) using TMS as int. standard. EI-MS were measured at 20eV accelearating voltage. FAB-MS were recorded on VG ZAB-HS mass spectrometers. Solvent systems of TLC and CC: ① . $CHCl_3$-MeOH-H_2O(8:2:0.1; 7:3:0.5 V/V), ② . petrol: EtOAc(1:1; 4:6 V/V), ③ . (8:2 V/V), ④ . $CHCl_3$-MeOH-H_2O(7:3:1, 9mL+HOAc 1mL). TLC were by spraying with 7%H_2SO_4 followed by heating.

Plant material: *Paris polyphylla* var. *yunnanensis* was collected at Luopin(Yunnan), China in october 1987 and identified by Prof. Li Heng (Kunming Institute of Botany, Academia Sinica). The voucher specimen is kept in KUN.

Extraction and isolation of saponins The dried aerial parts of *Paris polyphylla* var. *yunnanensis* (1.94kg) were extracted with hot MeOH. The extracts were subjected to a D-101 highly porous polymer column chomatography with 75% MeOH to afford saponin fraction (113g). The crude saponis were chromatographed on silica gel column with solvent a to give three fractions. The third fraction (2.1g) was further chromatographed on reversed phase highly porous polymer and RP-18 yielding saponins 1 (205mg) and 2 (184mg).

Saponin 1 Colorless (from MeOH), mp 287—289℃. IR$\nu_{max}^{KBr}cm^{-1}$: 3300—3500, 1000—1100(OH), 1650(C=C). ^1H NMR (δ) 0.97(3H, s, H-18), 1.08(3H, s, H-19), 1.22 (3H, d, J=6.2Hz, H-21) 1.55, 1.56, 1.57 (9H, each dd, J=6.2Hz, 3× rha-CH_3) and 4.92(1H, d, J=7.7Hz, glc-H-1), 5.78, 6.22, 6.33 (3H br, each 3× rha-H_1). The ^{13}C NMR as table 1, FAB-MS m/z: 1047[M+1] 899[M-rha]$^+$, 752[M-2rha]$^+$, 753[M-2(rha)$^+$], 570[M-3rha-$2H_2O$]$^+$

Saponin 2 Needles (from MeOH), mp 281—283℃. IR$\nu_{max}^{KBr}cm^{-1}$: 3500—3300, 1100—1000(-OH), 1625(C=C). ^1H NMR (δ, ppm) 1.03(3H, s, H-19) 1.17(3H, s, H-18), 1.33 (3H, d, J=7Hz, H-21), 1.58, 1.59, 1.61(9H, d, J=6Hz, each, 3× rha-CH_3), 4.92(1H, d, J=7.5Hz, glc-H-1) 5.82, 6.27, 6.38(3H, br, each, 3× rha-H_1). FAB-MS m/z: 1063[M+H], 915[M-rha]$^+$, 768[M-2rha]$^+$.

Acid Hydrolysis of 1 and 2 A soln of each saponin (60mg) in 2 mol/L HCl-50% MeOH 10 mL was refluxed on a water bath for 4h. The reaction mixt was diluted with H_2O (5 mL) and removed MeOH. The reaction mixt was extracted with EtOAc. The crude sapogenin was subjected to column

chromatography eluting with soln ㈡ to afford 3(35mg) and 4(31mg), respectively.

3, mp 205—207℃, ^{13}C NMR as table 1. ^{1}H NMR (δ) 0.98(3H, s, H−18), 1.08(3H, s, H−19) 1.28(3H, d, J=7.2Hz H−21), 4.50(1H, t, J=6 2Hz, H−6). EI−MS m/z: 446 $C_{27}H_{42}O_5$, 428[M−H_2O]$^+$, 410[M−H_2O]$^+$, 171[$C_9H_{15}O_3$]$^+$, 169[$C_9H_{13}O_3$]$^+$, 142[$C_8H_{14}O_2$]$^+$.

4, mp 231—232℃. ^{13}C NMR as table 1. ^{1}H NMR (δ) 1.02(3H, s, H−18), 1.17(3H, s, H−19), 1.32(3H, d, J=7.2Hz, H−21), 4.57(1H, t, J=7.0Hz, H−16), 5.36(1H, d, J=4.6Hz H−6), 5.96(3H, 3× OH). EI−MS: 462. $C_{27}H_{42}O_6$, 444[M−H_2]$^+$, 426[M−2H_2O]$^+$, 187[$C_9H_{15}O_4$]$^+$, 185[$C_9H_{13}O_4$]$^+$, 158[$C_8H_{14}O_3$]$^+$.

The aq. layer was neutralized with solid $AgCO_3$, filtered, evaporated to dryness in vacuo, then the residue was examined on TLC and PC with solvent ㈢, ㈣ used for identifying the sugars Sugars of saponins 1 and 2 were detenmined identical, both are glucose and rhamnose (1:3).

Acetylation of sapongenin 3 and 4 Each sapogenin (10 mg) was dissolved in pyridine (1 mL) and $(ACO)_2O$ (2 mL). The soln was allowed to stand 24 h at room temp. The reaction mixt was poured into ice water and the ppt. was collected by filtration, dissolved in $CHCl_3$ and filtered, then added MeOH and removed $CHCl_3$ to give 5 and 6, respectively.

5, Needles (from MeOH), mp 129—131℃ EI−MS m/z: 530[M]$^+$, 213($C_{11}H_{17}O_4$)$^+$, 211($C_{11}H_{15}O_4$)$^+$, 184($C_{18}H_{16}O_3$)$^+$. ^{1}H NMR ($CDCl_3$, δ, ppm), 0.83(3H, s, H−18), 0.90(3H, d, J=7.0Hz H−21), 1.04(3H, s, H−19), 2.05 2.07(6H, s, 2×$COCH_3$), 3.74(1H, dd, J=5.2, 11Hz, H−26α), 3.91(1H, t, J=11.2Hz, H−26β), 5.40(1H, d, J=5.0Hz, H−6).

6, Needles (from MeOH), mp 198—199℃. EI−MS m/z: 572[M]$^+$, 255($C_{13}H_{19}O_5$)$^+$, 253($C_{13}H_{17}O_5$)$^+$, 226($C_{12}H_{18}O_4$)$^+$. ^{1}H NMR ($CDCl_3$, δ, ppm), 0.84 (3H, s, H−18), 0.89(3H, d, J=7.2Hz, H−21), 1.04(3H, s, H−19), 2.04, 2.05, 2.06(9H, s, 3×$COCH_3$), 3.55(1H, t, J=11.2Hz, H−26α) 3.65(1H, dd, J=3.6, 11.0Hz, H−26β), 3.94(2H, m, J=5.6Hz, H−3), 4.04(1H, t, J=7.3Hz, H−16), 4.88(1H, dd, J=5.0, 11.8Hz, H−23α), 5.38(1H, d, J=4.8Hz, H−6).

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《云南植物研究》植物化学论文作者须知

为使本期刊植物化学论文格式规范化，除按本刊征稿简则外，另补充如下规定，务请作者参阅本规定撰写论文。

1.研究论文及简报的基本格式参照本刊 1993 年（15 卷）第 1—2 期。

2.植物材料应附正确的拉丁学名、产地、数量和制备方法。

3.化学结构图须另页绘制，基团标注无误，在文稿内注明插图位置。常见化合物的结构不必给出。表插入文中适当位置，图表应附相应的英文。

4.参考文献按出现的先后顺序在文中注明，著录格式见本刊"征稿简则"，其中，英文期刊名的缩写参照 CA，但不加点，不可随意缩写，如：Phytochem（正确为 Phytochemistry），Tetra（正确为 Tetrahedron）。

5.实验部分必须简明扼要，但要使实验化学家能够据此重复出该实验，可以省略的一些实验细节：(1) 常规衍生物(如乙酰化物)的制备方法；(2) 化合物分离的细节，如装柱，TLC 板，柱子及分馏的大小等；(3) 仪器（不包括型号）及化学试剂的商业来源。

6.新化合物采用 IUPAC 命名规则给出一个完整的系统名，若有必要可再取一个得体的俗名。文中化合物第一次出现时若注有编号，下文均以编号代表。

7 每个化合物尽可能标出得率，如：化合物 3（510mg；0.0031%）。结晶须指明所用溶剂，如：白色针晶（MeOH），熔点的表示法，如：mp 259—261 ℃。液体化合物的折射率表示法，如 n_D^{22}1.653。

8. 元素分析表示法，如：已知化合物(Found: C, 62.9; H, 5.4. Calc. for $C_{13}H_{13}ON_4$: C, 62.9; H, 5.3%)。新化合物(Found: C, 62.9; H, 5.4. $C_{13}H_{13}ON_4$requires: C, 62.9; H, 5.3%)。

9. 比旋度的表示法：$[\alpha]_D^{温度}$ 测定值 °（所用溶剂：c 指 100ml 溶剂里化合物的克数），如$[\alpha]_D^{23}$+32.2 °(EtOH; c 0.3210)。

旋光色散谱 (ORD)可用一系列不同波长下的[α]值或分子比旋[θ]值表示。

园二色散谱 (CD) 可用分子椭率值如$[\theta]_{256}$+21780、$[\theta]_{307}$−16113 或微分子色散吸收值如Δε253−1.02(MeOH; c 0.164)表示。

10. NMR 表示为^{1}H NMR 或^{13}C NMR，须注明仪器的频率、溶剂及内标物。化学位移以 δ 值(对 TMS)表示，注明峰形，如：单峰(s)，宽单峰(brs)，双峰(d)，双二重峰(dd)，复峰(m)等。^{13}C NMR 及^{1}H NMR 数所须注明所对应的碳和氢的位置，采用 IUPAC 定位，标为 C−1，C−2；H−1，H−2。例如：^{13}C NMR(21.15Mz, $CDCl_3$): δ30.1(t, C−5), 74.1(d, C−6), 121.3(d, C−3), 144.2(s, C−4)。^{1}H NMR(100MHz, $CDCl_3$): δ0.681(3H, s, H−18), 0.884(6H, d, J = 6.0Hz, H−26 and H−27), 0.901(3H, d, J = 5.0Hz, H−21), 4.342(1H, q, J6α, 7α = 4.5Hz, J6α, 7β = 2.0Hz, H−6), 4.211(1H, m, $W_{1/2}$ = 18.0Hz, H−3α)。所用仪器频率及溶剂若在实验部分的总论中已注明，则以下皆可省略。

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