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黄花远志的新齐墩果烷型三萜皂甙*

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摘要 从云南产远志科药用植物黄花远志 (*Polygala arillata* Buch.-Ham.ex D.Don) 茎皮的乙醇提取物中分离得到4个新的齐墩果烷型三萜 皂甙, 命名为黄花远志皂甙 (arillatanoside) A ~ D。同时还分离得到1个已知的三萜皂甙远志甙 (polygalasaponin) XXXV。它们的结构通过波谱方法推定。

关键词 远志科, 黄花远志, 三萜皂甙, 黄花远志皂甙 A ~ D
分类号 Q 946

New Oleanane Triterpenoid Saponins from *Polygala arillata* *

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Abstract Four new oleanane triterpenoidal saponins, arillatanoside A ~ D, together with a known saponin polygalasaponin XXXV were isolated from the stem bark of *Polygala arillata*. The structures of new saponins were established to be 28 - O - α - L - arabinopyranosyl - (1→3) - β - D - xylopyranosyl - (1→4) - α - L - rhamnopyranosyl - (1→2) - β - D - fucopyranosyl presenegenin - 3 - O - β - D - glucopyranoside, 28 - O - β - D - galactopyranosyl - (1→4) - [α - L - arabinopyranosyl - (1→3)] - β - D - xylopyranosyl - (1→4) - α - L - rhamnopyranosyl - (1→2) - [4 - O - acetyl] - β - D - fucopyranosyl presenegenin - 3 - O - β - D - glucopyranoside, 28 - O - β - D - galactopyranosyl - (1→4) - [α - L - arabinopyranosyl - (1→3)] - β - D - xylopyranosyl - (1→4) - α - L - rhamnopyranosyl - (1→2) - β - D - fucopyranosyl presenegenin 3 - O - β - D - glucopyranoside and 28 - O - β - D - galactopyranosyl - (1→4) - [α - L - arabinopyranosyl - (1→3)] - β - D - xylopyranosyl - (1→4) - [β - D - apiofuranosyl - (1→3)] - α - L - rhamnopyranosyl - (1→2) - β - D - fucopyranosyl presenegenin - 3 - O - β - D - glucopyranoside, respectely, by FAB - MS and NMR spectroscopy.

Key words Polygalaceae, *Polygala arillata*, Triterpenoidal saponins, Arillatanoside A ~ D

Polygala arillata Buch.-Ham. ex D. Don is a moderate size tree in the family Polygalaceae, distributed in southern China. It as a folk herb is used for treating coughs, expectorants, stomach trouble and rheumatism (Jiangsu College of New Medicine, 1979). Chemical studies on this plant have in-

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dicated the presence of some xanthones, polygalitol, stigmasterol and stigmasterol – 3 – O – β – glucopyranoside (Mao *et al*, 1997,1996; Shbuth *et al*, 1977). In this paper we describe the isolation of five oleanane triterpenoidal saponins (1 ~ 5) from the stem bark of *P. arillata* and the structure of four new saponins together with a known saponin.

RESULTS AND DISCUSSIONS

Five triterpenoidal saponins were isolated from the polar part of EtOH extract of *P. arillata*. One of them was identified as the known polygalasaponin XXXV (5) on the basis of its NMR and FAB – MS spectra, and comparison with literature data which was isolated from *Polygala fallax* Hemsl. (Zhang *et al*, 1996a).

The structure of four novel triterpenoidal saponins, which named arillatanoside A ~ D (1 ~ 4), were established by concerted application of NMR and MS studies.

Arillatanoside A (1) was obtained as a colorless amorphous powder. It gave a molecular ion peak at m/z 1236($C_{58}H_{92}O_{20}$) in the negative FAB – MS and main fragment ion peaks at m/z 1103 $[M-132-H]^-$, 1073 $[M-162-H]^-$, 971 $[M-2\times132-H]^-$, 679 $[M-2\times133-2\times145-H]^-$. The ^1H NMR spectrum of 1 showed the presence of seven singlet methyl signals at δ 0.76, 0.85, 1.10, 1.47, 1.51, 1.63 and 1.90; a pair of hydroxymethyl signals at δ 3.58 and 3.95; a trisubstituted olefinic proton signal at δ 5.79 (s, br.); and five anomeric proton signals at δ 6.45 (s, br.), 6.00 (s, br.), 5.12 (s, br.), 5.05 (s, br.) and 5.02 (s, br.). The ^{13}C NMR spectrum of **1** showed the presence of one carboxylic carbon signal at δ 182.15, one ester carbonyl carbon signal at δ 176.75 and five anomeric carbon signals at δ 106.84, 105.86, 105.30, 101.08 and 94.89. The ^{13}C and ^1H NMR spectral data of **1** were homologous to those of polygalasaponin XXVIII (**6**), an oleanane triterpenoidal saponin which isolated from *Polygala japonica* Houtt. (Zhang *et al*, 1996b; Masayuki *et al*, 1995). The carbon signals for aglycone skeleton and sugar moiety of **1** were very similar to those of **6** (Table 1). It is indicated that both of them have the same aglycone as presenegenin and similar sugar linkages. However, in the comparison between the ^{13}C NMR spectrum of **1** and those of **6**, the spectrum of **1** showed one set additional signals of α – L – arabinopyranosyl unit. A careful analysis of the glycosylation shift led us observed that the signal C – 3 of terminal β – D – xylopyranosyl unit of oligosaccharide chain of **1** was downfield shifted to δ 87.79 from δ 78.8 of **6**, while other carbon signals were almost unaffected. It was suggested that the additional α – L – arabinopyranosyl unit of **1** could be linked to C – 3 position of the terminal β – D – xylopyranosyl unit of **6**. This was confirmed by two – dimensional NMR techniques. HMQC and HMBC experiments showed correlation between H – 3 of β – D – xylopyranosyl unit and C – 1 of α – L – arabinopyranosyl unit. Based on the above evidence, the structure of saponin **1** was established to be 28 – O – α – L – arabinopyranosyl – (1→3) – β – D – xylopyranosyl – (1→4) – α – L – rhamnopyranosyl – (1→2) – β – D – fucopyranosyl presenegenin – 3 – O – β – D – glucopyranoside.

Arillatanoside B (2) was obtained as a white amorphous powder and exhibited a molecular ion

peak at m/z 1440 by negative FAB – MS. To comparison with ^{13}C NMR spectrum suggested its molecular formula could be $C_{66}H_{104}O_{34}$. The ^{13}C NMR spectrum of **2** showed the presence of one carboxylic carbon signal at δ 185.91, two ester carbonyl carbon signals at δ 176.07 and 171.25, and six anomeric carbon signals at δ 106.64, 105.39 (2 × C), 103.25, 102.23 and 94.57. It is noticed that the ^{13}C NMR spectrum of **2** closely resembled that of polygalasaponin XXXIV (**7**) (Zhang *et al*, 1996) except one more α – L – arabinopyranosyl unit in **2** (Table 1). By comparison of the ^{13}C NMR spectral data of **2** with that of **7**, all the carbon signals overlapped with each other except for C – 3 of β – D – xylopyranosyl unit. The chemical shift C – 3 of β – D – xylopyranosyl unit went downfield from δ 76.7 in **7** to δ 87.23 in **2**, indicated that this additional α – L – arabinopyranosyl unit was located at C – 3 of β – D – xylopyranosyl unit in **2**. Therefore, the structure of saponin **2** was shown to be 28 – O – β – D – galactopyranosyl – (1→4) – [α – L – arabinopyranosyl – (1→3)] – β – D – xylopyranosyl – (1→4) – α – L – rhamnopyranosyl – (1→2) – [4 – O – acetyl] – β – D – fucopyranosyl presenegenin – 3 – O – β – D – glucopyranoside.

Arillatanoside C (**3**) was obtained as a white amorphous and exhibited a molecular ion peak at m/z 1398 $[M(C_{64}H_{102}O_{33})]^-$ in its negative FAB – MS. The ^1H and ^{13}C NMR spectra of **3** showed six anomeric proton signals at δ 6.62 (s, br.), 6.01 (d, J = 8.0Hz), 5.01 (s, br.), 4.90 (s, br.), 4.78 (s, br.) and 4.78 (s, br.); and six anomeric carbon signals at δ 106.55, 105.99, 105.17, 103.16, 100.93 and 94.87. The ^{13}C NMR spectrum of **3** closely resembled that of **1**. Comparison of the ^{13}C NMR spectral data of 3 with that of saponin **1**, showed that there is one more β – D – galactopyranosyl unit in **3** (Table 1). The C – 4 carbon signal of β – D – xylopyranosyl unit was downfield shift from δ 70.45 in **1** to δ 78.03 in **3**. It indicated that this additional β – D – galactopyranosyl unit should be linked at the position C – 4 of β – D – xylopyranosyl unit in **3**. Moreover, the chemical shift pattern of **3** are most overlapped with that of saponin **2**, except less a set signals of an acetyl group in C – 4 position of α – L – rhamnopyranosyl unit. Thus, the structure of saponin **3** is 28 – O – β – D – galactopyranosyl – (1→4) – [α – L – arabinopyranosyl – (1→3)] – β – D – xylopyranosyl – (1→4) – α – L – rhamnopyranosyl – (1→2) – β – D – fucopyranosyl presenegenin 3 – O – β – D – glucopyranoside.

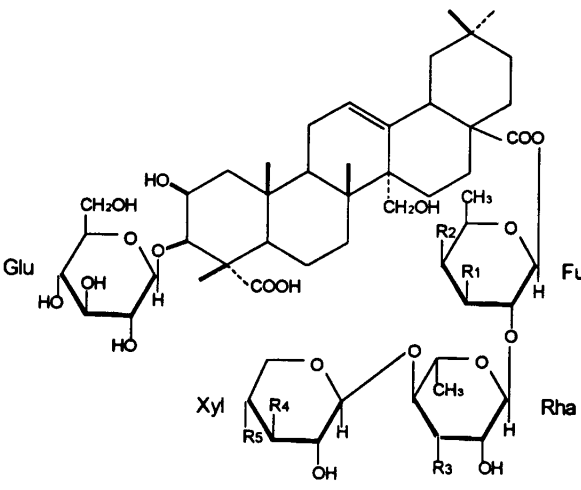
Arillatanoside D (**4**) exhibited a molecular ion peak at m/z 1530 $[M(C_{69}H_{110}O_{37})]^-$ in its negative FAB – MS. The ^{13}C NMR spectrum of **4** showed seven anomeric carbon signals at δ 111.77, 105.08 (2 × C) 104.40, 103.27, 101.65 and 94.56. Its ^{13}C NMR spectrum showed a similar pattern to those of saponins **3** and desacylsenegasaponin A (**8**), later was isolated from *Polygala senega* var. *latifolia* Torrey et Gray (Masayuki *et al*, 1995). However, **4** exhibited one more α – L – arabinopyranosyl unit at C – 3 position of β – D – xylopyranosyl unit in **8**, and one more β – D – apiofuranosyl unit at C – 3 position of α – L – rhamnopyranosyl unit in **3** (Table 1). Therefore, the structure of **4** was determined to be 28 – O – β – D – galactopyranosyl – (1→4) – [α – L – arabinopyranosyl – (1→3)] – β – D – xylopyranosyl – (1→4) – [β – D – apiofuranosyl – (1→3)] – α – L – rhamnopyranosyl – (1→2) – β – D – fucopyranosyl presenegenin – 3 – O – β – D – glucopyranoside.

Though, the structures of all four new saponins were deduced by comparison with that of known

saponins, as characters, they are the same aglycone and similar pattern of sugar chain. It is noticed that the triterpenoidal saponins of *Polygala* species shown biological activity such as inhibitory activity of increasement of serum glucose level has been reported recently (Masayuki *et al*, 1995 and Yoshigawa *et al*, 1999). The screening of biological actives for these new saponins is interesting.

EXPERIMENTAL

General experimental procedures ^1H and ^{13}C NMR spectra were obtained with Bruker AM – 400, DRX – 500 spectrometer. FAB – MS spectra were taken on VG Autospec – 3000 system spectrometer. The chemical shifts (δ) were expressed in ppm with reference to the solvent signals. Coupling constants (J) were given in Hz. Chromatographic materials were used Rp – 8 (40 ~ 60 μm, Merck), Sephadex LH – 20 (25 ~ 100 μm, Pharmacia Fine Chemical Co. Ltd.), MCI – gel CHP20P (75 ~ 150 μm, Mitsubish Chemical Industries, Ltd.) and silica gel (200 ~ 300 mesh, Qingdao Marine Chemical Factory). TLC was developed with $CHCl_3$ – MeOH – H_2O (65:35:9, 7:3:0.5, 7:3:1). The ratio of solvents was given in v/v in each case. Spot of TLC were detected by spraying 5% H_2SO_4 following by heating.



	R1	R2	R3	R4	R5
6	OH	OH	OH	OH	OH
1	OH	OH	OH	Ara(p)	OH
7	OH	OAc	OH	OH	Gal
2	OH	OAc	OH	Ara(p)	Gal
3	OH	OH	OH	Ara(p)	Gal
8	OH	OH	Api(f)	OH	Gal
4	OH	OH	Api(f)	Ara(p)	Gal
5	OAc	OAc	OH	OH	Gal

Ara(p): α-L-arabinopyranosyl
Gal: β-D-galactopyranosyl
Api(f): β-D-apiofuranosyl
OAc: acetyl

Extraction and isolation *Polygala arillata* Buch. – Ham. was collected in Kunming, Yunnan Province in March 1997. The dried bark (20kg) was powdered and extracted with 95% EtOH at room temperature (4 × 30L), then concentrated in vacuum (60℃) to evaporate the solvent to give a small volume. After extracting with $CHCl_3$(3 × 2L), the water layer portion was subjected to D101 resin column chromatography, after washing by H_2O, eluting with EtOH to give 200g polar fraction. 150g of them was chromatographed on silica gel column with the solvent system ($CHCl_3$ – MeOH – H_2O, 7:3:1) to give fractions A ~ F. The fraction A (50g) was rechromatographed over Sephadex LH – 20 (30% ~ 90% MeOH) and MCI – gel CHP20P (30% ~ 80% MeOH, 30% ~ 50% CH_3COCH_3) to give compound **1** (100mg), **2** (70mg), **3** (80mg), **4** (80mg) and **5** (90mg) respectively.

Table 1 ^{13}C NMR spectral data of the aglycone moieties of saponins (in C_5D_5N)

C	6*	7*	5*	8*	1	2	3	4	5
1	44.3	44.3	44.3	44.3	44.50	44.23	44.47	44.33	44.29
2	70.3	70.4	70.4	70.1	70.74	70.40	67.97	70.45	70.70
3	86.0	86.0	86.0	86.0	85.45	86.61	86.14	86.45	86.23
4	52.9	52.5	52.9	52.9	53.50	53.49	53.40	53.26	53.38
5	52.5	52.5	52.5	52.6	52.60	52.46	52.41	52.68	52.48
6	21.4	21.5	21.5	21.3	21.85	21.74	21.85	21.28	21.72
7	33.6	33.6	33.5	33.9	34.10	33.66	34.03	33.99	34.00
8	41.2	41.2	41.2	41.2	41.26	41.18	41.23	41.15	41.13
9	49.4	49.4	49.3	49.4	49.50	49.34	49.47	49.34	49.27
10	37.1	37.0	37.0	37.1	37.07	37.06	36.84	37.18	37.00
11	23.6	23.7	23.7	23.7	23.30	23.42	23.33	23.50	23.43
12	127.9	127.9	127.8	127.8	127.94	128.28	128.12	127.80	128.20
13	138.9	139.0	138.9	139.1	193.11	138.80	139.09	139.49	138.96
14	47.0	47.0	47.1	47.0	47.06	47.23	47.07	47.02	47.22
15	24.6	24.5	24.5	24.5	24.95	24.59	24.94	24.64	24.55
16	24.1	24.0	23.9	24.0	24.90	23.94	23.64	24.64	24.19
17	48.0	48.1	48.0	48.0	48.23	48.21	48.40	48.11	48.17
18	42.0	42.0	41.9	42.0	42.15	42.03	42.09	41.81	41.80
19	45.4	45.4	45.4	45.5	45.50	45.41	45.41	45.71	45.48
20	30.8	30.8	30.8	30.8	30.89	30.82	30.75	30.85	30.75
21	33.8	33.9	33.9	33.9	34.10	34.10	34.03	33.99	33.59
22	32.4	32.4	32.4	32.4	32.40	32.64	32.42	32.44	32.51
23	180.8	180.8	180.7	180.9	182.15	185.91	185.50	186.00	186.00
24	14.2	14.2	14.2	14.2	14.41	14.31	14.19	14.73	14.87
25	17.5	17.5	17.5	17.5	17.63	17.70	17.60	17.56	17.53
26	18.8	18.7	18.6	18.8	18.91	18.80	18.94	19.08	18.85
27	64.5	64.5	64.4	64.6	64.20	64.15	64.18	64.72	64.31
28	176.7	176.7	176.4	176.6	176.75	176.87	176.54	176.65	176.54
29	33.1	33.1	33.0	33.1	33.19	33.19	33.10	33.18	33.07
30	24.1	24.0	23.9	24.1	24.01	23.94	23.80	24.01	23.88

* ref. data

Arillatanoside A (1): The colorless amorphous powder. FAB - MS m/z 1236[M ($C_{58}H_{92}O_{20}$)]$^-$, 1218[M - H_2O]$^-$, 1103[M - 132 - H]$^-$, 1073[M - 162 - H], 971[M - 2X132 - H]$^-$. ^1H NMR spectrum: δ 0.76, 0.85, 1.10, 1.47, 1.51, 1.63 and 1.90 (Me × 7); 5.79 (1H, s, br., 12 - H); 6.45(1H, s, br.), 6.00(1H, s, br.), 5.12(1H, s, br.), 5.05(1H, s, br.) and 5.02(1H, s, br.)(anomeric protons). See ^{13}C NMR data in Table 1 and 2.

Arillatanoside B (2): The white amorphous powder. FAB - MS: m/z 1440[M ($C_{66}H_{104}O_{34}$)]$^-$, 1308 [M - 132]$^-$, 1278 [M - 162]$^-$, 1145 [M - 132 - 163]$^-$, 1116 [1278 - 162]$^-$,

982 [1145 – 162]⁻. See ^{13}C NMR data in Table 1 and 2.

Table 2 ^{13}CNMR spectral data of sugar moieties of saponins (in C_5D_5N)

C	6*	7*	5*	8*	1	2	3	4	5
Glu – 1	105.4	105.4	105.4	105.3	105.30	105.39	105.17	105.08	105.01
2	75.3	75.3	75.3	75.3	75.27	75.21	75.30	75.12	75.32
3	78.4	78.3	78.3	78.3	78.28	77.54	77.81	78.54	77.86
4	71.6	71.7	71.7	71.4	71.57	71.50	71.50	71.65	71.58
5	78.4	78.3	78.3	78.3	78.19	77.35	77.53	78.54	77.67
6	62.7	62.8	62.8	62.7	62.68	62.39	62.52	62.70	62.58
Fuc – 1	94.8	9436	94.2	94.8	94.89	94.57	94.87	94.96	94.05
2	74.0	74.1	73.0	75.0	73.50	74.34	74.55	74.80	72.50
3	76.7	74.7	74.6	76.3	76.90	74.51	76.00	76.58	74.96
4	73.2	74.8	71.2	73.1	73.32	74.76	73.39	73.27	71.33
5	72.5	70.6	70.1	72.3	72.54	70.74	72.44	72.47	70.27
6	16.9	16.5	16.1	16.9	17.02	16.61	16.92	17.00	16.09
3 – Ac			20.6						20.64
			170.1						170.12
4 – Ac		20.7	20.4			20.90			20.43
		171.1	170.8			171.25			170.84
Rha – 1	101.2	101.8	102.1	101.5	101.08	102.23	100.93	101.65	102.24
2	71.8	71.8	71.4	71.6	71.78	71.77	71.78	71.65	71.59
3	72.5	72.5	72.4	82.1	72.54	72.61	72.63	81.95	72.50
4	85.1	85.2	84.7	78.7	85.41	85.49	86.15	78.54	84.52
5	68.3	68.5	69.0	68.3	68.04	68.21	67.58	68.02	68.81
6	18.6	18.8	18.8	18.6	18.54	18.99	18.94	18.88	18.67
Xyl – 1	170.4	107.0	106.8	104.8	106.84	106.64	106.55	105.08	106.70
2	76.2	75.7	75.6	75.1	76.90	75.83	75.30	76.82	75.77
3	78.8	76.7	76.6	76.2	87.79	87.23	87.48	83.80	76.77
4	70.9	78.3	78.2	78.6	70.45	77.71	78.03	78.18	77.67
5	67.5	65.0	65.0	64.6	67.00	66.30	66.28	65.21	64.85
Api – 1				111.7				111.77	
2				77.6				77.46	
3				79.6				80.09	
4				74.6				74.80	
5				64.6				65.73	
Gal – 1		104.5	104.5	104.4		103.25	103.16	104.40	103.89
2		71.8	71.8	71.8		71.50	71.50	70.45	71.79
3		75.1	75.1	75.0		75.21	75.30	75.41	75.32
4		70.1	70.0	70.1		70.47	69.82	69.94	70.07
5		77.3	77.3	77.3		77.35	77.23	77.46	77.09
6		62.3	62.3	62.3		62.39	62.39	62.31	62.40
Ara – 1					105.86	105.39	105.99	103.27	
2					72.54	72.61	72.63	72.47	
3					75.41	74.76	74.55	75.62	
4					68.86	70.27	69.82	68.02	
5					67.32	66.64	67.10	66.64	

* ref. Data

Arillatanoside C (3): The white amorphous. FAB - MS m/z 1398[M($C_{64}H_{102}O_{33}$)]$^-$ 1266[M - 132]$^-$, 1236[M - 162]$^-$. ^{1}H NMR spectrum δ 6.62 (1H, s, br.), 6.01 (1H, d, J = 8.0Hz), 5.01 (1H, s, br.), 4.90 (1H, s, br.), 4.78 (1H, s, br.), 4.78 (1H, s, br.)(anomeric protons). See ^{13}C NMR data in Table 1 and 2.

Arillatanoside D (4): The white amorphous. FAB - MS am/z 1530 [M($C_{69}H_{110}O_{37}$)]$^-$. See ^{13}C NMR data in Table 1 and 2.

Polygalasaponin XXXV (5): The white amorphous powder. FAB - MS m/z 1349 [M($C_{63}H_{98}O_{31}$) - H]$^-$. ^{1}H NMR δ 2.04 (2 × CH_3). See ^{13}C NMR data in Table 1 and 2.

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