Triterpenoids from *Rhaponticum uniflorum*

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The isolation and identification of twenty-one components (including four new triterpenoid saponins and one new triterpenoid acid) from the root of Rhaponticum uniflorum (L.) DC. (Compositae) are described. Their structures were determined on the basis of spectral analysis and chemical transformation. The new compounds were identified as 3-*O*-α-L-arabinopyranosyl-urs-12,18(19)-dien-28-oic acid β-D-glucopyranosyl ester, 3β-hydroxy urs-12,18(19)-dien-28-oic acid β-D-glucopyranosyl ester, 3β-hydroxyurs-12,19(29)-dien-28-oic acid β-D-glucopyranosyl ester, 3-*O*-α-L-arabinopyranosyl-urs-9(11),12-dien-28-oic acid β-D-glucopyranosyl ester and 2α,3α,19α,25-tetrahydroxyurs-12-en-23,28-dioic acid.

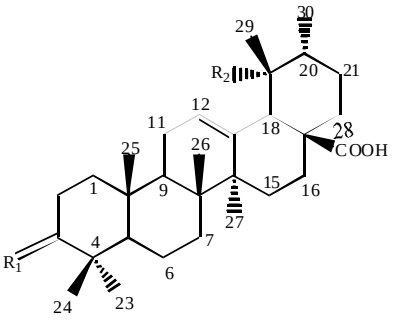
INTRODUCTION

Rhaponticum uniflorum (L.) DC. (Compositae) is distributed in northern China. Its root is a Chinese traditional medicine and has been used for intoxication and for the treatment of fever.[1] Recently, it was demonstrated that its ethyl acetate extract inhibits peroxidation of membrane lipids and posseses antiatherosclerotic activity.[2] Some lipophilic components of sulfur-containing acetylene compounds have been isolated from this plant.[3] Many phytoecdysteroids were isolated from its roots and aerial parts.[4] We have investigated the chemical constituents of its root, leading to the isolation of twenty-one components including five triterpenoid acids, nine triterpenoid saponins, three phytoecdysteroids, one phenols, one thiophene, one flavonoid, and one steroid. Of these components, four triterpenoid saponins and one triterpenoid acid are new compounds. In this paper, we describe the structural elucidation of isolated components.

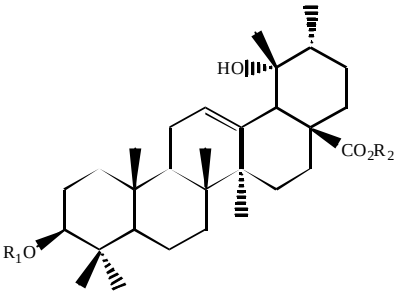
RESULTS AND DISCUSSION

Separation of the methanolic extract of roots of *Rhaponticum uniflorum* over silica gel and Sephadex LH-20 yielded twenty-one compounds. Sixteen of them were identified as known compounds, ursolic acid (**1**),[5] 3-oxo-19α-hydroxyurs-12-en-28-oic acid (**2**),[6] pomolic acid (**3**),[7] ziyuglycoside II (**4**),[8] 28-*O*-β-D-glucopyranosyl pomolic acid ester (**5**),[6] ziyuglycoside I (**6**),[8] 2α,3α,19α-trihydroxyurs-12-en-28-oic acid (**7**),[9] rosmutin (**8**),[10] sauvissimoside R_1 (**9**),[11] ecdysterone (**15**),[12] ajugasterone C (**16**),[13] ajugasterone C-20,22-monoacetonide (**17**),[13] 3,3′,4-tri (*O*-methyl) ellagic acid (**18**),[14] arctic acid (**19**),[3] (+)-catechin (**20**),[15] and daucosterol (**21**)[16] on the basis of their NMR and MS spectra, and comparison with authentic samples and literature data. Five of them were identified as new compounds, 3-*O*-α-L-arabinopyranosyl-urs-12,18(19)-dien-28-oic acid β-D-glucopyranosyl ester (**10**), 3β-hydroxyurs-12,18(19)-dien-28-oic acid β-D-glucopyranosyl ester (**11**), 3β-hydroxyurs-12,19(29)-dien-28-oic acid β-D-glucopyranosyl ester (**12**), 3-*O*-α-L-arabinopyranosyl-urs-9(11),12-dien-28-oic acid β-D-glucopyranosyl ester (**13**), and 2α,3α,19α,25-tetrahydroxyurs-12-en-23,28-dioic acid (**14**) by various NMR techniques, including COSY, NOESY, HMQC and HMBC experiments and chemical methods. These five compounds gave positive response to the Liebermann-Burchard test and compounds **10**-**13** also showed positive coloration to molish test, indicating **10**-**13** to be triterpenoid saponins and **14** to be a triterpene.

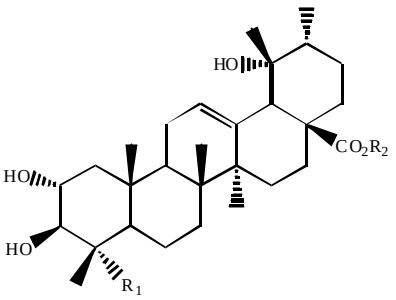
Compound **10** was obtained as an amorphous powder, mp 203-205 °C. The IR spectrum showed the absorption for hydroxyl groups (3354 cm^{-1}), ester carbonyl (1727 cm^{-1}) and double bond (1640 cm^{-1}). Acid hydrolysis of **10** in refluxing 15% HCl benzene afforded D-glucose and L-arabinose, identified by PC. The HR-FABMS showed the molecular ion at *m/z* 748.4392, corresponding to the molecular formula $C_{41}H_{64}O_{12}$. **10** had ultravio let absorption maximum at 238 nm, indicating the existence of a conjugated diene system. Its ^{1}H NMR spectrum (400 MHz, CD_3OD) showed the presence of one vinyl hydrogen (δ 5.37, t, *J* = 4.0 Hz) and one vinyl-attached methyl group (δ 1.73, s). These data concluded compound **10** to be a 12,18(19)-diene ursane type triterpene.[17] The ^{1}H NMR spectrum showed two anomeric protons at δ 6.20 (d, *J* = 8.1 Hz, glc-1) and δ 4.26 (d, *J* = 6.9 Hz, ara-1), in-



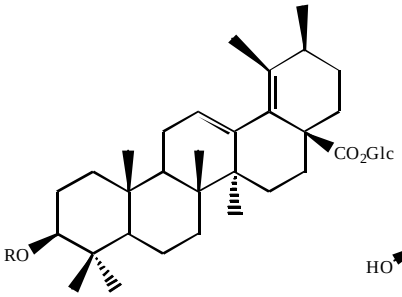
1 R_1= R_2=H
2 R_1=O R_2=OH



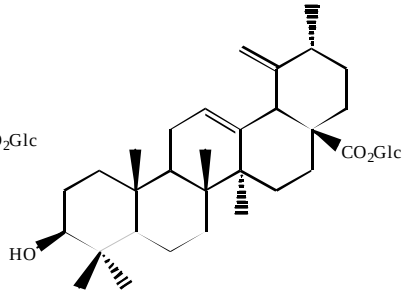
3 R_1=R_2=H
4 R_1=Ara R_2=H
5 R_1=H R_2=Glc
6 R_1=Ara R_2=Glc



8 R_1=CH_3 R_2=Glc
9 R_1=CO_2H R_2=Glc



10 R=Ara
11 R=H



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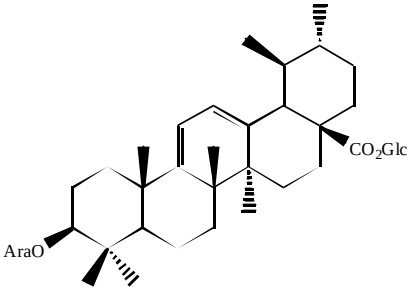

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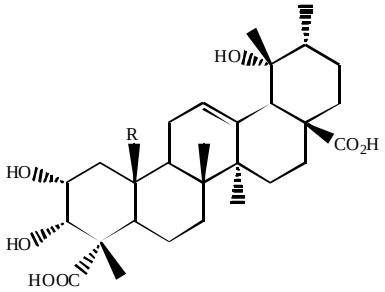
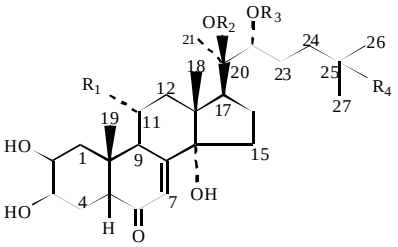
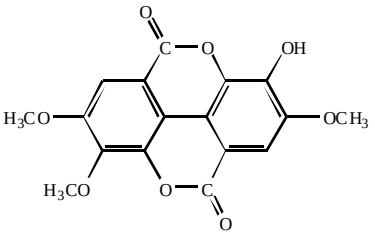


7 R=CH_3
14 R=CH_2OH



15 R_1=R_2=R_3=H R_4=OH
16 R_1=OH R_2=R_3=R_4=H
17 R_1=OH R_2R_3=CMe_2 R_4=H



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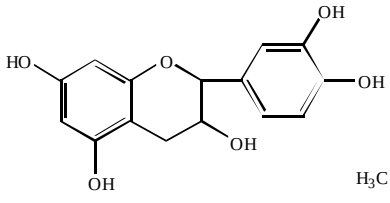

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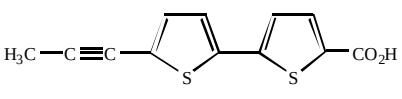

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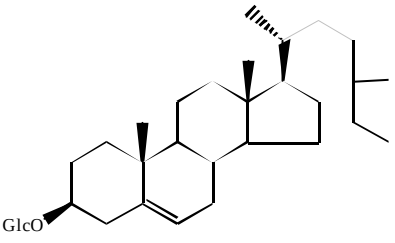

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dic a tive of the pres ence of a β-glucosyl and a α-arabinosyl moi ety. On acid hy dro ly sis, **10** fur nished an aglycone, mp 293-295 °C, *m/z*: 454 $[M]^+$. Many fea tures in its EI mass spectrum in di cated that the aglycone was closely re lated in struc-

Table 1. ^{13}C NMR Spectral Data of Compounds **10**~**12** (100 MHz, **10** in CD_3OD, **11**~**12** in C_5D_5N)

C	**10**	**11**	**12**
1	40.23 t	39.36 t	39.05 t
2	27.47 t	28.15 t	28.15 t
3	90.66 d	79.08 d	79.32 d
4	40.35 s	39.45 s	39.45 s
5	57.20 d	55.96 d	55.96 d
6	19.27 t	18.67 t	18.67 t
7	35.85 t	35.11 t	35.11 t
8	40.64 s	39.81 s	39.45 s
9	48.58 d	48.32 d	48.10 d
10	37.82 s	37.51 s	37.51 s
11	24.23 t	23.48 t	23.85 t
12	127.70 d	126.65 d	128.56 d
13	139.54 s	138.75 s	138.75 s
14	45.69 s	44.91 s	42.80 s
15	29.24 t	29.05 t	29.05 t
16	27.14 t	26.74 t	25.77 t
17	48.36 s	49.90 s	49.80 s
18	134.04 s	133.84 s	52.23 d
19	137.53 s	137.51 s	153.45 d
20	35.63 d	34.58 d	37.40 s
21	31.61 t	30.97 t	30.63 t
22	35.85 t	35.31 t	37.18 t
23	28.66 q	28.79 q	28.79 q
24	17.14 q	16.60 q	16.51 q
25	16.70 q	16.31 q	15.77 q
26	18.74 q	18.56 q	18.68 q
27	22.35 q	22.11 q	22.11 q
28	176.60 s	174.74 s	176.28 s
29	19.79 q	19.53 q	110.37 t
30	18.74 q	18.68 q	19.38 q
Sugar moieties			
	Glc-28	Glc-28	Glc-28
1	95.77 d	95.80 d	95.90 d
2	74.03 d	74.11 d	74.05 d
3	78.63 d	78.87 d	78.87 d
4	71.26 d	71.18 d	71.18 d
5	78.39 d	78.06 d	78.14 d
6	62.61 t	62.30 t	62.30 t
	Ara-3		
1	107.09 d		
2	72.83 d		
3	74.33 d		
4	69.47 d		
5	66.32 t		

ture to Ilexolic acid.[17] Thus **10** was de ter mined to be Ilexolic acid 3-*O*-α-L-arabinopyranosyl-28-*O*-β-D-glucopyranoside (3-*O*-α-L-arabinopyranosyl-18-dehydro-20-epiursolic acid 28-*O*-β-D-glucopyranosyl es ter).

Com pounds **11** and **12** were iso lated as an in sep a ra ble mix ture in a ra tio of 3:2, based on the in te gra tion of the olefinic pro tons cor re spond ing to the aglycone groups in the ^{1}H NMR spec trum of **11**+**12**. The IR spec trum showed the presence of hydroxyl groups (3433 cm^{-1}), ester carbonyl (1723 cm^{-1}) and dou ble bond (1631 cm^{-1}). Acid hy dro ly sis of the mix ture af forded D-glucose as the sole sugar, and HR-FABMS (*m/z* 616.3969; calc.: 616.3969), in di cated that the mo lec u lar for mula should be $C_{36}H_{56}O_8$. The NMR spec trum of **11**+**12** showed that **11** and **12** were struc tural iso mers. The ^{1}H NMR spec trum (400 MHz, pyridine-d_5) in di cated that **11** was closely re lated to **10**, ex cept for the ab sence of arabinosyl moi ety at C-3. The ^{13}C NMR spec trum of **11**+**12** ex hib ited sig nals for two Δ^{12}-dou ble bond (δ 126.65, 138.75; 128.56, 138.75), one $\Delta^{18(19)}$-dou ble bond (δ 133.84, 137.51) and one ter mi nal dou ble bond [δ 153.45(s), δ110.37(t)]. Com pari son of the ^{13}C NMR and DEPT spec tral data of **11** and **12** with those of re lated com pounds found com pound **11** and **12** to have a con ju gated $\Delta^{12,18}$,[17] and $\Delta^{12,19(29)}$ func tions, re spec-tively.[15] The ^{1}H NMR spec trum of **11**+**12** showed sig nals for two anomeric pro tons of glu cose (δ 6.32, 6.31, d, *J* = 8.1 Hz), H-29 (δ 1.79, 3H, s; δ 5.53, 5.18, 2H, br s), H-12 (δ 5.75, 1H, t; δ 5.65, 1H, t), and H-3 (δ 3.45, 2H, dd, *J* = 11.1, 4.1 Hz). Thus, **11** was elu ci dated as Ilexolic acid 28-*O*-β-D- glu co-pyranoside (18-dehydro-20-epiursolic acid 28-*O*-β-D- gluco-pyranosyl ester) and **12** was deduced as 3β-hydroxyurs-12,19(29)-dien-28-oic acid β-D-glucopyranosyl es ter.

The com pound **13**, platelet crys tals, mp 247-249 °C, had a mo lec u lar for mula, $C_{41}H_{64}O_{12}$, based on the HR- FABMS (*m/z* 748.4394; calc.: 748.4392). The IR spec trum (KBr) in di-cated the pres ence of hydroxyl groups (3437 cm^{-1}), es ter car-bonyl (1729 cm^{-1}) and dou ble bond (1645 cm^{-1}). Acid hy dro-ly sis of **13** af forded D-glucose and L-arabinose, iden ti fied by PC. The ^{1}H NMR spec trum of **13** showed the pres ence of two trisubstituted dou ble bonds. That these two trisubstituted dou ble bonds form a homoannular diene sys tem was ev i dent from its UV ab sorp tion max i mum at 280 nm char ac ter is tic of such a sys tem.[17] The fol low ing ^{1}H NMR spec tral data of **13** (400 MHz, pyridine-d_5) sug gested the struc tural fea tures of an urs-9(11),12-dien-28-oic acid bioside triterpene: a broad sin glet at δ 1.97 (H-18), two olefinic pro tons at δ 5.70 (d, *J* = 10.7 Hz, H-11) and δ 6.49 (d, *J* = 10.5 Hz, H-12), which were con firmed by the cross peaks be tween H-11 and H-12 in the ^{1}H-^{1}H COSY spec trum, and H-29 (δ 0.75, d, *J* = 6.4 Hz, 3H), H-30 (δ 0.97, d, *J* = 6.7 Hz, 3H) and two anomeric pro tons at δ 6.20 (d, *J* = 8.1 Hz, glc-1) and δ 4.75 (d, *J* = 7.0 Hz, ara-1). The ^{13}C NMR spec trum showed four olefinic car bons at δ 135.49 (s, C-9), 127.34 (d, C-11) and 125.99 (d, C-12), 138.25 (s, C-13), and a car boxyl car bon at δ 176.58 (s, C-28). The as sign ments of the ^{13}C NMR sig nals of **13** were made by

Table 2. ^{1}H and ^{13}C NMR Spectral Data of Compound **13** (400 MHz, C_5D_5N)

No.	H	C	Observed connectivities in HMBC spectrum
1	0.97 m, 1.81 m	38.29 t	H-2, H-25
2	1.91 m, 2.20 m	26.54 t	H-1
3	3.35 dd (11.8, 4.1)	88.56 d	H-1, H-2, Ara-1′, H-23, H-24
4		39.64 s	H-23, H-24
5		55.32 d	H-24, H-23, H-1
6		26.61 t	H-26
7		32.82 t	H-26
8		40.86 s	H-11, H-18, H-6, H-26, H-27
9		135.49 s	H-11, H-12, H-18, H-27
10		36.65 s	H-1, H-2, H-25
11	5.70 d (10.7)	127.34 d	H-18
12	6.49 d (10.5)	125.99 d	H-18
13		138.25 s	H-12, H-26, H-27
14		42.48 s	H-12, H-15, H-26, H-27
15	1.67 m, 2.15 m	32.00 t	H-26, H-27, H-16
16	1.65 m, 2.01 m	25.68 t	H-15, H-27
17		47.16 s	H-22
18	1.97	54.67 d	H-12
19		27.80 d	H-29, H-21, H-22
20	2.81 m	34.67 d	H-19, H-29, H-30
21		32.60 t	H-30
22		24.99 t	H-20, H-29
23	1.26 s	27.90 q	H-3, H-24
24	0.92 s	16.66 q	H-3, H-23
25	0.86 s	18.37 q	H-1
26	1.14 s	17.00 q	
27	1.00 s	21.23 q	H-26
28		176.58 s	Glc-1″, H-22, H-21
29	0.75 d (6.4)	19.46 q	H-28
30	0.97 d (6.7)	16.42 q	
Ara-3			
1′	4.75 d (7.0)	107.47 d	
2′	4.45 m	72.88 d	
3′	4.16 m	74.58 d	
4′	4.32 m	69.47 d	
5′	4.02 m, 3.98 m	66.70 t	
Glc-28			
1″	6.20 d (8.1)	96.37 d	
2″	4.17 m	74.09 d	
3″	4.42 m	79.25 d	
4″	4.37 m	71.25 d	
5″	3.83 m	78.81 d	
6″	4.28 m, 4.24 m	62.36 t	

comparison with those of model triterpenes[18] and were confirmed by the HMQC and HMBC spectral analysis (see Table 2). On the basis of these data, the structure of **13** was elucided as 3-*O*-α-L-arabinopyranosyl-urs-9(11),12-dien-28-oic acid β-D-glucopyranosyl ester.

The compound **14**, amorphous powder, mp 293-295°C, has a molecular formula, $C_{30}H_{46}O_8$, based on the HR-FABMS (*m/z* 534.3191; calc.: 534.3189). The IR spectrum showed the absorption for hydroxyl groups (3412 cm^{-1}) and a carboxylic group (1689 cm^{-1}). The EI-MS exhibited significant ions at *m/z* 264, 246, 201, 187, and 146, which indicated the presence of a tertiary hydroxyl function on C-19 in the urs-12-en-28-oic acid skeleton in accord with its ^{13}C NMR spectrum.[19] The ^{1}H NMR spectrum of **14** showed signals for two protons on C-1 (δ 1.47, 2.28, m, 2H) and two geminal protons on C-25 (δ 4.17, 4.22, dd, *J* = 13.8,1.5 Hz, 2H), which were

Table 3. ^{1}H and ^{13}C NMR Spectral Data of Compound **14** (400 MHz, C_5D_5N)

No.	H	C	Observed connectivities in HMBC spectrum
1	1.47 m, 2.28 m	48.26 t	
2	4.23 m	68.69 d	H-1, H-3
3	4.62 d (8.4)	81.24 d	H-1, H-24
4		54.70 s	H-3, H-5, H-24
5	2.23 m	52.34 d	H-24, H-26
6		21.37 t	H-5, H-26
7		33.31 t	H-26
8		40.44 s	H-26, H-27
9		48.07 d	
10		38.54 s	H-1, H-25, H-26
11	2.08 m, 2.23 m	24.10 t	H-12, H-27
12	5.54 m	127.63 d	H-11, H-18
13		140.08 s	H-18, H-27
14		42.09 s	H-12, H-18, H-26, H-27
15	1.16 m, 2.21 m	29.25 t	H-27
16	2.02 m, 3.10 m	26.96 t	
17		48.07 s	H-15, H-18
18	3.02 br s	54.70 d	H-11, H-29
19		72.70 s	H-18, H-29, H-30
20	1.30 m	42.31 d	H-29, H-30
21	1.40 m	26.40 t	H-30
22	2.04 m	38.54 t	
23		181.05 s	
24	1.68 s	13.73 q	H-3, H-5
25	4.17, 4.22 dd (13.8, 1.5)	64.79 t	H-2
26	1.06 s	17.31 q	H-11
27	1.62 s	24.61 q	H-30
28		181.05 s	H-18
29	1.39 s	27.08 q	
30	1.08 d (6.6)	16.74 q	

con firmed by the cross peaks be tween H-1 and H-25 in the ^{1}H-^{1}H COSY spec trum.[15] Since the sig nal of C-4 was shifted to lower field (δ 54.70) than that of **7** (δ 38.67),[6] and was very sim i lar to that of the co-occurring known triterpene **9**,[11] the car boxyl group was assigned to C-23 on the ba sis of HMBC and NOESY dif fer ence spec tra (see Ta ble 3). Thus, **14** was elu ci dated as 2α,3α,19α,25-tetrahydroxyurs-12-en-23,28-dioic acid.

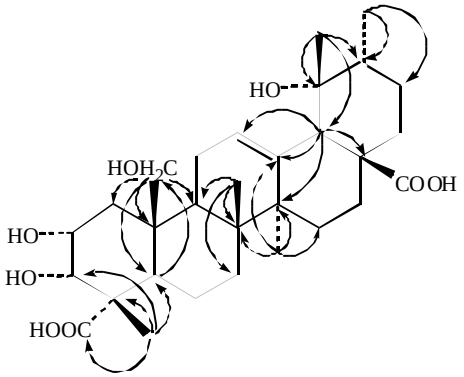

Fig. 1. Se lected HMBC cor re la tions of **14**.

The above twenty-one com pounds con tained seven dif-fer ent skel e tons: five ursane type triterpenoid ac ids (**1**, **2**, **3**, **7**, and **14**), nine ursane type triterpenoid sapo nins (**4**, **5**, **6**, **8**, **9**, **10**, **11**, **12**, and **13**), three ecdysteroids (**15**, **16**, and **17**), one phe nol (**18**), one thiophene (**19**), one flavonoid (**20**), and one ste roid (**21**). Triterpenoid is an other ma jor prod uct in this plant ex cept the phytoecdysones.

EXPERIMENTAL SECTION

General Methods

Melting points were de ter mined on a Kofler micro-melting point ap pa ra tus and are un cor rected. Op ti cal ro ta-

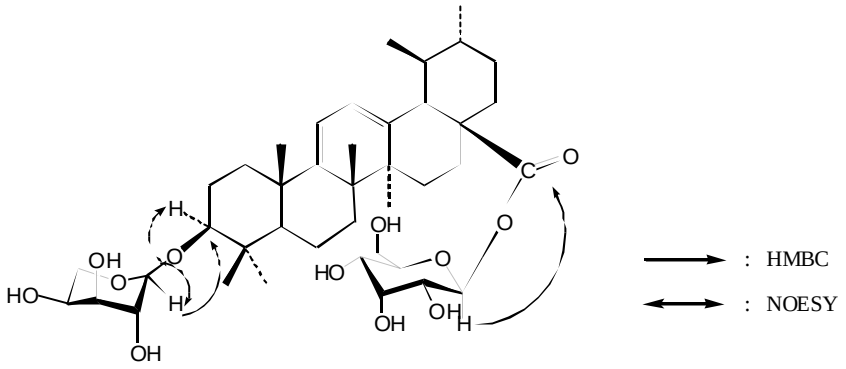

Fig. 2. Key HMBC and NOESY cor re la tions of **13**.

tions were ob tained with a JASCO-20 polarimeter. IR spec tra were re corded on a Bio-Rad FTS spec trom e ter and UV spectra on an UV-210A spec trom e ter. NMR spec tra were performed on a Bruker AM-400 us ing TMS as an in ter nal standard. NMR ex per i ments in cluded ^{1}H-^{1}H COSY, NOESY, HMQC, and HMBC. HR-FABMS was mea sured on a Bruker APEX II, and FABMS and EIMS were mea sured on a VG-ZAB-HS mass spec trom e ter.

Plant Material

The roots of *Rhaponticum uniflorum* (L.) DC. (Compositae) were pur chased from a com pany of Chi nese me dic i-nal ma te ri als in Gansu Prov ince, China, and were iden ti fied by Prof. Yin-Shou Zhou, Lanzhou Medical College. A voucher spec i men No. 98001 was de pos ited in the Her bar ium of the Phar macy De part ment, Lanzhou Med i cal Col lege, and in the Lab o ra tory of Nat u ral Prod ucts, Lanzhou Uni ver sity, P. R. China.

Extraction and Isolation

The roots of *Rhaponticum uniflorum* (3 kg) were extracted with MeOH (×6) at room tem per a ture, and con centrated to give a dark brown syrup (156 g). The MeOH ex tract was sus pended in wa ter and sub jected to se quen tial ex traction with petrol, EtOAc and n-BuOH, successively. The EtOAc layer was con cen trated un der re duced pres sure to leave a brown syrup (41 g) which was sub jected to chro matog ra phy on sil ica gel (2.1 Kg, 200-300 mesh) and eluted with a gra di ent of petrol and EtOAc (9:1) to af ford five frac tions. Frac tion II (16 g) un der went col umn chro ma tog ra phy on silica-gel (1.6 Kg, 300-400 mesh) and eluted with n-hexane-EtOAc (9:1) to ob tain **19** (25 mg), **1** (10 mg), **2** (14 mg), **3** (56 mg), **7** (41 mg), **14** (46 mg), **18** (65 mg), and **20** (45 mg), successively. Frac tion III was chromatographed on Sephadex LH-20 and eluted with MeOH or H_2O-MeOH to yield **21** (36 mg), **4** (50 mg), **5** (42 mg), **11** and **12** (50 mg). Frac tion IV was purified by repeated chromatography on Sephadex LH-20 and eluted with a gra di ent of H_2O-MeOH to give **8** (45 mg), **6** (80 mg), **10** (55 mg), **13** (56 mg), **15** (31 mg), **16** (23 mg) and **17** (25 mg).

The n-BuOH layer was con cen trated un der re duced pres sure to leave a brown syrup (36 g) which was sub jected to chro ma tog ra phy on sil ica gel (1.8 Kg, 200-300 mesh) and eluted with a gra di ent of $CHCl_3$ and MeOH (8:1) to af ford **9** (46 mg).

3-*O*-α-L-Arabinopyranosyl-urs-12,18(19)-dien-28-oic acid β-D-glucopyranosyl ester (10)

Amor phous pow der (MeOH), mp 203-205 °C; $[\alpha]_D^{20}$ +67.1° (MeOH; c 0.31); UV (MeOH) λ_{max} (log ε): 238 (3.75) nm; IR (KBr, cm^{-1}): 3354 (OH), 1727 (C=O), 1449, 1386, 1074; ^{1}H NMR (400 MHz, CD_3OD): δ 3.15 (1H, dd, *J* = 11.1, 4.1 Hz, H-3), 5.37 (1H, t, *J* = 4.0 Hz, H-12), 1.73 (3H, s, H-29), 0.99 (3H, d, *J* = 6.4 Hz, H-30), 0.84, 0.92, 0.98, 1.04, 1.10 (each 3H, s, Me × 5), 4.26 (1H, d, *J* = 6.9 Hz, H-Ara1), 6.20 (1H, d, *J* = 8.1 Hz, H-Glc1); ^{13}C NMR (100 MHz, CD_3OD) data is listed in Ta ble 1; EIMS *m/z* (rel. Int.): 586 (M-Glc, 2.1), 454 (M-Glc-Ara, 5.3), 437 (5.6), 408 (2.4), 246 (26.6), 208 (3.6), 207 (14.7), 201 (51.6), 190 (54.8), 189 (50.0), 145 (35.0), 119 (48.0); FAB-MS *m/z*: 771 $[M+Na]^+$, 749 $[M+H]^+$; HR-FABMS *m/z* 748.4400, calcd for $C_{41}H_{64}O_{12}$: 748.4392.

3β-Hydroxyurs-12,18(19)-dien-oic acid β-D-glucopyranosyl es ter (11) and 3β-hydroxyurs-12,19(29)-dien-28-oic acid β-D-glucopyranosyl es ter (12)

Amor phous pow der (MeOH). IR (KBr, cm^{-1}): 3433 (OH), 1723 (C=O), 1631 (C=C), 1454, 1387, 1198, 1071; ^{1}H

NMR (400 MHz, C_5D_5N): δ 3.45 (1H, dd, *J* = 11.0, 4.0 Hz, H-3), 5.69, 5.53, t, H-12; 1.79 (3H, s, H-29), 5.53, 5.18 (2H, br s, H-29'), 1.00 (3H, d, *J* = 6.2 Hz, H-30), 0.91, 1.00, 1.08, 1.15, 1.21 (each 3H, s, Me×5), 6.31, 6.32 (each 1H, d, *J* = 8.1 Hz, glc-1); ^{13}C NMR (100 MHz, C_5D_5N) data is listed in Table 1; EIMS *m/z* (rel. Int.): 454 (M-Glc, 5.0), 408 (2.9), 246 (27.2), 208 (4.2), 207 (16.0), 201 (53.0), 190 (56.0), 189 (51.0), 145 (34.2), 119 (47.5); FAB-MS *m/z*: 639 $[M+Na]^+$, 617 $[M+H]^+$; HR-FABMS *m/z* 616.3969, calcd for $C_{36}H_{56}O_8$: 616.3969.

3-*O*-α-L-Arabinopyranosyl-urs-9(11),12-dien-28-oic acid β-D-glucopyranosyl ester (13)

Platelet crystals (MeOH), mp 247-249 °C; $[\alpha]_D^{20}$ +21° (pyridine; c 0.12); IR (KBr, cm^{-1}): 3437 (OH), 1729 (C=O), 1645 (C=C), 1468, 1370, 1068; UV (MeOH) λ_{max} (log ε): 280 (3.91) nm; ^{1}H NMR, ^{13}C NMR (400 MHz, C_5D_5N) data is listed in Table 2; FABMS *m/z*: 771 $[M+Na]^+$, 749 $[M+H]^+$, 586 $[M-Glc]^+$, 454 $[M-Glc-Ara]^+$; HR-FABMS *m/z* 748.4394, calc.: 748.4392.

2α,3α,19α,25-Tetrahydroxyurs-12-en-23,28-dioic acid (14)

Amorphous powder (MeOH), mp 293-295 °C; $[\alpha]_D^{20}$ +43.6° (pyridine; c 0.21); IR (KBr, cm^{-1}): 3412 (OH), 1689 (COOH), 1605 (C=C), 1558, 1461, 1398, 1051; ^{1}H NMR, ^{13}C NMR (400 MHz, C_5D_5N) data is listed in Table 3. EIMS *m/z*: 517 ($M+H-H_2O$, 100), 498 ($M-2H_2O$, 13.0), 264 (3.0), 246 (3.5), 201 (5.0), 187 (2.7), 146 (4.0); FABMS *m/z*: 534 $[M]^+$, 517 $[M+H-H_2O]^+$; HR-FABMS *m/z* 534.3191, calcd for $C_{30}H_{46}O_8$: 534.3189.

Total hydrolysis of compounds 8,9,10,11+12,13

Each compound (20 mg), 15% HCl (20 mL) and C_6H_6 (20 mL) were mixed and refluxed for 10 hr. After neutralization of the aq. layer, the soln was filtered and concd. D-Glucose in compounds **8**, **9**, **10**, **11**+**12**, and **13** was identified by PC using EtOAc-pyridine-H_2O (12:5:4) as developing solvent. L-Arabinose in compounds **10** and **13** was detected by PC.

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Key Words

Rhaponticum uniflorum; Compositae; Triterpenoid saponins; Triterpenoid acids.

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