New Triterpenoid Saponins and Neolignans from *Morina kokonorica*

by **Ying Zhu***[a]), **Zhang-Ping Lü**[a]), **Cai-Bin Xue**[a]), and **Wang-Suo Wu**[b])

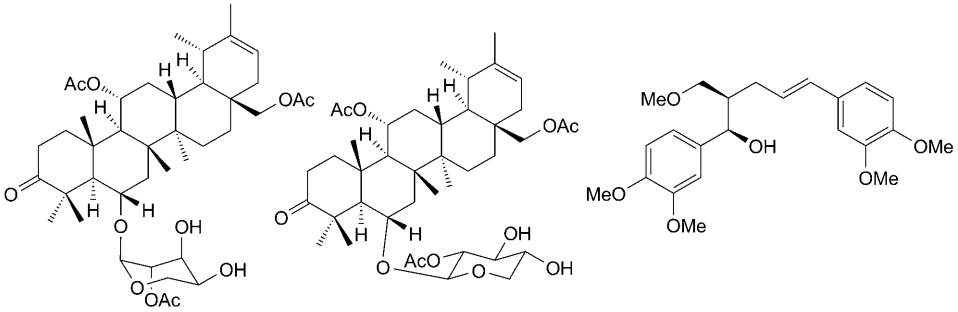
[a]) State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China (phone: +86-931-3698769; fax: +86-931-8912582; e-mail: zhuy@lzu.edu.cn)

[b]) Radiochemistry Laboratory, Lanzhou University, Lanzhou 730000, P. R. China

Two new taraxastane-type triterpenoid saponins and two new neolignans, (6α,11α)-6-[(2-*O*-acetyl-α-L-arabinopyranosyl)oxy]-3-oxotaraxast-20-ene-11,28-diyl diacetate (**1**), (6α,11α)-6-[(2-*O*-acetyl-β-D-xylopyranosyl)oxy]-3-oxotaraxast-20-ene-11,28-diyl diacetate (**2**), (1*R*,2*R*,4*E*)-1,5-bis(3,4-dimethoxyphenyl)-2-(methoxymethyl)pent-4-en-1-ol (**3**), and 1,1′-[(1*E*,4*R*,5*R*)-5-methoxy-4-(methoxymethyl)pent-1-ene-1,5-diyl]bis(3,4-dimethoxybenzene) (**4**), together with six known compounds were isolated from the Chinese medicinal plant *Morina kokonorica* HAO. Their structures were determined on the basis of spectral data, especially 2D-NMR and HR-ESI-MS.

Introduction. – The genus *Morina* (Dipsacaceae) consists of *ca.* 15 species growing in plateau regions of temperate zones in the world. Six species, *M. chinensis*, *M. chlorantha*, *M. kokonorica*, *M. nepalensis* var. *alba, M. nepalensis* var. *delavayi*, and *M. nepalensis* var. *nepalensis*, mainly occur in mountainous regions at the altitude between 2800 and 4900 m in the northwest and southwest of China [1]. Some species of this genus have been used as Chinese traditional medicine for the treatments of cerebral apoplexy, arthralgia, lumbago, megrim, and tumors, such as *M. chinensis*, *M. kokanica*, *M. nepalensis* var. *alba*, and *M. nepalensis* var. *delavayi* [2]. Up to now, the chemical constituents of *M. chinensis* [3], *M. nepalensis* var. *alba* [4], *M. kokanica* [5], *M. longifolia* [6], *M. officinalis* [7], and *M. persica* [8] were reported as triterpenoids, triterpenoid saponins, lignanoids, phenylpropanoids, caffeoylquinic acids, flavonoids, and essential oils. In this article, we present the results of our systematic investigation of *M. kokonorica*. Two new taraxastane-type triterpene saponins, **1** and **2**, two new neolignans, **3** and **4**, together with six known compounds, **5**–**10**, were isolated from the MeOH extract of the whole plant. Their structures were determined on the basis of spectral data, including 1D- and 2D-NMR, HR-ESI-MS, as well as IR, UV, and CD. The known compounds are elucidated as 3β-hydroxyurs-12-en-28-al (= ursolaldehyde) (**5**) [9][10], 3β-hydroxyurs-11-en-28,13β-olide (**6**) [11], morinol G (**7**) [12], (+)-pinoresinol (**8**) [13], (−)-lariciresinol (**9**) [14], and balanophonin (**10**) [15] by comparison of their physical and spectral data with those reported in the literature.

Results and Discussion. – Compound **1** was obtained as a crystalline powder. The HR-ESI-MS showed a *pseudo*-molecular ion peak at *m*/*z* 748.4633 ($[M+NH_4]^+$, $C_{41}H_{66}NO_{11}^+$; calc. 748.4630), corresponding to the molecular formula $C_{41}H_{62}O_{11}$. The IR spectrum of **1** showed absorption bands at 3435 (OH), 1735 (C=O), and 1639



(C=C) cm^{-1}. From ^1H- and ^{13}C-NMR (*Table 1*), ^1H,^1H-COSY, HSQC, and HMBC, 1D-NOE, and NOESY data, the structure of **1** was determined as (6α,11α)-6-[(2-*O*-acetyl-α-L-arabinopyranosyl)oxy]-3-oxotaraxast-20-ene-11,28-diyl diacetate.

The ^{13}C-NMR spectrum (*Table 1*) of **1** showed 41 C-atoms, including seven characteristic Me groups of a triterpenoid moiety, a CO group (δ(C) 218.5), a CH_2O group (δ(C) 61.4), two O–CH groups (δ(C) 79.8 and 72.7), two olefinic C-atoms (δ(C) 117.9 (C(21)), 139.8 (C(20))), three AcO groups, and a sugar residue. The ^1H-NMR spectrum (*Table 1*) showed the presence of six tertiary Me groups at δ(H) 0.79, 1.11, 1.22, 1.24, 1.03, and 1.60, one secondary Me group at δ(H) 0.94 (d, J = 6.6, Me(29)), an olefinic H-atom at δ(H) 5.23 (br. d, J = 6.6, H–C(21)), H-atoms of two O–CH groups (δ(H) 3.72 (br. dd, J = 10.5, 3.0), 4.92–4.94 (m)), H-atoms of a CH_2O group (δ(H) 3.77 (d, J = 10.5), 4.27 (d, J = 10.5)) and an anomeric H-atom (δ(H) 4.60 (d, J = 6.0)).

Table 1. *^{1}H- and ^{13}C-NMR* (DEPT) *Data*[a]) *of* **1** *and* **2** ($CDCl_3$, δ in ppm, J in Hz)

	δ(H)		δ(C)	
	1	**2**	**1**	**2**
CH_2(1)	1.93–1.95 (m, H_α), 2.22–2.24 (m, H_β)	1.95–1.97 (m, H_α), 2.19–2.21 (m, H_β)	42.1 (t)	42.2 (t)
CH_2(2)	2.76 (br. dd, J = 11.5, 12.6, H_α), 2.17–2.19 (m, H_β)	2.76–2.78 (m, H_α), 2.16–2.18 (m, H_β)	33.1 (t)	33.2 (t)
C(3)	–	–	218.5 (s)	218.6 (s)
C(4)	–	–	47.5 (s)	47.6 (s)
H–C(5)	1.94–1.96 (m)	1.95–1.97 (m)	56.8 (d)	56.9 (d)
H–C(6)	3.72 (br. dd, J = 10.5, 3.0)	3.69–3.71 (m)	79.8 (d)	79.5 (d)
CH_2(7)	1.51–1.53 (m, H_α), 1.99–2.01 (m, H_β)	1.51–1.53 (m, H_α), 1.98–2.00 (m, H_β)	34.4 (t)	35.1 (t)
C(8)	–	–	41.9 (s)	41.9 (s)
H–C(9)	1.83–1.85 (m)	1.84–1.86 (m)	51.3 (d)	51.4 (d)
C(10)	–	–	39.6 (s)	39.6 (s)
H–C(11)	4.92–4.94 (m)	4.97–4.99 (m)	72.7 (d)	72.8 (d)
CH_2(12)	1.26–1.35 (m, H_α), 1.74–1.82 (m, H_β)	1.28–1.32 (m, H_α), 1.76–1.84 (m, H_β)	35.0 (t)	35.1 (t)
H–C(13)	1.80–1.82 (m)	1.79–1.81 (m)	36.6 (d)	36.7 (d)
C(14)	–	–	43.0 (s)	43.1 (s)
CH_2(15)	0.99 (br. d, J = 8.8, H_α), 2.14–2.15 (m, H_β)	1.00 (br. d, J = 8.8, H_α), 2.12–2.14 (m, H_β)	26.5 (t)	26.5 (t)
CH_2(16)	1.55–1.57 (m, H_α), 1.13–1.15 (m, H_β)	1.56–1.58 (m, H_α), 1.14–1.16 (m, H_β)	30.0 (t)	30.1 (t)
C(17)	–	–	37.1 (s)	37.2 (s)
H–C(18)	1.33–1.35 (m)	1.33–1.35 (m)	48.0 (d)	48.0 (d)
H–C(19)	1.66–1.68 (m)	1.67–1.69 (m)	35.4 (d)	35.5 (d)
C(20)	–	–	139.8 (s)	139.7 (s)
H–C(21)	5.23 (br. d, J = 6.6)	5.24 (br. d, J = 6.6)	117.9 (d)	118.0 (d)
CH_2(22)	1.98–2.00 (m, H_α), 2.05–2.07 (m, H_β)	1.99–2.01 (m, H_α), 2.04–2.06 (m, H_β)	41.6 (t)	41.7 (t)
Me(23)	1.24 (s)	1.24 (s)	31.3 (q)	31.3 (q)
Me(24)	1.22 (s)	1.23 (s)	18.7 (q)	18.8 (q)
Me(25)	0.79 (s)	0.81 (s)	19.1 (q)	19.1 (q)
Me(26)	1.11 (s)	1.13 (s)	17.4 (q)	17.4 (q)
Me(27)	1.03 (s)	1.03 (s)	14.4 (q)	14.4 (q)
CH_2(28)	3.77 (d, J = 10.5, H_a), 4.27 (d, J = 10.5, H_b)	3.78 (d, J = 10.5, H_a), 4.28 (d, J = 10.5, H_b)	61.4 (t)	61.5 (t)
Me(29)	0.94 (d, J = 6.6)	0.95 (d, J = 6.6)	22.6 (q)	22.7 (q)
Me(30)	1.60 (s)	1.62 (s)	21.4 (q)	21.4 (q)
sugar	Ara	Xyl	Ara	Xyl
H–C(1′)	4.60 (d, J = 6.0)	4.61 (d, J = 6.3)	101.0 (d)	101.7 (d)
H–C(2′)	4.96 (t, J = 7.0)	4.78 (t, J = 7.2)	72.6 (d)	73.7 (d)
H–C(3′)	3.69–3.71 (m)	3.54 (t, J = 8.2)	71.7 (d)	75.5 (d)
H–C(4′)	3.89–3.91 (m)	3.81–3.83 (m)	67.0 (d)	70.3 (d)
CH_2(5′)	3.55 (dd, J = 13.5, 4.2, H_a), 3.91–3.93 (m, H_b)	3.31 (dd, J = 11.7, 2.1, H_a), 4.03 (dd, J = 11.4, 4.5, H_b)	63.5 (t)	64.3 (t)
C(1″)	–	–	171.4 (s)	171.4 (s)
Me(2″)	2.10 (s)	2.12 (s)	21.0 (q)	21.1 (q)
C(1*)	–	–	171.2 (s)	171.2 (s)
Me(2*)	2.02 (s)	2.04 (s)	21.2 (q)	21.3 (q)
C(1#)	–	–	171.0 (s)	170.0 (s)
Me(2#)	2.00 (s)	2.00 (s)	21.9 (q)	21.9 (q)

[a]) The assignments of the signals of **1** and **2** were performed by ^{1}H,^{1}H-COSY, HMBC, and NOESY experiments.

The ^{1}H- and ^{13}C-NMR data of **1** were similar to those of taraxast-20-en-3-one [16–18], indicating that **1** is a taraxastane-type triterpene saponin.

The ^{1}H- and ^{13}C-NMR spectra showed signals of the sugar residue at δ(H) 4.60 (*d*, $J = 6.0$), 4.96 (*t*, $J = 7.0$), 3.69–3.71 (*m*), 3.89–3.91 (*m*), 3.55 (*dd*, $J = 13.5, 4.2$), and 3.91–3.93 (*m*); and at δ(C) 101.0, 72.6, 71.7, 67.0, and 63.5, which closely resembled those of arabinopyranose (Ara) [19][20]. The L-configuration for Ara was assumed from biogenetic considerations. Furthermore, the characteristic anomeric H-atom signal (δ(H) 4.60 and $J(1',2') = 6.0$) indicated an α-configuration in comparison with the values reported for α-L-Ara (δ(H) 4.45, $J = 7$) and β-L-Ara (δ(H) 5.23, $J = 3$) in the literature [20]. The signals for H–C(2′) and C(2′) were shifted downfield because of the effect of an AcO group [20]. This was supported by HMBCs from H–C(2′) at δ(H) 4.96 to C(1′), C(3′), and an AcO group (C(1″) at δ(C) 171.4). ^{1}H,^{1}H-COSY correlations, between H–C(1′) at δ(H) 4.60 and H–C(2′) at δ(H) 4.96, and between H–C(2′) and H–C(3′) at δ(H) 3.69–3.71, further confirmed the position of the AcO group in the sugar residue.

The structure of **1** and its ^{1}H- and ^{13}C-NMR assignment were confirmed by ^{1}H,^{1}H-COSY, HSQC, and HMBC experiments (*Fig. 1*). The C=C bond was located between C(20) and C(21), which was confirmed by HMBCs from C(20) to H_α–C(22) at δ(H) 1.98–2.00, Me(29) and Me(30), from C(21) to Me(30) and H_α–C(22), and from H–C(21) to C(17), C(19), and C(30). The CO group was located at C(3) due to HMBCs from the CO group at δ(C) 218.5 to CH_2(1), CH_2(2), H–C(5), Me(23), and Me(24). Two AcO groups were assigned to the C(11) and C(28) positions, respectively, based on the HMBCs from H–C(11) at δ(H) 4.92–4.94 to an AcO group with C(1#) at δ(C) 171.0 and from the CH_2O group with H_a–C(28) at δ(H) 3.77 and H_b–C(28) at δ(H) 4.27 to C(16), C(17), C(19) and the other AcO group with C(1*) at δ(C) 171.2. The arabinopyranosyloxy residue was located at the C(6) position, based on the

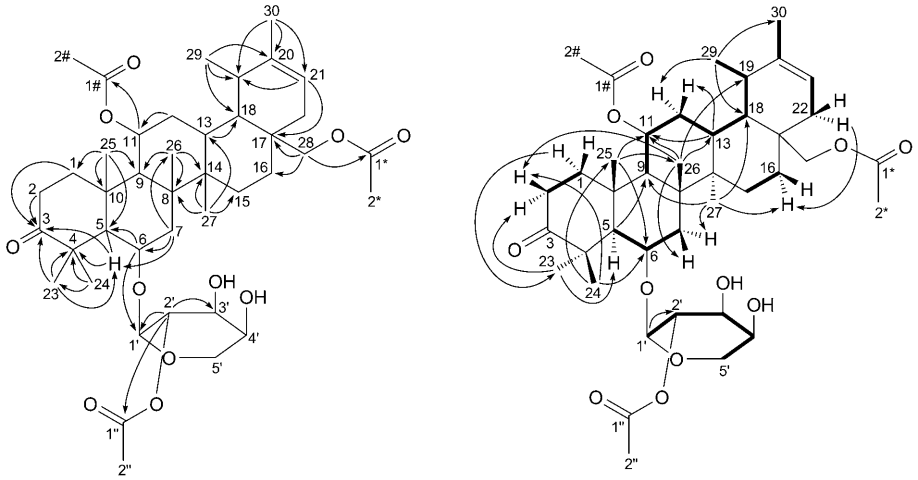


Fig. 1. *Key correlations from HMBC* (H → C), *^{1}H,^{1}H-COSY* (—), *and NOESY* (H → H) *experiments of* **1**

HMBCs observed between H–C(6) at δ(H) 3.72 and the anomeric C-atom C(1′) at δ(C) 101.0.

The relative configuration of **1** was elucidated by coupling constants, NOE, and NOESY experiments. The orientation of the (arabinopyranosyl)oxy residue at C(6) was assigned to be α due to the coupling constants of H–C(6) (δ(H) 3.72, br. *dd*, J = 10.5, 3.0) in the ^{1}H-NMR. This coupling pattern was similar to that found in other 6α-OH triterpenes such as missourin, which shows a *doublet* of *triplet* (J = 11.4, 7.2) pattern [21], in contrast to 6β-OH triterpenes (*m*, $W_{1/2}$ = 6 Hz or br. *s*) [16][22]. In NOE experiments, irradiation of Me(25) lead to the enhancement of Me(24) (+10.38%), Me(26) (+10.48%), H_a–C(28) at δ(H) 3.77 (+7.09%) and H–C(11) (+5.90%) and irradiation of H–C(18) lead to the enhancement of Me(27) (+8.78%) and Me(29) (+6.68%). A NOESY experiment showed key correlations as shown (*Fig. 1*), especially significant correlations from Me(23) to H_α–C(1) at 1.93–1.95 and H_α–C(2) at δ(H) 2.76, correlations from Me(24) to Me(25), H–C(6), and H_β–C(12) at δ(H) 1.74–1.82, correlations from Me(25) to Me(26), H_β–C(7) at δ(H) 1.99–2.01, and H–C(11), correlations from Me(26) to Me(24), H_β–C(1) at δ(H) 2.22–2.24, H–C(11), and H–C(19) at δ(H) 1.66–1.68, correlations from Me(27) to H–C(9), H_α–C(12) at δ(H) 1.26–1.35, H_α–C(16) at δ(H) 1.55–1.57, and H–C(18), correlations from Me(29) to Me(27), H_α–C(12) at δ(H) 1.26–1.35, and H–C(18), correlation between H_α–C(16) at δ(H) 1.55–1.57 and H_α–C(22) at δ(H) 1.98–2.00. If Me(25) was β-oriented as in all natural taraxastane-type triterpenoids, H–C(6), H–C(11), Me(24), Me(25), Me(26), and CH_2(28) should be β-oriented, but H–C(5), H–C(9), H–C(18), Me(23), Me(27), and Me(29) should be α-oriented. The signals of H_α– and H_β–C(15) were assigned by comparison with reported values [17][23].

Compound **2** was obtained as a crystalline powder. The HR-ESI-MS (positive ion mode) showed a *pseudo*-molecular-ion peak at *m*/*z* 748.4671 ($[M+NH_4]^+$, $C_{41}H_{66}NO_{11}^+$; calc. 748.4630), corresponding to the molecular formula $C_{41}H_{62}O_{11}$. The IR spectrum showed absorption bands at 3436 (OH), 1734 and 1711 (C=O) cm^{-1}. From ^{1}H- and ^{13}C-NMR (*Table 1*), ^{1}H,^{1}H-COSY, HMBC (*Fig. 2*), and 1D-NOE data, the structure of **2** was elucidated as (6α,11α)-6-[(2-*O*-acetyl-β-D-xylopyranosyl)oxy]-3-oxotaraxast-20-ene-11,28-diyl diacetate.

The ^{1}H- and ^{13}C-NMR spectral data of **2** were similar to those of **1** except for the signals of the sugar residue (*Table 1*), indicating that both compounds possess the same aglycone. The ^{1}H- and ^{13}C-NMR spectra showed the sugar residue signals at δ(H) 4.61 (*d*, J = 6.3), 4.78 (*t*, J = 7.2), 3.54 (*t*, J = 8.2), 3.81–3.83 (*m*), 3.31 (*dd*, J = 11.7, 2.1), and 4.03 (*dd*, J = 11.4, 4.5); and at δ(C) 101.7, 73.7, 75.5, 70.3, and 64.3 (*Table 1*), which closely resembled those of β-xylopyranose (Xyl) [24]. The NOE experiment confirmed the sugar residue to be β-Xyl. Irradiation of H–C(1′) led to the enhancement of H–C(3′) (+4.57%) and irradiation of H–C(3′) led to the enhancement of CH_2(5′) at δ(H) 3.31 (+2.18%). The D-configuration of Xyl was assumed from biogenetic considerations. HMBCs, from H–C(2′) to C(1′), C(3′), and C(1″) (δ(C) 171.4), revealed the substitution of HO–C(2′) by an AcO group as in compound **1**.

Compound **3** was obtained as a colorless oil. The HR-ESI-MS (positive ion mode) showed a *pseudo*-molecular-ion peak at *m*/*z* 420.2379 ($[M+NH_4]^+$, $C_{23}H_{34}NO_6^+$; calc. 420.2381), corresponding to the molecular formula $C_{23}H_{30}O_6$. The IR spectrum showed absorption bands at 3514 (OH), 2931 (MeO), 1710 (conjugated C=C bond with

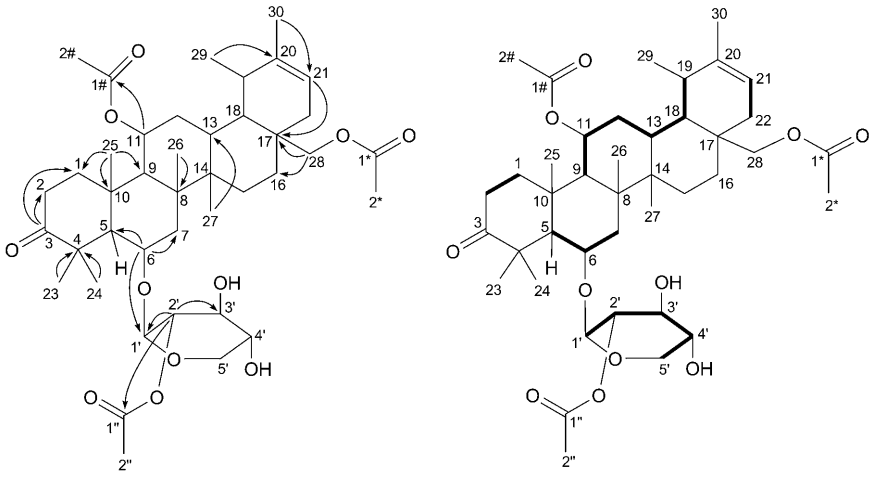


Fig. 2. *Key correlations from HMBC* (H → C) *and* ^{1}*H,*^{1}*H-COSY* (—) *experiments of* **2**

MeO), 1601 and 1514 (aromatic moiety) cm^{-1}. From ^{1}H- and ^{13}C-NMR (*Table 2*), ^{1}H,^{1}H-COSY, HMBC, and 1D-NOE data, the structure of **3** was elucidated as (1*R*,2*R*,4*E*)-1,5-bis(3,4-dimethoxyphenyl)-2-(methoxymethyl)pent-4-en-1-ol.

The ^{13}C-NMR spectrum of **3** showed 23 signals (*Table 2*), assigned to twelve C-atoms of two Ph groups, five MeO groups, an CH_2O group, an O–CH group, two olefinic and two non-oxygenated aliphatic C-atoms. The ^{1}H-NMR spectrum of **3** displayed the presence of two 1,3,4-trisubstituted Ph groups (δ(H) 6.92 (*s*), 6.82 (*d*, *J* = 7.0), 6.86 (*d*, *J* = 7.1), 6.86 (*s*), 6.80 (*d*, *J* = 7.2), and 6.85 (*d*, *J* = 7.2)), a (*E*)–C=C bond (δ(H) 6.28 (*d*, *J* = 15.6), 5.95 (*dt*, *J* = 15.6, 7.5)), one CH_2O (δ(H) 3.45 (*dd*, *J* = 9.3, 6.3), 3.59 (*dd*, *J* = 9.3, 3.6)), one CH_2 group at δ(H) 2.15 (*ddd*, *J* = 12.6, 7.5, 6.0) and 2.24 (*ddd*, *J* = 12.9, 7.5, 6.6), one O–CH group at δ(H) 4.69 (*d*, *J* = 6.3), one CH group at δ(H) 1.98–2.04 (*m*), as well as five MeO groups at δ(H) 3.36, 3.86, 3.87, 3.89, and 3.89. The ^{1}H- and ^{13}C-NMR spectra of **3** were similar to those of morinol G (**7**) with the exception of the signals of an additional MeO group appearing at δ(H) 3.36 and δ(C) 59.1 [12].

The HMBC experiment showed correlations within two C_6–C_3 units. The first unit showed correlations from C(7)[1]) at δ(C) 77.2 to H–C(6), H–C(8), H_a–C(9) and H_b–C(9); from C(8) at δ(C) 44.5 to H_a–C(9), H_b–C(9), H_a–C(9′), and H_b–C(9′); from CH_2(9) at δ(H) 3.45 and 3.59 to C(7), C(8), and a MeO C-atom at δ(C) 59.1, which indicated the presence of a MeO at C(9). The second unit showed correlations from C(7′) at δ(C) 131.4 to H–C(6′), H–C(8′), H_a–C(9′), and H_b–C(9′); from C(8′) at δ(C) 126.0 to H–C(7′), H_a–C(9′), and H_b–C(9′); from CH_2(9′) at δ(H) 2.15 and 2.24 to C(7′), C(8′), C(8), and C(9), respectively. The two C_6–C_3 units are connected between C(8) and C(9′) by a C–C bond. This was confirmed by ^{1}H,^{1}H-COSY correlations, between H–C(7) and H–C(8), from H–C(8) to CH_2(9) and CH_2(9′), and from H–C(8′) to H–C(7′) and CH_2(9′).

The relative configuration of **3** was deduced from the coupling constant and an NOE experiment. The coupling constant between H–C(8) and H–C(7) was 6.6 Hz,

Table 2. *^{1}H- and ^{13}C-NMR* (DEPT) *Data*[a]) *of* **3** *and* **4** ($CDCl_3$, δ in ppm, J in Hz)[1])

	δ(H)		δ(C)	
	3	**4**	**3**	**4**
C(1)	–	–	136.0 (*s*)	135.6 (*s*)
H–C(2)	6.92 (*s*)	6.83–6.85 (*m*)	109.4 (*d*)	110.0 (*d*)
C(3)	–	–	148.2 (*s*)	148.2 (*s*)
C(4)	–	–	148.9 (*s*)	148.9 (*s*)
H–C(5)	6.82 (*d*, J = 7.0)	6.82 (*d*, J = 7.1)	111.1 (*d*)	111.0 (*d*)
H–C(6)	6.86 (*d*, J = 7.1)	6.85–6.87 (*m*)	118.8 (*d*)	120.1 (*d*)
H–C(7)	4.69 (*d*, J = 6.3)	4.18 (*d*, J = 6.6)	77.2 (*d*)	83.1 (*d*)
H–C(8)	1.98–2.04 (*m*)	1.96–2.04 (*m*)	45.5 (*d*)	45.5 (*d*)
CH_2(9)	3.45 (*dd*, J = 9.3, 6.3, H_a), 3.59 (*dd*, J = 9.3, 3.6, H_b)	3.25–3.40 (*m*, H_a), 3.55 (*dd*, J = 9.6, 4.8, H_b)	74.2 (*t*)	71.5 (*t*)
C(1′)	–	–	130.5 (*s*)	130.8 (*s*)
H–C(2′)	6.86 (*s*)	6.83–6.85 (*m*)	108.5 (*d*)	108.4 (*d*)
C(3′)	–	–	148.3 (*s*)	148.3 (*s*)
C(4′)	–	–	148.9 (*s*)	148.9 (*s*)
H–C(5′)	6.80 (*d*, J = 7.2)	6.80 (*d*, J = 7.2)	110.7 (*d*)	110.5 (*d*)
H–C(6′)	6.85 (*d*, J = 7.2)	6.83–6.85 (*m*)	118.7 (*d*)	118.8 (*d*)
H–C(7′)	6.28 (*d*, J = 15.6)	6.21 (*d*, J = 15.9)	131.4 (*d*)	131.0 (*d*)
H–C(8′)	5.95 (*dt*, J = 15.6, 7.5)	5.92 (*dt*, J = 15.3, 7.2)	126.0 (*d*)	126.8 (*d*)
CH_2(9′)	2.15 (*ddd*, J = 12.6, 7.5, 6.0, H_a), 2.24 (*ddd*, J = 12.9, 7.5, 6.6, H_b)	2.04–2.15 (*m*, H_a), 2.17–2.21 (*m*, H_b)	32.2 (*t*)	30.5 (*t*)
MeO–C(3)	3.86 (*s*)	3.86 (*s*)	55.7 (*q*)	55.7 (*q*)
MeO–C(4)	3.89 (*s*)	3.89 (*s*)	55.8 (*q*)	55.8 (*q*)
MeO–C(3′)	3.87 (*s*)	3.87 (*s*)	55.7 (*q*)	55.7 (*q*)
MeO–C(4′)	3.89 (*s*)	3.89 (*s*)	55.8 (*q*)	55.9 (*q*)
MeO–C(7)	–	3.21 (*s*)	–	56.8 (*q*)
MeO–C(9)	3.36 (*s*)	3.35 (*s*)	59.1 (*q*)	58.9 (*q*)

[a]) The assignments of the signals of **3** and **4** were performed by ^{1}H,^{1}H-COSY, HMBC, and NOE experiments.

which suggested that the configuration is *threo* in comparison with the values reported for *threo* (J = 6.9) and *erythro* (J = 4.1) configurations [25]. In the NOE experiment, irradiation of H–C(8) lead to the enhancement of H–C(7) (+3.15%). The CD spectrum of **3** showed a negative excition chirality by negative excition coupling (λ ([θ]) = 256.8 (+125.7), 265.5 (−3660)).

Compound **4** was obtained as a colourless oil. The HR-ESI-MS (positive ion mode) showed a *pseudo*-molecular-ion peak at m/z 434.2532 ($[M+NH_4]^+$, $C_{24}H_{36}NO_6^+$; calc. 434.2537), corresponding to the molecular formula $C_{24}H_{32}O_6$. Its IR spectrum showed absorption bands at 2927 (MeO), 1713 (conjugated C=C bond with MeO), 1652, 1597, and 1513 (aromatic moiety) cm^{-1}. From ^{1}H- and ^{13}C-NMR (*Table 1*), ^{1}H,^{1}H-COSY, HMBC (*Fig. 3*), and 1D-NOE data, compound **4** was elucidated as 1,1′-[(1*E*,4*R*,5*R*)-5-methoxy-4-(methoxymethyl)pent-1-ene-1,5-diyl]bis(3,4-dimethoxybenzene).

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[1]) Arbitrary atom numbering. For systematic names, see *Exper. Part.*

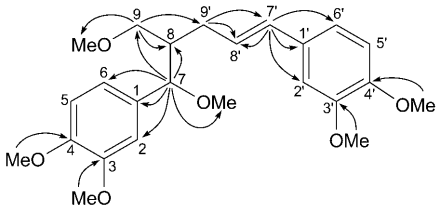

Fig. 3. *Key correlations from HMBC* (H → C) *experiments of* **4**[1])

The ^{1}H- and ^{13}C-NMR spectral data of **4** were very similar to those of **3** with the exception that signals of an additional MeO group appeared at δ(H) 3.21 and δ(C) 56.8. The only other difference in the ^{13}C-NMR spectral data between **3** and **4** occured for the C-atoms C(7) and C(9)[1]). In the ^{13}C-NMR spectrum, the signal of C(7) was shifted downfield (δ(C) 83.1) and that of C(9) upfield because of the additional MeO group located at C(7) in **4** (*Table 2*). In the ^{1}H-NMR spectrum, the signals of H–C(7) (δ(H) 4.18 (d, $J = 6.3$)), H–C(9), and H–C(9′) were all shifted upfield in comparison to the corresponding signals in **3**. The HMBC between the MeO group at δ(C) 56.8 and H–C(7) also confirmed the position of the MeO substituent. In the NOE experiment, irradiation of H–C(8) lead to the enhancement of H–C(7) (+2.98%), which indicated that the configuration of C(7) and C(8) was *threo*. The CD spectrum of **4** showed a negative excition chirality by negative excition coupling (λ ([θ]) = 266.5 (−19.6), 269.5 (−1700)). The CD spectra of **3** and **4** revealed that both compounds possess the same absolute configurations at C(7) and C(8), respectively [25].

Phytochemical studies on the genus *Morina* mainly focused on two species, *M. chinensis* and *M. nepalensis* var. *alba*. Flavonoid glycosides, neolignans, sesquineolignans, phenylpropanoid derivatives, and ursane-type saponins were isolated from *M. chinensis.* Acylated flavonoid glycosides, caffeoylquinic acids, oleanane- and ursane-type saponins were isolated from *M. nepalensis* var. *alba.* In this work, we isolated lignans, neolignans, taraxastane- and ursane-type triterpenes from *M. kokonorica*. Except for **7**, compounds were all isolated from the genus *Morina* for the first time. To our knowledge, compounds **1** and **2** are the first taraxastane-type triterpenes glycosylated at C(6).

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh, *Qingdao Marine Chemical Factory*, P. R. China); SiO_2 GF_{254} (10–40 μm, *Qingdao Marine Chemical Factory*), detection at 254 nm UV light or by heating after spraying with 5% H_2SO_4 in EtOH (*v*/*v*). M.p.: *Kofler* melting point apparatus; uncorrected. Optical rotations: *Perkin-Elmer-341* polarimeter. CD Spectra: *Jasco-J-810* circular dichroism spectropolarimeter, λ ([θ]) in nm. UV Spectra: *Shimadzu* spectrometer *UV-260,* λ_{max} (log ε) in nm. IR Spectra: *Nicolet NEXUS-670* FT-IR spectrometer, in cm^{-1}. NMR Spectra: *Varian Mercury plus-300* spectrometer at 300 (^{1}H-NMR) and 75 MHz (^{13}C-NMR), δ in ppm, J in Hz, Me_4Si (TMS) as internal standard. HR-ESI-MS: *Bruker Daltonics APEX-II* mass spectrometer.

Plant Material. The whole plant of *M. kokonorica* was collected in the south of Gansu Province, P. R. China, in September 2005. It was identified by Prof. *Guo-Liang Zhang*, Department of Life Science, Lanzhou University. A voucher specimen (No. Mk20050906) has been deposited with the State Key Laboratory of Applied Organic Chemistry, Lanzhou University.

Extraction and Isolation. The powder of the air-dried whole plant of *M. kokonorica* (4 kg) was extracted with MeOH (25 l each time) at *ca.* 5° for four times, 7 d each. After concentration of the extracts under reduced pressure, the residue (643 g) was suspended in H_2O (5.5 l) and then extracted with $CHCl_3$ (4×3.5 l). The $CHCl_3$ extract (213.5 g) was subjected to CC (SiO_2, 1900 g) by gradient elution with petroleum ether (PE; 60–90°)/acetone (100:1 to 1:1) and finally washed with MeOH, to give 20 fractions (*Fr. 1–Fr. 20*). *Fr. 3* (16 g; PE/acetone 20:1) was resubjected to CC (SiO_2; PE/acetone 50:1 to 10:1) and further separated by CC (PE/AcOEt 10:1), to obtain **5** (7 mg). *Fr. 6* (4.0 g, PE/acetone 5:1) was subjected to CC (SiO_2; PE/acetone 8:1 to 5:1) and further separated by CC (PE/AcOEt 8:1), to give **6** (8 mg) and **4** (7 mg). *Fr. 12* (5.1 g; PE/acetone 3:1) was subjected to CC (SiO_2, PE/AcOEt 5:1 to 1:1) and further separated by CC (PE/AcOEt 3:1) to give **3** (21 mg). *Fr. 14* (3.8 g; PE/acetone 2:1) was subjected to CC (SiO_2; PE/AcOEt 5:1 to 1:1) and further purified by CC (PE/acetone 3:1) to give **8** (9 mg). *Fr. 15* (2.1 g; PE/acetone 2:1) was subjected to CC (SiO_2; PE/AcOEt 3:1 to 1:1) and further separated by CC (PE/acetone 2:1) to obtain **10** (6 mg), **7** (10 mg), and **1** (22 mg). *Fr. 16* (3.1 g; PE/acetone 1:1) was subjected to CC (SiO_2; PE/AcOEt 1:1) and further separated by CC (PE/acetone 2:1) to give **2** (7 mg) and **9** (6 mg).

*(6α,11α)-6-[(2-*O*-Acetyl-α-*L*-arabinopyranosyl)oxy]-3-oxotaraxast-20-ene-11,28-diyl Diacetate* (**1**). White crystalline powder (acetone). M.p. 235–236°. $[\alpha]_D^{20} = +15$ ($c = 1.0$, acetone). IR (KBr): 3435, 2962, 2929, 1735, 1639, 1564, 1456, 1369, 1239, 1089, 1053, 1029, 967, 773. ^{1}H- and ^{13}C-NMR (DEPT): see *Table 1*. HR-ESI-MS: 748.4633 ($[M + NH_4]^+$, $C_{41}H_{66}NO_{11}^+$; calc. 748.4630).

*(6α,11α)-6-[(2-*O*-Acetyl-β-*D*-xylopyranosyl)oxy]-3-oxotaraxast-20-ene-11,28-diyl Diacetate* (**2**). White crystalline powder (acetone). M.p. 233–234°. $[\alpha]_D^{20} = +12$ ($c = 1.1$, acetone). IR (KBr): 3436, 2960, 2930, 2876, 1734, 1711, 1514, 1458, 1368, 1239, 1080, 1033, 984. ^{1}H- and ^{13}C-NMR (DEPT): see *Table 1*. HR-ESI-MS: 748.4671 ($[M + NH_4]^+$, $C_{41}H_{66}NO_{11}^+$; calc. 748.4630).

*(1*R*,2*R*,4*E*)-1,5-Bis(3,4-dimethoxyphenyl)-2-(methoxymethyl)pent-4-en-1-ol* (**3**). Colorless oil. $[\alpha]_D^{20} = +1$ ($c = 0.30$, MeOH). CD (MeOH): 256.8 (+125.7), 265.5 (−3660), 274.8 (−1681). UV (MeOH): 262 (2.72), 225 (2.98). IR (film): 3514, 2997, 2931, 2835, 1710, 1601, 1514, 1462, 1417, 1358, 1263, 1235, 1139, 1027, 967, 859, 812, 765. ^{1}H- and ^{13}C-NMR (DEPT): see *Table 2*. HR-ESI-MS: 420.2379 ($[M + NH_4]^+$, $C_{23}H_{34}NO_6^+$; calc. 420.2381).

*1,1′-[(1*E*,4*R*,5*R*)-5-Methoxy-4-(methoxymethyl)pent-1-ene-1,5-diyl]bis(3,4-dimethoxybenzene)* (**4**). Colorless oil. $[\alpha]_D^{20} = +2$ ($c = 1.00$, MeOH). CD (MeOH): 266.5 (−19.6), 269.5 (−1700). UV (MeOH): 267 (3.36), 231 (3.38). IR (film): 2927, 2835, 1713, 1652, 1597, 1513, 1461, 1417, 1357, 1263, 1235, 1138, 1099, 1028, 966, 859, 809, 764. ^{1}H- and ^{13}C-NMR (DEPT): see *Table 2*. HR-ESI-MS: 434.2532 ($[M + NH_4]^+$, $C_{24}H_{36}NO_6^+$; calc. 434.2537).

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