Huangqiyenins G – J, Four New 9,10-Secocycloartane (= 9,19-Cyclo-9,10-secolanostane) Triterpenoidal Saponins from *Astragalus membranaceus* BUNGE Leaves

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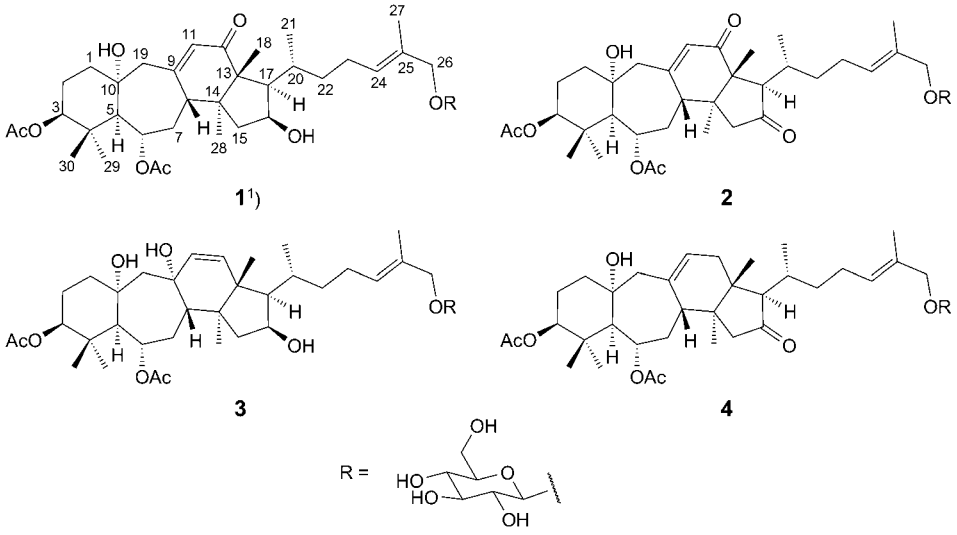
Four new 9,10-secocycloartane (= 9,19-cyclo-9,10-secolanostane) triterpenoidal saponins, named huangqiyenins G – J (**1** – **4**, resp.), were isolated from *Astragalus membranaceus* BUNGE leaves. The acid hydrolysis of **1** – **4** with 1M aqueous HCl yielded D-glucose, which was identified by GC analysis after treatment with L-cysteine methyl ester hydrochloride. The structures of **1** – **4** were established by detailed spectroscopic analysis as (3*β*,6*α*,10*α*,16*β*,24*E*)-3,6-bis(acetyloxy)-10,16-dihydroxy-12-oxo-9,19-cyclo-9,10-secolanosta-9(11),24-dien-26-yl *β*-D-glucopyranoside (**1**), (3*β*,6*a*,10*α*,24*E*)-3,6-bis(acetyloxy)-10-hydroxy-12,16-dioxo-9,19-cyclo-9,10-secolanosta-9(11),24-dien-26-yl *β*-D-glucopyranoside (**2**), (3*β*,6*α*,9*α*,10*α*,16*β*,24*E*)-3,6-bis(acetyloxy)-9,10,16-trihydroxy-9,19-cyclo-9,10-secolanosta-11,24-dien-26-yl *β*-D-glucopyranoside (**3**), and (3*β*,6*α*,10*α*,24*E*)-3,6-bis(acetyloxy)-10-hydroxy-16-oxo-9,19-cyclo-9,10-secolanosta-9(11),24-dien-26-yl *β*-D-glucopyranoside (**4**).

Introduction. – *Astragalus membranaceus* BUNGE belongs to the family Leguminosae and has long been one of the most important tonic herbs used in traditional Chinese medicine. Pharmacological investigations demonstrated that extracts of the leaves possess biological activities, including antioxidation, anti-aging, and anti-inflammatory activity [1], and protection against pancreatic injury [2]. The dried leaves of *A. membranaceus* (named beiqishengcha) has been authorized as a functional food by the *State Food and Drug Administration* of P. R. China in 1998.

Known biologically active components of *A. membranaceus* are triterpenoidal saponins, flavonoids, and polysaccharides. Chemical studies on *Astragalus* saponins have reported the presence of cycloartane-type triterpenoid glycosides which were found to exert many biological activities (*e.g.*, hepatoprotection, cardioprotection, antidiabetic nephropathy, anti-inflammatory, gastroprotection, and neuroprotection against ischemic brain injury) [3 – 8].

In the earlier investigations of *A. membranaceus* leaves, we have reported four cycloartane-type and two secocycloartane triterpenoid saponins named huangqiyenins A – F [9 – 12] (cycloartane = 9,19-cyclolanostane). As a continuing phytochemical study on this natural medicine, we further isolated four new 9,10-secocycloartane (= 9,19-cyclo-9,10-secolanostane = 9(10)a-homo-19-norlanostane) triterpenoidal saponins, huangqiyenins G – J (**1** – **4**, resp.). It is worth mentioning that 9,10-secocycloartanes are less common than their cycloartane counterparts. They represent a small group of compounds comprising *ca.* 20 representatives in the Ranunculaceae,

Buxaceae, and Leguminosae families [13–15]. This article deals with the isolation and structure elucidation of these newly isolated triterpenoids.

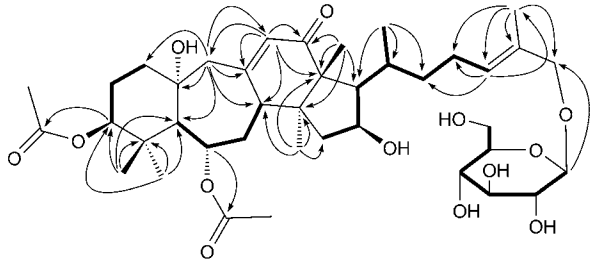


1[1]) **2** **3** **4**

Results and Discussion. – Compound **1**, named huangqiyenin G, was obtained as a white amorphous powder (MeOH). The molecular formula was determined as $C_{40}H_{62}O_{13}$ by HR-FAB-MS ($[M+Na]^+$ at m/z 773.4087), indicating ten degrees of unsaturation. The ^{1}H-NMR spectrum of **1** (*Table 1*) showed seven Me *s* at δ(H) 0.91, 1.08, 1.20, 1.55, 1.78, 2.06, and 2.08, a Me *d* at δ(H) 1.38 ($J = 6.5$ Hz), an olefinic H-atom *s* at δ(H) 5.92, and an olefinic H-atom *t* at δ(H) 5.72 ($J = 6.4$ Hz). No signals due to H-atoms of a cyclopropane ring were observed. The typical downfield CH *d* at δ(H) 4.90 ($J = 7.8$ Hz) was assigned to the anomeric H-atom of the β-D-glucopyranosyl moiety. The acid hydrolysis of **1** with 1M aqueous HCl yielded D-glucose, which was identified by GC analysis after treatment with L-cysteine methyl ester hydrochloride in pyridine [16]. The ^{13}C-NMR data (*Table 2*) showed the presence of 40 C-atoms that were sorted by a DEPT experiment as eight Me, nine CH_2, and 14 CH groups, as well as nine quaternary C-atoms, including four olefinic C-atoms at δ(C) 128.3, 129.5, 131.9, and 157.6, and three C=O groups at δ(C) 170.4, 170.5, and 203.8. The ^{1}H- and ^{13}C-NMR signals were assigned by HSQC, ^{1}H,^{1}H-COSY, and HSQC-TOCSY data. The full connectivity was deduced from the HMBC data (*Fig.*). In particular, the key long-range correlations H_α–C(19)/C(5), C(8), C(9), C(10), and C(11), and H_β–C(19)/C(8), C(9), C(10), and C(11) showed that the CH_2(19) group must be located between C(9) and C(10), and the coupling constants $J = 14.7$ and 1.2 Hz of H_α–C(19) indicated that C(19) was connected to two quaternary C-atoms (C(9) and C(10)), and H_α–C(19) showed allylic coupling with H–C(11). The HMBCs Me(18)/C(12), C(13), C(14), and C(17), and H–C(11)/C(8), C(9), C(12), C(13), and C(19) indicated that the C=O group at δ(C) 203.8 must be located at C(12). Furthermore, the correlation from the

[1]) Trivial atom numbering; for systematic names, see *Exper. Part.*

anomeric H-atom of the glucosyl moiety at δ(H) 4.90 to δ(C) 75.2 could also be observed, which confirmed that the glucosyloxy group should be attached to C(26). In addition, in the HMBC spectrum of **1**, H–C(3) and H–C(6) showed connectivity with the C=O of the AcO groups at δ(C) 170.4 and 170.5, respectively. Compound **1** was thus determined to represent a 9,19-cyclo-9,10-secolanostane-type triterpenoid with two Ac groups and a glucosyl group.



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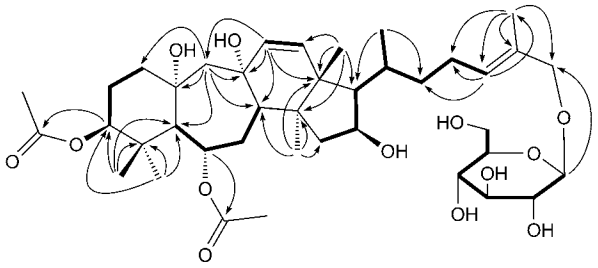

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Figure. *Key HMBC* (H → C) *and* ^{1}*H,*^{1}*H-COSY* (—) *features of* **1** *and* **3**

The relative configuration of **1** was determined on the basis of ^{1}H,^{1}H-coupling constants, NOESY experiments, and comparison of NMR data with those of huangqiyenin F [12], a compound previously isolated from *A. membranaceus* which possessed a (24*E*) side-chain moiety. In particular, the ^{13}C-NMR data of the side chain were almost identical in both compounds, and the correlations between H–C(23) and Me(27) were observed in the NOESY experiment, which enabled the assignment of the C(24)=C(25) bond configuration as (*E*) in **1**. The configuration at C(3) of **1** could be assigned as β, according to the coupling constant of H–C(3) at δ(H) 4.93 (*dd*, $J = 10.4$, 2.0 Hz). The NOESY correlations Me(30)/H–C(6), Me(29)/H–C(5), Me(29)/H–C(3), Me(28)/H–C(16), Me(28)/H–C(17), Me(18)/H–C(8), H–C(5)/H–C(3), H–C(6)/H$_\beta$–C(19), H–C(6)/H–C(8) were observed. From these data, H–C(3), H–C(5), H–C(16), H–C(17), and H$_\alpha$–C(19) could be placed in α-position, H–C(6), and H–C(8), and H$_\beta$–C(19) in β-position. Furthermore, the interaction Me(30)/H$_\beta$–C(19) indicated that the CH$_2$(19) group was in β-position with respect to ring *A*, and hence OH–C(10) was in α-position. In addition, The NOESY correlations Me(18)/H–C(20), H–C(17)/CH$_2$(22), H–C(16)/CH$_2$(22) confirmed the configuration at C(20) as (*R*) [17–19]. Thus, the structure of **1** was established as (3β,6α,10α,16β,24*E*)-3,6-

Table 1. *^{1}H-NMR Data* (500 MHz, C_5D_5N) *of Compounds* **1**–**4**. δ in ppm, J in Hz.

	1	**2**	**3**	**4**
CH_2(1)	1.87–1.95 (*m*, H_α), 1.87–1.95 (*m*, H_β)	1.80–1.87 (*m*, H_α), 1.80–1.87 (*m*, H_β)	1.32–1.40 (*m*, H_α), 1.32–1.40 (*m*, H_β)	1.90–1.96 (*m*, H_α), 1.90–1.96 (*m*, H_β)
CH_2(2)	1.71–1.79 (*m*, H_α), 1.93–1.98 (*m*, H_β)	1.70–1.77 (*m*, H_α), 1.85–1.90 (*m*, H_β)	1.67–1.74 (*m*, H_α), 1.86–1.93 (*m*, H_β)	1.73–1.80 (*m*, H_α), 1.93–1.98 (*m*, H_β)
H–C(3)	4.93 (*dd*, *J* = 10.4, 2.6)	4.93 (*dd*, *J* = 9.5, 4.2)	4.86 (*dd*, *J* = 11.6, 4.0)	4.95 (*dd*, *J* = 9.3, 2.0)
H–C(5)	2.32 (*d*, *J* = 6.9)	2.33 (*d*, *J* = 6.2)	2.42 (*d*, *J* = 6.8)	2.30 (*d*, *J* = 6.1)
H–C(6)	5.58–5.62 (*m*)	5.61 (*ddd*, *J* = 11.0, 6.2, 4.3)	5.49 (*ddd*, *J* = 11.6, 6.8, 2.4)	5.50–5.56 (*m*)
CH_2(7)	1.88–1.95 (*m*, H_α), 1.88–1.95 (*m*, H_β)	1.71–1.77 (*m*, H_α), 1.71–1.77 (*m*, H_β)	2.15–2.21 (*m*, H_α), 3.12 (*dt*, *J* = 9.5, 6.0, H_β)	1.78–1.83 (*m*, H_α), 1.78–1.83 (*m*, H_β)
H–C(8)	2.97 (br. *d*, *J* = 11.7)	3.04 (br. *d*, *J* = 10.2)	2.32–2.39 (*m*)	2.46 (br. *d*, *J* = 11.4)
H–C(11)	5.92 (br. *s*)	6.03 (br. *s*)	5.75 (*d*, *J* = 9.9)	5.46 (*dd*, *J* = 3.8, 1.2)
H–C(12) or CH_2(12)	–	–	6.40 (*d*, *J* = 9.9)	2.04–2.31 (*m*)
CH_2(15)	2.29 (*dd*, *J* = 14.3, 6.1, H_α), 2.38 (*dd*, *J* = 14.3, 7.6, H_β)	2.30 (*d*, *J* = 17.5, H_α), 2.71 (*d*, *J* = 17.5, H_β)	2.00–2.05 (*m*, H_α), 2.35–2.41 (*m*, H_β)	2.20 (*d*, *J* = 19.0, H_α), 2.40 (*d*, *J* = 19.0, H_β)
H–C(16)	4.66 (*ddd*, *J* = 7.9, 7.6, 6.1)	–	4.82 (*ddd*, *J* = 7.3, 6.4, 6.3)	–
H–C(17)	2.50 (*dd*, *J* = 10.7, 7.9)	2.98 (*d*, *J* = 5.0)	2.30–2.36 (*m*)	2.37 (*d*, *J* = 9.5)
Me(18)	1.55 (*s*)	1.35 (*s*)	1.43 (*s*)	0. 93 (*s*)
CH_2(19)	2.73–2.77 (*m*, H_α), 3.12 (br. *d*, *J* = 14.8, H_β)	2.73 (*dd*, *J* = 15.2, 1.2, H_α), 3.20 (*dd*, *J* = 15.2, 1.2, H_β)	2.00–2.05 (*m*, H_α), 2.27 (*dd*, *J* = 14.3, 1.0, H_β)	2.65 (*dd*, *J* = 15.0, 1.2, H_α), 2.98 (*dd*, *J* = 15.0, 1.2, H_β)
H–C(20)	2.28–2.34 (*m*)	1.95–2.20 (*m*)	2.37–2.43 (*m*)	1.83–1.89 (*m*)
Me(21)	1.38 (*d*, *J* = 6.5)	1.30 (*d*, *J* = 6.8)	1.19 (*d*, *J* = 6.6)	1.01 (*d*, *J* = 6.8)
CH_2(22)	1.32–1.38 (*m*), 2.11–2.16 (*m*)	1.60–1.67 (*m*), 1.82–1.89(*m*)	1.28–1.35 (*m*), 2.04–2.30 (*m*)	1.39–1.44 (*m*), 2.10–2.17 (*m*)
CH_2(23)	2.20–2.27 (*m*), 2.31–2.37 (*m*)	2.09–2.16 (*m*), 2.20–2.26 (*m*)	2.12–2.19 (*m*), 2.29–2.35 (*m*)	2.11–2.17 (*m*), 2.18–2.25 (*m*)
H–C(24)	5.72 (*t*, *J* = 6.4)	5.66 (*t*, *J* = 6.6)	5.72 (*t*, *J* = 6.4)	5.71 (*t*, *J* = 6.3)
CH_2(26)	4.21 (*d*, *J* = 11.4), 4.48 (*d*, *J* = 11.4)	4.23 (*d*, *J* = 11.5), 4.50 (*d*, *J* = 11.5)	4.24 (*d*, *J* = 11.6), 4.51 (*d*, *J* = 11.6)	4.26 (*d*, *J* = 11.3), 4.52 (*d*, *J* = 11.3)
Me(27)	1.78 (*s*)	1.78 (*s*)	1.80 (*s*)	1.83 (*s*)
Me(28)	0.91 (*s*)	1.07 (*s*)	1.27 (*s*)	1.04 (*s*)
Me(29)	1.08 (*s*)	1.07 (*s*)	1.05 (*s*)	1.04 (*s*)

Table 1 (cont.)

	1	**2**	**3**	**4**
Me(30)	1.20 (*s*)	1.21 (*s*)	1.15 (*s*)	1.21 (*s*)
*Ac*O–C(3)	2.06 (*s*)	2.08 (*s*)	2.08 (*s*)	2.06 (*s*)
*Ac*O–C(6)	2.08 (*s*)	2.08 (*s*)	2.03 (*s*)	2.08 (*s*)
H–C(1′)	4.90 (*d*, *J* = 7.8)	4.90 (*d*, *J* = 7.9)	4.92 (*d*, *J* = 7.6)	4.93 (*d*, *J* = 7.5)
H–C(2′)	4.09 (*t*, *J* = 7.8)	4.08 (*t*, *J* = 7.9)	4.09 (*t*, *J* = 7.6)	4.10 (*t*, *J* = 7.5)
H–C(3′)	4.26–4.33 (*m*)	4.25–4.32 (*m*)	4.26–4.33 (*m*)	4.24–4.32 (*m*)
H–C(4′)	4.26–4.33 (*m*)	4.25–4.32 (*m*)	4.26–4.33 (*m*)	4.24–4.32 (*m*)
H–C(5′)	3.94–4.01 (*m*)	3.92–4.00 (*m*)	3.92–4.00 (*m*)	3.90–3.99 (*m*)
CH_2(6′)	4.57 (*dd*, *J* = 11.7, 2.0), 4.41 (*dd*, *J* = 11.7, 4.6)	4.57 (*dd*, *J* = 11.7, 2.0), 4.40 (*dd*, *J* = 11.7, 5.0)	4.57 (*dd*, *J* = 11.9, 2.0), 4.40 (*dd*, *J* = 11.9, 5.5)	4.57 (*dd*, *J* = 11.5, 2.0), 4.41 (*dd*, *J* = 11.5, 4.6)

Table 2. *^{13}C-NMR Data* (125 MHz, C_5D_5N) *of Compounds* **1**–**4**. δ in ppm.

	1	**2**	**3**	**4**
C(1)	44.5 (*t*)	44.2 (*t*)	30.1 (*t*)	44.5 (*t*)
C(2)	25.3 (*t*)	25.2 (*t*)	25.3 (*t*)	25.0 (*t*)
C(3)	79.5 (*d*)	79.4 (*d*)	80.0 (*d*)	79.7 (*d*)
C(4)	39.5 (*s*)	39.5 (*s*)	40.4 (*s*)	39.5 (*s*)
C(5)	57.9 (*d*)	57.8 (*d*)	60.8 (*d*)	58.0 (*d*)
C(6)	76.0 (*d*)	75.5 (*d*)	75.6 (*d*)	76.6 (*d*)
C(7)	32.9 (*t*)	33.3 (*t*)	27.9 (*t*)	33.0 (*t*)
C(8)	45.8 (*d*)	44.4 (*d*)	42.3 (*d*)	42.5 (*d*)
C(9)	157.6 (*s*)	159.9 (*s*)	76.0 (*s*)	137.4 (*s*)
C(10)	72.3 (*s*)	72.3 (*s*)	73.2 (*s*)	72.3 (*s*)
C(11)	128.3 (*d*)	127.7 (*d*)	133.4 (*d*)	123.9 (*d*)
C(12)	203.8 (*s*)	201.8 (*s*)	136.7 (*d*)	36.4 (*t*)
C(13)	58.0 (*s*)	57.3 (*s*)	47.5 (*s*)	44.4 (*s*)
C(14)	50.7 (*s*)	46.2 (*s*)	49.9 (*s*)	42.5 (*s*)
C(15)	46.7 (*t*)	48.6 (*t*)	45.1 (*t*)	48.9 (*t*)
C(16)	70.3 (*d*)	216.0 (*s*)	71.4 (*d*)	217.6 (*s*)
C(17)	49.5 (*d*)	55.8 (*d*)	52.2 (*d*)	60.5 (*d*)
C(18)	14.3 (*q*)	15.6 (*q*)	21.8 (*q*)	16.2 (*q*)
C(19)	48.4 (*t*)	48.5 (*t*)	49.9 (*t*)	48.7 (*t*)
C(20)	30.6 (*d*)	32.3 (*d*)	31.1 (*d*)	31.9 (*d*)
C(21)	19.7 (*q*)	20.9 (*q*)	18.5 (*q*)	18.8 (*q*)
C(22)	36.9 (*t*)	34.9 (*t*)	36.5 (*t*)	35.6 (*t*)
C(23)	26.0 (*t*)	26.4 (*t*)	25.6 (*t*)	25.8 (*t*)
C(24)	129.5 (*d*)	128.4 (*d*)	129.4 (*d*)	128.7 (*d*)
C(25)	131.9 (*s*)	132.5 (*s*)	132.0 (*s*)	132.7 (*s*)
C(26)	75.2 (*t*)	75.2 (*t*)	75.3 (*t*)	75.2 (*t*)
C(27)	14.2 (*q*)	14.2 (*q*)	14.3 (*q*)	14.2 (*q*)
C(28)	19.4 (*q*)	18.2 (*q*)	21.3 (*q*)	18.2 (*q*)
C(29)	28.4 (*q*)	27.9 (*q*)	27.1 (*q*)	28.4 (*q*)
C(30)	18.9 (*q*)	18.4 (*q*)	18.0 (*q*)	18.8 (*q*)
*Ac*O–C(3)	21.7 (*q*), 170.4 (*s*)	21.6 (*q*), 170.4 (*s*)	21.5 (*q*), 170.5 (*s*)	21.7 (*q*), 170.4 (*s*)
*Ac*O–C(6)	21.1 (*q*), 170.5 (*s*)	21.0 (*q*), 170.5 (*s*)	21.0 (*q*), 170.0 (*s*)	21.1 (*q*), 170.5 (*s*)
C(1′)	103.6 (*d*)	103.8 (*d*)	103.9 (*d*)	103.6 (*d*)
C(2′)	75.2 (*d*)	75.3 (*d*)	75.3 (*d*)	75.5 (*d*)
C(3′)	78.7 (*d*)	78.6 (*d*)	78.7 (*d*)	78.8 (*d*)
C(4′)	71.8 (*d*)	72.0 (*d*)	71.9 (*d*)	71.8 (*d*)
C(5′)	78.5 (*d*)	78.6 (*d*)	78.7 (*d*)	78.5 (*d*)
C(6′)	62.9 (*t*)	62.8 (*t*)	63.0 (*t*)	62.9 (*t*)

bis(acetyloxy)-10,16-dihydroxy-12-oxo-9,19-cyclo-9,10-secolanosta-9(11),24-dien-26-yl β-D-glucopyranoside[1]).

Compound **2**, named huangqiyenin H, was obtained as a white amorphous powder, with a molecular formula $C_{40}H_{60}O_{13}$ based on the HR-FAB-MS (*m*/*z* 771.3936 ($[M+Na]^+$)). The ^{1}H-NMR spectrum (*Table 1*) showed seven Me *s*, a Me *d*, and two olefinic H-atom signals at δ(H) 6.03 (br. *s*) and 5.66 ($J = 6.6$ Hz). The ^{13}C-NMR spectrum (*Table 2*) revealed 40 C-atoms including two ketonic C=O groups at δ(C) 216.0 and 201.8, four olefinic C-atoms at δ(C) 127.7, 128.4, 132.5, and 159.9, two Ac

groups at δ(C) 21.6, 170.4, 21.0, and 170.5, and a glucosyl group at δ(C) 103.8, 75.3, 78.6, 72.0, 78.6, and 62.8. The acid hydrolysis of **2** gave D-glucose [16]. Detailed comparison of the ^{1}H- and ^{13}C-NMR data of **2** and **1** indicated they have identical rings *A* – *C* and side chain but a different ring *D*. The appearance of a C=O signal at δ(C) 216.0 in the ^{13}C-NMR spectrum of **2** and the disappearance of the signal of H–C(16) in the ^{1}H-NMR spectrum revealed the presence of a C=O group at C(16), which was further confirmed by the HMBC data. The HMBCs H_α–C(15)/C(13), C(14), C(16), and C(17), and H–C(20)/C(13), C(16), and C(17) confirmed the connectivity of ring *D*. Therefore, **2** was elucidated as (3β,6α,10α,24*E*)-3,6-bis(acetyloxy)-10-hydroxy-12,16-dioxo-9,19-cyclo-9,10-secolanosta-9(11),24-dien-26-yl β-D-glucopyranoside[1]).

Huangqiyenin I (**3**) was obtained as a white amorphous powder, and the molecular formula was determined as $C_{40}H_{64}O_{13}$, on the basis of the HR-FAB-MS (*m*/*z* 775.4249 ([*M* + Na]$^+$)). The acid hydrolysis of **3** liberated D-glucose, which was identified by GC analysis [16]. The ^{1}H-NMR spectrum (*Table 1*) showed the presence of three olefinic H-atoms at δ(H) 6.40 (*J* = 9.9 Hz), 5.75 (*J* = 9.9 Hz), and 5.72 (*J* = 6.4 Hz), of seven tertiary Me groups at δ(H) 1.05, 1.15, 1.27, 1.43, 1.80, 2.03, and 2.08, and of a secondary Me group at δ(H) 1.19 (*J* = 6.6 Hz). In the ^{13}C-NMR spectrum (*Table 2*), the 40 C-atoms were assigned to eight Me, nine CH_2, and 15 CH groups and to eight quaternary C-atoms by a DEPT experiment. The spectroscopic data of **3** were similar to those of huangqiyenin F [12]. However, olefinic H-atoms of a disubstituted C=C bond were observed in the ^{1}H-NMR spectrum of **3**. In the HMBC spectrum, the correlation of the olefinic H–C(12) to C(9), C(11), C(13), and C(14), of H–C(11) to C(8), C(9), C(12), and C(13), and of Me(18) to C(12), C(13), C(14), and C(17) indicated that the C=C bond is located between C(11) and C(12) (*Fig.*). The key NOE correlations H_β–C(19)/Me(30), H_β–C(19)/H–C(6), H_β–C(19)/H–C(8), and H–C(6)/H–C(8) indicated that CH_2(19) was in β-orientation with respect to ring *A*, and the OH groups at C(9) and C(10) were α-orientated. The configuration at C(20) was determined as (*R*) by the NOESY correlations Me(18)/H–C(20), H–C(17)/CH_2(22), and H–C(12)/Me(21) [17 – 19]. Accordingly, compound **3** was assigned as (3β,6α,9α,10α,16β,24*E*)-3,6-bis(acetyloxy)-9,10,16-trihydroxy-9,19-cyclo-9,10-secolanosta-11,24-dien-26-yl β-D-glucopyranoside[1]).

Huangqiyenin J (**4**) was obtained as a white amorphous powder. The molecular formula was determined as $C_{40}H_{62}O_{12}$ by positive-mode HR-FAB-MS (*m*/*z* 757.4114 ([*M* + Na]$^+$)). The ^{1}H-NMR spectrum of **4** (*Table 1*) showed seven Me *s* at δ(H) 0.93, 1.04 (6 H), 1.21, 1.83, 2.06, and 2.08, a Me *d* at δ(H) 1.01 (*J* = 6.8 Hz), and two olefinic H-atom signals at δ(H) 5.46 (*J* = 3.8, 1.2 Hz) and 5.71 (*J* = 6.3 Hz). The ^{13}C-NMR spectrum (*Table 2*) exhibited 40 C-atoms including four olefinic C-atoms at δ(C) 123.9, 128.7, 132.7, and 137.4, and three C=O groups at δ(C) 170.4, 170.5, and 217.6. The acid hydrolysis of **4** gave D-glucose [16]. Comparison of the ^{1}H- and ^{13}C-NMR data of **4** with those of huangqiyenin F [12] and **2** showed that **4** has the same rings *A* – *C* as huangqiyenin F, and the same ring *D* and side-chain moiety as **2**, which was further established by the key HMBC, HSQC-TOCSY, and NOESY features. The key HMBC cross-peaks Me(18)/C(12), C(13), C(14), and C(17), and Me(28)/C(8), C(13), C(14), and C(15) indicated the connection between ring *C* and *D*. Thus, **4** was established as (3β,6α,10α,24*E*)-3,6-bis(acetyloxy)-10-hydroxy-16-oxo-9,19-cyclo-9,10-secolanosta-9(11),24-dien-26-yl β-D-glucopyranoside[1]).

Experimental Part

General. Column chromatography (CC): silica gel *60* (SiO_2; 200–300 mesh; *Merck*, Germany). HPLC: *Waters-Delta-600* pump and *Waters-2414* refractive-index detector; *TSK-gel ODS-120T* column (10 μm, 40 × 300 mm; *Tosoh*, Japan). GC: *Fuli-9790* H_2 flame detector; *DM-5* column (0.25 μm, 30 m × 0.25 mm; *Dikma*, China). IR Spectra: *Shimadzu FI-IR-8100* spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *JNM-LA-500* spectrometer; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. HR-FAB-MS: *Jeol-JMS-DX-302* mass spectrometer; in *m*/*z*.

Plant Material. The leaves of *A. membranaceus* BUNGE were collected in Daxing'anling, Heilongjiang Province, P. R. China, in August 1995, and identified by Prof. *Zhenyue Wang*, Heilongjiang University of Chinese Medicine, P. R. China. A voucher specimen (No. 19950026) is deposited with the Herbarium of Heilongjiang University of Chinese Medicine, P. R. China.

Extraction and Isolation. The dried leaves of *A. membranaceus* BUNGE (1.2 kg) were defatted with petroleum ether (2 × 5 l) for 2 h each time (80°). Then, the residue was extracted with MeOH under reflux (3 × 5 l) for 3 h each time, and the extract was concentrated to a syrup. A suspension of the MeOH extract (310 g) in H_2O (5 l) was extracted with BuOH (3 × 5 l) sat. with H_2O. The BuOH layer was concentrated to give the BuOH extract (119 g). The BuOH extract (60 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH/H_2O 6:1:0.1 and then $CHCl_3$/MeOH/H_2O 3:1:0.1): *Fractions I–X*, in order of elution. *Fr. IV* (6.8 g) was resubjected to CC (SiO_2, $CHCl_3$/MeOH/H_2O 5:1:0.1) and separated further by HPLC (*TSK*-gel *ODS-120T*, flow-rate 8 ml/min, MeOH/H_2O 3:7): **1** (123 mg; t_R 9.0 min), **2** (42.1 mg; t_R 14.5 min), **4** (30.4 mg; t_R 19.3 min), and **3** (80.8 mg; t_R 25.1 min).

Acid Hydrolysis of **1**–**4**. Each of compounds **1**–**4** (each 4 mg) was hydrolyzed in 1M HCl (1.0 ml) for 2 h at 85°. The mixture was cooled and partitioned between $CHCl_3$ (2.0 ml) and H_2O (2.0 ml). The aq. layer was washed with $CHCl_3$ (3 × 3.0 ml), neutralized with $Ba(OH)_2$, filtered, and evaporated. The residue was dissolved in pyridine (1.0 ml), and 0.1M L-cysteine methyl ester hydrochloride in pyridine (2.0 ml) was added. The mixture was heated at 60° for 1 h. An equal volume of Ac_2O was added under heating, and incubation was continued for 1 h. The acetylated thiazolidine derivatives was compared with authentic samples by GC (*DM-5* column; injector and detector temp. 280°; temp. gradient for the oven from at 160° to 195° at a rate of 5°/min). The sugar unit in compounds **1**–**4** was determined by the retention time t_R of the peak of the hydrolysates and that of an authentic sample of D-glucose (t_R 15.1 min).

Huangqiyenin G (=*(3β,6α,10α,16β,24*E*)-3,6-Bis(acetyloxy)-10,16-dihydroxy-12-oxo-9,19-cyclo-9,10-secolanosta-*9(*11*)*,24-dien-26-yl β-*D*-Glucopyranoside* = *(2*E*,6*R*)-6-[2*S*,3*R*,3a*R*,6a*R*,9*S*,10a*R*,11*S*,12a*R*,12b*S*)-9,11-Bis(acetyloxy)-1,2,3,3a,4,6,6a,7,8,9,10,10a,11,12,12a,12b-hexadecahydro-2,6a-dihydroxy-3a,10,10,12b-tetramethyl-4-oxobenzo[4,5]cyclohept[1,2-*e*]inden-3-yl]hex-2-en-1-yl β-*D*-Glucopyranoside*; **1**): White amorphous powder. $[\alpha]_D^{21} = +55.1$ ($c = 1.0$, MeOH). IR (KBr): 3430, 2959, 1729, 1713, 1658, 1371, 1078, 1022. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (neg.): 749 ($[M-H]^-$). HR-FAB-MS (pos.): 773.4085 ($[M+Na]^+$, $C_{40}H_{62}NaO_{13}^+$; calc. 773.4088).

Huangqiyenin H (=*(3β,6α,10α,24*E*)-3,6-Bis(acetyloxy)-10-hydroxy-12,16-dioxo-9,19-cyclo-9,10-secolanosta-*9(*11*)*,24-dien-26-yl β-*D*-Glucopyranoside* = *(2*E*,6*R*)-6-[3*R*,3a*R*,6a*R*,9*S*,10a*R*,11*S*,12a*R*,12b*S*)-9,11-Bis(acetyloxy)-1,2,3,3a,4,6,6a,7,8,9,10,10a,11,12,12a,12b-hexadecahydro-6a-hydroxy-3a,10,10,12b-tetramethyl-2,4-dioxobenzo[4,5]cyclohept[1,2-*e*]inden-3-yl]hex-2-en-1-yl β-*D*-Glucopyranoside*; **2**): White amorphous powder. $[\alpha]_D^{21} = +61.5$ ($c = 1.0$, MeOH). IR (KBr): 3425, 2945, 1745, 1729, 1713, 1650, 1078, 1022. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (pos.): 748 (M^+), 771 ($[M+Na]^+$). HR-FAB-MS (pos.): 771.3936 ($[M+Na]^+$, $C_{40}H_{60}NaO_{13}^+$; calc. 771.3932).

Huangqiyenin I (=*(3β,6α,10α,16β,24*E*)-3,6-Bis(acetyloxy)-9,10,16-trihydroxy-9,19-cyclo-9,10-secolanosta-11,24-dien-26-yl β-*D*-Glucopyranoside* = *(2*E*,6*R*)-6-[2*S*,3*R*,3a*R*,5a*R*,6a*R*,9*S*,10a*R*,11*S*,12a*R*,12b*S*)-9,11-Bis(acetyloxy)-1,2,3,3a,5a,6,6a,7,8,9,10,10a,11,12,12a,12b-hexadecahydro-2,5a,6a-trihydroxy-3a,10,10,12b-tetramethylbenzo[4,5]cyclohept[1,2-*e*]inden-3-yl]hex-2-en-1-yl β-*D*-Glucopyranoside*; **3**): White amorphous powder. $[\alpha]_D^{21} = +65.3$ ($c = 1.0$, MeOH). IR (KBr): 3440, 2943, 1719, 1709, 1079, 1026. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (neg.): 751 ($[M-H]^-$). HR-FAB-MS (pos.): 775.4249 ($[M+Na]^+$, $C_{40}H_{64}NaO_{13}^+$; calc. 775.4245).

Huangqiyenin J (= *(3β,6α,10α,24*E*)-3,6-Bis(acetyloxy)-10-hydroxy-16-oxo-9,19-cyclo-9,10-secolanosta-*9*(11),24-dien-26-yl β-*D*-Glucopyranoside* = *(2*E*,6*R*)-6-[3*R*,3a*R*,5a*R*,6a*R*,9*S*,10a*R*,11*S*,12a*R*,12b*S*)-9,11-Bis(acetyloxy)-1,2,3,3a,4,6,6a,7,8,9,10,10a,11,12,12a,12b-hexadecahydro-5a-hydroxy-3a,10,10,12b-tetramethyl-2-oxobenzo[4,5]cyclohept[1,2-*e*]inden-3-yl]hex-2-en-1-yl β-*D*-Glucopyranoside*; **4**): White amorphous powder. $[\alpha]_D^{21} = +69.6$ ($c = 1.0$, MeOH). IR (KBr): 3441, 2938, 17.44, 1720, 1715, 1080, 1026. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. FAB-MS (neg.): 733 ($[M-H]^-$). HR-FAB-MS (pos.): 757.4143 ($[M+Na]^+$, $C_{40}H_{62}NaO_{12}^+$; calc. 757.4139).

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