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TRITERPENE GLYCOSIDES FROM *Astragalus* AND THEIR GENINS. XC. ASKENDOSIDE K FROM *Astragalus taschkendicus*

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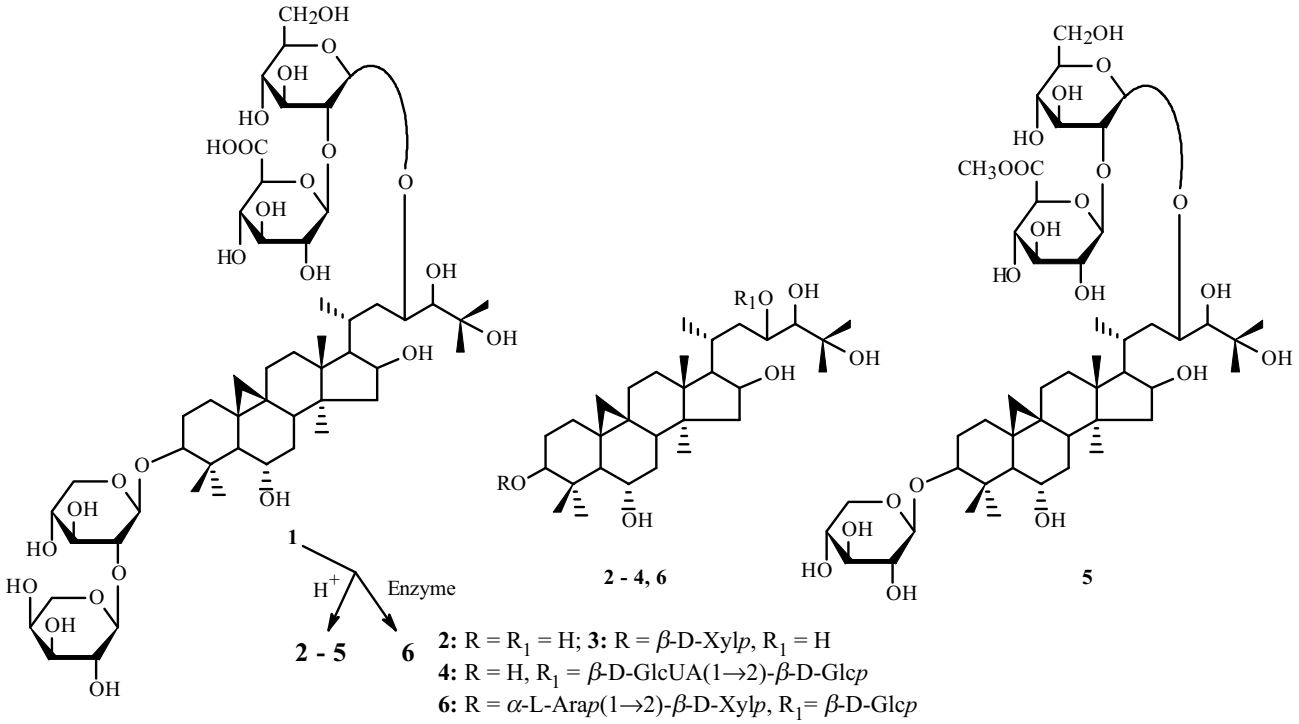
A new triterpene cycloartane glycoside called askendoside K was isolated from roots of Astragalus taschkendicus *Bunge (Leguminosae). The structure of this glycoside was established using chemical and biochemical transformations and spectral data. Askendoside K was a bisdesmoside of cycloorbigenin C and had the structure 23*R,*24*R-*cycloartan-3*β,6α,*16*β,*23,24,25-hexaol 3*-O-*[(*α-*L-arabinopyranosyl)(1→2)-*β-*D-xylopyranoside],23*-O-*[(*β-*D-glucuronopyranosyl)(1→2)-*β-*D-glucopyranoside].*

Keywords: *Astragalus taschkendicus*, Leguminosae, triterpene glycosides, askendoside K, cycloorbigenin C, PMR, ^{13}C NMR, DEPT, COSY, Hetcor, and NOE spectra.

In continuation of research on polar triterpene glycosides from *Astragalus taschkendicus* Bunge (Leguminosae) [1], we isolated one more new glycoside from roots of this plant and called it askendoside K (**1**). Herein we report the structure determination of this glycoside.

The PMR spectrum of **1** (Table 1) exhibited at strong field 1H doublets for an AX system at δ 0.06 and 0.35 that belonged to the isopropane methylene of a cyclopropane ring in addition to resonances for seven methyls. As expected, the ^{13}C NMR spectrum of this same glycoside showed resonances at δ 21.12, 29.03, and 30.23 for quaternary C-9 and C-10 and methylene C-19 composing the three-membered ring, indicating that the studied glycoside was a cycloartane triterpenoid [2–5].



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In fact, acid hydrolysis of **1** produced the genin, which was identified as cycloorbigenin C (**2**) [6, 7]. Paper chromatography (PC) of the products in the carbohydrate part of the acid hydrolysate in the presence of authentic samples and taking into account biogenetic considerations detected D-xylose, D-glucose, D-glucuronic acid, and L-arabinose. The observance of four sets of resonances for monosaccharide units in the PMR and ^{13}C NMR spectra of **1** indicated that these monosaccharides occurred in this glycoside in a 1:1:1:1 ratio and that **1** was a tetraoside.

Stepwise acid hydrolysis of **1** isolated progenins **3–5** in addition to cycloorbigenin C. Progenin **3** was identical to cycloorbicoside D according to PMR and ^{13}C NMR spectra and direct comparison with an authentic sample [7–9].

Comparison of ^{13}C NMR spectra of **1**, cycloorbigenin C, and progenins **3**–**5** suggested that **1** was a bisdesmoside glycoside, the glycosylation centers of which were C-3 and C-23. The production of cycloorbicoside D as a progenin defined the location of the D-xylose as C-3, thereby confirming the conclusion that C-3 was one of the glycosylation centers.

As expected, a negative Overhauser effect on the H-3 resonance (δ 3.44) was observed in a difference PMR spectrum for measuring the nuclear Overhauser effect (NOE) upon pre-irradiation of the D-xylose anomeric proton of **1** (δ 4.79) [10, 11].

A comparison of the ^{13}C NMR spectra of **1** and cycloorbicoside D indicated that the D-xylose in **1** was not terminal. The C-1 resonance of the D-xylose in the ^{13}C NMR spectrum of **1** underwent a strong-field shift to δ 105.45; the C-2 resonance, a weak-field shift to δ 84.37 compared with the resonances of cycloorbicoside D. This meant that D-xylose C-2 was glycosylated in **1**.

Progenin **4** contained D-glucose and D-glucuronic acid. This provided evidence that the L-arabinose was located on C-2 of the D-xylose. Therefore, the carbohydrate chain of **1** that was situated on C-3 consisted of pentoses whereas that on C-23, hexoses. In fact, the difference PMR spectrum for measuring the NOE from irradiation of the L-arabinose anomeric proton in **1** (δ 5.07) exhibited an Overhauser effect on the D-xylose H-2 resonance (δ 4.00). The spin–spin coupling constant (SSCC) of the L-arabinose anomeric proton (^{3}J = 6.7 Hz) defined the pyranose form, the $^4C_1$-conformation, and the α-configuration of this monosaccharide in **1**. This meant that the carbohydrate chain on C-3 had the structure (α-L-arabinopyranosyl)(1→2)-β-D-xylopyranose.

Experiments on measurement of the NOE were conducted in order to find the structure of the carbohydrate chain on C-23. Irradiation of H-23 (δ 4.74) in **1** exhibited a NOE in the PMR spectrum on the resonance of the D-glucose anomeric proton (δ 5.25). Consistent with this, irradiation of the D-glucose anomeric proton produced in the PMR spectrum a NOE on the H-23 resonance. Therefore, the D-glucose was bonded directly to C-23 and the D-glucuronic acid was the terminal monosaccharide. The SSCC of the D-glucose anomeric proton (^{3}J = 7.4) defined the pyranose form, the $^4C_1$-conformation, and the β-configuration of this hexose. This conclusion and structure for the carbohydrate chain on C-23 was confirmed by the production of askendoside H (**6**) from **1** as a result of enzymatic hydrolysis of the latter. Enzymatic hydrolysis of **1** by β-D-glucuronidase produced **6**, which was identified as askendoside H [1] based on PMR and ^{13}C NMR spectral data and direct comparison with an authentic sample.

The site of attachment of the D-glucuronic acid was found by comparing ^{13}C NMR spectra of askendosides H and K. The resonance of the D-glucose anomeric C atom in the ^{13}C NMR spectrum of **1** underwent a strong-field shift to δ 101.80; that of C-2, a weak-field shift to δ 81.72 compared with those resonances in askendoside H. This indicated unambiguously that D-glucose C-2 was glycosylated. Therefore, the D-glucuronic acid was bonded to C-2 of the D-glucose. This was confirmed by the difference PMR spectrum of **1** taken upon irradiation of the D-glucuronic acid anomeric proton (δ 5.61), where a NOE was observed on the H-2 resonance of D-glucose (δ 4.14).

The SSCC of the D-glucuronic acid anomeric proton (^{3}J = 7.5) defined its pyranose form, $^4C_1$-configuration, and β-configuration.

As already noted, progenin **4** was a bioside that contained D-glucose and D-glucuronic acid and should have had the structure 23*R*,24*R*-cycloartan-3β,6α,16β,23,24,25-hexaol 23-*O*-[(β-D-glucuronopyranosyl)(1→2)-β-D-glucopyranoside]. This was in full agreement with the PMR and ^{13}C NMR spectra.

Progenin **5** was a triose and contained D-xylose, D-glucose, and D-glucuronic acid. The PMR spectrum of **5** showed a resonance for a methoxyl at δ 3.67. This was consistent with the ^{13}C NMR spectrum of this glycoside that exhibited a resonance for a methoxyl C atom at δ 51.99. The chemical shift of the methoxyl resonance in the PMR spectrum indicated that this group originated from an ester. A strong-field shift of the D-glucuronic acid carbonyl resonance to δ 170.29 was also indicative of this. This meant that the D-glucuronic acid carboxylic acid was methylated. This occurred during methanolysis. Glycoside **5** was 23*R*,24*R*-cycloartan-3β,6α,16β,23,24,25-hexaol 3-*O*-β-D-xylopyranoside,23-*O*-[(β-D-(6-*O*-Me)-glucoronopyranosyl(1→2)]-β-D-glucopyranoside].

TABLE 1. Chemical Shifts of C and H Atoms in Askendoside K (**1**), Parameters of Its 2D ^1H–^1H COSY and Hetcor NMR Spectra, Chemical Shifts of C Atoms in **2**–**5**, DEPT Data for All Compounds (δ, ppm, J/Hz, C_5D_5N, 0 = TMS for δ_C, 0 = HMDS for δ_H)

C atom	DEPT	**1**		**2**	**3**	**4**	**5**	**6**
		δ_C	δ_H	δ_C	δ_C	δ_C	δ_C	δ_C
1	CH_2	32.37		32.74	32.42	32.74	32.45	32.53
2	CH_2	29.66		31.40	29.80	31.30	30.25	29.78
3	CH	88.43	3.44 dd (11.6, 4.4)	78.30	88.66	78.48	88.69	88.55
4	C	42.61	–	42.42	42.67	42.43	42.62	42.76
5	CH	53.93	1.57 d (9.2)	53.91	54.00	53.87	54.04	54.10
6	CH	67.00	3.56 td (9, 3.9)	68.16	67.77	68.26	68.01	67.89
7	CH_2	38.14		38.54	38.32	38.46	38.37	38.31
8	CH	46.63[a]	1.70 dd (11.9, 4.8)	47.06	46.82	47.05	47.01	46.82
9	C	21.12	–	21.18	21.25	21.08	21.24	20.51
10	C	29.03	–	29.51	29.13	29.47	29.20	29.20
11	CH_2	26.17		26.24	26.16	26.22	26.19	26.29
12	CH_2	33.07		32.92	32.86	33.09	33.10	33.14
13	C	45.75	–	45.59	45.56	45.72	45.73	45.84
14	C	46.63[a]	–	46.78	46.74	46.67	46.68	46.78
15	CH_2	48.13	1.51, 1.91	47.66	47.56	48.00	48.06	47.88
16	CH	71.76[b]	4.54 td (7.6, 4.8)	72.08	72.05	71.71	71.70[a]	72.17
17	CH	57.60	1.62 dd (10.8, 7.5)	57.37	57.31	57.85	57.92	57.47
18	CH_3	19.08	1.25 s	18.85	18.70	18.94	18.95	19.66
19	CH_2	30.23	0.06 и 0.35 d (4)	30.24	30.33	30.30	30.10	30.34
20	CH	27.39	2.55 m	27.29	27.27	27.73	28.20	27.60
21	CH_3	18.72.	1.14 d (6.4)	20.27	20.24	19.16	19.21	18.85
22	CH_2	37.78	2.62 dd (14.8, 9.9)	42.88	42.85	38.09	37.99	39.02
23	CH	79.39	4.74 dt (9.2, 2.8)	73.10	73.08	79.02	78.38*	82.79
24	CH	80.10	4.42 d (4)	79.03	79.01	79.87	79.03*	80.64
25	C	72.63	–	74.29	74.29	72.88	72.92	72.68
26	CH_3	26.50	1.50 s	24.56	24.54	26.46	26.47	26.45
27	CH_3	28.20	1.54 s	28.93	28.91	28.19	27.95	28.35
28	CH_3	19.95	0.79 s	20.13	20.05	20.11	20.13	20.12
29	CH_3	28.51	1.82 s	29.31	28.80	29.28	28.81	28.61
30	CH_3	16.16	1.27 s	16.14	16.65	16.09	16.63	16.27
			β-D-Xyl*p* unit					
1	CH	105.45	4.79 d (7)		107.62		107.47	105.58
2	CH	83.47	4.00 dd (9, 7)		75.61		75.50[b]	83.53
3	CH	77.39	4.07		78.52		78.22	77.59
4	CH	70.86	4.06		71.21		71.16	71.02
5	CH_2	67.78	3.50 dd (11, 9), 4.16		67.04		66.91	66.98
			α-L-Ara*p* unit					
1	CH	106.57	5.07 d (6.7)					106.57
2	CH	73.59	4.45					73.63
3	CH	74.15	4.10					74.33
4	CH	69.08	4.21 td (3.1, 1.8)					69.13
5	CH_2	66.42	3.69 dd (12.3, 1.9)					66.58
			4.27 dd (12.3, 3.2)					
			β-D-Glc*p* unit					
1	CH	101.80	5.25 d (7.4)			101.33	99.49	106.63
2	CH	81.72	4.14			82.35	83.69	75.90
3	CH	78.22	4.16			78.30	77.91	78.25
4	CH	71.76[b]	3.89 dd (9.8, 7.7)			71.88	71.70[a]	72.32
5	CH	78.50	3.85 m			77.71	77.47	78.25
6	CH_2	62.67	4.10, 4.43			62.72	62.70	63.18
			β-D-GlcUA unit					
1	CH	104.94	5.61 d (7.5)			105.15	106.04	
2	CH	75.25	4.14			75.41	75.50[b]	
3	CH	77.70	4.16			78.23	78.14	
4	CH	73.13	4.36			73.21	72.81	
5	CH	76.95	4.40			77.29	77.38	
6	C	173.54	–			173.00	170.29	
CH_3O	CH_3	–	–			–	51.99	

Chemical shifts of protons given without multiplicities and SSCC were found using 2D spectra. Resonances marked by the same letter were overlapped; by an asterisk, ambiguous.

Thus, the new triterpene cycloartane glycoside askendoside K (**1**) was 23*R*,24*R*-cycloartan-3β,6α,16β,23,24,25-hexaol 3-*O*-[(α-L-arabinopyranosyl)(1→2)-β-D-xylopyranoside],23-*O*-[(β-D-glucuronopyranosyl)(1→2)-β-D-glucopyranoside].

EXPERIMENTAL

General comments have been published [12]. The following solvent systems were used: $CHCl_3$:MeOH:H_2O (65:35:7, 1); $CHCl_3$:MeOH (10:1, 2); *n*-BuOH:Py:H_2O (6:4:3, 3); $CHCl_3$:MeOH:H_2O (70:12:1, 4); 70:25:4, 5). PMR and ^{13}C NMR spectra were obtained on UNITYplus 400 (Varian) and DRX-500 (Bruker) spectrometers from Py-d_5 solutions of the compounds. Data for spectra of **1** that were obtained with added trifluoroacetic acid are also given. ^{13}C NMR spectra were recorded with full C–H decoupling and under DEPT conditions. 2D spectra of **1** were taken using standard Varian programs. Chemical shifts of protons are given versus HMDS; of C atoms, relative to the resonance of the β-C atoms of Py-d_5 (δ 123.493 vs. TMS).

Isolation and separation of triterpenoids from *Astragalus taschkendicus* Bunge were reported [13–15]. Fractions eluted after askendoside H and several more polar glycosides that contained askendoside K (**1**) were combined and rechromatographed over a column using system 1 to isolate **1** (1.5 g, 0.0285% of air-dried raw material).

Askendoside K (1), $C_{52}H_{86}O_{25}$, white non-crystalline powder. Table 1 lists the PMR and ^{13}C NMR spectra.

Cycloorbigenin C (2) from 1. Compound **1** (300 mg) was hydrolyzed by methanolic H_2SO_4 (30 mL, 0.5%) on a boiling-water bath for 6 h. The mixture was diluted with H_2O. The MeOH was evaporated. The resulting solid was filtered off, washed with H_2O, and dried. The dry solid was chromatographed over a column of silica gel with elution by system 2 to afford genin **2** (120 mg), $C_{30}H_{52}O_6$, mp 256–258°C (MeOH), which was identified as cycloorbigenin C [6, 7].

PMR spectrum of cycloorbigenin C (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.19 and 0.47 (d, ^2J = 4, 2H-19), 0.90 (s, CH_3), 1.08 (d, ^3J = 6.4, CH_3-21), 1.26, 1.27, 1.57, 1.61, 1.79 (s, 5 × CH_3), 3.56 (dd, $^3J_1$ = 11.5, $^3J_2$ = 4.7, H-3), 3.65 (d, ^3J = 8.5, H-24), 3.70 (td, $^3J_1$ = $^3J_2$ = 9.4, $^3J_3$ = 3.8, H-6), 4.22 (td, $^3J_1$ = $^3J_2$ = 8.7, $^3J_3$ = 2, H-23), 4.59 (td, $^3J_1$ = $^3J_2$ = 7.8, $^3J_3$ = 4.9, H-16). Table 1 lists the ^{13}C NMR spectrum of cycloorbigenin C.

The filtrate was evaporated to a small volume and heated on a water bath for 1 h to destroy methylglycosides. The solution was cooled and neutralized with $BaCO_3$. A precipitate formed. The aqueous solution was concentrated and analyzed by PC using system 3 and comparison with authentic samples. PC detected D-glucose, D-xylose, D-glucuronic acid, and L-arabinose. PMR and ^{13}C NMR spectra of **1** showed that these monosaccharides were present in the glycoside in a 1:1:1:1 ratio.

Partial Hydrolysis of 1. Compound **1** (500 mg) was hydrolyzed by methanolic H_2SO_4 (50 mL, 0.25%) for 8 h at 40°C. The mixture was diluted with H_2O. The MeOH was evaporated. The aqueous solution was treated with *n*-BuOH. The BuOH extract was washed with H_2O and evaporated to dryness. The dry solid was chromatographed over a column with elution by system 2 to afford **2** (90 mg), which was identified as cycloorbigenin C by direct comparison and PMR spectral data.

Further elution of the column by system 4 produced progenin **3** (27 mg). Continued elution of the column by system 5 gave progenin **4** (35 mg). Further elution of the column by the same solvent system isolated progenin **5** (30 mg).

23*R*,24*R*-Cycloartan-3β,6α,16β,23,24,25-hexaol 3-*O*-β-D-Xylopyranoside or Cycloorbicoside D (3) from 1. Progenin **3**, $C_{35}H_{60}O_{10}$, mp 285–287°C (MeOH), $[\alpha]_D^{28}$ 0 ± 3° (*c* 0.44, MeOH), identified as cycloorbicoside D based on spectral data and comparison with an authentic sample [7–9].

PMR spectrum of cycloorbicoside D (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.13 and 0.42 (d, ^2J = 4, 2H-19), 0.88 (s, CH_3), 1.06 (d, ^3J = 6.6, CH_3-21), 1.21, 1.24, 1.56, 1.60, 1.88 (s, 5 × CH_3), 3.52 (dd, $^3J_1$ = 11.6, $^3J_2$ = 4.4, H-3), 3.61 (dd, ^2J = 11.6, ^3J = 10, D-xylose H-5a), 3.64 (m, H-6), 3.64 (d, ^3J = 8.4, H-24), 3.95 (dd, $^3J_1$ = 8.8, $^3J_2$ = 7.2, D-xylose H-2), 4.05 (t, $^3J_1$ = $^3J_2$ = 8.8, D-xylose H-3), 4.13 (m, D-xylose H-4), 4.21 (m, H-23), 4.25 (dd, ^2J = 11.2, ^3J = 5.2, D-xylose H-5e), 4.58 (td, $^3J_1$ = $^3J_2$ = 7.3, $^3J_3$ = 4.7, H-16), 4.79 (d, ^3J = 7.5, D-xylose H-1). Table 1 lists the ^{13}C NMR spectrum of cycloorbicoside D.

23*R*,24*R*-Cycloartan-3β,6α,23,24,25-hexaol 23-*O*-[(β-D-Glucuronopyranosyl)(1→2)-β-D-glucopyranoside] (4) from 1. Progenin **4**, $C_{42}H_{70}O_{17}$, $[\alpha]_D^{28}$ –7.4 ± 2° (*c* 1.35, MeOH).

PMR spectrum of progenin **4** (500 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.14 and 0.40 (d, ^2J = 4, 2H-19), 0.82 (s, CH_3), 1.21 (d, ^3J = 6, CH_3-21), 1.25, 1.28, 1.56, 1.57, 1.79 (s, 5 × CH_3), 3.55 (dd, $^3J_1$ = 12, $^3J_2$ = 4, H-3), 3.64 (td, $^3J_1$ = $^3J_2$ = 9, $^3J_3$ = 3, H-6), 4.56 (m, H-16), 4.75 (m, H-23), 5.51 (d, ^3J = 7, D-glucuronic acid H-1). The resonance of D-glucose H-1 overlapped the H_2O resonance at δ 5.28. Table 1 lists the ^{13}C NMR spectrum of progenin **4**.

23*R*,24*R*-Cycloartan-3β,6α,23,24,25-hexaol 3-*O*-β-D-Xylopyranoside,23-*O*-[β-D-(6-*O*-Me)-glucuronopyranosyl(1→2)]-β-D-glucopyranoside (5) from 1. Progenin **5**, $C_{48}H_{80}O_{21}$, $[\alpha]_D^{28}$ –16.3 ± 2° (*c* 1.1, MeOH).

PMR spectrum of progenin **5** (500 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.15 and 0.42 (d, ^2J = 4, 2H-19), 0.88, 1.24 (s, 2 × CH_3), 1.25 (d, ^3J = 6.5, CH_3-21), 1.27, 1.55, 1.59, 1.88 (s, 4 × CH_3), 3.53 (dd, $^3J_1$ = 12, $^3J_2$ = 4, H-3), 3.61 (m, D-xylose H-5a and H-6), 3.67 (s, CH_3O), 4.53 (m, H-16), 4.73 (m, H-23), 4.79 (d, ^3J = 7, D-xylose H-1), 5.35 (d, ^3J = 7.5, D-xylose H-1), 5.39 (d, ^3J = 7.5, D-glucuronic acid H-1). Table 1 lists the ^{13}C NMR spectrum of progenin **5**.

Askendoside H (6) from 1. Glycoside **1** (74 mg) in H_2O (15 mL) was treated with several milligrams of β-D-glucuronidase. The solution was stirred, treated with benzene (1 drop), and left at 30°C for 37 d, after which the solution was evaporated to dryness. The dry solid was chromatographed over a column with elution by system 5 to isolate **6** (29 mg), $C_{46}H_{78}O_{19}$, which was identified as askendoside H [1] by direct comparison with an authentic sample and spectral data.

PMR spectrum of askendoside H (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.12 and 0.45 (d, ^2J = 4, 2H-19), 0.88 (s, CH_3), 1.15 (d, ^3J = 6.4, CH_3-21), 1.28, 1.29, 1.51, 1.53, 1.84 (s, 5 × CH_3), 1.61 (d, ^3J = 9, H-5), 4.80 (d, ^3J = 7, D-xylose H-1), 5.01 (d, ^3J = 7.7, D-glucose H-1), 5.09 (d, ^3J = 6.5, L-arabinose H-1). Table 1 lists the ^{13}C NMR spectrum of askendoside H.

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