TWO NEW CYCLOARTANE-TYPE GLUCOSIDES, MONGHOLICOSIDE I AND II, FROM THE AERIAL PART OF ASTRAGALUS MONGHOLICUS BUNGE

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Two new cycloartane-type glucosides, mongholicoside I (**1**) and II (**2**), were isolated from the aerial part of Astragalus mongholicus Bunge and characterized as 9,19-cyclolanost-24E-ene-1α,3β,16β,27-tetraol 27-O-β-D-glucopyranoside and 3β-acetoxy-9,19-cyclolanost-24E-ene-1α,3β,12β,16β,27-pentaol 27-O-β-D-glucopyranoside based on the chemical and spectral evidence.

KEYWORDS Astragalus mongholicus; Leguminosae; cycloartane-type glucoside; mongholicoside I; mongholicoside II

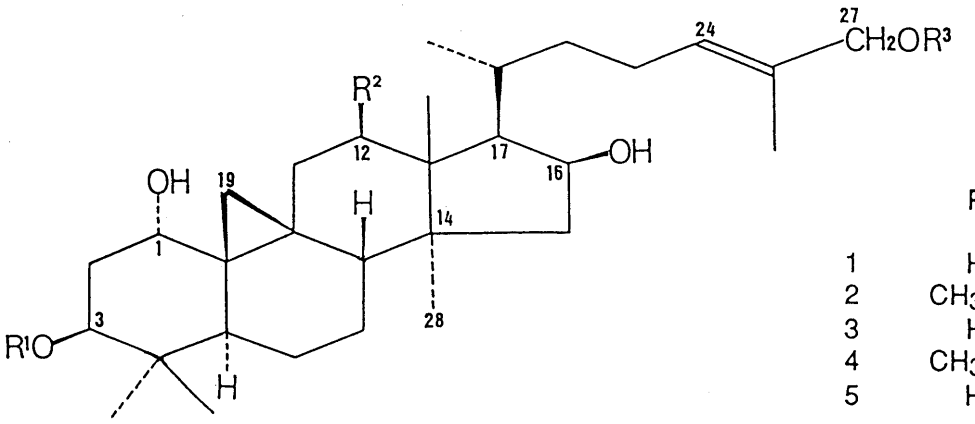
A number of chemical studies on the constituents of Astragaluous plants (Leguminosae) have been reported. A number of cycloartane-type triterpenoid glycosides named astragalosides were isolated from the root and the aerial part of A. membranaceus[1-3] and the root of A. mongholicus.[4] However, no work has been reported on the constituents of the aerial part of A. mongholicus. This paper describes the structural elucidation of two new glucosides. The n-butanol-soluble portion derived from the ethanolic extract of the aerial part was subjected to column chromatography on Sephadex LH-20 (MeOH) and then on silica gel to afford several fractions, which comprised crude glycosides. These fractions were further separated and purified by HPLC to give two new glucosides, mongholicoside I (**1**) and mongholicoside II (**2**), along with β-sitosterol β-D-glucoside.

Compound **1**, colorless needles, mp 143-145°C, $[\alpha]_D$+47.9°, showed a strong hydroxy absorption band at 3400cm^{-1} in the infrared (IR) spectrum. The positive fast atom bombardment mass spectrum (FAB-MS) displayed a peak at m/z 659 $(M+Na)^+$, and negative FAB-MS displayed a peak at m/z 635 $(M-H)^-$, which revealed 636 as its molecular weight. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum (400 MHz, in C_5D_5N) showed five tertiary and a secondary methyls (δ 1.05, 1.07, 1.14, 1.30, 1.47, 1.79). The ^{1}H-NMR signals at δ0.48 and 0.75 ppm (each 1H,d,J=4.0 Hz) established the presence of a cyclopropane methylene moiety. It also gave an anomeric proton signal at δ4.86 ppm (1H,d,J=7.6 Hz). Thus **1** was considered to be a cycloartane-type triterpene glycoside. This observation was supported by ^{13}C-NMR data. Acidic hydrolysis of **1** gave the complex mixture, while a genuine aglycone (**3**) of **1** was effected by the enzy-

matic hydrolysis with cellulase and the sugar component was presumed to be glucose on the basis of thin layer chromatography (TLC) and ^{13}C-NMR spectrum. The EI-MS spectrum of **3** gave an M^+ ion at m/z 474, and the molecular formula of **3** was determined to be $C_{30}H_{50}O_4$ by means of high MS spectrum. The ^{1}H-NMR spectrum of **3** revealed a primary hydroxyl group, three secondary hydroxyl groups and an olefinic proton : δ3.56 (1H,t, J=3.1,1-H), 3.74(1H,dd,J=4.7 and 12.1,3-H), 4.40(1H,m,16-H), 3.99(2H,s,27-H), 5.47 (1H,t,J=7.3,24-H); these observations are in close agreement with those of ^{13}C-NMR spectrum : δ 73.6(C-1), 36.8(C-2), 73.8(C-3), 40.5(C-4), 39.6(C-5), 20.7(C-6), 24.7 (C-7), 48.0(C-8), 20.7(C-9), 30.5(C-10), 25.85(C-11), 32.8(C-12), 45.4(C-13), 46.8 (C-14), 48.2(C-15), 72.7(C-16), 56.5(C-17), 19.1(C-18), 30.2(C-19), 29.6(C-20), 17.9 (C-21), 36.3(C-22), 25.9(C-23), 126.4(C-24), 135.4(C-25), 13.7(C-26), 68.8(C-27), 20.2(C-28), 25.2(C-29), 13.1(C-30). The structure of **3** was considered by the comparison of ^{13}C-NMR spectra with the cycloartenol and similar compounds. Furthermore, ^{1}H-^{1}H shift correlation spectroscopy (^{1}H-^{1}H COSY), ^{1}H-^{13}C COSY, and long-range ^{1}H-^{13}C COSY experiments were carried out to establish the definite positions of hydroxyl groups to be C-1, C-3, C-16 and C-27. The stereochemistry of 24-ene and 16-OH were determined based on the results of different nuclear Overhauser effect (NOE) experiments. A different NOE was observed between the olefinic proton of 24-H and 27-H, and the stereochemical feature of 24-ene could be assigned to be E. In addition, 16-OH was determined to be β by significant NOE enhancement between 16-H and 14-CH_3. From the coupling patterns of 1-H (t,J=3.1Hz) and 3-H (dd, J=4.7 and 12.1 Hz), the 1α-OH and 3β-OH configurations in **3** were substantiated. The ^{13}C-NMR spectrum of **1** indicated the occurrence of significant glycosylation shift[5] at the C-27; and from the coupling constant of the anomeric proton at δ4.86 ppm (1H d, J=7.6 Hz) in the ^{1}H-NMR spectrum, the glucopyranosyl residue was suggested to attach in the β-form. Based on the above-mentioned evidence the structure of **1** was established to be 9,19-cyclolanost-24E-ene-1α,3β,16β,27-tetraol 27-O-β-D-glucopyranoside.

Compound **2**, white powder, mp.128-130°C (dec.), showed $[\alpha]_D$+42.1°, and its molecular weight 694, was determined by positive FAB-MS $(M+Na)^+$ and negative FAB-MS $(M-H)^-$ measurement. Two doublet signals at δ0.67 and 0.77 ppm (each 1H,J=4.4 Hz) in the ^{1}H-NMR spectrum were attributable to the protons of the cyclopropane ring. The structure of **2** was deduced to be glycoside, having a similar cycloartane-type triterpene. On the basis of spectroscopic evidence, an IR absorption at 1715 cm^{-1}, ^{1}H-NMR signal at δ2.05 ppm (3H,s) and ^{13}C-NMR signal at δ170.6 ppm, **2** showed the presence of an acetyl group in its molecule. Enzymatic hydrolysis of **2** with cellulase yielded **4** and glucose. The ^{1}H-NMR spectrum of **4** revealed a primary and four secondary hydroxyl groups : δ 3.56(1H,t,J=2.8,1-H), 5.07(1H,dd,J=4.7 and 12.1,3-H), 3.90(1H,dd,J=2.0 and 8.1,12-H), 4.43(1H,m,16-H), 3.98(2H,s, 27-H). From two-dimensional (2D)-NMR spectra and ^{13}C-NMR spectrum : δ 72.5(C-1), 33.9(C-2), 76.5(C-3), 39.3(C-4), 39.4(C-5), 20.28(C-6), 25.0*

(C-7), 46.4(C-8), 20.4(C-9), 29.3(C-10), 39.1(C-11), 72.47(C-12), 50.5(C-13), 47.7 (C-14), 48.2(C-15), 72.3(C-16), 57.2(C-17), 12.3(C-18), 29.0(C-19), 29.4(C-20), 18.7 (C-21), 36.5(C-22), 25.2*(C-23), 126.1(C-24), 135.1(C-25), 13.5(C-26), 68.5(C-27), 20.3(C-28), 25.1(C-29), 14.1(C-30), 21.0($\underline{C}H_3CO$-), 170.6($CH_3\underline{C}O$-) (* Assignments may be interchangeable), **4** was deduced to be monoacetate at the C-3 of aglycone of **2**, having five hydroxyl groups at the C-1, C-3, C-12, C-16 and C-27. The stereochemistry of the 24-ene was confirmed to be E since NOE was observed between 24-H and 27-H. From the significant NOE observation between 12-H and 14-CH_3 and 16-H and 14-CH_3, each orientation of 12-OH and 16-OH was established to be β-form. The 1-OH and 3-OH were deduced to be α and β orientation from their coupling constants of the 1-H (t,J=2.8 Hz) and 3-H (dd,J=4.7 and 12.1 Hz) in its ^{1}H-NMR spectrum, respectively. Hydrolysis of **4** with 10% K_2CO_3 yielded **5**. The position of an acetyl moiety was attributable to 3-OH, because the ^{1}H-NMR signal of 3-H in **5** was observed at δ3.74 ppm. From the glycosylation shift values of C-27 in ^{13}C-NMR spectrum and the coupling constant of the anomeric proton signal at δ4.86 ppm (1H,d,J=7.7 Hz) in ^{1}H-NMR spectrum, glucopyranosyl residue was suggested to attach in the β-form. On the basis of the above-mentioned spectral and chemical data, **2** was characterized to be 3β-acetoxy-9,19-cyclolanost-24E-ene-1α,3β,12β,16β,27-pentaol 27-O-β-D-glucopyranoside. Studies on other glycosides are in progress.



	R^1	R^2	R^3
1	H	H	Glc
2	CH_3CO	OH	Glc
3	H	H	H
4	CH_3CO	OH	H
5	H	OH	H

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