Triterpenoids from *Astragalus armatus* subsp. *numidicus* and their chemotaxonomic significance

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Abstract

In continuation of our chemical studies on the secondary metabolites of Algerian Saharan species, we report the isolation of three undescribed cycloartane saponins named astragalarmosides A–C (**1-3**) together with eleven known compounds that were obtained from the aerial parts of *Astragalus armatus* subsp. *numidicus* (Murb.) Emb. & Maire. Among the known compounds, nine cycloartane saponins and one oleanane were isolated for the first time in *Astragalus* species. Their structures were assigned based on extensive 1D- and 2D NMR experiments (^{1}H, ^{13}C, COSY, ROESY, HSQC, HMBC), mass spectrometry HR-ESI-MS and by comparison of their spectral data with those of literature values. The chemotaxonomic of the genus *Astragalus* is summarized in this study to show its interesting chemodiversity throughout the world.

Keywords: Fabaceae, *Astragalus armatus* subsp. *numidicus* (Murb.) Emb. & Maire, cycloartane glycoside, chemotaxonomic studies

1 Introduction

Astragalus, a genus in the Fabaceae family, includes more than 3000 species of herbs and small shrubs found in arid and continental regions of Asia, America, and Africa (Li et al., 2014). In Algeria, the genus *Astragalus* is well represented, with the Algerian flora comprising 40 *Astragalus* species (Quézel & Santa, 1962). Previous chemical studies performed on this genus have resulted in the isolation of flavonoids (Khalfallah et al., 2014; Khalfallah et al., 2024; Li et al., 2025), several cycloartane and oleanane type triterpene glycosides (Bedir et al., 1999a; Polat et al., 2010; Li et al., 2025), alkaloids, and polysaccharides (Li et al., 2025). *Astragalus* species have long been used in traditional Chinese medicine for their anti-perspirant, tonic, and diuretic properties. They have also been employed in treating various conditions, including diabetes mellitus, nephritis, leukemia, and uterine cancer (Sevimli-Gür et al., 2011). Some bioactive compounds from *Astragalus* species exhibit reported hemolytic and immunostimulatory effects (Aslanipour et al., 2017), cytotoxic activities (Gülcemal et al., 2012), antioxidant, antiapoptotic and antiviral (Lu et al., 2017) anti-inflammatory, antitumor, neuroprotective, and hypoglycemic activities (Li et al., 2025). In continuation of our works on *Astragalus* (Khalfallah et al., 2024; Labed et al., 2016), we report here, the phytochemical investigation of the exudate from the subspecies *Astragalus armatus* subsp. *numidicus* (Murb.) Emb. & Maire. Three new cycloartane glycosides (**1-3**) as well as eleven known compounds were isolated.

2 Results and discussion

2.1 Isolation and structural elucidation

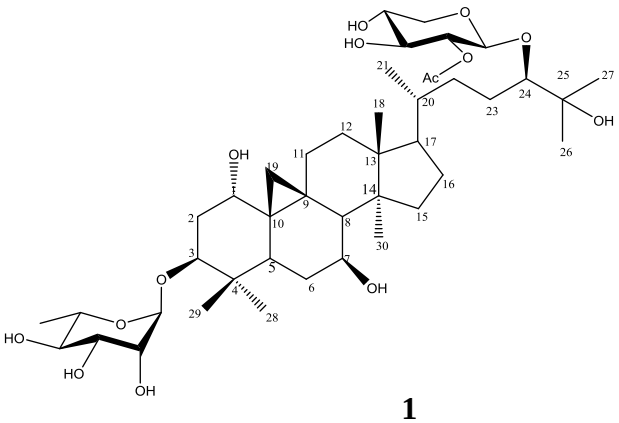
The purification of the ethyl acetate and *n*-butanol parts of the hydroethanol extract of the aerial parts of *Astragalus armatus* subsp. *numidicus* led to three undescribed compounds (**1-3**) (Fig. 1) and eleven known compounds (**4**–**14**).

Compound **1** was obtained as a white amorphous powder, with a molecular formula of $C_{46}H_{76}O_{17}$ based on HR-ESI-MS (*m/z* 901.5165 $[M-H]^+$, calcd for 901.5161). The ^1H and ^{13}C NMR spectra (Table 1) in combination with the HSQC and ^1H–^1H COSY correlations of compound **1** were characteristic of cycloartane glycoside type. The ^1H NMR spectrum of **1** showed six signals of tertiary methyl groups characterized as singlets at δ_H 0.82 (H3-29), 0.98 (H_3-28), 1.03 (H_3-18), 1.05 (H_3-30), 1.10 (H_3-27), and 1.15 (H_3-26). One secondary methyl was also observed at δ_H 0.92 (d, J = 5.2 Hz, H_3-21). The characteristic doublets of

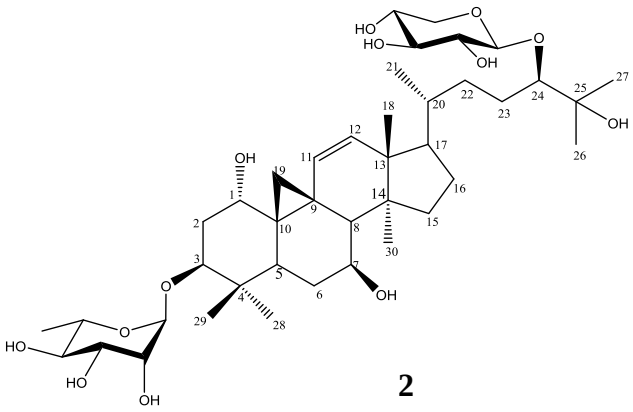
cyclopropane methylene hydrogen signals at δ_H 0.43 (d, J = 4.1 Hz, H- 19a) and δ_H 0.78 (d, J = 4.1 Hz, H-19b) were also observed indicating a cycloartane type triterpenoid (Iskenderov et al., 2009a). Furthermore, the ^{1}H NMR spectrum of **1** revealed signal from four oxymethine hydrogen signals at δ_H 3.65 (m, H-3), δ_H 3.53 (m, H-1), δ_H 3.55 (m, H-7) and δ_H 3.38 (m, H-24). The ^{13}C NMR spectra of **1** contained 46 signals including seven methyl carbons at δ_C 13.1(C-29), 16.9 (C-28), 17.4 (C-21), 17.9 (C-30), 23.8 (C-27) 24.5 (C-18), and 24.6 (C-26). Additionally, there were four oxymethine carbon signals at δ_C 69.7 (C- 7), 72.3 (C-1), 83.7 C-3) and 88.2 (C-24).

Furthermore, two anomeric hydrogens at δ_H 4.75 (s, H-1') and 4.48 (d, J = 7.8 Hz, H-1'') were observed in the ^{1}H NMR spectrum. Two sugar units were ascertained from COSY spectrum analyses, and ^{13}C chemical shifts of their relative attached carbons were assigned unambiguously from the HSQC spectrum (Table 2). The presence of an α-rhamnose unit was revealed by a broad singlet of an anomeric hydrogen H-1' at δ_H 4.75 and a methyl group at δ_H 1.24 (d, J = 6.1 Hz, H-6'). The broad singlet or small J-value of an anomeric hydrogen of rhamnose and chemical shift of Rha-C-5 at δ_C 67-69 indicated its α configuration (Bendamene et al., 2020). The second sugar with an anomeric hydrogen at δ_H 4.48 (d, J = 7.8 Hz, H-1'') was a pentose identified as a xylose, whose anomeric configuration (*β*) was determined by the large coupling constant value (J_{H1-H2} = 7.8 Hz) (Lehbili et al., 2017). The linkage sites were determined by the HMBC spectrum analysis, which showed the key correlations between H-1 (δ_H 4.75) of rhamnose and C-3 (δ_C 83.7) of the aglycone, and between H-1'' (δ_H 4.48) of the xylose and C-24 (δ_C 88.2) of the aglycone like in Cyclomacroside D (**10**) (Iskenderov et al., 2009a). The difference between compound **1** and **10** was the presence of an acetoxy group which was confirmed in the ^{1}H-NMR spectrum (δ 2.11 s, 3H, $COCH_3$). The site of acylation was clear from the downfield shift of H-2'' (δ 4.72 t, J = 8.4 Hz) of the xylose moiety and the HMBC cross peaks between this hydrogen H-2'' and the carbonyl at δ_C 170.5. The relative configuration of compound **1** was deduced by analysis of its ROESY spectrum. In this spectrum, ROE correlations observed between H-5 (δH 2.14) and H-3 (δH 3.65)/H-7 (δH 3.55), as well as between H-3 (δH 3.65) and H3-28 (δ_H 0.98), supported their *α*-orientation and therefore the OH at C-3 and C-7 is *β*-oriented. Furthermore, ROE correlations between H-19 (δ_H 0.43) and H-1 (δ_H 3.53) supported their *β*-orientation. The absolute configuration of C-24 could be determined to be *R* by the ^{13}C NMR chemical shift of C-24 (δ_C 88.2). According to the

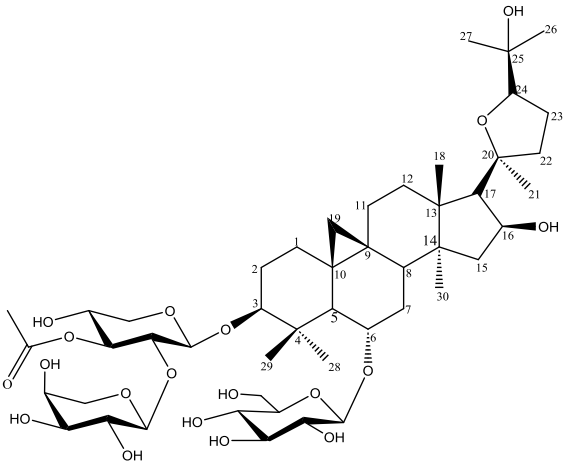
literature data, while the chemical shift of C-24 is in the range of 77.1-78.6 ppm for the 24*S* configuration (Kim et al., 2008; Horo et al., 2012; Çaliş et al., 1996), it is in the range of 79.6–81.0 ppm for the 24*R* configuration (Karabey et al., 2012; Naubeev et al., 2014; Lu et al., 2012). Thus, the structure of compound **1** was elucidated as 3-*O*-α-L-rhamnopyranosyl-24-*O*-(2''-*O*-acetyl)-*β*-D-xylopyranosyl-1α,3*β*,7*β*,24(*R*),25-pentahydroxycycloartane,named Astragalarmoside A.



1



2



3

Fig. 1: Structures of compounds **1-3** isolated from *Astragalus armatus* subsp. *numidicus*

Compound **2** was obtained as a white amorphous powder. The HR-ESI–MS spectrum of **2** showed a pseudo-molecular ion peak $[M\text{-}H_2\ O+H]^+$ at *m/z* 751.4638 (calcd for 751.4638) supporting a molecular formula of $C_{41}H_{67}O_{12}$. It was evident by the comparison of the ^{13}C NMR spectra of compounds **2** and **1** that the two compounds differed by the absence of acetyl group signals and the chemical shifts of C-11 (δ_C 130.4) and C-12 (δ_C 135.1) for compound **2** indeed of C-11 (δ_C 25.5) and C-12 (δ_C 32.6) for compound **1** (Table 1), indicating the presence

of a double bond between C-11 and C-12. This was confirmed by the HMBC cross peaks observed from the first olefinic hydrogen H-12 (δ_H 6.05) with carbons C-18 (δ_C 16.3), C-9 (δ_C 24.1), C-13 (δ_C 48.3), C-14 (δ_C 49.5), and CH_2-19 (δ_C 25.7), and between the second olefinic hydrogen H-11 (δ_H 5.32) with carbons C-18, C-9, C-10 (δ_C 33.1), C-13, and C-8 (δ_C 52.6). However, the linkage sites of the sugar units were the same as that of compound **1** (Table 2). This deduction was further confirmed by the assignment of all the ^{1}H and ^{13}C NMR signals of **2** with the assistance of ^{1}H-^{1}H COSY, HSQC, HMBC and ROESY experiments. The absolute configuration of C-24 could be determined to be *R* by the ^{13}C NMR chemical shift of C-24 (90.5) (Yalçın et al., 2012; Polat et al., 2009). The structure of compound **2** was established as 3-*O*-α-L-rhamnopyranosyl-24-*O*-*β*-D-xylopyranosyl-1α,3*β*,7*β*,24(*R*),25-pentahydroxycycloart-11-en and denoted as Astragalarmoside B.

Compound **3** was obtained as a white amorphous powder. The ESI/MS of the compound exhibited the quasi-molecular ion peak at *m/z* 981.50308 $[M+Na]^+$ (calcd for $C_{48}H_{78}O_{19}Na$, 981.5035), which is well-matched with the molecular formula $C_{48}H_{78}O_{19}$. The ^{1}H and ^{13}C NMR data of compound **3** were characteristic of a cycloartane-type-glycoside and to the presence of cycloastragenol as the aglycone (Fathiazad et al., 2010) (Table 1). The ^{1}H NMR spectrum of **3** showed signals typical of cyclopropane methylene hydrogens at δ_H 0.28 and 0.62 (each d, J = 4.0 Hz, H_2-19), seven tertiary methyl groups at δ_H 1.01, 1.04, 1.15, 1.22, 1.25, 1.27, 1.28, and three oxygen bearing methine hydrogen signals at δ 3.18 (m, H-3), 3.56 (m, H-6), and 4.67 (t, J = 7.6 Hz, H-16) (Table 1). Additionally, the resonances for three anomeric hydrogens at δ_H 4.34 (d, J=7.7 Hz, H-1'), 4.72 (d, J=4.3 Hz, H-1''), and 4.40 (d, J= 6.28 Hz, H-1''') were observed, demonstrating the presence of three-linked sugar units, and one 3H signal at δ_H 2.11 indicative of the presence of an acetoxyl group (Table 2). The ^{13}C NMR data showed 48 signals, 32 of which were attributed to the aglycone and the acetyl (δ_C 19.8 and 170.5) moieties and the remaining 16 were due to three sugar units (Table 2). The combinate analysis of HSQC and ^{1}H–^{1}H COSY correlations allowed the assignment of signals of the sugar moieties and revealed the presence of one xylose, one arabinose and one glucose. However, the carbon resonances attributed to C-3 (88.7) and C-6 (78.7) in comparison with those of cycloastragenol (Fathiazad et al., 2010) were found to be shifted downfield by +9–7ppm. As a result, C-3 and C-6 were the sites of glycosidation, confirming the bidesmosidic structure of compound **3**. The HMBC correlations observed between H-1'' (δ_H 4.72) of xylose and C-3 (δ_C 88.7), and H-1' (δ_H 4.34) of glucose and C-6 (δ_C 78.7) confirmed these assignments. The third anomeric hydrogen signal at δ_H 4.40 (H-1''') assigned to the arabinose unit showed correlation with the C-2'' atom (δ_C 75.0) of the xylose moiety attached to C-3.

The downfield shift of H-3'' (δ_H 4.96, t, J = 6.1 Hz) of the xylose moiety and the HMBC cross peaks between this hydrogen and the carbonyl at δ_C 169.9, indicated the presence of an acetyl group in C-3''' of xylose. The NMR data of **3** were superimposable with those reported for Trojanoside H (Bedir et al., 1999b), with exception of the acetylation of the xylose moiety. Thus, compound **3** was identified as 3-*O*-[α-L-arabinopyranosyl-(1→2)-*β*-D-(3-*O*-acetyl)-xylopyranosyl-6-*O*-*β*-D-glucopyranosyl]- 20(S), 24(R) epoxy-3*β*,6*β*,16*β*,25-tetrahydroxycycloastragenol, and named Astragalarmoside C.

Eleven known compounds were identified as Astrasieversianin II (**4**) (Çaliş et al., 1997; Baratta & Ruberto, 1997; Bedir et al., 1999a), Astrasieversianine IV (**5**) (Peng et al., 2008; Verotta et al., 2002; Kim et al., 2008), Astrasieversianine VI (**6**) (Verotta et al., 2002)**,** Astrasieversianine X (**7**) (Çaliş et al., 1997; Verotta et al., 2002; Polat et al., 2010), Astragaloside II (**8**) (Peng et al., 2008; Tappe et al., 1994), Astragaloside IV (**9**) (Lee et al., 2013; Fathiazad et al., 2010; Peng et al., 2008), Cyclomacroside D (**10**) (Iskenderov et al., 2009a; Labed et al., 2016)**,** Cycloaraloside E (**11**) (Isaev, 1991), Cyclomacroside C (**12**) (Iskenderov et al., 2009b), Agroastragaloside IV (**13**) (Hirotani, 1999), Soyasaponin I (**14**) (Cui et al., 1992)**,** by comparison of their physical and spectral data with those of literature values.

2.2 Chemotaxonomic study

Cycloartane triterpenoids constitute a distinct class of saponins. Bibliographic studies indicate their predominant occurrence in several plant families, including Meliaceae, Orchidaceae, Passifloraceae, Combretaceae, Araliaceae, Ranunculaceae, and Fabaceae (Ekiz Dinçman et al., 2024). The genus *Astragalus* (Fabaceae family) represents a major source of these cycloartane saponins (Stambolov et al., 2023; Stambolov et al., 2023). Recent research has identified over 140 cycloartane-type triterpene glycosides from various *Astragalus* species. Additionally, studies have shown that genus also contains oleanane-type saponins, including at least 18 oleanane derivatives, alongside various other secondary metabolites (Li et al., 2014; Ghasemian-Yadegari et al., 2017).

Cycloartane glycosides in *Astragalus* species exhibit remarkable structural diversity, primarily driven by variations in: Glycosylation patterns (mono-, di-, or oligosaccharide attachments), and linkage positions on the cycloartane aglycone (C-3, C-6, C-24, or C-25). In contrast, oleanane glycosides isolated from *Astragalus* display limited structural variation, predominantly featuring skeletons common throughout the Fabaceae family. While their presence affirms the genus taxonomic placement, these oleanane glycosides offer less utility

for interspecies differentiation compared to their cycloartane counterparts (Benchadi et al., 2013). The present study, which was carried out on the Algerian subspecies *Astragalus armatus* subsp. *numidicus* (Murb.) Emb. & Maire, allowed the isolation and identification of 3 undescribed saponins (Astragalarmoside A (**1**), Astragalarmoside B (**2**), Astragalarmoside C (**3**)) (Fig. 1), as well as 11 known saponins (Astrasieversianine II (**4**)**,** Astrasieversianine IV (**5**), Astrasieversianine VI (**6**)**,** Astrasieversianine X (**7**), Astragaloside II (**8**), Astragaloside IV (**9**), Cyclomacroside D (**10**), Cycloaraloside E (**11**)**,** Cyclomacroside C (**12**), Agroastragaloside IV (**13**), Soyasaponine I (**14**).

Cycloartanes can be present as the free aglycone, or they can be found as mono-, bi-, and tridesmosidic glycosides. The most common sugar found on the structure of glycosides is β-D-xylose. Additional monosaccharide are β-D-glucose, α-L-rhamnose, α-L-arabinose (Isaev et al., 1989).

Some of the saponins isolated from *A. armatus* subsp. *numidicus* (Murb.) Emb. & Maire, which are Astragalarmoside A (**1**), Astrasieversianine VI (**6**), Astragaloside II (**8**) has for each an acetate group linked to C-2' of the xylose, while the acetate group of Astragalarmoside C (**3**) is linked to C-3' of the xylose sugar, however Astrasieversianine II (**4**) and Astrasieversianine IV (**5**) that contains also two acetate group for each which linked to C-2' and C-3' of the xylose.

Previous studies report the presence of Astrasieversianine II (**4**) in three species: *A. melanophrurius* (Çaliş et al., 1997), *A. siculus* (Baratta & Ruberto, 1997), and *A. trojanus* (Bedir et al., 1999a). Similarly, Astrasieversianine IV (**5**) and Astragaloside II (**8**) have been documented in several *Astragalus* sources, including: roots of *A. mongholicus* Bunge (Peng et al., 2008), *A. melanophrurius* (Çaliş et al., 1997), *A. mongholicus Bge* (Tappe et al., 1994), *A. kahiricus DC* (Verotta et al., 2002), *A. membranaceus* (Kim et al., 2008), *A. wiedemannianus* Fischer (Polat et al., 2010), and *A. membranaceus* Bunge (Kitagawa et al., 1983). Astrasieversianine VI (**6**) was described from one species**,** *A. kahiricus DC* (Verotta et al., 2002), while Astrasieversianine X (**7**) have been found in three species *A. melanophrurius* (Çaliş et al., 1997), *A. kahiricus DC* (Verotta et al., 2002) and *A. wiedemannianus Fische* (Polat et al., 2010). Astragaloside IV (**9**) has been isolated from several *Astragalus* species, including roots of *A. mongholicus* Bunge (Peng et al., 2008), *A. caspicus* Bieb (Fathiazad et al., 2010), *A. melanophrurius* (Çaliş et al., 1997), *A. membranaceus* (Lee et al., 2013; Kim et al., 2008), *A. wiedemannianus* Fischer (Polat et al., 2010), *A. membranaceus* Bunge (Kitagawa et al., 1983), *A. trojanus* (Bedir et al., 1999a).

Cycloaraloside E (**11**) was isolated only from *A. armatus* (Isaev, 1991)**,** while Cyclomacroside C (**12**) (Iskenderov et al., 2009b) and Cyclomacroside D (**10**) were both isolated from *A. macropus* (Iskenderov et al., 2009a), and Agroastragaloside IV (**13**) from *A. membranaceus* (Hirotani, 1999).

Whereas Soyasaponine I (**14**) was identified in *A. sinicus* L. (Cui et al., 1992), *A. membranaceus* Bunge (Kitagawa et al., 1983), *A. depressus* L. (Maamria et al., 2015), *A. shikokianus* (Yahara et al., 2000), *A. trimestris* (Kitagawa et al., 1983), *A. monspessulanus* L. (Bourezzane et al., 2018), besides some other genera of Fabaceae family such as *Pisum* (Taylor et al., 2004), *Hedysarum* (Liu et al., 2007), *Melilotus* (Hirakawa et al., 2000), *Trifolium* (Jurzysta et al., 1989), *Lupinus* (Woldemichael & Wink, 2002), *Glycine* (Hosny & Rosazza, 1999), and *Medicago* (Bialy et al., 1999). Due to its broad occurrence in Fabaceae family and more specifically in *Astragalus* species, this compound could serves as a chemotaxonomic marker for the genus *Astragalus* (Oleszek & Stochmal, 2002).

3 Conclusion

In conclusion, the systematic phytochemical study on the aerial parts of *A. armatus* subsp. *numidicus* (Murb.) Emb. & Maire. afforded three undescribed components, astragalarmoside A-C (**1-3**) (Fig. 1), ten known cycloartane saponin (**4-13**) and one oleanane (**14**). These results expand our knowledge of chemical diversity and provide evidence to further analysis of their potential chemotaxonomic significance. Compounds **5**, **8** and **9** have been previously reported from different species of the genus *Astragalus* (Peng et al., 2008; Fathiazad et al., 2010; Çaliş et al., 1997; Lee et al., 2013; Kitagawa et al., 1983; Bedir et al., 1999a), might reveal the close chemotaxonomic relationships between *A. armatus* subsp. *numidicus* (Murb.) Emb. & Maire and other *Astragalus* species. It is also interesting to note that ten cycloartane (**4-13**) are described for the first time in the *A. armatus* subsp. *numidicus* (Murb.) Emb. & Maire.

4 Experimental

4.1 General experimental procedures

1D and 2D-NMR spectra (^{1}H and ^{13}C-NMR, ^{1}H–^{1}H COSY, HSQC, HMBC and ROESY) were recorded in CD_3OD on a 500 MHz Bruker Avance Neo spectrometer equipped with a SP & ^{19}F/^{1}H Iprobe (^{1}H at 500.28 MHz and ^{13}C at 125.8 MHz) and III-600 spectrometer

(Karlsruhe, Germany) (^{1}H at 600 MHz and ^{13}C at 150 MHz) equipped with a 5 mm TCI cryoprobe. 2D-NMR experiments were performed using a standard Bruker microprogram (Top Spin 4.4.1 software). HR-ESIMS experiments were performed using a Micromass Q-TOF micro instrument (Manchester, UK). Flash chromatography was performed on a Puri Flash® 5.050 equipped with a Inter Soft® X Navigator and dual UV and DEDL detection using Puri Flash® cartridges (silica gel or RP-C18). Preparative high-performance liquid chromatography (HPLC) was performed on a Gilson PLC 2050 equipped with Gilson Glider Prep® software, Armen pump and Ecom UV detector, using a RP-C18 column (Interchim C18-HQ, 5 µm, 250 × 21.2 mm). The mobile phase was composed of CH_3CN/ H_2O with TFA (0.0025%) with a flow rate 50 mL/min. The chromatograms were monitored at 205, 215 and 360 nm. Semi-preparative HPLC was performed on a Vanquish Core / UltiMate instrument equipped with an VC-P20-A pump with a built-in degasser, VC-A12-A autosampler, UltiMate TCC-3000 oven, Ultimate DAD 3000 thermofisher detector, UltiMate AFC-3000 automatic fraction collector and chromeleon® software. An RP-C18 prep column (Interchim 5 µm C18 100 A° 250-10.0 mm, Montlucon, France). The mobile phase for semi-preparative HPLC was a mixture of H_2O with TFA (0.0025%) and CH_3CN with a flow rate of 4.7 mL/min. The chromatograms were monitored at 205, 215 and 360 nm. Analytical HPLC experiments were performed using a Dionex Ultimate 3000, equipped with an LPG-3000 SD pump, a WPS-3000 injector and a UV-DAD-3000 detector with Chromeleon® software and an Interchim C18-2.5 µm, 100 Å (250 × 4,6 mm, using the same eluent as semi-preparative HPLC with a flow rate of 1 mL/min. The chromatograms were monitored at 205, 215 and 360 nm.

4.2 Plant material

The aerial parts of *Astragalus armatus* subsp. *numidicus* (Murb.) Emb. & Maire, were collected in June 2018 in Batna (Northeastern Algeria). The plant was authenticated by Prof. Gérard De Bélair (University of Annaba, Algeria) and a voucher specimen (LOST.Aan.06.18) was deposited at the Herbarium of the laboratory of Therapeutic Substances (LOST), University frères Mentouri-Constantine 1.

4.3 Extraction and isolation

The dried aerial parts of *Astragalus armatus* subsp. *numidicus* (Murb.) Emb. & Maire (1.2 kg) were subjected to maceration at room temperature in a hydroalcoholic mixture (EtOH/H_2O, 70:30 v/v). After filtration, the solvent was removed under reduced pressure at a temperature not exceeding 40°C to obtain a crude dry extract (228 g). This extract was diluted with

distilled water (700 mL**)**, then successively extracted with petroleum ether (PE), dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc), and *n*-butanol (*n*-BuOH) (3 × 300 mL, each) to give 0.104 g of PE, 1.33 g of CH_2Cl_2, 6.14 g of EtOAc and 20.56 g of *n*-BuOH extracts.

A part of the EtOAc extract (5.5 g) was fractionated by vacuum liquid chromatography (VLC) over C18 reverse phase, eluted with H_2O / MeOH (70 :30, 60 :40, 50 :50, 40 :60, 30 :70, 20 :80, 10 :90, 0 :100) to obtain 9 fractions (A-I). Fraction G (638.5 mg) was fractionated by flash chromatography over silica gel, eluted by a gradient system of CH_2Cl_2 /MeOH (100/0% to 0/100%), in 25 min to afford 13 sub-fractions. Sub-fractions G2, G4, G5 and G7 were separated by semi-prep HPLC for 30 min. Sub-fraction G2 (14.5 mg) eluted by a gradient system of 45–55% of ACN in H_2O give compound **4** (1 mg, R_t 15.3 min). Sub-fraction G4 (19.4 mg) eluted by a decreasing gradient system 60–45% of H_2O in ACN give compound **5** (14.2 mg, R_t 17.4 min). Sub-fractions G5 (22.4 mg) and G7 (17.2 mg) eluted by a gradient system 40–50% of ACN in H_2O give compound **6** (3.9 mg, R_t 12.4 min), compound **7** (1.4 mg, R_t 7.5 min) and compound **8** (7.2 mg, R_t 9.5 min). Sub-fraction G8 yielded a white precipitate which was identified as compound **9** (2.1 mg).

A part of the *n*-BuOH extract (15.3 g) was subjected to C_{18} reverse phase VLC, eluting successively with 300 mL of H_2O/ MeOH using a solvent gradient from 70% H_2O to 100% MeOH in 10% MeOH increments, yielding 8 fractions *(*I–VIII). The fraction III (806 mg) was purified by silica gel flash chromatography using a CH_2 Cl_2 /MeOH gradient 95 :5*%* to 0 :100*%* over 60 minutes, affording 18 sub-fractions. Three sub-fractions III-7, III-10, III-15 affording three compounds as pure substances: **1** (42.5 mg), **10** (101.8 mg), and **11** (22.9 mg). Sub-fraction III-4 was purified by semi-prep HPLC eluted with the isocratic system 25 % of CH_3CN for 15min and a gradient system 30-60% CH_3CN for 15 min to yield compound **12** (4.4 mg, R_t 11.11min). The semi-prep HPLC purification of sub-fraction III-13, eluted with binary gradient CH_3CN:H_2O, from 25% to 35% of CH_3CN, for 30 min, afford compound **13** (4 mg, R_t 12.23 min). With the same last binary gradient system, sub-fraction III-9 was purified by preparative HPLC to yield compound **2** (3.5 mg, R_t 19.12 min). The fraction V (600 mg) was fractionated by flash chromatography over silica gel, eluted by a gradient system of CH_2Cl_2 /MeOH (100/0% to 0/100%), in 120 min to afford 9 sub-fractions. Sub-fraction V-5 was separated by semi-prep HPLC using a gradient from 35% to 45% CH_3CN, in 30 min to led compound **3** (1.2 mg, R_t 17.83 min). The last sub-fraction V-9 yielded compound **14** (29.1 mg) in its pure form.

4.3.1 Astragalarmoside A (1)

White amorphous solid; [α] +3.11 (c 0.90, MeOH); ^{1}H NMR (CD_3OD, 600 MHz) and ^{13}C NMR (CD_3OD, 150 MHz) data, see Tables 1 and 2. HR-ESIMS $[M-H]^+$ *m/z* 901.5165 (calcd for $C_{46}H_{76}O_{17}$, 901.5161).

4.3.2 Astragalarmoside B (2)

White amorphous solid; [α] +16.2 (c 0.21, MeOH); ^{1}H NMR (CD_3OD, 600 MHz) and ^{13}C NMR (CD_3OD, 150 MHz) data, see Tables 1 and 2. HR-ESIMS $[M-H_2O+H]^+$ *m/z* 751.4638 (calcd for $C_{41}H_{67}O_{12}$, 751. 4633)

4.3.3 Astragalarmoside C (3)

White amorphous solid; [α] +1.18 (c 0.16, MeOH); ^{1}H NMR (CD_3OD, 600 MHz) and ^{13}C NMR (CD_3OD, 150 MHz) data, see Tables 1 and 2. HR-ESIMS $[M+Na]^+$ *m/z* 981,5030 (calcd for $C_{48}H_{78}O_{19}Na$, 981,5035), $[M+Na-CH_2O]^+$ *m/z* 951.5270 , $[M+Na-CO_2]^+$ *m/z* 937.5126 , $[M+Na-CO_2-H_2O]^+$ *m/z* 919.4929 .

CRediT authorship contribution statement

Hadjer Boubertakh: Data curation, Investigation, Writing – original draft. **Assia Khalfallah**: Methodology, Supervision, Writing – original draft. **Ahmed Kabouche**: Validation, Writing – review & editing. **Zahia Kabouche**: Project administration, Validation, Writing – review & editing. **Charlotte Sayagh**: Methodology, Data curation, Software, Supervision. **Anthony Abou Dib :** Data curation. **Laurence Voutquenne-Nazabadioko**: Data curation, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare no conflict of Interest

Supplementary Information

Experimental part with HR-ESI–MS, ^{1}H NMR,^{13}C NMR, COSY, HMBC and ROESY spectra of compounds **1-3**

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Table 1

^{13}C NMR and ^{1}H NMR spectroscopic data of aglycone moieties for compounds **1**-**3** in CD_3OD.[a.]

	1		**2**		**3**	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	72.3	3.53 m	71.2	3.66 m	31.5	1.57; 1.28 m
2	35.6	2.04; 1.84 m	35.2	2.14 ; 1.89 dd (1.04, 2.3)	29.1	1.95 ; 1.71 m
3	83.7	3.65 m	83.4	3.67 m	88.7	3.18 m
4	40.05	-	40.0	-	41.7	-
5	38.7	2.14 dd (9.9, 3.9)	39.1	2.06 m	51.9	1.62 m
6	30.7	1.73 ; 1.01 m	29.7	1.74 ; 1.12 m	78.7	3.56 m
7	69.7	3.55 m	69.6	3.56 m	33.6	1.91; 1.61 m
8	54.6	1.56 d (9.5)	52.6	1.93 d (10.0)	45.2	1.88 m
9	20.7	-	24.1	-	20.7	-
10	29.9	-	33.1	-	28.8	-
11	25.5	2.25; 1.34 m	130.4	5.32 d (9.9)	25.8	1.93; 1.37 m
12	32.6	1.68 m	135.1	6.05 d (9.9)	32.7	1.70; 1.60 m
13	45.5	-	48.3	-	44.5	-
14	48.3	-	49.5	-	45.9	-
15	37.1	1.58 m	35.4	1.62 ;1.68 m	44.7	2.05; 1.40 m
16	28.3	1.96 ;1.34 m	28.4	2.06 ;1.40 m	73.4	4.67 t (7.6)
17	51.9	1.57 m	47.0	1.77 m	57.6	2.39 d (7.6)
18	16.9	1.03 s	16.3	1.01 s	19.9	1.27 s
19	28.0	0.78 d (4.1); 0.43 d (4.1)	25.7	1.07 d (4.4); 0.61 d (4.4)	28.1	0.62 d (4.0) ; 0.28 d (4.0)
20	36.2	1.41 m	36.9	1.46 m	87.0	-
21	17.4	0.92 d (5.2)	17.7	0.93 s	27.1	1.22 s
22	33.0	1.52; 1.26 m	32.8	1.67 ;1.62 m	34.0	2.63; 1.65 m
23	28.06	1.53 ; 1.36 m	28.2	1.64 ;1.53 m	25.5	2.04 m
24	88.2	3.38 m	87.9	3.43 d (8.2)	81.2	3.78 m
25	72.2	-	72.1	-	71.1	-
26	24.6	1.15 s	25.2	1.17 s	26.4	1.28 s
27	23.8	1.10 s	23.8	1.17 s	25.3	1.15 s
28	24.5	0.98 s	24.6	1.03 s	27.1	1.25 s
29	13.1	0.82 s	13.3	0.86 s	15.4	1.01 s
30	17.9	1.05 s	19.3	0.93 s	18.7	1.04 s

[a] ppm, *J* in parentheses in Hz.

Table 2:

^{13}C NMR and ^{1}H NMR spectroscopic data in CD_3OD of the sugar moieties of compounds **1**-**3**. [a.]

	1		**2**		**3**	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
	Rha		**Rha**		**Glc**	
1’	102.9	4.75 s	102.9	4.78 s	103.5	4.34 d (7.7)
2’	70.9	3.85 m	70.8	3.86 m	74.3	3.19 t (8.3)
3’	71.3	3.64 m	71.0	3.64 m	77.1	3.34 m
4’	72.7	3.37 m	72.4	3.37 t (9.4)	70.4	3.29 m
5’	68.5	3.68 m	68.4	3.69 m	76.4	3.26 m
6’	16.4	1.24 d (6.1)	16.5	1.26 d (6.18)	61.5	3.87 dd (10.5, 3.4); 3.67 dd (11.4, 5.08)
Xyl						
1’’	102.0	4.48 d (7.8)	104.0	4.32 d (7.56)	102.8	4.72 d (4.3)
2’’	74.2	4.72 t (8.4)	73.8	3.22 m	75.0	3.74 t (4.8)
3’’	74.9	3.45 t (9.4)	76.5	3.33 m	72.8	4.96 t (6.1)
4’’	69.7	3.56 m	69.8	3.51dt (5.2, 9.4)	67.1	3.63 m
5’’	65.6	3.91 dd (11.2, 5.09) ; 3.24	65.7	3.87 dd (11.3, 5.1); 3.20 t (11.3)	62.7	4.06 dd (11.9, 2.5); 3.40 dd (11.9, 5.6)
CO	170.5	-			169.9	-
Ac-CH_3	19.8	2.11 s			20.1	2.11 s
Ara						
1’’’					103.5	4.40 d (6.28)
2’’’					71.1	3.56 m
3’’’					72.8	3.54 m
4’’’					68.3	3.81 m
5’’’					65.7	3.90; 3.53

[a] ppm, *J* in parentheses in Hz.