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TRITERPENOIDS FROM *Astragalus* PLANTS

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Advances in the chemistry of Astragalus *triterpenoids based on worldwide literature appearing mainly after 1988 were reviewed. The review was dedicated to the memory of Professor N. K. Abubakirov.*

Key words: *Astragalus*, Leguminosae, triterpenoids, cycloartanes, lanostanes, oleananes, chemical and spectral properties, chemical transformation, biological activity.

INTRODUCTION

Astragalus is a well represented species in the legume family (Leguminosae) that numbers more than 2200 species growing worldwide [1].

The *Flora of the USSR* lists 849 *Astragalus* species; the *Flora of Uzbekistan*, 239 [2, 3].

Certain *Astragalus* species have been used since antiquity in folk medicine of many peoples; several representatives of this genus, in conventional medicine. Triterpenoids are often found among secondary plant metabolites. Triterpenoids of the cycloartane, lanostane, and oleanane types are observed. They all originate biogenetically from a single precursor, squalen-2,3-oxide. Nevertheless, whereas cycloartanes and lanostanes are biogenetically related, oleananes have no biogenetic link to them. A peculiarity of phytosteroid biosynthesis is the generation of an additional 9,19-three-membered ring during cyclization of squalen-2,3-oxide with subsequent opening of this ring. This is responsible for the biogenetic relationship of cycloartane and lanostane triterpenoids.

Cycloartane triterpenoids were first discovered in *Astragalus* plants [4-6]. Plants of this genus drew attention to themselves after it was established that they produce cycloartane triterpenoids. These studies turned a new page in the study of *Astragalus* plants. Since then, their content of cycloartane methylsteroids and glycosides came under intense scrutiny in many scientific centers of the world. Cycloartanes are derivatives of 9β,19-cyclolanostane and are produced exclusively by photosyntheic eukaryotes [7]. Cycloartanes dominate the known triterpenoids in plants of this genus. At present, 152 cycloartanes have been described from *Astragalus* plants. Of these, 45 were included in our previous review [8]. This review includes compounds appearing after the previous review [8].

CYCLOARTANE TRITERPENOIDS: CLASSIFICATION AND CHEMICAL AND SPECTRAL PROPERTIES

A total of 30 structurally distinct genins have been found in the plants under discussion (**1**-**30**). Some of these (**1**, **2**, **10**, **28**, **30**) have not been characterized as pure compounds but as the corresponding glycosides. Methylsteroids **6**, **7**, **14**, and **16** have been found only in the free state.

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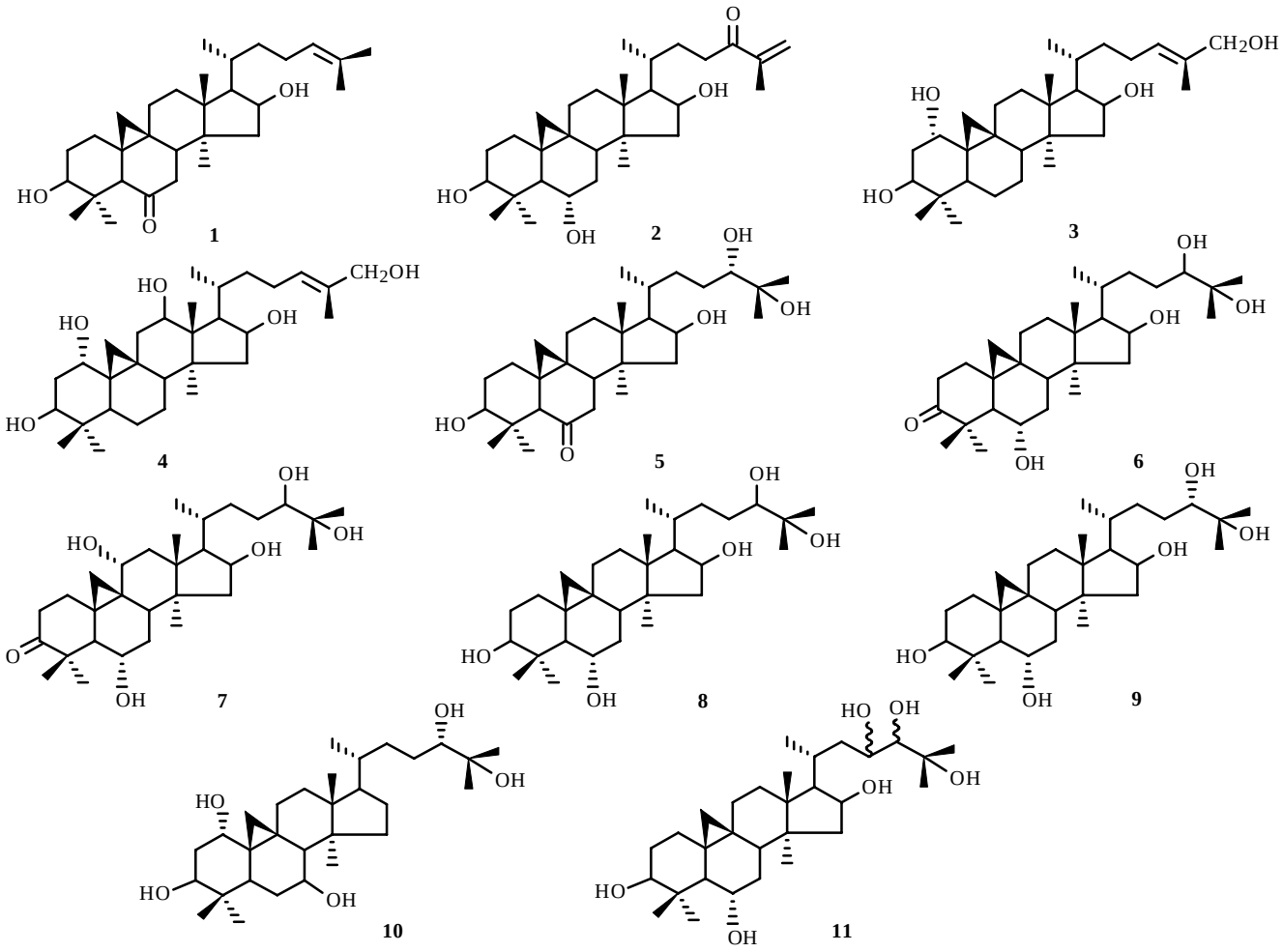
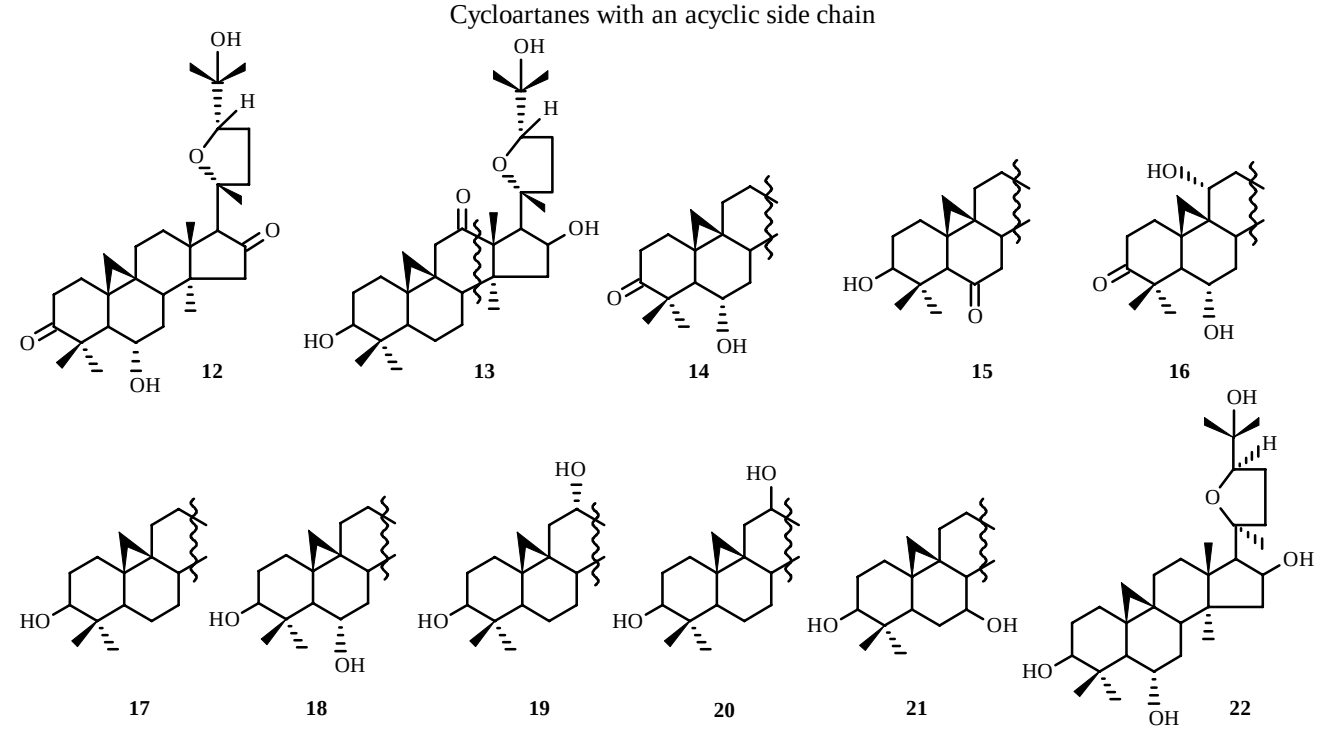
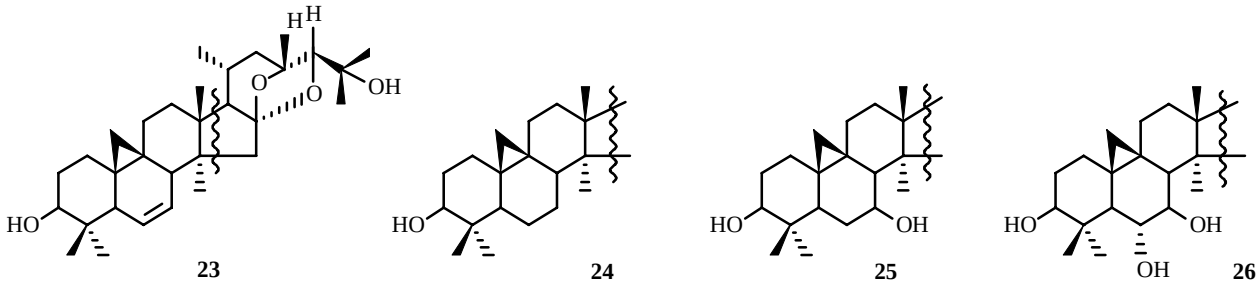


Cycloartanes with an acyclic side chain

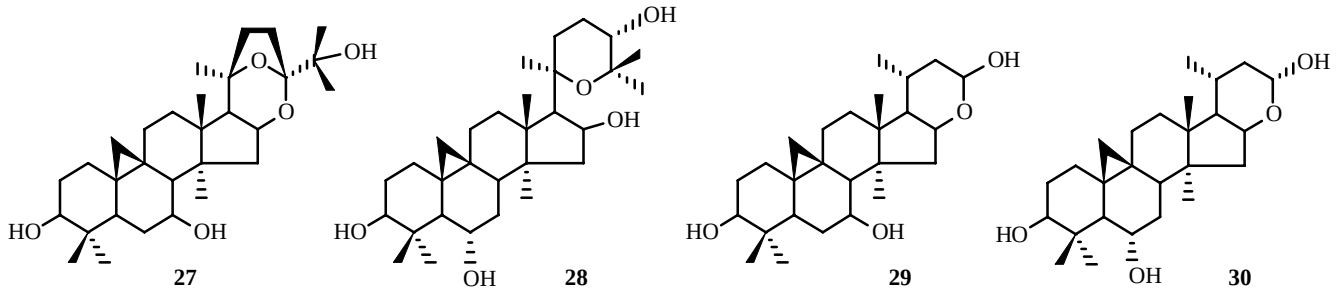


20,24-Epoxycycloartanes



23 **24** **25** **26**

16β,23;16α,24-Diepoxycycloartanes



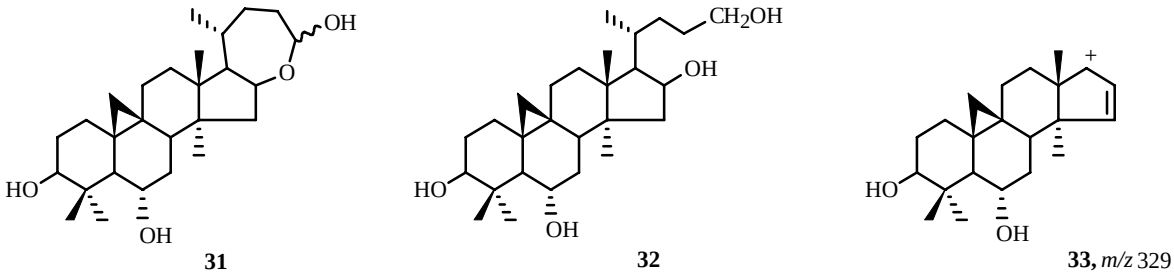
27 **28** **29** **30**

16β,24;20,24-Diepoxycycloartanes, 20,25-epoxycycloartanes, 24-nor-16β,23-epoxycycloartanes

The structures of **1**-**30** show that the side chains of the compounds differ substantially. Therefore, our classification of these substances is based on structural features of the side chains. The known cycloartane methylsteroids of *Astragalus* plants can be divided into six structural types according to the side-chain structure: 1) cycloartanes with an acyclic side chain (**1**-**11**), 2) 20,24-epoxycycloartanes (**12**-**22**), 3) 16β,23;16α,24-diepoxycycloartanes (**23**-**26**), 4) 16β,24;20,24-diepoxycycloartanes (**27**), 5) 20,25-epoxycycloartanes (**28**), 6) 24-nor-16β,23-epoxycycloartanes (**29**,**30**).

Triterpenoids of *Astragalus* plants are polyhydroxycompounds. Only genin **1** retains the intact side chain of cycloartenol. The side chain of the remaining compounds is oxidized to one degree or another. Most of the compounds contain in the acyclic side chain an α-diol on C-24–C-25 and a 16β-hydroxyl.

The presence of an α-glycol is easily determined by periodate oxidation. A 25-norhemiacetal of type **31** is formed in the presence of a 16β-hydroxyl [9, 10]. If the 16-hydroxyl is acylated or glycosylated, the hemiacetal does not form. In the first instance, periodate oxidation with subsequent reduction by $NaBH_4$ leads to a 25-noralcohol of type **32** [11]. Smith degradation [12] of glycosides containing a C-16 carbohydrate followed by acid hydrolysis also forms a 25-nor-product of the **32**-type tetraol [13-17]. These chemical properties of cycloartan-16β,24,25-triols were used to correlate chemical structures of cycloasgenin C (**8**) and cyclocanthogenin (**9**) [11]. This enabled the stereochemistry of asymmetric C-24 in cyclocanthogenin to be unambiguously determined. This correlation consists essentially of converting genins **8** and **9** by two routes to the same nor-products **31** and **32**.



31 **32** **33,** *m/z* 329

A 24,25-glycol is readily converted in quantitative yield to the isopropylidene derivative, which also proves the presence of an α-diol.

On one hand the C-16 secondary hydroxyl is sterically shielded by a *cis*-oriented side chain; on the other, it creates an intramolecular H-bond (IHB) with the oxygenated functional groups of the side chain. Therefore, the reactivity of the 16β-hydroxyl toward alkylation and acylation is much less than the 1α-, 3β-, 6α-, 7β-, and 11α-hydroxyls. Only 12α- and 12β-hydroxyls and the C-25 tertiary hydroxyl are less reactive than the 16β-hydroxyl [18, 19]. The difference in the reactivities of the hydroxyls enables derivatives with a free C-16 hydroxyl to be prepared. Oxidation to the ketone and subsequent measurement of the Cotton effect in the circular dichroism (CD) spectrum unambiguously determines the location of the ketone and, therefore, the corresponding C-16 secondary hydroxyl. The C-16 ketone exhibits a negative Cotton effect near 302-305 nm ($\Delta\varepsilon$ = -5.09—5.8) [9, 11, 20, 21].

A β-orientation of the acetoxyl and, therefore, the C-16 hydroxyl, gives a positive increment of molecular rotations between the 16-acetoxy and 16-hydroxy derivatives [9, 11, 20, 22].

Electron-impact mass spectrometry of cycloartanes with an acyclic side chain gives a characteristic peak for the ion resulting from loss of the side chain owing to rupture of the C-17–C-20 bond and elimination of a water molecule including the C-16 hydroxyl. This ion with *m*/*z* 329 has structure **33** or its isomeric structure corresponding to the polycyclic part of the molecule, depending on the number and position of the ketone and hydroxyl [9-11, 20]. The corresponding ion forms upon fragmentation of lanost-9(11)-ene isomers of cycloartanes [11, 20].

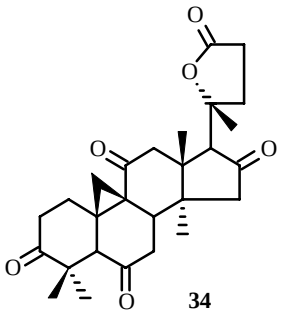
A common structural element for cycloartanes with an acyclic side chain, 16β,23;16α,24-diepoxycycloartanes, and 24-nor-16β,23-epoxycycloartanes is a secondary CH_3-21 methyl. This was easily recognized in the PMR spectrum as a single 3H-doublet at strong field. The orientation of the CH_3-21 was the same in these compounds. The C-20 retained the initial absolute configuration of the cycloartenol. Therefore, the stereochemistry of asymmetric C-20 in the three structural types under discussion was not examined. For the three remaining structural types, asymmetric C-20 is bonded to an epoxy oxygen. Therefore, the stereochemistry of C-20 must also be established.

20,24-Epoxycycloartanes (**12-22**) represent the most numerous group. Of the four possible side-chain stereoisomers [two pairs of enantiomers: 20*R*,24*S* and 20*S*,24*R* (1) and 20*R*,24*R* and 20*S*,24*S* (2)], at present only the first pair has been found in *Astragalus* plants. Side chains in 10 genins (**12-21**) have identical stereochemistry (20*R*,24*S*) whereas that of **22** is enantiomeric.

Cyclosiversigenin (**18**) is the most widely distributed genin of *Astragalus* plant glycosides. Thus, it is not surprising that it was discovered first [4, 8]. Cyclosiversigenin is also known as cycloastragenol [23] and astramembrangenin [24, 25].

Chemical and spectral investigations of cyclosiversigenin [4] and cyclogalegigenin [26] led convincingly to the conclusion that the side chains of these genins are enantiomers and have the alternate stereochemistry 20*R*,24*S* and 20*S*,24*R*. However, the erroneous selection of the stereochemistry of cyclosiversigenin [4] led to the incorrect configuration for cyclogalegigenin also [26]. X-ray structural analysis found the 20*S*,24*R* configuration for cyclogalegigenin, which, in turn, determined the 20*R*,24*S* configuration for cyclosiversigenin [27]. X-ray structural studies of the nona-O-methyl ether of astragaloside IV (cyclosiversioside F, which is cyclosiversigenin 3-O-β-D-xylopyranoside, 6-O-β-D-glucopyranoside) [23] and astramembrangenin 3,6-diacetate (cyclosiversigenin 3,6-diacetate) [25] agree with the stereochemistry of cyclosiversigenin.

The fundamental property of cyclopropane to impart to a compound certain attributes of a double bond was used to correlate chemically the structures of cycloasgenin A (**16**) and cyclosiversigenin (**18**) [6]. Oxidation of **16** and **18** by chromic anhydride in glacial acetic acid produced tetraketolactone **34**.



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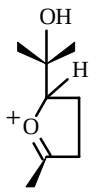
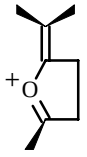
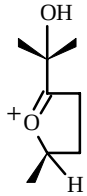


35, *m*/*z* 143



36, *m*/*z* 125



37, *m*/*z* 143

The cyclopropane ring is similar to a double bond with respect to electron delocalization. Therefore, C-1 and C-11 of the cycloartane skeleton are allylic positions. Introducing a ketone at C-11 in cyclosiversigenin is essentially allylic oxidation. The C-11 position is preferentially oxidized owing to the ability of the C ring to adopt the conformation necessary for conjugation of the ketone and the cyclopropane ring. This directs the reaction. Conjugation of the C-11 ketone and the cyclopropane ring is clearly seen in IR spectra [6, 28].

Unambiguous determination of the absolute configuration of cyclosiversigenin and cyclogalegigenin enabled a correlation to be found between the stereochemistry of the asymmetric centers of the side chain and the parameters of the PMR and ^{13}C spectra [8]. However, 12α- and 12β-hydroxyls have a substantial influence on the chemical shifts of the atoms in the side chain. A 12-ketone also has some effect on the observed NMR parameters. As a result, chemical conversion from genins **19** and **20** to genin **13** and from **13** to quisvagenin (**17**) played an integral role in proving the structures of cycloalpigenins A (**13**) [29], B (**19**) [18], and C (**20**) [19].

Cycloalpigenins B and C are epimers at C-12. The similarity of the spectral parameters for asymmetric C-12 (δ 72.76 and 72.10, respectively) and H-12 [for **19**, δ 4.11 dd (J = 10, 6 Hz) and δ 3.86 dd (J = 9, 6 Hz); in **20**, δ 4.09 m and δ 3.77 dd (J = 9, 5 Hz)] is striking [19]. The practically identical spin—spin coupling constants (SSCC) for H-12 in methylsteroids **19** and **20** are consistent with either the axial or pseudoaxial orignation of the H. Therefore, the corresponding hydroxyl is either equatorial or pseudoequatorial. Therefore, the C ring should be flexible and change confirmation upon a change of configuration at C-12. Conformational analysis [19] showed that the C ring is in fact flexible. In **19** it has the boat conformation (B11); in **20**, chair (C12). Thus, adjusted parameters of NMR spectra cannot be used to determine the stereochemistry of C-12. For this, proof of the orientation of the 12α-hydroxyl in cycloalpigenin B is essential [18]. For this, the *γ-gauche* coupling of the H-17 hydroxyl is used. Its signal is found at lower field at δ 3.15 (C_5D_5N) and δ 2.63 ($CDCl_3$). This proton in the PMR of cycloalpigenin C, which has a 12β-hydroxyl, resonates at δ 2.49 (C_5D_5N) and δ 2.14 ($CDCl_3$) [19]. A C-12 carbonyl also has a deshielding *γ-gauche* coupling to H-17 that shifts the signal for this proton to δ 3.19 (C_5D_5N) [29]. Therefore, it can be proposed that ring C in cycloalpigenin A has the same conformation as that in cycloalpigenin B, i.e., the boat conformation (B11).

A C-20 oxygen of the epoxy group is a common structural feature of compounds of structure types *2*, *4*, and *5*. This gives rise to a singlet for CH_3-21 in the PMR spectra and, as a result, all methyls of methylsteroids that belong to the aforementioned three structural types resonate as singlets. The signal for H-24 that is observed at δ 3.89-4.09 (C_5D_5N, TMS) and δ 3.77-3.88 ($CDCl_3$, TMS) as a doublet of doublets or a triplet is a characteristic feature of PMR spectra of 20,24-epoxycycloartan-25-ols that is also caused by the side chain [18, 19, 29-31].

Known 20,24-epoxycycloartanes, except for cycloadsurgenin (**12**), which is a 3,16-dione, contain a 16β-hydroxyl. The proton geminal to this group resonates in PMR spectra at rather low field compared with the same proton of other structural types and is observed at δ 4.87-5.02 (C_5D_5N, TMS) [18, 19, 29, 30], δ 4.70-4.90 (C_5D_5N, HMDS) [6, 26], and δ 4.46-4.67 ($CDCl_3$, TMS) [18, 19, 31]. However, the signal for H-16 of cycloartanes with an acyclic side chain appears at rather high field of δ 4.74-4.75 (C_5D_5N, TMS) [10, 20] and δ 4.54-4.58 (C_5D_5N, HMDS) [9, 11]. The signal for H-16 in PMR spectra of **27** and **29**, where C-16 is bonded to an oxygen of the epoxy, is shifted to strong field even more and is observed at δ 4.56 (C_5D_5N, TMS) [32] and 4.30 [5].

Fragmentation by electron-impact mass spectrometry of 20,24-epoxycycloartan-25-ols provides useful information on the structure of the side chain. As a rule, the base peak in these spectra is the ion with *m*/*z* 143 (**35**) and elemental composition $C_8H_{15}O_2$, which corresponds to the side chain [4, 6, 18, 19, 26, 31, 33-35]. This peak arises upon cleavage of the C-17–C-20 bond. The ion with *m*/*z* 125 (**36**) is a daughter ion generated from **35** by elimination of a water molecule.

A ketone on C-12 and C-16 causes significant changes in the fragmentation pathway in the electron-impact mass spectra of the genins [29]. The peak for **35** is not the base peak in mass spectra of cycloalpigenin A (**13**) [29] and cycloadsurgenin (**12**) [36]. The intensity of the peak for this ion in the mass spectrum of cycloalpigenin A is only 28.9%. A peak of reduced intensity with *m*/*z* 143 is also observed in mass spectra of certain 12- and 16-keto derivatives of 20,24-epoxycycloartanes [6, 18, 26, 33]. The peak for the corresponding side chain with *m*/*z* 99 becomes the base peak in mass spectra of tetraketolactone derivatives such as **34**.

It should be noted that the ion with *m*/*z* 143 also arises upon fragmentation of cycloalpigenin (**27**), which is 16β,24;20,24-diepoxycycloartane [32]. However, in this instance the ion with *m*/*z* 143 has the isomeric structure of **37**. This is confirmed by the lack of a peak for the daughter ion with *m*/*z* 125 (**36**).

TABLE 1. Dihedral Angles in Newman Projections and SSCC Associated with Them Calculated using the Karplus Equation ($^3J = 7 - \cos\varphi + 5\cos 2\varphi$)

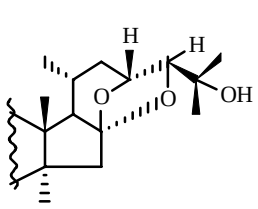
Isomer	φ (H-23/H-24), °	Multiplicity and SSCC (J/Hz) for H-24	φ (H-22/H-23), °	φ (H-22′/H-23), °	Multiplicity and SSCC (J/Hz) for H-23
38	96	d (J = 2.2)	26	94	dd (J = 9.2, 2.1)
39	24	d (J = 9.4)			
40	94	d (J = 2.1)	60	60	t (J = 4)
41	28	d (J = 8.9)			

Evidently the peak for the ion with *m*/*z* 143 is also seen in the spectrum of cyclocephalogenin (**28**) with an isomeric side chain.

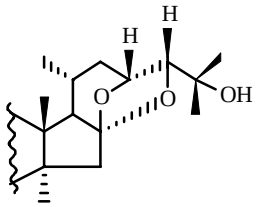
Thus, correct assignment of a triterpenoid to a certain structural type based on mass spectral data requires confirmation by additional information. This could be PMR and ^{13}C NMR spectral data. The aforementioned signal for H-24 in PMR spectra and signals for C-20 (δ 87.27), C-24 (δ 81.75), and C-25 (δ 71.27) in ^{13}C NMR spectra, assignment of which is not difficult, enables the compound to be unambiguously identified as a 20,24-epoxycycloartane. However, 16*β*,24;20,24-diepoxycycloartanes do not have an H-24 but a C-24 ketal, which is recognized easily in the ^{13}C NMR spectrum (δ 110.60) [32]. The chemical shifts of H-24 (δ 3.70, C_5D_5N, TMS), C-20 (δ 78.97), C-24 (δ 68.84), and C-25 (δ 75.25) of 20,25-epoxycycloartanes differ substantially from those of the corresponding atoms of 20,24-epoxycycloartanes [37-39].

16*β*,23;16*α*,24-Diepoxycycloartanes **23-26** are anomalies among secondary metabolites of *Astragalus* plants. Compounds of this structural group are typical of plants of the *Cimicifuga* genus and are observed as yet only in *Astragalus orbiculatus* Ledeb. Genins of **23-26** have identical stereochemistries, 16*β*,23*R*;16*α*,24*S*. The determination of the stereochemistry of the side chain of these compounds is especially interesting.

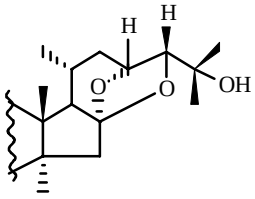
An examination of molecular models indicates that the heterocycles can be fused in two ways: 16*β*,23*R*;16*α*,24 and 16*α*,23*S*;16*β*,24. Depending on the stereochemistry of C-24, each type of fusion can give two stereoisomers. As a result, four isomers are possible: 16*β*,23*R*;16*α*,24*S* (**38**), 16*β*,23*R*;16*α*,24*R* (**39**), 16*α*,23*S*;16*β*,24*R* (**40**), and 16*α*,23*S*;16*β*,24*S* (**41**).



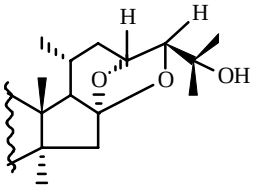
38: 16*β*, 23*R*; 16*α*, 24*S*



39: 16*β*, 23*R*; 16*α*, 24*R*



40: 16*α*, 23*S*; 16*β*, 24*R*

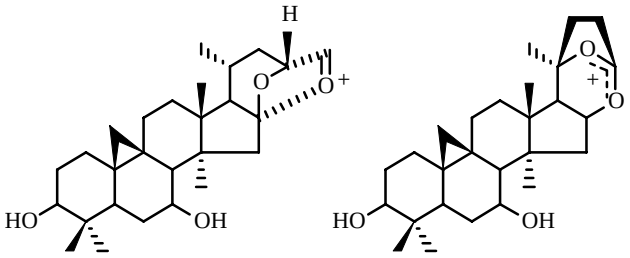


41: 16*α*, 23*S*; 16*β*, 24*S*

Table 1 presents results from a conformational analysis of the possible stereoisomers of **38**-**41**. It can be seen that H-24 in **39** and **41** gives a doublet with SSCC 7-9 Hz whereas that for H-24 in the PMR spectra of **23**, **25**, and **26** is observed as a singlet [40-42]. Therefore, the stereoisomers of **39** and **41** were not investigated further. Analogous arguments for H-23 exclude **40** also since the SSCC and the multiplicity of H-23 in PMR spectra of **23**, **25**, and **26** agree with those calculated for **38**.

It should be noted that the PMR spectrum of dihydrocycloorbigenin A (**24**) (400 MHz, C_5D_5N, TMS, δ, ppm, J/Hz) has SSCC 1 Hz with the signal for H-24 at 3.72 as a doublet (J = 1); for H-23, at 4.79 as a doublet of doublets of doublets (ddd, J = 9, 1.5, 1). Signals for H-24 and H-23 in PMR spectra are usually observed as a singlet and doublet of doublets (J = 9, 2 Hz or a doublet with broad components). This can be used as a diagnostic feature of this structural type [40-42]. This is consistent with the ^{13}C NMR spectrum, which has the signal for the C-16 ketal at δ 114.60-115.27 [43].

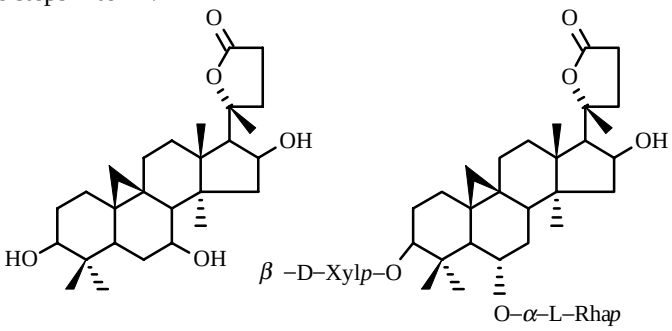
Mass spectral fragmentation of compounds of this type gives typically an ion of type **42** with *m*/*z* 429 [40]. This and corresponding ions in mass spectra of **23**, **24**, and **26** are the base peaks. Ion **43** with *m*/*z* 429 is also formed upon fragmentation of cycloalpigenin (**27**) owing to cleavage of the C-24–C-25 bond [32]. However, in this instance the peak is not the base peak.



42, *m/z* 429 **43,** *m/z* 429

The method for proving the configuration of chiral atoms C-20 and C-24 of **27**, the basis of new structural type 4, deserves attention [32]. An examination of molecular models indicates that the heterocycles can be fused as the 20*R*,24*R*- and 20*S*,24*S*-configurations. Therefore, establishing the stereochemistry of one of these asymmetric centers defines the configuration of the other chiral atom.

Cycloalpigenin was converted by acid hydrolysis with subsequent periodate oxidation into lactone **44** in order to determine the configuration of C-20. The analogous lactone **45** was prepared from the known glycoside cyclocarposide, which has the 20*R*-configuration. C-20 in ^{13}C NMR spectra of **44** and **45** resonates at δ 90.43 and 90.23, respectively. The good agreement of these values indicates that the configuration of C-20 is identical in **44** and **45**. This means that **27** has 20*R*,24*R*-stereochemistry. This conclusion is confirmed by chemical correlation of the structures of cycloalpigenin and cycloalpigenin D (**21**) by converting it in three steps into **44**.



44 **45**

The developed method and chemical correlation of the structures of **27** and **21** are good reasons for using ^{13}C NMR spectroscopy to resolve issues of the stereochemistry of C-20 and C-24 in 16*β*,24;20,24-diepoxycycloartanes without involving chemical conversions. Therefore, chemical shifts of asymmetric C-20 and C-24 of δ 84.87 and 110.60 can indicate the *R*-configuration for these side-chain atoms.

20,25-Epoxycycloartane genins are represented only by cyclocephalogenin (**28**), the structure of which was established in cyclocepholoside I [37].

Finally, the last structural type, 24-nor-16*β*,23-epoxycycloartane, is rare and includes dasyanthogenin (**29**) [5] and the genin of tomentoside I (**30**) [44]. The latter was not prepared in the free state but was determined as the glycoside. Compounds of this structural type are hemiacetals. Therefore, native genins cannot be prepared by methods such as acid catalysis. Under acid catalysis conditions, hemiacetals are readily alkylated to form acetals. Conditions favorable for forming acetals arise often during isolation and separation of plant substances. During isolation of acetals of type **29** and **30** genins, the question of the authenticity of the isolated substance must be resolved.

Early structural investigations of natural compounds were performed using several chemical and instrumental methods. The rapid development of the latter, especially NMR spectroscopy in one and two directions, reduced the use of organic chemical methods to a minimum for studying low-molecular-weight natural compounds and in most instances even replaced them. Nevertheless, the chemical correlation of the structures, as determined from the presented data, is still significant and in certain instances can play a decisive role with no alternatives.

TABLE 2. Cycloartane Methylsteroids of *Astragalus* Plants Found by [8]

Compound, molecular formula	mp, °C; $[\alpha]_D$, deg (solvent)	*Astragalus* species	Reference
3. Mogholicoside I genin, $C_{30}H_{50}O_4$		*A. mongholicus* Bunge	47
4. Mogholicoside II genin, $C_{30}H_{50}O_5$		*A. mongholicus* Bunge	47
5. Huangqiyenin II, $C_{30}H_{50}O_5$	+112.5 (chloroform)	*A. membranaceus* Bunge	35
11. Cycloorbigenin C, $C_{30}H_{50}O_6$	256-258	*A. orbiculatus* Ledeb.	48, 125
12. Cycloadsurgenin, $C_{30}H_{46}O_5$	249-251; -47.06 (chloroform)	*A. adsurgens* Pall.	36
13. Cycloalpigenin A, $C_{30}H_{48}O_5$	223-226; -43.2 (methanol)	*A. alopecurus* Pall.	29
14. Cyclopicnanthogenin, $C_{30}H_{48}O_5$	233-235	*A. pycnanthus* Boriss.	34
15. Huangqiyenin I, $C_{30}H_{48}O_5$	+74.4 (chloroform)	*A. membranaceus* Bunge	35
19. Cycloalpigenin B, $C_{30}H_{50}O_5$	210-211; +18.7 (methanol)	*A. alopecurus* Pall.	18
20. Cycloalpigenin C, $C_{30}H_{50}O_5$	242-244; -34.5 (methanol)	*A. alopecurus* Pall.	19
21. Cycloalpigenin D, $C_{30}H_{50}O_5$	209-211; +46.7 (methanol)	*A. alopecurus* Pall.	33
23. Cycloorbigenin A, $C_{30}H_{46}O_4$	207-209; -101.3 (methanol)	*A. orbiculatus* Ledeb.	42
24. Dihydrocycloorbigenin A, $C_{30}H_{48}O_4$	237-238	*A. orbiculatus* Ledeb.	43
26. Cycloorbigenin B, $C_{30}H_{48}O_6$	201-203; +20.7 (methanol)	*A. orbiculatus* Ledeb.	41
27. Cycloalpigenin, $C_{30}H_{48}O_5$	224-226; 0 (methanol)	*A. alopecurus* Pall.	32

It seems likely that total and partial syntheses of natural compounds will still be significant and attractive in the future because they are important methods for confirming structures and inventing accessible pathways for preparing them. Thus, partial syntheses of 3-dehydrocycloasgenin C (**6**) and cyclopycnanthogenin (**14**) are notable. The synthesis of **6** in six steps from cycloasgenin C (**8**) confirmed the structure of the former [45]. Cyclopycnanthogenin (**14**) was also synthesized from cyclosiversigenin (**18**) in four steps [46].

Table 2 lists genins (15 compounds) appearing in the literature after the prior review [8], their physicochemical constants, and the plants from which they were isolated for the first time.

The physicochemical constants and certain chemical and spectral properties of 10 genins [3-dehydrocycloasgenin C (**6**), cycloasgenin B (**7**), cycloasgenin C (**8**), cyclocanthogenin (**9**), cycloasgenin A (**16**), quisvagenin (**17**), cyclosiversigenin (**18**), cyclogalegigenin (**22**), cyclorbigenin (**25**), and dasyanthogenin (**29**)] have been reviewed in [8].

Owing to the advance of NMR spectroscopy to primary significance not only for the proof of structures of new compounds but also for the identification of known compounds, we present ^{13}C NMR spectral data of known cycloartane triterpenoid genins of *Astragalus* plants (Tables 3a-c).

Triterpenoids **3** and **4** typically have a double bond at C-24. Genins **3** and **4** in experiments for measuring the differential nuclear Overhauser effect (NOE) show effects between H-24 and protons geminal to the primary hydroxyl, thereby determining its position on C-27. Consequently, the double bond in these compounds has the 24*E*-configuration [47].

Huangqiyenins I (**15**) and II (**5**) can be viewed as 6-keto derivatives of **18** and **9**, respectively [35]. The structures of these genins were proved using spectral data. A significant high-field shift of the signals for C-18 and C-19 in the ^{13}C NMR spectrum of **15** compared with those of cyclosiversigenin is characteristic of this spectrum. These signals in the spectrum of **15** are obsserved at δ 18.7 and 22.9; in the spectrum of **18**, at δ 21.66 and 31.02. Obviously, this is a consequence of the effect of the 6-ketone. It seems that an analogous effect should be observed in the ^{13}C NMR spectrum of **5**. In fact, C-19 in the spectrum of **5** resonates at δ 21.9; C-18 and C-21, at δ 18.5 and 15.7. Let us remember that the signals for C-18 and C-21 in the ^{13}C NMR spectrum of **9** are found at δ 18.24 and 18.94, respectively. We see that the signal for C-21 underwent a high-field shift and not that of C-18, as would be expected. This is improbable. Apparently the signals for C-18 and C-21 should be exchanged in the spectrum of **5** by exchanging the chemical shifts.

A high-field shift of the signal for C-19 to δ 20.94 was observed in the ^{13}C NMR spectrum of **23**, which contains a Δ^6-double bond. Furthermore, one of the H atoms of the cyclopropane methylene also is shielded by the anisotropy of the Δ^6-double bond and resonates in the PMR of **23** at δ -0.14 [42].

TABLE 3a. Chemical Shifts of C Atoms in Cycloartane Genins of *Astragalus* Plants (δ, ppm, C_5D_5N, 0 = TMS)

C atom	Compound							
	3	**4a**	**5** [35]	**6** [34]	**7***	**8** [17]	**9** [54]	**11** [125]
1	73.6	72.5	30.7	31.91	29.66	32.81	32.78	32.85
2	36.8	33.9	30.4	35.88	36.38	31.45	31.34	31.49
3	73.8	76.5	77.6	216.77	216.90	78.37	78.34	78.41
4	40.5	39.3	41.4	50.57	50.70	42.44	42.33	42.51
5	39.6	39.4	57.9	53.63	54.69	54.01	53.96	54.01
6	20.7	20.28	211.8	69.21	68.72	68.31	68.29	68.29
7	24.7	25.0*	41.6	38.30	38.77	38.62	38.45	38.62
8	48.0	46.4	43.0	48.29	48.21	47.24	47.17	47.19
9	20.7	20.4	21.8	21.50	28.34	21.31	21.35	21.30
10	30.5	29.3	30.4	28.28	28.72	30.37	30.37	29.64
11	25.85	39.1	26.7	26.23	64.05	26.40	26.43	26.36
12	32.8	72.47	33.2	33.03	48.02	33.23	33.33	33.05
13	45.4	50.5	45.8	45.67	46.28	45.74	45.76	46.18
14	46.8	47.7	47.8	46.83	46.97	46.98	46.85	46.90
15	48.2	48.2	45.9	49.18	48.86	48.81	48.41	47.78
16	72.7	72.3	71.5	71.67	71.65	71.78	72.02	72.20
17	56.5	57.2	56.6	57.35	57.35	57.27	57.39	57.51
18	19.1	12.3	18.5	18.72	18.63	18.81	18.24	18.94
19	30.2	29.0	21.9	30.73	29.29[a]	29.36	29.70	30.11
20	29.6	29.4	28.8	31.56	31.54	31.64	28.78	27.41
21	17.9	18.7	15.7	19.70	19.51	19.09	18.97	20.36
22	36.3	36.5	32.9	29.35	29.29[a]	29.62	33.07	42.97
23	25.9	25.2*	28.0	34.79	34.72	34.84	27.99	73.17
24	126.4	126.1	77.2	80.55	80.52	80.59	77.22	79.19
25	135.4	135.1	72.6	72.68	72.64	72.69	72.49	74.37
26	13.7	13.5	25.7	25.94	25.94	25.90	25.43	24.70
27	68.8	68.5	26.5	26.16	26.11	26.20	26.46	28.98
28	20.2	20.3	19.1	20.43	21.56	20.30	20.18	20.25
29	25.2	25.1	27.5	28.60	28.54	29.37	29.17	29.41
30	13.1	14.1	14.9	20.55	20.62	16.13	15.98	16.20
$C\underline{H}_3COO$		21.0						
CH_3COO		170.6						

These features of the ^{13}C NMR and PMR spectra are caused by the location of the double bond and have analytical significance. The presence of a ketone or hydroxyl on C-12 of compounds of structural type 2 is characteristically reflected in the chemical shift of C-17 in the ^{13}C NMR spectra. This can be a diagnostic feature. Thus, C-17 in the ^{13}C NMR spectrum of **14**-**18**, **21**, and **22**, which are not oxygenated on C-12, resonates at δ 56.49-58.55 (Table 3) [29, 34, 35] whereas the signal for C-17 in the ^{13}C NMR spectrum of **19**, which contains a 12α-hydroxyl, is shifted to high field and is observed at δ 52.29 [18]. The effect of a 12-ketone on the chemical shift of C-17 is even stronger. In the ^{13}C NMR spectrum of **13**, C-17 resonates at δ 49.85. On the other hand, the presence of a 12β-hydroxyl shifts the signal for C-17 to weak field to δ 60.17 in the ^{13}C NMR spectrum of **20** [19].

TABLE 3b. Chemical Shifts of C Atoms in Cycloartane Genins of *Astragalus* Plants (δ, ppm, C_5D_5N, 0 = TMS)

C atom	Compound							
	12 [36]	**13** [29]	**14** [34]	**15** [35]	**16***	**17** [29]	**18** [34]	**19** [18]
1	35.4	32.84	31.85	30.8	30.00	32.42	32.81	32.60
2	32.4	31.00[a]	35.86	30.3	36.41	31.33	31.47	31.28
3	217.0	77.59	216.82	77.7	217.08	77.99	78.32	77.93
4	50.1	40.95	50.56	41.1	50.69	41.13	42.47	41.10
5	54.2	47.05	53.55	58.1	54.66	47.56	54.00	47.74
6	69.1	20.71	69.17	211.5	68.70	20.33[a]	68.38	21.58
7	37.6	26.54	38.39	41.7	38.86	26.60	38.85	25.98
8	47.0	47.62	48.19	43.5	48.19	48.20	47.30	48.96
9	20.0	19.99	21.21	21.7	28.29	21.33	20.99	19.93
10	28.6	28.14	28.49	31.0	28.96	29.98	29.92	26.95
11	26.4	45.91	26.07	26.7	63.76	26.47[b]	26.32	38.80
12	32.5	211.25	33.20	33.4	48.35	33.53	33.47	72.76
13	44.4	60.95	45.00	45.6	45.65	45.13	45.09	49.90
14	44.1	47.54	46.06	47.3	46.20	47.08[c]	46.21	50.84
15	51.5	46.02	47.04	44.6	46.82	47.08[c]	46.81	46.49
16	218.4	73.01	73.41	73.0	73.43	73.48	73.48	72.83
17	65.2	49.85	58.50	57.9	58.53	58.55	58.44	52.29
18	20.4	14.98	22.14	18.7	21.87	21.92	21.66	21.95
19	31.3	31.00[a]	31.08	22.9	29.61	30.61	31.02	30.35
20	84.4	87.22	87.22	87.2	87.11	87.28	87.27	87.51
21	26.9	28.74	28.57	28.6	28.53[a]	28.57	28.59	26.18
22	31.6	36.02	34.93	35.2	34.98	35.00	34.97	38.40
23	26.5	25.92	26.45	26.5	26.38	26.47[b]	26.47	26.92
24	81.9	82.32	81.73	81.9	81.81	81.79	81.75	83.54
25	71.1	70.67	71.27	71.4	71.20	71.24	71.27	70.76
26	28.0	27.26	27.18	27.1	27.13	27.18	27.17	26.59
27	27.9	28.22	28.22	28.1	28.15	28.22	28.21	27.45
28	26.2	20.78	20.43	19.2	21.54	20.33[a]	20.27	21.20
29	29.6	26.12	28.65	27.3	28.53[a]	26.20	29.44	27.40
30	17.9	14.79	20.45	14.7	20.68	14.60	16.14	14.89

Table 3c. Chemical Shifts of C Atoms in Cycloartane Genins of *Astragalus* Plants (δ, ppm,C_5D_5N, 0 = TMS)

C atom	Compound							
	20 [19]	**21***	**22** [29]	**23** [43]	**24** [43]	**25** [43]	**26** [43]	**27** [32]
1	32.14	32.20	32.78	30.90	32.41	32.34	32.72	32.13
2	31.02	31.14	31.43	30.05	31.31	31.22	31.68	31.13
3	77.84	77.74	78.30	77.33	77.93	77.94	78.05	77.68
4	40.95	40.82	42.43	40.85	41.15	40.93	42.46	40.82
5	46.87	46.34	53.99	43.46	47.44	46.57	51.67	46.31
6	20.92	32.12	68.35	128.87	21.30	32.18	72.88	32.01
7	25.68	70.42	38.73	127.52	26.75	70.35	75.00	70.07
8	45.34	55.34	47.20	47.15	47.79	55.46	53.58	54.78
9	20.64	19.96	21.01	18.80	19.51	19.78	19.53	19.48

Table 3c. (Continued)

C atom	Compound							
	20 [19]	**21***	**22** [29]	**23** [43]	**24** [43]	**25** [43]	**26** [43]	**27** [32]
10	27.36	27.36	29.79	28.75	27.01	27.64	29.03	27.66
11	37.24	26.48	26.48	25.35	26.66	26.96	26.61	26.91
12	72.10	33.40	33.76	33.77	33.11	33.24	32.97	33.12
13	48.68	45.55	46.50	44.44	44.59	44.34	44.19	45.75[a]
14	52.01	46.35	46.80	46.41	46.32	46.97	46.75	45.75[a]
15	48.25	48.86	49.02	46.77	46.62	48.93	48.84	45.16
16	72.27	73.86	72.84	114.60	114.87	115.27	115.15	74.38
17	60.17	57.95	56.49	60.02	61.20	60.70	60.59	61.33
18	13.65	21.41	21.23	17.33	19.33	19.01	18.72	22.23
19	29.56	29.33	30.88	20.94	30.75	30.00	31.37	30.14
20	87.32	87.30	86.62	23.73	23.95	23.89	23.61	84.87
21	25.96	28.69	26.32	20.32	19.83	20.17	19.97	30.56
22	38.98	35.02	37.53	38.16	38.25	38.52	38.34	31.84
23	26.10	26.75	24.30	71.96	71.83	71.87	71.73	33.58
24	84.56	81.67	84.90	90.44	90.60	90.57	90.52	110.60
25	71.05	71.31	70.28	70.98	71.01	71.16	71.01	72.83
26	26.20	27.11	26.87	27.84	27.91	27.80	27.95	25.59
27	26.26	28.24	28.10	24.73	24.77	24.83	24.64	25.25
28	19.98	19.90	20.49	16.08	19.41	19.10	19.28	19.64
29	27.43	26.21	29.41	26.19	26.22	26.25	29.15	26.18
30	14.66	14.79	16.11	15.23	14.90	14.80	16.00	14.75

*Spectra of genins that are published for the first time. **4a** is the 3-monoacetate of **4**. The spectrum of **12** was recorded in $CDCl_3$. Signals denoted by the same letters can be mutually interchanged within columns, *signals assigned arbitrarily.

These features of the ^{13}C NMR and PMR spectra are caused by the location of the double bond and have analytical significance. The presence of a ketone or hydroxyl on C-12 of compounds of structural type 2 is characteristically reflected in the chemical shift of C-17 in the ^{13}C NMR spectra. This can be a diagnostic feature. Thus, C-17 in the ^{13}C NMR spectrum of **14**-**18**, **21**, and **22**, which are not oxygenated on C-12, resonates at δ 56.49-58.55 (Table 3) [29, 34, 35] whereas the signal for C-17 in the ^{13}C NMR spectrum of **19**, which contains a 12α-hydroxyl, is shifted to high field and is observed at δ 52.29 [18]. The effect of a 12-ketone on the chemical shift of C-17 is even stronger. In the ^{13}C NMR spectrum of **13**, C-17 resonates at δ 49.85. On the other hand, the presence of a 12β-hydroxyl shifts the signal for C-17 to weak field to δ 60.17 in the ^{13}C NMR spectrum of **20** [19].

CYCLOARTANE GLYCOSIDES

The chemistry of glycosides has undergone radical changes during the last decade and a half. As a result, all progress in methodology achieved in the past has been stripped of practical use, retaining only historical value owing to the total incorporation of modern methods of 1D and 2D NMR spectroscopy (PMR, ^{13}C NMR, J-modulation, DEPT, ^{1}H-^{1}H COSY, HSQC, HMBC, TOCSY, ROESY). These methods enable fundamental questions of glycoside structure determination to be resolved, with the exception of special questions of stereochemistry, without using chemical procedures. Various types of mass spectrometry (EIMS, FDMS, FABMS, HRESIFTMS) and IR spectroscopy supplement information obtained by NMR spectroscopy.

The principal drawback of all modern work on establishing glycoside structures is the assignment a priori of an absolute configuration to monosaccharide units, i.e., the assignment of monosaccharides to D- or L-series is unfounded. The enantiomers of monosaccharides occurring in triterpene glycosides are not found in plants. This is the only problem of this approach. Its resolution usually involves laborious chemical procedures for preparing pure monosaccharides in order to measure the specific rotation. In addition to being labor-intensive, it consumes a large quantity of glycoside.

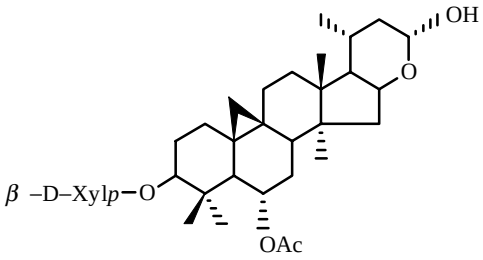
A chromatographic method for determining the absolute configuration of certain monosaccharides has been developed [49].

The displacement of labor- and resource-intensive chemical methods from structural analysis of glycosides by physical research methods not only offset in some instances the observed tendencies toward less research but also ensured a certain growth of newly discovered substances. This is clearly seen by studying the *Astragalus* genus. During the first decade of research on the triterpenoid content of these plants, about 40 cycloartane glycosides were discovered. A review published in 1989 [8] includes 35 glycosides isolated from *Astragalus* plants. The number reached 122 in subsequent years.

Table 4 lists new cycloartane glycosides isolated from *Astragalus* plants since the appearance of the previous review [8]. The glycoside composition of these plants is more varied, as witnessed by their number.

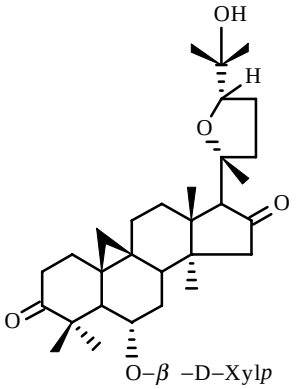
As a rule, the carbohydrate parts of the glycosides consist of D-glucose, D-xylose, L-arabinose, and L-rhamnose. The branched monosccharide D-apiose is rather rare and found in two glycosides. These are cycloaralosides C (**83**) [73] and F (**121**) [95], which were isolated from *A. amarus* Pall. and *A. villosissimus* Bunge. Cycloaraloside C was also isolated from *A. iliensis* by Chinese researchers and named astrailienine A [74].

TABLE 4. Cycloartane Glycosides of *Astragalus* Plants



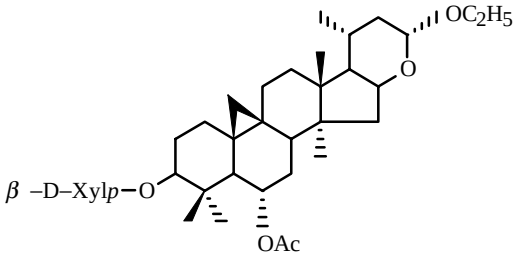
46. Tomentoside II

Astragalus tomentosus
Lam. [50]
$C_{33}H_{52}O_9$, mp 217°C (methanol)



47. Cycloadsurgenin 6-O-β-D-xylopyranoside

Astragalus adsurgens Pall. [51]
$C_{35}H_{54}O_9$, mp 238-239°C



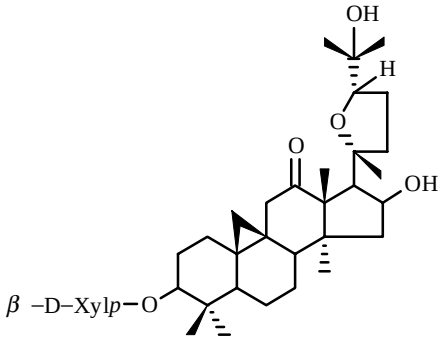
48. Tomentoside I

Astragalus tomentosus Lam. [44]

$C_{35}H_{56}O_9$, mp 247-250°C, $[\alpha]_D$ -18.7° (methanol)

δ_C (C_5D_5N)

C-1	31.9	C-11	26.0	C-21	20.6	β-D-Xyl*p*-1	107.0
2	29.9	12	33.0	22	33.2	2	75.5
3	87.5	13	44.8	23	99.0	3	78.6
4	42.2	14	46.0	28	19.3	4	71.2
5	56.5	15	43.3	29	26.8	5	67.2
6	70.2	16	70.4	30	16.4		
7	38.1	17	44.5	Ac	21.7		
8	49.9	18	19.8	Ac	170.3		
9	20.9	19	27.8	Et	15.4		
10	28.2	20	25.6	Et	62.7		



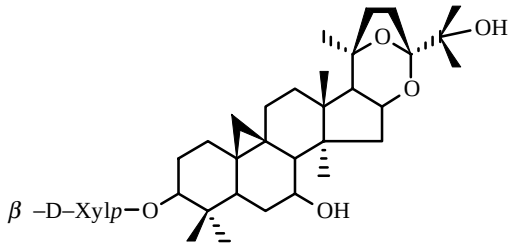
49. Cycloalpioside A

Astragalus alopecurus Pall. [29]

$C_{35}H_{56}O_9$, mp 287-288°C (methanol), $[\alpha]_D^{27}$ -15.1° (*c* 0.53, pyridine)

δ_C (C_5D_5N)

C-1	32.61	C-11	45.79	C-21	25.70	β-D-Xyl*p*-1	107.50
2	30.49	12	211.22	22	36.00	2	75.55
3	88.03	13	60.93	23	26.43[a]	3	78.58
4	41.20	14	47.18	24	82.30	4	71.23
5	47.49	15	45.96	25	70.68	5	67.10
6	20.75	16	73.01	26	27.26[b]		
7	25.70	17	49.82	27	27.84		
8	47.60	18	14.96	28	20.45		
9	20.02	19	30.86	29	27.26		
10	26.43[a]	20	87.21	30	15.38		



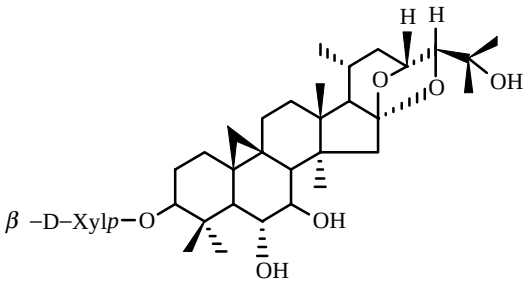
50. Cycloalpioside

Astragalus alopecurus Pall. [32]

$C_{35}H_{56}O_9$, mp 277-278°C (methanol), $[\alpha]_D^{26}$ -25.1° (*c* 0.71, pyridine)

δ_C (C_5D_5N)

C-1	31.83[a]	C-11	26.85	C-21	30.57	β-D-Xyl*p*-1	107.56
2	29.92	12	33.10	22	31.67	2	75.52
3	88.13	13	45.11	23	33.54	3	78.59
4	41.03	14	45.59	24	110.58	4	71.20
5	46.40	15	45.74	25	72.80	5	67.12
6	31.83[a]	16	74.33	26	25.59		
7	69.95	17	61.29	27	25.23		
8	54.63	18	22.14	28	19.60		
9	19.52	19	29.93	29	25.70		
10	27.35	20	84.86	30	15.32		



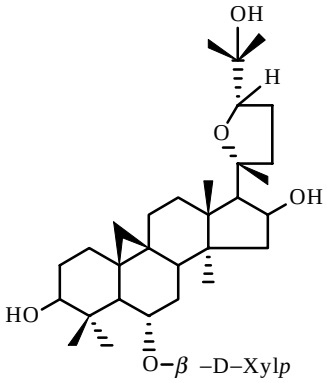
51. Cycloorbicoside B

Astragalus orbiculatus Ledeb. [43, 52]

$C_{35}H_{56}O_{10}$, mp 242-244°C (methanol), $[\alpha]_D^{24}$ +20.6° (*c* 0.87, methanol)

δ_C (C_5D_5N)

C-1	32.42	C-11	26.53	C-21	19.95	*β*-D-Xyl*p*-1	107.72
2	28.75	12	32.94	22	38.31	2	75.65
3	88.51	13	44.18	23	71.73	3	78.56
4	42.70	14	46.72	24	90.50	4	71.22
5	51.79	15	48.74	25	71.00	5	67.08
6	72.64	16	115.12	26	27.93		
7	74.94	17	60.57	27	24.63		
8	53.50	18	18.64	28	19.17		
9	19.64	19	31.54	29	28.66		
10	30.30	20	23.78	30	16.52		



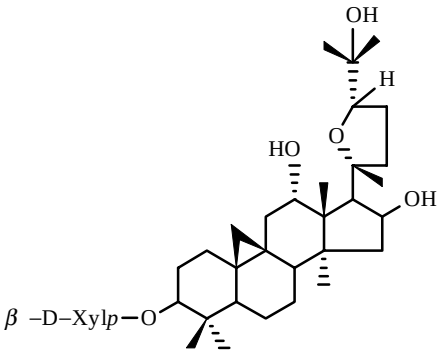
52. Trigonoside I

Astragalus trigonus [53]

$C_{35}H_{58}O_9$, mp 226°C (ethylether), $[\alpha]_D^{25}$ +25° (*c* 0.58, methanol)

δ_C (C_5D_5N)

C-1	32.55	C-11	26.53	C-21	28.86	*β*-D-Xyl*p*-1	105.82
2	31.23	12	33.67	22	36.16	2	75.45
3	78.35	13	45.40	23	26.68	3	78.55
4	42.59	14	46.07	24	81.94	4	71.19
5	52.38	15	46.44	25	71.58	5	67.12
6	78.80	16	73.67	26	28.31		
7	34.33	17	58.40	27	27.26		
8	45.17	18	21.05	28	28.99		
9	21.33	19	28.10	29	16.47		
10	29.23	20	87.62	30	20.02		



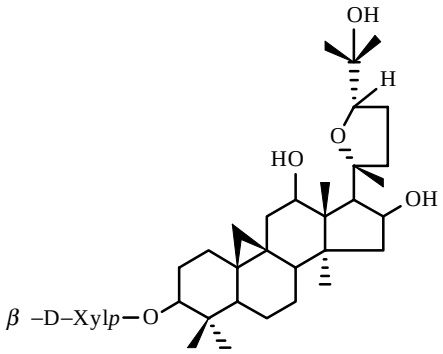
53. Cycloalpioside B

Astragalus alopecurus Pall. [18]

$C_{35}H_{58}O_9$, mp 253-254°C (methanol), $[\alpha]_D^{23}$ -26.3° (*c* 0.53, methanol)

δ_C (C_5D_5N)

C-1	32.36	C-10	26.81	C-19	30.12[a]	C-28	21.19
2	30.12[a]	11	38.76	20	87.53	29	27.47[c]
3	88.47	12	72.77	21	25.75	30	15.50
4	41.35	13	49.85	22	38.38	*β*-D-Xyl*p*-1	107.55
5	47.65	14	50.76	23	26.29	2	75.54
6	21.30	15	46.44	24	83.48	3	78.57
7	26.03	16	72.77[b]	25	70.78	4	71.22
8	48.90	17	52.20	26	27.03	5	67.09
9	19.94	18	21.97	27	27.47[c]		



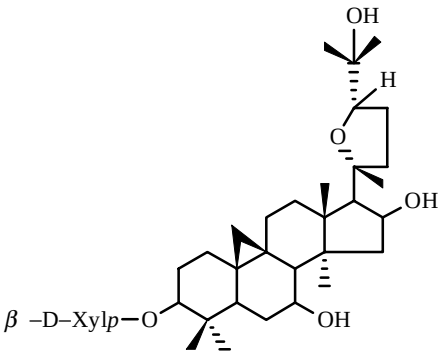
54. Cycloalpioside C

Astragalus alopecurus Pall. [19]

$C_{35}H_{58}O_9$, mp 223-225°C (methanol), $[\alpha]_D^{26}$ +25.7° (*c* 0.71, pyridine)

δ_C (C_5D_5N)

C-1	31.81	C-11	37.05	C-21	25.90	β-D-Xyl*p*-1	107.36
2	29.76	12	72.01	22	38.93	2	75.41
3	88.22	13	48.53	23	26.06	3	78.43
4	41.12	14	51.93	24	84.53	4	71.14
5	46.90	15	48.16	25	71.05	5	66.96
6	20.90	16	72.22	26	25.68		
7	25.41	17	60.11	27	26.15		
8	45.04	18	13.56	28	19.87		
9	20.23	19	29.16	29	27.37		
10	26.96	20	87.27	30	15.19		



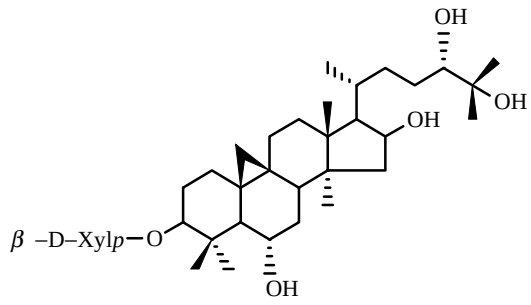
55. Cycloalpioside D

Astragalus alopecurus Pall. [33]

$C_{35}H_{58}O_9$, mp 300-301°C (methanol), $[\alpha]_D^{26}$ -18.3° (*c* 0.87, pyridine)

δ_C (C_5D_5N)

C-1	31.74[a]	C-11	26.67[e]	C-21	28.61	β-D-Xyl*p*-1	107.49
2	29.88	12	33.31	22	34.96	2	75.44
3	88.22	13	45.49	23	26.67[e]	3	78.51
4	40.93	14	46.31[b]	24	81.64	4	71.19[f]
5	46.31[b]	15	48.70	25	71.19[f]	5	67.0
6	31.74[a]	16	73.73	26	27.04[d]		
7	70.21	17	57.96	27	28.16		
8	55.05	18	21.21	28	19.94[c]		
9	19.94[c]	19	28.83	29	25.70		
10	27.04[d]	20	87.25	30	15.23		



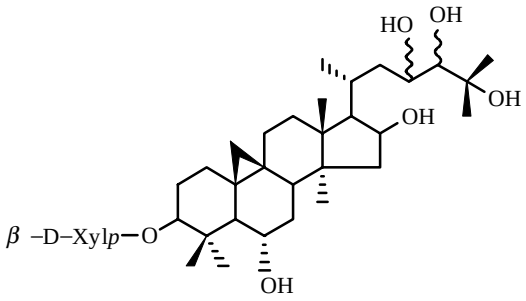
56. Cyclocanthoside A

Astragalus tragacantha Habl. [54]

$C_{35}H_{60}O_9$, mp 154-155°C (ethylacetate), $[\alpha]_D^{24}$ +27° (*c* 0.8, methanol)

δ_C (C_5D_5N)

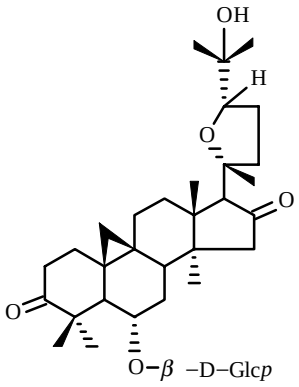
C-1	32.52	C-11	26.28	C-21	18.91	β-D-Xyl*p*-1	107.59
2	28.65	12	33.19	22	33.03	2	75.61
3	88.74	13	45.73	23	27.91	3	78.49
4	42.71	14	46.81	24	77.19	4	71.26
5	54.11	15	46.99	25	72.54	5	67.04
6	67.93	16	72.01	26	25.71		
7	38.42	17	57.35	27	26.47		
8	48.36	18	18.28	28	20.14		
9	21.36	19	29.53	29	29.25		
10	30.35	20	28.86	30	16.15		



57. Cycloorbicoside D

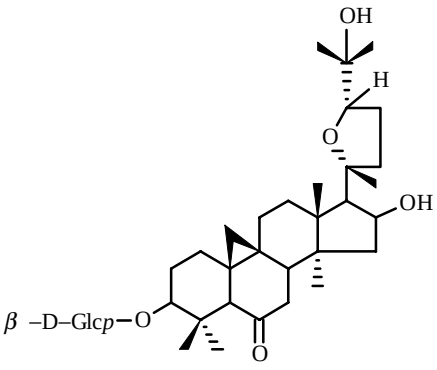
Astragalus orbiculatus Ledeb. [48]
$C_{35}H_{60}O_{10}$, mp 285-287°C (methanol)
δ_C (C_5D_5N), published for the first time

C-1	32.48	C-11	26.28	C-21	20.17	*β*-D-Xyl*p*-1	107.06
2	30.01	12	33.07	22	42.82	2	75.16
3	88.61	13	45.67	23	72.90	3	77.95
4	42.56	14	46.79	24	79.21	4	71.02
5	54.01	15	47.61	25	74.04	5	66.61
6	67.88	16	72.08	26	24.73		
7	38.24	17	57.42	27	28.60		
8	46.90	18	18.68	28	20.12		
9	21.41	19	30.10	29	28.75		
10	29.37	20	27.37	30	16.59		



58. Cycloadsurgenin 6-O-*β*-D-glucopyranoside

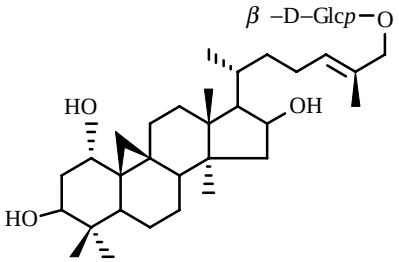
Astragalus adsurgens Pall. [51]
$C_{36}H_{56}O_{10}$, mp 260-261°C



59. Huangqiyenin A

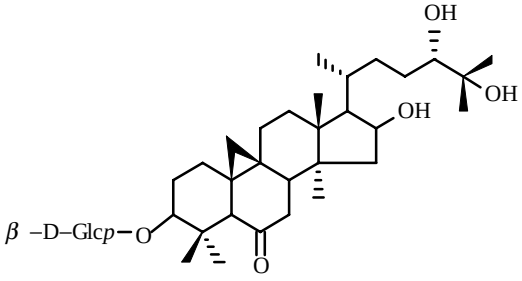
Astragalus membranaceus Bunge [35]
$C_{36}H_{58}O_{10}$, mp 265-268°C (methanol), $[\alpha]_D$ +32.1° (*c* 0.56, methanol)
δ_C (C_5D_5N)

C-1	29.0	C-11	26.4	C-21	28.6	*β*-D-Glc*p*-1	106.8
2	30.3	12	33.2	22	35.0	2	75.8
3	87.8	13	45.3	23	26.8	3	78.7
4	41.4	14	47.2	24	81.7	4	71.8
5	57.8	15	44.2	25	71.3	5	78.3
6	211.2	16	72.9	26	27.1	6	63.1
7	41.5	17	57.7	27	28.1		
8	42.8	18	18.5	28	19.1		
9	21.5	19	22.1	29	26.8		
10	30.2	20	87.1	30	15.3		



60. Mongholicoside I

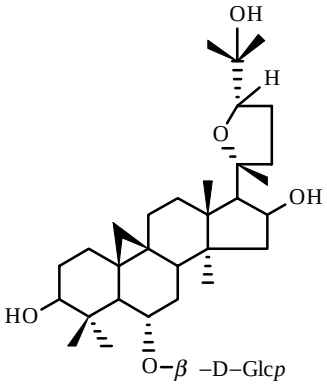
Astragalus mongholicus Bunge [47]
$C_{36}H_{60}O_9$, mp 143-145°C, $[\alpha]_D$ +47.9°



61. Huangqiyenin B

Astragalus membranaceus Bunge [35]
$C_{36}H_{60}O_{10}$, mp 272-274°C (methanol), $[\alpha]_D$ +54.4° (*c* 0.60, pyridine)
δ_C (C_5D_5N)

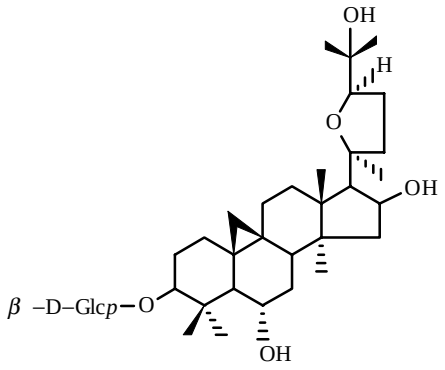
C-1	29.1	C-11	26.7	C-21	18.4	*β*-D-Glc*p*-1	106.9
2	30.4	12	33.2	22	32.9	2	75.8
3	87.9	13	45.9	23	28.0	3	78.7
4	41.3	14	47.8	24	77.3	4	71.8
5	57.9	15	46.0	25	72.5	5	78.3
6	211.4	16	71.4	26	25.7	6	63.1
7	41.6	17	56.6	27	26.4		
8	42.7	18	15.7	28	19.1		
9	21.8	19	22.7	29	27.0		
10	30.1	20	28.8	30	15.4		



62. Brachyoside B

Astragalus spinosus Vahl. [55], *Astragalus brachypterus* Fischer [56]
$C_{36}H_{60}O_{10}$, mp 259°C (methanol)
δ_C (C_5D_5N)

C-1	32.0	C-11	25.7	C-21	26.5	*β*-D-Glc*p*-1	104.6
2	28.9	12	32.8	22	34.4	2	74.9
3	77.7	13	44.5	23	25.9	3	78.4
4	41.4	14	45.7	24	81.1	4	71.1
5	52.0	15	45.5	25	70.9	5	77.5
6	79.4	16	72.9	26	27.6	6	62.3
7	34.4	17	57.7	27	28.1		
8	45.7	18	20.7	28	19.4		
9	20.8	19	30.5	29	28.6		
10	28.9	20	86.8	30	15.7		



63. Sieberoside I

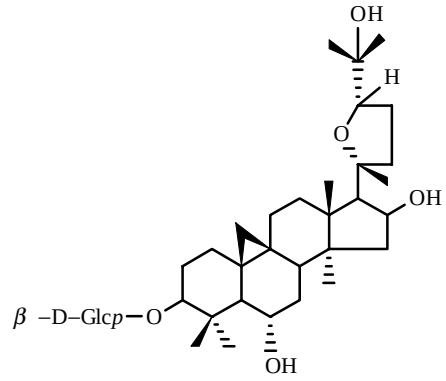
Astragalus sieberi [57]

$C_{36}H_{60}O_{10}$, mp 177°C (methanol), $[\alpha]_D^{25}$ +29.9° (*c* 0.62, pyridine)

δ_C (C_5D_5N)

C-1	32.3	C-11	26.4	C-21	26.1	*β*-D-Glc*p*-1	106.7
2	30.5	12	33.5	22	37.3	2	75.6
3	88.9	13	46.3	23	24.1	3	78.4
4	42.4	14	46.6	24	85.5	4	71.5
5	53.8	15	48.6	25	70.2	5	77.9
6	67.9	16	72.7	26	27.8	6	62.7
7	38.9	17	56.2	27	26.6		
8	46.6	18	21.0	28	20.3		
9	20.8	19	30.0	29	28.8		
10	29.3	20	86.5	30	16.5		

64. Cycloaraloside A



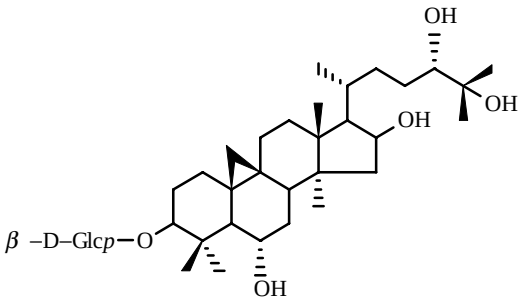
Astragalus amarus Pall. [58, 73]

$C_{36}H_{60}O_{10}$, mp 240-242°C ($CHCl_3$-CH_3OH-H_2O, 140:14:1), $[\alpha]_D^{25}$ +33° (*c* 1.15, methanol)

δ_C (C_5D_5N)

C-1	32.41	C-11	26.37[a]	C-21	28.41	*β*-D-Glc*p*-1	106.82
2	30.16	12	33.31	22	34.88	2	75.82
3	88.96	13	44.97	23	26.37[a]	3	78.66
4	42.58	14	45.91	24	81.64	4	71.78
5	53.93	15	46.09	25	71.26	5	78.06
6	67.97	16	73.43	26	27.04	6	62.87
7	38.54	17	58.26	27	28.53		
8	47.06	18	21.51	28	20.09		
9	20.84	19	30.55	29	28.91		
10	29.50	20	87.17	30	16.66		

65. Alexandroside I



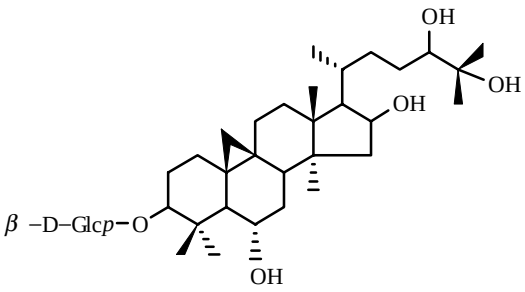
Astragalus alexandrinus Boiss. [59]

$C_{36}H_{62}O_{10}$, mp 288-290°C (EtOH-Et_2O), $[\alpha]_D$ +43.2° (*c* 1.4, methanol)

We measured the stereochemistry of C-24 using ^{13}C NMR spectra.

δ_C (C_5D_5N)

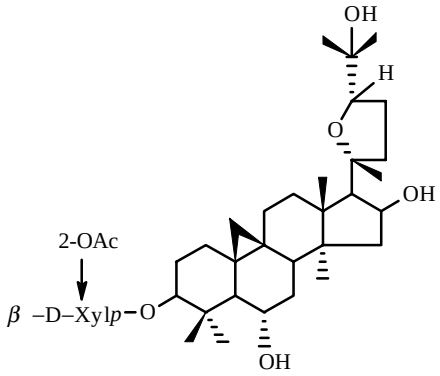
C-1	32.8	C-11	26.6	C-21	18.7	*β*-D-Glc*p*-1	107.1
2	30.6	12	33.5*	22	33.6*	2	76.0
3	89.5	13	46.0	23	28.4	3	78.7*
4	43.0	14	47.1	24	77.9	4	72.3
5	54.2	15	48.6	25	72.3	5	78.3*
6	68.4	16	71.9	26	26.3	6	63.1
7	38.7	17	57.6	27	26.3		
8	47.5	18	19.4	28	20.5		
9	21.5	19	30.5	29	29.3		
10	29.6	20	29.2	30	17.1		



66. Cyclounifolioside C

Astragalus unifoliolatus Bunge [60]
$C_{36}H_{62}O_{10}$, mp 192-195°C (methanol)
δ_C (C_5D_5N)

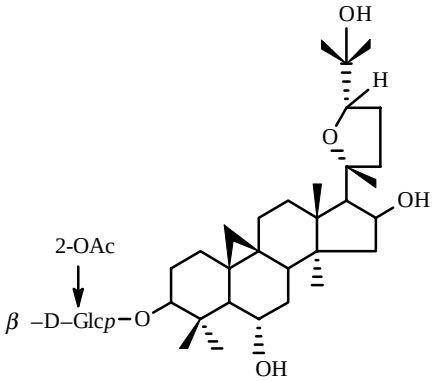
C-1	32.16	C-11	26.06	C-21	18.69	*β*-D-Glc*p*-1	106.66
2	32.91	12	32.91	22	34.58	2	75.66
3	88.81	13	45.45	23	29.70	3	78.48
4	42.36	14	46.64	24	80.29	4	71.61
5	53.83	15	48.43	25	72.46	5	77.89
6	67.70	16	71.47	26	25.62		62.79
7	38.16	17	56.99	27	25.86		
8	46.76	18	18.51	28	19.95		
9	21.02	19	29.14	29	28.66		
10	29.91	20	31.35	30	16.44		



67. Cycloexoside B

Astragalus exilis A. Kor. [97]
$C_{37}H_{60}O_{10}$
δ_C (C_5D_5N)

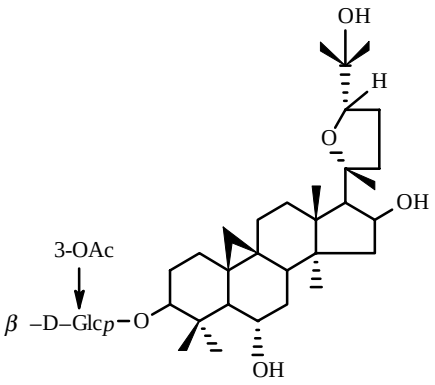
C-1	32.25	C-11	26.10	C-21	28.63	*β*-D-Xyl*p*-1	104.79
2	30.08	12	33.30	22	34.86	2	76.15
3	89.01	13	44.96	23	26.35	3	75.63
4	42.24	14	46.05	24	81.67	4	71.27
5	53.80	15	46.61	25	71.22	5	67.02
6	68.09	16	73.40	26	27.03	Ac	21.21
7	38.66	17	58.32	27	28.08	Ac	170.09
8	47.14	18	21.54	28	20.12		
9	20.95	19	30.70	29	28.47		
10	29.43	20	87.18	30	16.39		



68. Astraverrucin II

Astragalus verrucosus Moris [61]
$C_{38}H_{62}O_{11}$, $[\alpha]_D^{20}$ +2.27° (*c* 1.94, pyridine)
δ_C (C_5D_5N)

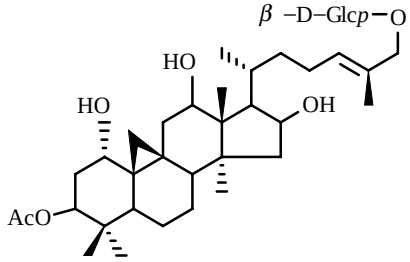
C-1	32.2	C-11	26.2	C-21	27.1	*β*-D-Glc*p*-1	104.0
2	30.0	12	33.4	22	34.9	2	75.8
3	89.3	13	45.0	23	26.5	3	76.3
4	42.6	14	46.1	24	81.7	4	71.8
5	54.0	15	46.7	25	71.3	5	78.4
6	67.9	16	73.5	26	28.2	6	62.6
7	38.7	17	58.4	27	28.6	Ac	21.5
8	47.1	18	21.5	28	28.8	Ac	170.1
9	21.0	19	30.6	29	16.5		
10	29.4	20	87.3	30	20.2		



69. Astraverrucin III

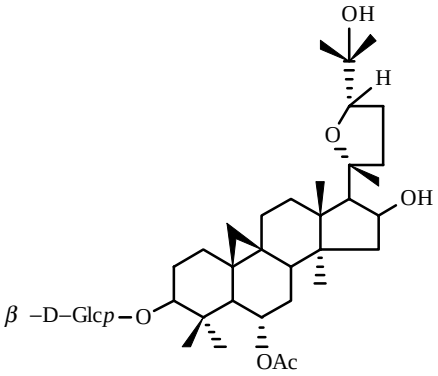
Astragalus verrucosus Moris [61]
$C_{38}H_{62}O_{11}$, $[\alpha]_D^{20}$ +1.10° (*c* 0.92, pyridine)
δ_C (C_5D_5N)

C-1	32.3	C-11	26.2	C-21	27.1	*β*-D-Glc*p*-1	106.7
2	30.1	12	33.3	22	34.9	2	73.4
3	89.3	13	45.0	23	26.4	3	79.7
4	42.6	14	46.1	24	81.6	4	69.4
5	54.0	15	46.6	25	71.3	5	78.1
6	67.9	16	73.7	26	28.2	6	62.3
7	38.6	17	58.3	27	28.6	Ac	21.3
8	47.0	18	21.5	28	20.1	Ac	170.9
9	20.9	19	30.5	29	28.9		
10	29.5	20	87.2	30	16.6		



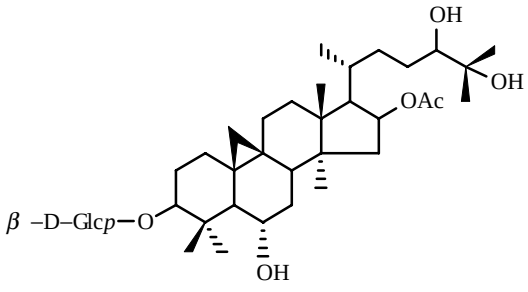
70. Mongholicoside II

Astragalus mongholicus Bunge [47]
$C_{38}H_{62}O_{11}$, mp 128-130°C, $[\alpha]_D$ +42.1°



71. Huangqiyenin D

Astragalus membranaceus Bunge [62]
$C_{38}H_{62}O_{11}$

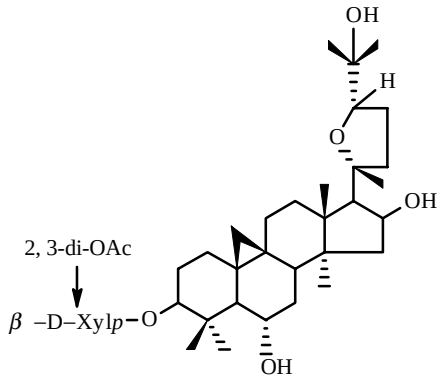


72. Cyclounifolioside D

Astragalus unifoliolatus Bunge [63]
$C_{38}H_{64}O_{11}$, mp 171-173°C (methanol)
δ_C (C_5D_5N)

C-1	32.19	C-11	25.97	C-21	18.33	*β*-D-Glc*p*-1	106.68
2	29.74	12	33.19	22	33.95	2	75.69
3	88.84	13	46.82	23	30.13	3	78.50
4	42.42	14	45.68	24	79.18	4	71.66
5	53.8	15	46.51	25	72.59	5	77.93
6	67.63	16	75.42	26	25.74	6	62.83
7	32.56	17	55.26	27	25.68	Ac	21.21
8	45.68	18	18.23	28	19.76	Ac	170.6
9	20.89	19	29.08	29	27.41		
10	28.66	20	31.59	30	16.51		

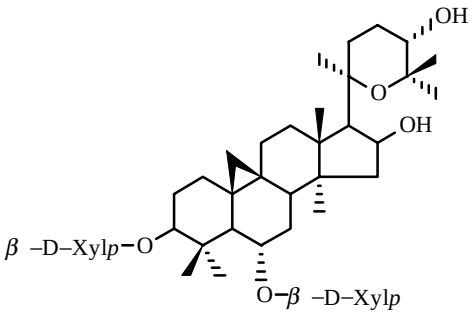
There is evidently a mistake in the chemical shift for C-7.



73. Cycloexoside

Astragalus exilis A. Kor. [64]
$C_{39}H_{62}O_{11}$, mp 193-196°C (methanol), $[\alpha]_D^{25}$ -56° (*c* 0.5, methanol)
δ_C (C_5D_5N)

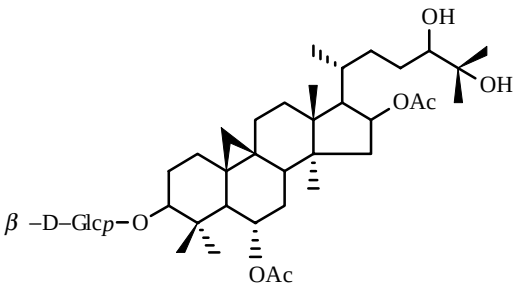
C-1	32.24	C-11	26.18	C-21	28.63	*β*-D-Xyl*p*-1	104.10
2	29.98	12	33.36	22	34.91	2	73.15
3	89.30	13	45.02	23	26.40	3	76.61
4	42.21	14	46.11	24	81.71	4	68.81
5	53.81	15	46.71	25	71.23	5	66.67
6	68.05	16	73.41	26	27.11	Ac	20.74
7	38.71	17	58.37	27	28.14	Ac	21.04
8	47.17	18	21.58	28	20.19	Ac	169.82
9	20.81	19	30.76	29	28.52	Ac	170.47
10	29.44	20	87.20	30	16.39		



74. Cyclodissectoside

Astragalus dissectus B. Fedtsch. et N. Ivanova [39]
$C_{40}H_{66}O_{13}$
δ_C (C_5D_5N)

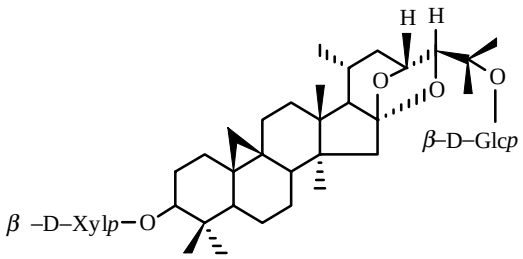
C-1	32.11	C-11	26.70	C-21	28.84	3-O-*β*-D-Xylp-1	107.61
2	30.11	12	34.14	22	26.79	2	75.60
3	88.42	13	46.03	23	24.11	3	78.55[a]
4	42.60	14	46.80	24	68.77	4	71.26
5	52.35	15	47.26	25	75.25	5	67.05
6	78.55[a]	16	73.98	26	28.63	6-O-*β*-D-Xylp-1	105.74
7	34.24	17	60.76	27	28.16	2	75.36
8	44.91	18	20.43	28	19.96	3	78.29
9	21.19	19	29.59	29	28.16	4	71.10
10	28.16	20	79.00	30	16.71	5	66.99



75. Cyclounifolioside A

Astragalus unifoliolatus Bunge [65]
$C_{40}H_{66}O_{14}$, mp 208-210°C (methanol)
δ_C (C_5D_5N)

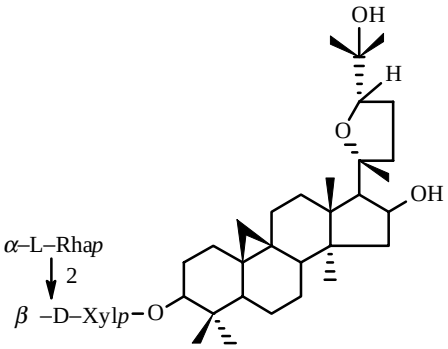
C-1	32.00	C-11	25.90	C-21	18.50	*β*-D-Glc*p*-1	106.70
2	29.80	12	33.25	22	34.10	2	75.50
3	87.95	13	46.90	23	30.10	3	78.40
4	42.10	14	45.95	24	79.30	4	71.70
5	50.00	15	45.60	25	72.10	5	78.10
6	70.70	16	75.50	26	25.90	6	62.80
7	32.60	17	55.30	27	25.70	Ac	21.45
8	45.30	18	18.10	28	19.80	Ac	21.8
9	20.80	19	28.80	29	27.00	Ac	170.70
10	28.40	20	31.70	30	16.60	Ac	171.1



76. Cycloorbicoside C

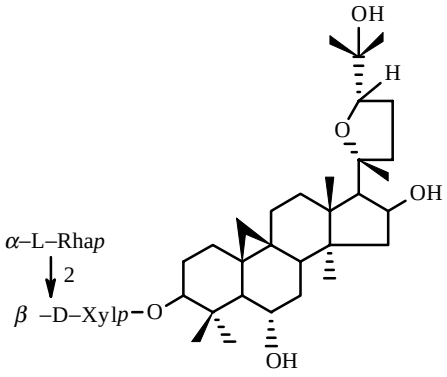
Astragalus orbiculatus Ledeb. [66]
$C_{41}H_{66}O_{13}$, mp 265-266°C (methanol)
δ_C (C_5D_5N)

C-1	32.16	C-11	26.56	C-21	19.79	β-D-Xylp-1	107.52
2	30.08	12	33.07	22	38.16	2	75.55
3	88.47	13	44.60	23	71.86	3	78.56
4	41.36	14	46.27	24	88.28	4	71.24
5	47.54	15	46.61	25	78.76	5	67.08
6	20.98	16	114.89	26	22.22	β-D-Glcp-1	98.81
7	26.59	17	61.30	27	24.47	2	75.23
8	47.57	18	19.21	28	19.33	3	78.83
9	19.60	19	30.46	29	25.76	4	71.81
10	26.77	20	23.91	30	15.43	5	78.19
						6	62.92



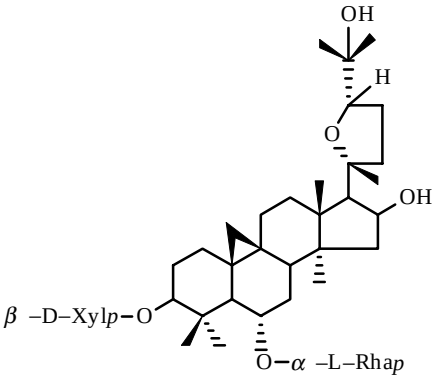
77. Quisvaloside B

Astragalus quisqualis Bunge [67]
$C_{41}H_{68}O_{12}$



78. Astrachrysoside A

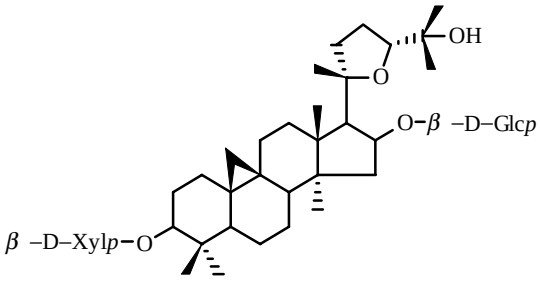
Astragalus chrysopterus Bunge [68, 69]
$C_{41}H_{68}O_{13}$



79. Cyclocarposide

Astragalus coluteocarpus Boiss. [70, 82]
$C_{41}H_{68}O_{13}$, mp 284-285°C (methanol), $[\alpha]_D^{24}$ -28° (*c* 1.0, pyridine)
δ_C (C_5D_5N)

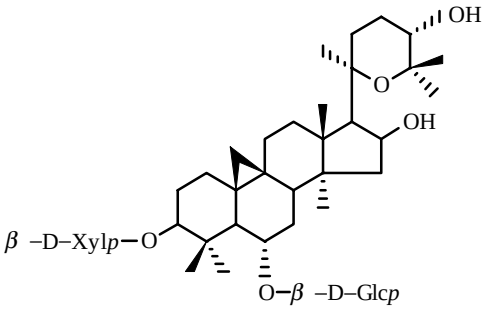
C-1	32.20	C-11	26.38	C-21	28.42	β-D-Xylp-1	107.43
2	30.06	12	33.27	22	34.88	2	75.38
3	87.83	13	45.00	23	25.95	3	78.44
4	42.26	14	46.16[a]	24	81.67	4	71.14
5	52.03	15	46.67	25	71.22	5	66.96
6	79.16	16	73.33	26	27.05	α-L-Rhap-1	103.88
7	34.55	17	58.23	27	28.11	2	72.87
8	46.16[a]	18	21.47	28	20.16	3	72.56
9	20.65	19	30.22	29	28.51	4	73.71
10	28.70	20	87.15	30	17.05	5	70.06
						6	18.16



80. Prusianoside B

Astragalus prusianus DC [71]
$C_{41}H_{68}O_{13}$, $[\alpha]_D^{25}$ +20.0° (*c* 0.004, methanol)
δ_C (C_5D_5N)

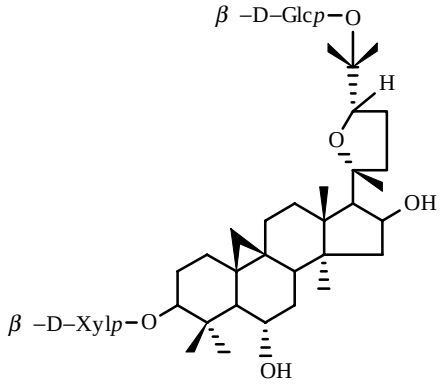
C-1	32.2	C-11	26.8	C-21	26.3	β-D-Xylp-1	107.6
2	30.2	12	33.1	22	39.0	2	75.7
3	88.7	13	46.9	23	26.4	3	78.7
4	41.5	14	47.0	24	84.5	4	71.6
5	47.7	15	48.0	25	71.4	5	67.2
6	21.0	16	83.7	26	26.3	β-D-Glcp-1	106.7
7	26.2	17	60.1	27	27.7	2	75.7
8	47.8	18	21.7	28	20.7	3	79.0
9	20.0	19	30.2	29	26.3	4	72.0
10	25.9	20	87.2	30	15.6	5	78.5
						6	63.1



81. Cyclocephaloside I

Astragalus microcephalus Willd. [37]
$C_{41}H_{68}O_{14}$, $[\alpha]_D$ +6.1° (*c* 0.42, methanol)
δ_C (C_5D_5N)

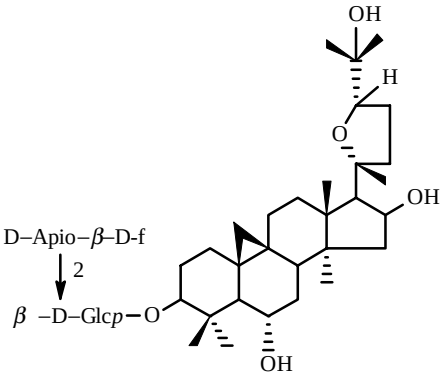
C-1	32.3	C-11	24.1	C-21	28.8	β-D-Xylp-1	107.7
2	30.2	12	34.2	22	26.7	2	75.6
3	88.6	13	45.9	23	26.3	3	78.5
4	42.7	14	46.8	24	68.7	4	71.8
5	52.7	15	47.4	25	75.2	5	67.1
6	79.5	16	74.0	26	28.6	β-D-Glcp-1	105.1
7	34.8	17	60.8	27	28.0	2	75.6
8	46.1	18	20.9	28	20.1	3	79.2
9	21.1	19	29.5	29	28.8	4	71.3
10	29.1	20	78.9	30	16.7	5	78.1
						6	63.1



82. Isoastragaloside IV

Astragalus membranaceus Bunge [72]
$C_{41}H_{68}O_{14}$, mp 279-283°C, $[\alpha]_D$ +17° (*c* 0.4, water)
δ_C (C_5D_5N)

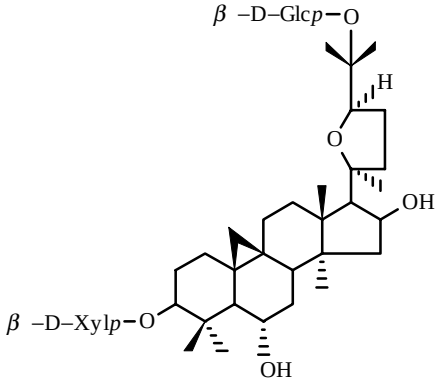
C-1	32.4	C-11	26.3	C-21	27.9	*β*-D-Xyl*p*-1	107.4
2	30.3	12	33.3	22	35.0	2	75.3
3	88.7	13	45.1	23	25.9	3	78.1
4	42.6	14	46.0	24	82.1	4	71.0
5	53.7	15	46.8	25	78.2	5	66.8
6	68.1	16	73.4	26	23.0	*β*-D-Glc*p*-1	98.6
7	38.4	17	58.0	27	25.7	2	74.7
8	47.1	18	21.6	28	19.9	3	78.8
9	20.8	19	30.8	29	28.8	4	71.1
10	29.9	20	87.3	30	16.6	5	77.7
						6	62.4



83. Cycloaraloside C (astrailienin A)

Astragalus amarus Pall., *Astragalus iliensis* [73, 74]
$C_{41}H_{68}O_{14}$, mp 242-244°C (methanol), $[\alpha]_D^{30}$ +4.9° (*c* 1.63, methanol)
δ_C (C_5D_5N)

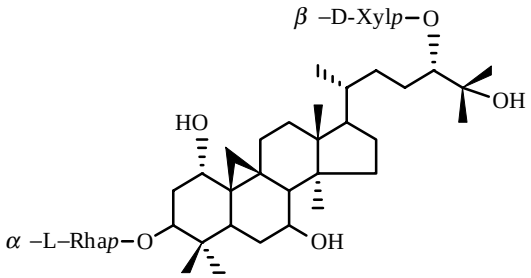
C-1	32.42	C-11	26.37[a]	C-21	28.16	*β*-D-Glc*p*-1	105.47
2	30.15	12	33.39	22	34.88	2	79.40
3	88.87	13	45.04	23	26.37[a]	3	78.66
4	42.58	14	46.09	24	81.72	4	72.01
5	54.01	15	46.61	25	71.26	5	78.21
6	67.97	16	73.43	26	27.12	6	62.89
7	38.54	17	58.34	27	28.53	D-Apio-*β*-D-f-1	111.15
8	46.98	18	21.51	28	20.17	2	77.83
9	20.84	19	30.47	29	28.76	3	80.52
10	29.43	20	87.25	30	16.58	4	75.59
						5	66.11



84. Cyclogaleginoside E

Astragalus galegiformis L. [108]
$C_{41}H_{68}O_{14}$, mp 187-188°C (methanol)
δ_C (C_5D_5N)

C-1	33.30	C-11	27.17	C-21	24.84	*β*-D-Xyl*p*-1	107.48
2	30.58	12	34.26	22	38.00	2	75.50
3	89.91	13	47.85	23	24.27	3	77.95
4	43.15	14	47.47	24	86.38	4	71.29
5	54.66	15	49.23	25	78.93	5	66.70
6	69.60	16	74.42	26	25.01	*β*-D-Glc*p*-1	99.04
7	38.85	17	56.31	27	23.51	2	75.04
8	48.50	18	21.40	28	20.90	3	77.63
9	21.91	19	32.18	29	28.73	4	71.80
10	30.58	20	88.93	30	16.55	5	77.63
						6	62.84



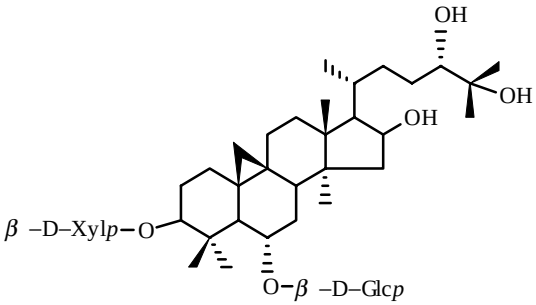
85. Macrophyllosaponin B

Astragalus oleifolius DC [75]

$C_{41}H_{70}O_{13}$, $[\alpha]_D^{20}$ +2.8° (*c* 0.58, methanol)

δ_C (CD_3OD)

C-1	74.7	C-11	28.0	C-21	19.9	α-L-Rhap-1	105.4
2	38.0	12	35.0	22	35.4	2	73.5
3	86.1	13	47.9	23	30.5	3	73.6
4	42.5	14	50.7	24	90.2	4	75.1
5	41.1	15	39.5	25	74.5	5	71.0
6	33.1	16	30.7	26	26.2	6	18.9
7	72.1	17	54.1	27	27.5	β-D-Xylp-1	106.4
8	57.0	18	19.3	28	20.3	2	76.2
9	23.0	19	30.3	29	27.0	3	78.9
10	32.1	20	38.7	30	15.5	4	72.1
						5	68.0



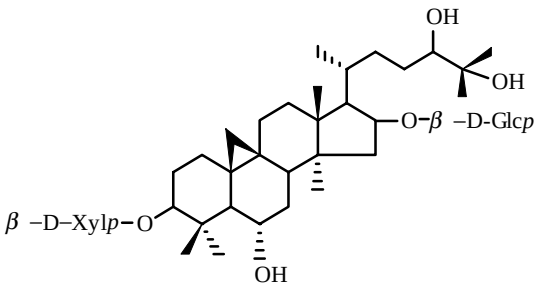
86. Cyclocanthoside E

Astragalus tragacantha Habl. [54]

$C_{41}H_{70}O_{14}$, mp 282-284°C (ethanol), $[\alpha]_D^{25}$ +23.5° (*c* 0.5, pyridine)

δ_C (C_5D_5N)

C-1	32.27	C-11	26.30	C-21	18.48	β-D-Xylp-1	107.60
2	28.77	12	33.21	22	33.00	2	75.61
3	88.59	13	45.82	23	27.90	3	78.48
4	42.68	14	46.94	24	77.14	4	71.25
5	52.52	15	47.88	25	72.58	5	67.02
6	79.13[a]	16	72.02	26	25.77	β-D-Glcp-1	105.18
7	34.32	17	57.20	27	26.50	2	75.56
8	45.61	18	18.37	28	19.84	3	79.13
9	21.45	19	28.21	29	28.65	4	71.95
10	30.20	20	28.57	30	16.71	5	78.06
						6	63.20



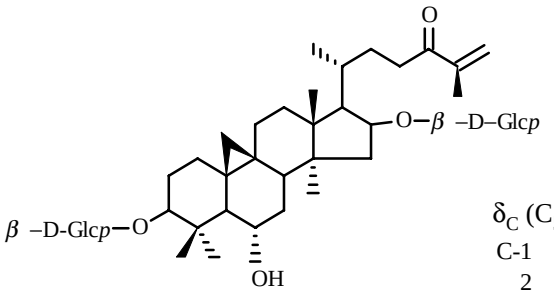
87. Cyclopycnanthoside

Astragalus pycnanthus Boriss. [16]

$C_{41}H_{70}O_{14}$, mp 280-282°C (methanol), $[\alpha]_D^{19}$ +17.5° (*c* 0.6, methanol)

δ_C (C_5D_5N)

C-1	32.57	C-11	26.25	C-21	19.06	β-D-Xylp-1	107.67
2	29.26	12	32.79	22	30.33[b]	2	75.68
3	88.79	13	45.60	23	34.40	3	78.57
4	42.74	14	46.86[a]	24	79.99	4	71.29
5	54.05	15	47.77	25	72.73	5	67.10
6	67.94	16	83.10	26	25.40	β-D-Glcp-1	106.64
7	38.42	17	57.52	27	26.32	2	75.81
8	46.86	18	18.06	28	20.19	3	78.84
9	21.29	19	30.33[b]	29	28.95	4	71.78
10	30.41	20	31.97	30	16.76	5	78.12
						6	62.89



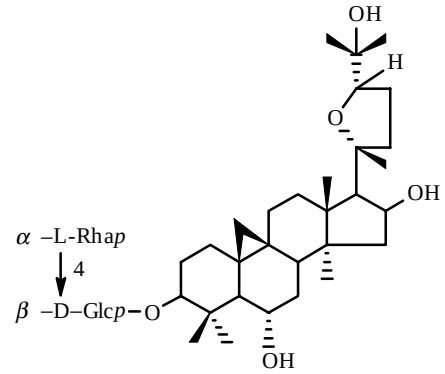
88. 3*β*,6α,16*β*-Trihydroxy-9,19-cyclolanost-24-oxo-25-ene, 3*β*,16*β*-diglucopyranoside

Astragalus trigonus DC [76]

$C_{42}H_{68}O_{14}$, mp 229°C (Et_2O—MeOH, 2:1), $[\alpha]_D^{25}$ -74° (*c* 0.61, MeOH)

δ_C (C_5D_5N)

C-1	32.2	C-12	32.4	C-23	35.5	3	78.3
2	29.9	13	45.8	24	203.0	4	71.6
3	88.9	14	46.6	25	145.0	5	77.9
4	42.7	15	48.1	26	124.6	6	62.6
5	53.7	16	82.3	27	17.6	16-O-*β*-D-Glc*p*-1	106.6
6	67.6	17	56.8	28	19.9	2	75.3
7	38.0	18	18.7	29	28.6	3	78.2
8	46.6	19	30.0	30	16.4	4	71.6
9	21.3	20	29.9	3-O-*β*-D-Glc*p*-1	106.7	5	77.8
10	29.4	21	17.5	2	75.6	6	62.6
11	25.9	22	31.8				



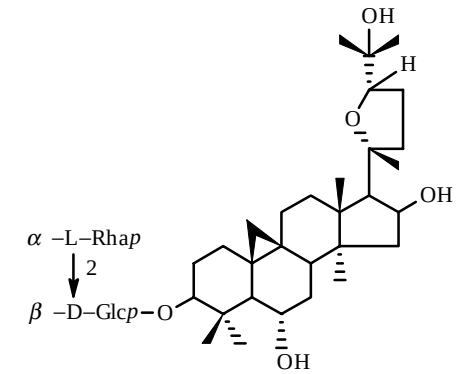
89. Astraverrucin IV

Astragalus verrucosus Moris [77]

$C_{42}H_{70}O_{14}$, $[\alpha]_D^{20}$ +10.5° (*c* 0.18, methanol)

δ_C (C_5D_5N)

C-1	32.4	C-12	34.9	C-23	26.2	3	76.8
2	30.1	13	45.0	24	81.7	4	78.4
3	89.2	14	46.9	25	71.3	5	77.0
4	42.6	15	46.1	26	28.2	6	63.0
5	54.0	16	73.5	27	28.6	*α*-L-Rha*p*-1	102.7
6	68.0	17	58.4	28	20.2	2	72.6
7	38.7	18	20.9	29	29.0	3	72.8
8	47.2	19	30.6	30	16.7	4	74.0
9	21.6	20	87.2	*β*-D-Glc*p*-1	106.8	5	70.3
10	29.5	21	27.1	2	76.1	6	19.0
11	26.5	22	33.4				



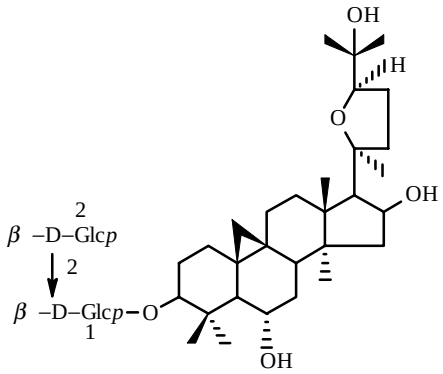
90. Cycloaraloside D

Astragalus amarus Pall. [78]

$C_{42}H_{70}O_{14}$, mp 226-228°C (methanol), $[\alpha]_D^{28}$ -11.9° (*c* 0.84, methanol)

δ_C (C_5D_5N)

C-1	32.72	C-12	33.66	C-23	26.34	3	78.42
2	30.25	13	45.38	24	82.03	4	72.60
3	88.55	14	46.35	25	71.19	5	77.51
4	42.61	15	46.87	26	27.08	6	63.21
5	54.31	16	73.40	27	28.40	*α*-L-Rha*p*-1	101.51
6	67.99	17	58.56	28	20.23	2	72.22
7	38.36	18	21.35	29	28.69	3	72.55
8	46.96	19	30.51	30	16.71	4	74.28
9	21.06	20	87.20	*β*-D-Glc*p*-1	105.09	5	69.46
10	29.63	21	27.99	2	79.57	6	18.47
11	26.48	22	35.21				



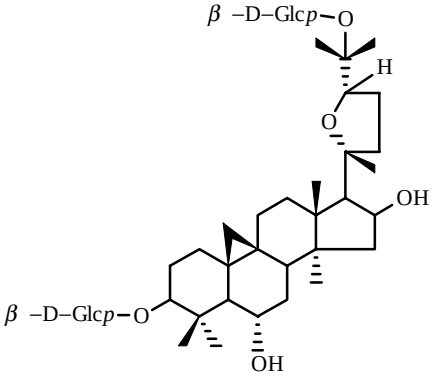
91. Sieberoside II

Astragalus sieberi Pall. [57]

$C_{42}H_{70}O_{15}$, mp 250°C (methanol), $[\alpha]_D^{25}$ -82° (*c* 0.5, methanol)

δ_C (C_5D_5N)

C-1	32.5	C-12	33.9	C-23	24.5	3	78.5
2	30.4	13	46.6	24	85.1	4	71.7
3	89.1	14	47.0	25	70.4	5	78.1
4	42.9	15	49.0	26	28.3	6	63.0
5	54.2	16	73.0	27	27.0	β-D-Glcp_2-1	106.2
6	67.9	17	56.6	28	20.6	2	77.2
7	38.6	18	21.2	29	29.0	3	78.2
8	46.9	19	30.4	30	16.7	4	72.0
9	21.2	20	86.8	β-D-Glcp_1-1	105.1	5	78.3
10	29.5	21	26.5	2	83.7	6	63.0
11	26.6	22	37.7				



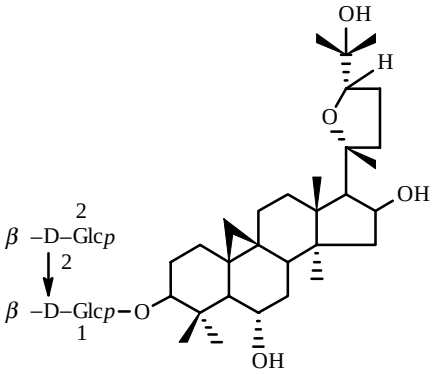
92. Cycloaraloside E

Astragalus amarus Pall. [79]

$C_{42}H_{70}O_{15}$, mp 180-182°C ($CHCl_3$—CH_3OH, 1:1), $[\alpha]_D^{28}$ -5° (*c* 0.5, methanol)

δ_C (C_5D_5N)

C-1	32.40	C-12	33.45	C-23	25.80	3	78.45[b]
2	30.00	13	45.15	24	82.05	4	71.85
3	88.95	14	46.05[a]	25	78.45[b]	5	77.85[c]
4	42.60	15	46.05[a]	26	22.80	6	62.83
5	53.85	16	73.80	27	25.50	25-O-β-D-Glc*p*-1	98.70
6	68.10	17	58.20	28	19.95	2	75.15
7	38.55	18	21.45	29	28.65	3	78.45[b]
8	46.95	19	30.45	30	16.50	4	71.25
9	20.70	20	87.15	3-O-β-D-Glc*p*-1	106.95	5	77.85[c]
10	29.25	21	27.75	2	75.75	6	62.70
11	26.10	22	34.95				



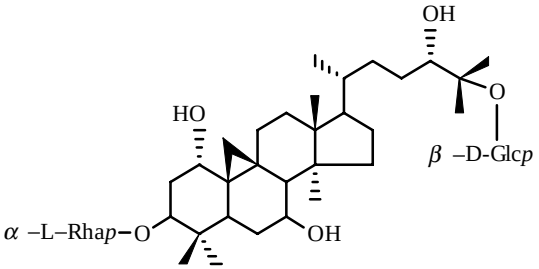
93. Cyclounifolioside B

Astragalus unifoliolatus Bunge [80]

$C_{42}H_{70}O_{15}$, mp 210-215°C

δ_C (C_5D_5N)

C-1	32.38	C-12	33.47	C-23	26.47	3	78.42
2	30.62	13	45.10	24	81.75	4	71.67
3	88.93	14	46.19	25	71.28	5	77.95
4	42.76	15	46.66	26	28.21	6	62.89
5	53.97	16	73.47	27	27.15	β-D-Glcp_2-1	106.12
6	67.80	17	58.40	28	20.16	2	77.05
7	38.51	18	21.44	29	28.87	3	78.15
8	46.81	19	30.21	30	16.59	4	71.88
9	21.02	20	87.28	β-D-Glcp_1-1	105.05	5	78.08
10	29.42	21	28.59	2	83.61	6	62.95
11	26.28	22	34.96				



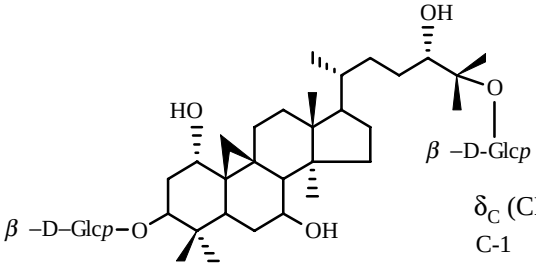
94. Macrophyllosaponin C

Astragalus oleifolius DC [75]

$C_{42}H_{72}O_{14}$, $[\alpha]_D^{20}$ +15° (*c* 0.32, methanol)

δ_C (CD_3OD)

C-1	74.8	C-12	35.0	C-23	30.0	3	73.6
2	38.0	13	47.9	24	79.0	4	75.1
3	86.1	14	50.7	25	82.5	5	71.0
4	42.5	15	39.5	26	24.0	6	18.8
5	41.1	16	30.6	27	23.6	β-D-Glcp-1	99.0
6	33.1	17	54.2	28	27.0	2	76.4
7	72.1	18	19.3	29	15.5	3	79.3
8	57.0	19	30.3	30	20.2	4	72.7
9	23.0	20	38.3	α-L-Rhap-1	105.4	5	78.8
10	32.4	21	19.9	2	73.5	6	63.8
11	28.0	22	35.7				



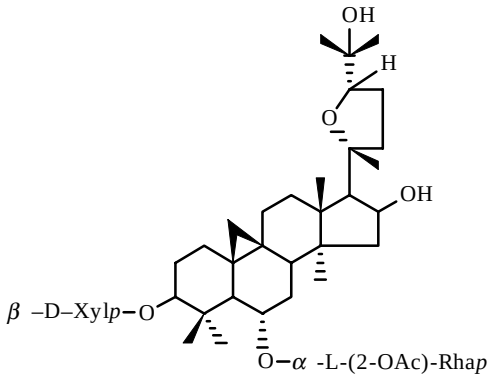
95. Macrophyllosaponin E

Astragalus oleifolius DC [81]

$C_{42}H_{72}O_{15}$

δ_C (CD_3OD)

C-1	73.1	C-12	33.0	C-23	28.0	3	77.2[a]
2	36.4	13	45.9	24	77.0	4	70.8
3	84.1	14	48.9	25	80.5	5	76.8[b]
4	40.7	15	37.5	26	22.0	6	61.8
5	39.3	16	28.6	27	21.6	25-O-β-D-Glcp-1	97.0
6	31.0	17	52.2	28	24.8	2	74.7
7	70.2	18	17.4	29	13.5	3	77.3[a]
8	55.1	19	28.4	30	18.2	4	70.6
9	21.0	20	36.2	3-O-β-D-Glcp-1	105.7	5	77.0[b]
10	30.4	21	17.9	2	74.3	6	62.1
11	26.0	22	33.7				



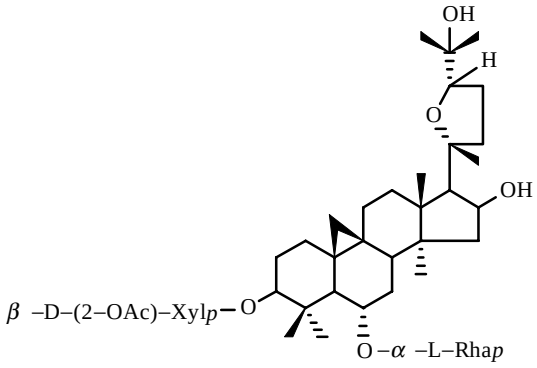
96. Cyclocarposide B

Astragalus coluteocarpus Boiss. [82]

$C_{43}H_{70}O_{14}$, mp 271-273°C (methanol), $[\alpha]_D^{24}$ 0° (*c* 0.5, pyridine)

δ_C (C_5D_5N)

C-1	32.16	C-12	33.28	C-23	25.94	3	78.46
2	30.06	13	45.02	24	81.71	4	71.18
3	87.85	14	46.19	25	71.22	5	66.99
4	42.27	15	46.71	26	27.07	α-L-Rhap-1	100.41
5	51.93	16	73.35	27	28.13	2	74.49
6	79.90	17	58.29	28	20.18	3	70.45
7	34.33	18	21.47	29	28.51	4	73.80
8	46.22	19	30.26	30	16.98	5	69.97
9	20.64	20	87.18	β-D-Xylp-1	107.49	6	18.16
10	28.77	21	28.42	2	75.50	Ac	21.03
11	26.39	22	34.90			Ac	170.76

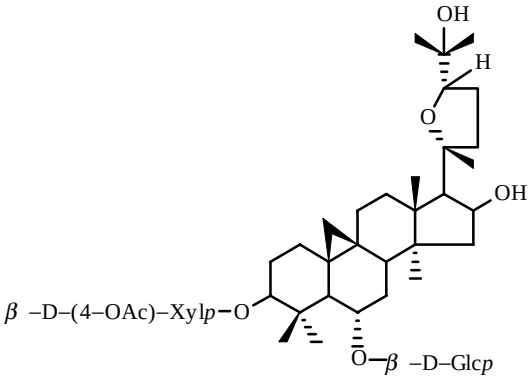


97

97. Cyclocarposide C

Astragalus coluteocarpus Boiss. [83]
$C_{43}H_{70}O_{14}$, mp 257-259°C (methanol), $[\alpha]_D^{23}$ -21° (*c* 0.59, pyridine)
δ_C (C_5D_5N)

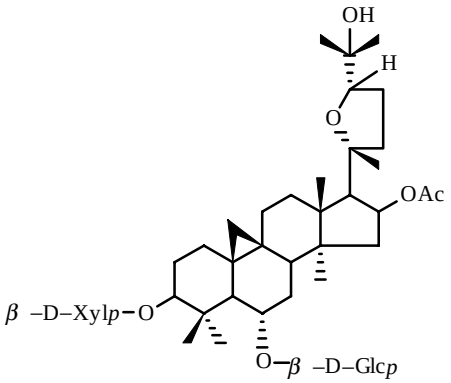
C-1	32.06	C-12	33.29	C-23	25.92	4	71.23
2	29.93	13	45.03	24	81.72	5	67.10
3	88.05	14	46.19	25	71.30	α-L-Rhap-1	104.00
4	41.95	15	46.30	26	27.07	2	72.98
5	51.98	16	73.36	27	28.13	3	72.60
6	79.25	17	58.30	28	20.21	4	73.81
7	34.70	18	21.57	29	28.52	5	70.12
8	46.77	19	30.38	30	16.96	6	18.17
9	20.73	20	87.18	β-D-Xylp-1	104.95	Ac	21.17
10	28.69	21	28.02	2	76.21	Ac	169.95
11	26.40	22	34.90	3	75.55		



98. Cyclocephaloside II

Astragalus microcephalus Willd. [56]
$C_{43}H_{70}O_{15}$, $[\alpha]_D^{23}$ +12.5° (*c* 0.1, methanol)
δ_C (C_5D_5N)

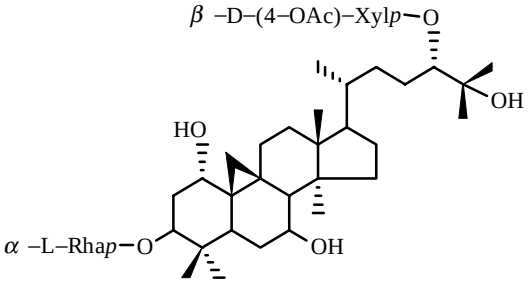
C-1	32.7	C-12	33.8	C-23	26.4	4	73.0
2	30.3	13	46.3	24	82.5	5	63.1
3	89.8	14	47.0	25	72.9	β-D-Glcp-1	104.9
4	42.8	15	46.0	26	26.4	2	75.3
5	53.7	16	74.4	27	27.4	3	78.4
6	79.8	17	58.6	28	20.0	4	71.5
7	35.0	18	21.1	29	29.0	5	77.8
8	46.7	19	29.3	30	16.2	6	62.7
9	22.0	20	88.1	β-D-Xylp-1	107.0	Ac	20.6
10	30.0	21	29.0	2	75.1	Ac	171.9
11	26.8	22	35.4	3	74.7		



99. Trojanoside A

Astragalus trojanus Stev. [84]
$C_{43}H_{70}O_{15}$, $[\alpha]_D^{25}$ +20.1° (*c* 0.1, methanol)
δ_C (CD_3OD)

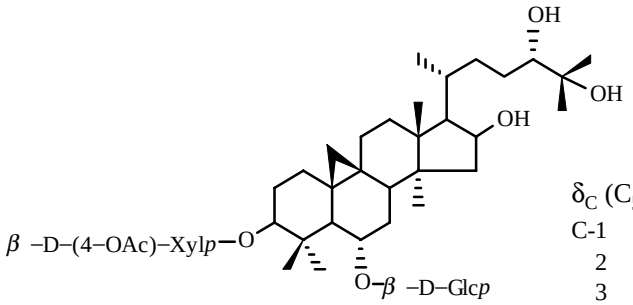
C-1	32.6	C-12	33.4	C-23	27.1	4	70.9
2	30.0	13	45.9	24	83.0	5	66.5
3	89.9	14	47.4	25	72.4	β-D-Glcp-1	104.7
4	42.9	15	45.3	26	25.8	2	75.1
5	52.8	16	77.6	27	25.8	3	78.1
6	79.2	17	58.4	28	20.1	4	70.4
7	33.6	18	20.3	29	28.1	5	77.6
8	45.4	19	28.0	30	16.3	6	62.7
9	22.4	20	87.0	β-D-Xylp-1	107.1	Ac	20.6
10	29.5	21	27.8	2	75.1	Ac	171.2
11	26.8	22	37.1	3	77.8		



100. Macrophyllosaponin A

Astragalus oleifolius DC [75]
$C_{43}H_{72}O_{14}$, $[\alpha]_D^{20}$ -5.0° (*c* 0.28, methanol)
δ_C (CD_3OD)

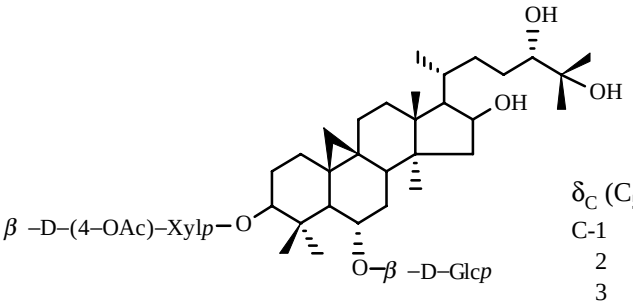
C-1	74.7	C-12	35.0	C-23	30.4	4	75.1
2	38.0	13	47.9	24	90.0	5	70.9
3	86.1	14	50.7	25	74.0	6	18.8
4	42.5	15	39.5	26	26.4	β-D-Xylp-1	106.2
5	41.1	16	30.6	27	27.4	2	75.0
6	33.1	17	54.0	28	20.2	3	76.3
7	72.1	18	19.2	29	27.0	4	74.5
8	57.0	19	30.3	30	15.5	5	64.6
9	23.0	20	38.7	α-L-Rhap-1	105.3	Ac	21.8
10	32.4	21	19.9	2	73.5	Ac	173.2
11	28.0	22	35.4	3	73.6		



101. Agroastragaloside II

Astragalus membranaceus Bunge [85]
$C_{43}H_{72}O_{15}$, mp 267-269°C (methanol),
$[\alpha]_D^{25}$ +48° (*c* 0.22, methanol)
δ_C (C_5D_5N)

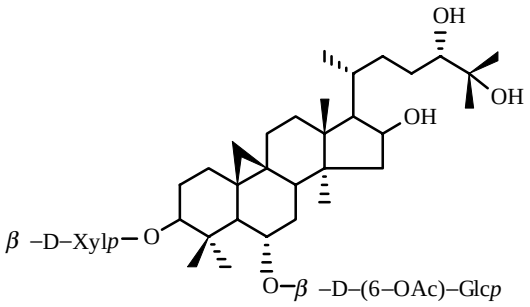
C-1	32.2	C-12	33.3	C-23	28.0	4	71.5
2	30.1	13	45.9	24	77.2	5	67.3
3	89.1	14	47.0	25	72.6	β-D-Glcp-1	105.3
4	42.4	15	48.1	26	25.9	2	75.8
5	52.6	16	72.1	27	26.6	3	79.3
6	79.3	17	57.3	28	20.0	4	72.0
7	34.6	18	18.7	29	28.4	5	78.3
8	45.9	19	28.5	30	16.7	6	63.3
9	21.6	20	28.7	β-D-Xylp-1	104.9	Ac	21.4
10	28.8	21	18.5	2	75.8	Ac	170.2
11	26.3	22	33.1	3	76.4		



102. Cyclocanthoside B

Astragalus tragacantha Habl. [54]
$C_{43}H_{72}O_{15}$, mp 235-237°C (methanol),
$[\alpha]_D^{23}$ +12.6° (*c* 0.96, methanol)
δ_C (C_5D_5N)

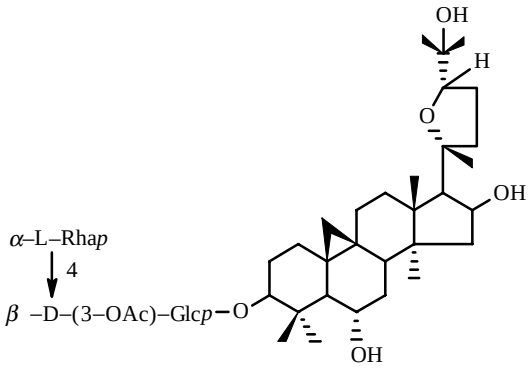
C-1	32.19	C-12	33.18	C-23	27.87	4	73.23
2	28.74	13	45.79	24	77.11	5	63.17[b]
3	88.61	14	46.91	25	72.52	β-D-Glcp-1	105.15
4	42.64	15	47.88	26	25.74	2	75.60
5	52.48	16	71.93	27	26.46	3	79.15[a]
6	79.15[a]	17	57.19	28	19.82	4	71.98
7	34.35	18	18.48	29	28.61	5	78.07
8	45.65	19	28.26	30	16.62	6	63.17[b]
9	21.41	20	28.52	β-D-Xylp-1	107.38	Ac	20.86
10	30.09	21	18.32	2	75.74	Ac	170.57
11	26.26	22	32.97	3	74.91		



103. Cyclocanthoside C

Astragalus tragacantha Habl. [54]
$C_{43}H_{72}O_{15}$, mp 240-242°C ($CHCl_3$—CH_3OH, 1:1),
$[\alpha]_D^{20}$ +30.6° (*c* 1.11, methanol)
δ_C (C_5D_5N)

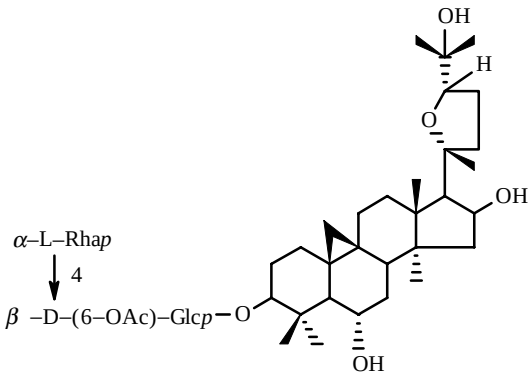
C-1	32.09	C-12	33.18	C-23	27.14	4	71.24
2	28.52	13	45.83	24	77.18	5	67.01
3	88.44	14	46.82	25	72.55	*β*-D-Glc*p*-1	105.07
4	42.60	15	47.53	26	25.63	2	75.49
5	52.19	16	72.05	27	26.49	3	78.71[a]
6	78.71[a]	17	57.16	28	19.77	4	71.51
7	33.59	18	18.08	29	28.30	5	74.98
8	44.93	19	27.85	30	16.69	6	65.06
9	21.46	20	28.70	*β*-D-Xyl*p*-1	107.54	Ac	21.03
10	30.12	21	18.32	2	75.55	Ac	170.97
11	26.31	22	33.04	3	78.48		



104. Astraverrucin V

Astragalus verrucosus Moris [77]
$C_{44}H_{72}O_{15}$, $[\alpha]_D^{20}$ +12.2° (*c* 0.27, methanol)
δ_C (C_5D_5N)

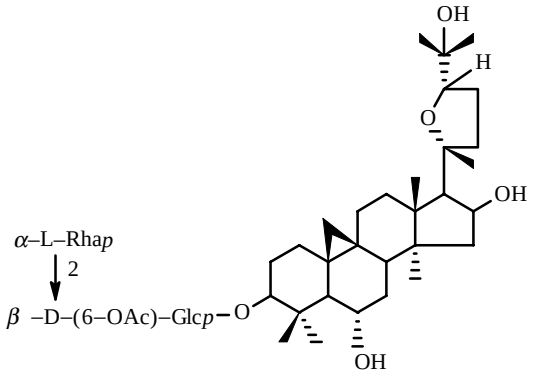
C-1	32.4	C-12	33.4	C-23	26.5	4	76.0
2	30.1	13	45.1	24	81.8	5	77.0
3	89.5	14	46.2	25	71.4	6	62.0
4	42.6	15	46.7	26	28.3	*α*-L-Rha*p*-1	103.0
5	54.0	16	73.6	27	28.7	2	73.0
6	68.2	17	58.4	28	20.2	3	72.5
7	38.8	18	21.0	29	29.0	4	74.0
8	47.3	19	30.8	30	16.7	5	72.5
9	21.4	20	87.3	*β*-D-Glc*p*-1	106.5	6	19.0
10	29.5	21	27.3	2	74.1	Ac	21.7
11	26.3	22	35.0	3	77.5	Ac	170.9



105. Astraverrucin VI

Astragalus verrucosus Moris [77]
$C_{44}H_{72}O_{15}$, $[\alpha]_D^{20}$ +2.86° (*c* 0.7, methanol)
δ_C (C_5D_5N)

C-1	32.7	C-12	34.9	C-23	26.2	4	77.6
2	30.0	13	45.0	24	81.7	5	74.8
3	89.2	14	46.1	25	71.3	6	64.5
4	42.6	15	46.6	26	28.2	*α*-L-Rha*p*-1	101.9
5	54.3	16	73.4	27	28.6	2	72.0
6	67.8	17	58.3	28	20.2	3	72.5
7	38.6	18	21.0	29	29.0	4	74.2
8	46.9	19	30.4	30	16.7	5	69.7
9	21.4	20	87.2	*β*-D-Glc*p*-1	105.5	6	18.8
10	29.5	21	27.1	2	74.2	Ac	21.5
11	26.5	22	33.4	3	79.7	Ac	170.8



106. Cycloaraloside B

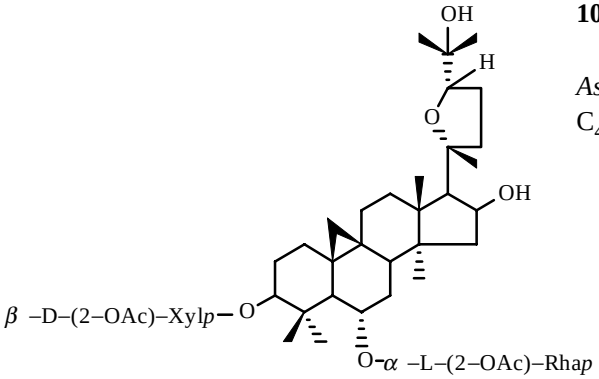
Astragalus amarus Pall. [86]

$C_{44}H_{72}O_{15}$, mp 181-183°C (ethylacetate—methanol, 5:1),

$[\alpha]_D^{24}$ 0° (*c* 0.7, methanol)

δ_C (C_5D_5N)

C-1	32.65	C-12	33.39	C-23	26.39	4	72.01
2	29.47	13	45.02	24	81.68	5	74.74
3	89.14	14	46.13	25	71.20	6	64.80
4	42.59	15	46.61	26	28.13	α-L-Rhap-1	101.81
5	54.25	16	73.40	27	28.50	2	72.50
6	67.87	17	58.34	28	20.11	3	72.42
7	38.47	18	21.38	29	28.65	4	74.13
8	46.85	19	30.40	30	16.70	5	69.64
9	20.86	20	87.21	β-D-Glcp-1	105.35	6	18.68
10	30.25	21	27.09	2	79.60	Ac	20.76
11	26.21	22	34.89	3	77.70	Ac	170.71



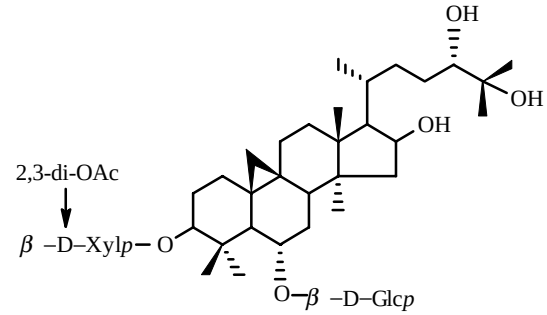
107. Cyclocarposide A

Astragalus coluteocarpus Boiss. [83]

$C_{45}H_{72}O_{15}$, mp 224-226°C (methanol), $[\alpha]_D^{23}$ -31.7° (*c* 0.57, methanol)

δ_C (C_5D_5N)

C-1	32.04	C-13	45.03	C-25	71.30	α-L-Rhap-1	100.65
2	29.99	14	46.16	26	27.09	2	74.34
3	88.25	15	46.74	27	28.15	3	70.60
4	41.95	16	73.36	28	20.21	4	73.91
5	51.95	17	58.32	29	28.63	5	70.09
6	79.75	18	21.56	30	16.95	6	18.07
7	34.62	19	30.34	β-D-Xylp-1	105.01	Ac	20.99
8	46.34	20	87.19	2	76.24	Ac	21.29
9	20.66	21	28.05	3	75.61	Ac	170.14
10	28.76	22	34.91	4	71.24	Ac	170.75
11	26.41	23	25.90	5	67.12		
12	33.28	24	81.74				



108. Agroastragaloside I

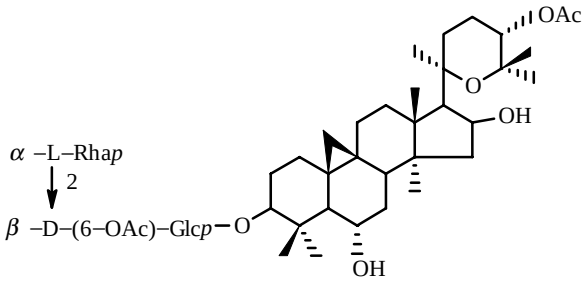
Astragalus membranaceus Bunge [87]

$C_{45}H_{74}O_{16}$, mp 237-239°C (methanol),

$[\alpha]_D^{25}$ +17.3° (*c* 0.15, methanol)

δ_C (C_5D_5N)

C-1	32.2	C-13	45.9	C-25	72.7	β-D-Glcp-1	105.3
2	29.9	14	47.0	26	25.9	2	75.8
3	89.4	15	48.1	27	26.6	3	79.3
4	42.4	16	72.1	28	20.0	4	72.0
5	52.5	17	57.3	29	28.4	5	78.3
6	79.4	18	18.8	30	16.7	6	63.3
7	34.7	19	28.6	β-D-Xylp-1	104.1	Ac	20.9
8	46.0	20	28.8	2	73.3	Ac	21.0
9	21.6	21	18.5	3	77.0	Ac	170.0
10	28.8	22	33.1	4	68.9	Ac	170.6
11	26.4	23	28.0	5	66.8		
12	33.3	24	77.3				



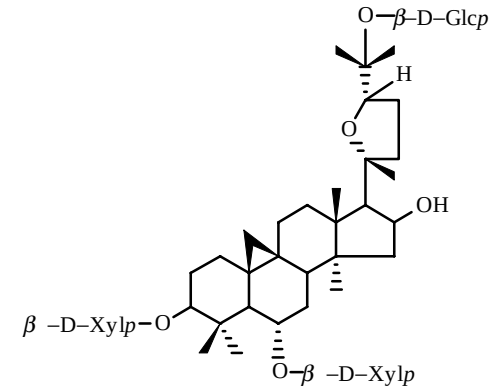
109. No name

Astragalus peregrinus [88]

$C_{46}H_{74}O_{14}$, amorphous, $[\alpha]_D^{20}$ +5.3° (*c* 0.4, methanol)

δ_C (C_5D_5N)

C-1	32.6	C-13	46.8	C-25	74.1	α-L-Rha*p*-1	101.8
2	30.1	14	46.3	26	27.4	2	72.36
3	89.1	15	48.4	27	27.6	3	72.40
4	42.5	16	73.6	28	20.6	4	74.1
5	54.4	17	60.5	29	28.7	5	69.5
6	68.1	18	20.6	30	16.6	6	18.6
7	38.5	19	30.6	β-D-Glc*p*-1	105.4	Ac	20.7
8	47.1	20	79.8	2	77.6	Ac	20.8
9	21.3	21	27.4	3	79.6	Ac	169.8
10	29.4	22	26.9	4	71.8	Ac	176.0
11	26.3	23	20.7	5	74.6		
12	34.5	24	71.6	6	64.3		



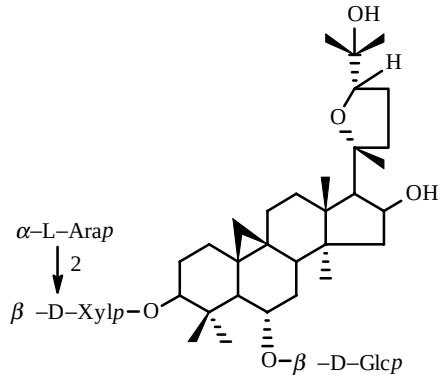
110. Trojanoside B

Astragalus trojanus Stev. [84]

$C_{46}H_{76}O_{18}$, $[\alpha]_D^{25}$ +13.2° (*c* 0.1, methanol)

δ_C (CD_3OD)

C-1	32.6	C-15	45.5	C-28	19.7	β-D-Glc*p*-1	98.4
2	30.1	16	74.5	29	28.1	2	75.0
3	90.0	17	58.5	30	16.3	3	77.9
4	42.6	18	20.9	3-O-β-D-Xyl*p*-1	105.2	4	71.1
5	52.8	19	28.5	2	75.0	5	77.5
6	79.1	20	87.0	3	77.6	6	62.5
7	35.0	21	27.5	4	70.8		
8	45.4	22	35.1	5	66.1		
9	21.9	23	26.1	6-O-β-D-Xyl*p*-1	102.2		
10	29.5	24	82.8	2	75.0		
11	26.7	25	79.9	3	77.6		
12	33.6	26	22.7	4	70.8		
13	46.1	27	25.0	5	66.1		
14	46.9						



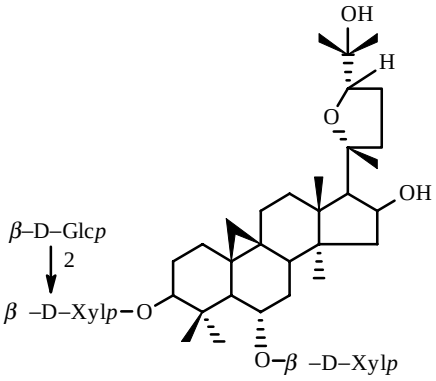
111. Trojanoside H

Astragalus trojanus Stev. [89]

$C_{46}H_{76}O_{18}$, $[\alpha]_D^{25}$ +14.2° (*c* 0.1, methanol)

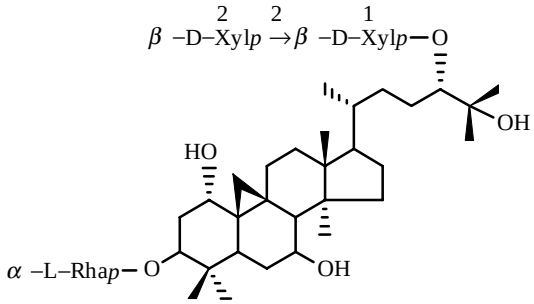
δ_C (CD_3OD)

C-1	33.0	C-13	46.3	C-25	72.4	α-L-Ara*p*-1	106.7
2	30.5	14	47.0	26	27.7	2	73.5
3	89.8	15	46.2	27	26.6	3	74.1
4	42.9	16	74.7	28	20.3	4	69.6
5	53.3	17	59.0	29	28.4	5	67.2
6	80.0	18	21.1	30	16.4	β-D-Glc*p*-1	105.8
7	35.0	19	29.3	β-D-Xyl*p*-1	105.6	2	75.7
8	46.5	20	87.0	2	83.2	3	78.6
9	22.4	21	27.8	3	76.9	4	71.8
10	29.5	22	35.5	4	71.0	5	77.8
11	27.0	23	26.7	5	66.0	6	62.9
12	34.1	24	82.7				



112. No name

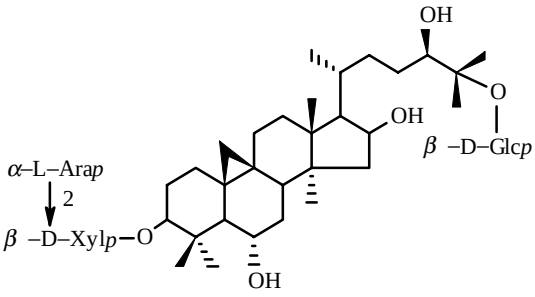
Astragalus adsurgens Pall. [90]
$C_{46}H_{76}O_{18}$



113. Macrophyllosaponin D

Astragalus oleifolius DC [75]
$C_{46}H_{78}O_{17}$, $[\alpha]_D^{20}$ -1.0° (*c* 0.32, methanol)
δ_C (CD_3OD)

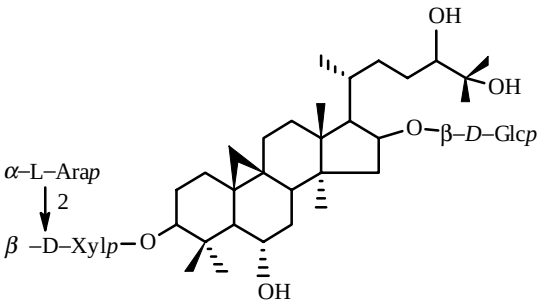
C-1	74.8	C-13	47.9	C-25	74.6	β-D-Xylp_1-1	104.9
2	38.0	14	50.7	26	26.3	2	84.3
3	86.1	15	39.5	27	27.3	3	78.6
4	42.5	16	30.7	28	20.4	4	71.9
5	41.1	17	54.0	29	27.0	5	67.5
6	33.1	18	19.3	30	15.5	β-D-Xylp_2-1	107.5
7	72.1	19	30.1	α-L-Rha*p*-1	105.4	2	76.8
8	57.0	20	38.9	2	73.5	3	78.7
9	23.0	21	19.9	3	73.6	4	72.2
10	32.4	22	35.6	4	75.1	5	68.2
11	28.0	23	30.3	5	71.0		
12	35.0	24	89.7	6	18.8		



114. Askendoside F

Astragalus taschkendicus Bunge [91]
$C_{46}H_{78}O_{18}$, amorphous, $[\alpha]_D^{24}$ 0° (*c* 0.7, methanol)
δ_C (C_5D_5N)

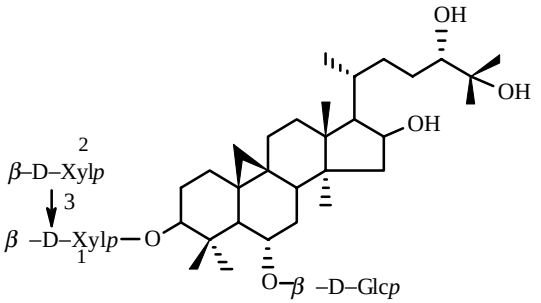
C-1	32.51	C-13	45.68	C-25	80.90	α-L-Ara*p*-1	106.61
2	29.22[a]	14	46.84	26	21.54	2	73.63
3	88.52	15	48.62	27	24.22	3	74.28
4	42.75	16	71.80	28	20.17	4	69.11
5	54.12	17	57.32	29	28.63	5	66.98
6	67.94	18	18.77	30	16.24	β-D-Glc*p*-1	98.69
7	38.40	19	29.93	β-D-Xyl*p*-1	105.59	2	75.34
8	46.94	20	31.53	2	83.55	3	78.73
9	21.34	21	18.93	3	77.58	4	71.71
10	30.35	22	29.22[a]	4	70.97	5	78.19
11	26.31	23	34.94	5	66.57	6	62.80
12	33.18	24	78.94				



115. Askendoside G

Astragalus taschkendicus Bunge [92]
$C_{46}H_{78}O_{18}$, mp 273-275°C (methanol),
$[\alpha]_D^{20}$ +11° (*c* 0.9, pyridine)
δ_C (C_5D_5N)

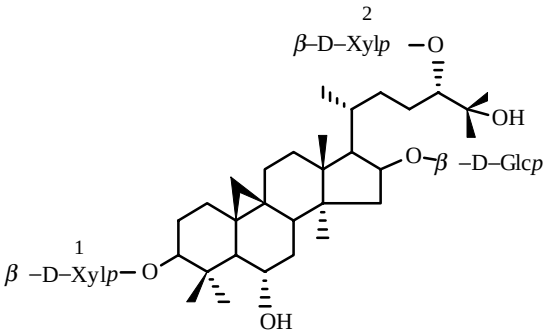
C-1	32.64[a]	C-13	45.57	C-25	72.76	α-L-Ara*p*-1	106.74[d]
2	30.33[b]	14	46.84	26	25.40	2	73.65
3	88.59	15	47.73	27	26.30[c]	3	74.32
4	42.80	16	83.14	28	20.17	4	69.17
5	54.01	17	57.52	29	28.69	5	67.08
6	67.98	18	18.08	30	16.36	β-D-Glc*p*-1	106.74[d]
7	38.40	19	30.33[b]	β-D-Xyl*p*-1	105.70	2	75.82
8	46.84	20	31.97	2	83.66	3	78.81
9	21.29	21	19.05	3	77.76	4	71.79
10	29.21	22	34.44	4	71.04	5	78.13
11	26.30[c]	23	30.33[b]	5	66.71	6	62.90
12	32.64[a]	24	80.00				



116. Brachyoside A

Astragalus brachypterus Fischer [56]
$C_{46}H_{78}O_{18}$, $[\alpha]_D$ +15.5° (*c* 0.1, methanol)
δ_C (CD_3OD)

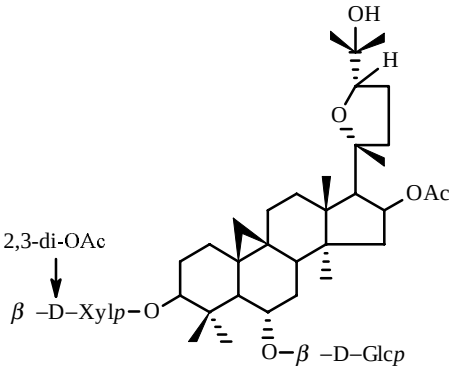
C-1	33.4	C-13	46.6	C-25	74.0	β-D-Xylp_2-1	106.8
2	30.9	14	47.6	26	25.7	2	74.1
3	90.1	15	48.0	27	26.4	3	77.0
4	43.0	16	73.8	28	28.7	4	71.3
5	53.7	17	58.3	29	16.8	5	66.5
6	80.4	18	18.8	30	20.8	β-D-Glc*p*-1	105.5
7	35.3	19	29.3	β-D-Xylp_1-1	106.1	2	75.8
8	46.1	20	32.6	2	74.5	3	78.7
9	22.0	21	19.2	3	83.6	4	72.2
10	30.0	22	35.8	4	69.9	5	77.8
11	27.4	23	30.0	5	67.8	6	63.5
12	34.2	24	81.2				



117. Cephalotoside A

Astragalus cephalotes var. *brevicalyx* [93]
$C_{46}H_{78}O_{18}$, $[\alpha]_D^{20}$ +20.9° (*c* 0.53, methanol)
δ_C (C_5D_5N)

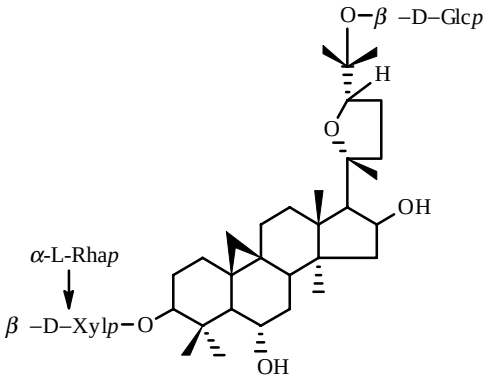
C-1	32.62	C-13	45.67	C-25	72.26	β-D-Xylp_2-1	106.97
2	30.43	14	46.83	26	25.83	2	75.36
3	88.82	15	48.18	27	26.85	3	78.50
4	42.76	16	82.75	28	20.34	4	71.03
5	54.08	17	57.40	29	28.99	5	67.25
6	67.98	18	19.15	30	16.78	β-D-Glc*p*-1	106.23
7	38.51	19	30.55	β-D-Xylp_1-1	107.68	2	75.81
8	47.01	20	31.32	2	75.68	3	78.62
9	21.26	21	17.83	3	78.58	4	71.82
10	29.30	22	34.43	4	71.29	5	77.95
11	26.26	23	30.00	5	67.10	6	62.97
12	32.76	24	90.67				



118. Trojanoside I

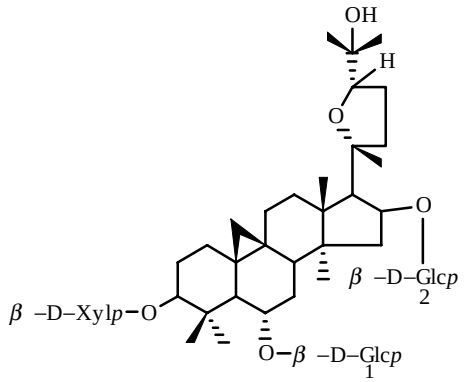
Astragalus trojanus Stev. [94]
$C_{47}H_{74}O_{17}$
δ_C (C_5D_5N)

C-1	32.3	C-13	46.8	C-25	71.3	β-D-Glc*p*-1	105.4
2	30.2	14	47.1	26	28.5	2	76.1
3	89.6	15	45.7	27	27.2	3	79.7
4	42.7	16	76.6	28	20.3	4	72.3
5	52.6	17	58.0	29	28.5	5	78.8
6	79.1	18	20.8	30	16.9	6	63.5
7	34.0	19	28.2	β-D-Xyl*p*-1	104.5	Ac	21.2
8	45.4	20	86.2	2	73.6	Ac	21.3
9	22.1	21	27.2	3	77.3	Ac	21.7
10	29.1	22	37.3	4	69.3	Ac	170.4
11	26.3	23	27.1	5	67.2	Ac	170.8
12	33.3	24	83.3			Ac	171.0



119. Asernestioside A

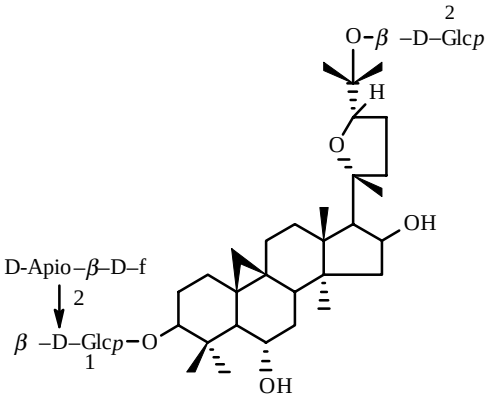
Astragalus ernestii Comb. [30, 68]
$C_{47}H_{78}O_{18}$



120. Trojanoside K

Astragalus trojanus Stev. [94]
$C_{47}H_{78}O_{19}$
δ_C (C_5D_5N)

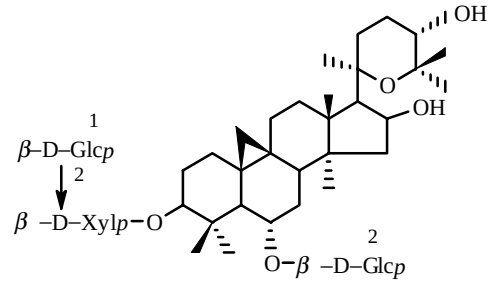
C-1	32.4	C-13	46.9	C-25	72.0	β-D-Glcp_1-1	105.7
2	30.3	14	46.9	26	27.6	2	75.7
3	88.8	15	47.4	27	26.5	3	79.4
4	42.8	16	83.7	28	20.3	4	72.2
5	52.7	17	59.9	29	28.9	5	78.1
6	80.1	18	21.3	30	16.8	6	63.0
7	35.1	19	29.6	β-D-Xyl*p*-1	107.8	β-D-Glcp_2-1	106.6
8	46.1	20	87.2	2	75.8	2	75.7
9	20.3	21	26.4	3	78.7	3	79.0
10	29.4	22	38.8	4	71.4	4	72.0
11	26.7	23	25.9	5	67.2	5	78.5
12	33.2	24	84.5			6	63.4



121. Cycloaraloside F

Astragalus amarus Pall., *Astragalus villosissimus* Bunge [95]
$C_{47}H_{78}O_{19}$, amorphous, $[\alpha]_D^{28}$ -26.1° (*c* 0.84, methanol)
δ_C (C_5D_5N)

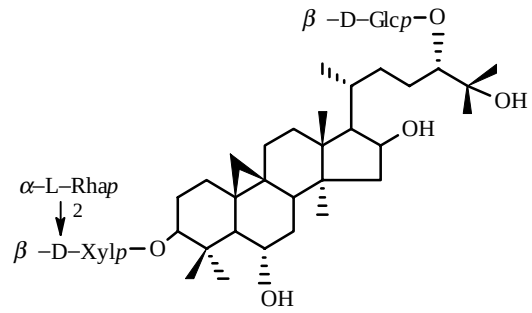
C-1	32.35	C-13	45.13	C-25	78.52	D-Apio-β-D-f-1	111.13
2	30.19	14	45.97	26	22.97	2	77.91
3	88.84	15	46.01	27	25.60	3	80.56
4	42.58	16	73.47	28	19.96	4	75.58
5	53.90	17	58.06	29	28.75	5	66.11
6	67.81	18	21.43	30	16.56	β-D-Glcp_2-1	98.76
7	38.45	19	30.34	β-D-Glcp_1-1	105.46	2	75.09
8	46.69	20	87.14	2	79.39	3	78.44
9	20.73	21	27.80	3	78.71	4	71.28
10	29.37	22	34.95	4	71.95	5	77.86
11	26.14	23	25.90	5	78.28	6	62.67
12	33.41	24	82.03	6	62.85		



122. Cyclocanthoside F

Astragalus tragacantha Habl. [38]
$C_{47}H_{78}O_{19}$, amorphous
δ_C (C_5D_5N)

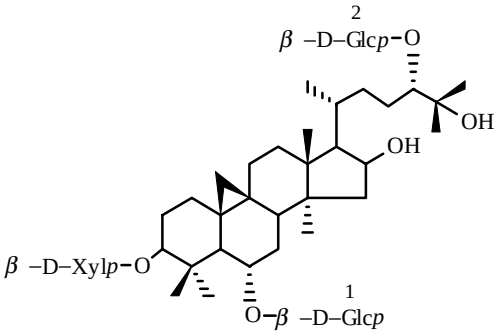
C-1	32.26	C-13	45.99	C-25	75.25	β-D-Glcp_1-1	106.24
2	30.12	14	46.86	26	28.63	2	76.94
3	88.52	15	47.32	27	28.02	3	77.98
4	42.65	16	74.00	28	20.07	4	72.00
5	52.54	17	60.86	29	28.56	5	78.14
6	79.33	18	20.75	30	16.58	6	63.03
7	34.56	19	29.01	β-D-Xyl*p*-1	105.42	β-D-Glcp_2-1	105.02
8	45.72	20	78.97	2	83.87	2	75.66
9	21.20	21	28.88	3	77.72	3	78.97
10	29.01	22	26.74	4	70.93	4	71.95
11	26.38	23	24.11	5	66.55	5	77.98
12	34.24	24	68.84			6	63.19



123. Trojanoside C

Astragalus trojanus Stev. [84]
$C_{47}H_{80}O_{18}$, $[\alpha]_D^{25}$ -5.0° (*c* 0.1, methanol)
δ_C (CD_3OD)

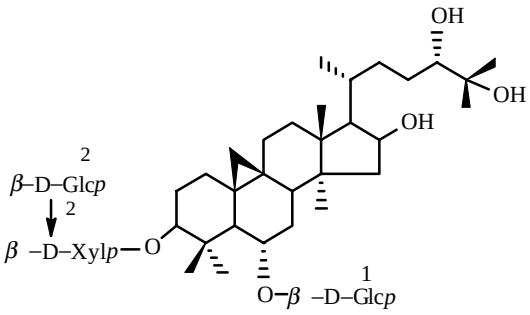
C-1	33.1	C-13	46.1	C-25	73.9	α-L-Rha*p*-1	101.7
2	30.1	14	46.8	26		2	71.8
3	89.5	15	48.8	27	26.3	3	71.7
4	43.0	16	72.3	28	19.9	4	73.6
5	54.5	17	57.8	29	28.2	5	69.7
6	69.2	18		30	16.3	6	18.0
7	38.5	19	31.5	β-D-Xyl*p*-1	105.9	β-D-Glc*p*-1	104.7
8	48.4	20	30.7	2	78.5	2	75.2
9	21.4	21	17.7	3	78.5	3	77.7
10	29.9	22	32.9	4	71.2	4	71.2
11	26.6	23	29.3	5	65.9	5	77.7
12	33.7	24	89.8			6	62.2



124. Brachyoside C

Astragalus brachypterus Fischer [56]
$C_{47}H_{80}O_{19}$, $[\alpha]_D$ +12.5° (*c* 0.1, methanol)
δ_C (CD_3OD)

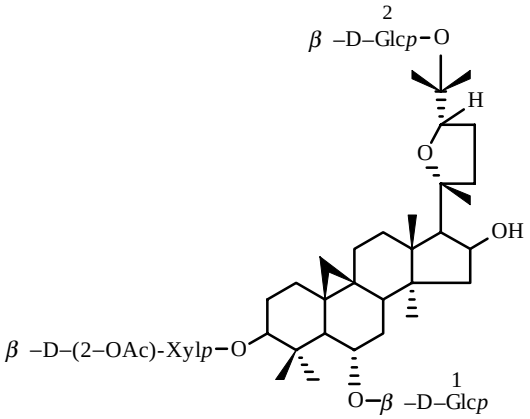
C-1	32.7	C-13	46.3	C-25	73.5	β-D-Glcp_1-1	104.6
2	30.1	14	47.1	26	26.5	2	75.2
3	89.8	15	48.1	27	24.0	3	78.2
4	42.7	16	72.5	28	19.8	4	71.3
5	52.9	17	57.6	29	28.1	5	77.6
6	79.9	18	18.0	30	16.2	6	62.7
7	34.8	19	28.9	β-D-Xyl*p*-1	107.1	β-D-Glcp_2-1	104.6
8	46.6	20	30.9	2	75.2	2	75.2
9	21.9	21	17.5	3	77.7	3	77.8
10	29.8	22	33.0	4	71.0	4	71.3
11	26.8	23	29.4	5	66.4	5	78.2
12	33.7	24	89.7			6	62.2



125. Cyclocanthoside G

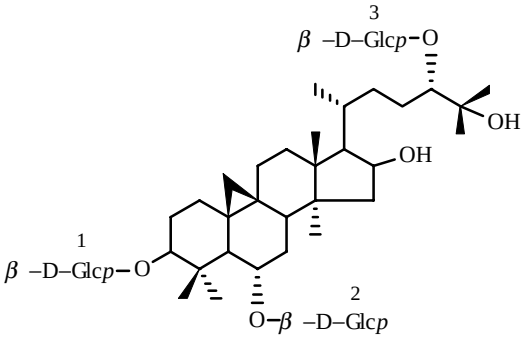
Astragalus tragacantha Habl. [54]
$C_{47}H_{80}O_{19}$, mp 190-195°C ($CHCl_3$—CH_3OH—H_2O, 70:23:4), $[\alpha]_D^{28}$ 0° (*c* 1.18, methanol)
δ_C (C_5D_5N)

C-1	32.10	C-13	45.82	C-25	72.55	β-D-Glcp_1-1	105.11
2	28.56	14	46.89	26	25.75	2	75.66[a]
3	88.39	15	47.69	27	26.43	3	78.85
4	42.63	16	71.98	28	19.72	4	71.95
5	52.28	17	57.11	29	28.64	5	77.97
6	78.87	18	18.23	30	16.56	6	63.20
7	33.95	19	27.88	β-D-Xyl*p*-1	105.36	β-D-Glcp_2-1	106.25
8	45.09	20	28.28	2	83.86	2	75.66[a]
9	21.43	21	18.34	3	76.93	3	78.15
10	30.06	22	32.98	4	70.90	4	71.91
11	26.29	23	27.70	5	66.58	5	77.79
12	33.19	24	77.12			6	63.02



126. Agroastragaloside IV

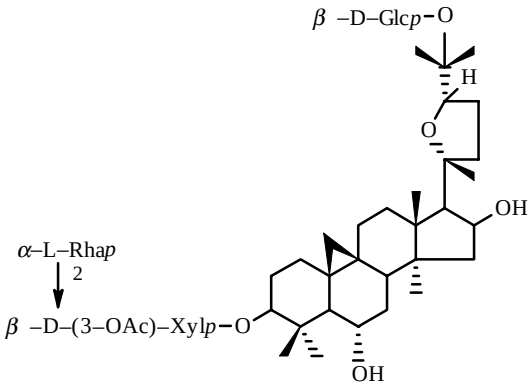
Astragalus membranaceus Bunge [96]
$C_{47}H_{80}O_{20}$



127. Trojanoside D

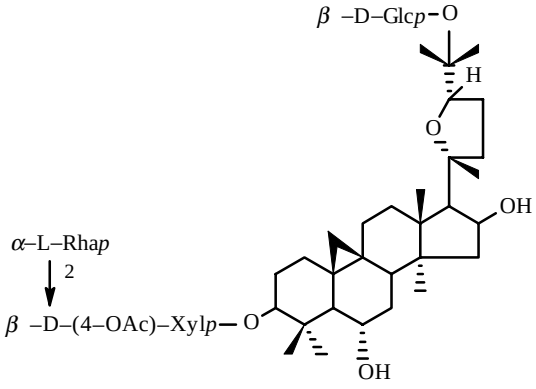
Astragalus trojanus Stev. [84]
$C_{48}H_{82}O_{20}$, $[\alpha]_D^{25}$ +22.5° (*c* 0.1, methanol)
The ^{13}C NMR spectrum of the genin part agrees with that of brachyoside C (**124**).
δ_C (CD_3OD)

β-D-Glcp_1-1	104.8	β-D-Glcp_2-1	105.8	β-D-Glcp_3-1	104.8
2	75.2	2	75.2	2	75.0
3	78.2	3	78.2	3	77.9
4	71.4	4	71.4	4	71.4
5	77.5	5	77.5	5	77.8
6	62.5	6	62.2	6	62.5



128. Asernestioside B

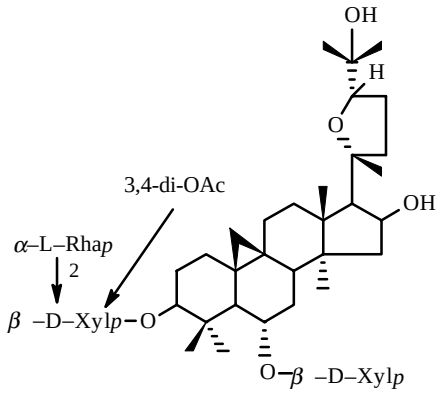
Astragalus ernestii Comb. [30, 68]
$C_{49}H_{80}O_{19}$



129. Asernestioside C

Astragalus ernestii Comb. [30, 68]
$C_{49}H_{80}O_{19}$, mp 204-207°C (methanol), $[\alpha]_D$ -13.22° (*c* 0.32, methanol)
δ_C (C_5D_5N)

C-1	32.4	C-15	46.0	C-29	28.6	β-D-Glc*p*-1	98.8
2	30.3	16	73.5	30	16.6	2	75.1
3	88.4	17	58.1	β-D-Xyl*p*-1	105.4	3	78.4
4	42.6	18	21.4	2	77.6	4	71.3
5	54.0	19	30.4	3	74.6	5	77.9
6	67.7	20	87.2	4	73.3	6	62.7
7	38.4	21	27.8	5	62.5	Ac	20.8
8	46.7	22	35.0	α-L-Rha*p*-1	101.9	Ac	170.5
9	20.8	23	25.9	2	72.3		
10	29.9	24	82.0	3	72.5		
11	26.2	25	78.5	4	74.0		
12	33.4	26	23.0	5	69.9		
13	45.1	27	25.6	6	18.6		
14	46.0	28	20.0				



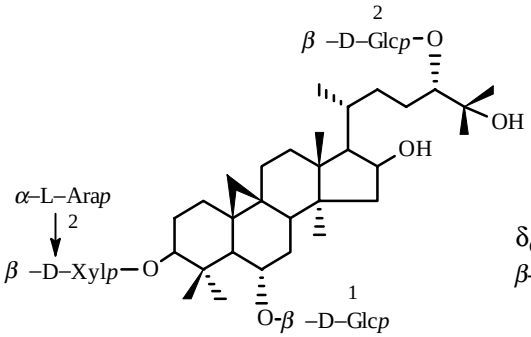
130. Trojanoside J

Astragalus trojanus Stev. [94]

$C_{50}H_{80}O_{19}$

δ_C (C_5D_5N)

C-1	32.7	C-15	46.6	C-29	28.7	β-D-Xylp-1	106.6
2	30.4	16	74.3	30	17.3	2	76.2
3	89.2	17	59.0	β-D-Xylp-1	104.5	3	79.3
4	43.2	18	21.2	2	75.2	4	71.9
5	52.8	19	27.3	3	72.6	5	67.8
6	78.5	20	88.2	4	70.3	Ac	21.2
7	34.3	21	29.5	5	61.7	Ac	21.7
8	44.6	22	35.8	α-L-Rhap-1	102.9	Ac	171.0
9	22.1	23	27.2	2	71.5	Ac	171.1
10	29.0	24	82.5	3	73.3		
11	27.2	25	72.1	4	74.6		
12	34.1	26	29.0	5	72.9		
13	46.1	27	28.0	6	19.5		
14	47.0	28	20.5				



131. Trojanoside F

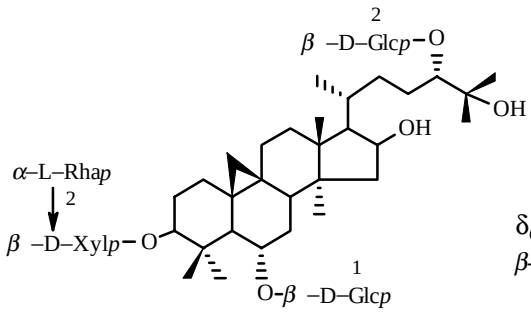
Astragalus trojanus Stev. [84]

$C_{52}H_{88}O_{23}$, $[\alpha]_D^{25}$ +5.2° (*c* 0.1, methanol)

The ^{13}C NMR spectrum of the genin part agrees with that of brachyoside C (**124**).

δ_C (CD_3OD)

β-D-Xylp-1	105.6	β-D-Glcp$_1$-1	104.7	β-D-Glcp$_2$-1	104.7	α-L-Arap-1	106.2
2	82.8	2	75.3	2	75.2	2	73.1
3	76.6	3	78.2	3	77.6	3	74.7
4	70.6	4	71.4	4	71.1	4	69.1
5	65.7	5	77.4	5	77.7	5	66.8
		6	62.2	6	62.5		



132. Trojanoside E

Astragalus trojanus Stev. [84]

$C_{53}H_{90}O_{23}$, $[\alpha]_D^{25}$ +2.6° (*c* 0.1, methanol)

The ^{13}C NMR spectrum of the genin part agrees with that of brachyoside C (**124**).

δ_C (CD_3OD)

β-D-Xylp-1	105.9	β-D-Glcp$_1$-1	104.6	β-D-Glcp$_2$-1	104.6	α-L-Rhap-1	101.6
2	78.7	2	75.3	2	75.2	2	71.9
3	78.1	3	78.2	3	77.7	3	71.7
4	71.1	4	71.3	4	71.3	4	73.5
5	66.1	5	77.5	5	77.7	5	69.5
		6	62.2	6	62.2	6	18.0

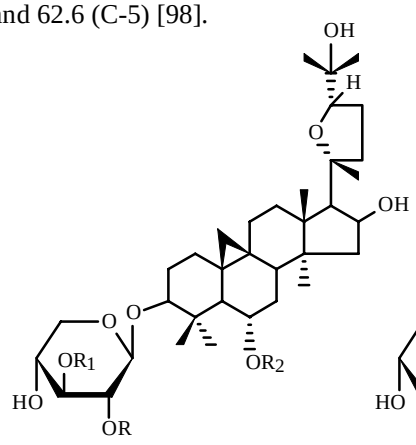
TABLE 5. Effect of an Acetyl Group in the 3-O-β-D-Xylopyranoside of Cycloartane Glycosides on Chemical Shifts of Pentose C Atoms (δ, ppm,C_5D_5N, 0 = TMS)

C atom	Effect								
	2-OAc			3-OAc			4-OAc		
	δ_{133} [97]	δ_{67} [97]	$\Delta\delta=\delta_{67}-\delta_{133}$	δ_{135} [98]	δ_{134} [98]	$\Delta\delta=\delta_{134}-\delta_{135}$	δ_{86} [54]	δ_{102} [54]	$\Delta\delta=\delta_{102}-\delta_{86}$
1	107.63	104.79	-2.84	107.1	106.6	-0.5	107.60	107.38	-0.22
2	75.63	76.15	+0.52	75.2	72.8	-2.4	75.61	75.74	+0.13
3	78.50	75.63	-2.87	77.7	78.7	+1.0	78.48	74.91	-3.57
4	71.26	71.27	+0.01	71.3	69.1	-2.2	71.25	73.23	+1.98
5	67.05	67.02	-0.03	66.6	66.2	-0.4	67.02	63.17	-3.85
	δ_{79} [83]	δ_{97} [83]	$\Delta\delta=\delta_{97}-\delta_{79}$	δ_{137} [99]	δ_{136} [99]	$\Delta\delta=\delta_{136}-\delta_{137}$	δ^*_{124} [56]	δ^*_{98} [56]	$\Delta\delta=\delta_{98}-\delta_{124}$
1	107.43	104.95	-2.48	107.4	107.3	-0.1	107.1	107.0	-0.1
2	75.38	76.21	+0.83	75.2	73.2	-2.0	75.2	75.1	-0.1
3	78.44	75.55	-2.89	78.6	79.4	+0.8	77.7	74.7	-3.0
4	71.14	71.23	+0.09	71.1	69.3	-1.8	71.0	73.0	+2.0
5	66.96	67.10	+0.14	66.8	66.7	-0.1	66.4	63.1	-3.3

*Spectra recorded in CD_3OD.

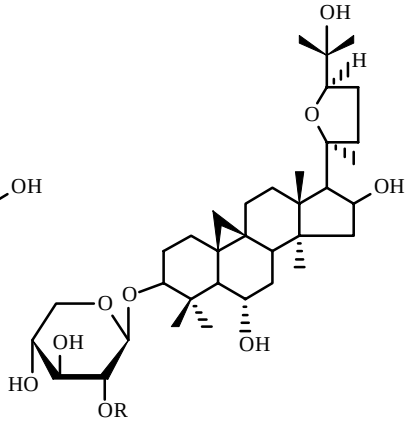
Acetylated glycosides are common for *Astragalus* plants. The acetic-acid residues are localized both in the genin part and in the carbohydrate chain of the glycosides. Acetyls are located mainly in the D-xylose situated on C-3 of the genins. Glycosides with three acetyls in the 3-O-β-D-xylopyranoside are known [98, 99].

The presence of a fully acetylated terminal D-xylose in a molecule can be rather simply proven. A peak for tri-O-acetylxylopyranosoxonium with *m*/*z* 259 is observed in the electron-impact mass spectrum (EIMS) and the fast-atom bombardment mass spectrum (FABMS) of the glycoside [75, 93, 98]. The PMR spectrum of the glycoside with resonance lines for acetoxyls can confirm this structural fragment by a low-field shift of the signals for D-xylose H-2, H-3, and H-4, which are geminal to acetoxyls. The ^{13}C NMR spectrum of the acetylated glycoside can lead to the analogous conclusion. Since the size of the β-effects from acetylation in monosaccharides is greater than that of α-effects, signals of all C atoms in fully acetylated β-D-xylopyranosides undergo a significant high-field shift and are observed at δ 103.4 (C-1), 72.5 (C-2), 72.9 (C-3), 70.0 (C-4), and 62.6 (C-5) [98].

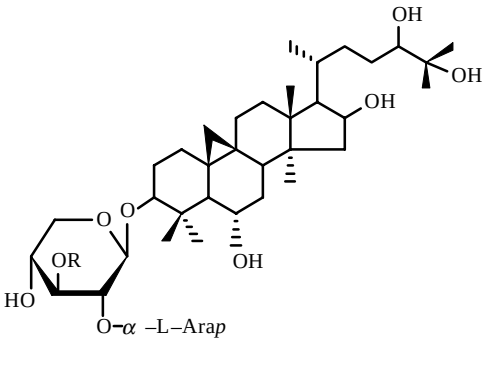


133 - 144

133: R = R_1 = R_2 = H;
134: R = H, R_1 = Ac, R_2 = β-D-Glc*p*;
135: R = R_1 = H, R_2 = β-D-Glc*p*;
136: R=H, R_1=Ac, R_2 = β-D-Xyl*p*;
137: R = R_1 = H, R_2 = β-D-Xyl*p*;
138: R = Ac, R_1 = H, R_2 = β-D-Glc*p*;
139: R = Ac, R_1 = H, R_2 = β-D-Xyl*p*;
140: R = H, R_1 = Ac, R_2 = β-D-Glc*p*;
141: R = R_1 = Ac, R_2 = β-D-Glc*p*;
142: R = R_1 = Ac, R_2 = β-D-Xyl*p*;
143: R = α-L-Ara*p*, R_1 = Ac, R_2 = β-D-Xyl*p*;
144: R = α-L-Ara*p*, R_1 = H, R_2 = β-D-Xyl*p*



145: R = Ac;
146: R = H



147: R = Ac;
148: R = H

TABLE 6. Increments of Molecular Rotations of Glycosides Caused by Acetyl Groups on C-2 and C-3 of the β-D-Xylopyranoside

Compound	M	$[\alpha]_D$, deg	$[M]_D$, deg	$\Delta[M]_D$, (Contribution of Ac on C-2)	$\Delta[M]_D$, (Contribution of Ac on C-3)	Reference
138	826	+31	+256			98
135	784	+24	+188	+68		98
145	664	+40	+266			101
146	622	+32	+199	+67		101
139	796	+30	+239			102
137	754	+24	+181	+58		103, 104
140	826	+15	+124			98
135	784	+24	+188		-64	98
141	868	+13	+113			98
138	826	+31	+256		-143	98
147	798	0	0			105
148	756	+27	+204		-204	106
143	928	-46	-427			107
144	886	-9	-80		-347	103
142	838	+21	+176			102
139	796	+30	+239		-63	102

A structural analysis of mono- and diacetylated β-D-xylopyranosides is interesting because each of them has three isomers. The signal for H-4, which is geminal to an acetoxyl, is observed in the PMR spectrum at δ 5.25-5.35 as a triplet of doublets with SSCC 9 and 5.6 Hz (C_5D_5N, TMS) [30, 54] and is easily recognized. Therefore, the position of the acetyl on C-4 of the β-D-xylopyranoside is easily determined from the routine PMR spectrum. Atoms H-2 and H-3 of a β-D-xylopyranoside containing acetyls on C-2 and C-3 resonate in the PMR spectrum at δ 5.26-5.49, often as triplets with identical SSCCs [64, 100]. Thus, unambiguous assignment of these signals and determination of the location of the acetyl requires additional data. These could be parameters of multi-frequency PMR spectra and results of periodate oxidation for monoacetyl glycosides. Data from ^{13}C NMR spectra can also be used.

Table 5 lists chemical shifts of C atoms in the 3-O-β-D-xylopyranoside of cycloartane glycosides and its monoacetates. It can be seen that the acetyl has a significant effect on the chemical shifts of only three C atoms. Signals of α-C atoms undergo low-field shifts; of β-C atoms, high-field.

A correlation exists between the position of the acetyl in the β-D-xylopyranoside and its contribution to the molecular rotation of the glycosides. Increments of molecular rotation between acetylated and the corresponding de-acetylated glycosides (Table 6) indicate that the contribution of a 2-O-acetyl to the molecular rotation is positive whereas that of a 3-O-acetyl is negative. Therefore, this parameter is interesting for choosing the location of the acetyl between the alternative positions C-2 and C-3 in the β-D-xylopyranoside.

Asernestioside C (**129**) is a cyclosiversigenin trioside with one acetyl in the carbohydrate. It is the first cycloartane glycoside for which the structure was proved without using chemical methods [30]. A negative NOE between H-3 of the genin and the anomeric proton of the monosaccharide bonded to C-3 of the genin was first observed in NMR spectroscopy of triterpene glycosides using this glycoside as an example. A negative NOE was also measured by these same authors in several triterpene glycosides of various classes. This phenomenon was used to prove the structure of cyclocanthoside E (**86**) [54].

The advantage of using β-effects of glycosylation to determine the position of a glycosyl substituent on C-6 of cycloartanes was based on an analysis of experimental results [38]. Several factors make it difficult to establish glycosylation of cycloartanes at the 6α-hydroxyl using ^{13}C NMR spectra of glycosides containing more than two monosaccharides. A nonglycosylated C-6 atom of 6α-hydroxycycloartanes resonates in the ^{13}C NMR spectrum at δ 68.29-68.39; C-5 of pentosopyranose, C-4 of L-arabinopyranose, and C-5 of L-rhamnopyranose, close to this range; and C-24 of cyclocephalogenin, in this same range (glycosides **74**, **81**, **121**).

The signal for a glycosylated C-6 of cycloartanes is observed at δ 78.30-79.69. This part of the spectrum is even more densely populated. This same interval contains signals for D-glucopyranose C-3 and C-5, D-xylopyranose C-3, nonglycosylated genin C-3, and cyclocephalogenin C-20. At times, the C-6 signal overlaps exactly one of these signals. Even DEPT experiments are useless for analyzing this spectral region because these C atoms are identical chemically with the exception of cyclocephalogenin C-20. Obviously, unambiguous assignment of signals in this part of the spectrum is not a simple matter. Therefore, it seemed possible to use the β-effects of glycosylating C-6 of cycloartanes, i.e., the effect of a glycosyl substituent on C-6 on the spectral properties of C-5 and C-7.

The signal for C-5 in ^{13}C NMR spectra of cycloartanes that are not glycosylated at C-6 is observed at δ 53.96-54.01 as a rather isolated singlet and is readily identified. In spectra of cycloartanes glycosylated at C-6, C-5 undergoes a glycosylation β-effect and appears at higher field, at δ 52.03-52.52. The magnitude of the β-effect is approximately 1.5-2.0 ppm to the negative side.

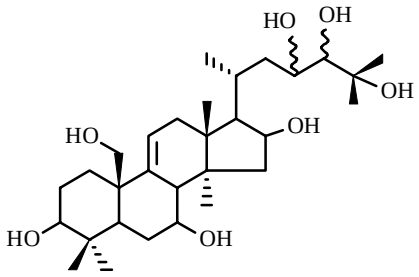
Glycosylation has a more substantial effect on the other β-atom, C-7. The signal for C-7 in spectra of unsubstituted compounds occurs at δ 38.45-38.85; in spectra of glycosides, at δ 33.50-35.05. In this instance, the magnitude of the β-effect is 3.4-5.3 ppm, also to the negative side.

An examination of the spectra of many glycosides indicates that these β-effects are regular, do not depend on the nature of the glycosylating carbohydrate, and can be reliably used in structural investigations.

The anomeric proton of D-apio-β-D-furanoside resonates as a doublet with SSCC J = 2 Hz or a broad singlet [73, 95]. This fact prompted a slight broadening of the conclusions about the SSCC of an anomeric proton, equal to 7-8 Hz [79]. This constant indicates an axial orientation of the anomeric proton, suggesting the $^4C_1$-conformation and, therefore, the pyranose form of the monosaccharide.

LANOSTANE AND 9,10-SECOCYCLOARTANE TRITERPENOIDS

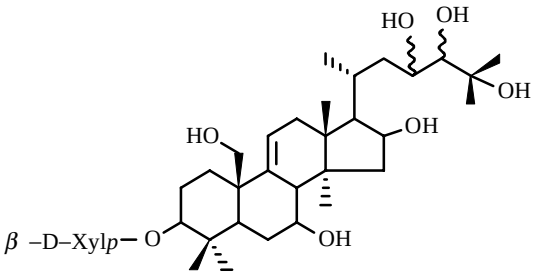
Astragalus lanostane triterpenoids are not common. At present, they are represented by orbigenin (**149**) and orbicoside (**150**), which occur in aerial organs of *Astragalus orbiculatus* Ledeb. [48, 109, 110]. Orbicoside is orbigenin 3-O-β-D-xylopyranoside. This is the first instance for *Astragalus* plants where lanostane compounds were found with cycloartane triterpenoids.



149. Orbigenin

Astragalus orbiculatus Ledeb. [48, 109]
$C_{30}H_{52}O_7$, mp 298-301°C (methanol)
δ_C (C_5D_5N)

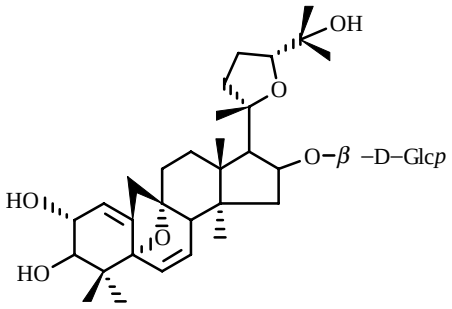
C-1	30.99	C-9	142.01	C-17	55.50	C-24	79.13
2	28.66	10	45.30	18	15.72	25	74.24
3	78.20	11	121.57	19	60.54	26	24.69
4	39.71	12	37.54	20	27.42	27	28.90
5	50.34	13	45.37	21	20.47	28	19.28
6	32.22	14	45.38	22	43.03	29	29.18
7	71.84	15	49.56	23	73.21	30	17.70
8	50.87	16	72.63				



150. Orbicoside

Astragalus orbiculatus Ledeb. [48, 110]
$C_{35}H_{60}O_{11}$, mp 281-283° C (methanol)
δ_C (C_5D_5N)

C-1	30.87	C-10	44.93	C-19	60.54	C-28	19.28
2	27.22	11	121.58	20	27.42	29	28.57
3	88.87	12	37.54	21	20.47	30	18.10
4	39.84	13	45.37	22	43.03	β-D-Xylp-1	107.73
5	50.44	14	45.37	23	73.20	2	75.48
6	31.85	15	49.52	24	79.14	3	78.60
7	71.79	16	72.63	25	74.25	4	71.23
8	50.87	17	55.50	26	24.70	5	67.14
9	141.86	18	15.69	27	28.89		



151. Prusianoside A

Astragalus prusianus DC [71]
$C_{36}H_{56}O_{11}$, $[\alpha]_D^{25}$ -112.5° (*c* 0.004, methanol)
δ_C (CD_3OD)

C-1	112.9	C-10	147.5	C-19	46.5	C-28	22.1
2	73.8	11	34.7	20	88.3	29	22.6
3	81.6	12	31.8	21	25.5	30	21.7
4	37.8	13	46.7	22	39.8	β-D-Glcp-1	106.7
5	84.9	14	47.4	23	26.4	2	75.6
6	135.5	15	46.5	24	85.3	3	78.6
7	127.1	16	84.8	25	73.0	4	71.8
8	49.5	17	60.0	26	26.3	5	77.8
9	80.0	18	19.3	27	27.1	6	62.9

The first 9,10-secocycloartanoid prusianoside A (**151**) from this genus was isolated from roots of *Astragalus prusianus* DC [71].

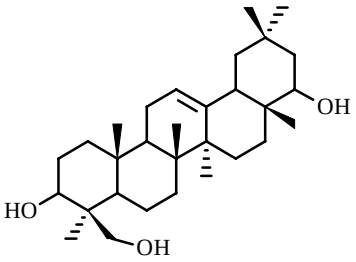
4-Monomethyl- and 4,4-demethylcycloartanes have not yet been found in *Astragalus* plants.

OLEANANE TRITERPENOIDS

Oleanane triterpenoids from *Astragalus* plants are also not common. Soyasapogenol B (**152**) [111] and the new triterpenoid sapogenin II (**153**) [112] were obtained from the total triterpenoids of the aerial organs of *Astragalus glycyphyllos* L., which is used in folk medicine in Bulgaria.

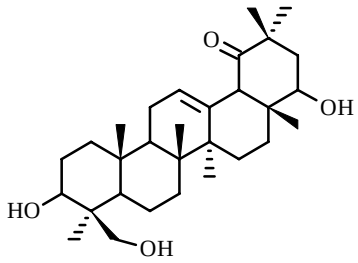
Astragaloside VIII (**154**) is a trioside of soyasapogenol B and was isolated from roots of *Astragalus membranaceus* Bunge [113]. Its structure differs from that of soyasaponin I (**155**), which is found in certain representatives of the bean family, in that it has a β-D-xylopyranose instead of a β-D-galactopyranose.

In addition to methyl ethers of astragaloside VIII (**154a**) and soyasaponin I (**155a**), four new unnamed glycosides **156**-**159** were isolated from seeds of *Astragalus complanatus* R. Br. [114]. Glycosides **154a**, **155a**, and **156**-**159** are methyl ethers of the corresponding glycosides that are formed and separated after treatment of the total glycosides with diazomethane. Glycosides **154**, **155**, **158**, and **159** are derivatives of soyasapogenol B; **156** and **157**, of the new sapogenin.



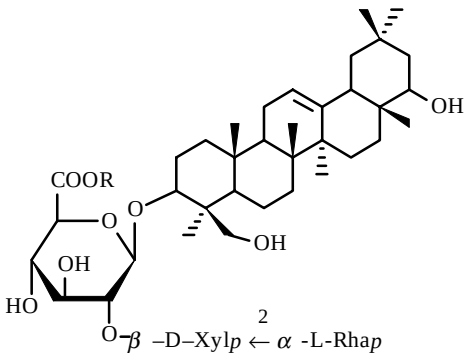
152.Soyasapogenol B

Astragalus glycyphyllos L. [111]
$C_{30}H_{50}O_3$, mp 255-257°C, $[\alpha]_D$ +62.5° (*c* 0.4, methanol) [114]



153. Sapogenin II

Astragalus glycyphyllos L. [112]
$C_{30}H_{48}O_4$, mp 299-301°C (ethylacetate—methanol, 1:1)

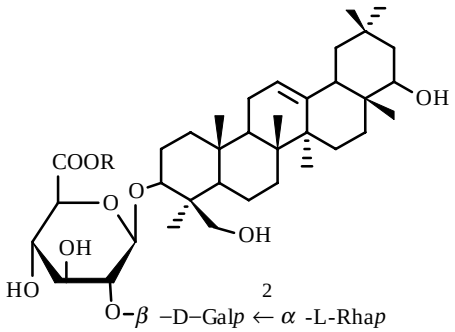


154: R = H; **154a:** R = Me

154. Astragaloside VIII

Astragalus membranaceus Bunge [113],
Astragalus complanatus R. Br. [114]
$C_{47}H_{76}O_{17}$, mp 223-224°C (methanol),
$[\alpha]_D^{18}$ -12.1° (*c* 1.0, methanol) [113]
154a: $C_{48}H_{78}O_{17}$, mp 278-280°C (methanol),
$[\alpha]_D^{18}$ -12.9° (*c* 1.0, methanol) [113]
δ_C (C_5D_5N) [114]

C-1	38.8	C-13	144.8	C-25	15.6	Me	52.1
2	26.7[a]	14	42.4	26	17.0	β-D-Xylp-1	102.5
3	91.1	15	26.4[a]	27	25.6	2	79.5
4	44.3	16	28.6	28	28.6	3	78.2[b]
5	56.4	17	38.0	29	33.3	4	70.8
6	18.6	18	45.3	30	21.1	5	66.8
7	33.3	19	46.7	β-D-GlcUA-1	105.4	α-L-Rhap-1	102.3
8	39.9	20	30.9	2	78.6[b]	2	72.4[d]
9	47.7	21	42.4	3	76.8	3	72.8[d]
10	36.5	22	75.5	4	73.6	4	74.3
11	24.0	23	23.0	5	77.5	5	69.4
12	122.4	24	62.8	6	170.4	6	18.9

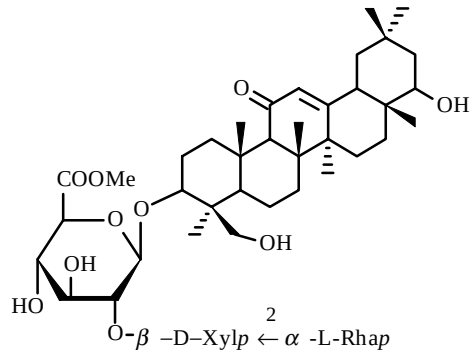


155: R = H; **155a:** R = Me

155. Soyasaponin I

Astragalus complanatus R. Br. [114]
$C_{48}H_{78}O_{18}$, mp 238-240°C (methanol),
$[\alpha]_D$ -8.5° (*c* 1.0, methanol) [139]
155a: $C_{49}H_{80}O_{18}$, $[\alpha]_D$ -4.1° (*c* 1.0, methanol) [114]
δ_C (C_5D_5N) [114]

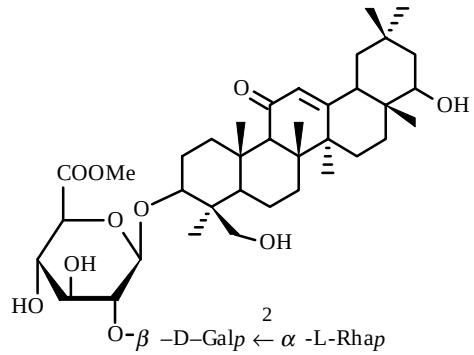
C-1	38.6	C-13	144.9	C-25	15.8	Me	52.2
2	26.7[a]	14	43.9	26	17.0	β-D-Gal*p*-1	101.8
3	91.3	15	26.4[a]	27	25.7	2	76.8[b]
4	43.9	16	28.6	28	28.7	3	76.6[b]
5	56.1	17	38.0	29	33.2	4	71.2
6	18.5	18	45.3	30	21.2	5	76.9[b]
7	33.2	19	46.8	β-D-GlcUA-1	105.5	6	61.6
8	39.9	20	30.9	2	78.6	α-L-Rha*p*-1	102.5
9	47.8	21	42.3	3	76.5[b]	2	72.4[d]
10	36.5	22	75.6	4	73.6	3	72.8[d]
11	24.1	23	23.0	5	77.7	4	74.3
12	122.3	24	63.6	6	170.4	5	69.4
						6	19.0



156. No name

Astragalus complanatus R. Br. [114]
$C_{48}H_{76}O_{18}$, $[\alpha]_D$ +13.3° (*c* 0.5, methanol)
δ_C (C_5D_5N)

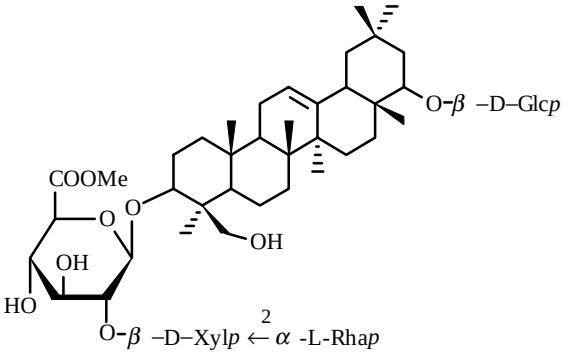
C-1	39.5	C-13	169.3	C-25	16.5	Me	52.1
2	26.7	14	45.4	26	18.7	β-D-Xyl*p*-1	102.6
3	91.0	15	26.7	27	23.1[a]	2	79.5
4	44.7	16	27.9	28	28.3	3	78.2[b]
5	56.1	17	37.8	29	33.2	4	70.9
6	17.9	18	45.5	30	21.7	5	66.9
7	33.2	19	45.2	β-D-GlcUA-1	105.5	α-L-Rha*p*-1	102.4
8	44.0	20	30.9	2	78.6[b]	2	72.4[c]
9	61.8	21	42.0	3	76.8	3	72.8[c]
10	37.0	22	74.9	4	73.6	4	74.3
11	199.4	23	23.0[a]	5	77.5	5	69.5
12	128.4	24	62.8	6	170.3	6	19.0



157. No name

Astragalus complanatus R. Br. [114]
$C_{49}H_{78}O_{19}$, $[\alpha]_D$ +8° (*c* 0.2, methanol)
δ_C (C_5D_5N)

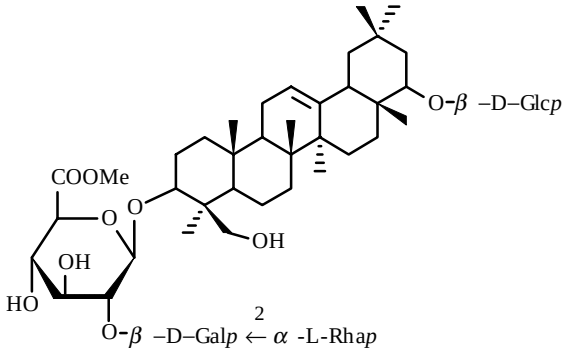
C-1	39.3	C-13	169.7	C-25	16.7	Me	52.0
2	26.7[a]	14	45.0	26	18.5	β-D-Gal*p*-1	101.5
3	90.9	15	26.5[a]	27	22.8[b]	2	76.3[c]
4	44.5	16	27.7	28	28.1	3	76.2[c]
5	55.9	17	36.8	29	32.9	4	71.0
6	17.7	18	45.2	30	21.5	5	76.7[c]
7	33.0	19	45.0	β-D-GlcUA-1	105.3	6	61.6
8	43.8	20	30.7	2	78.4	α-L-Rha*p*-1	102.2
9	61.6	21	41.8	3	76.3[c]	2	72.2[d]
10	36.6	22	74.7	4	73.4	3	72.5[d]
11	199.3	23	22.7[b]	5	77.5	4	74.1
12	128.2	24	63.3	6	170.1	5	69.2
						6	18.7



158. No name

Astragalus complanatus R. Br. [114]
$C_{54}H_{88}O_{22}$, $[\alpha]_D$ -68.3° (*c* 0.4, methanol)
δ_C (C_5D_5N)

C-1	38.8	C-15	26.6[a]	C-29	32.3	α-L-Rha*p*-1	102.3
2	25.9[a]	16	28.6	30	21.0	2	72.4[c]
3	91.1	17	37.4	β-D-GlcUA-1	105.4	3	72.7[c]
4	44.3	18	45.8	2	78.8[b]	4	74.3
5	56.3	19	46.4	3	76.8	5	69.4
6	18.6	20	30.5	4	73.6	6	18.9
7	33.3	21	37.4	5	77.5	β-D-Glc*p*-1	102.6
8	39.7	22	82.5	6	170.4	2	75.2
9	47.7	23	22.9	Me	52.0	3	78.2[b]
10	36.5	24	63.0	β-D-Xyl*p*-1	102.5	4	71.9
11	23.9	25	15.6	2	79.4	5	78.5[b]
12	122.5	26	16.9	3	78.1[b]	6	62.8
13	144.3	27	25.2	4	70.8		
14	42.2	28	28.6	5	66.8		



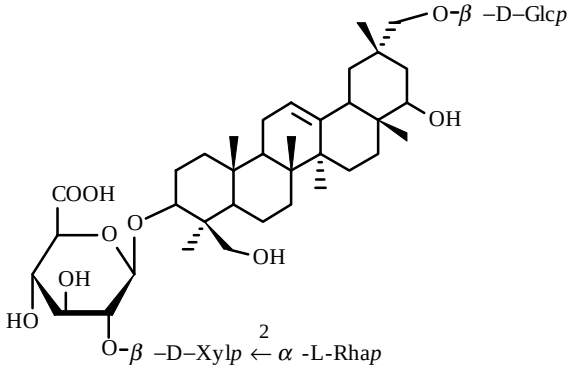
159. No name

Astragalus complanatus R. Br. [114]
$C_{55}H_{90}O_{23}$, $[\alpha]_D$ -37.0° (*c* 0.8, methanol)
δ_C (C_5D_5N)

C-1	38.6	C-16	28.6	β-D-GlcUA-1	105.5	α-L-Rha*p*-1	102.4
2	26.0[a]	17	37.4	2	78.9	2	72.4[c]
3	91.1	18	45.8	3	76.4[b]	3	72.8[c]
4	43.9	19	46.4	4	73.6	4	74.3
5	56.1	20	30.6	5	77.7	5	69.4
6	18.5	21	37.5	6	170.4	6	19.0
7	33.3	22	82.5	Me	52.1	β-D-Glc*p*-1	102.6
8	39.8	23	23.0	β-D-Gal*p*-1	101.7	2	75.3
9	47.8	24	63.6	2	76.6[b]	3	78.2[d]
10	36.4	25	15.8	3	76.5[b]	4	72.0[c]
11	24.0	26	16.9	4	71.2	5	78.3[d]
12	122.5	27	25.3	5	76.9[b]	6	63.1
13	144.4	28	28.7	6	61.6		
14	42.3	29	32.5				
15	26.7[a]	30	21.1				

The new sapogenin differs from soyasapogenol B by the presence of an additional ketone on C-11. All glycosides contain β-D-glucuronic acid bonded to C-3 of the genins. Glycosides **156** and **157** have a bisdesmosidic structure. A β-D-glucopyranose located on C-22 of soyasapogenol B makes up the second carbohydrate chain in these glycosides.

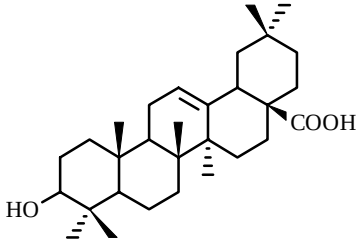
The new oleanane bisdesmosidic tetraoside astrojanoside A (**160**) was isolated from *Astragalus trojanus* Stev. [84]. Oleanolic acid (**161**) was found in *Astragalus unifoliolatus* Bunge [65].



160. Astrojanoside A

Astragalus trojanus Stev. [84]
$C_{53}H_{86}O_{23}$, $[\alpha]_D^{25}$ +16.7° (*c* 0.1, methanol)
δ_C (C_5D_5N)

C-1	39.9	C-16	30.1	β-D-GlcUA-1	105.2	α-L-Rhap-1	102.0
2	26.9	17	38.7	2	78.6	2	72.2
3	92.1	18	46.1	3	76.8	3	72.0
4	45.5	19	42.1	4	74.0	4	74.0
5	57.5	20	36.0	5	77.0	5	69.0
6	20.1	21	37.1	6	176.0	6	18.0
7	34.4	22	77.0	β-D-Xylp-1	102.9	β-D-Glcp-1	104.8
8	40.8	23	22.8	2	79.1	2	75.1
9	48.9	24	63.8	3	78.4	3	78.1
10	37.6	25	16.2	4	71.0	4	70.6
11	24.5	26	17.5	5	66.5	5	77.9
12	124.0	27	25.1			6	62.6
13	144.8	28	20.0				
14	43.5	29	80.1				
15	26.6	30	24.9				



161. Oleanolic acid

Astragalus unifoliolatus Bunge [65]
$C_{30}H_{48}O_3$, mp 301-302°C (ethanol),
$[\alpha]_D^{24}$ +75° (*c* 1.2, $CHCl_3$—CH_3OH, 1:1) [115]
δ_C (C_5D_5N)

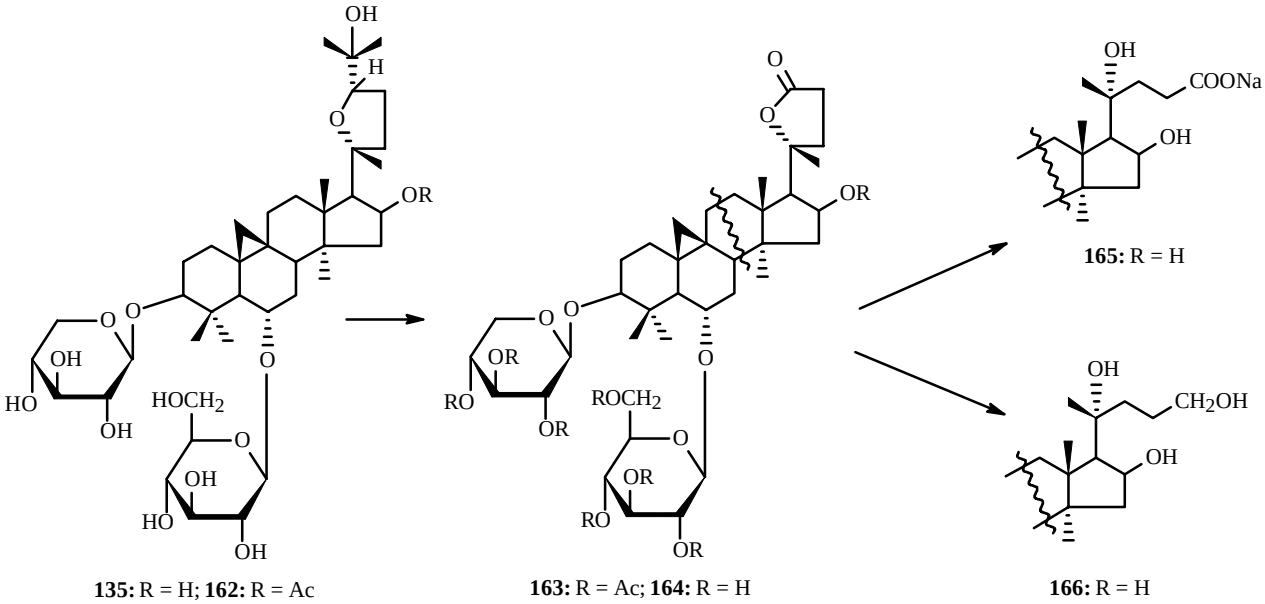
C-1	38.95	C-9	48.04	C-17	46.70	C-24	16.52
2	28.34	10	37.39	18	42.04	25	15.55
3	78.09	11	23.82	19	46.54	26	17.46
4	39.37	12	122.48	20	30.96	27	26.16
5	55.82	13	144.90	21	34.26	28	180.38
6	18.81	14	42.18	22	32.22	29	33.28
7	32.22	15	28.09	23	28.77	30	23.78
8	39.76	16	23.74				

CHEMICAL TRANSFORMATIONS OF CYCLOARTANE GLYCOSIDES

Several cycloartane glycosides exhibit a wide spectrum of physiological activity. Therefore, the available glycosides of this class deserve attention as starting materials for chemical transformations to reveal structure—activity relationships and create biologically active compounds. Transformations of certain cyclosiversigenin glycosides are notable. Methods for chemical transformation of cycloartane glycosides have been developed in two directions: 1) transformation of the genin part of glycosides with retention of the carbohydrate components and 2) regioselective glycosylation. The first method has been used to transform the widely distributed glycoside cyclosiversioside F (**135**) and askendoside D (**144**) [116-118]; the second, askendoside D (**144**) [119, 120] and cyclosiversiosides A (**142**) and H (**178**) [121].

The first transformation method is based on loss of an isohydroxyisopropyl fragment of the side chain with the 20,24-epoxy-25-ol structure upon oxidation by chromic acid. This produces a γ-lactone in the side chain. Selective acetylation of primary and secondary hydroxyls in cyclosiversioside F produces the octaacetate **162** with a free tertiary hydroxyl on C-25, which then undergoes Jones oxidation [122] to give a γ-lactone in the side chain. Octaacetate lactone **163** is a key synthon for further transformations. Saponification of **163** by methanolic KOH and subsequent acidification of the reaction mixture with

H_2SO_4 produced lactone **164** in 58.5% yield based on starting material **135** [116]. Nonaacetate lactone **170** was prepared from askendoside D (**144**) using this scheme. Treatment of **170** with methanolic NaOH (0.1%) at room temperature for 15 min gave monoacetate lactone **174** in 47.4% yield based on **144** [117]. After saponification of octaacetate lactone **163** by methanolic NaOH (1%) at room temperature for more than a day, the sodium salt (**165**) crystallized in 50% yield based on octaacetate **162** [117].

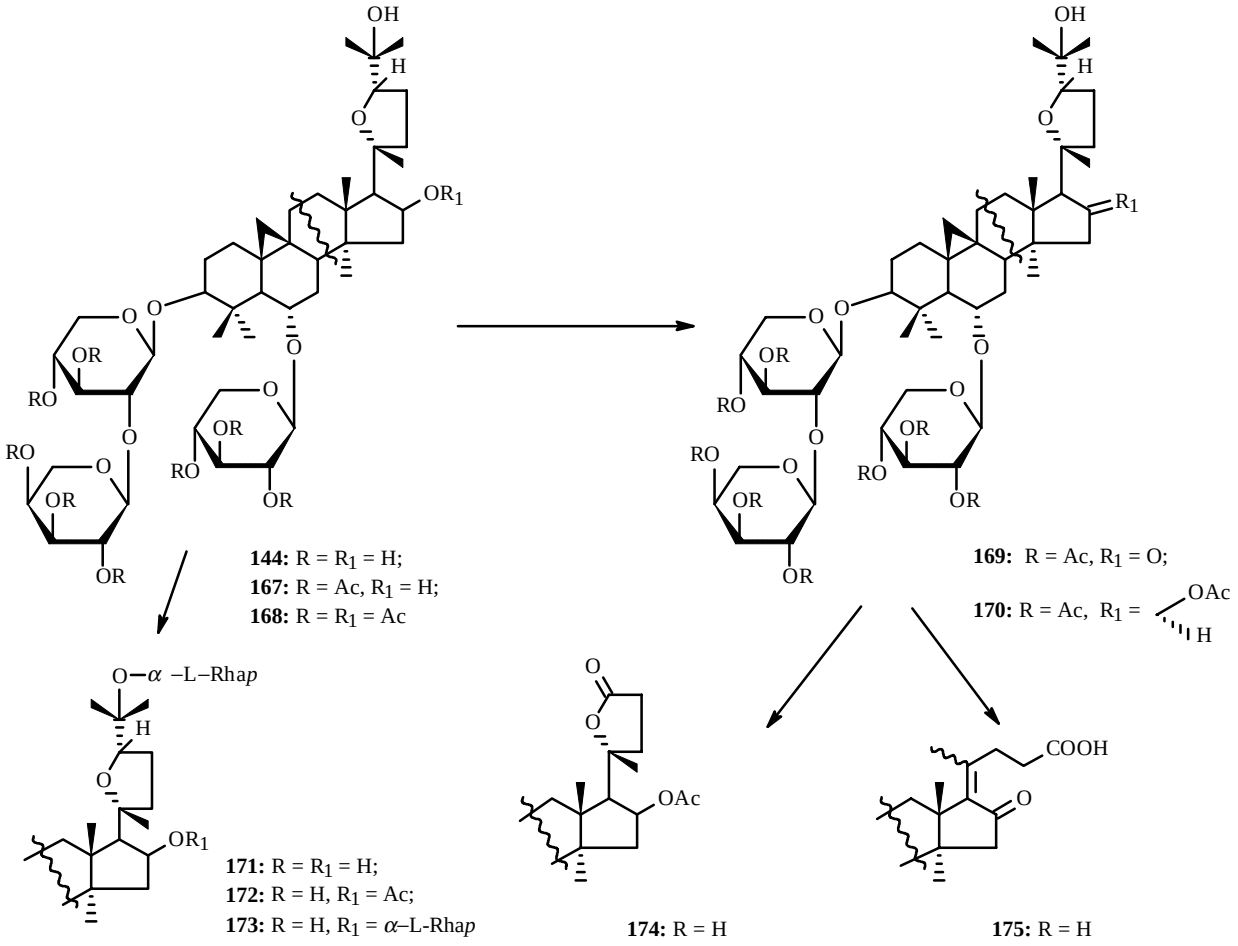


135: R = H; **162:** R = Ac

163: R = Ac; **164:** R = H

165: R = H

166: R = H



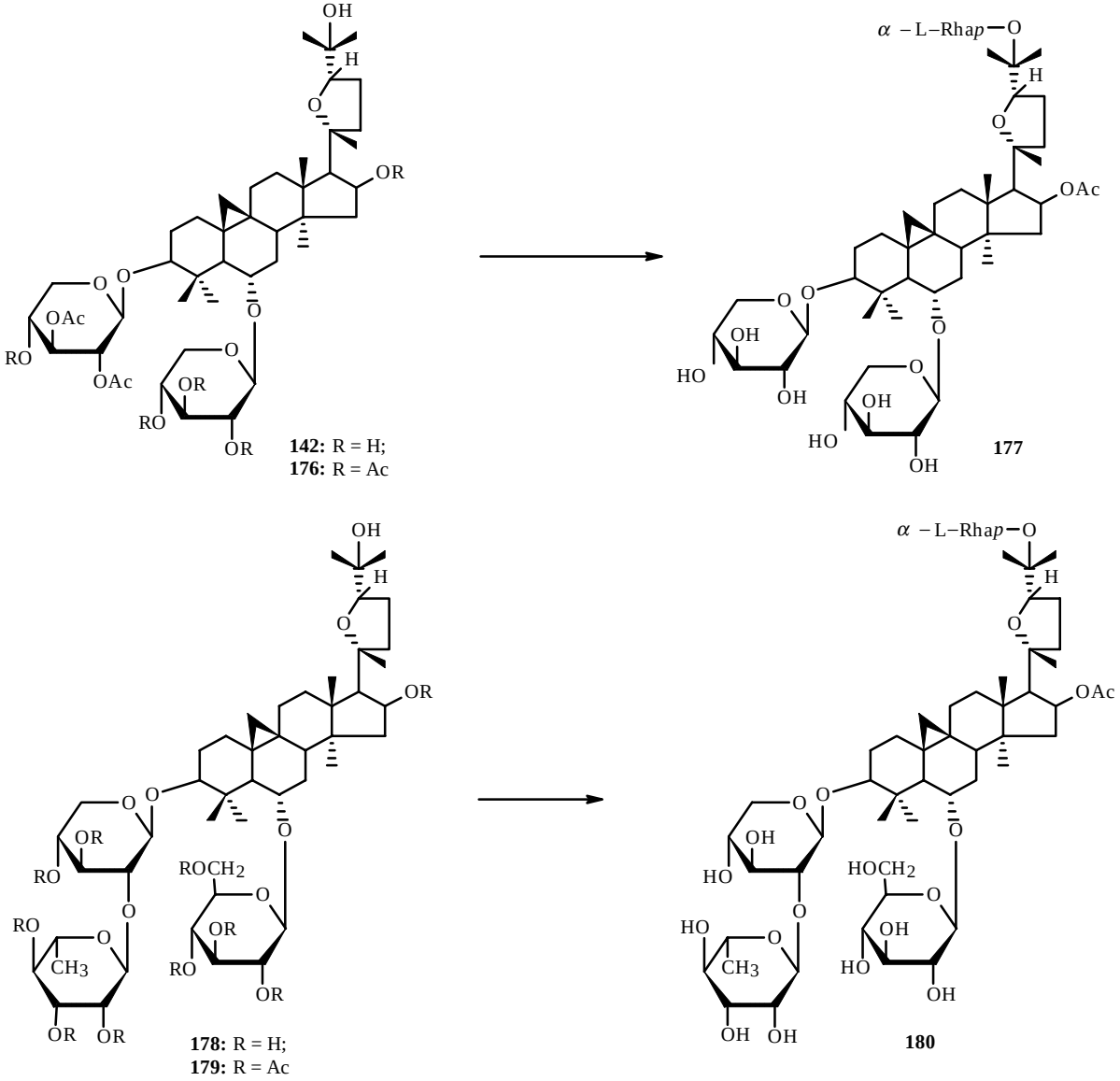
144: R = R_1 = H;
167: R = Ac, R_1 = H;
168: R = R_1 = Ac

169: R = Ac, R_1 = O;
170: R = Ac, R_1 =

171: R = R_1 = H;
172: R = H, R_1 = Ac;
173: R = H, R_1 = α–L-Rha*p*

174: R = H

175: R = H



Reductive opening of the lactone ring of octaacetate lactone **163** by $NaAlH_4$ produced norglycoside **166** in 10% yield based on **163** [117].

The octaacetate of askendoside D (**167**) was transformed through ketolactone **169** by basic hydrolysis and subsequent acidification into a mixture of 17*E*- and 17*Z*-isomers of carboxylic acid **175** [118].

Regioselective glycosylation of cycloartane glycosides is achieved by selective protection of primary and secondary hydroxyls via acetylation using acetic anhydride in pyridine. Depending on the reaction conditions, the acetylation can produce acetates with a free tertiary hydroxyl on C-25 (**168**, **176**, **179**) or acetates with free hydroxyls on C-16 and C-25 (**167**). Koenigs—Knorr condensation [123] of these acetates with acetobromorhamnose in dichloroethane under a stream of N_2 in the presence of mercury cyanide and molecular sieves (4 Å) followed by removal of the protecting groups produces rhamnosides **171-173** [119, 120], **177**, and **180** [121] in rather high yields of 72-82%.

Partial synthesis of trojanoside A (**99**) [124] from cyclosiversioside F (**135**) is interesting from the viewpoint of transformations and confirmation of chemical structures.

BIOLOGICAL ACTIVITY

Early biological investigations of glycosides from *Astragalus* plants have been reviewed [7, 8]. Later studies are reviewed in this section.

Semisynthetic glycosides **164** [116] and **171** [119] possess cardiotonic activity and have several advantages over cardenolides owing to the lack of toxicity and cumulative effects. In continuation of these studies, the positive inotropic activity of several natural cycloartane glycosides and their synthetic analogs **165** and **172-174** was evaluated [126]. It was found that the studied triterpenoids exhibit cardiotonic activity to various degrees.

A comparison of the effects of cycloartane and cardiac glycosides on certain indicators of myocardium metabolism in animals determined that askendoside D intensifies the lipolytic activity of myocardium and the oxidative metabolism of lipids. Askendoside D and cyclosiversioside F induce a hypoglycemic effect [127].

Askendosides C and D in tests using animals with experimental endogenous hypercholesterinemia exhibit high hypocholesterinemic activity. Cycloorbicoside A and askendoside D have distinct interferon-inducing activities [128].

Glycosides from *Astragalus melanophrurius* Boriss. roots were tested biologically in vitro [129]. It was noted that the immunomodulating activity of these compounds is interesting.

Astragaloside II (**138**, cyclosiversioside D) protects 100% of T-lymphocytes from the pathogenic effect of HIV infection in vitro [55]. The EC_{50} is about 2.5×10^{-5} mole, which unfortunately is difficult to attain in vivo. Prelimiary antitumor screening of astragaloside II in vitro showed that colon cancer (SW-620) and leukemia (CCRF-CEM, HL-60) are the cell lines most sensitive to this glycoside [55].

Astrasieversianin XI exerts an inhibitory action on the central nervous system by decreasing the number of responses to stimuli. As a result, it can be used in depression [130].

The effects of cyclosiversioside F and astrasieversianin XI on leucocytopenia caused by cyclophosphamide and γ-rays have been studied. The results indicate that these glycosides taken perorally and continuously significantly increase the amount of leucocytes and lymphocytes in the studied pathology models. Further observations found that these compounds possess also antistress activity in animal experiments [131]. Cyclosiversioside F and astrasieversianin XI exhibit antioxidant, immunostimulating, and hepatoprotective effects [132].

High concentrations of cyclosiversioside F and astrasieversianin XI (250 μg/mL) suppress and normal concentrations (0.05-5 μg/mL) stimulate natural killer activity of lymphocytes in peripheral human blood. Recombinant α-interferon or recombinant interleukin-2 potentiate the stimulation of natural killer activity by these glycosides. The studied glycosides reduce the inhibition of natural killer activity by dexamethasone. Apparently these glycosides are immunomodulators [133].

The effects of various doses of *Astragalus* glycosides were studied using a hemodynamic method and in rat models of experimental cardiac insufficiency induced by sodium pentobarbital. It was found that weak doses of glycosides (2 mg) intensify cardiac insufficiency whereas moderate (4 mg) and high (8 mg) doses are antagonistic to it [134].

The methanol extract of roots (*Astragali Radix*) increases the humoral and cellular immune response, phagocytic activity, and amount of leucocytes formed [135].

***

Thus, *Astragalus* plants are promising sources of cycloartane methylsteroids and their glycosides. *Astragalus* species that have not yet been studied for triterpenoid content are *A. ephemerotorum* Gontsch., *A. kulabensis* Lipsky [136], *A. stipulosus* Boriss. [137], *A. siculus* Biv. [138], *A. falcatus* Lam. [140], and *A. aitosensis* MB [141]. From these, known compounds have been isolated. *Astragalus* species that have been more or less thoroughly studied for triterpenoid content are listed below.

1. *A. taschkendicus* Bunge
2. *A. adsurgens* Pall.
3. *A. aitosensis* MB
4. *A. alexandrinus* Boiss.
5. *A. alopecurus* Pall.
6. *A. amarus* Pall.
7. *A. babatagi* M. Pop.
8. *A. basineri* Trautv.
9. *A. brachypterus* Fischer
10. A. cephalotes var. Brevicalyx
11. *A. chrysopterus* Bunge
12. *A. coluteocarpus* Boiss.
13. *A. complanatus* R. Br.
14. *A. dasyanthus* Pall.
15. *A. dissectus* B. Fedtsch. et N. Ivanova
16. *A. ephemerotorum* Gontsch.
17. *A. ernestii* Comb.
18. *A. exilis* A. Kor
19. *A. falcatus* Lam.
20. *A. galegiformis* L.
21. *A. glycyphyllos* L.
22. *A. iliensis*
23. *A. kuhitangi* (Nevski) Sirj.
24. *A. kulabensis* Lipsky
25. *A. melanophrurius* Boiss.
26. *A. membranaceus* Bunge
27. *A. microcephalus* Willd.
28. *A. mongholicus* Bunge
29. *A. oleifolius* DC
30. *A. orbiculatus* Ledeb.
31. *A. pamirensis* Ovcz. et Rassulova
32. *A. peregrinus*
33. *A. prusianus* DC
34. *A. pterocephalus* Bunge
35. *A. pycnanthus* Boriss.
36. *A. qusqualis* Bunge
37. *A. schahrudensis* Bunge
38. *A. siculus* Biv.
39. *A. sieberi*
40. *A. sieversianus* Pall.
41. *A. spinosus* Vahl
42. *A. stipulosus* Boriss.
43. *A. tomentosus* Lam.
44. *A. tragacantha* Habl.
45. *A. trigonus* DC
46. *A. trojanus* Stev.
47. *A. unifoliolatus* Bunge
48. *A. uninodus* M. Pop. et Vved.
49. *A. verrucosus* Moris
50. *A. villosissimus* Bunge

These are wild plants. Thus, their practical use depends to a large extent on natural resources and distributions. Therefore, conservation investigations in addition to biological testing of newly discovered natural compounds and their synthetic analogs are needed. A biotechnology method for producing plant material containing biologically active compounds is attractive and promising.

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