TRITERPENOIDS OF THE CYCLOARTANE SERIES

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In this review on triterpenoids of the cycloartane series, new achievements in this field of natural compounds are considered, the literature up to 1983 and, in part, 1984 being covered.

Two large groups of plant substances having a steriod skeleton and a 9,19-three-membered ring are known. These are the Buxus alkaloids [1, 2] and the cycloartane triterpenoids.

The ideal of the triterpenoids of the cycloartane series combines compounds produced by plants the structure of which is based on the cycloartane skeleton – 9,19-cyclo-5α,9β-lanostane (I, shceme 1). The 4α,14α-dimethyl- and 14α-methyl-9,19-cyclosteroids (II, III) are biologically connected with the cycloartanes.

Interest in the cycloartanes is largely due to the fact that one of the simplest representatives – cycloartenol (Table 3, 28) – is the key intermediate in the biosynthesis of the phytosteroids (see, for example, [3, 4]). In view of this, cycloartenol and some of its weakly polar derivatives are widely distributed in plants [5]. More highly oxidized compounds of this class are found more rarely. However, in recent years the number of cycloartanes with various oxygen functions that have been described has risen considerably. Many of them have been isolated in the form of glycosides.

Early investigations to determine the structures of the cycloartanes are reflected in the monographs [6, 7] and the results of later investigations are given in the reviews [5, 8]. Information on individual representatives of this class can be found in review papers on triterpenoids [9-11]. The last most complete summary of the triterpenoids of the cycloartane series was given in a paper [5] published in 1975 showing the structures of about 50 compounds. At the present time, more than 160 substances of this type are known. It must be assumed that this is far from the limit and it is possible to expect a large variety of structural type, particularly among the glycosylated forms.

The present paper considering recent advances in the field of natural triterpenoids covers the literature up to 1983 and only individual publications for 1984. Table 3 gives the known cycloartanes and their 4-monomethyl and 4,4-dimethyl analogs, and also compounds of glycoside nature.

ISOLATION

In plants, cycloartanes are found in the free form and in the form of glycosides. The methods of isolation from plant raw materials developed for various types of triterpenoids [11, 12] are fully applicable to the cycloartane derivatives.

The weakly polar cycloartanes present in the lipid fraction of a plant can be extracted with chloroform, ethyl ether, or petroleum ether [13-17]. The extraction of the polar compounds is carried out with methanol or ethanol. The primary extract is fequently subjected to preliminary purification to eliminate accompanying substances. In each concrete case the method of treatment depends on the features of the plant under investigation [18-20].

As a rule, the separation of the complex combination of extractive substances is performed by column chromatography on alumina or silica gel. Alumina is used for the chromatographic fractionation of the weakly polar compounds [21, 22]. Good results on the separation of the weakly polar cycloartanes in the form of acetates [23-25] and benzoates [26] have been obtained by the use of silica gel impregnated with silver nitrate. Polyhydroxy compounds, substances of glycosidic nature, and polyhydroxycycloartanes having acyl residues

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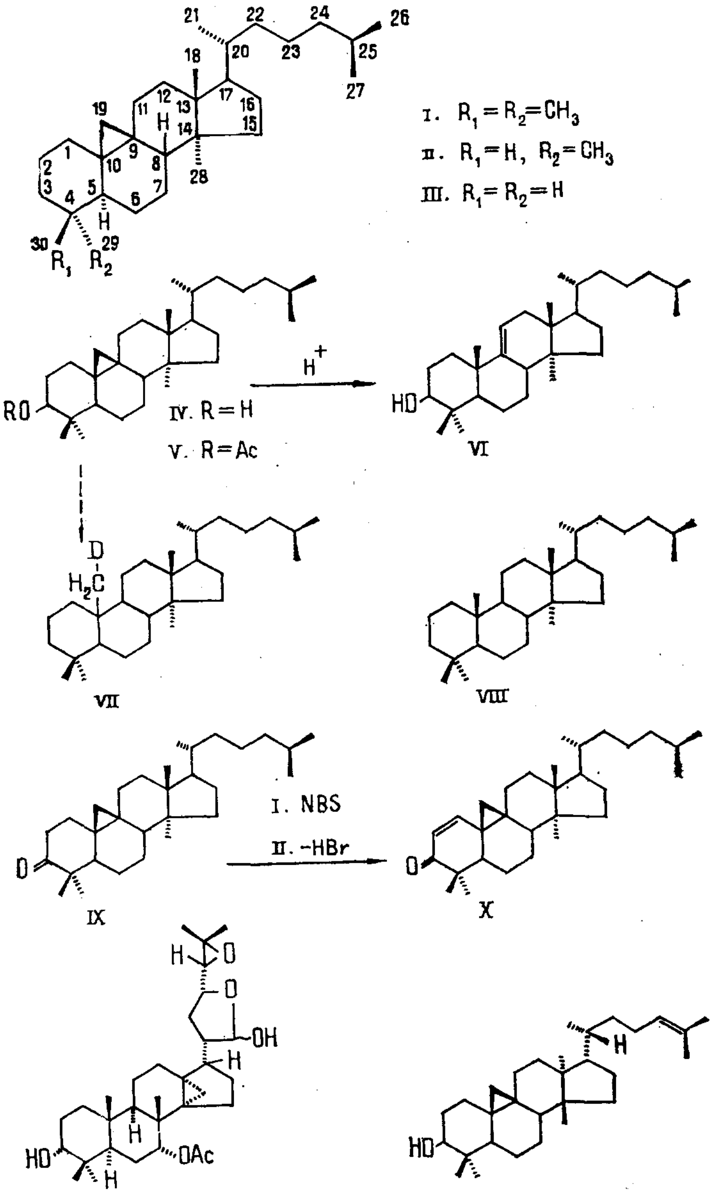
are chromatographed on silica gel. The use of GLC has been described for the determination of cycloartenol (28) and some of its close analogs [27, 28].

STRUCTURE DETERMINATION

The structure of cycloartenol (28) was the first to be shown among the series of triterpenoids under consideration [29]. Barton [29] showed that cycloartanol (24, 25-dihydrocycloartenol, IV) isomerizes under the action of acid forming a mixture of unsaturated lanostenes. Spring et al [30] established that the main component of the mixture was lanost-9(11)-enol (VI). The izomerization reaction convincingly showed the presence of a cyclopropane ring.



Schme 1

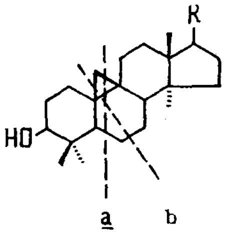
To determine the position of the cyclopropane ring, Barton et al. [31] isomerized cycloartanol acetate (V) with deuterium chloride and then by reduction obtained deuteropanostane (VII). They performed comparative quantitative measurements of the intensities of absorption in the UV spectra of lanostane (VIII) and the deutero product (VII) in the region characteristic for methyl groups at 1380 cm^{-1}. It was found that the deuterated compound possessed a smaller intensity of absorption. This was possible only if a deuteromethyl group had been formed, which showed the presence of a 9,19-ring.

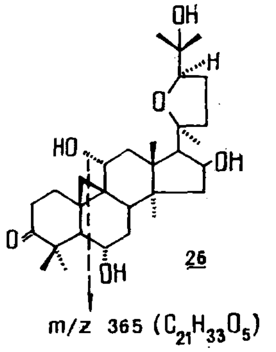
Spring et al. [32] came to the same conclusion, having shown that in the unsaturated ketone (X) obtained from cycloartanone (IX) the cyclopropane ring was, according to the UV spectrum, present in a chain of conjugation with the keto group.

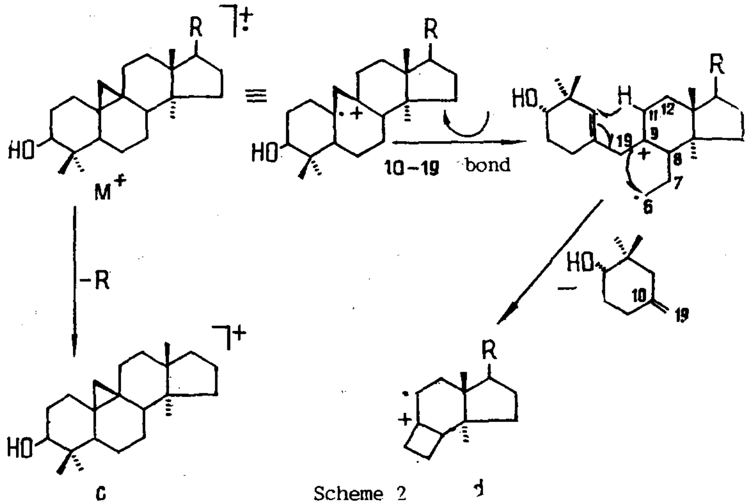
At the present time, to establish the structure of the cycloartanes instrumental methods have a decisive value. The cyclopropane group introduces characteristics features into the spectral behavior of the triterpenoids. However, the presence of a three-membered ring in the molecule of a triterpenoid is not an indisputable criterion of its membership of the cycloartane series. It must be mentioned that the tetracyclic triterpenoids glabretal (XI) [33] and cycloroylenol (XII) [34], each having a three-membered ring in the nucleus but not belonging to the cycloartane group have recently been isolated from plants.

Preliminary information on the presence of a three-membered ring in the molecule of a terpenoid can be obtained from its IR spectrum. The absorption of the CH_2 group of a cyclopropane ring is observed at 3040-3060 cm^{-1} [35, 36], although with low intensity. Very frequently, the required band appears in the form of a shoulder or a plateau on the intense band of the stretching vibrations of the CH_2 groups of alkanes. Furthermore, the stretching vibrations of the CH groups of other compounds such as alkanes, aromatic substances, and the methylene of an epoxide group, appear in this region. This must borne in mind in an analysis of IR spectra, and a conclusion on the presence of a cyclopropane ring based on absorption at 3040-3060 cm^{-1} must be confirmed by other information.

Mass spectrometry is of great value in the investigation of the cycloartanes. It was first shown, using cycloartenol (28) and cyclolaudenol (59) as examples that in the cycloartanes, in addition to the fragmentation characteristic for isoprenoid alcohols (the splitting out of one or more molecules of water, a methyl group, and the side chain) cleavages due to the presence of the 9,19-cyclopropane ring are observed [37, 38]. The influence of this group leads to the ejection of a neutral fragment containing ring A and to the formation of the ion d (scheme 2). Alternatively, cleavage may take place in the type a or b [13, 15, 17, 21, 23, 26, 37-51]. The detection of an ion with m/z 365 ($C_{21}H_{33}O_5$) in the mass spectrum of cycloasgenin A (26) [19] shows that route a is more probable.







Scheme 2

A possible mechanism for the formation of ion d consists in the initial ionization of the 9–10 bond, as a consequence of which the steric strain of ring B decreases. The cleavage of the activated 5–6 bond with the subsequent migration of one of the hydrogen atoms at C-11 through a McLafferty rearrangement leads to an ion of type d [37].

The intensity of the peak of the ion d is fairly high and in some cases amounts to 100%. This is particularly characteristic for the monohydroxycycloartane alcohols. In those cases

TABLE 1. Chemical Shifts of the Cyclopropane Protons of Cycloartanes with Various Substituents, ppm*

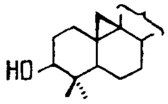
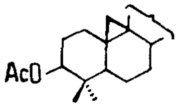
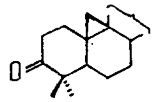
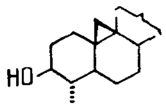
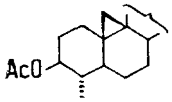
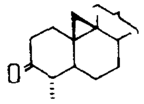
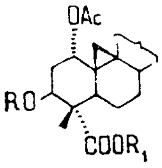
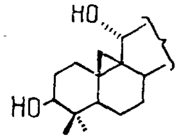
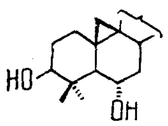
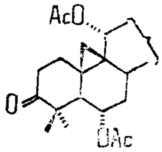
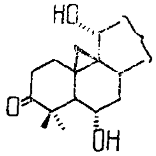
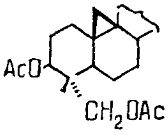
Compound	δ_A	B	Literature
 XIII (59)	0 32	0,58	55
 XIV	0.33	0,60	55
 XV	0,56	0.80	55
 XVI (149)	0,11	0,36	55
 XVII	0,13	0.40	55
 XVIII (147)	0,44	0,63	55
			
XIX. R=β-*D*-tetra)Ac-Glcp, R_1=H	0,50 (0.17)	0.73 (0,54)	56
XX. R=Ac, R_1=Me	(0,12)	(0,50)	58

TABLE 1 (continued)

Compound	δ_A	δ_B	Literature
 XXI (19)	0.47	0,64	41
 XXII (37)	[0,23] 0,36	[0,51] 0,52	19
 XXIII	[0,63]	[0 81]	19
 XXIV ([illegible])	[0,45] 0.46	[1,63] 1.22	19
 XXV	0.22	0,44	57

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*The figures given in round brackets were obtained with deuterobenzene as solvent; those in square brackets with deuteropyridine using HMDS as internal standard; and the others with deuterochloroform using TMS as internal standard.

TABLE 2. Chemical Shifts of the Cyclopropane Carbons of Some Cycloartane Derivatives and the Corresponding Carbon Atoms of 5α-Cholestan-3β-ol

Compound	C-9	C-10	C-19	Literature
5α-Cholestan-3β-ol (XXVIII)	55.1	35.9	12,3	62
Cycloartanol (IV)	20,0	26,0	29.8	64
Cycloeucalenol (146)	23,5	29,5	26,9	64
Pollinastanol acetate (XXIX)	23.5	29.8	25,7	64

where there are functions competing with the ion d for the localization of the charge, the intensity of the latter falls considerably [13, 19]. For example, in the mass spectrum of cycloartenone (11), the intensity of the peak of fragment d amounts to only 14% [37]. In polyfunctional cycloartanes, competing fragmentation reactions may lead to an even more considerable decrease in the probability of the appearance of the ion d and sometimes even to its practical absence [18, 20, 52, 53].

Thanks to its high informativeness ^{1}H and ^{13}C NMR spectroscopy is widely used in spectral studies of the cycloartane triterpenoids.

One of the features of the PMR spectra of the cycloartanes consists of the resonance signals of the cyclopropane methylene group. They appear in the strong field in the form of two one-proton doublets interacting in the manner of a AB system with a typical geminal spin-spin coupling constant ($^2J = 4$ Hz). The observation of these doublets shows the presence of a 1,1,2,2-tetrasubstituted cyclopropane ring such as the 9.19-ring is. For many representatives of the class under consideration, the centers of the doublets of the cyclopropane protons are located between 0.30 and 0.60 ppm [40, 54].

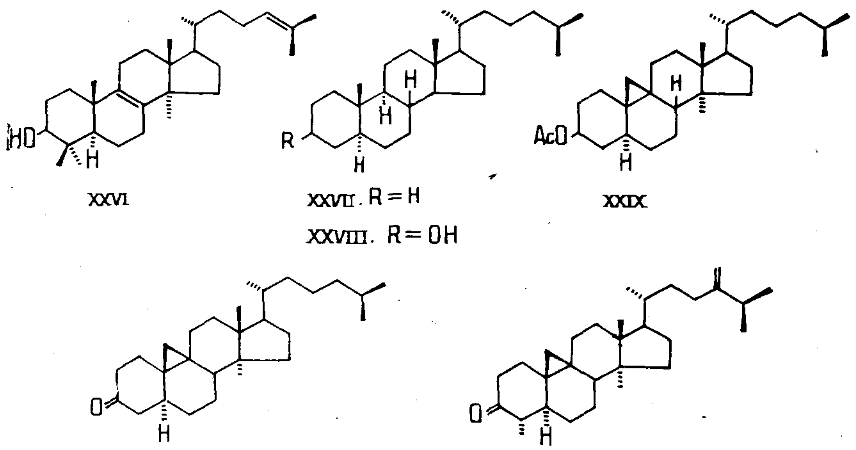
Some substituents present in rings A and C may affect the value of the chemical shift of the signals of the protons at C-19. Examples of such an effect are given in Table 1. Thus, when $CDCl_3$ is used as the solvent, a keto function at C-3 and hydroxy groups at C-1 and C-11 cause a paramagnetic effect [19, 41, 55, 56], while a 4α-hydroxymethylene group [57] or the absence of the 4β-methyl group [55] causes a diamagnetic shift of the signals of the cyclopropane protons.

The degree of influence of functional groups on the magnitude of the chemical shifts of the cyclopropane protons depends to a certain extent on the solvent used. It can be seen (Table 1, XIX, XX) that on passing from $CDCl_3$ to C_6D_6 there is small upfield shift of the signals [56, 58].

The most substantial effect of a solvent appears when pyridine is used. In the case of compound (XXIV) it has been shown that pyridine considerably intensifies the descreening action of an 11α-hydroxy group, and the signal of one of the cyclopropane protons shifts downfield to 1.63 ppm.

It must be mentioned that the use of pyridine as solvent can give additional information on the structure of a triterpenoid in the analysis of the chemical shifts of the methyl groups. The signals of the methyl groups of cycloartane derivatives usually appear in the 0.7-1.5 ppm region and their assignment is difficult and does not have the same analytical value as in the chemistry of other classes of steroid compounds. However, if the protons of the hydroxy and methyl groups are spatially close it is possible to use the pyridine-evoked downfield shift [59]. In a number of investigations [18, 52, 53], the authors, basing their choice on the paramagnetic shift of the signals of one of the methyl groups by about 1.8 ppm, were able to choose between the two possible positions, 6α and 7β, for the hydroxy group.

A prerequisite for the use of ^{13}C NMR spectroscopy in the investigation of the cycloartane triterpenoids was the interpretation of the spectra of lanosterol (XXVI, scheme 3) [60, 61] and of 5α-cholestane (XXVII) [62, 63]. The ^{13}C NMR spectra of some cycloartanes were first considered by Khuong-Huu et al. [64]. This method was subsequently developed [65, 66] and at the present time it is being widely used for solving structural problems [19, 20, 42, 53, 67-69].



XXVI

XXVII. R = H

XXVIII. R = OH

XXIX

XXX

XXXI

Scheme 3

The specificity of the ^{13}C NMR spectra of the cycloartanes as compared with derivatives of the 5α-cholestane series is due to the presence of a β-orientated strained three-membered ring and, as a consequence of this, the cis-linkage of rings B/C.

The peculiar nature of the carbon-carbon bonds of the cyclopropane ring and also the difference in the degree of substitution of its carbon atoms from the corresponding atoms in 5α-cholestane are shown both in the values of the chemical shifts and in the multiplicities of the signals of these carbon atoms.

It can be seen from Table 2 that the signals of the C-9 and C-10 atoms of pollinastanol acetate (XXIX) undergo a considerable diamagnetic shift (by 31.6 and 6.1 ppm, respectively) as compared with those of the atoms of 5α-cholestan-3β-ol (XXVIII), while the signal of the C-19 atom undergoes a paramagnetic shift by 13.4 ppm. The chemical shifts of the carbon atoms under consideration are affected by the methyl groups at C-4. Thus, for example, on passing from pollinastanol acetate (XXIX) to cycloeucalenol (146), which has a 4α-methyl group, a small (1.2 ppm) paramagnetic shift of the C-19 signal is observed but the chemical shifts of the C-9 and C-10 atoms scarcely change. The action of a gem-dimethyl group is more considerable. On passing from pollinastanol acetate (XXIX) to cycloartanol (IV) the diamagnetic shifts of the C-9 and C-10 signals are 3.5 and 3.8 ppm, respectively, and the paramagnetic shift of the C-19 signal is 4.1 ppm.

In structural investigations of the cycloartane triterpenoids a definite role is played by the use of chiroptic methods - optical rotatory dispersion (ORD) and circular dichroism (CD) [70, 71].

It is known that 3-keto-5-α-steroids and their 4-monomethyl derivatives have a positive Cotton effect, while in 3-keto-4,4-dimethyl-5α-isoprenoids an inversion of the sign of the curve is observed [72].

These characteristics are retained in a series of compounds having a 9,19- three-membered ring. The introduction of a 9,19-cyclopropane ring does not affect the basic nature of the CD and ORD curves. Thus, for example, pollinastanone (XXX) [73] and cycloeucalenone (XXXI) [44] show a positive Cotton effect, while cycloartenol (11) shows the curve with a negative Cotton effect that is characteristic for 4,4-dimethyl-3-keto-5α-steroids [72].

The determination of the sign of the Cotton effect of 3-keto derivatives is one of the methods of establishing the configuration at C-5. However, it must be borne in mind that the presence of substituents in ring B may affect the conformational features of rings A/B and thereby change the form of the CD curves. It has been reported that the presence of a 6α-hydroxy group in a cycloartane imparts a complex form to the CD curve of the 3-ketocycloartanes — a small negative minimum appears on the long-wave side and a considerable positive maximum in the short-wave region [19, 74]. This is possibly explained by a disturbance of the interaction characteristic of cycloartanes unsubstitued at C-6 between the equatorial CH_3 group at C-4 and the hydrogen atom at C-6 [70, pp. 125-128].

Chiroptic methods are used to elucidate some other features of the structure of the cycloartanes. THus, a negative Cotton effect at 305 nm, which is characteristic for 16-oxo steroids [75], provides the possibility of unambiguously choosing the site of a hydroxy group present in ring D [18, 52, 53].

The use of a method based on CD measurements [76, 77] permits the determination of the stereochemistry of the C-24 chiral center in compounds containing a C-24—C-25 glycol group [52].

The conformational features of the cycloartanes have been elucidated by x-ray structural analysis for the case of compounds (43, 45, 81, 138-140 and 158) [14, 78-81]. It has been shown that ring A has the form of a slightly distorted chair. The 9,19- three-membered ring imparts to ring B the form of a distorted half-chair and to ring C that of a highly deformed boat. The five-membered ring D has the envelope form.

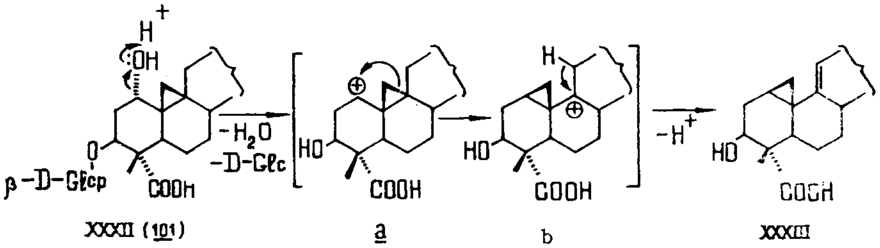
GLYCOSIDES OF THE CYCLOARTANE TRITERPENOIDS

At the present time about 40 glycosides of the cycloartane series have been described, and of them only (156) and (157) belong to the 4-monomethyl analogs. Scarcely any glycosides have been found among representatives of the pollinastanol (158) group. As a rule, all the glycosides are derivatives of polyhydroxycycloartanes. Glycosylated forms of the cycloartanes have been detected in plants belonging mainly to the two families Ranunculaceae and Leguminosae.

The carbohydrate components of the glycosides of the class under consideration are represented by D-xylose, D-glucose, D-galactose, L-arbinose, and L-rhamnose. The pentoses are found more frequently than the hexoses.

In contrast to many steroid and triterpene glycosides not of acyloside nature in which the carbohydrate chain is located predominately at C-3, the cycloartanes are found extremely frequently in the form of bis- or trisdesmosides.

Because of the presence of a 9,19-three-membered ring sensitive to the action of acids in the proof of the structure of the glycosides, the isolation of the native genins acquires particular importance. Dilute mineral and organic acids are used for hydrolysis. However, hydrolysis with acids in low concentration does not always take place [82] and the use of more severe conditions may lead not only to the opening of the cyclopropane ring [18, 20, 57] but also to some other changes. Thus, for example, in the case of thalicoside A (121), in addition to the opening of the three membered ring a ring-closure of the side chain also took place [57].



Scheme 4

If there is a hydroxy group in the α position with respect to the cyclopropane ring, this system becomes particularly vulnerable [56, 58]. In the case of substances similar to (XXXII) (scheme 4), in acid medium the α-hydroxy group is eliminated with the subsequent migration of the cyclopropane ring. The carbonium ion of the allyl type (a) formed on the elimination of the hydroxy group is stabilized by the migration of the cyclopropane ring and charge transfer to the tertiary carbon atom (ion b). The latter, losing a proton, is converted into the olefin (XXXIII).

If they do not contain free α-diol groups, the genins can be obtained by the Smith degradation of the corresponding glycosides [83], by oxidation with sodium periodate followed by treatment with alkali [57], or by periodate oxidation in the presence of cylcohexylamine and acetic acid [84, 85]. The last-mentioned permits the retention in the genin molecule of such labile groupings as ester and acetal groupings. Another advantage of theis method consists in the fact that, in addition to the genin, a certain amount of the corresponding formate is formed, and this permits the position of the sugar residue to be determined.

The enzymatic cleavage of the carbohydrate components is the mildest method for obtaining genins and progenins [13, 20, 68, 86-89].

The usual methods of carbohydrate chemistry are used to establish the structure of the sugar chain, such as complete and partial hydrolysis, methylation, and periodate oxidation [90-92, pp. 9-54; 102]. In demonstrating the structures of glycosides, wide use is made of exhaustive methylation [92(pp. 276-280), 103(pp. 485-465), 104-106]. TLC [92(pp. 37-46)], and, particularly GLC [92(pp. 26-37), 107, 108] are used for identifying monosaccharide methyl ethers. Individual derivatives of sugars can be determined with the aid of mass spectrometry [109]. Chromato-mass spectrometry is effective for the analysis of complex mixtures [110-116].

The information obtained by the study of the products of methylation can be confirmed and supplemented by periodate oxidation [103, pp. 58-77] and partial hydrolysis. The configurations of the glycosidic bonds are determined on the basis of a calculation of the molecular rotation increment for each monosaccharide residue [117], and also with the aid of PMR results [118, 119].

The majority of questions connected with determining the structures of glycosides can be solved with the aid of ^{13}C NMR spectroscopy. A comparison of the ^{13}C NMR spectra of the genin, of progenins, and of a glycoside enables the structure of the glycoside to be established reliably [120-123].

It is known that the carbon atom of the genin bearing the sugar residue experiences a glycosylation effect consisting in a paramagnetic shift of its resonance signal by approximately 10 ppm [120, 121]. This makes it possible to determine the position of attachment of the carbohydrate chain without error.

The size of the oxide ring is found by assigning the resonance signals of the carbohydrate residue in the spectrum of the corresponding progenin. The values of the chemical shifts of the anomeric carbon atoms are used for determining the configurations of the glycosidic bonds [122].

The contribution of ^{13}C NMR spectroscopy in the investigation of the cycloartane glycosides, especially their acyl derivatives, is considerable [87-89, 124-132].

Table 3 gives the structures of 164 compounds. It is not excluded that among them are some which are identical. For example, isocycloartenol (27) and β-cyclooristerol (29) have been ascribed the same structure. It is possible that triphyllol (83), the stereochemistry of the chiral centers of which at C-20 and C-24 has not been determined, is identical with one of the substances (82) and (84).

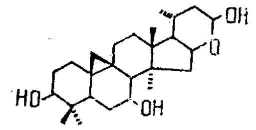
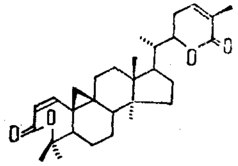
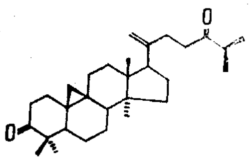
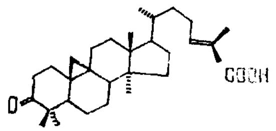
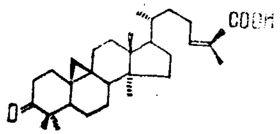
The glycosides of the genus Cimicifuga (95), (102), and (105) and the corresponding genins (22), (56), and (72) are artifacts [133, 134]. In all probability the list of artifacts of cycloartane derivatives isolated from the genus Cimicifuga is not limited to the compounds mentioned.

Attention is also directed to the fact that cyclogalegigenin (36) and cycloastragenol (38) are assigned the same structure while their physicochemical constants and spectral characteristics differ widely. The cyclosiversigenin (37) isolated from Astragalus sieversianus Pall. and the cycloastragenol (38) and astramembrangenin (37a) isolated from Astragalus membranaceus have close constants. At the same time, while identical stuctures are given for compounds (37) and (37a), cycloartane (38) differs from them by the sterochemistry of the C-20 and C-24 atoms. However, the identity of these three substances has not been established.

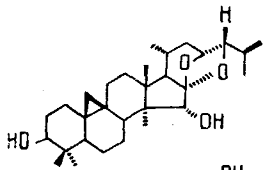
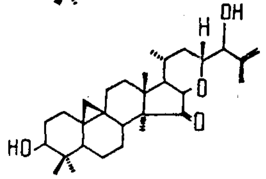
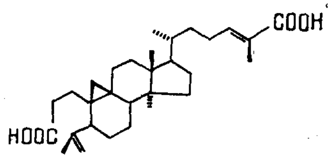
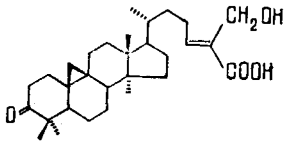
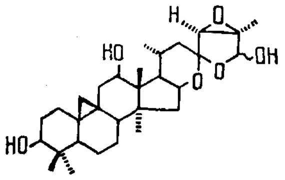
Plants of the genera Cimicifuga [135, pp. 103, 104] and Astragalus [135 (pp. 161, 163) and 136] have long been used in folk medicine for the treatment of various diseases. A tincture of Dahurian bugbane (Cimicifuga dahuria (Turcz.) Maxim.) is used in folk medicine as a sedative and hypotensive agent [137]. Individual species of Astragalus are also used in scientific medicine [138-140].

The neogalenical preparation Astragalozid, which consists of the combined glycosides of Astragalus sieversianus Pall. has shown hypocholesteremic activity, being capable of normalizing the lipid metabolism and improving the cardiac activity of animals in experimental endogenous hypercholesteremia [141].

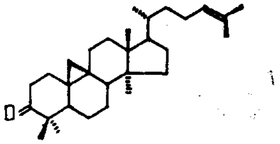
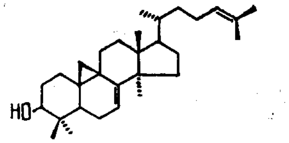
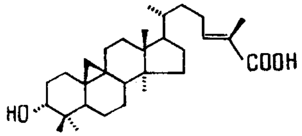
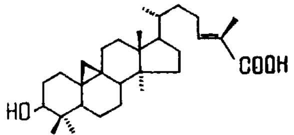
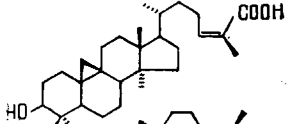
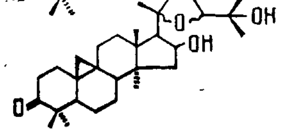
TABLE 3. Cycloartane Triterpenoids and their Glycosides having Established Structures

Name and molecular formula	Structure	mp, °C; $[\alpha]_D$ degree (solvent)	Source (family)	Literature
1	2	3	4	5
1. Dasyanthogenin $C_{26}H_{42}O_4$		210—214; 0 (ethanol)	Astragalus dasyanthus Pall. (Leguminosae)	149
2. Schizanlactone B $C_{30}H_{42}O_4$		205—207; +80,2 (chloroform)	genus Schizandra Rich. (Magnoliaceae)	150
3. Schizandraflorin $C_{30}H_{46}O_2$		107; +20,1 (chlorofrom)	Schizandra grandiflora Hook. f et Thom. (Magnoliaceae)	43
4. Magniferonic acid $C_{30}H_{46}O_3$		187—189; +23,5	Mangifera indica L. (Anacardiaceae), Shorea acuminata (Dipterocarpaceae)	151, 152
5. Schizandronic acid $C_{30}H_{46}O_3$		167—168,5 +15 (chloroform)	Schizandra nigra Max. (Magnoliaceae)	48

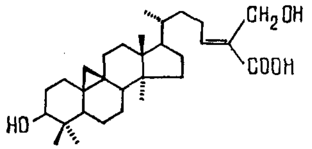
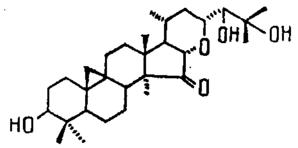
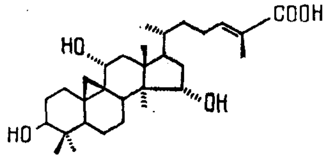
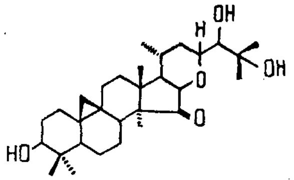
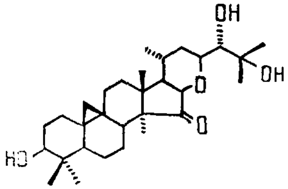
Continuation of Table 3

1	2	3	4	5
6. 25-Anhydrocimigenol $C_{30}H_{46}O_4$		194,5; +61,3	Cimicifuga japonica (Ranunculaceae)	85
7 Anhydrodahurinol $C_{30}H_{46}O_4$		216—217; —	Cimicifuga simplex Wormsk. (Ranunculaceae)	153
8. Nigranic acid $C_{30}H_{46}O_4$		Oil ; +55,8 methanol	Schizandra nigra Max. (Magnoliaceae)	154
9. Hydroxymangiferonic acid $C_{30}H_{46}O_4$		190—192; +18,2	Mangifera indica L. (Anacardiaceae)	155
10. Acteol $C_{30}H_{46}O_6$		126—133; —4	Actaea racemosa (Ranunculaceae)	156, 157

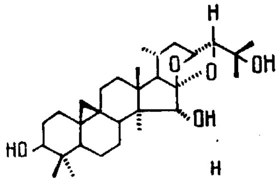
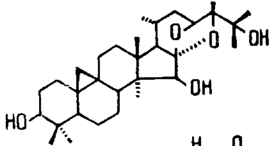
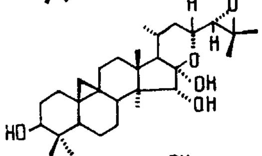
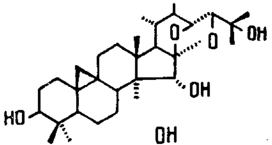
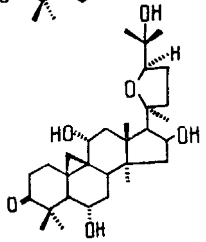
Continuation of Table 3

1	2	3	4	5
11. **Cycloartenone** $C_{30}H_{48}O$		109; +24 (chloroform)	Artocarpus integrifolia L. (Moraceae)	29
12. **Cimicifugenol** $C_{30}H_{48}O$		112–113; +21,4 (chloroform)	genus Cimicifuga (Ranunculaceae)	158
13. **Isomagniferolic acid** $C_{30}H_{48}O_3$		168–170; +29	Mangifera indica L. (Anacardiaceae)	151
14. **Mangiferolic acid** $C_{30}H_{48}O_3$		181–183; +49	Mangifera indica L. (Anacardiaceae)	159
15. **Schizandrolic acid** $C_{30}H_{48}O_3$		164–165; +35 (chloroform)	Schizandra nigra Max. (Magnoliaceae)	48, 160
16. **Argentatin A** $C_{30}H_{48}O_4$		—	Parthenium argentatum (Compositae)	161

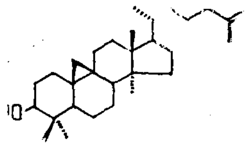
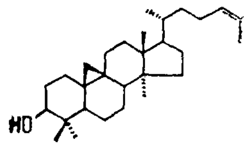
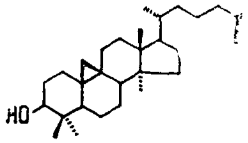
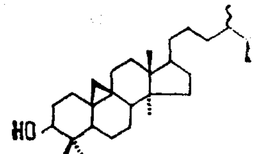
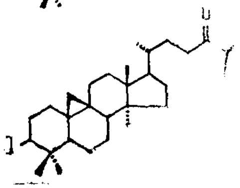
Continuation of Table 3

1	2	3	4	5
17. **Hydroxymangiferolic acid** $C_{30}H_{48}O_4$		201 - 204; + 39	Mangifera indica L. (Anacardiaceae)	151
18 **Aglycone A** $C_{30}H_{48}O_5$		220—225; +46	Actaea racemosa (Ranunculaceae)	162
19. **Ananasic acid** $C_{30}H_{48}O_5$		194—197,5 + 4,23 **(methanol)**	Ananas comosus (Stickm) Merr. (Bromeliaceae)	41
20. **Dahurinol** $C_{30}H_{48}O_5$		248—250; +54 5 **(chloroform)**	**genus** Cimicifuga (Ranunculaceae)	153, 163
21. **Isodahurinol** $C_{30}H_{48}O_5$		216 - 222 —	Cimicifuga simplex Wormsk., C. acerina Sieb. et Zucc. (Ranunculaceae)	153

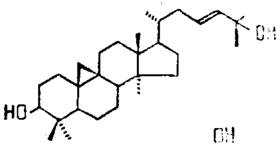
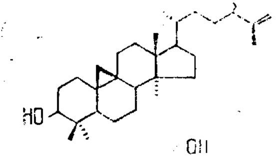
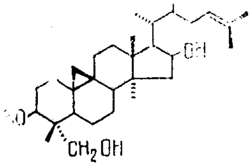
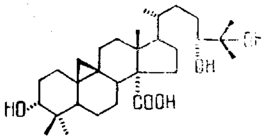
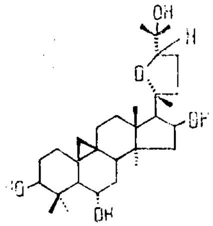
Continuation of Table 3

1		3	4	5
22. Cimigenol $C_{30}H_{48}O_5$		227,5 – 228,5; + 38	Actaea racemosa, Cimicifuga acerina Sieb. et Zucc. (Ranunculaceae)	164 – 167
23. Cimigol $C_{30}H_{48}O_5$		277—278; + 42 5 (ethanol)	genus Cimicifuga (Ranunculaceae)	168
24. Shengmanol $C_{30}H_{48}O_5$		153,5 - 154,5; + 0,5 (chlorofom)	Cimicifuga japonica (Ranunculaceae)	133
25. 22-Hydroxycimigenol $C_{30}H_{48}O_6$		274—276; + 45 (chloroform–methanol (1:1))	Cimicifuga japonica (Ranunculaceae)	86
26. Cycloasgenin A $C_{30}H_{48}O_6$		235—236; + 130 (methanol)	Astragalus taschkendicus Bunge (Leguminosae)	19

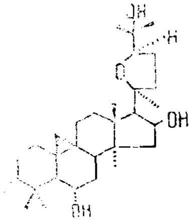
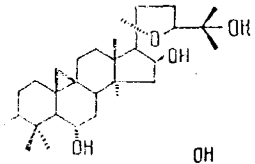
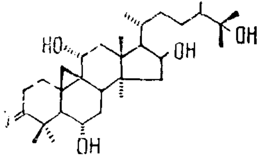
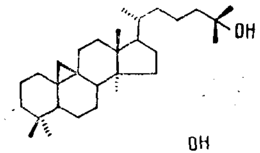
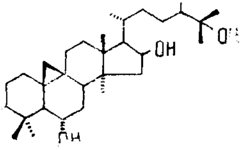
Continuation of Table 3

1	2	3	4	5
27. Isocycloartenol $C_{30}H_{50}O$		92—94; +44,9	Artocarpus chaplasha Roxb. (Moraceae)	21
28. Cycloartenol $C_{30}H_{50}O$		115; +54 (chloroform)	Strychnos nux-vomica L. (Loganiaceae)	30
29. β-Cyclooristerol $C_{30}H_{50}O$		112—113; +49	Rice bran oil	169
30. Cyclopeltenol $C_{30}H_{50}O$		192; +51 (chloroform)	Macaranga peltata Muell. (Euphorbiaceae)	170
31. Lagerenol $C_{30}H_{50}O_2$		92; +44,6 (chloroform)	Lagerstroemia langosteri (Lythraceae)	171

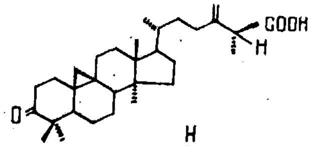
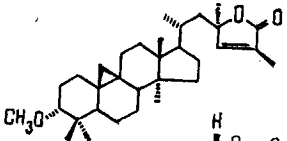
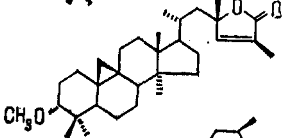
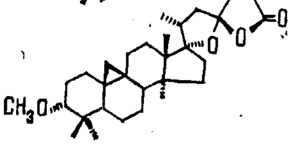
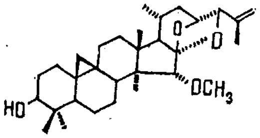
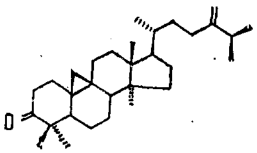
Continuation of Table 3

1	2	3	4	5
32. Cycloart-23-ene-3β, 25-diol $C_{30}H_{50}O_2$		200–204; +38 (chloroform)	Tillandsia usneoides L. (Bromeliaceae)	54, 172
33. Cycloart-25-ene-3β, 24ξ-diol $C_{30}H_{50}O_2$		184–188; + 48 (chloroform)	Tillandsia usneoides L. (Bromeliaceae)	172
34. Thalicogenin $C_{30}H_{50}O_4$		201–202; +34.5 (pyridine)	Thalictrum minus L. (Ranunculaceae)	57
35. Protolyofoligenic acid $C_{30}H_{50}O_5$		216,5–218; –10 (methanol)	Lyonia ovalifolia Drude var. elliptica Hand.–Mazz (Ericaceae)	173, 174
36. Cyclogalegigenin $C_{30}H_{50}O_5$		195–196; +28,7 methanol	Astragalus galegiformis L. (Leguminosae)	53

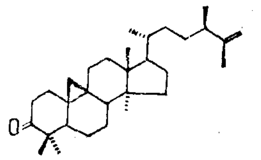
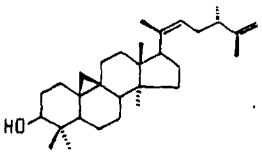
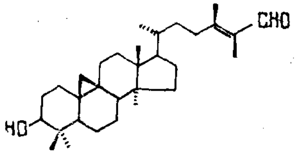
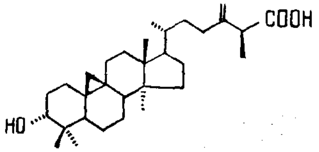
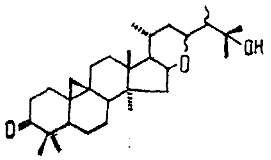
Continuation of Table 3

1	2	3	4	5
37. Cyclosiversigenin $C_{30}H_{50}O_5$		239—241; +50,6 (methanol)	Astragalus sieversianus Pall. (Leguminosae) Astragalus taschkendicus Bunge (Leguminosae)	18, 52
37a. Astramembrangenin $C_{30}H_{50}O_5$		237—237,5; +51,6 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	222
38. Cycloastragenol $C_{30}H_{50}O_5$		243—244; +49 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	20
39. Cycloasgenin B $C_{30}H_{50}O_6$		232—233; +98,9 (methanol)	Astragalus taschkendicus Bunge (Leguminosae)	74
40. 25-Hydroxycycloartanol $C_{30}H_{52}O_5$		181,5; +48,7	Rice bran oil	175, 176
41. Cycloasgenin C $C_{30}H_{52}O_5$		244 246; +33,7 (methanol)	Astragalus taschkendicus Bunge (Leguminosae)	52

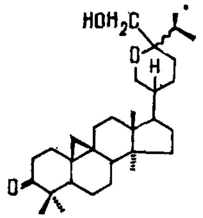
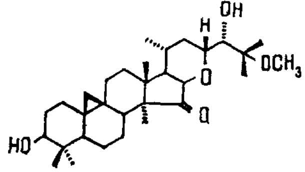
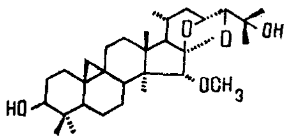
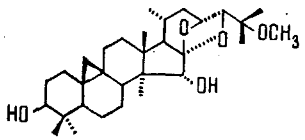
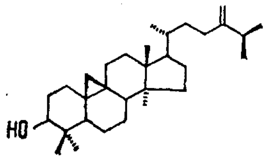
Continuation of Table 3

1		3	4	5
42. Ambonic acid $C_{31}H_{48}O_3$		149—150; +9,4	Mangifera indica L. (Anacardiaceae)	177, 178
43. Cyclograndisolide $C_{31}H_{48}O_3$		191—193; —	Abies grandis (Dougl.) Lindi (Pinaceae)	49, 179
44. Epicyclograndiisolide $C_{31}H_{48}O_3$		194 195; —	Abies grandis (Dougl.) Lindi (Pinaceae)	49, 179
45. Abietospiran $C_{31}H_{48}O_4$		219—221; —16,8 (chloroform)	Abies alba (Pinaceae)	81
46. Anhydro-15-O-methylcimigenol $C_{31}H_{48}O_4$		222—223; +38,5	Cimicifuga acerina Sieb. et Zucc. (Ranunculaceae)	180
47. 24-Methylenecycloartanone $C_{31}H_{50}O$		103—105; +24 (chloroform)	Spondias pinnata (Koen. et L. f) Kurz (Anacardiaceae)	181, 182

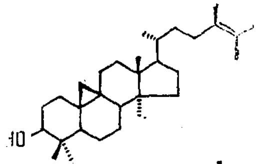
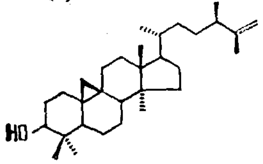
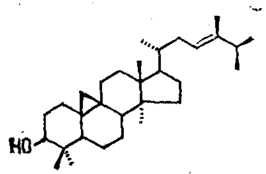
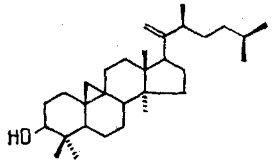
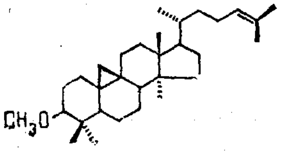
Continuation of Table 3

1	2	3	4	5
48. 24R-Cyclolaudenone $C_{31}H_{50}O$		105; +14,2 chloroform	Polypodium formosanum (Polypodiaceae)	183
49. Cycloeuphoronl $C_{31}H_{50}O$		95–96; —	Euphorbia tirucalli L. (Euphorbiaceae)	184
50. 3β-Hydroxy-24-methylcyclcarten-26-al $C_{31}H_{50}O_3$		166–170; +41	Mangifera indica L. (Anacardiaceae)	185
51. Ambolic acid $C_{31}H_{50}O_3$		167–169; +31	Mangifera indica L. (Anacardiaceae)	177
52. Argentatin B $C_{31}H_{50}O_3$		—	Parthenium argentatum (Compositae)	161

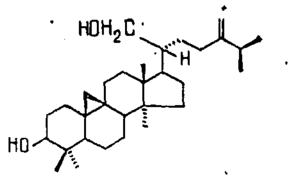
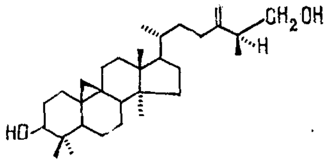
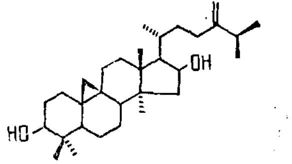
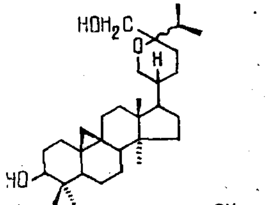
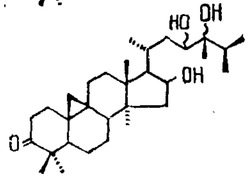
Continuation of Table 3

1	2	3	4	5
53. Lithocarpolone $C_{31}H_{50}O_3$		190–192; +28	Lithocarpus polystachya (Fagaceae)	46
54. 25-O-Methylisodahurinol $C_{31}H_{50}O_5$		237–239; —	Cimicifuga acerina Sieb. et Zucc. (Ranunculaceae)	153
55. 15-O-Methylcimigenol $C_{31}H_{50}O_5$		199,5–200,5; +38,9	Cimicifuga acerina Sieb. et Zucc. (Ranunculaceae)	180
56. 25-O-Methylcimigenol $C_{31}H_{50}O_5$		228–230; —	Cimicifuga acerina Sieb. et Zucc., C. japonica (Ranunculaceae)	86, 187
57. 24-Methylenecycloartanol $C_{31}H_{52}O$		121–122; +43	Rice bran oil	182

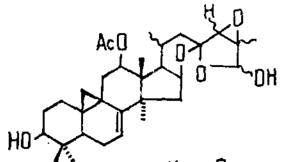
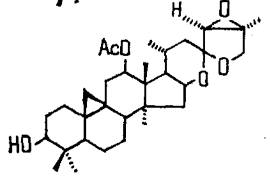
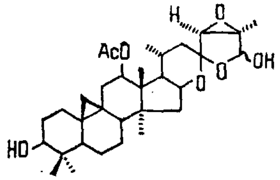
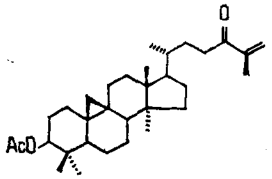
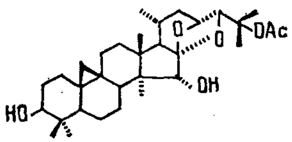
Continuation of Table 3

1	2	3	4	5
58. Cyclobranol $C_{31}H_{52}O$		156,5—157,5; +38,4 (chloroform)	Rice bran oil	
59. Cyclolaudenol $C_{31}H_{52}O$		125; +46	Opium	189, 190
60. Cyclosadol $C_{31}H_{52}O$		132—134; +41 (chloroform)	Zea mays L. (Gramineae)	191, 192
61. Cycloswietenol $C_{31}H_{52}O$		143—145; +55 (chloroform)	Swietenia mahagoni Linn. (Meliaceae)	193, 194
62. Methyl ether of cycloartenol $C_{31}H_{52}O$		118—120; +66 (chloroform)	genus Chionochloa (Gramineae)	40, 195

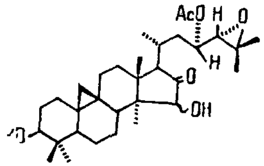
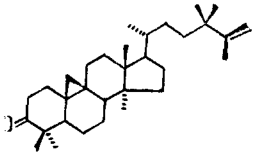
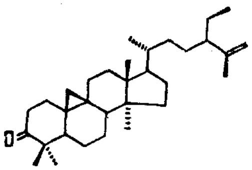
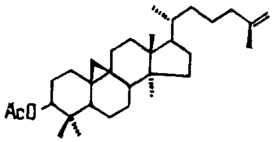
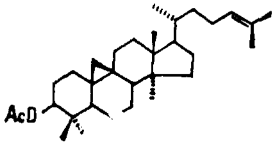
Continuation of Table 3

1	2	3	4	5
63. 24-Methylenecycloartane-3β, 21-diol $C_{31}H_{52}O_2$		165—168; +42	Lithocarpus polystachya (Fagaceae)	46
64. 24-Methylenecycloartane-3β, 26-diol $C_{31}H_{52}O_2$		154—157; +54	Mangifera indica L. (Anacardiaceae)	178, 1
65. Cyclomahogenol $C_{31}H_{52}O_2$		151—152; +42 (chloroform)	Swietenia mahagoni Linn. (Meliaceae)	196
66. Lithocarpodiol $C_{31}H_{52}O_3$		179—180; +54	Lithocarpus polystachia (Fagaceae)	46
67. Argentatin C $C_{31}H_{52}O_4$		—	Parthenium argentatum (Compositae)	161

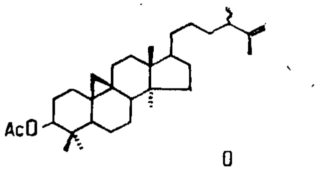
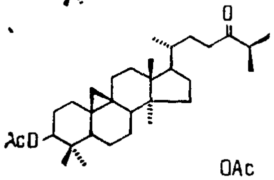
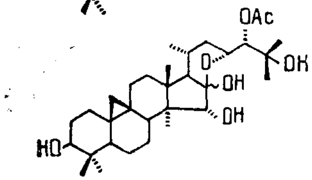
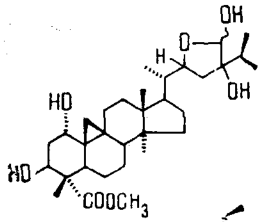
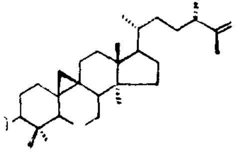
Continuation of Table 3

1	2	3	4	5
68. Genin of cimicifugoside $C_{32}H_{46}O_7$		251–253; —	Cimicifuga simplex Wormsk. (Ranunculaceae)	197
69. 27-Deoxyacetylacteol $C_{32}H_{48}O_6$		289–292; —87,5 (chloroform)	Cimicifuga racemosa (Ranunculaceae)	13
70. Acetylacteol $C_{32}H_{48}O_7$		247–249; —80	Actaea racemosa (Ranunculaceae)	157, 198
71. 3β-Acetoxycycoart-25-en-24-one $C_{32}H_{50}O_3$		133–136; +5,8 (chloroform)	Tillandsia usneoides L. (Bromeliaceae)	172
72. 25-O-Acetylcimigenol $C_{32}H_{50}O_5$		193–194; +39,5	Cimicifuga acerina Sieb. et Zucc. (Ranunculaceae)	180

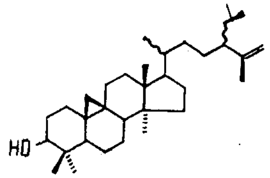
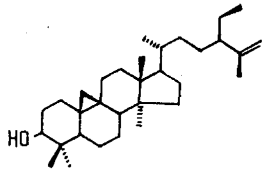
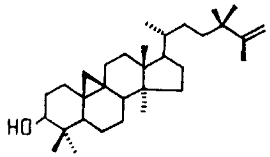
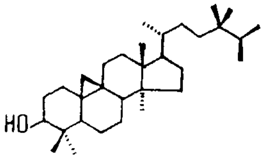
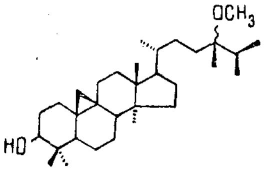
Continuation of Table 3

1	2	3	4	5
73. Acetylshengmanol $C_{32}H_{50}O_6$		(Amorphous) —16,1 (chloroform)	Cimicifuga japonica (Ranunculaceae)	199
74. Cyclobalanone $C_{32}H_{52}O$		187—190; +20	Quercus glauca Thunb.-Cyclobalanopsis glauca Qerst. (Fagaceae)	16
75. 24R-Cyclomargenone $C_{32}H_{52}O$		122—124; +13,4 (chloroform)	Polypodium formosanum (Polypodiaceae)	183
76. Isocycloartenyl acetate $C_{32}H_{52}O_2$		112—113; +53,8 (chloroform)	Artocarpus chaplasha Roxb. (Moraceae)	21
77. Cycloartenyl acetate $C_{32}H_{52}O_2$		118—120; +57 (chloroform)	Artocarpus chaplasha Roxb. (Moraceae)	21

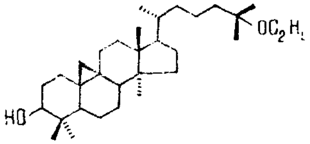
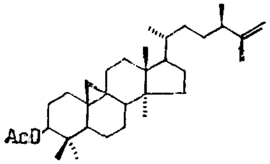
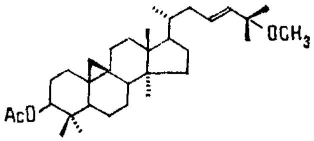
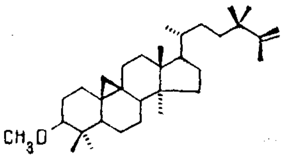
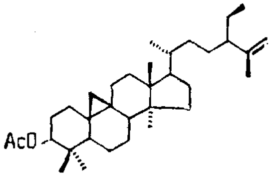
Continuation of Table 3

1	2	3	4	5
78 Cyclopeltenyl acetate $C_{32}H_{52}O_2$		189; +41 (chloroform)	Macaranga peltata Muel. (Euphorbiaceae)	170
79. Lagerenyl acetate $C_{32}H_{52}O_3$		122—123; +57.8 (chloroform)	Lagerstroemia langosteri (Lythraceae)	171
80. 24-O-Acetylhydroshengmanol $C_{32}H_{52}O_7$		200—202; +9 (methanol)	Cimicifuga japonica (Ranunculaceae)	86
81. Methyl passiflorate $C_{32}H_{52}O_7$		224; +78,6 (pyridine)	Passiflora edulis Sims. (Passifloraceae)	58. 80
82. Polysthicol $C_{32}H_{54}O$		— +42 (chloroform)	Polysthicum aculeatum (L.) Roth. (Polypodiaceae)	15

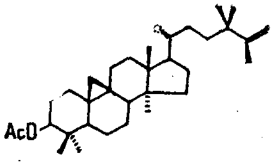
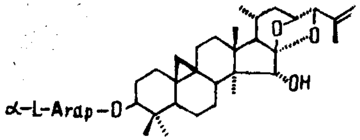
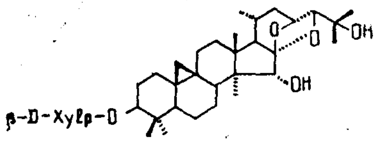
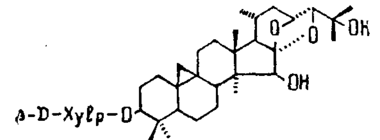
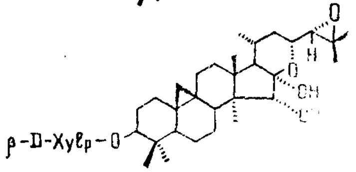
Continuation of Table 3

1	2	3	4	5
83. Tripyllol $C_{32}H_{54}O$		127—133; +44,8 (chloroform)	Adenophora triphylla var. japonica (Campanulaceae)	69
84. 24R-Cyclomargenol $C_{32}H_{54}O$		134—136; +34,3 (chloroform)	Polypodium formosanum (Polypodiaceae)	183
85. Cycloneolitsol $C_{32}H_{54}O$		120—122, 183—185; +42, +48 (chloroform)	Polypodium juglandifolium H. B. Willd (Polypodiaceae)	200, 201
86. 24,24-Dimethyl-9, 19-cyclolanostan-3β-ol $C_{32}H_{56}O$		134—136; +34,4 (chloroform)	Polypodium juglandifolium H. B. Willd (Polypodiaceae)	39
87. 24-Methoxy-24-methylcycloartanol $C_{32}H_{56}O_2$		151; +42,7	Rice bran oil	175, 176

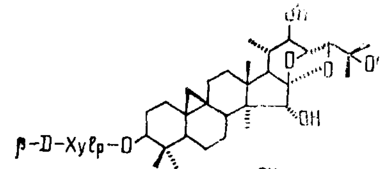
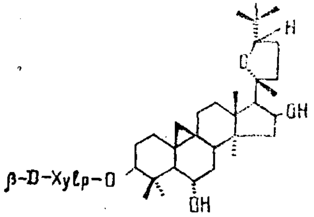
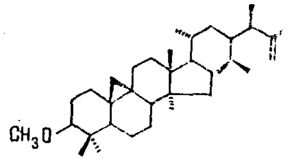
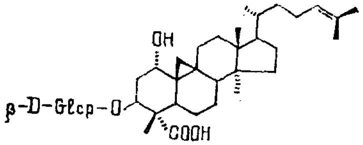
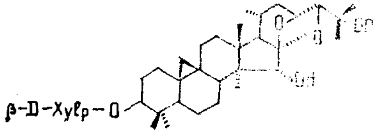
Continuation of Table 3

1	2	3	4	5
88. 25-Ethoxycycloartanol $C_{32}H_{56}O_2$		109; +47,7	Rice bran oil	175, 176
89. 24R-Cyclolaudenyl acetate $C_{33}H_{54}O_2$		127—128; +53.5 (chloroform)	Polypodium formosanum (Polypodiaceae)	183
90. 3β-Acetoxy-25-methoxycycloart-23-ene $C_{33}H_{54}O_3$		152—154; +48 (chloroform)	Tillandsia usneoides L. (Bromeliaceae)	172
91. Cycloneolitsin $C_{33}H_{56}O$		169—174; +63 (chloroform)	Neolitsea dealbata R. Br. Meer. (Lauraceae)	40
92. 24R-Cyclomargenyl acetate $C_{34}H_{56}O_2$		144—145; +50.5 (chloroform)	Polypodium formosanum (Polypodiaceae)	183

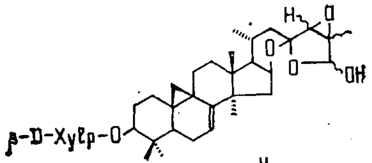
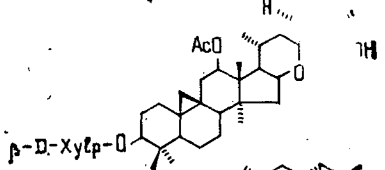
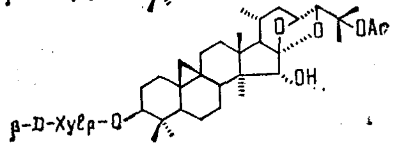
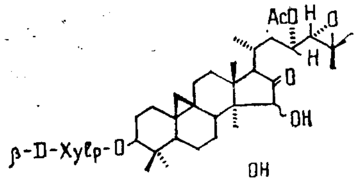
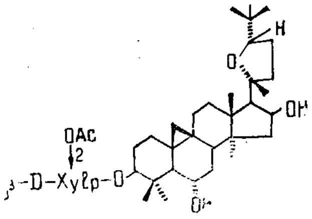
Continuation of Table 3

1	2	3	4	5
93. Cycloneolitsol acetate $C_{34}H_{56}O_2$		112 - 113; +48 (chloroform)	Polypodium juglandifolium H. B. Willd (Polypodiaceae)	200,201
94. 25-Anhydrocimigenol arbinoside $C_{35}H_{56}O_8$		272—274; +29,7	Cimicifuga japonica (Ranunculaceae)	85
95. Cimigenol xyloside $C_{35}H_{56}O_9$		261—264; +8 (pyridine)	Actaea racemosa (Ranunculaceae)	164
96. Cimigol xyloside $C_{35}H_{56}O_9$		297—299; +23,7 (dichloromethane-methanol (1:1))	Cimicifuga japonica (Ranunculaceae)	199
97. Shengmanol xyloside $C_{35}H_{56}O_9$		244—245,3; −10,2 (chloroform-methanol(1:1))	Cimicifuga japonica (Ranunculaceae)	133

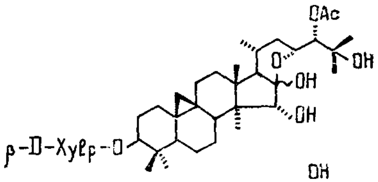
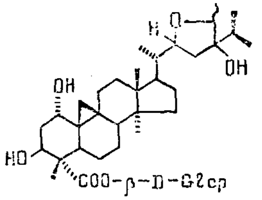
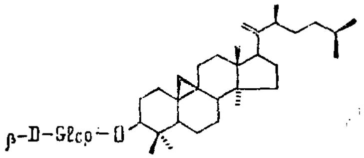
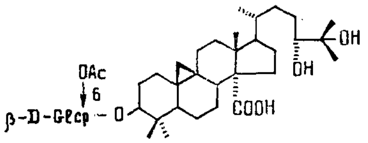
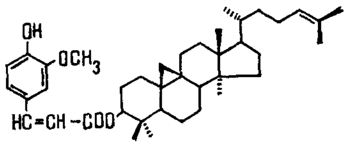
Continuation of Table 3

1	2	3	4	5
98. **22-Hydroxycimigenol xyloside** $C_{35}H_{56}O_{10} \cdot H_2O$		282—284; +17.7 (chloroform—methanol (1:1))	Cimicifuga japonica (Ranunculaceae)	86
99. **Cyclogaleginoside B** $C_{35}H_{58}O_9$		252 -254; +32 (pyridine)	Astragalus galegiformis L. (Leguminosae)	131
100. **Skimmiwallichin** $C_{35}H_{60}O$		152—154; +67.3 (chloroform)	Skimmia wallichii Hook. f. et Thoms (Rutaceae)	17
101. **3-O-β-D-Glucoside of mollic acid** $C_{36}H_{58}O_9$		248—250; +38 (pyridine)	Combretum molle (Combretaceae)	56
102. **25-O-Methylcimigenoside** $C_{36}H_{58}O_9$		268—270; —	Cimicifuga acerina, C. japonica (Ranunculaceae)	202

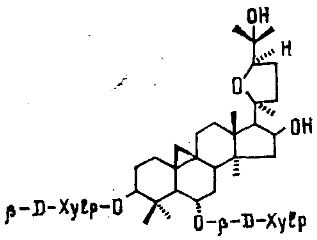
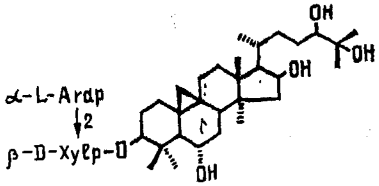
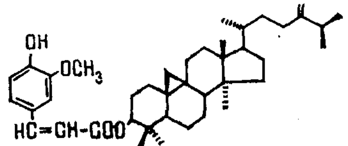
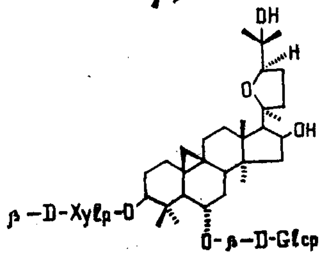
Continuation of Table 3

1		3	4	5
103. Cimicifugoside $C_{37}H_{54}O_{11}$		237–238; —	Cimicifuga simplex Wormsk (Ranunculaceae)	197
104. Actein $C_{37}H_{56}O_{11}$		246–250; 75,7	Actaea racemosa-Cimicifuga racemosa (Ranunculaceae)	156, 157, 198, 203, 204,
105. 25-O-Acetylcimigenoside $C_{37}H_{58}O_{10}$		234–235; —	Cimicifuga acerina (Ranunculaceae)	202
106. Acetylshengmanol xyloside $C_{37}H_{58}O_{10}\cdot H_2O$		280–281; –23,7 (dichloromethane–methanol (1:1))	Cimicifuga japonica (Ranunculaceae)	199
107. Cyclogaleginoside A $C_{37}H_{60}O_{10}$		224–226; +40 (pyridine)	Astragalus galegiformis L. (Leguminosae)	131

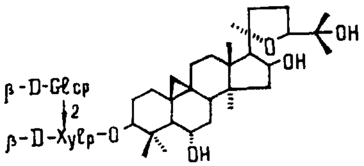
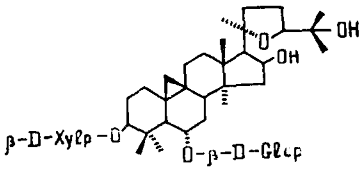
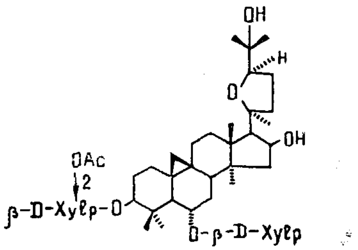
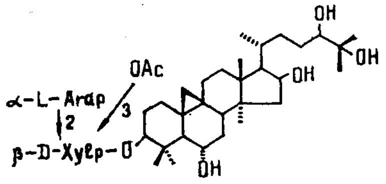
Continuation of Table 3

1	2	3	4	5
108. 24-O-Acetylhydroshengmanol xyloside $C_{37}H_{60}O_{11}$		235–237; +6,6 (chloroform-methanol (1:1))	Cimicifuga japonica (Ranunculaceae)	86
109. Passiflorin $C_{37}H_{60}O_{12}$		183; +47,1 (pyridine)	Passiflora edulis Sims. (Passifloraceae)	58
110. Cycloswietenol 3-O-β-D-glucopyranoside $C_{37}H_{62}O_6$		— +45 (methanol)	Swietenia mahagoni (Meliaceae)	205
111. Lyofolic acid $C_{38}H_{62}O_{11}$		130–140; —	Lyonia ovalifolia (Drude) var. elliptica (Hand—Mazz) (Ericaceae)	173, 206
112. Oryzanol A $C_{40}H_{68}O_3$		150,5–151,5; +40	Rice bran oil	207, 208

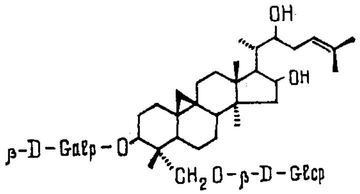
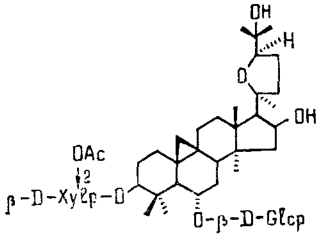
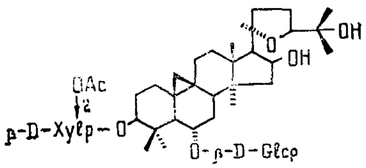
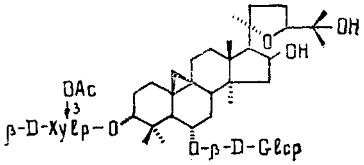
Continuation of Table 3

1	2	3	4	5
113. Cyclosiversioside E $C_{40}H_{66}O_{13}$		218—220; +29.9 (methanol)	Astragalus sieversianus Pall. (Leguminosae)	209
114. Askendoside C $C_{40}H_{68}O_{13}$		197—158; +27.3 (methanol)	Astragalus taschkendicus Bunge (Leguminosae)	210
115. Oryzanol A $C_{41}H_{60}O_2$		162—164; +36	Rice bran oil	182, 211, 212,
116. Cyclosiversioside E $C_{41}H_{68}O_{14}$		247—249; +36.6 (methanol)	Astragalus sieversianus Pall. (Leguminosae)	124

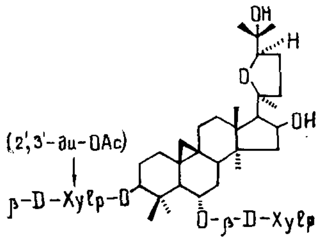
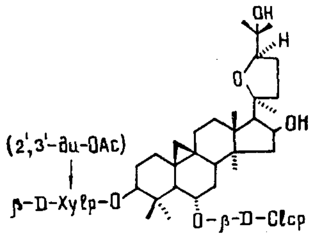
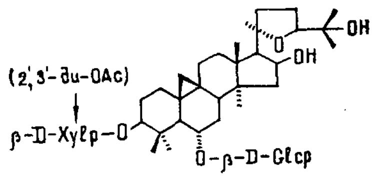
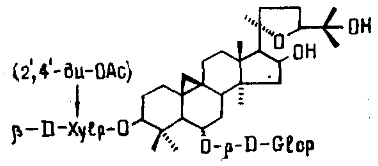
Continuation of Table 3

1	2	3	4	5
117. Astragaloside III $C_{41}H_{68}O_{14}\cdot H_2O$		245—247; +21,4 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	88
118. Astragaloside IV $C_{41}H_{68}O_{14}\cdot 2H_2O$		299—301; +24.4 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	87
119. Cyclosiversioside C $C_{42}H_{68}O_{14}$		253 -255; +30,1 (methanol)	Astragalus sieversianus Pall. (Leguminosae)	125
120. Askendoside A $C_{42}H_{70}O_{14}$		213—214; 0 (methanol)	Astragalus taschkendicus Bunge (Leguminosae)	129

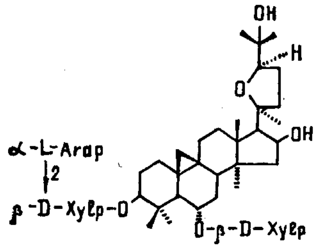
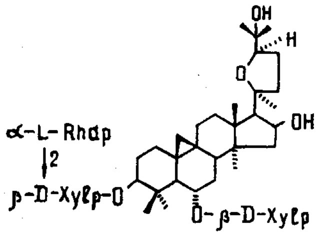
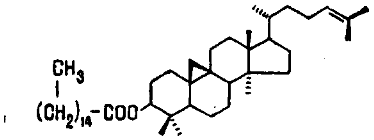
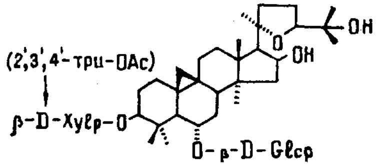
Continuation of Table 3

1	2	3	4	5
121. Thalicoside A $C_{42}H_{70}O_{14}$		255—258; +8,94 (methanol)	Thalictrum minus L. (Ranunculaceae)	132
122. Cyclosiversioside D $C_{43}H_{70}O_{15}$		266—268; +46,0 (methanol)	Astragalus basineri Trautv., Astragalus sieversianus Pall. (Leguminosae)	130
123. Astragaloside II $C_{43}H_{70}O_{15} \cdot H_2O$		251—253; +31,2 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	87
124. Isoastragaloside II $C_{43}H_{70}O_{15} \cdot H_2O$		223—224; +15,0 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	87

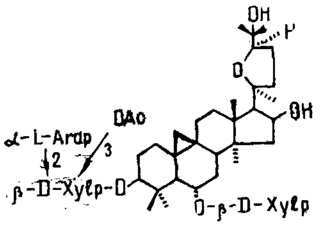
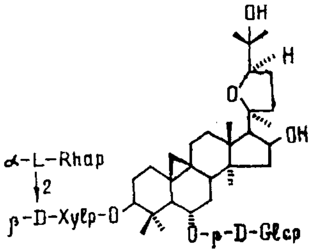
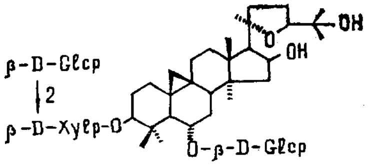
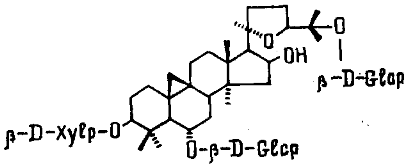
Continuation of Table 3

1	2	3	4	5
125. Cyclosiversioside A $C_{44}H_{70}O_{16}$		230–232; +23.8 (methanol)	Astragalus sieversianus Pall. (Leguminosae)	125
126. Cyclosiversioside B $C_{45}H_{72}O_{16}$		198–200; +10.7 (methanol)	Astragalus basineri Trautv., Astragalus sieversianus Pall. (Leguminosae)	130
127. Astragaloside I $C_{45}H_{72}O_{16} \cdot H_2O$		184–186; +12.7 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	87
128. Isoastragaloside I $C_{45}H_{72}O_{16} \cdot H_2O$		218–220; +17.9 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	87

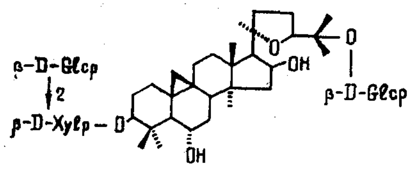
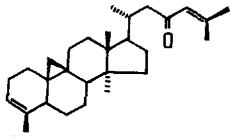
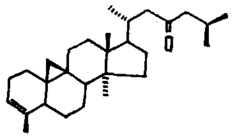
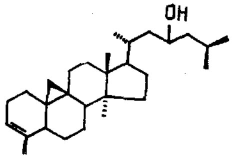
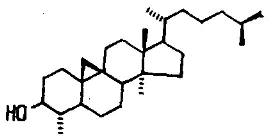
Continuation of Table 3

1	2	3	4	5
129. Askendoside D $C_{45}H_{74}O_{17}$		235–236; —9.1 (pyridine)	Astragalus taschkendicus Bunge (Leguminosae)	213
130. Cyclosiversioside G $C_{46}H_{76}O_{17}$		222—224; —5.42 (methanol)	Astragalus sieversianus Pall. (Leguminosae)	126
131. Cycloartenyl palmitate $C_{46}H_{80}O_2$		52—54; —	Strychnos nux-vomica L. (Loganiaceae), Musa sapientum L. (Musaceae)	214
132. Acetylastragaloside I $C_{47}H_{74}O_{17}$		280—281; +1.8 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	87

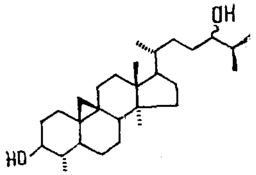
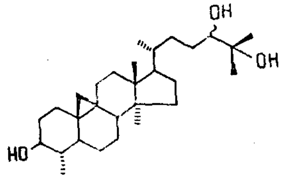
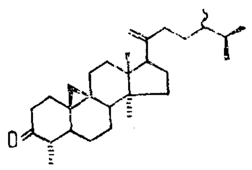
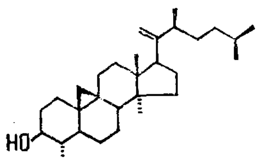
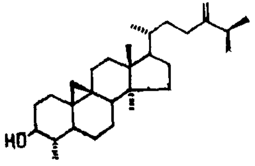
Continuation of Table 3

1	2	3	4	5
133. Askendoside B $C_{47}H_{78}O_{18}$		215—218; —45,5 (pyridine)	Astragalus taschkendicus Bunge (Leguminosae)	127
134. Cyclosiversioside H $C_{47}H_{78}O_{18}$		262—264; —30,0 (methanol)	Astragalus sieversianus Pall. (Leguminosae)	128
135. Astragaloside VI $C_{47}H_{78}O_{19}\cdot H_2O$		290—291; +17,3 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	88
136. Astragaloside VII $C_{47}H_{78}O_{19}\cdot 2H_2O$		292—293; +10,3 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	88

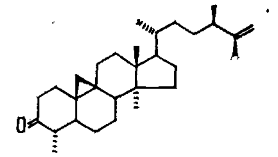
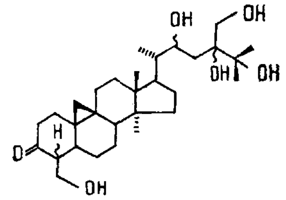
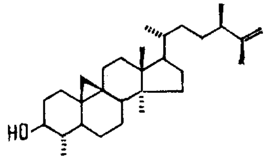
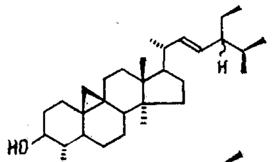
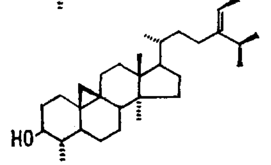
Continuation of Table 3

1	2	3	4	5
137. Astragaloside V $C_{47}H_{78}O_{19} \cdot 3H_2O$		202–204; +7,2 (methanol)	Astragalus membranaceus Bunge (Leguminosae)	88
138. Norcycloartene 1 $C_{29}H_{44}O$		— +5.6 (chloroform)	Tydemania expeditionitis (Chlorophyta)	14
139. Norcycloartene 2 $C_{29}H_{46}O$		— +16,1 (chloroform)	Tydemania expeditionitis (Chlorophyta)	14
140. Norcycloartene 3a $C_{29}H_{48}O$		— +12,6 (chloroform)	Tydemania expeditionitis (Chlorophyta)	14
141. 31-Norcycloartanol $C_{29}H_{50}O$		128–132; +49 (chloroform)	Polypodium vulgare (Polypodiaceae)	26

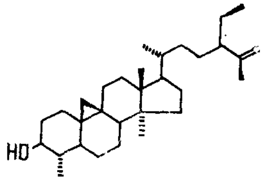
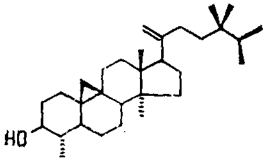
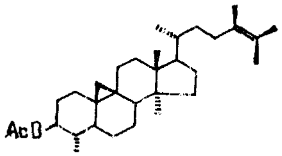
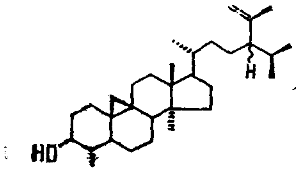
Continuation of Table 3

1	2	3	4	5
142. 4α,14α-Dimethyl-9,19-cyclocholestane-3β,24ξ-diol $C_{29}H_{50}O_2$		146–148; +11,7 (chloroform)	Ambrosia elatior L. (Compositae)	42
143. 4α,14α-Dimethyl-9,19-cyclocholestane-3β,24ξ, 25-triol $C_{29}H_{50}O_3$		104; +23,4 (chloroform)	Ambrosia elatior L. (Compositae)	42
144. 4α,14α-Trimethyl-9,19-Cyclocholestane-20-en-3-one $C_{30}H_{48}O$		138–139; +51,2	Musa paradisiaca L. (Musaceae)	215
145. 31-Norcycloswietenol $C_{30}H_{50}O$		131–133; +89,5 (chloroform)	Swietenia mahagoni L. (Meliaceae)	47
146. Cycloeucalenol $C_{30}H_{50}O$		138–139; +45	Eucalyptus microcorys (Myrtaceae)	216, 217

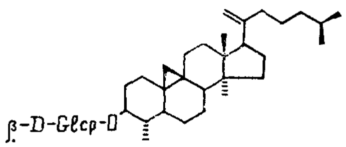
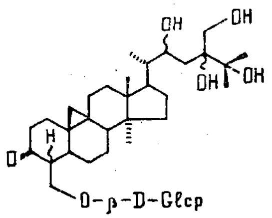
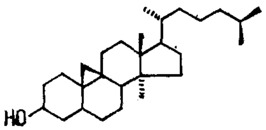
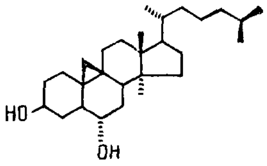
Continuation of Table 3

1	2	3	4	5
147. 31- **Norcyclolaudenone** $C_{30}H_{50}O$		130–132; +49,0	Musa sapientum L. (Musaceae)	44, 55
148. **Cymbidosone** $C_{30}H_{50}O_6$		226–229; +28 **(pyridine)**	Cymbidium giganteum (Orchidaceae)	68
149. **31-Norcyclolaudenol** $C_{30}H_{52}O$		139–140; +44	Polypodium vulgare (Polypodiaceae)	44, 55
150. **Cyclonervilol** $C_{31}H_{52}O$		166–169; +37,9 **(chloroform)**	Nervilia purpurea Schlechter (Orchidaceae)	24
151. **Cyclofuntumienol** $C_{31}H_{52}O$		143–145; +50	Funtumia elastica (Apocinaceae)	45

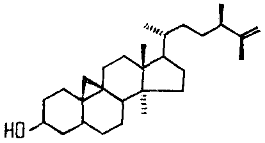
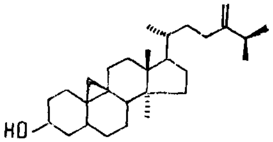
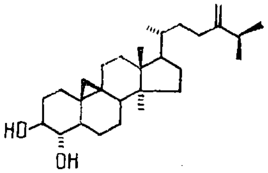
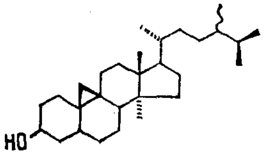
Continuation of Table 3

1	2	3	4	5
152. Cyclotrichosantol $C_{31}H_{52}O$		143—144; +42	Trichosantes palmata L. (Cucurbitaceae)	218
153. 24,24-Dimethyl-4β-demethyl-9,19-cyclolanost-20(21)-en-3β-ol $C_{31}H_{52}O$		142—144; +35,7 (chloroform)	Polypodium juglandifolium H. B. Willd (Polypodiaceae)	39
154. 4α,14α,24-Trimethyl-9β,19-cyclo-5α-cholest-24-en-3β-ol acetate $C_{32}H_{52}O_2$		159—160; —	Brassica napus L. (Cruciferae)	23
155. Cyclohomonervilol $C_{32}H_{54}O$		166—167; +40,5 (chloroform)	Nervilia purpurea Schlechter (Orchidaceae)	24

Continuation of Table 3

1	2	3	4	5
156. 31-Norcycloswietenol 3-O-β-D-glucopyranoside $C_{36}H_{60}O_6$		165—169; +79,5	Swietenia mahagoni L. (Meliaceae)	47
157. Cymbidoside $C_{36}H_{60}O_{11}$		150—152; +24 (methanol)	Cymbidium giganteum (Orchidaceae)	68
158. Pollinastanol $C_{28}H_{48}O$		95; +35 (chloroform)	The pollen of various plants	73, 79
159. Cyclostenol $C_{28}H_{48}O_2$		222—223; +42 (chloroform)	Stenocereus thurberi (Cactaceae)	219

Continuation of Table 3

1	2	3	4	5
160. 14 α-Methyl-9β,19-cyclo-5α-ergost-25-en-3β-ol $C_{29}H_{48}O$		—	Chlorella sorokiniana (Chlorococcales)	220
161. 24-Methylenepollinastanol $C_{29}H_{48}O$		115–117; —	Musa sapientum L. (Musaceae) Astasia longa	51, 221
162. Surianol $C_{29}H_{48}O_2$		173–174,5; +39	Suriana maritima L. (Surianaceae)	50
163. 24-Methylpollinastanol $C_{29}H_{50}O$		—	Astasia longa	221

The glycosides of Astragalus membranaceus Bunge possess a hypotensive, diuretic, and cardiotonic activity. An inhibiting action of these glycosides on lipid oxidation processes has been shown.

Some cycloartame triterpenoids and their derivatives exhibit tranquilizing [143-145], sedative [146], and analeptic and antiinflammatory activities [147, 148].

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STRUCTURE OF A GLUCURONOXYLAN OF THE STEMS OF Symphytum asperum

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The results are given of an investigation of the structure of a glucuronoxylan of the stems of Symphytum asperum Ler. The xylan was isolated by alkaline extraction and was purified by reprecipitation via the copper complex. The polysaccharide was homogeneous according to the results of gel filtration and electrophoresis. It was shown by hydrolysis, periodate oxidation, methylation, oxidation with chromium trioxide and IR and ^{13}C NMR spectroscopy that the macromolecules were based on a β-(1→4)-polyxyloside chain having side chains at the second carbon atoms in the form of 4-O-Me-D-glucuronic acid. To each side chain there were not less than 12 xylose residues.

Continuing a study of the polysaccharides of Symphytum asperum Ler. (prickly comfrey) [1], we have investigated the structure of a glucuronoxylan from the stems of this plant.

The xylan was isolated by alkaline extraction and was purified by two reprecipitations via the copper complex. Its homogeneity was shown by electrophoresis and by gel chromatography on Sephadex G-200. On the gel-filtration elution curve, the protein component coincided with the carbohydrate component, which indicates the possibility of a chemical bond between them.

The preparation isolated was characterized by a high polysaccharide content and a minor amount of impurities of noncarbohydrate nature: ash 1.2%; nitrogen 0.32%.

Complete acid hydrolysis showed the presence in the polysaccharide of D-oxylose, D-glucuronic acid and 4-O-methylglucuronic acid residues.

The negative specific optical activity, $[\alpha]_D^{20}$ −68.0, and the results of IR spectroscopy permitted the assumption of the presence of a β-bond between the monomeric residues in the macromolecule of the glucuronoxylan.

To determine the configuration of the glycosidic bonds we used the method of oxidation with chromium trioxide, which is based on the different behaviors of completely acetylated α- and β-hexopyranosides in relation to CrO_3 [2]. Under the action of chromium trioxide on the acetates of polysaccharides, only β-glycosidic bonds undergo oxidation. The completeness of oxidation was checked by IR spectroscopy from the absence of absorption bands of hydroxy groups, while there were well-defined absorption band at 1240 and 1750 cm^{-1} in the spectrum. Analysis of the oxidation products of the xylan by PC and GLC showed that the reaction mixture contained no monosaccharides, which indicates the presence of β-glycosidic bonds between the xylose residues.

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