

PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Silene*

Z. Saatov, M. B. Gorovits, and N. K. Abubakirov

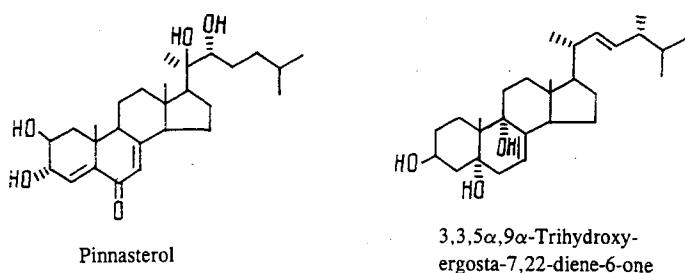
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Ecdysteroids produced by plants of the genus Silene are considered. The discussion covers 17 species of plants, from which 45 ecdysteroids have been isolated. It has been shown that ecdysterone is the most characteristic representative of the biosynthesis of ecdysteroids in the Silene series.

Ecdysteroids form a fairly large group (about 120) of steroid compounds which are found in the animal (Invertebrata) and vegetable kingdoms [1, 2]. Depending on the source of isolation, they are subdivided into zooecdysteroids and phytoecdysteroids. This division must be regarded as somewhat arbitrary, since many ecdysteroids (α -ecdysone, ecdysterone, makiosterone A, and others) are found in animals and plants. In the animal kingdom, ecdysteroids have been found among the Proto-stomia and in arthropods, mollusks, worms (platyhelminths, nemathelminths, and annelids) and echinoderms. It is known that in arthropods, ecdysteroids, as hormones, regulate at least three periods of development embryonic, post-embryonic, and the period of multiplication [4, 4a, 5]. The question of their role in the ontogenesis of other invertebrates still remains open [4].

About a quarter of a century ago, Japanese [6] and Australian [7, 8] chemists reported on the isolation of ecdysteroids from plants. Subsequently, the undisputed advantage of plant raw material as a source of ecdysteroids over animal organisms became apparent. It is expressed not only in the large structural diversity of the phytoecdysteroids but also in their incomparably high level in plant sources reaching, for example, 2.9% of the dry weight of the roots of the plant *Cyanothis arachnoidae* [9]. At the same time, the amount of ecdysteroids in animal organisms does not exceed hundredths of a percentage part [1].

At the present time, the presence of ecdysteroids is known in a large number of families (about 90) in the main orders of higher plants Polypodiophyta, Gymnospermae, and Angiospermae [1]. There is no information on the presence of ecdysteroids in lower plants (Thallophyta). Nevertheless, it must be borne in mind that pinnasterol has been isolated from the red marine alga *Laurentia pinnata* [10], and $3\beta,5\alpha,9\alpha$ -trihydroxyergosta-7,22-dien-6-one [11] from the fungus *Polyporus versicolor*, these being substances with structures close to those of the ecdysteroids



The importance of the ecdysteroids in the life of plants has still not yet been elucidated. It is generally considered that they play an important role in the plant-insect ecological system [12], acting in some cases as allelochemical toxins for insects [1, 4, 13]. Ecdysteroids are attracting the attention of researchers not only by their biological activity in relation to invertebrates, but also as substances exhibiting an anabolic and tonic action on mammals [14, 15].

From the point of view of the search for ecdysone-containing plants among representatives of the domestic flora, plants of the genus *Silene* (catchfly, Caryophyllaceae family). This genus, numbering about 400 representatives in the world flora, is represented by 153 species in the former Union and by 84 species in Central Asia [16, 17].

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TABLE 1. Plants of the Genus *Silene* from which Ecdysteroids have been Extracted

Plant	Ecdysteroid
1. <i>Silene brahuica</i>	(1,17,21,26,27,28,29,34,35) ^a , (7,9,11,15,17,26,27,28,30,35) ^b
2. <i>S. chamarensis</i>	35
3. <i>S. dioica</i>	25,35
4. <i>S. graminifolia</i>	35
5. <i>S. jenissensis</i>	35
6. <i>S. latifolia</i>	7,11,35
7. <i>S. longicalycina</i>	35
8. <i>S. multiflora</i>	35
9. <i>S. nutans</i>	(18,21,32,35) ^a ,(4,5,6,17, 19,20,21,35) ^b
10. <i>S. praemixta</i>	1,7,11,12,23,31,33,35
11. <i>S. oites</i>	3,7,9,11,13,16,17,20,22, 24,35,36,38,40,42
12. <i>S. repens</i>	35
13. <i>S. scabrifolia</i>	7,8,17,26,29,35,38,39, 41,43,44,45
14. <i>S. schafii</i>	21,35
15. <i>S. sobolevskajae</i>	35
16. <i>S. tatarica</i>	14 ^a ,37 ^b
17. <i>S. wallichiana</i>	1,2,7,10,11,35,38

*See note to Table 2.

In the present paper we describe ecdysteroids isolated from various species of *Silene*. The first to show the presence of ecdysteroids in plants of this genus, with *S. praemixta* as an example (9, Table 1), were N. K. Abubakirov et al., in 1979 [18]. This plant proved to be extremely rich in ecdysterone—the main molting and metamorphosis hormone of insects and the most widely distributed ecdysteroid in the animal and vegetable kingdoms (35, Tables 2 and 3) [19]. The results of an analysis performed by the method of [20] showed that ecdysterone accumulates in the greatest amount in the leaves, where its concentration reaches 2.5%, while the roots and inflorescences contain 0.34 and 1.7%, respectively.

Revina et al. [21] examined eight species of catchfly from the flora of the High Altai for the presence of ecdysterone. Ecdysterone was found in seven of them (2, 4, 5, 8, 9, 12, 15) [35]. Only one species *S. turgida* was distinguished by the absence of ecdysteroids. These authors [21] explained this by the assumption that it belongs to the section Auriculatae, morphologically distinct from the other species. Ecdysterone is undoubtedly the most characteristic representative of the biosynthesis of ecdysteroids in the order Silene [22]. It is found in all catchflies containing ecdysteroids, with a single exception *S. tatarica* [16]. However, there is a high probability that ecdysterone will be found in this plant, as well, when it is studied more carefully. Ecdysterone possesses a pronounced tonic and adaptogenic action on mammals. A drug used in medical practice has been created from it [23, 24]. As can be seen from Tables 1 and 2, plants of the genus *Silene* may be regarded as a good source of ecdysterone.

Ecdysteroids have been isolated from various species of catchfly with the exception of four compounds: poststerone (22), its dihydro analogue (16), rubrosterone (24), and sidisterone (25)* which belong to the C-27 steroids. Compounds 16 and 22 (C-21), 24 (C-19), and also (25)* (C-24) have been determined in the individual species in small amounts and their biosynthesis is obviously not representative for the genus *Silene*. We may note that sidisterone (25)* is the first known ecdysterone containing 24 carbon atoms [25].

Characteristic for plants of this genus is the presence of deoxyecdysteroids. This relates in the first place to 2-deoxy- α -ecdysone [7] and 2-deoxyecdysterone (11), which have been detected in appreciable amounts in many of the *Silene* species investigated. In all probability, the 2-deoxyecdysteroids (7) and (11), together with ecdysterone, must also be ascribed to some of the main products of biosynthesis. Their presence may be expected in other catchfly species, as well.

Another group of deoxy derivatives includes 22-deoxyecdysteroids (4), (5), (6), and (32). In contrast to the 2-deoxy-steroids, their level in the plants is low, and they have been identified only in individual representatives. 2-Deoxy- and 22-deoxyecdysteroids are known as metabolites of animal origin [2, 4, 26-28], while 2-deoxyecdysteroids and, in particular, 2-deoxy- α -ecdysone play an important role in the regulation of the processes of reproduction in arthropods [29, 30]. It is interesting to note that 22-deoxy-26-hydroxyecdysterone (6) and taxisterone (3) have been isolated from individuals of *Pycnogonum litorale* [28], which belongs to the class of marine spiders (*Pantopoda*)—ancient representatives of marine arthropods.

*There is some confusion over the compound "sidisterone" (25) — Publisher.

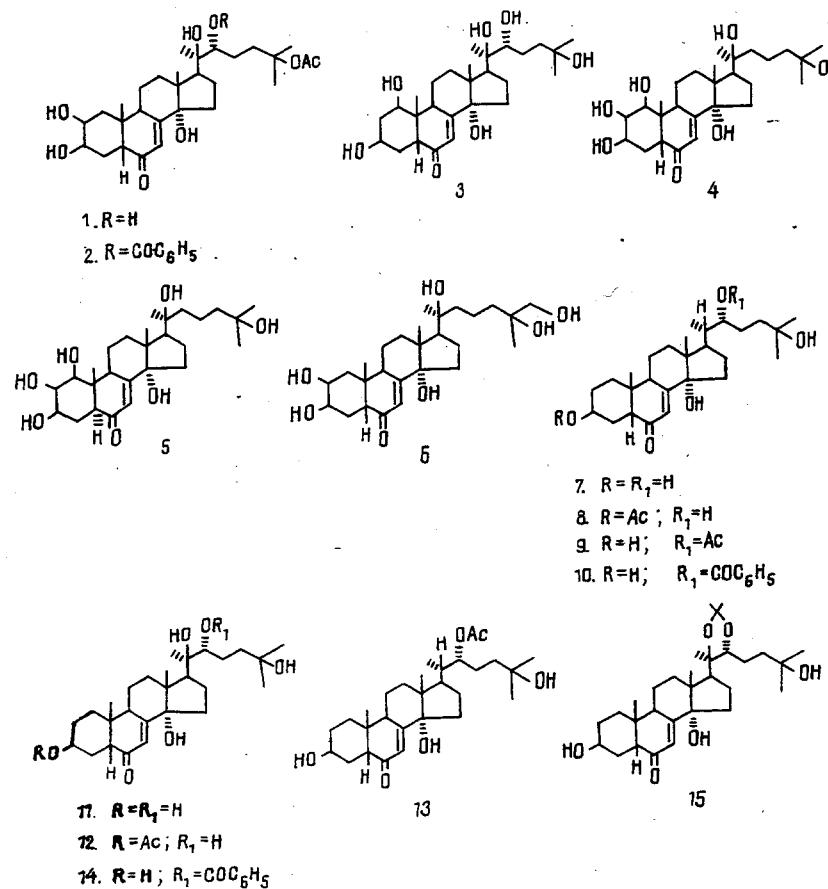
TABLE 2. Ecdysteroids Isolated from Plants of the Genus *Silene*

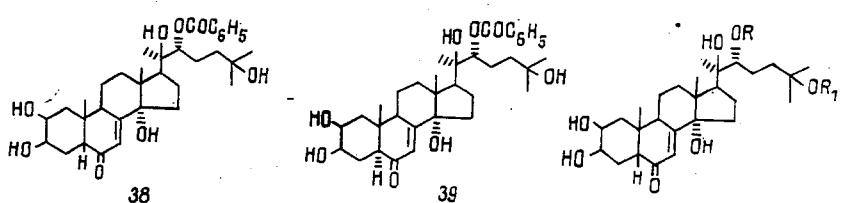
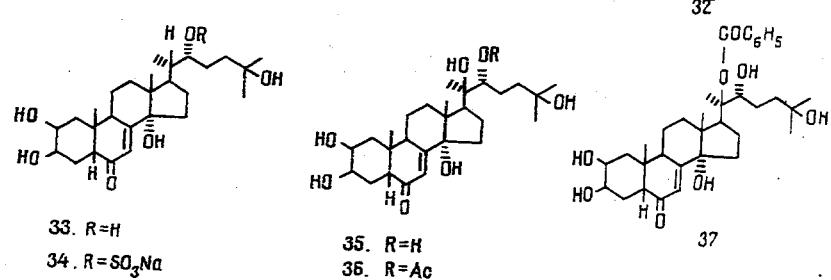
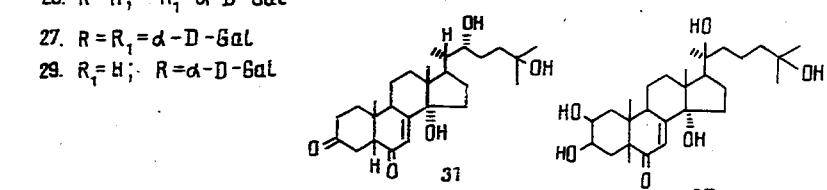
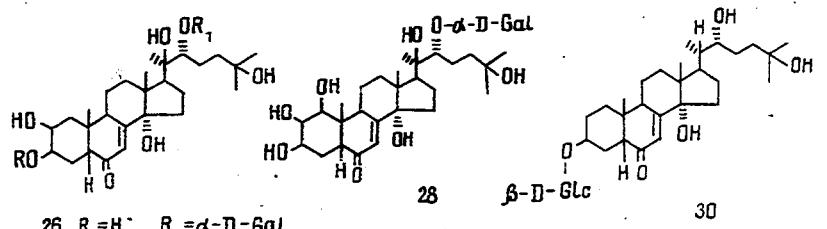
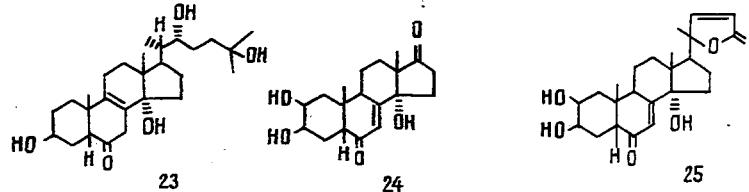
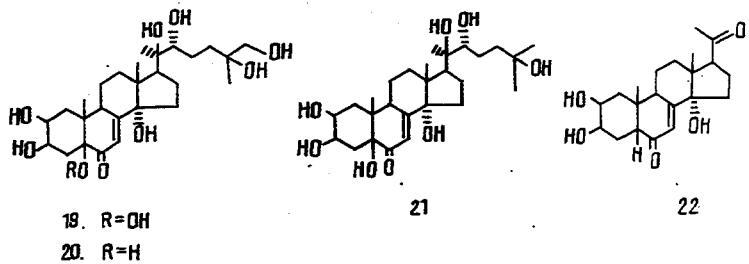
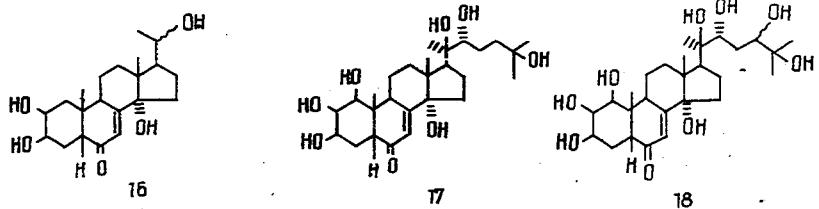
Ecdysteroid	Source, organ of the plant, yield (% on the air-dry raw material), literature
1. Viticosterone E	1 ^c (e.p. —0,0012) [34]; 10 (i,l —0,0017) [35]; 17 (e.p. —0,006) [36]
2. Viticosterone E 22-O-benzoate	17 (e.p. —0,0012) [37]
3. 2-Deoxyintegristerone A	11 (e.p.) ^d [32]
4. 22-Deoxyintegristerone A	9 (e.p.) ^d [32]
5. 5 α -22-Deoxyintegristerone A	9 (e.p.) ^d [32]
6. 22-Deoxy-26-hydroxyecdysterone	9 (e.p.) ^d [32]
7. 2-Deoxy- α -ecdysone	1 (e.p. —0,15) [38]; 1 (r. —0,06) [39]; 6 (i,l —TLC) [12]; 10 (i,l —0,12) [18]; 11 (e.p. —0,0009) [32,40]; 13 (e.p. —0,2) [41]; 17 (e.p. —0,71) [37]
8. 2-Deoxy- α -ecdysone 3-acetate	13 (e.p. —0,0011) [42]
9. 2-Deoxy- α -ecdysone 22-acetate	1 (r. —0,002) [39]; 11 (e.p.) ^d [32]
10. 2-Deoxy- α -ecdysone 22-O-benzoate	17 (e.p. —0,001) [36]
11. 2-Deoxyecdysterone	1 (e.p. —0,03) [38]; 1 (r. —0,02) [39]; 6 (e.p. —TLC) [12]; 10 (i,l —0,82) [18]; 11 (e.p.) ^d [32]; 17 (e.p. —0,40) [36]
12. 2-Deoxyecdysterone 3-acetate	10 (e.p. —0,002) [35]
13. 2-Deoxyecdysterone 22-acetate	11 (e.p.) ^d [32]
14. 2-Deoxyecdysterone 22-O-benzoate	16 (e.p.) ^d [32]
15. 2-Deoxyecdysterone 20; 22-monoacetonide	1 (r. —0,0014) [39]
16. Dihydropoststerone	11 (e.p.) ^d [32]
17. Integristerone A	1 (e.p. —0,20; r. —0,0045) [34]; 1 (r. —0,007) [39]; 9 (e.p.) ^d [32,43]; 11 (e.p.) ^d [32]; 13 (e.p. —0,001) [44]
18. Nusilsterone	9 (w.p. —0,002) [45]
19. 26-Hydroxypolypodine B	9 (e.p.) ^d [32,43]
20. 26-Hydroxyecdysterone	9 (w.p.) ^d [43]; 11 (e.p. —0,0034) [32,40]
21. Polypodine B	1 (e.p. 0,002) [34]; 9 (e.p. —0,010) [46]; 9 (w.p.) ^d [43]; 14 (w.p.) ^d [43]
22. Poststerone	11 (e.p.) ^d [32]
23. Premixisterone	10 (i,l —0,0026) [18,47]
24. Rubrosterone	11 (e.p.) ^d [32]
25. Sidisterone*	3 (e.p.) ^d [25]
26. Sileneoside A	1 (r. —0,02; 0,003) [34,39]; 13 (e.p. —0,001) [44]
27. Sileneoside B	1 (r. —0,0045; 0,003) [39,48]
28. Sileneoside C	1 (r. —0,0032; 0,002) [39,49]
29. Sileneoside D	1 (r. —0,0013) [50]; 13 (e.p. —0,001) [44]
30. Sileneoside E	1 (e.p. —0,15) [38]
31. Silenosterone	10 (i,l —0,003) [18]
32. Taxisterone (22-deoxyecdysterone)	9 (e.p. —0,0023) [51]
33. α -Ecdysone	10 (i,l —0,025) [35]
34. α -Ecdysone 22-sulfate	1 (r. —0,001) [52]

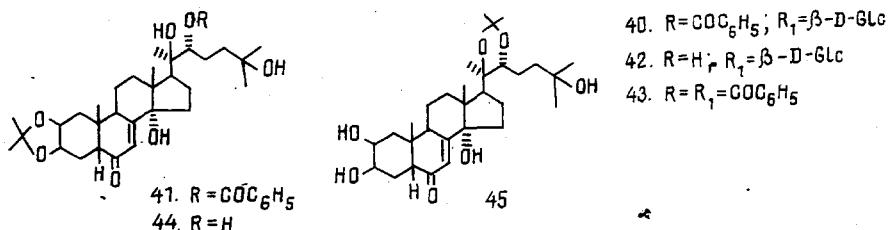
TABLE 2. (Continued)

Ecdysteroid	Source, organ of the plant, yield (% on the air-dry raw material), literature
35. Ecdysterone	1 (e.p. —0,03) [34]; 1 (r. —0,094; 0,004) [34,39]; 2 (e.p. —0,40)d [21]; 3 (e.p.)d [25]; 4 (e.p. —0,60)d [21]; 5 (e.p. —1,30)d [21]; 6 (i,l. —TCX) [12]; 7 (i,l. —TLC) [12]; 8 (e.p. —1,90)d [21]; 9 (e.p. —0,36) [46]; 9 (e.p. —0,27) [32]; 10 (i,l. —0,65) [19]; 11 (e.p. —0,98) [32]; 12 (e.p. —0,50)d [21]; 13 (e.p. —0,046) [41]; 14 (e.p.)d [43]; 15 (e.p. —0,50)d [21]; 17 (e.p. —0,46) [36]
36. Ecdysterone 22-acetate	11 (e.p.)d [32]
37. Ecdysterone 20-O-benzoate	16 (w.p. —0,0026) [53]
38. Ecdysterone 22-O-benzoate	11 (e.p.)d [32]; 13 (e.p. —0,16) [41]; 17 (e.p. —0,033) [36]
39. 5 α -Ecdysterone 22-O-benzoate	13 (e.p. —0,0001) [54]
40. Ecdysterone 22-O-benzoate 25-glucoside	11 (e.p.)d [32]
41. Ecdysterone 22-O-benzoate 2,3-monoacetonide	13 (e.p. —0,01) [55]
42. Ecdysterone 25-glucoside	11 (e.p.)d [32]
43. Ecdysterone 22,25-di-O-benzoate	13 (e.p. —0,0008) [55]
44. Ecdysterone 2,3-monoacetonide	13 (e.p. —0,02) [55]
45. Ecdysterone 20,22-monoacetonide	13 (e.p. —0,0026) [56]

Notes. a, b) Different growth sites of plants of the given species; c) the figure denotes the serial number of the name of the plant shown in Table 1; d) yields not given in the original paper; e) results of analysis; r) roots; e.p.) epigeal part; i) inflorescences; l) leaves; w.p.) whole plant.

TABLE 3. Structural Formulas of Ecdysteroids Isolated from Plants of the Genus *Silene*





Of the Central Asian species of catchflies, *S. brahuica*, which produces ecdysteroid glycosides, is attracting attention. Five different glycosides have been isolated from this plant silenosides A (26), B (27), C (28), D (29), and E (30). Before the work of Hikino et al. [31], only one carbohydrate-containing ecdysterone was known ponasteroside A, isolated from the plant *Pteridium aquilinum* [31]. At the present time, including the sileneosides, more than ten ecdysteroids bearing sugar residues have been described [1, 32, 33]. It is obvious that the presence of ecdysteroid glycosides in *S. brahuica* is not fortuitous for the catchfly genus. Similar substances have already been determined in two species *S. otites* and *S. scabrifolia*.

A large group of compounds is represented by ecdysteroids substituted in the hydroxy functions. Here are found esters of acetic acid (1, 8, 9, 12, 13, 36), benzoic acid (2, 10, 14, 37-41, 43), and sulfuric acid (34) and also isopropylidene derivatives (15, 41, 44, 45). Ecdysteroid esters are characteristic metabolites of animals organisms [4]. As can be judged from the facts given, they are largely characteristic of the biosynthetic processes of plants. It is known that ecdysteroid 22-O-glucosides are less active than their unsubstituted analogues [4]. Ecdysterone 22-O-galactoside, sileneoside A (26) [57], integristerone A 22-O-galactoside, sileneoside C (28), and 2-deoxyecdysterone 3-O-glucoside, sileneoside E (30) [58], have also proved to be inactive in relation to a specific biological effect.

The information on the amounts of ecdysteroids given in the present paper show only a general tendency to the biosynthesis of individual compounds by a particular species of plant. The ecdysteroid content (qualitative and quantitative) may change according to the growth site and the vegetation phase. We may be confident that the use of modern methods of separation will permit the detection of a large number of minor components. Indicative in this respect is a study of the plants *S. otites* and *S. scabrifolia*, from which about 15 ecdysteroids have been isolated.

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