SESQUITERPENE DERIVATIVES OF THE GENUS *Ferula*

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The review is devoted to a study of the sequiterpene derivatives of the plants of the genus *Ferula* (Apiaceae). Information is given on the determination of the structure, stereochemistry, and characteristic reactions of 78 coumarins, 39 esters, and six sesquiterpene alcohols isolated from plants of the genus *Ferula*. The possible biogenetic interrelationships and mutual transitions of the sesquiterpenes that are derivatives of aliphatic and of mono- and bicyclic hydrocarbons are discussed. Some information confirming the hypotheses made is given.

The genus *Ferula* Eug. Kor., family Apiaceae, is represented on the world scale by more than 150 species of plants [1], of which about 100 grow in the Soviet Union. The flora of central Asia include more than 70 species of *Ferula*. Extracts of some species of *Ferula* have long been used in folk medicine for treating various diseases [2], possess an antimicrobial and estrogenic action [3, 4], and are natural plant growth inhibitors and stimulators [5].

I. P. Tsukervanik et al. first began to occupy themselves with chemical investigations of plants of the genus *Ferula* as early as 1935. They limited themselves to the characteristic resin of certain species of *Ferula* [6-11]. From the beginning of the sixties, N. P. Kir'yalov et al. took up the study of the components of *Ferula*, having shown that this genus is a source of biologically active compounds [12-21]. They were the first to establish that ferulas contain not only terpenoid coumarins but also sesquiterpene lactones and alcohols [22, 23]. Thanks to the investigations of A. I. Ban'kovskii, M. E. Perel'son, K. S. Rybalko, V. I. Sheichenko, Yu. E. Sklyar, and others, the structures and stereochemistries of more than 30 *Ferula* coumarins and lactones have been demonstrated [24-37]. The sesquiterpene lactones of species of *Ferula* growing in Turkmenia are also being studied by N. P. Kir'yalov, S. V. Serkerov, and V. Yu. Bagirov [38-44].

A systematic study of the chemical compositions of various species of the genus *Ferula* growing in the territory of Uzbekistan and neighboring republics is being carried out in the Institute of the Chemistry of Plant Substances of the Academy of Sciences of the Uzbek SSR. As the result of investigations of about 30 species of *Ferula*, the structures of more than 70 new terpenoid coumarins and esters have been established.

All the compounds in plants of the genus *Ferula* are divided into three groups according to their chemical structure: coumarins, esters of terpene and sesquiterpene alcohols with aromatic and aliphatic acids, and sesquiterpene lactones [23, 45]. The compounds of all three groups each include a sesquiterpene residue $C_{15}H_{19-27}O_{1-4}$.

The present review gives information on the chemical and spectral properties of sesquiterpene derivatives of plants of the genus *Ferula* and methods of determining their structures and stereochemistries. Questions of the presence of these groups of substances in nature and methods for their detection and isolation have been considered elsewhere [45, 46].

Ferula COUMARINS

Up to the present time, more than 70 coumarins have been isolated from plants of the genus *Ferula* and their structures have been demonstrated (Table 1). The overwhelming majority of them are derivatives of umbelliferone — 7-hydroxycoumarin. Furocoumarins are found extremely rarely [47, 48], and pyranocoumarins have not yet been discovered [49, 50]. In accordance with the structure of the sesquiterpene moiety, the terpenoid coumarins of *Ferula* are divided into three types: a) coumarins having an aliphatic sesquiterpene substituent,

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TABLE 1. Terpenoid Coumarins (R = umbelliferone residue)

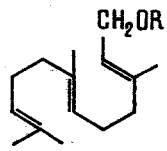
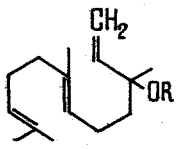
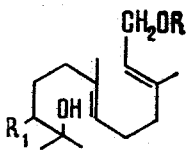
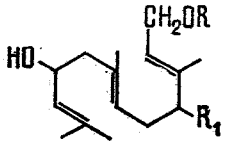
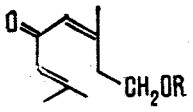
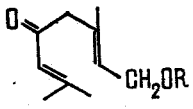
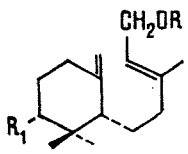
Compound	Structural formula	Literature
I. Coumarins having an aliphatic sesquiterpene substituent		
1. Umbelliprenin $C_{24}H_{30}O_3$, mp 61—63°		[55,66]
2. Cocanikin $C_{24}H_{30}O_3$, mp 34—35°		[15,66]
3. Karatavikin $C_{24}H_{30}O_5$, mp 59—60°		[15]
4. Karatavikinol $C_{24}H_{32}O_5$, mp 52—53°, $[\alpha]_D$ —12°	R_1=O R_1=O Ac	[16]
5. Tadzhiferin $C_{24}H_{30}O_4$, mp 68—70°		[67]
6. Tadzhikorin $C_{26}H_{32}O_6$, $[\alpha]_D$ + +15°	R_1=H R_1=OH	[67]
7. Reoselin $C_{36}H_{52}O_{15}$, mp 155—156°, $[\alpha]_D$ —22,5°	Glycoside of karatavikinol	[68]
8. Reoselin A $C_{36}H_{52}O_{15}$, mp 160—161°, $[\alpha]_D$ —73,5°	The same	[69]
9. Reoselin A $C_{36}H_{52}O_{15}$, mp 155—156°	The same	[70,71]
10. Feroside $C_{30}H_{42}O_{10}$, mp 110—111°, $[\alpha]_D$ +18,1°	Glycoside of karatavikin	[69]
11. Diversin $C_{19}H_{20}O_4$, mp 97—98°		[72,73]
12. Diversinin $C_{19}H_{20}O_{10}$, mp 55—57°		[77]
13. Diversoside $C_{23}H_{34}O_{10}$, mp 154—155°, $[\alpha]_D$ +10°	Glycoside of marmin	[74]
II. Coumarins with a monocyclic sesquiterpene substituent		
14. Farnesiferol B $C_{24}H_{30}O_4$, mp 113,5—114,4°, $[\alpha]_D$ +10°		[75]

TABLE 1 (Continued)

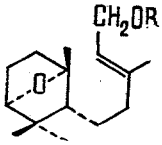
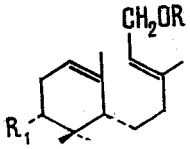
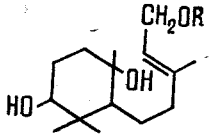
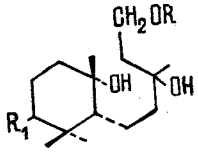
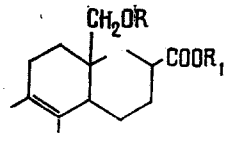
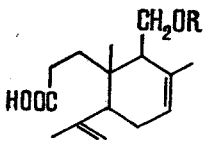
Compound	Structural formula	Literature
15. **Fekolone** $C_{24}H_{28}O_4$, $[\alpha]_D$ +47°	R_1=OH R_1=O	[76]
16. **Fernesiferol C** $C_{24}H_{30}O_4$, mp 84—85°, $[\alpha]_D$ −29°		[75]
17. Kopetdaghin $C_{24}H_{30}O_4$, mp 125,5°, $[\alpha]_D$ +28°	 R_1=OH	[77]
18. Fekolin $C_{26}H_{32}O_5$, $[\alpha]_D$ −29,8°	R_1=OAc	[76]
19. Kopeolin $C_{24}H_{32}O_5$, mp 146—147°, $[\alpha]_D$ −15,9°		[78]
20. Feropolol $C_{24}H_{34}O_6$, mp 96—98°, $[\alpha]_D$ +38,2°	 R_1=βOH	[79,80]
21. Feropolone $C_{24}H_{32}O_6$, mp 225—226°, $[\alpha]_D$ −7,5°	R_1=O	[79,80]
22. Feropolin $C_{26}H_{34}O_7$, mp 63—65°, $[\alpha]_D$ +8,5°	R_1=βOAc	[79,80]
23. Foliferin $C_{24}H_{34}O_6$, mp 240—241°, $[\alpha]_D$ +128°	R_1=αOH	[81]
24. Kopeoside $C_{30}H_{42}O_{10}$, mp 177—178°, $[\alpha]_D$ −22,1°		[78]
25. Galbanic acid $C_{24}H_{30}O_5$, mp 94—95°, $[\alpha]_D$ −25°	 R_1=H	[25]
26. Methyl galbanate $C_{25}H_{32}O_5$, $[\alpha]_D$ −25.8°	R_1=CH_3	[82]
27. Karatavikic acid $C_{24}H_{28}O_5$, mp 89—90°, $[\alpha]_D$ −105°		[17,83,84]

TABLE 1 (Continued)

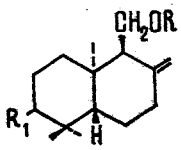
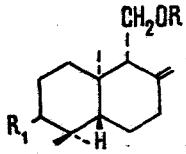
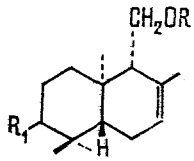
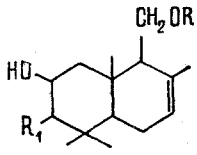
Compound	Structural formula	Literature
III. Coumarins having a bicyclic sesquiterpene substituent		
28. Farnesiferol A $C_{24}H_{30}O_4$, mp 154–155°, $[\alpha]_D$ −56°		[85,86]
	R_1=αOH	
29. Polyanthin $C_{26}H_{32}O_5$, mp 148–149°, $[\alpha]_D$ −50°	R_1=αOAc	[87,88]
30. Gummosin $C_{24}H_{30}O_4$, mp 176–177°, $[\alpha]_D$ −54°	R_1=βOH	[20,89]
31. Polyanthinin $C_{26}H_{32}O_5$, mp 127–129°, $[\alpha]_D$ −32°	R_1=βOAc	[87,88]
32. Mogoltedone $C_{24}H_{28}O_4$, mp 132–133°, $[\alpha]_D$ −41,7°	R_1=O	[90]
33. Colladonin $C_{24}H_{30}O_4$, mp 158–160°, $[\alpha]_D$ −60°		[24,63]
	R_1=αOH	
34. Colladin $C_{26}H_{32}O_5$, mp 153–154°, $[\alpha]_D$ −65°	R_1=αOAc	[24,63]
35. Colladonin isovalerate $C_{29}H_{38}O_5$, mp 86–88°, $[\alpha]_D$ −65°	R_1=αC_5H_9O	[63]
36. Badrakemin $C_{24}H_{30}O_4$, mp 199–200°, $[\alpha]_D$ −64°	R_1=βOH	[19]
37. Badrakemin acetate $C_{26}H_{32}O_5$, mp 173–174°, $[\alpha]_D$ −37,8°	R_1=βOAc	[91]
38. Badrakemone $C_{24}H_{28}O_4$, mp 185–186°, $[\alpha]_D$ −39,8°	R_1=O	[91]
39. Conferol $C_{24}H_{30}O_4$, mp 137–138°, $[\alpha]_D$ −84,2°		[31,92]
	R_1=βOH	
40. Moschatol $C_{24}H_{30}O_4$, mp 78–80°, $[\alpha]_D$ −77,4°	R_1=αOH	[93,94]
41. Moschatol angelate $C_{29}H_{36}O_5$, mp 66–68°, $[\alpha]_D$ −35,8°	R_1=αOAng	[95]
42. Conferone $C_{24}H_{28}O_4$, mp 142–143°, $[\alpha]_D$ −51°	R_1=O	[31,96]
43. Mogoltin $C_{24}H_{30}O_5$, mp 183–185°, $[\alpha]_D$ −68,3°		[60]
	R_1=OH	
44. Mogoltavin $C_{26}H_{32}O_6$, mp 196–197°, $[\alpha]_D$ −108°	R_1=OAc	[61]
45. Mogoltavinin $C_{29}H_{36}O_6$, mp 180–182°, $[\alpha]_D$ −119,2°	R_1=OAng	[62]

TABLE 1 (Continued)

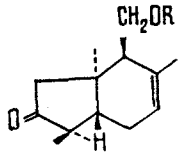
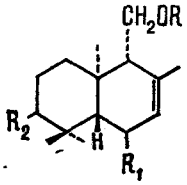
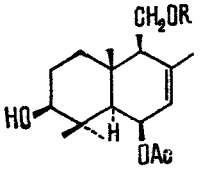
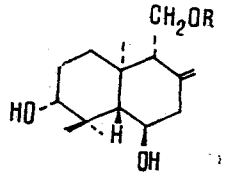
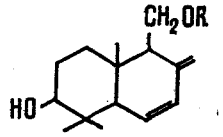
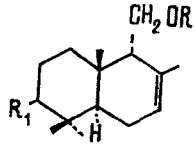
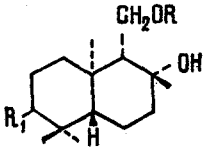
Compound	Structural formula	Literature
46. Tavicone $C_{23}H_{26}O_4$, mp 141—142°, $[\alpha]_D$ —77°		[97,98]
47. Conferin $C_{26}H_{32}O_6$, mp 141—142°, $[\alpha]_D$ —124°	 R_1=β OAc R_2=O	[34]
48. Conferdione $C_{24}H_{26}O_5$, mp 150—152°, $[\alpha]_D$ —51,9°	R_1=R_2=O	[33]
49. Ferocaulidin $C_{24}H_{28}O_5$, mp 75—77°, $[\alpha]_D$ —75°	R_1=O R_2=βOH	[99]
50. Ferocaulin $C_{24}H_{28}O_5$, mp 120—121°, $[\alpha]_D$ —20°	R_1=αOH R_2=O	[99]
51. Ferocaulicin $C_{26}H_{30}O_6$, mp 161—162,5°, $[\alpha]_D$ —120°	R_1=O R_2=βOAc	[99]
52. Ferocaulinin $C_{24}H_{28}O_5$, mp 84—85°, $[\alpha]_D$ —40°	R_1=βOH R_2=O	[99]
53. Feterin $C_{26}H_{32}O_5$, mp 160—162°, $[\alpha]_D$ —40°		[100]
54. Cauferin $C_{24}H_{30}O_5$, mp 104—105°, $[\alpha]_D$ —50°		[101]
55. Cauferidin $C_{24}H_{28}O_4$, mp 184—185,5°, $[\alpha]_D$ —60°		[101]
56. Feropolidin $C_{24}H_{30}O_4$, mp 154—155°, $[\alpha]_D$ +155°		[79,80]
57. Foliferidin $C_{24}H_{30}O_4$, mp 154—155°, $[\alpha]_D$ +217°	R_1=αOH R_1=βOH	[102]
58. Samarcandin $C_{24}H_{32}O_5$, mp 176—177°, $[\alpha]_D$ +24°		[18,24,106,157]

TABLE 1 (Continued)

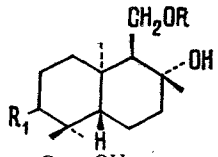
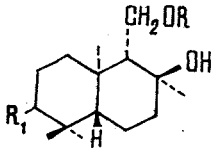
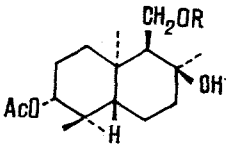
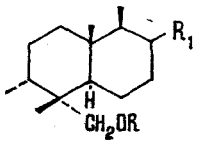
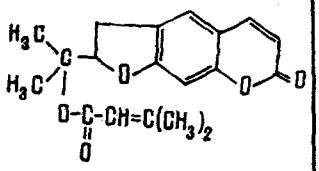
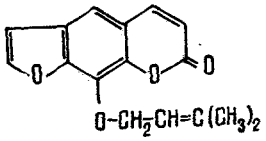
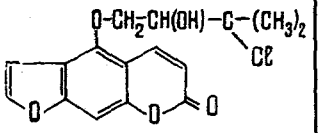
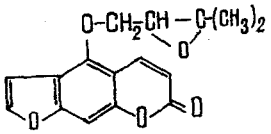
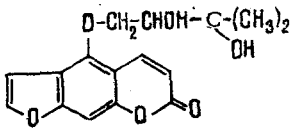
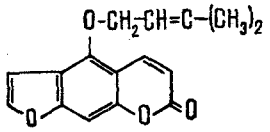
Compound	Structural formula	Literature
	R_1=βOH	
59. Samarcandin acetate $C_{26}H_{34}O_6$, mp 152–153°, $[\alpha]_D$ +29.4°	R_1=βOAc	[91,106,157]
60. Isosamarcandin $C_{24}H_{32}O_5$, mp 221°, $[\alpha]_D$ +26.75°	R_1=αOH	[26,106,157]
61. Isosamarcandin angelate $C_{29}H_{38}O_6$, mp 176–178°, $[\alpha]_D$ –26°	R_1=αOAng	[103]
62. Samarcandone $C_{24}H_{30}O_5$, mp 216–217°, $[\alpha]_D$ +25°	R_1=O	[18,24,106,157]
63. Ferucrin $C_{24}H_{32}O_5$, mp 213–215°, $[\alpha]_D$ +32°	 R_1=αOH	[104,105]
64. Ferucrin acetate $C_{26}H_{34}O_6$, mp 145–147°, $[\alpha]_D$ +20°	R_1=αOAc	[105]
65. Kellerin $C_{26}H_{34}O_6$, mp 76–78°, $[\alpha]_D$ +66.8°	R_1=βOAc	[35,105,106]
66. Nevskin $C_{24}H_{32}O_5$, mp 193–194°, $[\alpha]_D$ –79°	 R_1=αOH	[21,107,108]
67. Feshurin $C_{24}H_{32}O_5$, mp 213–215°, $[\alpha]_D$ –54°	R_1=βOH	[108,109]
68. Nevskone $C_{24}H_{30}O_4$, mp 183–184°	R_1=O	[110]
69. Colladocin $C_{26}H_{34}O_6$, mp 219°, $[\alpha]_D$ –4.58°		[27,108]
70. Kamolol $C_{24}H_{32}O_4$, mp 141–142°, $[\alpha]_D$ +55°	 R_1=αOH	[29,111,112]
71. Fecarpin $C_{24}H_{32}O_4$, mp 166–168°, $[\alpha]_D$ –20°	R_1=βOH	[113]
72. Kamolone $C_{24}H_{30}O_4$, mp 191–192°	R_1=O	[29,111,112]

TABLE 1 (Continued)

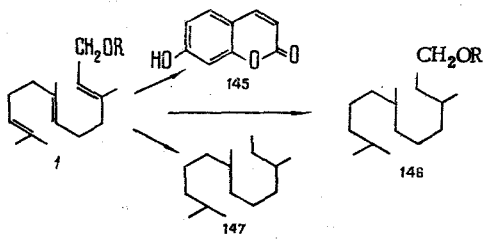
Compound	Structural formula	Literature
	Ferula furocoumarins	
73. Pranchimgin $C_{19}H_{20}O_5$, mp 138–140°		[47, 47a, 47b]
74. Imperatorin $C_{16}H_{14}O_4$, mp 102–103°		[47, 47a, 47c]
75. Saxalin $C_{16}H_{15}OCl$, mp 159–161°		[47a, 48]
76. Oxypeucedanin $C_{16}H_{14}O_5$, mp 141–143°		[47, 47a, 48a]
77. Oxypeucedanin hydrate $C_{16}H_{16}O_6$, mp 132–134°		[47a, 48b]
78. Isoimperatorin $C_{16}H_{14}O_4$, mp 109–110°		[47, 47a, 48c]

b) coumarins having a monocyclic sesquiterpene substituent, and c) coumarins with a bicyclic sesquiterpene substituent.

Thus, the diversity of *Ferula* coumarins is due to the structure of the sesquiterpene residue – different types of carbon skeleton, different positions and natures of the substituting groups (hydroxy, oxo, acyloxy groups), absence or presence and positions of double bonds, and different configurations at the asymmetric centers.

Since in all *Ferula* coumarins with the exception of the furocoumarins the aromatic moiety consists of an umbelliferone residue, the chemical study of one of these substances reduces to establishing the structure of the terpenoid part of the molecule. The chemical and spectral properties of umbelliferone have been described in monographs and reviews [51-59], and we shall therefore not discuss this question. Our review also includes coumarins from the genera *Peucedanum* [60-62] and *Colladonia* [24], since they are close in structure to the *Ferula* coumarins and some have even been isolated from *Ferula* species [63]. Terpenoid coumarins have also been isolated from representatives of the genera *Artemisia* [64], *Anthemis* [65], and others.

Coumarins Having an Aliphatic Sesquiterpene Substituent. Of this series 13 coumarins are known, and in three of them the terpenoid part is represented by a monoterpene [74-74]. The determination of the structures of the first representatives — umbelliprenin [55, 66], cocanikin [66], karatavikin [15], and karatavikinol [16] — reduced to a study of the products of acid and oxidative cleavage. The acid cleavage of umbelliprenin (1) gave umbelliferone (145) and a terpene oil. A determination of the number of C-CH_3 groups by the Kuhn–Roth method showed that the terpenoid part contained three C-CH_3 groups, and on hydrogenation it absorbed 4 moles of hydrogen. The hydrogenation of umbelliprenin gave hexahydroumbelliprenin (146), farnesane (147), and umbelliferone (145) (Scheme 1). Ozonization of the substance gave levulinic aldehyde, an umbelliferone ether, and hydroxyacetic acid. On the basis of the facts given it was established that umbelliprenin is the farnesyl ether of embelliferone [66]. This has been confirmed by a stereospecific synthesis [148].

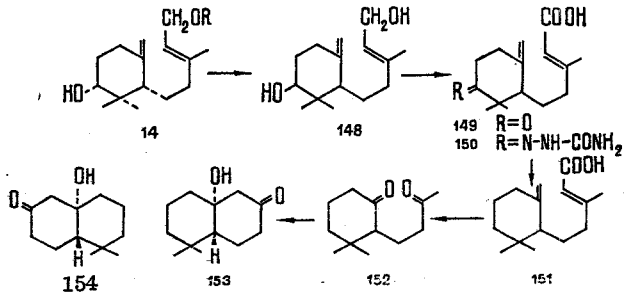


Scheme 1

Recently, in proving the structure and stereochemistry of coumarins, as of other natural compounds, spectral methods of investigation have been used to an increasing extent. A proof of the structure of tadzhiferin (5) — a hydroxy derivative of umbelliprenin — is an example of the possibilities of nuclear magnetic resonance spectroscopy in determining the structure of coumarine derivatives [6]. Perel'son et al. [67] convincingly showed the structures of the two fragments of the terpenoid moiety of tadzhiferin by the double-resonance and INDOR methods, and their linkage by two methylene groups enabled a structure to be suggested for the coumarin [67]. Among the coumarins with an aliphatic terpene substituent are diversin (11) and diversinin (12), which are isomers with respect to the position of a double bond. It must be mentioned that this series of coumarins also includes the coumarin glycosides diversoside [74], feroside [69], reoselin [68], and the reoselins A [69-71], the aglycones of which are marmin, karatavikin (3), and karatavikinol (4), respectively.

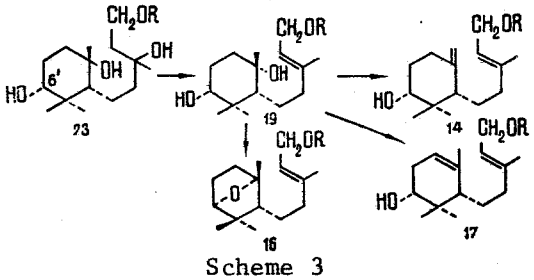
Coumarins with a Monocyclic Sesquiterpene Substituent. The coumarins of this series are represented by 14 compounds. The first two substances — farnesiferols B (14) and C (16) — were isolated as early as 1959, and their structures were shown by a chemical method [75]. The reduction of farnesiferol B (14) with sodium in liquid ammonia led to an unsaturated alcohol (148), the oxidation of which with chromium trioxide yielded the ketone (149). The reduction of the semicarbazone of the ketone by the Kizhner–Wolff [Wolff–Kishner] method gave compound (151), the subsequent oxidation of which with osmium tetraoxide and lead tetraacetate led to the diketone (152). The latter, on passage through alumina, cyclized to the hydroxy ketone (153), which proved to be an enantiomer of the hydroxy ketone (154) obtained from ambrein [75]. The structure and stereochemistry (14) of farnesiferol B are given in Scheme 2. The axial orientation of the hydroxy group at $C_{6'}$ was determined on the basis of biogenetic considerations, starting from farnesiferol A (28) [85].

The structure of other terpenoid coumarins have been proved by a combination of chemical and spectral methods [76-81]. Coumarins with two (kopeolin (12)) and three (foliferin (23) and feropolol (20)) hydroxy groups in the terpenoid moiety on dehydration under various conditions form coumarins with monocyclic and bicyclic terpenoid residues. The dehydration of feropolol (20) with sulfuric acid in ethanol likewise gave two anhydro derivatives — gummosin (30) and feropolidin (56), and the dehydration of foliferin (23) gave farnesiferol A (28)



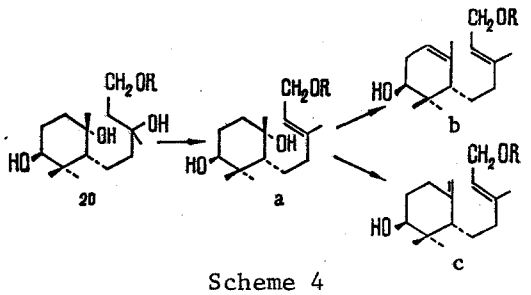
Scheme 2

and foliferidin (57). On the basis of the results obtained, absolute configurations shown were suggested for feropolol (20) and foliferin (23) [80]. A comparison of the established absolute configurations of hydroxy coumarins — foliferin (23) and farnesiferols B (14) and C (16) — permits the conclusion that foliferin (23), kopeolin (19), kopetdaghin (17), and farnesiferols B (14) and C (16) are products of a single chain of the biogenesis of terpenoid coumarins (Scheme 3).



Scheme 3

Another chain of hydroxycoumarins (20 → a → b → c) formed from feropolol (20) and differing from the preceding chain only by the orientation of the hydroxy group at C_6' has not yet been found in ferulas (Scheme 4).



Scheme 4

Coumarins Having a Bicyclic Sesquiterpene Substituent. Plants of the genus *Ferula* are the richest in coumarins with a bicyclic sesquiterpene substituent — 38 such coumarins have been found. They are derivatives of bicyclofarnesane with the exception of four coumarins — tavicone [97, 98], kamolol and kamolone [29, 111, 112], and fecarpin [113].

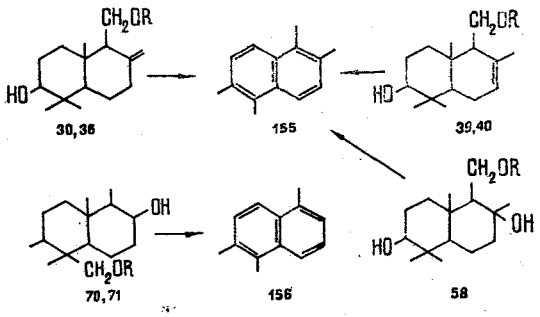
Coumarins of this type can be divided into three series according to the position of the double bonds and the presence or absence of a hydroxy group at C_2':

the farnesiferol A series with an exocyclic double bond at C_2' (10 coumarins); the conferol series with an endocyclic bond at C_2'-C_3' (15 coumarins); and the samarcandin series with a hydroxy group at C_2' (nine coumarins).

The structure of the first representatives of this series — farnesiferol A, badrakemin, gummosin, samarcandin, and colladonin — like those of coumarins with apiphatic and monocyclic terpenoid residues, has been shown on the basis of chemical transformations.

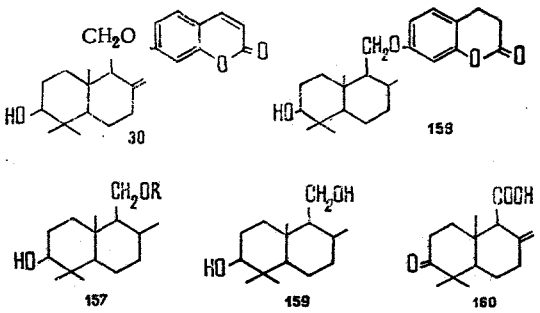
The selenium dehydrogenation of gummosin (30), badrakemin (36), and related compounds containing an oxygen function at C_6' led to 1,2,5,6-tetramethylnaphthalene (155). In this transformation, the angular methyl group was split out and the tetrasubstituted naphthalene

was formed as the result of a retropinacol rearrangement, which is a chemical proof of the carbon skeleton of the sesquiterpene part and of the position of the substituents (—OH, =O, —OAc) at C_6' of the respective coumarins (Scheme 5). Such coumarins as kamolol (70), kamolone (72), and fecarpin (71), which do not contain an oxygen function at C_6' of the substituent, give a trisubstituted naphthalene derivative on dehydrogenation, namely 1,5,6-trimethylnaphthalene (156).



Scheme 5

The hydrogenation of gummosin and badrakemin in alcoholic solutions in the presence of catalysts leads to the dihydro derivatives (157), and in acetic acid to the tetrahydro derivatives (158) with a reduced double bond in the α-pyrone ring and cleavage of the ether bond with the formation of saturated sesquiterpene diols (159) (Scheme 5). The hydrogenation of farnesiferol A, gummosin, badrakemin, and colladonin has yielded stereoisomeric diols with the composition $C_{15}H_{28}O_2$ differing in their physicochemical constants [19, 20, 24, 85].



Scheme 6

Oxidation of hydroxy groups in terpenoid coumarins with chromium trioxide in acetone and pyridine solutions gives oxo derivatives [20, 24, 85], and in acid solutions it leads to the cleavage of the ether bond and to the formation of keto acids. The oxidation of colladonin in an acetic acid medium with chromium trioxide gave the keto acid (160) [24]. An analysis of the PMR spectrum of the latter enabled the position of the aryloxymethyl group of C_1' to be determined and the structures of badrakemin, samarcandin, and samarcandone to be refined [24].

The dehydration of the tertiary hydroxy group in coumarins of the samarcandin series is usually carried out in 10% ethanolic sulfuric acid solution [18, 105], or with phosphorus pentoxide in benzene. Under these conditions one of the possible dehydration products is formed predominantly — with an endocyclic or an exocyclic double bond.

In the study of the structures and stereochemistries of coumarins with bicyclic terpenoid residues information from PMR spectroscopy is decisive. Analysis of the PMR spectra of a substance makes it possible to determine the coumarin series: in the spectra of coumarins of the farnesiferol A series there are signals from the protons of the exomethylene group in the 4.50-4.90 ppm region, in coumarins of the conferol series the signals of the vinyl methyl group and of an olefinic proton at 1.6-1.75 ppm and 5.4-5.9 ppm, respectively, and in the spectra of coumarins of the samarcandin series the signal of a methyl geminal to a hydroxy group at 1.16-1.33 ppm together with the signals of an angular methyl group and of gem-dimethyl groups.

The formation from mass spectrometry amounts to determining the molecular weights of the substance, of the terpenoid moiety, and of the ester groups and also the number of hydroxy and acyloxy groups [149-151].

The majority of acylated coumarins contain residues of acetic [60, 99, 110], angelic [62, 75], and tiglic and isovaleric [63] acids, the presence of which is demonstrated from the results of alkaline hydrolysis and PMR spectra [59, 152].

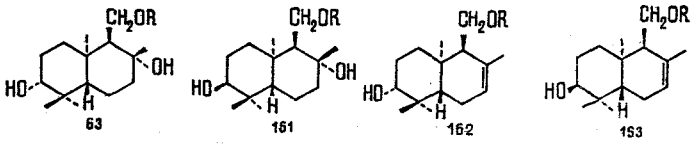
It is interesting to note that up to the present time no terpenoid coumarins esterified with aromatic acids have been found.

Stereochemistry of the Coumarins with a Bicyclic Sesquiterpene Residue. The diversity of the terpenoid coumarins with a bicyclofarnesyl residue is due to the presence of asymmetric centers in them at C_1', C_2', C_4', C_6', C_9', and C_{10}'. As mentioned above, they are subdivided into three series differing from one another in the position of the double bond and in the presence or absence of a hydroxy group in the terpenoid moiety.

Previously, because we had available an inadequate sample of farnesiferol A, we put forward an erroneous hypothesis concerning the relative configurations of gummosin, badrakemin, and colladonin [154a, 154b].

M. E. Perel'son et al. were the first to use PMR spectroscopy with a paramagnetic shift reagent (PSR) for determining the structures and stereochemistries of terpenoid coumarins, and they showed the relative configurations of gummosin, badrakemin, colladonin [32, 154], kellerin, samarcandin, and isosamarcandin [106]. They showed that in the coumarins of the farnesiferol A series with the axial orientation of the C_1'—CH_2OR group the signals of the C_2'=CH_2 protons in the PMR spectra are present at a distance of 0.1 ppm from one another, while in the case of the equatorial orientation this distance is 0.29-0.39 ppm [100]. By studying the circular dichroism curves of coumarins of this series it was found that the amplitude of the Cotton effect in the 200 nm region depends on the orientation of the substitutent at C_1' [155].

The absolute configuration of the first representative of coumarins of this type — farnesiferol A — was shown chemically by comparing the ORD curves of the diketones obtained from farnesiferol A and from α-amyrin [85]. Later, it was confirmed by an x-ray structural analysis of its epimer — gummosin [89]. The absolute configuration of ferucrin (63) has recently been established by passage to farnesiferol A (28) and deacetylkellerin (161) [105]. Thus, on the basis of chemical transformations, the passage to substances with established absolute configurations, the configurations of substances with the axial orientation of the C_1'—CH_2OR substituent — ferucrin (63), deacetylkellerin (161), anhydroferucrin (162), and anhydrodeacetylkellerin (163) — have been determined [105] (Scheme 7).

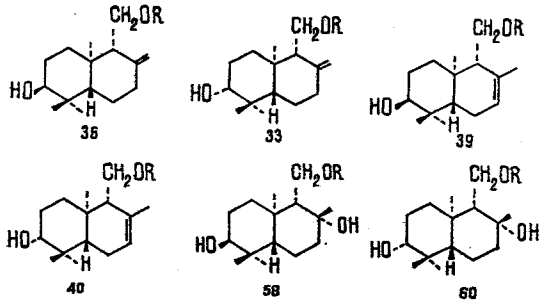


Scheme 7

Relative configurations have been put forward [31, 32, 106, 152, 154] for another group of terpenoid coumarins with the equatorial orientation of the substituent at C_1' — conferol (39), moschatol (40), samarcandin (58), isosamarcandin (60), badrakemin (36), and colladonin (33).

The passage from samarcandin (58) via conferol (39) to tetrahydrobadrakemin revealed the interconnection of the coumarins with the equatorial orientation of the C_1'—CH_2 OR group. These facts and also a comparison of the signs of the optical rotations of the coumarins of the three series by analogy with zonarol derivatives [156] have permitted the determination of the type of linkage of the bicyclofarnesyl group in the compounds under consideration as trans-nonsteroid and the proposal of absolute configurations for samarcandin (58), isosamarcandin (60), conferol (39), moschatol (40), badrakemin (36), and colladonin (33) [157] (Scheme 8).

A chemical proof of the absolute configuration of colladonin (33) recently provided by Spanish workers [63] has confirmed our results obtained on the basis of a comparison of the signs of specific rotation of the coumarins and their interconversions [157]. The same results have enabled us to identify mogoltavidin, mogoltavicin [79a], and mogoltacin [79c]

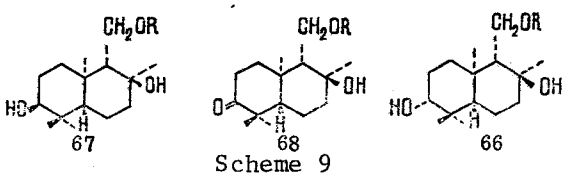


Scheme 8

with samarcandin (58), samarcandin acetate (59), and conferol (39), respectively [157]. Mogoltadin [79b] had previously been shown to be identical with farnesiferol A (28) [32].

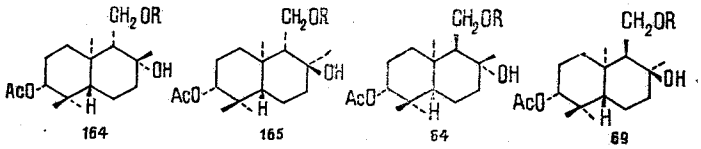
We have also shown that in coumarins of the samarcandin series the signs of the specific rotation depend on the orientation of the methyl group at C_2': substances with an equatorial methyl group rotate to the right and those with an axial methyl group rotate to the left [157]. Consequently, samarcandin (58) must have eight isomers with the trans-nonsteroid type of linkage in the bicyclofarnesane residue.

From Shurovskii's ferula we have isolated feshurin (67), which is an epimer of nevskin (66) at the secondary hydroxy group [108, 109]. The dehydration of (67) with sulfuric acid in ethanol led to conferol (39), and oxidation with chromium trioxide led to nevskone (68) [110]. The formation of conferol on the dehydration of samarcandin (58) and feshurin (67) shows that they are isomers with different orientations of the methyl group at C_2'. On the basis of these facts, feshurin and nevskin must have the absolute configurations 67 and 66, respectively (Scheme 9).



Scheme 9

The acylcoumarin colladocin has been described in the literature by authors who state that it differs from isosamarcandin acetate (164) [27] and nevskin acetate (165) [107]. According to recent results it is not identical, either, with ferucrin acetate (64) [105]. Taking into account the possibility of the existence of eight isomers of samarcandin, it may be concluded that colladocin has the absolute configuration (69) and is an isomer of ferucrin acetate at the C_2'—CH_3 group (Scheme 10).



Scheme 10

Thus, at the present time seven isomers of samarcandin, or their acetates, have been isolated — samarcandin (58), isosamarcandin (60), ferucrin (63), kellerin (65), nevskin (66), ferushin (67), and colladocin (69). In this series the isomer of deacetylkellerin at the C_2'—CH_3 group has not been discovered.

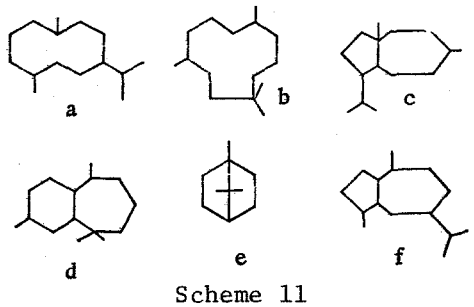
Previously, the determination of the orientation of the methyl group at C_2' in coumarins of the samarcandin series was based on the formation of anhydro products on the dehydration of the coumarins: from coumarins with an axial hydroxy group the main products were substances with an endocyclic double bond, while those with an equatorial hydroxy group gave mainly products with an exocyclic methylene [105, 158]. Since the dehydration of coumarins isomeric at C_2'—CH_3 (samarcandin and feshurin) led to conferol, the determination of the orientation of the methyl group at C_2' in this way is not, in our opinion, always reliable.

Recently, coumarins of the conferol and farnesiferol A series having two oxygen-containing substituents, at $C_{4'}$ and $C_{6'}$, have been found in ferulas. This permits the assumption that the possible variants of the structure of the terpenoid coumarins have still not yet been exhausted, and coumarins of the samarcandin series may be found with an oxygen function at $C_{4'}$.

ESTERS OF TERPENOID ALCOHOLS

Terpenoid alcohols in the free form have been isolated from various species of *Ferula* by Kir'yalov [23], Borisov [179], and Bagirov [180]. We are the first to have shown that the genus *Ferula* contains another group of natural compounds in addition to terpenoid coumarins and sesquiterpene lactones — esters of terpenoid alcohols with aromatic and aliphatic acids (Table 2).

The terpenoid alcohols entering into the composition of the esters are, like the coumarins, subdivided according to the structure of the carbon skeleton into derivatives of monocyclic and bicyclic sesquiterpenes. The monocyclic alcohols of *Ferula* are represented by derivatives of germacrane (a) and humulane (b), and the bicyclic alcohols are represented by derivatives of carotane (c), himachalane (d), camphane (e), and guaiane (f) (Scheme 11). We are the first to have isolated substances with humulane and himachalane skeletons from plants of the genus *Ferula* (125-129, 144).



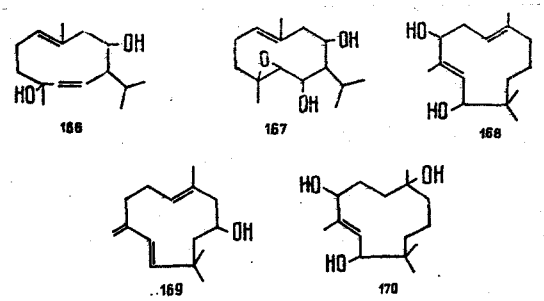
Scheme 11

As esterifying acids of these esters are found vanillic, isovanillic, p-hydroxybenzoic, trimethoxybenzoic, veratric, 3,4-dihydroxybenzoic, angelic, tiglic, and acetic acids.

The fact that a substance is an ester of an aromatic acid is shown by absorption bands in the IR spectrum at 1520-1620 cm^{-1} (benzene ring) and 1690-1710 cm^{-1} (ester carbonyl) and by maxima in the UV spectra at 255-262 and 292-300 nm. Esters with aliphatic acids have absorption bands in their IR spectra at 1720-1735 cm^{-1} [46].

Esters of sesquiterpene alcohols have also been isolated from representatives of the genera *Laserpitium* [159], *Buddleia* [160], *Selinium* [161], and others.

Derivatives of Monocyclic Sesquiterpenes. Among the esters, germacrane derivatives are represented by two alcohols — angrendiol (166) [23, 116] and ugamdiol (shiromodiol) (167) [162-164], and humulane derivatives by juniferol (168) [127], fecerol (169) [124], and fexerol (170) [128] (Scheme 12).



Scheme 12

Attempts to determine the carbon skeleton by dehydrogenation with selenium or sulfur do not give unambiguous results since in this process cyclization takes place and derivatives of guaiane, selinane, and other bicyclic hydrocarbons may be formed [165]. In establishing the skeletons of sesquiterpene alcohols, PMR and mass spectroscopy provide valuable information. Thus, the PMR spectra of germacrane derivatives show two three-proton doublets from

TABLE 2. Esters of *Ferula*

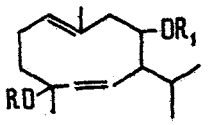
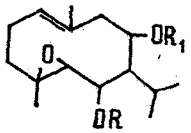
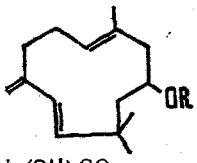
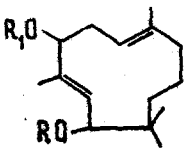
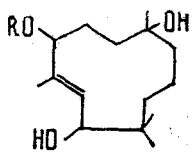
Compound	Structural formula	Literature
I. Esters of monocyclic alcohols		
79. **Ferolin** $C_{22}H_{30}O_4$, mp 189–190.5°, $[\alpha]_D$ −91.6°	 R_1=C_6H_4(OH)CO—; R=H	[114–117]
80. **Chimganidin** $C_{23}H_{32}O_5$, mp 140–141°, $[\alpha]_D$ −97.9°	R_1=C_6H_3(OH)(OCH_3)CO— R=H	[114–117]
81. **Federin** $C_{24}H_{32}O_5$, mp 179–180°, $[\alpha]_D$ −86.1°	R=Ac R_1=C_6H_4(OH)CO—	[118]
82. **Ugaferin** $C_{25}H_{36}O_7$, mp 123–124°, $[\alpha]_D$ −24.3°	 R=H R_1=C_6H_2(OCH_3)$_3$CO—	[119]
83. **Fekorin** $C_{22}H_{34}O_5$, $[\alpha]_D$ −29°	R=Ang R_1=Ac	[120]
84. **Rubaferinin** $C_{23}H_{32}O_6$, mp 105–106°, $[\alpha]_D$ −36°	R=H R_1=C_6H_3(OH)(OCH_3)CO—	[121]
85. **Rubaferidin** $C_{22}H_{30}O_5$, mp 162–164°, $[\alpha]_D$ −40°	R=H R_1=C_6H_4(OH)CO—	[121]
86. **Involucrin** $C_{27}H_{38}O_8$, mp 154–155°, $[\alpha]_D$ −33.4°	R=Ac R_1=C_6H_2(OCH_3)$_3$CO—	[122]
87. **Involucrinin** $C_{30}H_{42}O_8$, $[\alpha]_D$ −28.2°	R=Ang R_1=C_6H_2(OCH_3)$_3$CO—	[122]
88. **Ferocin** $C_{22}H_{28}O_3$, mp 127–128°, $[\alpha]_D$ −200°	 R=C_6H_4(OH)CO—	[123,124]
89. **Ferocinin** $C_{23}H_{30}O_4$, mp 107–108°, $[\alpha]_D$ −197.4°	R=C_6H_3(OH)(OCH_3)CO—	[123,124]
90. **Juferin** $C_{22}H_{28}O_3$, mp 90–91°, $[\alpha]_D$ +120.4°	R=C_6H_4(OH)CO—	[125,126]
91. **Juniferin** $C_{23}H_{32}O_5$, mp 85–86°, $[\alpha]_D$ −1.6°	 R=H R_1=C_6H_3(OH)(OCH_3)CO—	[125,127]
92. **Juniferinin** $C_{24}H_{32}O_5$, mp 164–165°, $[\alpha]_D$ +33.5°	R=Ac R_1=C_6H_4(OH)CO—	[125,127]
93. **Juniferidin** $C_{24}H_{32}O_5$, mp 162–163°, $[\alpha]_D$ +2.1°	R=Ac R_1=C_6H_4(OH)CO—	[126]
94. **Fexerin** $C_{20}O_{32}O_3$, $[\alpha]_D$ −2.4°	R=C_5H_7O R_1=H	[128]
95. **Fexerinin** $C_{23}H_{32}O_5$, $[\alpha]_D$ −64°	R=C_6H_3(OH)(OCH_3)CO— R_1=H	[129]
96. **Fexeridin** $C_{23}H_{34}O_6$, mp 141–143°, $[\alpha]_D$ +40°	 R=C_6H_3(OH)(OCH_3)CO—	[129]

TABLE 2 (Continued)

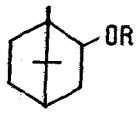
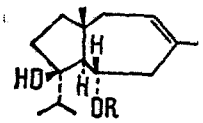
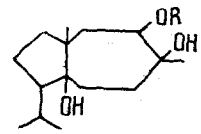
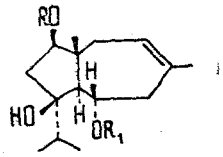
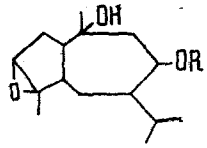
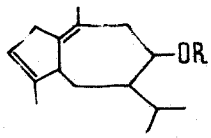
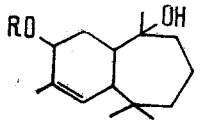
Compound	Structural formula	Literature
II. Esters of bicyclic alcohols		
97. d-Chimgin $C_{17}H_{22}O_3$, mp 155°, $[\alpha]_D$ +4,9°	 R=$C_6H_4(OH)CO$—	[130]
98. d-Chimganin $C_{18}H_{24}O_4$, mp 85°, $[\alpha]_D$ +5°	R=$C_6H_3(OH)(OCH_3)CO$—	[130]
99 l-Chimgin $C_{17}H_{22}O_3$ mp 158—159°, $[\alpha]_D$ —60,2°	R=$C_6H_4(OH)CO$—	[131]
100. l-Chimganin $C_{18}H_{24}O_4$, mp 85—86°, $[\alpha]_D$ —41,7°	R=$C_6H_3(OH)(OCH_3)CO$—	[114]
101. Rubaferin $C_{18}H_{24}O_4$, mp 106—107°, $[\alpha]_D$ —45,08°	R=$C_6H_3(OCH_3)(OH)CO$—	[121]
102. Ferutin $C_{23}H_{32}O_5$, mp 130—131°, $[\alpha]_D$ +101.8°	 R=$C_6H_3(OCH_3)(OH)CO$—	[132, 133]
103. Ferutinin $C_{22}H_{30}O_4$, mp 120—121°, $[\alpha]_D$ +66,1°	R=$C_6H_4(OH)CO$—	[133, 134]
104. Ferutidin $C_{23}H_{32}O_4$, mp 102—103°, $[\alpha]_D$ +103,5°	R=$C_6H_4(OCH_3)CO$—	[135]
105. Teferin $C_{23}H_{32}O_5$, mp 78—80°, $[\alpha]_D$ +86,5°	R=$C_6H_3(OH)(OCH_3)CO$—	[136]
106. Teferidin $C_{22}H_{30}O_3$, $[\alpha]_D$ +37,5°	R=C_6H_5CO—	[137]
107. Akiferin $C_{24}H_{34}O_5$, mp 102—103°, $[\alpha]_D$ +69,1°	R=$C_6H_3(OCH_3)_2CO$—	[138]
108. Akiferidin $C_{22}H_{30}O_5$, mp 87—88°, $[\alpha]_D$ +28,5°	R=$C_6H_3(OH)_2CO$—	[139]
109. Linkiol $C_{20}H_{34}O_4$, mp 123—125°, $[\alpha]_D$ —17°	 R=C_5H_7O	[140]
110. Akichenin $C_{27}H_{36}O_6$, mp 160—161°, $[\alpha]_D$ —8,3°	 R=C_5H_7O R_1=$C_6H_4(OH)CO$—	[141]
111. Akiferidinin $C_{27}H_{36}O_7$, mp 66—67°, $[\alpha]_D$ +46°	R=C_5H_7O R_1=$C_6H_3(OH)_2CO$—	[139]
112. Tenuferin $C_{23}H_{32}O_6$, mp 176—178°, $[\alpha]_D$ +134,6°	 R=$C_6H_3(OCH_3)(OH)CO$—	[142]
113. Tenuferinin $C_{23}H_{32}O_6$, mp 102—103°, $[\alpha]_D$ +106,8°	R=$C_6H_3(OH)(OCH_3)CO$—	[142]
114. Tenuferidin $C_{22}H_{30}O_5$, mp 164—165°, $[\alpha]_D$ +75°	R=$C_6H_4(OH)CO$—	[142]

TABLE 2. (Continued.)

Compound	Structural formula	Literature
115. **Akiferinin** $C_{24}H_{34}O_6$, mp 176—177°, $[\alpha]_D$ +73.1°	R=$C_6H_3(OCH_3)_2CO$—	[143]
116. **Microferin** $C_{22}H_{28}O_3$, mp 144—145°, $[\alpha]_D$ +122.9°	 R=$C_6H_4(OH)CO$—	[113]
117. **Microferinin** $C_{23}H_{30}O_4$, mp 152—154°, $[\alpha]_D$ +89.3°	R=$C_6H_3(OH)(OCH_3)CO$—	[113]
118. **Xeroferin** $C_{23}H_{32}O_5$, mp 118—120°	 R=$C_6H_3(OH)(OCH_3)CO$—	[144]

the isopropyl group [116, 119], and the mass spectra have the peaks of ions with m/e M − 43 $(M - C_3H_7)^+$. The absence of a singlet signal from an angular methyl in the PMR spectrum in the 0.8-1.1 ppm region permits the assumption that the substance belongs to the germacrane derivatives.

The germacrane skeleton of sesquiterpenes is also shown by pyrolysis. This process leads to a Cope rearrangement with the formation of elemane derivatives [166]. Thus, the pyrolysis of angrendiol gives isomeric elemane alcohols (166a, 166b), the formation of which shows the skeleton of angrendiol and the position of the secondary hydroxy group at C_8 [166] (Scheme 13).

166 166 a, 166 b

Scheme 13

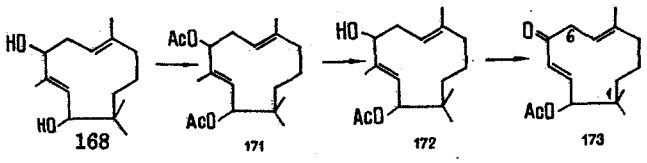
The PMR and mass spectra of humulane derivatives — juniferol, fecerol, and fexerol — show a different picture: in the PMR spectrum there are two three-proton singlets from the tertiary methyl groups at C_1. The multiplicity of the latter is determined by a comparison of the values of the CSs of the gem-dimethyls in the spectra of juniferol, fecerol, and fexerol derivatives. In addition, the mass spectra of humulane derivatives have no peak of an ion with m/e M − 43.

The position and nature of the double bonds are determined by the results of chemical transformations and by UV, IR, and PMR spectroscopy. The UV spectrum of fecerol has a maximum at 244 nm (log ε 4.44) due to a conjugated dienic group, and the PMR spectrum has the signals from the protons of an exocyclic methylene at 4.72 and 4.78 ppm and of trans-disubstituted olefinic protons at 5.32 and 5.74 ppm. The latter are also shown by an absorption band at 970-980 cm^{-1} in the IR spectrum [124, 167]. The protons of a cis-disubstituted double bond in the PMR spectrum of angrendiol appear with a SSCC of 6-7 Hz [116].

A characteristic feature of germacrane derivatives is their cyclization under the action of acidic reagents (10-50% sulfuric acid, perchloric and formic acids, p-toluenesulfonyl chloride) to form derivatives of guaiane and selinane. The cyclization of chimganidin by sulfuric acid in ethanol has given a guaiane derivative, which is explained by the position of the double bond at C_1-C_{10} and the hydroxy groups in angrendiol. The same substance has been isolated as a natural compound from *Ferula microcarpa* [113].

The cyclization of ugamdiol (167) has also given a guaiane derivative [164]. It must be mentioned that the position of the epoxy group (C_5-C_6 or C_1-C_{10}) affects the formation of cyclization products. Thus, C_5,C_6-epoxygermacranes cyclize into guaianes and the C_1-C_{10} compounds into selinanes [168].

The cyclization of humulane derivatives leads to mixtures of bi- and tricyclic sesquiterpenes: the treatment of humulene with perchloric acid has given bicyclic and tricyclic sesquiterpene alcohols. Thus, the study of the products of the cyclization of monocyclic sesquiterpenes gives useful information in structural investigations. As was to be expected, the oxidation of unsaturated monocyclic alcohols in an acid medium leads to bicyclic ketones, and therefore oxidation is carried out in pyridine, and ketones of the initial compounds are obtained. The Sarett oxidation [169] of the monoacetate of juniferol (172) forms the monoketone (173), in the PMR spectrum of which a displacement of the signals of the C_3-H end of the methylene protons at C_6 is observed. In addition to this, the UV spectrum shows the maximum at 225 nm (log ε 3.0) of an α,β-unsaturated ketone. On the basis of these facts, the position of the second hydroxy group in juniferol has been found to be at C_5 [127] (Scheme 14).

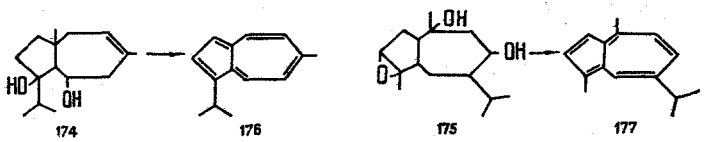


Scheme 14

Derivatives of monocyclic sesquiterpenes of *Ferula* are probably precursors of the bicyclic sesquiterpenes, as is confirmed by the finding of esters of one and the same acid with monocyclic and bicyclic alcohols [142, 170].

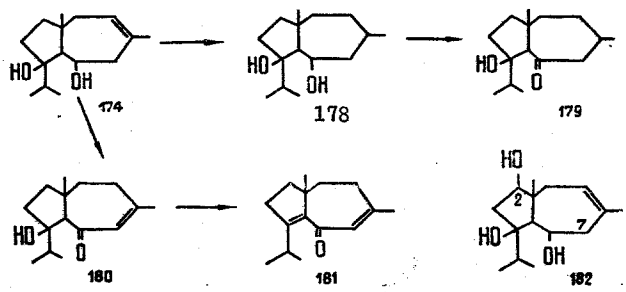
Derivatives of Bicyclic Sesquiterpenes. *Ferula* esters, the terpenoid moiety of which has a bicyclic carbon skeleton, are derivatives of carotane (ferutinol, akichenol) [132-139], of guaiane (microferol) [113], and of himachalane (xeroferol) [144].

In contrast to the monocyclic derivatives, the bicyclic sesquiterpenes form by dehydrogenation hydrocarbons the skeleton of which corresponds to that of the initial substance. Thus, the dehydrogenation of ferutinol (174) and of the alcohol from tenuferidin (175) with selenium gives 4-isopropyl-8-methylazulene (176) and guaiazulene (177), respectively (Scheme 15). Under these conditions, himachalane derivatives form cadalene, 2-methyl-6-p-toluylheptane, and ar-himachalene [171].



Scheme 15

Carotane derivatives are the most widespread in plants of the genus *Ferula* [132-139]. The structure of ferutinol (jaeschkeanadiol) was studied independently of one another by two groups of workers [132, 133, 172]. The oxidation of dihydroferutinol (178) with chromium trioxide led to the monoketone (179), in the IR spectrum of which an absorption maximum characteristic for a carbonyl group in a seven-membered ring appeared. The oxidation of ferutinol yielded an α,β-unsaturated ketone (180) with migration of the double bond from the C_8-C_9 to the C_7-C_8 position [133]. When jaeschkeanadiol was oxidized and then subjected to dehydration, the α,β-unsaturated ketone (181) was formed, which showed the 1,3-positions of the hydroxy groups, and structure (174) was proposed for it [133, 173] (Scheme 16). A comparison of the keto acids obtained from jaeschkeanadiol and from laserol, substances with known stereochemistries, showed the absolute configuration of jaeschkeanadiol [172].

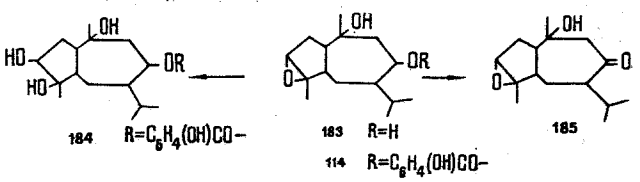


Scheme 16

Esters of akichenol (182) have been isolated from *Ferula akitschkensis* which also contains esters of ferutinol [139, 141]. The multiplicities of the olefinic and hemihydroxylic protons in the PMR spectra of the akichenol derivatives excluded the possibility that the second secondary hydroxy group was present at C_7 or C_{10}, and its stability to periodic acid excluded C_2, and the structure (182) was proposed for it.

The comparative study of the influence of aromatic acid residues in the PMR spectra of esters of ferutinol and akichenol on the CSs of the signals of the isopropyl group revealed a relationship which permits the determination of the position of the ester groups in akichenol esters. On the basis of these facts the relative configuration of akichenol has been suggested [173].

The presence of an epoxide ring in the alcohol from tenuferidin (183) was shown by its opening to form the glycol (184) on treatment with a solution of oxalic acid, and by the production of acetyl derivatives. The positions of the tertiary hydroxy group and of the epoxide ring were determined by the oxidation of the alcohol, which gave the monoketone (185) with its carbonyl group in the seven-membered ring [142] (Scheme 17).



Scheme 17

SESQUITERPENE LACTONES

From six species of *Ferula*, 21 lactones have been isolated and their structures have been shown (Table 3). They are derivatives of only two types of sesquiterpenes — guaiane and selinane. Of them, six have proved to be hydroxy lactones and the remainder esters of hydroxy lactones with aliphatic and aromatic acids. It must be mentioned that diversolide is the first sesquiterpene lactone esterified with an aromatic acid [146].

Biogenetic Link is the Series of *Ferula* Sesquiterpenes. The first hypotheses concerning the biosynthesis of sesquiterpenes were put forward by L. Ruzicka [174] and were subsequently confirmed by Hendrickson [175]. According to this hypothesis, sesquiterpenes are formed from 2,3-cis-farnesol or trans-farnesol — three isoprene units linked in series in the "head-to-tail" manner.

Up to the present time, derivatives of nine types of sesquiterpenes have been isolated from plants of the genus *Ferula* — acyclofarnesane (f), monocyclofarnesane (g), bicyclofarnesane (h), germacrane (a), humulane (b), carotane (c), guaiane (d), himachalane (e), and selinane (j), the precursors of which are apparently acyclofarnasane.

The terpenoid moiety of the coumarins is represented by only three types — f, g, and h. In this respect, the sesquiterpenes of the esters are far more diverse and so far five types have been found — a-e (Scheme 18). This permits the assumption that other types of sesquiterpene may be found among the esters.

A comparison of the structures that have been established for the terpenoid coumarins, esters, and sesquiterpene lactones permits the positions of the double bonds and of the hydroxy groups in the terpenoid part to be suggested hypothetically. Since the double bond in isoprene itself is present at C_3-C_4, in the majority of *Ferula* sesquiterpenes the double

TABLE 3. Sesquiterpene Lactones of *Ferula*

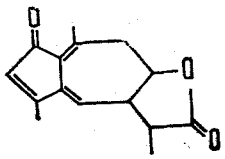
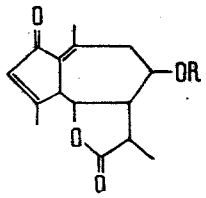
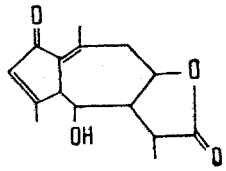
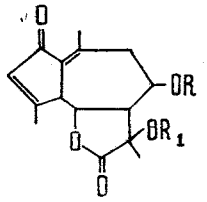
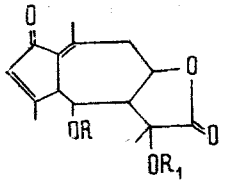
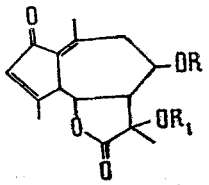
Compound	Structural formula	Literature
119. **Ferulin** $C_{15}H_{16}O_3$, mp 176–178°		[38]
120. **Badkhyzin** $C_{20}H_{24}O_5$, mp 139–140°, $[\alpha]_D$ +68°	 R=C_5H_7O	[16]
121. **Ferulidin** $C_{15}H_{18}O_4$		[145]
122. **Olgoferin** $C_{23}H_{36}O_7$, mp 240–244°, $[\alpha]_D$ +46,9°	 R=R_1=C_4H_5O	[47]
123. **Olgin** $C_{21}H_{24}O_7$, mp 176–178°, $[\alpha]_D$ +25°	R=C_4H_5O R_1=Ac	[37]
124. **Oferin** $C_{23}H_{28}O_7$, mp 214–216°, $[\alpha]_D$ +0°	R=C_4H_5O R_1=C_4H_7O	[37]
125. **Laferin** $C_{22}H_{26}O_7$, mp 142–144°, $[\alpha]_D$ –3,1°	R=C_5H_7O R_1=Ac	[37]
126. **Talassin A** $C_{24}H_{30}O_7$, mp 205–208°, $[\alpha]_D$ –72,1°	R=R_1=C_5H_7O	[37]
127. **Talassin B** $C_{23}H_{30}O_7$, mp 205–208°, $[\alpha]_D$ –29,6°	R=C_5H_7O R_1=C_4H_7O	[37]
128. **Diversolide** $C_{29}H_{32}O_9$, mp 185–186°, $[\alpha]_D$ –284°	 R=$C_6H_3(OCH_3)_2CO$– R_1=C_5H_7O	[146]
129. **Malaphyll** $C_{29}H_{32}O_9$, mp 204°–205°	 R=$C_6H_3(OCH_3)_2CO$– R_1=C_5H_7O	[44]
130. **Malaphyllin** $C_{26}H_{28}O_9$, mp 216–217°	R=$C_6H_3(OCH_3)_2CO$– R_1=Ac	[44]

TABLE 2 (Continued)

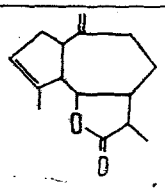
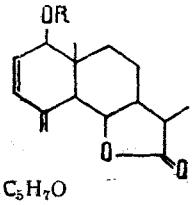
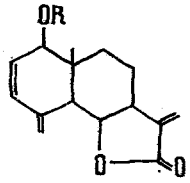
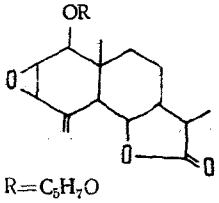
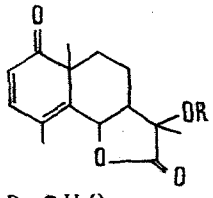
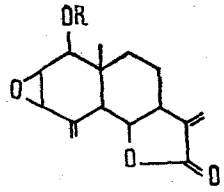
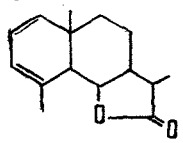
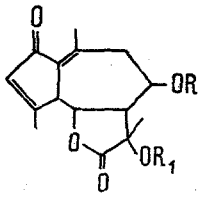
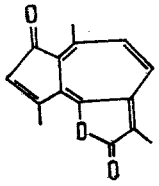
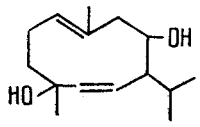
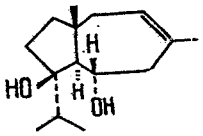
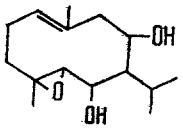
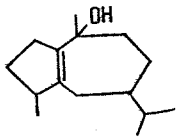
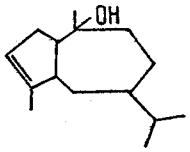
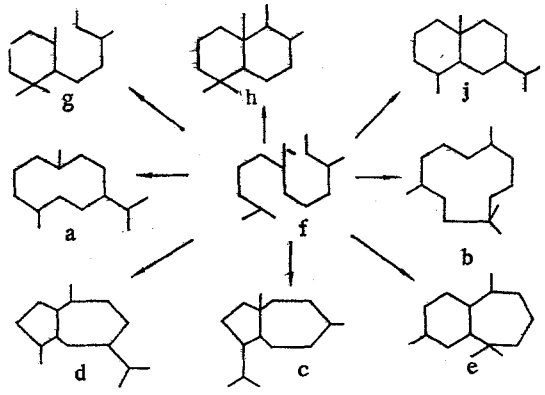
Compound	Structural formula	Literature
131. Grilactone $C_{15}H_{20}O_2$, mp 79,5–81°, $[\alpha]_D$ –125°		[147,148]
132. Oopodin $C_{20}H_{26}O_4$, mp 127–128°	 R=C_5H_7O	[42]
133. Dehydro-oopodin ($C_{20}H_{24}O_4$, mp 113-114°	 R=C_5H_7O	[42]
134. Badkhyzidin $C_{20}H_{26}O_5$, mp 117–118°	 R=C_5H_7O	[41]
135. Semopodin $C_{20}H_{24}O_5$, mp 177–178°	 R=C_5H_7O	[43]
136. Badkhyzinin $C_{20}H_{24}O_5$, mp 104–105°, $[\alpha]_D$ –212,4°	 R=C_5H_7O	[40]
137. Feropodin $C_{15}H_{20}O_2$, mp 140–141°		[39]
138. Malaphyllinin $C_{24}H_{24}O_7$, mp 208–209°	 R= C_6H_5CO R_1=Ac	[44a]

TABLE 3 (Continued)

Compound	Structural formula	Literature
138a. Malaphyllidin $C_{15}H_{12}O_3$ mp 256°		[446]
Sesquiterpine alcohols		
139. Angrendiol $C_{15}H_{26}O_2$, mp 135–137°, $[\alpha]_D$ −86°		[23, 116]
140. Jaeschkeanadiol (chimgandiol, ferutinol) $C_{15}H_{26}O_2$, mp 91–92°, $[\alpha]_D$ +38,8°		[23, 133, 172]
141. Ugamdiol (shiromodiol) $C_{15}H_{26}O_3$, mp 82–83°, $[\alpha]_D$ +47,5°		[23, 163]
142. Ovindiol $C_{15}H_{26}O_2$, mp 137–138°, $[\alpha]_D$ −74°		[23]
143. Guaiol $C_{15}H_{25}O$, mp 91°, $[\alpha]_D$ −26,3°		[47]
144. Karatavin $C_{15}H_{26}O$, mp 136–137°,		[26]



Scheme 18

bonds and the epoxy and tertiary hydroxy groups also occupy these positions in the carbon atoms of the isoprene units. For example, in umbelliferone (1), diversinin (12), ugamdiol (167), ferutinol (174), and juniferol (168) the double bond and the epoxy group (167) are present at C_3–C_4 of an isoprene unit. A deviation from these positions of the double bonds is apparently observed in those cases in which double bonds are formed by the dehydration of

tertiary hydroxy groups (coumarins of the farnesiferol A and conferol series) or by the migration of the double bond with the formation of conjugated systems (fecerol (169), diversin (11)).

The secondary hydroxy groups and carbonyl groups in *Ferula* sesquiterpenes also occupy definite positions in the isoprene chain. They are most frequently found at the first and fifth carbon atoms. For example, in mogoltin (43) and tadzhiferin (5) the hydroxy groups are present on the fifth carbon atoms of the first and third isoprene units, and in feracolin (50) and conferdione (48) the oxygen substituents are located on the fifth carbon atoms of the second and third units, and in tadzhikorin (6) and juniferol (168) on the first and fifth carbon atoms of the terminal isoprene unit. In all sesquiterpene lactones of *Ferula*, the hydroxy groups are present on the first and fifth carbon atoms of the first isoprene unit, forming the lactone ring [176].

It must be mentioned that in all *Ferula* coumarins the umbelliferone residue is connected to the terpenoid moiety by an ether bond with a primary hydroxy group, and the residues of aromatic and aliphatic acids in esters are connected with a secondary hydroxy group.

Up to the present time, it is mainly the epigeal organs of the plants that have been investigated. On this basis, it has been observed that, as a rule, ferulas producing esters do not contain terpenoid coumarins and sesquiterpene lactones, i.e., only one group of compounds is present in definite form [46]. But there is information in the literature which does not agree with this. For example, a given plant is found to contain both coumarins and esters in the case of *Ferula samarcandica, F. korshinskyi* [120, 177], and *F. microcarpa* [113], and coumarins and sesquiterpene lactones simultaneously in *F. diversivitata* [72-74, 146] and *F. malacophylla* [44, 178]. It may be assumed that when the same species of *Ferula* from different growth sites and in different phases of vegetation in each of them are investigated, these three main groups of natural compounds will probably be detected, although one of them may be quantitatively predominating.

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POLYSACCHARIDES OF IRIS

I. GLUCOMANNAN FROM *Iris sogdiana*

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Several fractions of alkali-soluble polysaccharides have been isolated from the seeds of *Iris sogdiana* Bge. The separation of one of the fractions has yielded a glucomannan consisting of glucose and mannose residues in a ratio of 1:1.2. On the basis of the results of oxidation with chromium trioxide of the acetate of the glucomannan, and of periodate oxidation and methylation, it has been established that its molecule consists of a linear chain composed of β-D-glucopyranose and β-D-mannopyranose residues connected by β-1→4 bonds, although the presence of branching is not excluded. The possibility has been shown of isolating D-mannose by the hydrolysis of the seeds.

In Uzbekistan, the genus *Iris* (family Iridaceae) is represented by nine wild-growing species [1]. There are reports in the literature on the study of the monosaccharide composition of the alkali-soluble polysaccharides from the seeds of *I. versicolor* L. and *I. mandschurica* Meissn. [2]. Andrews et al. [3] have studied a glucomannan from the seeds of

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