a distinctly acid reaction. The liberated acids were extracted with diethyl ether, and the extracts were dried over calcined Na_2SO_4 and evaporated. This gave the free fatty acid fraction.

The neutral extract was subjected to alkaline hydrolysis with 10% ethanolic NaOH on the water bath at 80°C for 60 min.

The unsaponifiable fraction was extracted from the cooled hydrolysate repeatedly with diethyl ether. The ethereal extracts were combined, washed with water to neutrality, dried over calcined Na_2SO_4, and evaporated to give the unsaponifiable fraction.

The soaps were combined with the wash-waters from the unsaponifiables and the mixture was acidified with 10% HCl to a distinctly acid reaction. The acid components of the esters (the bound acids) were extracted with diethyl ether. The ethereal extracts were combined, dried over calcined Na_2SO_4, and evaporated to give the bound-acid fraction.

The free and bound acids were methylated separately and the methyl esters were analyzed by GLC.

SUMMARY

1. The lipoid components of a new product — a CO_2 extract from tea production wastes — have been studied.

2. The group composition of the lipoids has been established and the qualitative and quantitative characteristics have been given for individual groups of lipoids: carotenoids, tocopherols, sterols, and fatty acids, and also the alkaloid caffeine accompanying them.

LITERATURE CITED

1. M. S. Umanskii, in: Abstracts of Lectures at the IVth Scientific Conference of Young Scientific Biologists [in Russian], Moscow (1960), p. 65.
2. B. G. Savinov, Carotene [in Russian], Kiev (1948).
3. V. A. Devyatnin, Methods of Chemical Analysis in the Manufacture of Vitamins [in Russian], Moscow (1964).
4. Handbook on Methods of Investigation, Technical and Chemical Control, and the Accounting of Production in the Oils and Fats Industry [in Russian], Leningrad, Part 1, Book 2 (1967), p. 820.

STEREOCHEMISTRY OF TERPENOID COUMARINS.

CRYSTAL AND MOLECULAR STRUCTURE OF SAMARCANDIN

S. M. Nasirov, A. I. Saidkhodzhaev,   UDC 547.582
T. Kh. Khasanov, M. R. Yagudaev, and
V. M. Malikov

The absolute configuration of samarcandin has been established on the basis of the results of a complete X-ray investigation. The absolute configurations of conferol, moscharol, badrakemin, and coladonin, and the absolute configurations of feshurin, nevskin, and isosamarcandin have been refined.

At the present time, more than 40 terpenoid coumarins with a bicyclofarnesyl residue have been isolated from plants of the genera *Ferula* and *Colladonia*, and these have been subdivided into two groups according to the orientation of the aryloxymethylene group at C_9: with the substitutuent C_9—CH_2OAr orientated axially (group I), and equatorially (group II). The absolute configurations of representatives of coumarins of group I — farnesiferol A and gummosin — have been determined on the basis of chemical transformations and the methods of optical rota-

TABLE 1. Equations of the Planes of Some Fragments of the
Molecule and Deviations from These Planes, Å. Ring A: 8.59 x −
5.53 y + 7.08 z = 5.42; ring B: 6.83 x − 6.58 y + 9.15 z =
5.74; O−Ar fragment: −9.36 x − 0.50 y + 7.45 z = 2.03

Ring A		Ring B		O−Ar fragment			
C (1)	0,02:6	C (5)*	0,7391	C (16)	0,00˙4	C (22)	0,0057
C (2)	−0˙0203	C (6)	0˙0091	C (17)	−0,0070	C (23)	0,0419
C (3)*	0˙6632	C (7)	−0,0094	C (18)	0,0301	O (4)	0,0063
C (4)	0,0200	C (8)*	−0˙6300	C (19)	0,0070	C (24)	−0,0311
C (5)	−0˙0204	C (9)	0,0093	C (20)	−0,0216	O (5)	0,1080
C (10)*	−0,707	C (10)	−0˙0090	C (21)	0,0085	O (3)	−0,0011

*Atoms not included in the calculation of the equations of
the planes.

tory dispersion and x-ray structural analysis [1–4]. The establishment of the absolute con-
figuration of the coumarins of this group is being carried out at the present time by passage
to gummosin or farnesiferol A. The absolute configurations of ferucrin and of kellerin have
been shown in this way [5–7].

Relative configurations with a trans-linked bicyclofarnesyl skeleton have been proposed
for the coumarins with an equatorially arranged substituent at C_9 (group II), two types of
linkage being assumed: C_5−αH, C_{10}−βCH$_3$, and C_5−βH, C_{10}−αCH$_3$ [8–10]. An absolute configuration
has been proposed only for one representative of this group — coladonin [11].
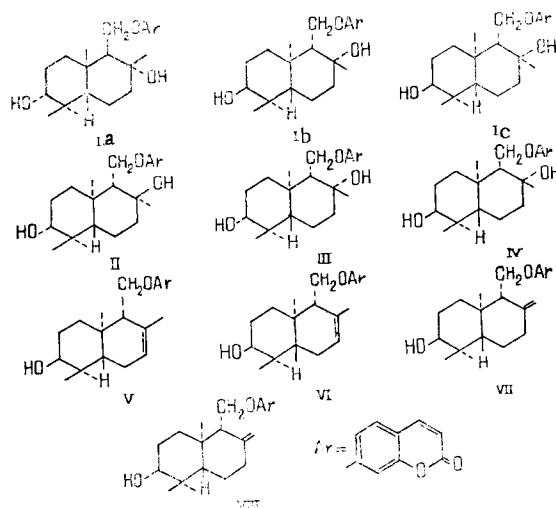
On the basis of the results of a study of the stereochemistry of samarcandin by PMR spec-
troscopy with the use of paramagnetic shift reagents, the relative configuration (Ia) in which
the bicyclofarnesyl residue has the trans-steroidal linkage and the C_8−OH group the equatorial
orientation has been proposed for it [9].

Recently, by passing from samarcandin through conferol to tetrahydrobadrakemin we showed
the interrelationship between the three series of terpenoid coumarins, and, by comparing the
signs of the specific rotations of the saturated diol from farnesiferol A and of the terpenoid
coumarins from *Ferula* genus, in which the bicyclofarnesyl residue has the second type of link-
age (C_5−βH, C_{10}−αCH$_3$), we have proposed absolute configurations for a number of coumarins. The
absolute configuration (Ib), in which the hydroxy group at C_8 has the axial orientation, was
established for samarcandin [10].

Passage between three terpenoid coumarins — farnesiferol A, conferol, and samarcandin —
has also been effected by the action of trifluoroacetic acid [12, 13].

In view of the contradictory nature of the information on the stereochemistry of samar-
candin, and also the significance of the transitions effected between the three series of cou-
marins, we have made an x-ray structural analysis of samarcandin. An unambiguous answer to
the question of the stereochemistry of samarcandin would permit the absolute configuration
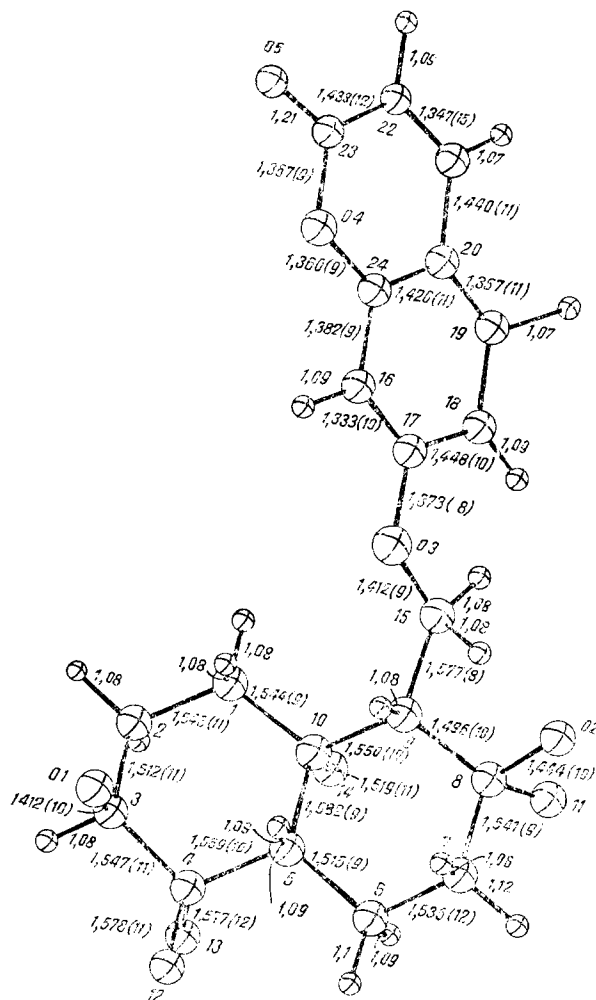
172

Fig. 1. Geometry of the samarcandin mole-
cule.

to be established not only of samarcandin itself but also of several interrelated terpenoid coumarins having an equatorially oriented aryloxymethylene group at C_9.

For the analysis we took samarcandin, $C_{24}H_{32}O_5$, mp 176–177°C, $[\alpha]_D$ + 30° (c 5.0; ethanol) isolated from *Ferula samarcandica* Korov. A general view of the samarcandin molecule is shown in Fig. 1.

The present investigation has shown the crystalline and molecular structure of samarcandin and the fact that the substituent at the C(9) atom (CH_2OAr, where Ar is a coumarin residue) is present in the equatorial orientation. The orientations of the other substituents are as follows: OH at C(3) — β-axial; OH at C(8) — β-equatorial; methyl groups at the C(8) and C(10) — α-axial (Ic) (Fig. 1).

The conformations of the rings can be judged from the figures of Table 1, which gives the equations of the planar fragments of the rings and the deviations of individual atoms from these planes, and also from Table 2, which gives the valence angles.

The oxycoumarin moiety of the molecule is planar. In the terpene moiety, the cyclohexane rings A and B are trans-linked and each has the chair conformation ($^3C_9$ and $^5C_2$, respectively). The C(3) and C(10) atoms of ring A deviate from the plane of the other four atoms by 0.663 and 0.707 Å; in ring B the C(9) and C(8) atoms deviate by 0.789 and 0.630 Å. These magnitudes are close to the ideal value for the chair conformation, which is 0.73 Å [14]. The almost ideal chair conformations of these rings is also indicated by the torsional angles (Table 3) which are close to the ideal value of 60°.

The structure of samarcandin is similar to that of gummosin, studied previously [3, 4], which differs from samarcandin by the presence of hydroxy and methyl groups at the C(8) atom

TABLE 2. Valence Angles, ω, deg

Angle	ω	Angle	ω	Angle	ω	Angle	ω (Ideal)
C(1) C(2) C(3)	109.8(7)	C(5) C(6) C(7)	109.1(8)	C(1) C(10) C(9)	109.2(6)	C(20) C(21) C(22)	119.7(8)
C(2) C(3) C(4)	113.1(6)	C(6) C(7) C(8)	112.1(7)	C(1) C(10) C(14)	109.9(6)	C(21) C(22) C(23)	121.9(9)
C(3) C(4) C(1)	108.4(6)	C(7) C(8) C(9)	109.3(6)	C(5) C(10) C(14)	114.5(6)	C(22) C(23) O(4)	118.1(8)
C(4) C(5) C(10)	114.8(6)	C(8) C(9) C(10)	117.7(6)	C(9) C(10) C(14)	112.2(6)	C(23) O(1) C(24)	121.6(6)
C(5) C(10) C(1)	106.5(5)	C(9) C(10) C(5)	104.3(6)	C(4) C(5) C(6)	114.0(6)	O(4) C(24) C(20)	121.5(6)
C(10) C(1) C(2)	112.5(6)	C(10) C(5) C(6)	112.8(5)			C(24) C(20) C(21)	117.2(7)
O(1) C(3) C(2)	112.3(7)	O(2) C(8) C(7)	106.7(7)	C(9) C(15) O(3)	108.1(6)	C(19) C(20) C(21)	125.5(7)
O(1) C(3) C(4)	109.9(7)	O(2) C(8) C(9)	108.8(6)	C(15) O(3) C(17)	119.2(6)	O(4) C(24) C(16)	118.0(6)
		O(2) C(8) C(11)	104.8(6)				
C(3) C(4) C(12)	107.0(6)	C(9) C(8) C(11)	110.2(7)	C(16) C(17) C(18)	123.1(6)	O(5) C(23) O(4)	116.5(7)
C(3) C(4) C(13)	110.1(7)			C(17) C(18) C(19)	113.2(7)	O(5) C(23) C(22)	125.4(9)
C(5) C(4) C(12)	106.7(7)	C(8) C(9) C(15)	111.0(6)	C(18) C(19) C(20)	125.3(7)		
C(5) C(4) C(13)	115.8(7)	C(10) C(9) C(15)	112.6(6)	C(19) C(20) C(24)	117.3(7)	O(3) C(17) C(16)	117.7(6)
C(12) C(4) C(13)	108.4(8)			C(20) C(24) C(16)	120.4(7)	O(3) C(17) C(18)	119.2(7)
				C(24) C(16) C(17)	120.7(6)		

TABLE 3. Comparison of the Torsion Angles, deg

Ring	Angle	Samarcandin	Gummosin	Ideal	Ring	Angle	Samarcandin	Gummosin	Ideal
A $^3C_{10}$	1—2—3—4*	−59	−59	−60	B $^5C_8$	5—6—7—8	−59	−59	−60
	2—3—4—5	+54	+54	+60		6—7—8—9	+52	+59	+60
	3—4—5—10	−53	−50	−60		7—8—9—10	−53	−60	−60
	4—5—10—1	+55	+48	+60		8—9—10—5	+56	+63	+60
	5—10—1—2	−57	−51	−60		9—10—5—6	−59	−66	−60
	10—1—2—3	+61	+59	+60		10—5—6—7	+64	+59	+60
	Total	+1	+1	0		Total	+1	−4	0

*Torsion angle relative to the C(2)—C(3) bond, i.e., dihedral angle between the C(1)C(2)C(3) and the C(2)-C(3)C(4) planes.

TABLE 4. Coordinates of the Atoms ($\times 10^4$) of the Samarcandin Molecule

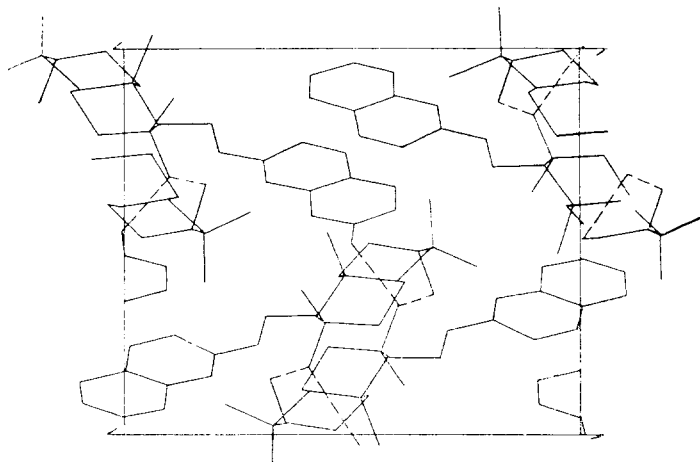| ATOM	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O (1)	1407(6)	—1810(4)	7433 (3)	175	75	50	34	2	3
O (2)	3298(5)	992(4)	4172(3)	149	74	59		—6	32
O (3)	2698(5)	2065(3)	6353 (3)	194	44	59	—6	—78	-11
O (4)	4315(5)	4120(4)	8574 (3)	137	55	55	—41	—32	—14
O (5)	5023(6)	498 (5)	9702 (4)	196	89	74	—87	—53	—44
C (1)	930(8)	325(6)	6816 (5)	140	63	40	7	16	—28
C (2)	25(8)	—370(6)	7312 (5)	142	81	52	30	31	—15
C (3)	278(8)	—1402(6)	7103 (5)	145	62	64	—36	59	—11
C (4)	19 (8)	—1726(6)	6109 (5)	139	65	55	-58	42	—22
C (5)	1049(7)	—931(5)	5601 (4)	134	44	38	-9	36	—29
C (6)	1094(9)	—1156(6)	4617 (5)	166	62	54	—26	13	—3
C (7)	2187(8)	—58(5)	4231 (5)	175	62	41	—5	14	—11
C (8)	2132(8)	578(5)	4409 (5)	161	53	45	8	—13	11
C (9)	1926(7)	756(4)	5370 (4)	103	41	50	13	—15	—5
C (10)	837(7)	206(5)	5807 (5)	123	53	52	37	10	—7
C (11)	1238(8)	1004(7)	3777 (6)	168	75	63	42	—55	27
C (12)	720(11)	—2841(6)	5974 (6)	240	55	65	—36	52	—8
C (13)	—1120(9)	—1727(9)	5817 (7)	120	133	98	—154	34	—31
C (14)	—367(8)	625(6)	5488 (6)	124	82	66	75	-40	6
C (15)	1975(8)	1938(5)	5595 (5)	167	44	52	—6	—18	—17
C (16)	3479(7)	3124(5)	7437 (5)	130	44	42	—7	—37	—3
C (17)	2900(8)	3037(5)	6671 (5)	150	35	57	—15	23	10
C (18)	2442(7)	3911(6)	6186 (4)	124	60	38	41	—15	0
C (19)	2725(9)	4867(5)	6586 (6)	172	44	69	14	16	4
C (20)	3340(8)	4985(5)	7351 (5)	130	48	54	—1	7	—8
C (21)	3602(12)	5952(6)	7772 (6)	259	53	80	5	16	—8
C (22)	4197(12)	5962(7)	8546 (7)	263	59	96	12	—89	—46
C (23)	4537(9)	5034(7)	8988 (5)	153	85	58	—56	—36	—26
C (24)	3733(7)	4080(6)	7786 (5)	121	55	55	—21	—4	—1
H1-1	740	1120	6980						
H1-2	1830	120	7020						
H2-1	—880	—180	7110						
H2-2	130	—250	8000						
H3	—440	—1920	7410						
H5	1940	—1100	5840						
H6-1	1189	—1980	4480						
H6-2	270	—880	4310						
H7-1	3000	—900	4480						
H7-2	2170	—700	3500						
H9	2690	370	5670						
H15-1	2570	1610	5100						
H15-2	1700	2700	5400						
H16	3750	2430	7790						
H18	1920	3840	5580						
H19	2468	5555	6244						
H21	3300	6660	7480						
H22	4410	6700	8850						

Fig. 2. Packing of the samarcandin molecules.

in place of an exomethylene group, and also by the equatorial orientation of the substituent at the C(9) atom.

With the exception of a few details, samarcandin has the same stereochemistry as gummosin. What has been said is illustrated by the closeness of the torsional angles [2] determining the conformation of the rings in samarcandin and gummosin. These magnitudes are given in Table 3, together with the ideal values for the corresponding cyclohexane conformations [14].

The lengths of the bonds and the valence angles (Table 2) are completely usual and are close to the corresponding standard values [15]. For example, the mean length of a C—C bond in the benzene ring (1.388 Å), just as in gummosin, is close to that found in crystalline benzene, 1.398 Å [16]. In the samarcandin molecule there are "active" hydrogen atoms that participate in the formation of hydrogen bonds. O(13)—H...O(7) H-bonds (2.668 Å) unite the molecules into an infinite helix around a second-order screw axis parallel to [001]. These helices are "cross-linked" by O(7)—H...O(20) H-bonds (2.845 Å) likewise forming helices around a second-order axis parallel to [100]. Thus, the absolute configuration (Ic) (Fig. 2) is proposed for samarcandin.

The x-ray structural analysis of the stereochemistry of samarcandin has permitted an unambiguous answer to the question of the configuration of the related compounds with an equatorially arranged substituent at C_9 (—CH$_2$OAr) isosamarcandin (II), nevskin (III), feshurin (IV), conferol (V), moschatol (VI), badrakemin (VII), and coladonin (VIII) and their natural oxo and acyloxy derivatives.

EXPERIMENTAL

The experimental investigation was carried out on a Syntex automatic four-circle diffractometer (Institute of Bioorganic Chemistry, Academy of Sciences of the Uzbek SSR, Tashkent) in Cu K_α radiation (graphite monochromator). The cell parameters were refined by the method of least squares from 12 reflections with $\nu \geqslant 30°$. These and other crystallographic characteristics were as follows:

$C_{24}H_{32}O_5$ $a = 20.3124$ Å $V = 2121.7$ Å^3

M 400, 815 $b = 14.4156$ Å $Z = 4$

Space group

P$2_1 2_1 2$ $c = 7.2116$ Å $d_{meas} = 1.27$ g/cm^3

$d_{calc} = 1.28$ g/cm^3

The intensities of the reflections with θ_{max} 64° ($\theta/2\theta$ scanning) were obtained on the diffractometer mentioned. In the interpretation and refinement of the structure, 1477 reflections with $|F^2| > 2\sigma$ were used.

The structure was interpreted by the direct method using the Rentgen-75 program [13] and was refined in the isotropic, and then in the anisotropic, approximation for the nonhydrogen atoms. The coordinates of the hydrogen atoms were given from geometrical considerations and were refined in the isotropic approximation. The parameters were given to equal B = 4 Å. The final value of R was 0.09.

SUMMARY

1. The spatial structure of samarcandin has been established on the basis of the results of a complete x-ray structural investigation.

2. The absolute configurations of conferol, moscharol, badrakemin, and coladin, have been confirmed.

3. The absolute configurations of isosamarcandin, feshurin, and nevskin have been refined.

LITERATURE CITED

1. L. Caglioti, H. Naef, D. Arigoni, and O. Jeger, Helv. Chim. Acta, 41, 2278 (1958).
2. N. P. Kir'yalov and S. D. Movchan, Khim. Prir. Soedin., 383 (1966).

3. S. M. Nasirov, V. G. Andrianov, Yu. T. Struchkov, T. Kh. Khasanov, A. I. Saidkhodzhaev, and G. K. Nikonov, Khim. Prir. Soedin., 657 (1976).
4. S. M. Nasirov, V. G. Andrianov, and Yu. T. Struchkov, Kristallografiya, 22, 1202 (1977).
5. M. E. Perel'son, Yu. E. Sklyar, N. V. Veselovskaya, and M. G. Pimenov, Khim.-farm. Zh., No. 3, 78 (1977).
6. N. V. Veselovskaya, Yu. E. Sklyar, M. E. Perel'son, and M. G. Pimenov, Khim. Prir. Soedin., 227 (1979).
7. A. A. Nabiev, Kh. Kh. Khasanov, and V. M. Malikov, Khim. Prir. Soedin., 17 (1979).
8. V. Yu. Bagirov, V. I. Sheichenko, and A. M. Ban'kovskii, Khim. Prir. Soedin., 450 (1976).
9. M. E. Perel'son, V. I. Sheichenko, Yu. E. Sklyar, and V. B. Andrianova, Khim.-farm. Zh., No. 8, 33 (1977).
10. A. I. Saidkhodzhaev and V. M. Malikov, Khim. Prir. Soedin., 707 (1978).
11. M. Pinar and B. Rodriguez, Phytochemistry, 1987 (1977).
12. A. A. Savina, Yu. E. Sklyar, V. I. Sheichenko, and I. A. Kir'yanova, Khim. Prir. Soedin., 630 (1979).
13. V. Yu. Bagirov, V. I. Sheichenko, A. A. Savina, and N. V. Veselovskaya, Khim. Prir. Soedin., 722 (1979).
14. International Tables for X-Ray Crystallography VIII. Kynoch Press, Birmingham (1962).
15. A. I. Chekhlov, Yu. T. Struchkova, and A. I. Kitaigorodskii, Zh. Strukt. Khim., 15, 754 (1974).
16. E. G. Cox, D. W. Cruickshank, and J. A. S. Smith, Proc. R. Soc., London A., 247, 1 (1958).

A PEUCEDANOL GLUCOSIDE FROM *Phlojodicarpus turczaninovii*

D. Gantimur, A. I. Syrchina,   UDC 547.992
and A. A. Semenov

The new coumarin peucedanol 3'-β-D-glucopyranoside (I), $C_{20}H_{26}O_{10} \cdot C_2H_5OH$, mp 160–162°C, has been isolated from an ethanolic extract of the epigeal part of *Phlojodicarpus turczanovii* growing in the Mongolian People's Republic (Gobi-Altai). The acid hydrolysis of (I) formed D-glucose and peucedanol (II), and also decursinol and marmesin. The results of IR, UV, PMR, and ^{13}C NMR spectroscopy are given.

The courmarins [1] peucenidin, libanorin, and buchtarmin have been isolated from *Phlojodicarpus turczaninovii* Sipl. growing in the south of Chitinskaya Province. The same plant collected in the mountains of the Gobi-Altai (Mongolian People's Republic) and erroneously identified previously as *Ph. sibiricus* [2] contains, instead of the coumarins mentioned, the epoxide derivatives phlojodicarpin and isophlojodicarpin.

We now report that in addition to the latter two compounds the Mongolian plant contains a polar coumarin which has been isolated by chromatography on silica gel of the butanol-soluble fraction of the ethanolic extract of the epigeal part of the plant followed by crystallization from ethanol. This compound has been assigned the structure of 3'-O-(β-D-glucopyranosyl)peucedanol (I) on the basis of the following facts.

The hydrolysis of (I) with dilute hydrochloric acid led to glucose and a mixture of three aglycones. Among them a substance with spectral and other characteristics identical with that of peucedanol (II) [3] predominated. It was shown by thin-layer chromatography on Silufol in the presence of markers (in the solvent system chloroform—methanol (10:1)) that minor components of the hydrolysate were decursinol (III) and marmesin (IV). We assume that they were artefacts formed during hydrolysis by the cyclization of (II). The phenolic hydroxyl in (I) is not glycosylated. This follows from the bathochromic shift of the long-wave absorption band in the UV region from 333 to 377 nm on the addition of sodium methanolate.