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Coumarins from *Peucedanum hystrix* growing in Mongolia

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Abstract: It is proved to be that of genus *Peucedanum hystrix* serve as a source of biologically valuable natural coumarins. Nine angular furocoumarins belonging to class of 2'-substituted and 2',3'-disubstituted 2',3'-dihydrofurocoumarins have been isolated and structurally isolated. For peucenidin data of X-ray analysis is obtained.

Keywords: *Peucedanum hystrix*, coumarins, oroselol, columbianetin, X-ray analysis.

Introduction

Plants of Umbelliferae family are known to be a good source of naturally occurring coumarins for producing of potential medicinal preparations [1]. Coumarins are considered as phytoalexins since plants produce them as defence substances when wounded or attacked by other organisms. Coumarins can be suggested to be beneficial for the plants themselves as natural biocontrolling antipathogenic compounds and for humans as remedy for hyperproliferative skin deseases and as reference compounds in various bioactive tests. Furthermore, coumarin containing plants are valuable as dietary supplements on the basis of their mild antimicrobial and anti-inflammatory effects. Coumarins are also active in plant metabolism, taking part in growth regulation.

Plants of genus *Peucedanum* sp. attract attention of scientists as source of coumarins. *Peucedanum hystrix* Bge. widely spread in Southern Siberia and Mongolia [2]. To our knowledge a systematic phytochemical investigation of this plant has not been properly carried out. Previously oroselon (**1**), oroselol (**2**) and 2'-(S)-O-senecioyl)-2',3'-dihydrooroselol (libanorin) (**3**) have been isolated from the *Peucedanum hystrix* Bge. [3].

Experimental

NMR spectra of compounds were obtained in $CDCl_3$ or CD_3OD obtained on spectrometers Bruker AV-300 [working frequency 300.13 (^{1}H) and 75.47 MHz (^{13}C)] and AV-600 [600.30 (^{1}H) и 150.96 MHz (^{13}C)]. Different types of proton-proton and carbon-proton shifting correlation spectroscopy (COSY, COXH, COLOC, NOESY) were used for assignment of signals in NMR spectra. Multiplesity of signals in ^{13}C NMR spectra determined in regime J modulation. High resolution mass-spectrometer DFS Thermo Scientific (energy

of ionizing electrons 70 eW, temperature of the evaporator 230-280°C) was used for recording mass-spectra, determining of molecular weight and elemental composition. Melting point determined on table Stuart SMF-38. Specific rotation $[\alpha]_D^{20}$ measured on polarimeter PolAAr3005.

X-ray analysis was carried out by ω-φ scanning (width of frames 0.5°) on difractometer KAPPA APEX II (Bruker) with doublecoordinate CCD detector by using of MoKα radiation (λ = 0.71073 Å).

Purified fractions were investigated by the method of chromato-mass-spectrometry on gas chromatograph Hewlett-Packard 5890/II MSD with quadrupol mass-spectrometer (HP MSD 5971) as detector. 30 meter quartz column HP-5MS (copolimer of 5% diphenyl-95% dimethylenesiloxane) with internal diameter 0.25 mm and film width of motionless phase 0.25 μм were used; temperature 50-280°C 4° per min, 15 min 280°C. The content of each compounds have been calculated by the area of GC peak without use of correcting factors and expressed in percentage.

Column chromatography on silica gel (firm Acros, 0.035-0.070 mm) (eluent – chloroform-ethanol) was used for isolation individual compounds. The purity of isolated compounds was checked thin layer chromatography method on plate Silufol UV-254, used system: chloroform – ethanol, 10:1; petroleum ether – ether, 4:1.

Fraction and Fractionation.

Air-dried, chopped roots and aerial parts of *Peucedanum hystrix* Bge. (500 г) exhaustively extracted with 96 % ethanol at room temperature. Alcoholic extract was concentrated until aqueous remainder, diluted by water in the ratio (1:1) and filtrated. Filtrate subjected to fractionation by solvents with increasing polarity: hexane, chloroform, diethyl ether and ethyl acetate, respectively. Triple extraction with solvents (3x100ml) by heating at reflux was carried out . Fractions were concentrated at rotatory evaporator. Yield of extractive compounds presented at table 1. Further each fractions were separated by column chromatography on silica gel.

Separation of the hexane fraction of the aerial parts of Peucedanum hystrix Bge. 0.9 g of the hexane fraction was chromatographed by column chromatography, consistently collected fractions. 144 mg eugenin **4**, 54 mg umbelliferon **5**, 27 mg oroselon **1**, 27 mg columbianetin **6**, 63 mg columbianadin **7**, 54 mg peucenidinи **8** and 45 mg libanotin **9** were isolated by crystallization from diethylether.

Separation of the hexane fraction of the root of Peucedanum hystrix Bge. 0.8 g of hexane extract was chromatographed by column chromatography. 64 mg libanorin **3**, 88 mg columbianetin **6**, 72 mg columbianadin **7**, 72 mg peucenidin **8**, 67 mg libanotin **9**, 16 mg furocoumarin **10** and 20 мг furocoumarin **11** were isolated.

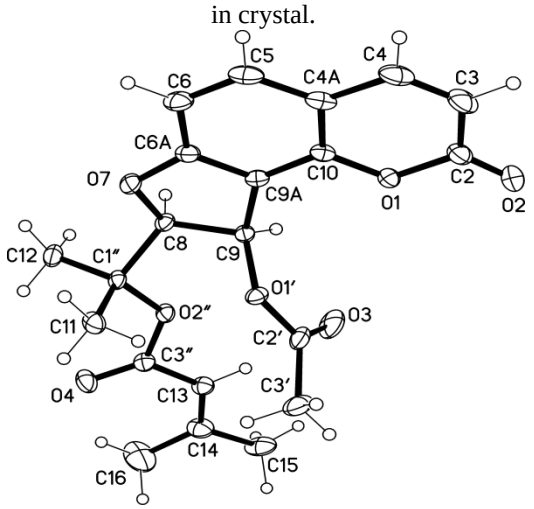
Separation of the chloroform fraction of the aerial parts of Peucedanum hystrix Bge. 0.7 g of chloroform extract was chromatographed by column chromatography. 70 mg umbelliferon **5**, 42 mg scopoletin **12**, 21 мг oroselon **1**, 35 mg libanorin **3**, 35 mg columbianetin **6**, 30 mg columbianadin **7**, 42 mg peucenidin **8** and 63 mg libanotin **9** were isolated by crystallization from diethylether.

Separation of the chloroform fraction of the roots of Peucedanum hystrix Bge. 0.8 g of chloroform extract was chromatographed by column chromatography. 16 mg angelicin **13**, 48 mg oroselol **2**, 24 mg coumarin **14**, 24 mg columbianetin **6**, 16 mg coumarin **11**, 64 mg umbelliferon **5** and 60 mg vaginidiol **15** were isolated.

Separation of the ether fraction of the aerial parts of Peucedanum hystrix Bge. 0.96 g of ether extract was chromatographed by column chromatography. 40 mg oroselol **2**, 30 mg columbianetin **6**, 20 mg libanorin **3**, 30 mg peucenidin **3**, 116 mg vanilic acid **16** and 20 mg trand-ferulic acid **17** were isolated by crystallization from diethylether.

Separation of the ether extract of the roots of Peucedanum hystrix Bge. 0.77 g of the chloroform extract was chromatographed by column chromatography. 92 mg mixture of coumarins **3**, **7**, **10** and **11**, 30 mg vaginidiol **15**, 60 mg umbelliferon **5** and 69 mglibanotin **9** were isolated.

Figure 1. Spatial structure of peucenidin (**8**) molecule in crystal.



Results and Discussion

We have investigated extractive compounds from *Peucedanum hystrix* Bge. collected from the place named Batkhaan uul, Uvurkhangai province. Concentrated ethanolic extract of the aerial parts and roots successively fractionated with hexane, chloroform, diethyl ether and ethyl acetate. The yield of extractive compounds and total content of coumarins in fractions after evaporation of hexane, chloroform and diethyl ether have shown at table 1. Total content of coumarins in the aerial parts and roots were 3.9 and 4.6%. The highest content of coumarins indicated in hexane and chloroform fractions. Extractive compounds separated by column chromatography on silica gel.

From the hexane fraction 5-hydroxy-7-methoxy-2-methyl chromon (eugenin) (**4**) (16% from extract weight) and coumarins: umbelliferon (**5**) (6% from extract weight), oroselon **1** (3%), 2',3'-dihydrooroselol (columbianetin) (**6**) (3%), 2'-O-angeloyl-2',3'-dihydrooroselol (sosimin, columbianadin) (**7**) (7%), (2'*S*,3'*R*)-3'-acetoxy-2'-O-senecioyl-2',3'-dihydrooroselol (peucenidin) (**8**) (6%) and (2'*S*,3'*R*)- 2'-O-angeloyl-3'-acetoxy-2',3'-dihydrooroselol (libanotin, edultin) (**9**) (5%) have been isolated. Oroselon **1** and (2'*S*)-2-methylbutanoyl-2',3'-dihydrooroselol (**10**) have been identified by spectral data. From the hexane fraction libanorin **3** (8%), columbianetin **6** (11%), columbianadin **7** (9%), peucenidin **8** (9%) and libanotin **9** (7%) have been isolated, respectively. Moreover the compound **10** (1.2% from fraction's weight) and (2'*S*,3'*R*)-2'-O-acetyl-3'-isobuteryloxy-2',3'-dihydrooroselol (**11**) (content 2.2% from fraction's weight).

Chromatographing of chloroformic fraction of ethanolic extract of the aerial parts of *Peucedanum hystrix* Bge. allow us to concentrate and isolate the main quantity of umbelliferon
5 (10% from extract's weight) and scopoletin (**12**) (6% from extract's weight), also to isolate oroselon **1** (3%), columbianetin **6** (5%), libanorin **3** (7%), columbianadin **7** (4%), peucenidin **8** (6%) and libanotin **9** (9%). From chloroformic fraction of ethanolic extract of roots angelicin (**13**) (2%), oroselol **2** (6%), columbianetin **6** (8%), libanorin **3** (4%), 2'*S*-isovaleryl-2',3'-dihydrooroselol (**14**) (3%), columbianadin **7** (3%), furocoumarin **11** (2%), umbelliferon **5** (8%), as well as (3'*R*)-hydroxy-2'*S*,3'*R*-dihydrooroselol (vaginidiol) (**15**) (8%) consequtively isolated.

Subsequent treatment of alcoholic extract of the aerial parts of *Peucedanum hystrix* Bge. with diethyl ether allow us to isolate additional quantity of oroselol **2** (4% from extract's weight), columbianetin **6** (3%), libanorin **3** (2%), peucenidin **8** (3%), vanilic acid (**16**) (yield 12%, content 23%) and trans-ferulic acid (**17**) (yield 2%, content 7%). From ether fraction of ethanolic extract consecutively isolated vanilic acid **16** (8%), derivatives of 2',3'-dihydrooroselol **3**, **7**, **10** and **11** (~12%), vaginidiol (**15**) (4%), umbelliferon **5** (8%), libanotin **9** (9%).
From data presented at table 1 we see that content of coumarins in ethyl acetate fractions was minimum.

Table 1. Yield of extractive compounds and total coumarins of *Peucedanum hystrix* Bge.

№	Solvent for extraction	Aerial parts		Root	
		Yield of extractive compounds, %	Total content of coumarins, %	Yield of extractive compounds, %	Total content of coumarins, %
1	Hexane	1.8	1.25	2.4	1.5
2	Chloroform	3.4	2.1	3.0	2.4
3	Diethyl ether	2.5	0.45	1.8	0.5
4	Ethylacetate	2.2	0.1	2.5	0.2

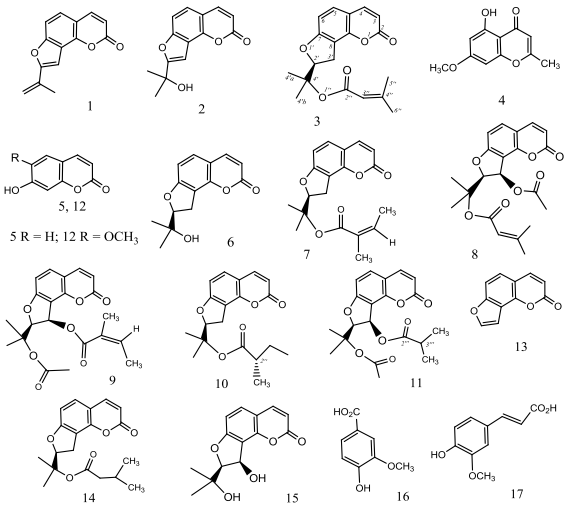


Figure 2. Isolated and identified compounds.

Structures of compounds have been established on the basis of their phusical, chemical and spectral characteristics, as well as comparison with literature data. For peucenidin **8** X-ray analysiswas done (Figure 2).

Geometric parameters of molecule of compound **8** have been proved by statistical data [4]. In Cambridge base of structural data [5] found seven identical structures with 2',3'-dihydrofurocoumarin skeleton including (2'*S*,3'*R*)-3'-senecoyl-2-O-acetyl-2',3'-dihydrooroselol (isopeucenidin) [6]. However in CBCD are absent 3D coordinates for isopeucenidin therefore we could not do comparisonal analysis of geometrical parameters of isopeucenidin with peucenidin **8**. In molecule of compound **8** observed intramolecular hydrogen bonds of C-H…O type which suggested to be formed due to presence of angeloyl and acetyl substituents (table 2).

Table 2. Parameters of intramolecular and intermolecular hydrogen bonds in the crystal of the compound **8**.

№	D-H...A	D–H, Å	H...A, Å	D...A, Å	Ungle D-H-A, °	Operation of symmetry
1.	C9-H9...O3	1.00	2.28	2.688(2)	103	-
2.	C11-H11A...O1'	0.98	2.33	3.008(3)	125	-
3.	C11-H11C...O4	0.98	2.55	3.088(2)	115	-
4.	C12-H12C...O4	0.98	2.39	2.928(2)	114	-
5.	C16-H16C...O4	0.98	2.18	2.942(3)	134	-
6.	C3-H3...O3	0.95	2.29	3.157(3)	152	3-x,-0.5+y,0.5-z
7.	C8-H8...O2	1.00	2.52	3.470(2)	160	-1+x, y, z

The investigation showed that *Peucedanum hystrix* Bge. represents as a reliable source of furocoumarins. In addition to oroselol **2** three groups of dihydrofurocoumarins: monoethers 8(*S*)-8,9-dihydrooroselol **3**, **7**, **8**, **10**, **14**, vaginidio l**5** and their 2,3-diethers **8**, **9**, **11** have been isolated. 2'-Substituted and 2',3'-disubstituted 2',3'-dihydrofurocoumarins attract attention in connection with known antitumour activity. Thus, 2'(*S*)-columbianetin sulphate possess antiproliferative activity [7]. Dihydrofurocoumarins vaginidiol **15** [6, 8] and angelmarin [9] also have antitumour activity.

Thus, we have obtained new data about metabolites composition of the plant *Peucedanum hystrix* Bge. It is proved to be that this plant might serve as source of *2'*-substituted and 2',3'-disubstituted 2',3'-dihydrofurocoumarins. Deserve attention isolation from *Peucedanum hystrix* Bge. highly distributed in plants chromone **4** [11] as well as vanilic **16** and trans-ferulic **17** acid.

Spectral data of individual compounds

Spectral and analytical data for umbelliferon **5** and scopoletin **12** correspond to literature data [12]. ^{13}C NMR spectral data of furocoumarins shown at table 3.

Oroselon {8-(prop-1-ene-2-yl)-2*H*-furo[2,3-*h*]chromen-2-one} (1). M. p. 177 - 180°C (from ethylacetate). In paper [2] m.p. 179-180°C. IR spectra (V, см -1): 760, 812, 831, 907, 1020, 1123, 1154, 1374, 1553, 1617, 1680. ^1H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 2.13 (3H, s, CH_3), 5.24 (1H, s, H-5′), 5.82 (1H, s, H-5′), 6.36 (1H, d, *J* = 9.6, H-3), 6.96 (1H, s, H-3'), 7.30, 7.34 (both d, 1H, J = 8.5, H-5,6), 7.77 (1H, d, *J* = 9.6, H-4). Mass-spectra, m/z (I_{comp}, %): 226 (100), 198 (82), 183 (48), 171 (24), 155 (53), 141 (28), 115 (43), 101 (12), 75 (26), 63 (78). Found, %: C 74.18; H 4.26. $C_{14}H_{10}O_3$. Calculated, %: C 74.33; H 4.46.

Oroselol {8-(2-hydroxypropane-2-yl)-2H-furo[2,3-*h*]chromen-2-one} (2). M.p. 150-154°C (from ether). In paper [2] m.p. 149-151°C. ^1H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 1.74 (s, 6H, 2×CH_3 at C-4'), 6.35 (1H, d, *J* = 9.8, H-3), 6.98 (1H, s, H-3'), 7.32 (1H, д, *J* = 8.5, H-6), 7.37 (1H, d, *J* = 8.5, H-5), 7.78 (1H, d, *J* = 9.8, H-4). Mass-spectra, m/z

(I_{comp}, %): 224 (32), 229 (100), 212 (5), 201 (15), 187 (8), 171 (14), 115 (15), 101 (18), 43 (23). Found: [*M*] 224.2034. $C_{14}H_{12}O_4$. Calculated: 244.2035.

Libanorin {8(*S*)-(2-senecioxypropane-2-yl)-8,9-dihydro-2*H*-furo[2,3-*h*]-chromen-2-one} (**3**). M.p. 75-77°C (from ether). $[\alpha]_D$ = +188.3 (c 0.88, $CHCl_3$). In paper [13] m.p. 79°C, $[\alpha]_D$ = +197 (c 2.2, $CHCl_3$). UV spectra (ethanol), λ_{max}/нм (lgε): 206 (4.11), 237 (3.68), 298 (2.77), 329 (4.13). IR spectra, (ν, cm^{-1}): 806, 832, 930, 980, 1024, 1069, 1263, 1385, 1460, 1506, 1620, 1720, 1736, 3090. ^{1}H NMR spectra ($CDCl_3$, δ, ppm, J/Hz):1.53, 1.61 (both s, 3H, CH_3 at C-4'), 1.86, 2.10 (both s, 3H, CH_3 at C-5"), 3.36 (2H, m, H-3'), 5.21 (1H, dd, *J* = 7.6, 8.2, H-2'), 5.58 (1H, broad s, H-4"), 6.23 (1H, d, *J* = 9.6, H-3), 6.80 (1H, d, *J* = 8.4, H-6), 7.27 (1H, d, *J* = 8.4, H-5), 7.62 (1H, d, *J* = 9.6, H-4). Mass-spectra, m/z (I_{comp}, %): 328 (10), 303 (10), 286 (5), 244 (16), 243 (11), 229 (42), 227 (15), 201 (8), 187 (16), 83 (100), 43 (25). Found: [*M*] 328.1314. $C_{19}H_{20}O_5$. Calculated: 328.1311. 5.58 (1H, broad s, H-4"), 6.23 (1H, d, *J* = 9.6, H-3), 6.80 (1H, d, *J* = 8.4, H-6), 7.27 (1H, d, *J* = 8.4, H-5), 7.62 (1H, d, *J* = 9.6, H-4). Mass-spectra, m/z (I_{comp}, %): 328 (10), 303 (10), 286 (5), 244 (16), 243 (11), 229 (42), 227 (15), 201 (8), 187 (16), 83 (100), 43 (25). Found: [*M*] 328.1314. $C_{19}H_{20}O_5$. Calculated: 328.1311.

Table 4.

Atom*	1	2	3	6	7	8	9	10	11	13	14	15
C-2	160.62	160.69	160.76	160.91	160.72	159.70	159.51	160.55	159.81	160.66	160.28	160.47
C-3	113.88	113.95	111.91	112.07	111.86	112.96	113.21	112.05	113.08	113.82	113.02	112.55
C-4	144.32	144.36	143.78	143.83	143.75	143.35	143.41	143.88	143.53	144.35	144.01	143.85
C-4a	118.29	113.42	113.24	113.88	112.88	113.15	113.24	113.31	113.27	116.75	113.21	113.10
C-5	123.79	123.41	128.21	128.61	128.43	131.22	131.21	127.12	131.32	124.66	127.24	130.77
C-6	108.21	108.48	106.48	106.53	106.41	107.46	107.60	106.43	107.03	108.64	106.56	107.95
C-7	156.90	156.91	163.70	163.56	163.71	163.48	163.39	163.05	163.52	157.19	163.18	163.50
C-8	132.18	117.41	112.75	112.96	112.96	112.42	112.94	112.88	112.85	113.35	112.91	116.35
C-8a	148.08	148.12	151.05	151.14	151.06	151.56	151.56	152.20	151.82	148.33	152.35	151.52
C-2'	157.94	164.22	88.84	91.12	89.05	88.46	88.32	88.68	88.19	145.72	88.59	90.97
C-3'	99.59	97.77	27.37	27.40	27.35	68.36	68.11	27.12	68.33	103.92	27.21	69.98
C-4'	113.40	69.11	81.04	71.63	81.56	80.13	81.02	81.79	78.26	-	81.93	72.15
$\underline{C}H_3$ при (C-4')	19.06 -	28.58 28.58	21.45 23.08	24.06 26.10	22.46 25.48	22.19 25.10	23.30 25.20	21.18 23.46	22.07 25.28	- -	21.26 22.34	26.33 27.49

* Used numeration of coumarin sceleton's atoms like in structure (**3**) (scheme 1). Note: *For compound
1: 114.46 (C= at C-4');
3: 165.61 (C-2"), 116.77 (C-3"), 156.27 (C-4"), 22.03 (C-5"), 21.88 (C-6");
7: 167.02 (C-2"), 128.11 (C-3"), 137.31 (C-4"), 20.26 (C-5"), 15.67 (C-6");
8: 165.82 (C-2"), 116.41 (C-3"), 156.89 (C-4"), 19.93 (C-5"), 20.75 (C-6"), 168.46 ($\underline{C}OCH_3$), 27.28 (CH_3);
9: 166.08 (C-2"), 128.46 (C-3"), 137.71 (C-4"), 15.62 (C-5"), 20.81 (C-6"), 170.51 ($\underline{C}OCH_3$), 22.32 (CH_3);
10: 174.62 (C-2"), 44.21 (C-3"), 26.75 (C-4"), 16.23 (CH_3), 11.31 (CH_3);
11: 11.15 (CH_3), 15.58 (CH_3), 22.15 (CH_3), 42.18 (C-3'"), 170.41 ($\underline{C}OCH_3$), 174.62 c (C-2'");
14: 12.65 (CH_3), 16.29 (CH_3), 28.46 (C-3"), 42.08 (C-4"), 173.33 ($\underline{C}$-2").

Eugenin (5-hydroxy-2-methyl-7-methoxy-4*H*-chromen-4-one) (**4**), oil. ^{1}H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 2.42 (3H, s, CH_3), 3.85 (3H, s, OCH_3), 6.03 (1H, s, H-3), 6.29 (1H, d, J = 2.0, H-6), 6.35 (1H, d, J = 2.0, H-8), 12.67 (1H, s, OH). ^{13}C NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 20.59 (CH_3), 55.75 (OCH_3), 92.32 (C-8), 98.22 (C-6), 105.24 (C-4a), 108.65 (C-3), 158.18 (C-8a), 162.54 (C-5), 165.41 (C-7), 166.49 (C-2), 182.44 (C-4). Mass-spectra, m/z (I_{comp}, %): 206 (100), 189 (35), 177 (20). Found: [*M*] 206.0579. $C_{11}H_{10}O_4$. Calculated: 206.0571.

Columbianetin {8(*S*)-(2-hydroxypropane-2-yl)-8,9-dihyhydro-2*H*-furo[2,3-*h*]-chromen-2-one} (**6**). M.p. 160-163°C (from ether). $[\alpha]_D$ = +195.36 (*c* 1.2, $CHCl_3$). In paper [7] m.p. 163°C, $[\alpha]_D$ = +264 (c 1.66, CH_3OH). ^{1}H NMR spectra ($CDCl_3$, δ, ppm, J/Hz):1.22, 1.35 (both s, 3H, CH_3 at C-4'), 3.30 (2H, m, H-3'), 4.77 (1H, t, *J* = 8.6, H-2'), 6.18 (1H, d, *J* = 9.6, H-3), 6.73 (1H, d, *J* = 8.2, H-6), 7.26 (1H, d, *J* = 8.2, H-5), 7.60 (1H, d, *J* = 9.6, H-4), 9.50 s (1H, OH). Mass-spectra, m/z (I_{comp}, %): 246 (56), 228 (10), 213 (14), 203 (10), 187 (100), 175 (25), 160 (48), 131 (21), 103 (12), 77 (22), 59 (69). Found: [*M*] 246.0264. $C_{14}H_{14}O_4$. Calculated: 246.0269.

Columbianadin {8(*S*)-(2-angeloyloxypropane-2-yl) -8,9-dihydro-2*H*-furo[2,3-*h*]-chromen-2-one} (**7**). M.p. 117-120°C (from ether). $[\alpha]_D$ = +225.6 (*c* 1.8, $CHCl_3$). In paper [14] m.p. 118.5-119°C, $[\alpha]_D$ = +227 (c 2.8, $CHCl_3$). ^{1}H NMR spectra ($CDCl_3$, δ, ppm, J/Hz):1.62 (3H, s, CH_3 at C-3"), 1.63 (both s, 3H, CH_3 at C-4'), 1.85 (3H, s, CH_3 at C-4"), 3.36 (2H, m, H-3'), 5.18 (1H, dd, *J* = 7.8, 8.2, H-2'), 5.98 (1H, m, H-4"), 6.20 (1H, d, *J* = 9.8, H-3), 6.68 (1H, d, *J* = 8.2, H-6), 7.22 (1H, d, *J* = 8.2, H-5), 7.60 (1H, d, *J* = 9.6, H-4). Mass-spectra, m/z

(I_{comp}, %): 328 (10), 270 (8), 257 (6), 246 (5), 228 (35), 213 (100), 187 (18), 131 (16), 83 (16), 55 (42). Found: [*M*] 328.1314. $C_{19}H_{20}O_5$. Calculated: 328.1311.

Peucenidin {**(8*S*,9*R*)-9-Acetoxy-8-(2-senecioyloxypropane-2-yl)-8,9-dihydro-2*H*-furo[2,3-*h*]chromen-2-one**} **(8)**. M.p. 122-125°C (from ethylacetate). $[\alpha]_D$ = –48.2 (c 1.23, $CHCl_3$). In papers [13, 15] $[\alpha]_D$ = –46°. UV spectra (ethanol), λ_{max}/nm (lgε): 207 (5.12), 226 (4.12), 298 (3.77), 322 (4.68). IR spectra, (ν, cm^{-1}): 806, 848, 862, 938, 980, 1005, 1024, 1053, 1075, 1114, 1132, 1320, 1354, 1490, 1576, 1620, 1647, 1727, 1752, 3093. ^{1}H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 1.61, 1.70 (both s, 3H, CH_3 at C-4'), 1.86, 2.11 (both s, 3H, CH_3 at C-5''), 2.02 (3H, s, C<u>H</u>$_3$C=O), 5.15 (1H, d, *J* = 7.0, H-2'), 5.58 (1H, broad s, H-4''), 6.21 (1H, d, *J* = 9.6, H-3), 6.82 (1H, d, *J* = 8.5, H-6), 6.97 (1H, d, *J* = 7.0, H-3'), 7.40 (1H, d, *J* = 8.5, H-5), 7.61 (1H, d, *J* = 9.6, H-4).Mass-spectra, m/z (I_{comp}, %): 386 (15), 326 (12), 311 (13), 303 (8), 286 (22), 261 (9), 244 (28), 243 (15), 229 (40), 227 (32), 201 (24), 187 (22), 83 (100), 43 (25). Found: [*M*] 386.1364. Calculated: 386.1360. Found, %: C 65,38; H 5,32. $C_{21}H_{22}O_7$. Calculated, %: C 65.28; H 5.74.

Libanotin (edultin) {(8*S*,9'*R*)-9-(angeloyloxypropane-2-yl)-8-acetoxy-8,9-dihydro-2*H*-furo[2,3-*h*]chromen-2-one} (**9**) M.p. 154-156°C (from hexane). $[\alpha]_D$ = +78.6 (c 1.3, $CHCl_3$). In paper [6] т.пл. 155-157°C, $[\alpha]_D$ = +79.5 (c 0.83, $CHCl_3$). UV spectra (ethanol), λ_{max}/nm (lgε): 207 (5.12), 232 (4.21), 300 (3.36), 318 (4.21). ^{1}H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 1.59, 1.71 (both s, 3H, CH_3 at C-4'), 1.81, 1.92 (both s, 3H, CH_3 at C-2''' and C-3'''), 2.01 (3H, s, C<u>H</u>$_3$C=O), 5.28 (1H, d, *J* = 7.0, H-2'), 6.08 (1H, m, H-3'''), 6.23 (1H, d, *J* = 9.6, H-3), 6.85 (1H, d, *J* = 8.5, H-6), 7.02 (1H, d, *J* = 7.0, H-3'), 7.41 (1H, d, *J* = 8.5, H-5), 7.62 (1H, d, *J* = 9.6, H-4). Mass-spectra, m/z (I_{comp}, %): 386 (18), 311 (12), 287 (12), 261 (8), 243 (32), 227 (18), 187 (73), 83 (100), 43 (54). Found: [*M*] 386.1368. Calculated: 386.1360.

{(8*S*,11*S*)-[2-(2-methylbutanoyl) oxypropane-2-yl)]-8,9-dihydro-2*H*-furo[2,3-*h*]-chromen-2-one} (**10**). M.p. 85-88°C (from ether). $[\alpha]_D$ = +192.6 (*c* 1.1, $CHCl_3$). In paper [7] m.p. 88-91°C, $[\alpha]_D$ = +194 (c 0.67, $CHCl_3$). ^{1}H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 0.85 (3H, t, *J* = 7.0, CH_3 at C-4''), 1.03 (3H, d, *J* = 7.0, CH_3 at C-3''), 1.30, 1.45 (1H, м, *J* = 7.0, H-4''), 1.50, 1.56 (both s, 3H, CH_3 at C-4'), 3.28 (1H, m, J_{gem} = 15.7, H-3'), 3.36 (1H, m, J_{gem} = 15.7, H-3'), 5.08 (1H, dd, *J* = 7.6, 9.4, H-2'), 6.18 (1H, d, *J* = 9.6, H-3), 6.71 (1H, d, *J* = 8.2, H-6), 7.22 (1H, d, *J* = 8.2, H-5), 7.60 (1H, d, *J* = 9.6, H-4). Mass-spectra, m/z (I_{comp}, %): 330 (16), 305 (8), 259 (6), 231 (30), 213 (100), 187 (31), 176 (28), 85 (32), 57 (46). Found: [*M*] 330.3459. $C_{19}H_{22}O_5$. Calculated: 330.3467.

{**(8*S*,9*R*)-8-(2-Acetoxypropane-2-yl)-9-(2-methyl)propanoyloxy)-8,9-dihydro-2*H*-furo[2,3-*h*]chromen-2-one** (**11**)}. M.p. 153-156°C (from ether). $[\alpha]_D$ = +100.2 (*c* 0.6, $CHCl_3$). In paper [8] m.p. 154-156°C, $[\alpha]_D$ = +97.9 (c 0.19, $CHCl_3$). ^{1}H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 1.17 (3H, d, *J* = 6.8, CH_3 at C-3'''), 1.19 (3H, d, *J* = 7.0, CH_3 at C-3'''), 1.59, 1.75 (both s, 3H, CH_3 at C-4'), 2.05 (3H, s, C<u>H</u>$_3$C=O), 2.53 (1H, m, H-3'''), 5.28 (1H, d, *J* = 6.7, H-2'), 6.20 (1H, d, *J* = 9.6, H-3), 6.84 (1H, d, *J* = 8.5, H-6), 7.00 (1H, d, *J* = 6.7, H-3'), 7.42 (1H, d, *J* = 8.5, H-5), 7.62 (1H, d, *J* = 9.6, H-4). Mass-spectra, m/z (I_{comp}, %): 374 (15), 314 (8), 299 (12), 286 (15), 261 (18), 244 (33), 229 (100), 213 (22), 187 (38), 158 (20), 71 (54), 43 (61). Found: [*M*] 374.2257. $C_{19}H_{22}O_5$. Calculated: 374.2259.

Angelicin (2*H*-furo[2,3-*h*]chromen-2-one) (**13**). M. p. 133-136°C (from ether). In paper [16] m.p. 136-137°C. UV spectra (ethanol), λ_{max}/nm (lgε): 251 (4.12), 302 (3.85), 326 (4.04). ^{1}H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 6.36 (1H, d, *J* = 9.6, H-3), 7.10 (1H, dd, *J* = 2.0, 1.6, H-3′), 7.34 (1H, d, *J*= 8.5, H-5), 7.41 (1H, dd, *J* = 8.5, 1.6, H-5), 7.68 (1H, d, *J* = 2.0, H-2′), 7.79 (1H, d, *J* = 9.6, H-4). Mass-spectra, m/z (I_{comp}, %): 186 (100), 158 (88), 149 (27), 130 (14), 102 (28). Found: [*M*] 186.0312. $C_{11}H_6O_3$. Calculated: 186.0317.

{8*S*-(2-isovaleryl)oxypropane-2-yl)]-8,9-dihudro-2*H*-furo[2,3-*h*]-chromen-2-one} (**14**). M.p. 72-74°C (from ether). $[\alpha]_D$ = +302.5 (*c* 1.1, $CHCl_3$). In paper [13] т.пл. 76-77°C, $[\alpha]_D$ = +305 (c 0.4, CH_3OH). ^1H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 0.91 (3H, t, *J* = 7.1, CH_3 at C-4"), 1.16 (3H, d, *J* = 7.0, CH_3 at C-4"), 1.48, 1.62 (1H, m, H-3"), 1.60, 1.68 (both s, 1H, CH_3 at C-4'), 2.36 m (1H, H-4"), 3.30 (1H, m, J_{gem} = 15.9, H-3'), 3.36 (1H, m, J_{gem} = 15.9, H-3'), 5.06 (1H, dd, *J* = 7.8, 9.6, H-2'), 6.19 (1H, d, *J* = 9.6, H-3), 6.72 (1H, d, *J* = 8.4, H-6), 7.22 (1H, d, *J* = 8.4, H-5), 7.61 (1H, d, *J* = 9.6, H-4). Mass-spectra, m/z (I_{comp}, %): 330 (10), 281 (5), 228 (30), 213 (100), 187 (28), 176 (20), 159 (11), 131 (18), 85 (25), 57 (31). Found: [*M*] 330.3461. $C_{19}H_{22}O_5$. Calculated: 330.3467.

Vaginidiol {**(8*S*,9*R*)-9-Hydroxy-8-(2-hydroxypropane-2-yl)-8,9-dihydro-2*H*-furo[2,3-*h*]chromen-2-one** (**15**)}. M.p. 170-173°C (from ethanol). $[\alpha]_D$ = +224.2 (*c* 1.2, $CHCl_3$). In paper [17] m.p. 168-169°C, $[\alpha]_D$ = +231 (c 0.01, EtOH). ^1H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 1.48, 1.55 (both s, 3H, CH_3 at C-4'), 4.20 (1H, broad s , 1H, OH), 4.35 (1H, d, *J* = 5.6,H-2'), 5.77 (1H, d, *J* = 5.6, H-3'), 6.20 (1H, d, *J* = 9.6, H-3), 6.82 (1H, d, *J* = 8.2, H-6), 7.35 (1H, d, *J* = 8.2, H-5), 7.63 (1H, d, *J* = 9.6, H-4). Mass-spectra, m/z (I_{comp}, %): 262 (30), 229 (19), 213 (15), 203 (19), 191 (27), 188 (22), 187 (50), 186 (100), 158 (62), 149 (27), 134 (22), 131 (32), 129 (17), 102 (34), 89 (19), 59 (61). Found: [*M*] 262.0832. $C_{14}H_{14}O5$. Calculated: 262.0836.

4-Hydroxy-3-methoxybenzoic acid (vanilic acid) (**16**), m.p. 210-213 °C (from ether) (in paper [18], 213-214°C). ^1H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 3.92 (3H, s, OCH_3), 6.84 (1H, d, J = 8.3, H-5), 7.59 (1H, dd, J = 8.3 and 1.9, H-6), 7.55 (1H, d, J = 1.9, H-2). ^{13}C NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 56.31 (OCH_3), 113.51 (C-2), 115.47 (C-5), 122.69 (C-4), 125.02 (C-6), 148.11 (C-3), 152.01 (C-1), 169.81 (C=O). Mass-spectra, m/z (I_{comp}, %): 168 (100), 153 (65), 125 (31), 97 (50), 77 (10).

***trans*-Ferulic acid** (**17**), m.p. 165-167 °C (from ether) (in paper [19], 168-169 °C). ^1H NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 3.92 (3H, s, OCH_3), 6.31 (1H, d, J = 16.1, H-α), 6.82 (1H, d, J = 8.3, H-5), 6.90 (1H, dd, J= 8.3 and 2.0, H-6), 7.11 (1H, d, J = 2.0, H-2), 7.59 (1H, d, *J* = 16.1, H-β). ^{13}C NMR spectra ($CDCl_3$, δ, ppm, J/Hz): 55.82 (OCH_3), 110.05 (C-2), 115.11 (C-α), 115.24 (C-5), 123.00 (C-6), 129.91 (C-1), 145.71 (C-β), 148.50 (C-4), 150.64 (C-3), 172.91 (C=O). Mass-spectra, m/z (I_{comp}, %): 194 (100), 179 (18), 148 (10), 133 (17), 105 (8), 77 (10).

Conclusions

1. It is proved to be that plants of genus Peucedanum hystrix might serve as source of biologically valuable natural coumarins.
2. Nine angular furocoumarins belonging to class of 2'-substituted and 2',3'-disubstituted 2',3'-dihydrofurocoumarins have been isolated and structurally isolated.
3. For peucenidin data of X-ray analysis is obtained.

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