Coumarin Compounds from Roots of Peucedanum (*Peucedanum morisonii* Bess.)

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Abstract

The composition of Coumarin compounds from roots of *Peucedanum morisonii* is investigated, 13 individual components are isolated and characterized.

INTRODUCTION

Peucedanum (*Peucedanum morisonii* Bess.) is a perennial herbaceous plant, widely spread in West Siberia, which has been used to obtain "Peutsedanin" preparation allowed for application to cure vitiligo and circumscribed alopecia, and as antitumour means as well. In folk medicine, decoction of roots is applied to cure diseases of the organs in gastrointestinal tract and osteoalgia. Extract of roots has antibacterial, protistocide and fungicide properties [1, 2].

Previous investigations of this plant, dealing with the studies of chemical composition, resulted in isolation of furocoumarin compounds from the alcohol extracts: peucedanin **1**, isoimperatorin **2** and bergaptol **3**, and also peucenol **8**, which is a 6,7-disubstituted coumarin [3, 4]. The authors of [5] discovered the presence of peucedanin **1** and imperatorin **4** in roots. In the present paper, we describe isolation of 13 coumarin derivatives from the roots of the indicated plant.

EXPERIMENTAL

Freshly distilled solvents and reagents of "ch." grade (pure) were used. Melting points were measured with Kofler instrument. The IR spectra were recorded with Vector 22 spectrometer in KBr tablet, UV spectra were recorded with Specord UV-Vis spectrophotometer in ethanol ($C = 10^{-4}$ mol/l). A 0.1 M KOH solution in ethanol was used for alkalization. Molecular masses and elemental composition were determined with a high-resolution mass spectrometer (Finnigan MAT 8200). The NMR spectra were recorded with Bruker AC 200 spectrometer (working frequency: 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C) and Bruker DRX 500 spectrometer (working frequency 500.13 MHz for ^{1}H and 125.76 MHz for ^{13}C) in $CDCl_3$, CD_3OD, $CDCl_3$–CCl_4, $(CD_3)_2SO$ or $(CD_3)_2CO$ solutions. Multiplicity of signals in NMR ^{13}C spectra was determined according to standard procedures of recording spectra in the J-modulation mode (JMOD) and with out-of-resonance irradiation of protons. To assign signals in NMR spectra, various types of proton-proton and carbon-proton shift correlation spectroscopy (COSY, COLOC, CORRD) were used.

Coumarin compounds were separated using column chromatography with KSK silica gel (0–140 mm).

The purity of target products was determined by means of HPLC with Milikhrom-4

microcolumn chromatograph of the "Nauchpribor" Plant in Orel. Chormatographing conditions: a steel column 2 × 64 mm, Nucleosil C-18 sorbent (5 μm), temperature: ~20 °C, elutriation rate: 100 μl/min, UV detection at 204 nm. Elutriator was a mixture 75 % MeOH + 25 % H_2O for the analysis of peucedanin **1**, isoimperatorin **2**, peucenol **8** and stenocarpin **9**.

Overall fractions of coumarin compounds were investigated by means of chromato-mass spectrometry with Hewlett-Packard 5890/II MSD gas chromatograph combined with HP MSD 5971 quadrupole mass spectrometer as a detector. A 30 m quartz column HP-5MS was used (copolymer of 5 % diphenyl- + 95 % dimethylsiloxane) with the inner diameter 0.25 mm and the thickness of immobile phase film 0.25 μm (temperature: 50–280 °C, 4 °C/min, 15 min 280 °C). Per cent composition of coumarin compounds was calculated using the area of gas chromatographic peaks without applying correcting coefficients.

Roots of Peucedanum were harvested in habitats with consumable resources sufficient for mass harvesting.

Investigation was carried out with the samples of Peucedanum roots collected in Vengerovo District of the Novosibirsk Region in August 1999. Extraction of the plant material was carried out with a series of solvents listed in Table 1. Components extractable with methanol were subjected to distributive extraction in ethylacetate – water system, which allowed separating sucrose and mannitol and isolating additionally 6,7-disubstituted coumarin compounds. The major amount of peucedanin **1** was isolated from extracts No. 1 and 2 by crystallization. Column chromatography of extracts No. 1–4 and isolation with ethylacetate from extract No. 5 followed by recrystallization were applied to isolate individual coumarin compounds. Their total yield and structures are shown in Table 2.

TABLE 1

Yield of extracted substances from *Peucedanum morisonii*

No.	Solvent for extraction	Yield of extracted substances, %
1	Hexane	10.9
2	Diethyl ether	4.5
3	Methyl-*tert*-butyl ether	2.4
4	Ethylacetate (EA)	1.4
5	Methanol	6.8

Treatment procedure for the plant material

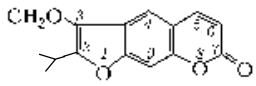
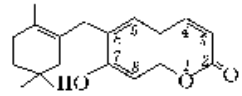
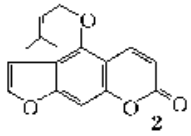
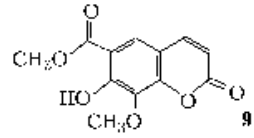
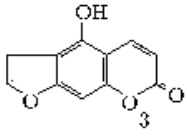
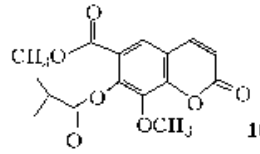
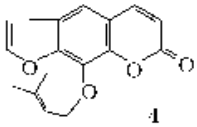
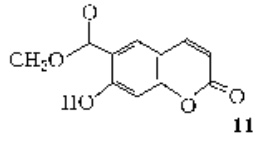
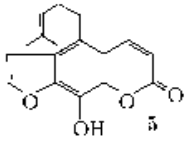
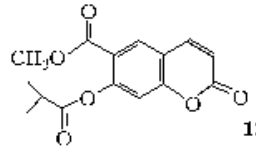
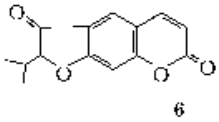
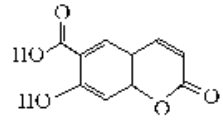
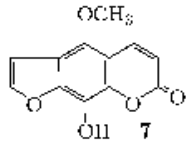
Air-dry ground (2–3 mm) roots of Peucedanum (100 g) were sequentially extracted with hexane, diethyl ether, methyl-*tert*-butyl ether, ethylacetate, methanol and butanol using trice-repeated extraction (3 × 150 ml) under heating with backflow condenser on water bath for 3 h in each case. The yield of a sum of extracted substances is listed in Table 1. Precipitate (1.35 g) which was filtered off the hexane extract (10.9 g) was a mixture of coumarin compounds as suggested by the data obtained by means of ^{1}H NMR, and chromato-mass spectrometry: peucedanin, isoimperatorin and alloimperatorin. After recrystallization of the extract from ethanol, 0.88 g of pure peucedanin **1** was separated by filtering.

Separation of ether extract. Four fractions were obtained by column chromatography of 4.5 g of the ether extract on silica gel (140 g) [eluent, chloroform – ethanol (10 : 0 → 10 : 2)]: fraction 1 (eluent, chloroform) – 0.5 g (oil, lipid part), fraction 2 (eluent – chloroform, chloroform : ethanol = 100 : 0.1 → 100 : 0.2) – 1.0 g, fraction 3 (eluent – chloroform : ethanol = 10 : 0.2 → 10 : 0.5) – 2.6 g, fraction 4 (eluent – chloroform : ethanol = 10 : 0.5 → 10 : 2) – 0.7 g. Fractions 2–4 were rechomatographed on silica gel (eluent, chloroform : ethanol = 10 : 0 → 10 : 0.5); 6 fractions were obtained from each experiment. Their crystallization from the corresponding solvents resulted in obtaining 0.80 g of peucedanin **1**, 0.20 g of isoimperatorin **2**, 0.03 g of imperatorin **4**, 0.02 g of alloimperatorin **5**, 0.05 g of oreoselon **6**, 0.05 g of peurhytenicin **11**, 0.06 g of peuruthenicin isobutyrate **12** and 0.08 g of peucenol **8**.

Separation of methyl-*tert*-butyl ether extract. By means of column chromatography on silica gel (2.40 g of the substance, 72 g of silica gel, eluent, chloroform : ethanol = 10 : 0 → 10 : 2), 12 fractions were collected sequentially; by means of crystallization from the corre-

TABLE 2

Structures of the isolated coumarin compounds

Structure	Yield, %	Structure	Yield, %
 **1**	3.22	 **8**	0.19
 **2**	0.53	 **9**	0.29
 **3**	0.21	 **10**	0.18
 **4**	0.03	 **11**	0.05
 **5**	0.04	 **12**	0.06
 **6**	0.18	 **13**	0.02
 **7**	0.04		

sponding solvents, the following compounds were isolated: 0.98 g of peucedanin **1**, 0.10 g of oreoselon **6**, 0.04 g of 5-methoxybergaptol **7**, 0.15 g of bergaptol **3**, 0.20 g of isoimperatorin **2**, 0.02 g of alloimperatorin **5** and 0.13 g of stenocarpin **9**.

Separation of ethylacetate extract. Chromatographing 1.4 g of ethylacetate ectract on 50 g of silica gel (eluent, chloroform : methanol = 10 : 0 → 10 : 2) leads to isolation of 0.56 g of peucedanin **1**, 0.13 g of stenocarpin isobutyrate **10**, 0.06 g of bergaptol **3**, 0.13 g of isoimperatorin **2**, 0.03 g of oreoselon **6**, 0.13 g of stenocarpin **9** and 0.018 g of umbellypheron-6-carboxylic acid **13**.

Separation of methanol extract. 60 ml of the mixture of ethylacetate and water (1 : 1 by volume) was added to partially evaporated methanol extract. After 30 min, the layers were separated from each other. Chromatographing of 0.58 g of the mixture isolated with methanol from the methanol extract (eluent, chloroform : ethanol = 10 : 0 → 10 : 2) resulted in obtaining 3 consequent fractions. From the 1st fraction (0.3 g), 0.11 g of peucenol **8** was isolated; from the 2nd fraction (0.2 g), 0.03 g of stenocarpin **10**, 0.05 g of stenocarpin isobutyrate **11** and 0.002 g of umbellypheron-6-carboxylic acid **13**.

By evaporating the mixture separated with water from methanol extract (5.8 g) followed by crystallization from ethanol, sequentially isolated compounds were: 1.38 g of crystal mannitol (m.p. 155–158 °C) and 0.92 g of sucrose (m.p. 170–176 °C).

RESULTS AND DISCUSSION

One can see from the data presented in Table 2 that the main coumarin compounds of Peucedanum are furocoumarin compounds (total content 4.25 %); alloimperatorin **5**, oreoselon **6** and 8-hydroxy-5-methoxy-psoralen **7** were isolated from this plant species for the first time. Attention should be paid to substantial content of 6,7-disubstituted coumarin compounds **8**–**13** in this Peucedanum species (0.81 of the weight of raw material was isolated). For the first time, C-6-carboxy-substituted coumarin compounds were isolated from *Peucedanum morisonii*: stenocarpin **9** and stenocarpin isobutyrate **10**, which were previously discovered in *peucedanum stenocarpum* Boiss. [6], and peuruthenicin **11**, which is present in *Peucedanum ruthenicum* Bieb. [7]. In addition, we isolated compounds which were not previously discovered in the plants of *Peucedanum* genus but were obtained by synthesis: peuruthenicin isobutyrate **12** and umbelliferon-6-carboxylic acid **13** [8].

Characterization of individual compounds

Peucedanin (2-isopropyl-3-methoxy-7H-furo[3,2-g][1]benzopyrane-7-on) 1. M. p. 108–109 °C (from ethanol). Mass spectrum, *m/z* (%): Calc. *m/z*: 258 (37.6), 243 (100), 228 (9.3), 200 (7.2). $C_{15}H_{14}O_4$. Exp. *m/z*: 258.0888. UV spectrum, λ_{max}, nm (lg ε) 219 (4.18), 255 (5.27), 301 (4.22). PMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 1.33 (6H, d, *J* = 7.2, 2×CH_3), 3.23 (1H, m, C<u>H</u>Me_2), 3.92 (3H, s, OCH_3), 6.34 (1H, d, *J* = 9.8, H-6), 7.31 (1H, s, H-9), 7.55 (1H, s, H-4), 7.77 (1H, d, $J_{5,6}$ = 9.8, H-5). The data of NMR ^{13}C spectrum are similar to those reported in [9].

Isoimperatorin [4-(3-methyl-2-butenyloxy-7H-furo[3,2-g][1]benzopyrane-7-on] 2. M. p. 104–105 °C (from ether). Mass spectrum, *m/z* (%): 270 (1.25), 243 (100), 202 (57.40), 174 (10.15), 69 (44.68), 41 (30.22). $C_{16}H_{14}O_4$. Calc. *m/z:* 270.08920. Exp. *m/z:* 270.08933. UV spectrum, λ_{max}, nm (lg ε): 223 (4.25), 244 shoulder (4.07), 251 (4.13), 260 (4.08), 269 (4.07), 310 (4.52). The data of the IR spectrum coincide with those reported in [10]. The data of NMR ^1H [11] and ^{13}C [12] spectra are similar to those reported in literature.

Bergaptol (4-hydroxy-7H-furo[3,2-g][1]benzopyrane-7-on) 3. M. p. 270–273 °C (from ethanol) [13]. UV spectrum, λ_{max}, nm (lg ε): 222 (4.26), 250 (4.12), 267 (5.28), 308 (5.02). NMR ^1H spectrum (CD_3OD, δ, ppm, *J*, Hz): 6.21 (1H, d, *J* = 10.2, H-6), 7.00 (1H, dd, $J_{9,5}$ = 0.7; $J_{9,3}$ = 0.8, H-9), 7.05 (1H, dd $J_{3,9}$ = 0.8; $J_{3,2}$ = 1.8, H-3), 7.56 (1H, s, OH), 7.68 (1H, d, $J_{2,3}$ = 1.8, H-2), 8.32 (1H, dd, $J_{5,6}$ = 10.2, $J_{5,9}$ = 0.7, H-5). NMR ^{13}C spectrum (δ_C, ppm): 92.18 (d, C-9), 104.90 (d, C-6), 105.40 (s, C-4a), 111.82 (d, C-3), 114.04 (s, C-3a), 141.54 (d, C-5), 145.70 (d, C-2), 149.28 (s, C-4), 154.14 (s, C-1a), 159.14 (s, C-8a), 163.76 (s, C-7).

Imperatorin [9-(3-methyl-2-butenyloxy)-7H-furo[3,2-g][1]benzopyrane-7-on] 4. M. p. 102–103 °C (from ether). Mass spectrum, *m/z* (%): 270 (26.28), 202 (100), 174 (25.23), 149 (22.30), 88 (11.84), 69 (20.52). $C_{16}H_{14}O_4$. UV spectrum, λ_{max}, nm (lg ε): 220 (4.41), 245 shoulder (4.34), 250 (4.42), 264 shoulder (4.12), 301 (4.08). The data of IR and PMR spectra coincide with those reported in [11]. The data of NMR ^{13}C spectrum of this compound are similar to those reported in [9].

Alloimperatorin {4-(3-methyl-2-butenyl)-9-hydroxy-7H-furo[3,2-g][1]benzopyrane-7-on} 5. M. p. 222–225 °C (from ether). Mass spectrum, *m/z* (%): 270 (100), 255 (62.80), 227 (38.60), 215 (22.25), 202 (36.60). $C_{16}H_{14}O_4$. UV spectrum, λ_{max}, nm (lg ε): 224 (4.46), 245 (4.14), 253 (4.21), 268 (4.28), 274 (4.17), 317 (4.04). The data of IR spectrum coincide with those reported in [14]. PMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 1.67 (3H, s, CH_3), 1.78 (3H, s, CH_3), 4.90 (2H, d, *J* = 7.0, C<u>H</u>$_2$), 5.52 (1H, t, *J* = 7.0, CH=), 6.25 (1H, d, *J* = 9.8, H-6), 6.90 (1H, d, *J* = 2.2, H-3), 7.55 (1H, s, H-4), 8.12 (1H, d, $J_{5,6}$ = 9.8, H-5).

Oreoselon {2-isopropyl-7H-furo[3,2-g][1]-benzopyrane-3,7-dion} 6. M. p. 174–177 °C (from ethyl acetate) [15]. Mass spectrum, *m/z* (%): 244.1 (33.31), 229.1 (30.58), 202.1 (100), 189.1 (23.87), 188.1 (23.27), 28.0 (30.43). $C_{14}H_{12}O_4$. Calc. *m/z:* 244.07355. Exp. *m/z:* 244.07420. UV spectrum, λ_{max}, nm (lg ε): 219 (4.56), 246 (5.12), 305 (3.09), 335 (3.42), 350 shoulder (2.18). The data of IR spectrum coincide with those reported in [14]. PMR spectrum (CD_3OD, δ, ppm, *J*, Hz): 0.92 (3H, d, *J* = 6.8, CH_3), 1.19 (3H, d, *J* = 6.8, CH_3), 2.37 (1H, m, CH), 4.70 (1H, d, *J* = 4.8, H-2), 6.38 (1H, d, *J* = 10.1, H-6), 7.13 (1H,

s, H-9), 7.98 (1H, s, H-4), 7.99 (1H, d, $J_{5,6}$ = 10.1, H-5). NMR ^{13}C spectrum (δ_C, ppm, CD_3OD): 15.53 (q, CH_3), 18.54 (q, CH_3), 30.96 (q, CH), 90.87 (d, C-2), 100.79 (d, C-9), 114.27 (s, C-3a), 114.51 (d, C-6), 119.09 (s, C-4a), 124.20 (d, C-4), 143.39 (d, C-5), 159.39 (s, C-1a), 160.87 (s, C-8a), 173.78 (s, C-7), 199.36 (s, C-3).

8-Hydroxy-5-methoxypsoralen {9-hydroxy-4-methoxy-7H-furo[3,2-g][1]benzopyrane-7-on } 7. M. p. 223–225 °C (from ether). Mass spectrum, *m/z* (%): 231 (100), 203 (33.08), 188 (43.65), 175 (26.32), 160 (28.30), 147 (12.73), 104 (25.68). $C_{12}H_8O_5$. UV spectrum, λ_{max}, nm (lg ε): 225 (4.14), 244 shoulder (4.05), 252 (4.16), 266 shoulder (4.22), 274 (4.30), 296 (4.01), 320 (4.12). The data of IR spectrum are similar to those reported in [16]. PMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 4.25 (3H, s, OCH_3), 6.23 (1H, d, *J* = 9.5, H-6), 6.99 (1H, dd, *J* = 2.4, 1.0, H-3), 7.59 (1H, d, *J* = 2.4, H-2), 8.10 (1H, d, $J_{5,6}$ = 9.5, H-5). NMR ^{13}C spectrum (δ_C, ppm, $CDCl_3$): 62.31 (q, CH_3), 105.62 (d, C-3), 108.11 (s, C-4a), 113.54 (d, C-6), 115.20 (s, C-3a), 140.15 (d, C-5), 143.12 (s, C-9), 145.18 (d, C-2), 150.34 (s, C-4), 152.80 (d, C-8a), 158.61 (d, C-1a), 160.91 (s, C-7).

Peucenol (peumorisin) {7-hydroxy-6-(2″,5″,5″-trimethyl-cyclohexene-1-yl-methyl)-benzo[1,2-b]pyrane-2-on} 8. M. p 135–137 °C (from ethanol). The data of IR and UV spectra are reported in [4, 17]. Mass spectrum, *m/z* (%): 298 (38.22), 281 (36.45), 279 (36.45), 227 (27.48), 175 (100), 147 (17.35), 123 (20.28), 121 (19.28), 64 (56.80), 48 (35.21), 40 (100). $C_{19}H_{22}O_3$. PMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 1.06 (3H, s, CH_3), 1.16 (3H, s, CH_3), 1.32 (2H, m, $C^{6'}H_2$), 1.69 (3H, s, CH_3), 1.83 (2H, m, $C^{4'}H_2$), 2.32 (2H, m, $C^{3'}H_2$), 3.39 (2H, s, CH_2), 6.19 (1H, d, *J* = 9.8, H-3), 6.95 (1H, s, H-8), 7.07 (1H, s, H-5), 7.60 (1H, d, $J_{5,6}$ = 9.8, H-4). NMR ^{13}C spectrum (δ_C, ppm): 19.44 (q, CH_3), 27.07 (t, C-4′), 28.98 (q, 2×CH_3), 29.12 (s, C-5′), 31.38 (t, C-3′), 33.92 (t, C-6′), 46.06 (t, CH_2), 103.02 (d, C-8), 112.06 (d, C-3), 124.50, 125.56 (both s, C-10,6), 128.08 (d, C-5), 130.10 (s, C-2′), 144.12 (d, C-4), 154.07 (s, C-1′), 158.96 (s, C-9′), 159.96 (s, C-7), 162.12 (s, C-2).

Stenocarpin [(7-hydroxy-8-methoxy-6-methoxycarbonyl-)-benzo[1,2-b]pyrane-2-on] 9. M. p. 190–193 °C (from ethanol). Mass spectrum, *m/z* (%): 250 (64.83), 219 (26.12), 218 (100), 190 (82.26), 189 (26.36), 188 (24.08), 28 (82.97). $C_{12}H_{10}O_6$. Calc. *m/z:* 250.04773. Exp. *m/z:* 250.04964. UV spectrum, λ_{max}, nm (lg ε): 245 (4.18), 285 (5.37), 375 (3.02), 400 (2.45). PMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 3.98 (3H, s, OCH_3), 4.02 (3H, s, OCH_3), 6.27 (1H, d, *J* = 9.8, H-3), 7.58 (1H, d, *J* = 9.8, H-4), 7.76 (1H, s, H-5), 11.24 (1H, s, OH). NMR ^{13}C spectrum (δ_C, ppm): 52.74 (q, CH_3), 61.29 (q, CH_3), 110.12 (s, C-6), 111.90 (s, C-10), 114.09 (d, C-3), 124.19 (d, C-5), 135.33 (s, C-7), 143.23 (d, C-4), 151.36 (s, C-8), 157.59 (s, C-9), 159.37 (s, C-2), 169.65 (s, C=O).

Stenocarpin isobutyrate {(7-isovaleryloxy-8-methoxy-6-methoxycarbonyl-)-benzo[1,2-b]pyrane-2-on] 10. M. p. 186–188 °C (from ethanol). Mass specrtum, *m/z* (%): 320 (3.40), 251 (15.67), 250 (100), 219 (22.14), 218 (69.38), 190 (49.02), 71 (49.42), 43 (65.10). $C_{16}H_{16}O_7$. Calc. *m/z:* 320.08959. Exp. *m/z*: 320.09044. UV spectrum, λ_{max}, nm (lg ε): 247 (4.46), 284 (3.97), 375 shoulder (3.12), 400 (2.86). PMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 1.35 (6H, d, *J* = 7.0, CH_3), 2.93 (1H, m, CH), 3.87 (3H, s, OCH_3), 4.02 (3H, s, OCH_3), 6.42 (1H, d, *J* = 9.8, H-3), 7.68 (1H, d, *J* = 9.8, H-4), 7.88 (1H, s, H-5). NMR ^{13}C spectrum (δ_C, ppm): 18.72 (q, 2×CH_3), 34.04 (d, CH), 52.36 (q, CH_3), 61.68 (q, CH_3), 116.70 (d, C-3), 117.03 (s, C-10), 120.70 (s, C-7), 125.12 (d, C-5), 140.46 (s, C-7), 143.00 (d, C-4), 146.58 (s, C-8), 150.33 (s, C-9), 158.69 (s, C-2), 163.70 (s, C=O), 174.53 (s, C=O).

Peuruthenicin [(7-hydroxy-6-methoxycarbonyl-)-benzo[1,2]pyrane-2-on 11. M p. 195–198 °C (from ethanol). Mass spectrum, *m/z* (%): 220 (44.13), 188 (100), 160 (38,12), 132 (22.28), 104 (28.46), 76 (55.12). $C_{11}H_8O_5$. PMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 3.97 (3H, s, OCH_3), 6.31 (1H, d, *J* = 9.8, H-3), 6.99 (1H, s, H-8), 7.65 (1H, d, *J* = 9.8, H-4), 7.76 (1H, s, H-5), 11.14 (1H, s, OH). NMR ^{13}C spectrum (δ_C, ppm): 52.61 (q, CH_3), 104.82 (d, C-8), 109.96 (s, C-6), 111.90 (s, C-10), 114.57 (d, C-3), 130.56 (d, C-5), 143.32 (d, C-4), 158.93 (s, C-7), 159.31 (s, C-9), 164.25 (s, C-2), 169.40 (s, C=O).

Peuruthenicin isobutyrate [(7-isovaleryloxy-6-methoxycarbonyl-)-benzo[1,2-b]-pyrane-2-on] 12. M. p/ 163–165 °C (from ethanol). Mass spectrum, *m/z* (%): 290 (2.02), 221 (15.93), 220 (14.57), 188 (28.38), 71 (53.86), 70 (16.12), 43 (100). $C_{15}H_{14}O_6$. Calc. *m/z:* 290.07903. Exp. *m/z:* 290.07873. IR spectrum, ν, cm^{-1}: 828, 844, 992, 1062, 1085, 1107, 1143, 1315, 1576, 1599, 1624,

1725, 1766, 3436. UV spectrum, λ_{max}, nm (lg ε): 245 (5.16), 284 (3.07), 317 (3.02), 400 (3.15). PMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 1.35 (6H, d, *J* = 7.0, CH_3), 2.89 (1H, m, CH), 3.87 (3H, s, OCH_3), 6.43 (1H, d, *J* = 9.8, H-3), 7.03 (1H, s, H-8), 7.70 (1H, d, *J* = 9.8, H-4), 8.17 (1H, s, H-5). NMR ^{13}C spectrum (δ_C, ppm): 18.60 (q, 2×CH_3), 34.08 (d, CH), 52.32 (q, CH_3), 112.43 (d, C-3), 116.44 (s, C-6), 116.91 (d, C-8), 120.31 (s, C-10), 131.75 (d, C-5), 142.35 (d, C-4), 153.27 (s, C-7), 156.90 (s, C-9), 159.28 (s, C-2), 163.61 (s, C=O), 174.86 (s, C=O).

Umbellipheron-6-carboxylic acid (6-carboxy-7-hydroxybenzo[1,2-b]pyrane-2-on) 13. M. p. 257–259 °C (from ethanol) [18]. Mass spectrum, *m/z* (%): 206 (46.23), 190 (100), 189 (35.38), 188 (34.12), 28 (42.15). $C_{10}H_6O_5$. UV spectrum, λ_{max}, nm (lg ε): 244 (4.88), 285 (5.37), 288 (4.08), 400 (2.85). PMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 6.20 (1H, d, *J* = 10.1, H-3), 6.80 (1H, s, H-8), 7.66 (1H, d, *J* = 10.1, H-4), 7.70 (1H, s, H-5), 11.20 (2H, broad s., OH). NMR ^{13}C spectrum (δ_C, ppm): 104.81 (d, C-8), 110.22 (s, C-6), 112.92 (s, C-10), 113.29 (d, C-3), 127.40 (d, C-5), 145.28 (d, C-4), 151.33 (s, C-7), 157.68 (s, C-9), 162.88 (s, C-2), 178.66 (s, C=O).

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