60. 4*H*-Chromenone Glycosides from *Eranthis hyemalis* (L.) SALISBURY

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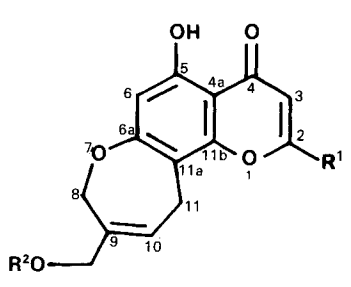
(19.II.91)

Investigation of the tubers of *Eranthis hyemalis* (*Ranunculaceae*) afforded six chromenone glycosides. Their structures have been elucidated mainly by spectroscopic (FAB-MS, 2D-NMR techniques) and chemical methods (acidic and enzymatic hydrolysis) as 9-{[(β-D-glucopyranosyl)oxy]methyl}-8,11-dihydro-5-hydroxy-2-methyl-4*H*-pyrano[2,3-*g*][1]benzoxepin-4-one (**1**), 9-{[(β-D-gentiobiosyl)oxy]methyl}-8,11-dihydro-5-hydroxy-2-methyl-4*H*-pyrano[2,3-*g*][1]benzoxepin-4-one (**2**), 9-{[(β-D-glucopyranosyl)oxy]methyl}-8,11-dihydro-5-hydroxy-2-(hydroxymethyl)-4*H*-pyrano[2,3-*g*][1]benzoxepin-4-one (**3**), 8-{(2*E*)-4-[(β-D-glucopyranosyl)oxy]-3-methylbut-2-enyl}-5,7-dihydroxy-2-methyl-4*H*-1-benzopyran-4-one (**4**), 8-{(2*E*)-4-[(β-D-glucopyranosyl)oxy]-3-methylbut-2-enyl}-5,7-dihydroxy-2-(hydroxymethyl)-4*H*-1-benzopyran-4-one (**5**), and 7-{[(β-D-glucopyranosyl)oxy]methyl}-2,3-dihydro-2-(1-hydroxy-1-methylethyl)-4-methoxy-5*H*-furo[3,2-*g*][1]benzopyran-5-one (**6**). Compound **2** exhibited negative inotropic activity.

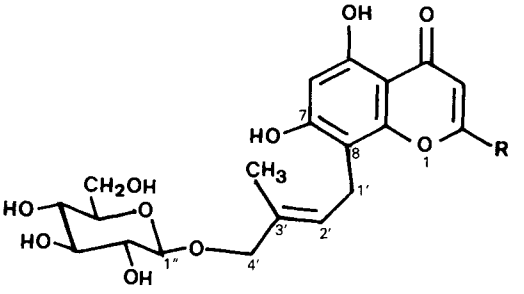
Introduction. – The genus *Eranthis* belongs to the tribe *Helleboreae*, subtribe *Helleborinae*, *Ranunculaceae*. This assignment is based on morphological similarities to the genus *Helleborus*. Investigations in comparative serology, though, have indicated a revision of the subtribe: *Eranthis* seems to be closely related to the genera *Actaea* and *Cimicifuga* [1]. This finding is compatible with several phytochemical studies which revealed the occurrence of chromenone derivates in *Eranthis hyemalis* [2] [3], *Eranthis pinnatifida* [4], and *Cimicifuga simplex* [5], whereas bufadienolides – like those of *Helleborus* – have not been found in any of these plants. The cardioactive fractions eranthin A and B prepared by *Schaub* [6] from *Eranthis hyemalis* did not contain any bufadienolides either [3] [7]. Nevertheless, up to now, *Eranthis hyemalis* is often described as a poisonous plant bearing cardiac glycosides [8–11]. For this reason, an investigation concerning the active substances of this plant has been started. The present work reports the isolation and structure elucidation of six chromenones from the tubers of *Eranthis hyemalis*.

Results. – The tubers (3.3 kg) were freeze-dried, powdered, and extracted successively with boiling EtOH/H_2O 7:3. The concentrated extracts were prepurified with petroleum ether and then extracted with $CHCl_3$/EtOH 9:1, $CHCl_3$/EtOH 2:1, and BuOH. The $CHCl_3$/EtOH 2:1 extract was submitted to column chromatography on silica gel using $CHCl_3$/MeOH/H_2O and H_2O-saturated AcOEt/MeOH mixtures. After crystallization, 4*H*-chromenones **1**–**6** were obtained.

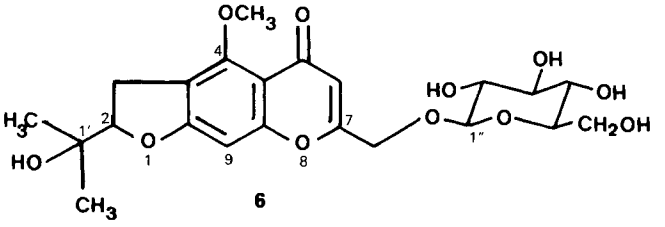
On both enzymatic (*Method B*, see *Exper. Part*) and acidic hydrolysis of **1**–**6**, each of the compounds afforded a carbohydrate unit which was identified as glucose by means of GLC [12]. Treatment of **2** with emulsine (*Method A*) yielded glucose, eranthin [3], and **1**.



1 $R^1 = CH_3$, $R^2 = \beta$-D-glucopyranosyl
2 $R^1 = CH_3$, $R^2 = \beta$-D-gentiobiosyl
3 $R^1 = CH_2OH$, $R^2 = \beta$-D-glucopyranosyl



4 $R = CH_3$
5 $R = CH_2OH$



6

After acidic hydrolysis of permethylated **2**, the sugar moiety of **2** was unambiguously identified as gentiobiose [13]. The structures of **1–6** finally were established by means of spectroscopic methods.

From the spectral data, the structure of 9-{[(β-D-glucopyranosyl)oxy]methyl}-8,11-dihydro-5-hydroxy-2-methyl-4*H*-pyrano[2,3-*g*][1]benzoxepin-4-one was derived for **1**. Chromenone **1** is identical with eranthin β-D-glucoside reported by *Junior* [3], although chemical-shift values of C(2), C(5), and C(6a), resp. C(4a) and C(11a), as assigned by *Junior* do not correspond to the ones we obtained. In these cases, however, definite assignments are only possible by application of 2D-NMR techniques (see below).

The FAB-MS of **1** showed the $[MH]^+$ peak at m/z 437. Elimination of the sugar moiety led to the $[MH - 162]^+$ peak at m/z 275. ^{1}H-NMR and ^{13}C-NMR experiments established the β-D-pyranosyl configuration of the sugar moiety and provided informations about the constitution of the aglycone of **1**. Additional 2D-NMR experiments allowed unambiguous assignment of all ^{1}H- and ^{13}C-NMR chemical-shift values. Starting with the Me signal at 2.41/19.4 ppm (*Me*–C(2)), the COSY spectrum showed a cross-peak at 6.25 ppm which we assigned to the olefinic proton H–C(3). The corresponding C-atom was derived from the 2D-SC spectrum. Moreover, the COLOC spectrum showed a correlation between the Me protons and C(3) at 107.5 ppm. The ^{13}C signal at 167.6 ppm was attributed to C(2) on the basis of COLOC crosspeaks with *Me*–C(2) (2.41 ppm) and *H*–C(3) (6.25 ppm). The large shift difference between C(2) and C(3) could only be explained by the presence of an O-atom at position 1 and a carbonyl group at position 4. The latter (C(4) at 181.9 ppm) was corroborated by a COLOC cross-peak with *H*–C(3). In the gated-decoupled ^{13}C-NMR spectrum, the signal of C(4a) was a clear *t* at 105.5 ppm with $J = 5.0$ Hz indicating two nearly identical coupling paths. In the COLOC spectrum, *H*–C(6) (6.40 ppm) gave 4 + 1 cross-peaks C(6a), C(5), C(11a), C(4a), and C(6) (at 163.5, 158.6, 109.8, 105.5, and 103.1 ppm (appeared in the 2D-SC spectrum, too), resp.) The resonance position of C(6) at 103.1 ppm indicated *o,o'*-substitution by RO fragments. The signal at 12.90 ppm was attributed to the intramolecularly H-bonded O*H*–C(5) (concentration-independent signal). O*H*–C(5) was also deduced by using the information provided by the COLOC spectrum which showed cross-peaks with C(5), C(4a), and C(6) (at 158.6, 105.5, and 103.1 ppm, resp.) leading to the assignments of these C-atoms. Remaining *s* at 163.5, 109.8, and 152.9 ppm had to be used for the ring closure of the chromenone fragment: the considerations given earlier referring to the substitution pattern and the cross-peaks of *H*–C(6)/

C(6a) and *H*–C(6)/C(11a) led to the assignments of C(6a) and C(11a) for the former two *s*; the remaining *s* at 152.9 ppm must, therefore, be assigned to C(11b).

A further fragment was constructed by starting at the olefinic *H*–C(10) at 6.05 ppm, correlated to C(10) at 125.1 ppm. The COSY spectrum displayed couplings with CH_2–C(9), CH_2(8), and CH_2(11) (at 4.75, 4.00 and 4.15, and 3.59 ppm, resp.). The *AB* system of CH_2–C(9) was established by a geminal coupling (J = 13 Hz), and its chemical-shift value, as well as that of CH_2(8), indicated the presence of an adjoining O-atom. The 2D-SC spectrum showed the expected correlations CH_2(11)/C(11) (20.6 ppm), CH_2–C(9)/CH_2–C(9) (69.6 ppm), and CH_2–C(8)/C(8) (69.6 ppm). Using the COLOC cross-peak of CH_2–C(8)/C(6a), the assignment of chemical-shift values was completed.

The aglycone of **2** was identified as eranthin by comparison with FAB-MS, ^{13}C-NMR, and ^{1}H-NMR data of **1**, in the course of which substitution by β-D-gentiobiose was corroborated too. The structure of **2** is 9-{[(β-D-gentiobiosyl)oxy]methyl}-8,11-dihydro-5-hydroxy-2-methyl-4*H*-pyranol[2,3-*g*][1]benzoxepin-4-one (eranthin β-D-gentiobioside).

With the aid of ^{13}C- and ^{1}H-NMR data, **3** was identified as a β-D-glucopyranoside, namely 9-{[(β-D-glucopyranosyl)oxy]methyl}-8,11-dihydro-5-hydroxy-2-(hydroxymethyl)-4*H*-pyrano[2,3-*g*][1]benzoxepin-4-one (= 2-*C*-hydroxyeranthin β-D-glucopyranoside).

The FAB-MS of **3** showed the $[MH]^+$ peak at *m/z* 453. An additional signal at *m/z* 291 ($[MH - 162]^+$) corresponded to the loss of the glucosyl unit and indicated the presence of an additional O-atom within the eranthin moiety. Comparison of the NMR spectra of **1** and **3** completed the following informations: The *Me*–C(2) of **1** at 2.41 and 19.4 ppm was missing in the spectra of **3**; instead, signals for a CH_2OH group showed up (4.47 (2 H) and 59.7 ppm). The downfield shift of C(2) (167.6→170.9 ppm) and the upfield shift of C(3) (107.5→105.6 ppm) also signalized an alteration in this area. Moreover, the COSY spectrum of **3** featured a cross-peak of CH_2OH/*H*–C(3) which supported the localization of CH_2OH at C(2). Due to the conformities of both **1** and **3** concerning the chemical-shift values of C(9) and CH–C(9), the glucosyloxy moiety had to be fixed to CH_2–C(9). Thus, glucosyl substitution at CH_2OH–C(2) had to be excluded.

The constitution of the aglycone of **4** was determined by comparison of NMR data of **1** and **4** which also showed it to be a β-D-glucopyranoside, *i.e.* 8-{(2*E*)-4-[(β-D-glucopyranosyl)oxy]-3-methylbut-2-enyl}-5,7-dihydroxy-2-methyl-4*H*-1-benzopyran-4-one (= 7,8-secoeranthin β-D-glucopyranoside).

In the FAB-MS of **4**, the $[MH]^+$ peak appeared at *m/z* 439. Elimination of the glucose moiety lead to the $[MH - 162]^+$ peak at *m/z* 277. The upfield shift in the ^{13}C-NMR spectrum of C(7) from 163.5 (C(6a) in **1**) to 159.9 ppm in **4** indicated a cleavage of the oxepin ring of **1** between C(8) and the O-atom. This was corroborated by the following assignments: Upfield shifts of C(6) (103.1→97.6 ppm) and C(8) (108.9 (C(11a) in **1**)→107.5 ppm) could be ascribed to a free OH group attached to C(7). The ^{1}H-NMR signal at 5.02 ppm indicated the presence of a phenolic OH group without H-bonding. Due to the open oxepin ring, the Me group at C(3′) of **4** had a *cis*-relationship to C(1′); signals at 13.1 (^{13}C-NMR) and, 1.78 ppm (3 H, ^{1}H-NMR) verified this assumption. This Me group was likely to cause the upfield shifts of C(2′) (125.1 (C(10) in **1**)→120.5 ppm), of *H*–C(2′) (6.05 (*H*–C(10) in **1**)→5.44 ppm) and of the CH_2(4′) group (69.6 (CH_2–C(9) in **1**)→65.9 ppm and 4.75 (CH_2–C(9) in **1**)→4.68 ppm). The remaining chemical-shift values were in agreement with the ones of **1**.

The structure of **5** was found to be 8-{(2*E*)-4-[(β-D-glucopyranosyl)oxy]-3-methylbut-2-enyl}-5,7-dihydroxy-2-(hydroxymethyl)-4*H*-1-benzopyran-4-one (= 2-*C*-hydroxy-7,8-secoeranthin β-D-glucopyranoside), as deduced from comparisons with the spectral data of **3** and **4**.

In the FAB-MS of **5**, signals were observed at *m/z* 455 ($[MH]^+$) and 293 ($[MH - 162]^+$). Due to the increase of 16 mass units compared to the aglycone of **4**, the presence of a hydroxylated secoeranthin derivative seemed possible. This assumption was corroborated by NMR data: Analogous to **3**, signals of a CH_2OH group at 4.40 (2 H) and 59.3 ppm appeared instead of the *Me*–C(2) signals of **4** at 2.40 and 19.5 ppm. The presence of

CH_2OH–C(11) caused chemical shifts of C(2) and C(3) similar to the ones appearing in the ^{13}C-NMR spectrum of **3**. Conformities with **4** concerning chemical-shift values assigned to C(6), C(7), C(8), C(2'), C(3'), CH_3–C(3'), and C(4') and the appropriate H-atoms indicated an open oxepin ring and substitution of the glucose *via* OH–C(4').

The aglycone of compound **6** was identified as cimifugin by means of FAB-MS and NMR experiments. This result was corroborated by enzymatic hydrolysis of **6** with β-glucuronidase (*Method B*) and ^1H-NMR and IR analysis of the obtained aglycone. Cimifugin has already been reported as a constituent of *Eranthis pinnatifida* [4] and *Cimicifuga simplex* [5]. Thus, the structure of **6** is 7-{[(β-D-glucopyranosyl)oxy]methyl}-2,3-dihydro-2-(1-hydroxy-1-methylethyl)-4-methoxy-5*H*-furo[3,2-*g*][1]benzopyran-5-one (= cimifugin β-D-glucopyranoside).

The FAB-MS of **6** showed the $[MH]^+$ peak at *m/z* 469. The signal at *m/z* 307 ($[MH - 162]^+$) corresponded to the elimination of 1 glucosyl moiety. The informations provided by 1D-NMR experiments were interpreted as follows: The benzopyranone skeleton was confirmed here, too. The substitution, though, appeared to be different from that of **1**–**5**: OH–C(5) was replaced by a MeO group (3.95 and 60.9 ppm), which caused a downfield-shift of the C(4a) signal of **1** from 105.5 to 117.6 ppm in **6**, and the *Me*–C(2) of **1** with signals at 2.41 and 19.4 ppm was missing and replaced by CH_2OR signals at 4.52 and 66.8 ppm. The resonance position of this CH_2OR indicated substitution by a glucosyloxy moiety. A CH_2 group (3.28 and 28.2 ppm) and a tertiary C-atom (4.74 and 91.7 ppm) with a neighbouring O-atom were used for the closure of a dihydrofuran ring. An isopropyl chain attached to this tertiary C-atom was deduced from signals of 2 Me groups (1.28 and 25.0 ppm, 1.40 and 25.0 ppm) and quaternary C-atom (71.5 ppm). The resonance position of the latter was ascribed to substitution by an OH group.

Discussion. – By means of column chromatography, six chromenone glycosides were isolated from tubers of *Eranthis hyemalis* and identified by GLC, FAB-MS, and NMR spectroscopy. Five of them, *i.e.* **2**–**6**, are new natural substances. In addition, the occurrence of eranthin [3] as well as khellol glucoside [2] in the tubers was proved by means of TLC.

The occurrence of chromenone **6** (cimifugin β-D-glucopyranoside), a furochromone derivative in *Eranthis hyemalis* might be a further indication of the relation to the genera *Actaea* and *Cimicifuga* [1], especially as the presence of bufadienolides in this plant can be excluded by all known odds.

Cardiac activity of extracts from *Eranthis hyemalis* – as described by *Schaub* [6] – appears to be due to the chromenones: pharmacological tests with eranthin β-D-gentiobioside (**2**) revealed negative inotropic effect on the isolated papillary muscle of the guinea pig [14]. The presence of other pharmacological properties inherent in these new natural substances, such as spasmolytic action [15] or antiviral phototoxicity [16], which are effects of the furochromone khellin, is to be examined in the course of further investigations.

We thank Prof. Dr. *P. Junior* for authentic eranthin and Dr. *K.K. Mayer*, Zentrale Analytik-Massenspektrometrie, University of Regensburg, for the FAB-MS. The NMR spectrometer *Bruker WM-250* was made available by the *Fonds zur Förderung der wissenschaftlichen Forschung in Österreich* (projekt No. 4009).

Experimental Part

General. TLC: silica gel *60* F_{254} precoated plates (*Merck*); system *1*: $CHCl_3$/MeOH/H_2O 70:22:3.5; system *2*: AcOEt/MeOH/H_2O 81:11:8; detection: after 15 min at 103–105°, the plate was sprayed with vanilline/H_2SO_4 reagent [17]. Column chromatography (CC): silica gel *60* (*Merck*, 0.063–0.200 mm). GLC: according to [12] [13]. M.p.: *Kofler* hotstage apparatus, uncorrected. IR (in cm^{-1}): *Perkin Elmer-257* spectrometer; 1 mg of compound in 200 mg of KBr. NMR: *Bruker-WM-250* spectrometer with *Aspect-2000* computer; ^1H, 250.13 MHz; ^{13}C, 62.9

MHz; TMS as internal standard; δ in ppm, J in Hz; J-modulation: $\tau = 7.1$ ms ($J = 141$ Hz). FAB-MS (positive-ion mode): *Varian Mat 311 A;* FAB canon from *Ion Tech Ltd.*, acceleration voltage 2.2 kV, E (neutral) = 6.0 keV; Xenon, $T = 40°$, $p < 10^{-5}$ Torr, T_{inlet} = r.t. glycerine matrix.

Acidic Hydrolysis. The compound (5 mg) was refluxed in 1.2 ml of 0.4N HCl for 30 min.

Enzymatic Hydrolysis. Method A: A mixture of compound (10 mg), emulsine (40 mg; EC 3.2.1.21; *Sigma Chemical Company*, product No. 0395), H_2O (2 ml), and 2 drops of toluene was stirred for 4 h at r.t. *Method B:* To a soln. of compound (12 mg) in MeOH (0.5 ml), acetate buffer pH 4.99 (12 ml) and β-glucuronidase (45 mg; EC 3.2.1.31; *Sigma Chemical Company*, product No. 1512) were added. After 2 days at 37°, the aglycone was extracted with $CHCl_3$/EtOH 9:1.

Plant Material. Tubers of *Eranthis hyemalis*, purchased from *Austrosaat AG*, Vienna, Austria, were cultivated in the garden of the Institute of Pharmacognosy; a voucher specimen of the plant material is retained at the herbarium of the Institute of Pharmacognosy, University of Vienna, Austria.

Extraction and Isolation. Lyophilized and powdered tubers (3.3 kg) were extracted with boiling EtOH followed by EtOH/H_2O 7:3. The solns. were concentrated, the residue was washed with petroleum ether and extracted with $CHCl_3$/EtOH 9:1, $CHCl_3$/EtOH 2:1, and BuOH. The $CHCl_3$/EtOH 2:1 extract (9.0 g) was separated by CC (5 × 67 cm, silica gel, $CHCl_3$/MeOH/H_2O 80:10:1; TLC monitoring). Repeated crystallisations of *Fraction I* in MeOH provided **1** in pure form (44.2 mg). Crystallisation of *Fraction II* and *III*, each in MeOH, afforded **3** (685.0 mg) and **2** (1755.7 mg), resp. *Fraction IV* was further separated by CC (silica gel, H_2O-sat. AcOEt/MeOH 95:5→93:7): pure **4** (80 mg) and **6** (44.5 mg). From *Fraction V*, **5** was obtained by CC (silica gel, H_2O-sat. AcOEt/MeOH 95:5); crystallisation from MeOH gave pure **5** (49.0 mg).

Eranthin β-D-Glucopyranoside (= *9-{[(β-D-Glucopyranosyl)oxy]methyl}-8,11-dihydro-5-hydroxy-2-methyl-4H-pyrano[2,3-g][1]benzoxepin-4-one*; **1**): Yellowish crystals. M.p. 191–192°. ^{1}H-NMR ((D$_6$)DMSO): 12.90 (*s*, OH–C(5)); 6.40 (*s*, H–C(6)); 6.25 (*s*, H–C(3)); 6.05 (*dd*, J(10,11) = 5, H–C(10)); 4.75 (*s*, 2 H–C(8)); 4.15, 4.00 (*AB*, J = 13, CH_2–C(9)); 4.11 (*d*, J(1′,2′) = 8, H–C(1′)); 3.59 (*d*, J(11,10) = 5, 2 H–C(11)); 3.4–2.9 (*m*, 6 H, sugar); 2.41 (*s*, Me–C(2)). ^{13}C-NMR ((D$_6$)DMSO): 181.9 (C(4)); 167.6 (C(2)); 163.5 (C(6a)); 158.6 (C(5)); 152.9 (C(11b)); 135.2 (C(9)); 124.7 (C(10)); 109.8 (C(11a)); 107.5 C(3)); 105.5 (C(4a)); 103.1 (C(6)); 101.2 (C(1′)); 76.8 (C(3′)); 76.6 (C(5′)); 72.8 (C(2′)); 70.1 (C(4′)); 69.6 (C(8), (CH$_2$–C(9)); 60.6 (C(6′)); 20.6 (C(11)); 19.4 (*Me*–C(2)). FAB-MS: 437 ([MH]$^+$), 275 ([MH − 162]$^+$).

Eranthin β-D-Gentiobioside (= *9-{[(β-D-Gentiobiosyl)oxy]methyl}-8,11-dihydro-5-hydroxy-2-methyl-4H-pyrano[2,3-g][1]benzoxepin-4-one*; **2**): Yellow crystals. M.p. 142–144°. ^{1}H-NMR ((D$_6$)DMSO): 12.80 (*s*, OH–C(5)); 6.44 (*s*, H–C(6)); 6.30 (*s*, H–C(3)); 6.06 (*d*, J(10,11) = 5, H–C(10)); 4.74 (*s*, 2 H–C(8)); 4.30 (*d*, J(1″,2″) = 8, H–C(1″)); 4.15, 4.00 (*AB*, J = 13, CH_2–C(9)); 4.12 (*d*, J(1′,2′) = 8, H–C(1′)); 3.60 (*d*, J(11, 10) = 5, 2 H–C(11)); 3.4–2.9 (*m*, 12 H, sugar); 2.44 (*s*, Me–C(2)). ^{13}C-NMR ((D$_6$)DMSO): 181.8 (C(4)); 167.6 (C(2)); 163.3 (C(6a)); 158.5 (C(5)); 152.7 (C(11b)); 135.0 (C(9)); 124.7 (C(10)); 109.9 (C(11a)); 107.4 (C(3)); 105.4 (C(4a)); 103.1 (C(6)); 102.7 (C(1″)); 100.9 (C(1′)); 76.1 (C(3′), C(3″)); 75.9 (C(5″)); 75.2 (C(5′)); 72.8 (C(2″)); 72.6 (C(2′)); 69.6 (C(8), CH$_2$–C(9)); 69.4 (C(4′), C(4″)); 67.7 (C(6′)); 60.4 (C(″)); 20.3 (C(11)); 19.2 (*Me*–C(2)). FAB-MS: 599 ([MH]$^+$), 275 ([MH − 162]$^+$).

2-C-Hydroxyeranthin β-D-Glucopyranoside (= *9-{[(β-D-Glucopyranosyl)oxy]methyl}-8,11-dihydro-5-hydroxy-2-(hydroxymethyl)-4H-pyrano[2,3-g][1]benzoxepin-4-one*; **3**): Yellow crystals. M.p. 227–228°. ^{1}H-NMR ((D$_6$)DMSO): 12.74 (*s*, OH–C(5)); 6.45 (*s*, H–C(6)); 6.34 (*s*, H–C(3)); 6.03 (*dd*, J(10, 11) = 5, H–C(10)); 4.74 (*s*, 2 H–C(8)); 4.47 (*s*, CH_2OH–C(2)); 4.15, 4.00 (*AB*, J = 13, CH_2–C(9)); 4.11 (*d*, J(1′,2′) = 8, H–C(1′)); 3.58 (*d*, J(11, 10) = 5, 2 H–C(11)); 3.4–2.9 (*m*, 6 H, sugar). ^{13}C-NMR ((D$_6$)DMSO): 182.5 (C(4)); 170.9 (C(2)); 164.1 (C(6a)); 159.2 (C(5)); 153.1 (C(11b)); 135.8 (C(9)); 125.2 (C(10)); 110.5 (C(11a)); 106.5 (C(4a)); 105.6 (C(3)); 103.8 (C(6)); 101.9 (C(1′)); 76.8 (C(3′)); 76.6 (C(5′)); 73.3 (C(2′)); 70.2 (C(8), CH$_2$–C(9)); 70.1 (C(4′)); 61.6 (C(6′)); 59.7 (CH$_2$OH–C(2)); 20.9 (C(11)). FAB-MS: 453 ([MH]$^+$), 291 ([MH − 162]$^+$).

7,8-Secoeranthin β-D-Glucopyranoside (= *8-{(2E)-4-[(β-D-Glucopyranosyl)oxy]-3-methylbut-2-enyl}-5,7-dihydroxy-2-methyl-4H-1-benzopyran-4-one*; **4**): Yellowish crystals. M.p. 205–206°. ^{1}H-NMR ((D$_6$)DMSO): 12.83 (*s*, OH–C(5)); 6.61 (*s*, H–C(6)); 6.25 (*s*, H–C(3)); 5.44 (*s*, H–C(2′)); 4.68 (*s*, H–C(4′)); 3.50 (*s*, 2 H–C(1′)); 3.4–3.0 (*m*, 6 H, sugar); 2.40 (*s*, Me–C(2)); 1.78 (*s*, Me–C(3′)). ^{13}C-NMR ((D$_6$)DMSO): 181.8 (C(4)); 167.6 (C(2)); 159.9 (C(7)); 158.8 (C(5)); 153.8 (C(8a)); 134.9 (C(3′)); 120.5 (C(2′)); 107.5 (C(8)); 107.4 (C(3)); 104.3 (C(4a)); 100.1 (C(1″)); 97.6 (C(6)); 76.7 (C(3″)); 76.1 (C(5″)); 72.9 (C(2″)); 69.2 (C(4″)); 65.9 (C(4′)); 60.2 (C(6″)); 20.3 (C(1′)); 19.5 (*Me*–C(2)); 13.1 (*Me*–C(3′)). FAB-MS: 439 ([MH]$^+$), 277 ([MH − 162]$^+$).

2-C-Hydroxy-7,8-secoeranthin β-D-Glucopyranoside (= *8-{(2E)-4-[(β-D-Glucopyranosyl)oxy]-3-methylbut-2-enyl}-5,7-dihydroxy-2-(hydroxymethyl)-4H-1-benzopyran-4-one*; **5**): Yellowish crystals. M.p. 225–228°. ^{1}H-NMR ((D_6)DMSO): 12.75 (*s*, OH–C(5)); 6.60 (*s*, H–C(6)); 6.31 (*s*, H–C(3)); 5.40 (*dd*, *J*(2′,1′) = 5, H–C(2′)); 4.68 (*s*, 2 H–C(4′)); 4.40 (*s*, CH_2OH–C(2)); 4.13 (*d*, *J*(1′,2′) = 8, H–C(1″)); 3.50 (*s*, 2 H–C(1′)); 3.4–3.0 (*m*, 6 H, sugar); 1.73 (*s*, Me–C(3′)). ^{13}C-NMR ((D_6)DMSO): 181.9 (C(4)); 170.7 (C(2)); 160.1 (C(7)); 158.9 (C(5)); 153.5 (C(8a)); 134.9 (C(3′)); 120.4 (C(2′)); 107.4 (C(8)); 104.85 (C(3)); 104.8 (C(4a)); 100.1 (C(1″)); 97.8 (C(6)); 76.7 (C(3″)); 76.1 (C(5″)); 72.9 (C(2″)); 69.2 (C(4″)); 65.8 (C(4′)); 60.2 (C(6″)); 59.3 (CH_2OH–C(2)); 20.3 (C(1′)); 13.1 (*Me*–C(3′)). FAB-MS: 455 ([*M*H]$^+$), 293 ([*M*H – 162]$^+$).

Cimifugin β-D-Glucopyranoside (= *7-{[(β-D-Glucopyranosyl)oxy]methyl}-2,3-dihydro-2-(1-hydroxy-1-methylethyl)-4-methoxy-5H-furo[3,2-g][1]benzopyran-5-one*; **6**): White crystals. M.p. 113–115°. IR (KBr): 3360, 2920, 2850, 1710, 1620. ^{1}H-NMR (aglycone; $CDCl_3$): 6.49 (*s*, H–C(9)); 6.32 (*s*, H–C(6)); 4.75 (*t*, *J*(2, 3) = 8.4, H–C(2)); 4.52 (*s* (*J* < 1), CH_2–C(7)); 3.95 (*s*, MeO–C(4)); 3.28 (*d*, *J*(3, 2) = 8.4, 2 H–C(3)); 1.40 (*s*, Me); 1.28 (*s*, Me). ^{1}H-NMR (glucoside; (D_6)acetone): additional signals at 4.48 (*d*, *J*(1″,2″) = 8, H–C(1″)); 3.4–3.0 (*m*, 6 H, sugar). ^{13}C-NMR ($CDCl_3$/CD_3OD 1:1): 178.7 (C(5)); 165.9 (C(7)); 163.5 (C(9a)); 160.1 (C(4)); 156.1 (C(8a)); 117.6 (C(4a)); 110.4 (C(6)); 103.2 (C(1″)); 94.1 (C(6)); 91.7 (C(2)); 76.9 (C(5″)); 76.8 (C(3″)); 73.9 (C(2″)); 71.5 (C(1′)); 70.5 (C(4″)); 66.8 (CH_2–C(7)); 62.0 (C(6″)); 60.9 (*Me*O–C(4)); 28.2 (C(3)); 25.0 (Me_2C). FAB-MS: 469 ([*M*H]$^+$), 307 ([*M*H – 162]$^+$).

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