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Chemical Studies of *Angelica japonica* A. Gray. I. On the Constituents of the Ethyl Acetate Extract of the Root

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The dried roots of *Angelica japonica* A. Gray (Umbelliferae) afforded three new chromones (VI, VIII and IX) together with six known chromones (I—V and VII) and fourteen known coumarins (X—XXIII) which were identified by comparison with authentic samples. The structure of VI, VIII and IX were established as (3*S*)-2,2-dimethyl-3,5-dihydroxy-8-hydroxymethyl-3,4-dihydro-2*H*,6*H*-benzo[1,2-*b*: 5,4-*b'*]dipyran-6-one, (3*S*)-2,2-dimethyl-3-*β*-D-glucosyloxy-5-hydroxy-8-methyl-3,4-dihydro-2*H*,6*H*-benzo[1,2-*b*: 5,4-*b'*]dipyran-6-one (*sec*-O-glucosylhamaudol) and (2*S*)-2-(1-hydroxy-1-methylethyl)-4-methoxy-7-*β*-D-glucosyloxymethyl-2,3-dihydro-5*H*-furo[3,2-*g*][1]benzopyran-5-one (*prim*-O-glucosylcimifugin).

Keywords——*Angelica japonica*; chromone; coumarin; dihydropyranochromone; dihydrofurochromone; *sec*-O-glucosylhamaudol; *prim*-O-glucosylcimifugin

Angelica japonica A. Gray. (Japanese name "hamaudo," Umbelliferae) is a stout perennial herb growing along the Pacific coast in the west of the Kanto region in Japan. In shape, it is similar to *A. keiskei* Koidzumi, which grows along the coast of Izu. However, it is easy to distinguish them, since the juice from the stock of the latter has a deep yellow color, while that of the former is nearly white in color.

It has been reported that the root of *Angelica japonica* afforded two chromones, hamaudol (I) and 3'-O-acetylhamaudol (II), together with six coumarins, osthol (X), psoralen (XI), isopimpinellin (XII), byak-angelicin (XIII), isoimperatorin (XIV), and bergapten (XV).[1] Recently, the authors reinvestigated this plant in order to study its chromones and coumarins, and were able to isolate seven chromones (III—IX) and eight coumarins (XVI—XXIII) in addition to hamaudol (I), 3'-O-acetylhamaudol (II) and the above six coumarins (X—XV). This paper describes in detail the identification and the structure elucidation of these compounds.

The roots of *A. japonica* collected on the Kada coast of Wakayama Pref. were treated as described in the experimental section and separated into hexane, ethylacetate, and methanol extracts. The ethyl acetate extract was chromatographed on silica gel to afford compounds I—XXIII. Six chromones (I—V and VII) were identified as hamaudol (I), 3'-O-acetylhamaudol (II), visamminol (III), 5-O-methylvisaminol (IV), cimifugin (V) and angelicain (VII), and fourteen coumarins (X—XXIII) were identified as osthol (X), psoralen (XI), isopimpinellin (XII), byak-angelicin (XIII), isoimperatorin (XIV), bergapten (XV), xanthotoxin (XVI), xanthotoxol (XVII), neobyakangelicol (XVIII), marmesin (XIX), oxypeucedanin hydrate (XX), umbelliferone (XXI), scopoletin (XXII) and pangeline (XXIII) by comparison with authentic samples.

The compound VI, mp 172—172.5°C, pale yellow needles, $C_{15}H_{16}O_6$, gave a deep green coloration with Gibbs reagent and a dark violet coloration with ferric chloride. The infrared (IR) spectrum of VI showed the presence of hydroxyl, carbonyl and aromatic ring moieties. The ultraviolet (UV) spectrum of VI showed absorption maxima at 222.5, 250, 256, 295 and 320 nm, which were shifted to longer wavelengths by addition of aluminium chloride.

On the basis of these spectral data and chemical properties, VI was considered to be a 5-hydroxychromone.

The proton nuclear magnetic resonance (^{1}H-NMR) spectrum (δ ppm, $CDCl_3$+DMSO-d_6) of VI exhibited signals due to a gem-dimethyl group at 1.34 (6H, s), ABX type signals assignable to adjacent methylene and methine protons at 3.72 (1H, dd, J=7.5 and 6.0 Hz), 2.47 (1H, dd, J=7.5 and 17.0 Hz), 2.93 (1H, dd, J=17.0 and 6.0 Hz), a hydroxymethyl group at 4.40 (2H, d, J=7.5 Hz), 5.25 (1H, t, J=7.5 Hz) and two hydroxyl groups at 4.46 (1H, s), 13.00 (1H, s), as well as a signal arising from an olefinic proton and a benzene proton at 6.25 (2H, s). These data indicate that VI is a 2-substituted chromone containing a dimethyldihydropyran ring, like hamaudol (I). However, the ^{1}H-NMR spectrum of VI exhibited signals arising from an allylic hydroxymethyl group, but showed no allylic methyl group like that of I. It is clear from these spectral data that VI is the structure in which a methyl group on the γ-pyrone ring of I is replaced with a hydroxymethyl group. Furthermore, the configuration at an asymmetric carbon of VI was confirmed to be S by comparison of the optical rotatory dispersion (ORD) curve with that of I.

Thus, VI was established as (3*S*)-2,2-dimethyl-3,5-dihydroxy-8-hydroxymethyl-3,4-dihydro-2*H*,6*H*-benzo[1,2-*b*: 5,4-*b*']dipyran-6-one.

The compound VII, mp 191—193°C, colorless needles, $C_{15}H_{16}O_6$, gave a blue coloration with Gibbs reagent and a dark violet coloration with ferric chloride. The IR spectrum of VII showed the presence of hydroxyl, carbonyl and aromatic ring moieties. The UV spectrum of VII showed absorption maxima at 233, 251, 256 and 298 nm, which were shifted to longer wavelengths by addition of aluminium chloride. Thus, VII also appears to be a 5-hydroxychromone. The ^{1}H-NMR spectrum (δ ppm, DMSO-d_6) of VII exhibited a signal attributable to a gem-dimethyl group at 1.17 (6H, s), A_2X signals assignable to adjacent methylene and methine groups at 3.06 (2H, d, J=9 Hz), 4.75 (1H, t, J=9 Hz), and signals attributable to a hydroxymethyl group at 4.40 (2H, d, J=7.5 Hz), 5.77 (1H, t, J=7.5 Hz), two hydroxy groups at 4.66 (1H, s), 13.10 (1H, s), an olefinic proton at 6.25 (1H, s) and an aromatic proton at 6.42 (1H, s). These data indicated the VII is a 2'-(1-hydroxy-1-methylethyl)-2',3'-dihydrofurochromone, like III or IV.

However, the ^{1}H-NMR spectrum of VII showed signals arising from an allylic hydroxymethyl group, but showed no signal due to an allylic methyl group like that in III. Therefore, the structure of VII is that in which the methyl group on the γ-pyrone ring of III is replaced with a hydroxymethyl group. The configuration at an asymmetric carbon of VII was confirmed to be *S* by comparison of the ORD curve with those of III and V.

From the results described above, VII was identified as angelicain (norcimifugin).

The compound VIII, mp 207—209°C, a colorless crystalline powder, gave a blue-green coloration with Gibbs reagent and a dark violet coloration with ferric chloride. The ^{1}H-NMR spectrum (δ ppm, DMSO-d_6) of VIII was very similar to that of I except that signals suggesting the presence of a sugar moiety were observed at 2.85—4.90 [anomeric H, 4.35 (d, J=7.5 Hz)]. On heating with 10% H_2SO_4, VIII gave I and glucose, which was identified by TLC and the preparation of D-glucose phenylhydrazone; thus, VIII is the glucoside of I. VIII gave a positive phenolic test and showed a signal due to chelated hydroxy group at 13.18 (1H, s) in the ^{1}H-NMR spectrum. Acetylation of VIII with acetic anhydride and pyridine at room temperature gave a tetraacetate (VIII—a), mp 209—210°C, $C_{29}H_{34}O_{14}$, whose IR and ^{1}H-NMR spectra indicated the presence of a chelated hydroxy group.

On the basis of these findings, VIII was confirmed to be a β-monoglucoside whose glucosyl group was linked at the secondary alcoholic hydroxyl group of I, and was identified as (3*S*)-2,2-dimethyl-3-β-D-glucosyloxy-5-hydroxy-8-methyl-3,4-dihydro-2*H*,6*H*-benzo[1,2-*b*: 5,4-*b*']-dipyran-6-one (*sec*-O-glucosylhamaudol).

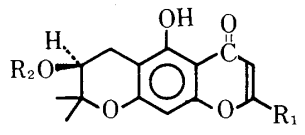
The compound IX, mp 118—120°C, a colorless crystalline powder, gave a negative phenolic test. The UV spectrum of IX showed absorption maxima at 230, 240, 243 and 296 nm, which were not shifted by addition of aluminium chloride. The ^{1}H-NMR spectrum of IX (δ ppm, DMSO-d_6) was similar to that of cimifugin (V) except that signals assignable to a sugar moiety

were observed at 3.2—5.3 [anomeric H, 4.35 (d, J=7.5 Hz)]. Upon heating with 10% H_2SO_4, IX gave cimifugin and glucose. The treatment of IX with acetic anhydride in pyridine afforded a colorless viscid oil (IX-a), $C_{32}H_{38}O_{16}$, which was shown to be a pentaacetate by the ^{1}H-NMR spectrum. From these results IX was considered to be a monoglucoside of cimifugin. The location of the glucosyl group was confirmed by the following results.

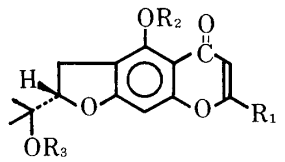
The hydrolysis of IX-a with 5% methanolic H_2SO_4 afforded cimifugin monoacetate (V-a-1) and cimifugin (V). The ^{1}H-NMR spectrum of V-a-1 (δ ppm, DMSO-d_6) showed signals attributable to allylic hydroxymethyl protons at 4.31 (CH_2) and 5.65 (OH) which were mutually coupled (J=7.0 Hz). Furthermore, the ^{1}H-NMR spectrum of V-a-1 was different from that of *prim*-O-acetylcimifugin (V-a-2) prepared from cimifugin by acetylation. On the basis of these findings, it became clear that the acetyl group of V-a-1 was bound to the tertiary hydroxyl group, and accordingly that the glucosyl group of IX was linked to the primary hydroxyl group.

Thus, the structure of IX was established as (2*S*)-2-(1-hydroxy-1-methylethyl)-4-methoxy-7-β-D-glucosyloxymethyl-2,3-dihydro-5*H*-furo[3,2-*g*][1]benzopyran-5-one (*prim*-O-glucosylcimifugin).

The authors have now isolated fourteen coumarins and nine chromones, including three new compounds, VI, VIII and IX, from the ethyl acetate extract of the roots of *Angelica japonica* A. GRAY growing in Japan and determined their structures.



I : R_1=CH_3, R_2=H
II : R_1=CH_3, R_2=$COCH_3$
VI : R_1=CH_2OH, R_2=H
VIII : R_1=CH_3, R_2=β-D-glucosyl



III : R_1=CH_3, R_2=R_3=H
IV : R_1=R_2=CH_3, R_3=H
V : R_1=CH_2OH, R_2=CH_3, R_3=H
VII : R_1=CH_2OH, R_2=R_3=H

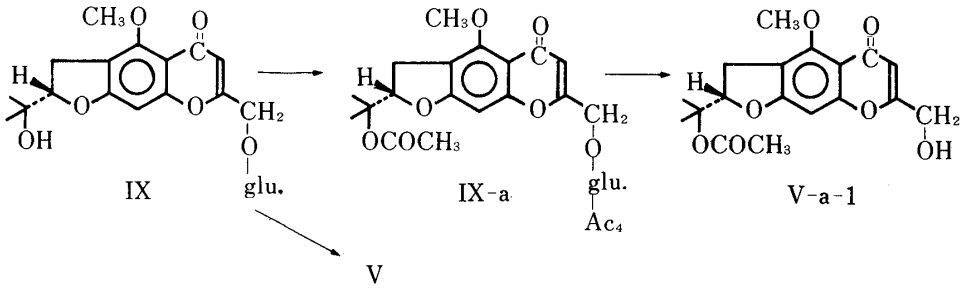


Chart 1

Experimental

Isolation of the Compounds——The dried and crushed roots (4.5 kg) of *Angelica japonica* A. GRAY collected on the Kada coast of Wakayama Pref. during June 1976 were extracted by refluxing three times with 10 l each of hexane, then with 10 l of methanol (5 h for each extraction). Each solution was concentrated under reduced pressure to give the corresponding extract: hexane extract (66.8 g), methanol extract (673 g). The methanol extract was further extracted with ethyl acetate under reflux and divided into the soluble part (EtOAc extract, 176 g) and insoluble part (MeOH extract, 497 g). The EtOAc extract (176 g) was chromatographed over silica gel (2.0 kg). Elution with mixtures of hexane–EtOAc, then a mixture of EtOAc–acetone, yielded the following five fractions: F-A (hexane–EtOAc, 3:1); F-B (2:1); F-C (1:1); F-D (1:2); F-E (EtOAc–acetone, 5:1) (figures in parentheses are the solvent ratios in v/v). F-A gave I, II, X, XI, XII, XIV, XV, XVI, XVII and XXIII, F-B gave III, XVIII and XXI, and F-D gave XIII. The materials from F-C were rechromatographed over silica gel with a mixture of hexane–EtOAc (1:1), yielding

VI, XIX, XX and XXII, and the materials from F-E were rechromatographed over silica gel with $CHCl_3$–MeOH (5: 1) to give IV, V, VII, VIII and IX.

Hamaudol (I)——Recrystallized from hexane–EtOAc to give pale yellow needles, mp 197—198°C. ORD (c=0.51, EtOH) $[\alpha]^{15}$ (nm): −19.6° (589), −23.5° (550), −47.1° (500), −78.4° (450), −137.3° (400). The melting point showed no depression on admixture with an authentic sample of hamaudol. The IR and ^{1}H-NMR spectra were identical with those of the authentic sample. Yield 0.014%.

3′-O-Acetylhamaudol (II)——Recrystallized from hexane–EtOAc to give pale yellow needles, mp 126—128°C. ORD (c=0.71, EtOH) $[\alpha]^{15}$ (nm): −27.3° (589), −31.3° (550), −39.1° (500), −42.2° (450), −64.9° (400). The melting point showed no depression on admixture with an authentic sample of 3′-O-acetylhamaudol. The IR and ^{1}H-NMR spectra were identical with those of the authentic sample. Yield 0.014%.

Visamminol (III)——Recrystallized from hexane–EtOAc to give colorless needles, mp 158—159°C. It gave a blue coloration with Gibbs reagent and ammonia aq. and gave a positive (dark violet coloration) ferric chloride reaction. ORD (c=0.08, EtOH) $[\alpha]^{17}$ (nm): +133.3° (589), +160.0° (550), +173.3° (500), +213.3° (450), +293.3° (400). IR ν_{max}^{Nujol} cm^{-1}: 3330 (OH), 1675 (CO), 1630, 1590 (arom.). UV λ_{max}^{EtOH} nm (log ε): 233.5 (4.33), 250.5 (4.27), 257.5 (4.26), 296.5 (4.15). UV $\lambda_{max}^{EtOH+AlCl_3}$ nm: 265, 314, 350. ^{1}H-NMR ($CDCl_3$) δ ppm:[2] 1.28, 1.37 (each 3H, s), 2.36 (3H, s), 2.80 (1H, br. s), 3.17 (2H, d, J=8.5 Hz), 4.80 (1H, t, J=8.5 Hz), 6.05 (1H, s), 6.35 (1H, s), 12.96 (1H, s). The UV, IR and ^{1}H-NMR spectra were identical with those of an authentic sample of visamminol. Yield 0.003%.

5-O-Methylvisamminol (IV)——Recrystallized from hexane–EtOAc to give pale yellow needles, mp 139—139.5°C. ORD (c=0.65, EtOH) $[\alpha]^{17}$ (nm): +86.8° (589), +105.4° (550), +192.2° (450), +279.1° (400). IR ν_{max}^{Nujol} cm^{-1}: 3380, 3150 (OH), 1650 (CO), 1630, 1610, 1595 (arom.). UV λ_{max}^{EtOH} nm (log ε): 224.1 (4.39), 237.7 (4.35), 241.5 (4.29), 387.5 (4.20). ^{1}H-NMR (acetone-d_6) δ ppm: 1.23, 1.26 (each 3H, s), 2.26 (3H, s), 2.76 (1H, s), 3.28 (2H, d, J=9.0 Hz), 3.86 (3H, s), 4.76 (1H, t, J=9.0 Hz), 5.90 (1H, s), 6.50 (1H, s). It gave a yellow coloration with conc. H_2SO_4 on TLC. The UV, IR and ^{1}H-NMR spectra were identical with those of an authentic sample of 5-O-methylvisamminol. Yield 0.006%.

Cimifugin (V)——Recrystallized from hexane–EtOAc to give colorless needles, mp 107—108.5°C, bitter taste. It gave a yellow coloration with conc. H_2SO_4 on TLC. ORD (c=0.81, EtOH) $[\alpha]^{24}$ (nm): +88.5° (589), +108.2° (550), +137.8° (500), +196.8° (450), +275.8° (400). IR ν_{max}^{Nujol} cm^{-1}: 3360 (OH), 1660 (CO), 1620, 1580 (arom.). UV λ_{max}^{EtOH} nm (log ε): 228.5 (4.41), 244 (4.39), 249.5 (4.35), 290 (4.22). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.24, 1.35 (each 3H, s), 3.23 (2H, d, J=8.5 Hz), 3.20 (1H, br. s), 3.86 (3H, s), 4.41 (2H, s), 4.66 (1H, t, J=8.5 Hz), 4.70 (1H, br. s), 6.15 (1H, s), 6.33 (1H, s). The IR, UV and ^{1}H-NMR spectra were identical with those of an authentic sample of cimifugin. Yield 0.033%.

(3*S*)-2,2-Dimethyl-3,5-dihydroxy-8-hydroxymethyl-3,4-dihydro-2*H*,6*H*-benzo[1,2-*b*: 5,4-*b*′]dipyran-6-one (VI)——Recrystallized from hexane–EtOAc to give pale yellow needles, mp 172—172.5°C. It gave a deep green coloration with Gibbs reagent and ammonia aq. and it gave a positive (dark violet coloration) ferric chloride reaction. *Anal.* Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.82; H, 5.38. ORD (c=0.72, EtOH) $[\alpha]^{18}$ (nm): −22.3° (589), −27.8° (550), −41.7° (500), −66.8° (450), −130.7° (400). IR ν_{max}^{Nujol} cm^{-1}: 3390 (OH), 1650 (CO), 1620, 1570 (arom.). UV λ_{max}^{EtOH} nm (log ε): 222.5 (4.47), 250 (4.48), 256 (4.48), 295 (4.23), 320 (3.86). UV $\lambda_{max}^{EtOH+AlCl_3}$ nm: 258, 306, 350. ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ ppm: 1.34 (6H, s), 2.47 (1H, dd, J=17.0 and 7.5 Hz), 2.93 (1H, dd, J=17.0 and 6.0 Hz), 3.72 (1H, dd, J=7.5 and 6.0 Hz), 4.40 (2H, d, J=7.5 Hz), 6.25 (2H, s), 4.46 (1H, s), 5.25 (1H, t, J=7.5 Hz), 13.00 (1H, s). Yield 0.006%.

Angelicain——Recrystallized from hexane–EtOAc to give colorless needles, mp 191—193°C. It gave a blue coloration with Gibbs reagent and ammonia aq. and gave a positive (dark violet coloration) ferric chloride reaction. *Anal.* Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.86; H, 5.42. ORD (c=0.60, EtOH) $[\alpha]^{27}$ (nm): +86.7° (589), +100.0° (550), +126.7° (500), +173.3° (450), +266.7° (400). IR ν_{max}^{Nujol} cm^{-1}: 3250 (OH), 1670 (CO), 1630, 1600 (arom.). UV λ_{max}^{EtOH} nm (log ε): 233 (4.35), 251 (4.29), 256 (4.30), 298 (4.17). UV $\lambda_{max}^{EtOH+AlCl_3}$ nm: 237, 266, 316, 370. ^{1}H-NMR (DMSO-d_6) δ ppm: 1.17 (6H, s), 3.06 (2H, d, J=9.0 Hz), 4.40 (2H, d, J=7.5 Hz), 4.66 (1H, s), 4.75 (1H, t, J=9.0 Hz), 5.77 (1H, t, J=7.5 Hz), 6.25 (1H, s), 6.42 (1H, s), 13.10 (1H, s). Yield 0.014%.

(3*S*)-2,2-Dimethyl-3-β-D-glucosyloxy-5-hydroxy-8-methyl-3,4-dihydro-2*H*,6*H*-benzo[1,2-*b*: 5,4-*b*′]dipyran-6-one (VIII) (*sec*-O-glucosylhamaudol)——Recrystallized from acetone to give a colorless crystalline powder, mp 207—209°C. It gave a blue-green coloration with Gibbs reagent and ammonia aq. and gave a positive (dark violet coloration) ferric chloride reaction. ORD (c=0.73, EtOH) $[\alpha]^{22}$ (nm): −40.8° (589), −51.7° (550), −65.3° (500), −81.6° (450), −122.5° (400). UV λ_{max}^{EtOH} nm (log ε): 297.5 (4.26), 257 (4.52), 251.5 (4.52), 236.5 (4.50). UV $\lambda_{max}^{EtOH+AlCl_3}$ nm: 364, 314.5, 265.5, 259. ^{1}H-NMR (DMSO-d_6) δ ppm: 1.30, 1.35 (each 3H, s), 2.36 (3H, s), 2.85 −4.90 [sugar moiety, anomeric H, 4.35 (d, J=7.5 Hz)], 6.18 (1H, s), 6.36 (1H, s), 13.18 (1H, s). Yield 0.018%.

VIII-tetraacetate (VIII-a)——A solution of VIII (500 mg) in a mixture of Ac_2O (10 ml) and pyridine (2 ml) was allowed to stand at room temperature overnight. After the reaction mixture had been treated in the usual way, the product was purified by column chromatography on silica gel with hexane–EtOAc (1: 1) and recrystallized from hexane–EtOAc to give colorless needles, mp 209—210°C. Yield 350 mg. *Anal.* Calcd for $C_{29}H_{34}O_{14}$: C, 57.42; H, 5.65. Found: C, 57.36; H, 5.56. MS m/e: 606 [M$^+$]. ORD (c=0.51, EtOH) $[\alpha]^{20}$ (nm): +1.96° (550), +1.96° (500), +3.92° (450), +11.76° (400), +23.53° (370). IR ν_{max}^{Nujol} cm^{-1}:

3500—2500 (OH), 1780, 1770, 1730, 1660 (CO), 1610, 1590 (arom.). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.30, 1.38 (each 3H, s), 1.86, 2.00, 2.05, 2.08 (each 3H, s), 2.34 (3H, s), 2.80 (2H, m), 3.80 (1H, m), 4.23—5.45 (7H, m), 6.00 (1H, s), 6.33 (1H, s), 13.13 (1H, s).

Hydrolysis of VIII——A solution of VIII (350 mg) in 10% H_2SO_4 (30 ml) was heated on a boiling water bath for 1 h. The reaction mixture was diluted with water (30 ml), and extracted with $CHCl_3$. The $CHCl_3$ solution was washed with water, dried and evaporated to dryness. The residue was chromatographed over silica gel using hexane–EtOAc (1: 1) as the eluent to give pale yellow needles, mp 197—198°C. Yield 70 mg. The IR, ^{1}H-NMR and ORD spectra were identical with those of an authentic sample of I. The aqueous layer was neutralized with $BaCO_3$, then filtered. The filtrate was evaporated to a syrup, and treated in the usual way to prepare the phenylosazone. The crude product was purified by chromatography on silica gel using EtOAc as the eluent to give yellow needles, mp 206—207°C. Yield 85 mg. The IR and ^{1}H-NMR spectra were identical with those of an authentic sample of D-glucose phenylosazone. A part of the syrup described above was subjected to TLC on avicel with HCOOH–MeCOEt–*n*-BuOH–H_2O (15: 30: 40: 15, v/v), and a spot corresponding to glucose was detected at Rf=0.22. Detection was effected with the Tollen reagent.

(2*S*)-2-(1-Hydroxy-1-methylethyl)-4-methoxy-7-*β*-D-glucosyloxymethyl-2,3-dihydro-5*H*-furo[3,2-*g*][1]-benzopyran-5-one (IX) (*prim*-O-glucosylcimifugin)——Recrystallized from $CHCl_3$ to give a colorless crystalline powder, mp 118—120°C. Bitter taste. It gave a yellow coloration with H_2SO_4 on TLC. ORD (c=0.60, EtOH) $[\alpha]^{24}$ (nm): +33.3° (589), +36.7° (550), +40.0° (500), +46.7° (450), +63.3° (400). UV λ_{max}^{EtOH} nm (log ε): 230 (4.42), 240 (4.38), 243 (4.33), 296 (4.22). ^{1}H-NMR (DMSO-d_6) δ ppm: 1.17 (6H, s), 3.86 (3H, s), 3.2—5.3 [15H, anomeric H, 4.35 (d, J=7.5 Hz)], 4.65 (2H, s), 6.37 (1H, s), 6.70 (1H, s). Yield 0.014%.

IX-pentaacetate (IX-a)——A solution of IX (200 mg) in a mixture of Ac_2O (10 ml) and pyridine (2 ml) was allowed to stand at room temperature overnight. After the reaction mixture had been treated in the usual way, the product was purified by column chromatography on silica gel with hexane–EtOAc (1: 1) to afford a colorless viscid oil (IX-a). Yield 210 mg. *Anal.* Calcd for $C_{32}H_{38}O_{16}$: C, 56.63; H, 5.64. Found: C, 56.55; H, 5.65. MS m/e: 678 [M$^+$]. ORD (c=0.44, EtOH) $[\alpha]^{20}$ (nm): +9.10° (589), +11.36° (550), +13.63° (500), +22.73° (450), +36.36° (400), +68.18° (350). ^{1}H-NMR ($CDCl_3$) δ ppm: 1.53, 1.56 (each 3H, s), 1.99, 2.02, 2.04, 2.08, 2.11 (each 3H, s), 3.15 (1H, dd, J=16 and 9 Hz), 3.40 (1H, dd, J=16 and 10 Hz), 5.15 (1H, dd, J=9 and 10 Hz), 3.97 (3H, s), 3.80—5.20 (9H, m), 6.23 (1H, s), 6.58 (1H, s).

Hydrolysis of IX——IX (350 mg) was dissolved in 10% H_2SO_4 (30 ml) and the solution was heated on a boiling water bath for 1 h, then treated in the same way as described previously to give V and glucose, which were identical with corresponding authentic samples (IR, ^{1}H-NMR and ORD spectra and TLC).

Hydrolysis of IX-a——IX-a (150 mg) was dissolved in 5% MeOH–H_2SO_4 (30 ml). The solution was heated on a boiling bath for 1 h, then cooled, diluted with water (50 ml), and extracted with $CHCl_3$. The $CHCl_3$ solution was washed with water, dried and evaporated to dryness. The residue was purified by chromatography on silica gel using EtOAc as the eluent to give V (5 mg) and a colorless viscid oil, V-a-1 (20 mg). ^{1}H-NMR of V-a-1 (DMSO-d_6) δ ppm: 1.48, 1.51 (each 3H, s), 1.93 (3H, s), 3.17 (1H, dd, J=15.0 and 6.5 Hz), 3.40 (1H, dd, J=15.0 and 9.0 Hz), 3.85 (3H, s), 4.31 (2H, d, J=7.0 Hz), 5.10 (1H, dd, J=6.5 and 9.0 Hz), 5.65 (1H, t, J=7.0 Hz), 6.07 (1H, s), 6.69 (1H, s).

Osthol (X)——Recrystallized from hexane–EtOAc to give colorless plates, mp 78—80°C. The melting point showed no depression on admixture with an authentic sample of osthol. The IR and ^{1}H-NMR spectra were identical with those of an authentic sample. Yield 0.003%.

Psoralen (XI)——Recrystallized from hexane–EtOAc to give colorless needles, mp 158—160°C. The melting point showed no depression on admixture with an authentic sample of psoralen. The IR and ^{1}H-NMR spectra were identical with those of the authentic sample. Yield 0.018%.

Isopimpinellin (XII)——Recrystallized from hexane-EtOAc to give pale yellow needles, mp 148—149°C. The melting point showed no depression on admixture with an authentic sample of isopimpinellin. The IR and ^{1}H-NMR spectra were identical with those of the authentic sample. Yield 0.016%.

Byak-angelicin (XIII)——Recrystallized from hexane–EtOAc to give yellow needles, mp 125—127°C. ORD (c=1.3, EtOH) $[\alpha]^{21}$ (nm): +17.7° (589), +21.5° (550), +26.2° (500), +33.8° (450), +40.0° (420). The melting point showed no depression on admixture with an authentic sample of byak-angelicin. The IR, ^{1}H-NMR and ORD spectra were identical with those of the authentic sample. Yield 0.02%.

Isoimperatorin (XIV)——Recrystallized from hexane–EtOAc to give colorless needles, mp 107—108°C. The melting point showed no depression on admixture with an authentic sample of isoimperatorin. The IR and ^{1}H-NMR spectra were identical with those of the authentic sample. Yield 0.018%.

Bergapten (XV)——Recrystallized from hexane–EtOAc to give colorless needles, mp 190—191°C. The melting point showed no depression on admixture with an authentic sample of bergapten. The IR and ^{1}H-NMR spectra were identical with those of the authentic sample. Yield 0.016%.

Xanthotoxin (XVI)——Recrystallized from hexane–EtOAc to give colorless needles, mp 144—145°C. The melting point showed no depression on admixture with an authentic sample of xanthotoxin. The IR and ^{1}H-NMR spectra were identical with those of the authentic sample. Yield 0.026%.

Xanthotoxol (XVII)——Recrystallized from hexane–EtOAc to give colorless needles, mp 239—240°C. The melting point showed no depression on admixture with an authentic sample of xanthotoxol. The IR

and ^{1}H-NMR spectra were identical with those of the authentic sample. Yield 0.003%.

Neobyakangelicol (XVIII)——Recrystallized from hexane–EtOAc to give yellow needles, mp 105—106°C. ORD (c=0.53, EtOH) $[\alpha]^{14}$ (nm): −7.5° (589), −11.2° (550), −14.9° (500), −18.7° (450). The melting point showed no depression on admixture with an authentic sample of neobyakangelicol. The IR, ^{1}H-NMR and ORD spectra were identical with those of the authentic sample. Yield 0.003%.

Marmesin (XIX)——Recrystallized from hexane–EtOAc to give colorless needles, mp 180—182°C. ORD (c=0.91, EtOH) $[\alpha]^{15}$ (nm): −15.4° (589), −21.9° (550), −46.2° (500), −96.7° (450), −241.5° (400). ORD (c=0.67, $CHCl_3$) $[\alpha]^{15}$ (nm): +23.9° (589), +29.8° (550), +35.8° (500), +44.8° (450), +74.6° (400). The melting point showed no depression on admixture with an authentic sample of marmesin. The IR, ^{1}H-NMR and ORD spectra were identical with those of the authentic sample. Yield 0.014%.

Oxypeucedanin Hydrate (XX)——Recrystallized from hexane–EtOAc to give colorless needles, mp 130—131°C. ORD (c=0.64, EtOH) $[\alpha]^{14}$ (nm): +25.0° (589), +31.4° (550), +37.5° (500), +50.8° (450), +78.1° (400). The melting point showed no depression on admixture with an authentic sample of oxypeucedanin hydrate. The IR, ^{1}H-NMR and ORD spectra were identical with those of the authentic sample. Yield 0.002%.

Umbelliferone (XXI)——Recrystallized from EtOAc to give a colorless crystalline powder, mp 218—222 °C. The melting point showed no depression on admixture with an authentic sample of umbelliferone. The IR and ^{1}H-NMR spectra were identical with those of the authentic sample. Yield 0.004%.

Scopoletin (XXII)——Recrystallized from EtOH to give a colorless crystalline powder, mp 202—204°C. The melting point showed no depression on admixture with an authentic sample of scopoletin. The IR and ^{1}H-NMR spectra were identical with those of the authentic sample. Yield 0.03%.

Pangeline (XXIII)——Recrystallized from hexane–EtOAc to give colorless needles, mp 123—125°C. ORD (c=0.46, EtOH) $[\alpha]^{18}$ (nm): +8.6° (589), +12.9° (550), +12.9° (500), +12.9° (450). ^{1}H-NMR (DMSO-d_6) δ ppm: 1.78 (3H, s), 4.45 (3H, m), 4.98 (1H, br. s), 5.15 (1H, br. s), 5.45 (1H, br. s), 6.40 (1H, d, J=9.5 Hz), 7.37 (1H, d, J=2.0 Hz), 7.43 (1H, s), 8.10 (1H, d, J=2.0 Hz), 8.38 (1H, d, J=9.5 Hz). The IR, ^{1}H-NMR spectra and $[\alpha]_D$ were identical with those of an authentic sample of pangeline. Yield 0.009%.

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References and Notes

1) *a*) K. Hata and A. Nitta, *Yakugaku Zasshi*, **80**, 742 (1960); *b*) A. Nitta, *ibid.*, **85**, 55 (1965); *c*) *Idem*, *ibid.*, **85**, 173 (1965); *d*) *Idem*, *ibid.*, **88**, 816 (1968); *e*) A. Nitta and H. Irie, *ibid.*, **88**, 819 (1968); *f*) *Idem*, *ibid.*, **88**, 1168 (1968).
2) The ^{1}H-NMR spectra were measured by means of a Hitachi R-40 spectrometer (90 MHz) with TMS as an internal standard.