# Isolation of Three New Sesquiterpene Lactones from the Pericarps of *Illicium majus*

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**Three new sesquiterpene lactones, majucin (3), neomajucin (4), and 2,3-dehydroneomajucin (5), have been isolated from the pericarps of Chinese *Illicium majus*, which is a toxic plant. The spectral features of compounds 3 and 4 were similar to those of anisatin (1), a convulsant from Japanese star anise. The structure of neomajucin (4) was determined by an X-ray crystallographic analysis, and the structures of the other compounds were deduced from the $^{1}$H- and $^{13}$C-nuclear magnetic resonance spectral data, aided by an extensive analysis of the $^{1}$H–$^{1}$H, $^{13}$C–$^{1}$H, and $^{13}$H–$^{1}$H long-range two dimensional shift-correlated spectra, on the basis of the structure of neomajucin. Only neomajucin exhibited picrotoxin-like toxicity, amounting to one-tenth of that of anisatin.**

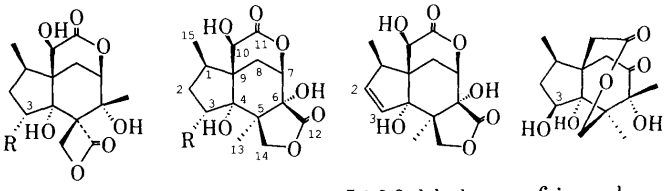
**Keywords** *Illicium majus*; Illiciaceae; majucin; anisatin; neomajucin; convulsive toxin; X-ray analysis

Japanese star anise, *Illicium anisatum* L. (Illiciaceae), is well known as a toxic plant, and is the sole species of *Illicium* genus growing in Japan. From the fruits of this plant, anisatin (**1**)[1–3] and neoanisatin (**2**)[3,4] were obtained as convulsive constituents; they are polyoxygenated sesquiterpene lactones, and have a $\beta$-lactone moiety in their structures. On the other hand, about 30 species of *Illicium* plants are known in China, and during our work on the isolation of sesquiterpene lactones from *Illicium*,[5,6] we became interested in these Chinese *Illicium* plants.[7,8] This paper deals with the isolation of three new sesquiterpene lactones together with anisatin from the pericarps of *Illicium majus* HOOK. f. *et* THOMS., which is distributed in the southern part of China and is regarded as toxic.

The MeOH extract of the pericarps (1.5 kg) of *I. majus* collected at Guangxi, China, was defatted with *n*-hexane, then partitioned between AcOEt and $H_2O$. After concentration of the AcOEt-soluble part, the major new compound, named majucin (**3**), was precipitated as crude crystals and its mother liquor was subjected to counter-current distribution to give five fractions. The separation and purification of fraction 4, achieved by chromatography over silica gel, yielded anisatin (**1**) (17 mg), **3**, and a new compound, named neomajucin (**4**) (496 mg). Another new compound, named 2,3-dehydroneomajucin (**5**), was obtained as an amorphous powder (5.3 mg) from fraction 3 by using medium-pressure liquid chromatography (MPLC). Crude majucin (**3**) was recrystallized from AcOEt to give colorless needles (2.16 g).

Compound **1** was identical (melting point, thin layer chromatography (TLC), proton and carbon-13 nuclear magnetic resonance ($^{1}$H- and $^{13}$C-NMR) spectra, and the infrared (IR) spectrum) with authentic anisatin obtained from the seeds or pericarps of *I. anisatum*.

The major compound, majucin (**3**), colorless needles (from AcOEt), mp 251—252 °C, $[\alpha]_D$ −74° ($c$=0.15, dioxane) was assigned the molecular formula $C_{15}H_{20}O_8$ from the electron impact mass (EI-MS) spectrum ($m/z$ 328 ($M^+$)) and the elemental analysis data. The IR spectrum of **3** exhibited $\gamma$- and $\delta$-lactone absorptions at 1760 and 1732 cm$^{-1}$, respectively. The $^{1}$H- and $^{13}$C-NMR spectra of **3** were very similar to those of anisatin (**1**), *i.e.*, a doublet methyl signal at $\delta$ 1.10, as well as H-10, H-7, and H-3 signals at $\delta$ 4.65, 5.14, and 5.21, respectively, were seen in the $^{1}$H-NMR spectrum of **3**, and the proton connectivities of H-15 (methyl)–H-1–H-2–H-3 and H-7–H-8 were revealed by the $^{1}$H–$^{1}$H two-dimensional shift-correlated spectrum (2D COSY) of **3**. However, it is noticeable that the singlet methyl signal (assignable to H-13 or H-14) at $\delta$ 1.95 was weakly coupled with one of the methylene signals (H-14 or H-13) of the $\gamma$-lactone at $\delta$ 5.11, indicating that they correlated with each other through the quaternary carbon C-5. These connectivities for the C-13, C-5, and C-14 carbons were also supported by the $^{13}$C–$^{1}$H long-range 2D



1 : anisatin R=OH
2 : neoanisatin R=H
3 : majucin R=OH
7 : R=OAc
4 : neomajucin R=H
5 : 2,3-dehydro-neomajucin
6 : pseudo-anisatin

Chart 1

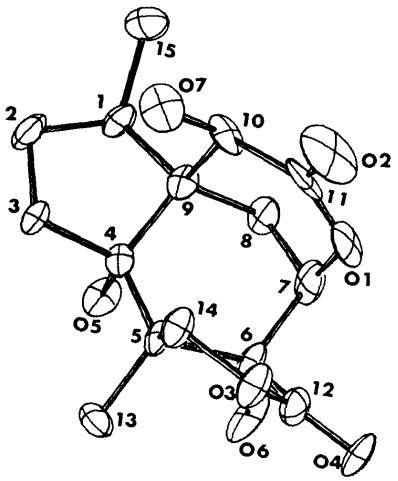


Fig. 1. Molecular Conformation for Compound **4** and Its Atomic Numbering

TABLE I. $^1$H-NMR Data for Anisatin (**1**), Majucin (**3**), Neomajucin (**4**), and 2,3-Dehydroneomajucin (**5**)

| Protons | Anisatin (**1**) | Majucin (**3**) | Neomajucin (**4**) | 2,3-Dehydroneomajucin (**5**) |
|---|---|---|---|---|
| 1 | 2.73 (qdd, 12.4, 11.0, 7.3) | 3.02 (qdd, 10.2, 9.5, 7.0) | 2.90 m | 2.96 (qdd, 7.3, 2.6, 1.5) |
| 2$\beta$ | 2.37 (ddd, 14.8, 12.4, 9.5) | 2.48 (dt, 12.6, 9.5) | 2.39 m | 5.82 (dd, 5.9, 1.5) |
| 2$\alpha$ | 2.18 (ddd, 14.8, 11.0, 4.4) | 2.21 (ddd, 12.6, 10.2, 4.4) | 2.29 m | |
| 3 | 5.57 (dd, 9.5, 4.4) | 5.21 (dd, 9.5, 4.4) | 1.85—2.05 (2H) m | 5.91 (dd, 5.9, 2.6) |
| 7 | 4.44 (dd, 3.7, 2.0) | 5.14 (dd, 3.3, 2.2) | 5.12 (dd, 2.6, 2.5) | 4.74 (dd, 6.6, 3.3) |
| 8$\beta$ | 2.04 (dd, 14.7, 3.7) | 2.05 (dd, 14.3, 3.3) | 2.00 (dd, 14.2, 2.6) | 2.29 (dd, 14.7, 3.3) |
| 8$\alpha$ | 2.73 (dd, 14.7, 2.0) | 3.11 (dd, 14.3, 2.2) | 3.01 (dd, 14.2, 2.5) | 2.83 (dd, 14.7, 6.6) |
| 10 | 4.49 (br d, 4.4) | 4.65 (br d, 4.5) | 4.66 (br d, 4.8) | 4.62 br s |
| 10-OH | 8.70 (br d, 4.4) | 8.95 (br d, 4.5) | 8.78 (br d, 4.8) | — |
| 12 | 1.79 s | — | — | — |
| 13 | — | 1.95 br s | 1.70 br s | 1.33 br s |
| 14a | 4.50 (d, 6.2) | 4.30 (d, 10.8) | 4.19 (d, 11.0) | 4.13 (d, 9.2) |
| 14b | 5.06 (d, 6.2) | 5.11 (br d, 10.8) | 5.02 (br d, 11.0) | 4.93 (br d, 9.2) |
| 15 | 1.10 (d, 7.3) | 1.10 (d, 7.0) | 1.18 (d, 7.0) | 1.24 (d, 7.3) |

400 MHz, $\delta$ from TMS in pyridine-$d_5$; $J$ (Hz) in parentheses. Assignments were aided by the $^1$H–$^1$H 2D COSY spectra.

TABLE II. $^{13}$C-NMR Data for Compounds **1**, **3**, **4**, and **5**

| Carbons | **1** | **3** | **4** | **5** |
|---|---|---|---|---|
| 1 | 37.4 | 38.0 | 39.4 | 49.5 |
| 2 | 41.9 | 42.9 | 31.4 | 140.4 |
| 3 | 71.1 | 72.7 | 31.6 | 130.5 |
| 4 | 85.4 | 82.8 | 84.1 | 97.0 |
| 5 | 26.0 | 47.5 | 47.5 | 48.6 |
| 6 | 74.8 | 79.9 | 79.6 | 78.5 |
| 7 | 81.5 | 80.6 | 80.5 | 71.8 |
| 8 | 27.5 | 27.1 | 27.5 | 29.2 |
| 9 | 50.6 | 51.5 | 51.0 | 53.7 |
| 10 | 70.0 | 70.3 | 70.7 | 73.2 |
| 11 | 174.6 | 174.7 | 174.8 | 176.6 |
| 12 | 22.0 | 177.6 | 177.2 | 177.9 |
| 13 | 168.6 | 20.9 | 21.4 | 17.9 |
| 14 | 65.2 | 72.4 | 72.6 | 74.1 |
| 15 | 13.7 | 14.1 | 14.3 | 13.5 |

Chemical shifts, $\delta$ from TMS in pyridine-$d_5$. Assignments were made with the aid of the $^{13}$C–$^1$H 2D COSY, and long-range $^{13}$C–$^1$H 2D COSY spectra.

TABLE III. Atomic Positional and Equivalent Isotropic Thermal Parameters for Compound **4** with Estimated Standard Deviations in Parentheses

| Atom | $x$ | $y$ | $z$ | $B_{eq}/B_{iso}$ |
|---|---|---|---|---|
| O1 | 0.8766 (3) | 0.0364 (3) | 0.5071 (7) | 3.3 |
| O2 | 0.7770 (3) | 0.0585 (4) | 0.3012 (8) | 4.9 |
| O3 | 0.9896 (3) | 0.1517 (3) | 0.2411 (6) | 2.7 |
| O4 | 1.0645 (3) | 0.0209 (3) | 0.3832 (7) | 3.2 |
| O5 | 0.9491 (2) | 0.3437 (3) | 0.8223 (6) | 2.5 |
| O6 | 1.0545 (3) | 0.1593 (4) | 0.7215 (7) | 3.2 |
| O7 | 0.7433 (3) | 0.2676 (4) | 0.4330 (7) | 3.6 |
| C1 | 0.7853 (4) | 0.3215 (5) | 0.8488 (9) | 2.2 |
| C2 | 0.7878 (4) | 0.4351 (5) | 0.7400 (1) | 2.8 |
| C3 | 0.8575 (3) | 0.4272 (4) | 0.5900 (9) | 2.2 |
| C4 | 0.9020 (3) | 0.3207 (4) | 0.6489 (9) | 1.7 |
| C5 | 0.9649 (3) | 0.2735 (4) | 0.5102 (9) | 1.8 |
| C6 | 0.9916 (3) | 0.1552 (5) | 0.5842 (9) | 2.2 |
| C7 | 0.9240 (4) | 0.0819 (5) | 0.6690 (1) | 2.8 |
| C8 | 0.8720 (4) | 0.1399 (5) | 0.8191 (9) | 2.5 |
| C9 | 0.8333 (3) | 0.2411 (5) | 0.7163 (9) | 2.0 |
| C10 | 0.7775 (4) | 0.1872 (5) | 0.5647 (9) | 2.6 |
| C11 | 0.8110 (4) | 0.0895 (5) | 0.4470 (1) | 3.2 |
| C12 | 1.0204 (4) | 0.1004 (5) | 0.3970 (1) | 2.4 |
| C13 | 1.0396 (3) | 0.3498 (5) | 0.4900 (1) | 2.6 |
| C14 | 0.9392 (4) | 0.2476 (5) | 0.2980 (9) | 2.3 |
| C15 | 0.7001 (4) | 0.2865 (5) | 0.9080 (1) | 3.4 |

$B_{eq} = 4/3 \times (B_{11} \times A \times A + B_{22} \times B \times B + B_{33} \times C \times C + B_{12} \times A \times B \times \cos(C) + B_{13} \times A \times C \times \cos(B) + B_{23} \times B \times C \times \cos(A))$.

COSY spectrum of **3**. As a result, it was suggested that the $\gamma$-lactone is formed between C-12 and C-14 (or C-13). The X-ray analysis of compound **4** clarified that C-14 (not C-13) is included in the $\gamma$-lactone moiety.

The stereostructures at C-1 and C-10 were elucidated by a nuclear Overhauser effect (NOE) experiment. When a doublet methyl signal (H-15) at $\delta$ 1.10 was irradiated, the H-10 signal at $\delta$ 4.65 was enhanced by 8%. Thus, the configurations at C-1 and C-10 were identical with those of anisatin (**1**).

Neomajucin (**4**), colorless octahedrons (from AcOEt), mp 220—222 °C, $[\alpha]_D$ −75° ($c$=0.25, dioxane) has the molecular formula, $C_{15}H_{20}O_7$, indicating one oxygen atom less than that of **3**. The absorptions of $\gamma$- and $\delta$-lactones were seen at 1770 and 1720 cm$^{-1}$, respectively, in the IR spectrum of **4**. The $^1$H- and $^{13}$C-NMR spectra of **4** have a strong resemblance to those of **3**, except for the appearance of the proton and carbon signals of a methylene group instead of the hydroxymethine (assigned to C-3) signals in the NMR spectra of **3**. Further, **4** gave no acetate upon usual acetylation, although **3** afforded a monoacetate (**7**). Thus, neomajucin (**4**) was considered to be the 3-deoxy compound of majucin (**3**). The structure of **4** was confirmed by an X-ray diffraction analysis. Crystallographic analysis for compound **4**, crystallized from AcOEt in the orthorhombic space group, was performed, and block-diagonal least-squares refinements with anisotropic nonhydrogen atoms and isotropic hydrogen atoms converged the $R$-value to 0.057. The atomic positional parameters, bond lengths, and bond angles are shown in Tables III, IV, and V, respectively.[9] An ORTEP drawing of **4** (nonhydrogen atoms) is shown in Fig. 1.

Consequently, the structure of **3** was elucidated as 3-hydroxy-neomajucin, and the configuration at C-3 was assigned as $\alpha$ (as shown in Chart 1) because the shape of the H-3 signal in the $^1$H-NMR spectrum of **3** was similar to that of anisatin (**1**), not to that of pseudoanisatin (**6**) which has the 3$\beta$-hydroxy group.[5]

The minor compound **5**, colorless amorphous solid, $[\alpha]_D$ −123.6° ($c$=0.11, dioxane) was suggested to have the molecular formula $C_{15}H_{18}O_7$ from the EI-MS ($m/z$ 310

Table IV. Bond Lengths (Å) for Compound **4**, with Estimated Standard Deviations in Parentheses

| | | | |
|---|---|---|---|
| O(1)–C(7) | 1.469 (8) | C(3)–C(4) | 1.530 (8) |
| O(1)–C(11) | 1.328 (8) | C(4)–C(5) | 1.522 (8) |
| O(2)–C(11) | 1.207 (9) | C(4)–C(9) | 1.558 (8) |
| O(3)–C(12) | 1.338 (8) | C(5)–C(6) | 1.570 (8) |
| O(3)–C(14) | 1.475 (7) | C(5)–C(13) | 1.548 (8) |
| O(4)–C(12) | 1.205 (7) | C(5)–C(14) | 1.547 (8) |
| O(5)–C(4) | 1.449 (7) | C(6)–C(7) | 1.540 (8) |
| O(6)–C(6) | 1.407 (7) | C(6)–C(12) | 1.516 (9) |
| O(7)–C(10) | 1.438 (8) | C(7)–C(8) | 1.511 (9) |
| C(1)–C(2) | 1.511 (8) | C(8)–C(9) | 1.543 (8) |
| C(1)–C(9) | 1.546 (8) | C(9)–C(10) | 1.535 (8) |
| C(1)–C(15) | 1.532 (9) | C(10)–C(11) | 1.527 (9) |
| C(2)–C(3) | 1.544 (9) | | |

Table V. Bond Angles (°) for Compound **4**, with Estimated Standard Deviations in Parentheses

| Atom | Angle (e.s.d.) | Atom | Angle (e.s.d.) |
|---|---|---|---|
| C(7)–O(1)–C(11) | 119.9 (4) | O(6)–C(6)–C(12) | 110.2 (3) |
| C(12)–O(3)–C(14) | 111.3 (5) | C(7)–C(6)–C(12) | 107.7 (4) |
| C(2)–C(1)–C(9) | 104.6 (5) | O(1)–C(7)–C(8) | 112.2 (3) |
| C(2)–C(1)–C(15) | 113.0 (3) | O(1)–C(7)–C(6) | 108.4 (7) |
| C(9)–C(1)–C(15) | 117.5 (4) | C(6)–C(7)–C(8) | 114.4 (4) |
| C(1)–C(2)–C(3) | 106.5 (3) | C(7)–C(8)–C(9) | 106.9 (6) |
| C(2)–C(3)–C(4) | 103.6 (5) | C(1)–C(9)–C(8) | 115.9 (7) |
| O(5)–C(4)–C(3) | 108.6 (4) | C(1)–C(9)–C(10) | 110.4 (2) |
| O(5)-C(4)–C(5) | 102.3 (2) | C(1)–C(9)–C(4) | 99.8 (3) |
| C(3)–C(4)–C)5) | 118.5 (6) | C(4)–C(9)–C(8) | 108.2 (2) |
| C(3)–C(4)–C(9) | 103.6 (2) | C(8)–C(9)–C(10) | 103.3 (3) |
| O(5)–C(4)–C(9) | 105.6 (5) | C(4)–C(9)–C(10) | 120.0 (7) |
| C(5)–C(4)–C(9) | 117.4 (4) | O(7)–C(10)–C(9) | 112.4 (4) |
| C(4)–C(5)–C(6) | 109.2 (5) | O(7)–C(10)–C(11) | 109.0 (7) |
| C(4)–C(5)–C(13) | 112.6 (4) | C(9)–C(10)–C(11) | 117.4 (3) |
| C(4)–C(5)–C(14) | 118.2 (3) | O(1)–C(11)–C(10) | 120.2 (9) |
| C(6)–C(5)–C(13) | 109.6 (3) | O(2)–C(11)–C(10) | 120.2 (5) |
| C(6)–C(5)–C(14) | 101.6 (3) | O(1)–C(11)–O(2) | 119.6 (8) |
| C(13)–C(5)–C(14) | 104.9 (5) | O(3)–C(12)–O(4) | 122.0 (12) |
| O(6)–C(6)–C(5) | 113.2 (4) | O(3)–C(12)–C(6) | 110.9 (4) |
| O(6)–C(6)–C(7) | 107.9 (6) | O(4)–C(12)–C(6) | 127.0 (12) |
| C(5)–C(6)–C(7) | 115.5 (3) | O(3)–C(14)–C(5) | 104.4 (4) |
| C(5)–C(6)–C(12) | 102.0 (5) | | |

($M^+$)) and proton and carbon counts in the $^1$H- and $^{13}$C-NMR spectra of **5**. In the IR spectrum of **5**, the absorptions of $\gamma$- and $\delta$-lactones were seen at 1770 and 1720 cm$^{-1}$, respectively. In addition to these data, the $^1$H- and $^{13}$C-NMR spectra of **5** indicated that **5** is an analogous compound to **3** and **4**; *i.e.* the signals for the six-membered ring, and $\gamma$-, and $\delta$-lactones have similarities to each other as shown in Tables I and II. But, in the signals for the five-membered ring, olefinic carbon signals were seen at $\delta$ 130.5 and 140.4 in the $^{13}$C-NMR spectrum of **5**, and the H-1 signal adjacent to a doublet methyl signal was coupled to olefinic protons, which were revealed by decoupling experiments in the $^1$H-NMR spectrum of **5**. As a result, **5** was concluded to be the 2,3-dehydro derivative of neomajucin (**4**). The assignment of two olefinic carbon signals was made from the $^{13}$C–$^1$H long-range COSY spectrum of **5**, as shown in Table II. The configurations at C-1 and C-10 were confirmed to be the same as in anisatin (**1**) by an NOE between the signals of a doublet methyl ($\delta$ 1.24) and H-10 ($\delta$ 4.62) (enhanced by 10%).

The toxicity of compounds **3** and **4** to mice was examined, and compared with that of anisatin (**1**) and neoanisatin (**2**), but compound **5** was not examined because of the small quantity available. When mice were treated with anisatin or neoanisatin, the animals exhibited picrotoxin-like convulsion, namely clonic convulsions followed by tonic extensive convulsions, in a dose-dependent manner. Neomajucin given i.p. also produced similar convulsions dose-dependently; however, majucin failed to produce any appreciable behavioral changes at doses up to 40 mg/kg. The convulsive toxicity of these compounds was the order of anisatin (**1**) ≥ neoanisatin (**2**) > neomajucin (**4**) as shown in Table VI.

Table VI. Picrotoxin-like Convulsion and Lethality Induced by Compounds **1**—**4**

| Compounds | Dose (mg/kg, i.p.) | Picrotoxin-like convulsion | Mortality | $LD_{50}$ value[a] (mg/kg) (95% confidence limits) |
|---|---|---|---|---|
| Anisatin | 0.5 | 3/5 | 0/5 | |
| (**1**) | 1 | 6/7 | 3/7 | 1.03 |
| | 2 | 7/7 | 7/7 | (0.84—1.27) |
| Neoanisatin | 1 | 4/6 | 0/6 | |
| (**2**) | 2 | 6/6 | 4/6 | 1.62 |
| | 3 | 6/6 | 6/6 | (1.01—2.59) |
| Majucin | 20 | 0/5 | 0/5 | |
| (**3**) | 40 | 0/5 | 0/5 | >40 |
| Neomajucin | 5 | 0/7 | 0/7 | |
| (**4**) | 10 | 4/6 | 1/6 | 12.2 |
| | 20 | 7/7 | 7/7 | (9.68—15.4) |

a) Litchfield–Wilcoxon method.

## Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were obtained with a JASCO IR-810 spectrophotometer, and optical rotations were measured with a JASCO DIP-181 digital polarimeter. $^1$H- and $^{13}$C-NMR spectra were recorded on a JEOL GX-400 spectrometer operating at 399.65 MHz for $^1$H and 100.40 MHz for $^{13}$C nuclei. NOE and 2D COSY experiments were performed on the same apparatus. Chemical shifts are given in $\delta$ relative to tetramethylsilane (TMS) as an internal standard. EI-MS were measured with a JEOL JMS-DX-303 spectrometer. TLC was performed on Merck precoated plate (Kieselgel 60 $F_{254}$). Column chromatography was carried out on Kieselgel 60 (Merck, Art. 7734 and 9385). MPLC was carried out on a JASCO 880-PU pump using a Kusano Si-5 column.

**Isolation** The pericarps (1.5 kg) of *Illicium majus*, collected at Guangxi, China, were extracted with MeOH three times. The combined extracts were evaporated to dryness. After being defatted with *n*-hexane, the residue was dissolved in $H_2O$, then extracted with AcOEt three times. Concentration of the AcOEt-soluble part gave crude majucin (**3**), and the mother liquor was subjected to counter-current distribution using a solvent system of $H_2O$ and AcOEt to give five fractions. Fraction 3 was purified by MPLC (solvent, $CHCl_3$–AcOEt–acetone (20:20:3)) to give majucin (**3**) and 2,3-dehydroneomajucin (**5**) (5.3 mg). A chromatographic separation of fraction 4 by silica gel (solvent, $CHCl_3$–MeOH (97:3)) afforded anisatin (**1**) (17 mg), majucin (**3**), and neomajucin (**4**) (496 mg) as crystals. Crude majucin (**3**) was combined and recrystallized from AcOEt to give colorless needles (2.16 g).

**Majucin (3)** Colorless needles from AcOEt, mp 251—252 °C, $[\alpha]_D^{24}$ −74° ($c$=0.15, dioxane). EI-MS *m/z*: 328 ($M^+$). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3550, 3520, 3400 (OH), 1760 ($\gamma$-lactone), 1732 ($\delta$-lactone). *Anal.* Calcd for $C_{15}H_{20}O_8$: C, 54.87; H, 6.14. Found: C, 54.73; H, 6.26.

**Acetylation of 3** A mixture of **3** (43 mg), dry pyridine (2 ml), and acetic anhydride (2 ml) was allowed to stand overnight at room temperature. The reaction mixture was evaporated to dryness, and the residue was chromatographed on silica gel with $CHCl_3$ as a solvent to give the monoacetate (**7**) (32 mg) as a colorless oil. EI-MS *m/z*: 370 ($M^+$). $^1$H-NMR $\delta$ ($CDCl_3$): 1.03 (3H, d, $J$=7.0 Hz, H-15), 1.31 (3H, s, H-13), 1.81 (1H, ddd, $J$=13.6, 4.8, 3.3 Hz, H-2$\alpha$), 1.93 (1H, dd, $J$=15.0, 3.3 Hz, H-8$\beta$), 2.12 (3H, s, AcO–),

2.19 (1H, dt, $J=13.6$, 9.9 Hz, H-2$\beta$), 2.66 (1H, dd, $J=15.0$, 2.2 Hz, H-8$\alpha$), 2.75 (1H, ddq, $J=9.9$, 3.3, 7.0 Hz, H-1), 4.04 (1H, d, $J=11.4$ Hz, H-14a), 4.25 (1H, br s, H-10), 4.26 (1H, br d, $J=11.4$ Hz, H-14b), 4.64 (1H, dd, $J=3.3$, 2.2 Hz, H-7), 5.45 (1H, dd, $J=9.9$, 4.8 Hz, H-3).

**Neomajucin (4)** Colorless octahedrons from AcOEt, mp 220—222 °C, $[\alpha]_D^{24}$ −75° ($c=0.25$, dioxane). EI-MS $m/z$: 312 ($M^+$). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3570, 3490 (OH), 1770 ($\gamma$-lactone), 1720 ($\delta$-lactone). *Anal.* Calcd for $C_{15}H_{20}O_7$: C, 57.68; H, 6.46. Found: C, 57.57; H, 6.58.

**Crystal Data for 4** $C_{15}H_{20}O_7$, orthorhombic, space group $P2_12_12_1$, $a=16.611$ (2), $b=11.985$ (1), $c=6.855$ (1) Å; $U=1364.7$ Å$^3$, $Z=4$, $D_c=1.52$ g·cm$^{-3}$, $\lambda$ (Cu$K_\alpha$) = 1.5418 Å. Intensity data were obtained on a Rigaku AFC-5R apparatus equipped with graphite monochromated Cu$K_\alpha$ radiation and using the $\theta$–$2\theta$ scan technique ($2\theta<128°$). Of 1318 independent reflections measured, only 1300 were considered as observed on the basis of the criterion $F_O>2\sigma(F_O)$. All intensities were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods with the MULTAN84[10] series of programs, in which RATAN was used to solve the phase problem. Refinements were made by a block-diagonal least-squares method and the hydrogen atoms were estimated from standard geometry except for those of the three hydroxy groups. The final refinements with anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors for the hydrogen atoms lowered the $R$ value to 0.057.

**2,3-Dehydroneomajucin (5)** Colorless amorphous powder, $[\alpha]_D^{23}$ −123.6° ($c=0.11$, dioxane). EI-MS $m/z$: 310 ($M^+$). IR $\nu_{max}^{Nujol}$ cm$^{-1}$: 3350 (OH), 1770 ($\gamma$-lactone), 1720 ($\delta$-lactone).

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**References and Notes**

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