# Constituents of the Seeds of *Swietenia mahagoni* JACQ. III.[1] Structures of Mahonin and Secomahoganin[2]

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**Two new tetranortriterpenoids, mahonin and secomahoganin, have been isolated from the cotyledons of seeds of *Swietenia mahagoni*. The structures of these compounds were determined by the use of two-dimensional nuclear magnetic resonance (2-D NMR) techniques ($^1$H–$^1$H correlation spectroscopy (COSY), $^1$H–$^{13}$C COSY, and $^1$H–$^{13}$C long-range COSY) and assignments of their $^1$H- and $^{13}$C-NMR signals were performed. A possible biosynthetic pathway to these tetranortriterpenoids is proposed.**

**Keywords** *Swietenia mahagoni*; Meliaceae; tetranortriterpenoid; mahonin; secomahoganin; 2-D NMR; $^1$H–$^1$H COSY; $^1$H–$^{13}$C COSY; $^1$H–$^{13}$C long-range COSY; biogenesis

In previous papers,[1,3] the structures of sixteen new tetranortriterpenoids, swietenins B—F, 3-*O*-acetyl- and 6-*O*-acetylswietenolide, 3-*O*-tigloyl-6-*O*-acetylswietenolide, swietemahonins A—G, and swietemahonolide, isolated from the cotyledons of seeds of *Swietenia mahagoni* JACQ (Meliaceae), were reported. In a continuing investigation of the oily fraction of the ether extract, we isolated two new tetranortriterpenoids, named mahonin (**1**) and secomahoganin (**2**), and their structures were determined by means of spectral methods involving two-dimensional nuclear magnetic resonance (2-D NMR) spectra. In this paper, we wish to report the structure determination of these two compounds.

Mahonin (**1**) is a minor component obtained as colorless needles, mp 148—150 °C, $[\alpha]_D$ +10.7° ($CHCl_3$), and its molecular formula was determined to be $C_{30}H_{36}O_7$ from the mass spectrum (MS) and high-resolution MS. It showed ultraviolet (UV) absorptions at 232 nm (log $\varepsilon$: 4.04) and 280 nm (log $\varepsilon$: 3.31) and infrared (IR) absorptions at 1740 (ester), 1700, 1670 ($\alpha$, $\beta$-unsaturated ketone), and 880 cm$^{-1}$

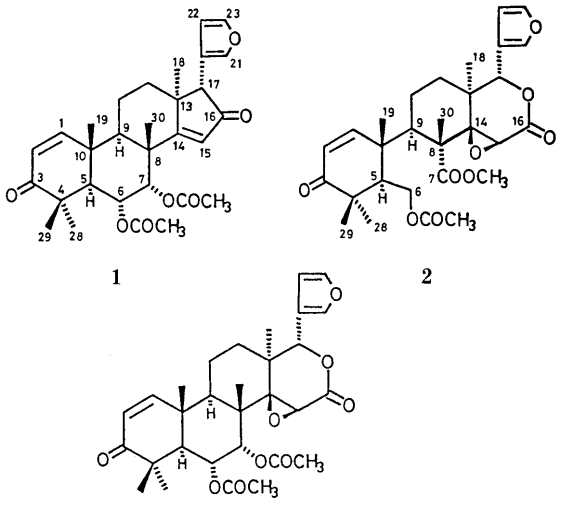

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Chart 1

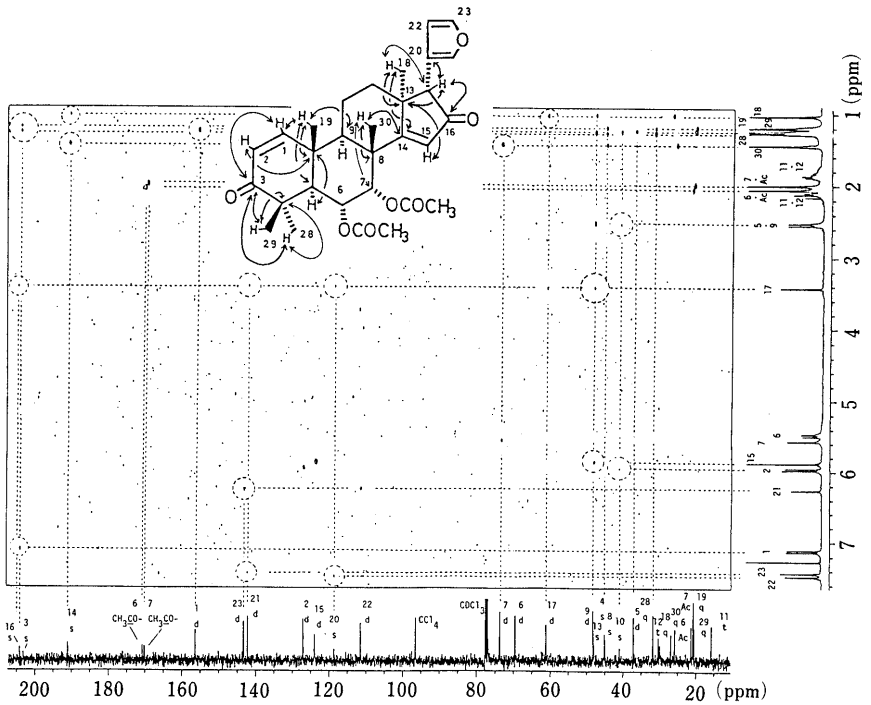

Fig. 1. Contour Map of the $^1$H–$^{13}$C Long-Range COSY Spectrum of Mahonin (**1**) in $CDCl_3$ ($J_{CH}$ = 10 Hz)

(furan). The proton nuclear magnetic resonance ($^1$H-NMR) spectrum of **1**, which was fully analyzed by the use of $^1$H–$^1$H carrelation spectroscopy (COSY),[4] indicated the presence of a $\beta$-substituted furan ($\delta$ 7.48, 6.26, and 7.43), two acetyl groups ($\delta$ 2.00 and 2.06), two acetoxyl-bearing methines ($\delta$ 5.48 and 5.57) and five *tert*-methyl groups ($\delta$ 1.03, 1.25, 1.28, 1.20, and 1.44). Further, it showed signals due to a pair of *cis*-coupled olefinic protons ($\delta$ 7.12 and 5.97, each d, $J$ = 10 Hz) and an isolated olefinic proton ($\delta$ 5.88, s), which could be ascribed to $\alpha,\beta$-unsaturated ketone groupings by considering the UV spectral data and the carbonyl absorptions in the IR spectrum. The spectral pattern fairly well resembled that of 6$\alpha$-acetoxygedunin (**3**)[3,5] except for the ring-D protons (15-H and 17-H) (Table I).

The carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectrum of **1**, analyzed with the aid of $^1$H–$^{13}$C COSY, also indicated the presence of two carbonyls ($\delta$ 203.99 and 204.60), a furan ($\delta$ 118.30, 141.72, 111.09, and 142.83), two acetyls ($\delta$ 170.17, 169.58, 21.28, and 20.81), two acetoxyl-bearing methines ($\delta$ 62.29 and 73.39), and three olefinic methines ($\delta$ 155.81, 126.67, and 123.57) along with five *tert*-methyls ($\delta$ 26.74, 20.75, 31.65, 20.46, and 25.73) (Table II). It also showed a signal at $\delta$ 190.66 (s), which may be assigned to the $\beta$-carbon of an $\alpha,\beta$-unsaturated ketone system.[6]

The above data led us to assume that the structure of mahonin might be **1**. Then, we measured the $^1$H–$^{13}$C

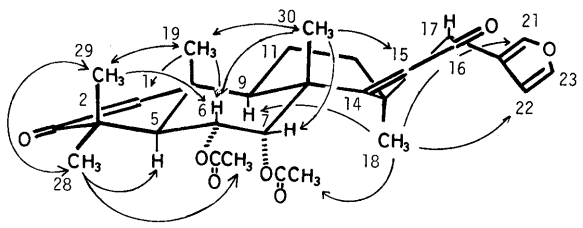


Fig. 2. NOE of Mahonin (**1**)

Table 1. $^1$H-NMR Spectral Data for Mahonin (**1**), Secomahoganin (**2**), and 6$\alpha$-Acetoxygedunin (**3**) from *Swietenia mahagoni*

| $^1$H | Compd. | | | $^1$H | Compd. | | |
|---|---|---|---|---|---|---|---|
| | **1**[a] | **2**[a] | **3**[a] | | **1**[a] | **2**[a] | **3**[a] |
| 1 | 7.12 d (10.0) | 6.68 d (10.5) | 7.07 d (10.0) | 15 | 5.88 s | 3.67 s | 3.62 s |
| 2 | 5.97 d (10.0) | 5.95 d (10.5) | 5.95 d (10.0) | 17 | 3.43[c] s | 5.43 s | 5.62 s |
| 5 | 2.54 d (12.5) | 2.07 dd (6.5, 3.5) | 2.53 d (12.5) | 21 | 7.48 dd (1.8, 0.8) | 7.39 dd (1.8, 0.8) | 7.42 dd (1.8, 1.0) |
| 6 | 5.48 dd (12.5, 2.5) | 4.23 dd (12, 6.5) | 5.28 dd (12.5, 2.5) | 22 | 6.26 dd (1.8, 0.8) | 6.35 dd (1.8, 0.8) | 6.33 dd (1.8, 1.0) |
| | | 4.68 dd (12, 3.5) | | 23 | 7.43 t (1.8) | 7.39 t (1.8) | 7.42 t (1.8) |
| 7 | 5.57 d (2.5) | — | 4.89 d (2.5) | 18[b] | 1.03 s | 1.27 s | 1.24 s |
| 9 | 2.53 m | 3.18 m | 2.54 dd (12.5, 5.0) | 19[b] | 1.25 s | 1.14 s | 1.22 s |
| 11 | 1.86 m | 1.44 m | 1.85 m | 28[b] | 1.28 s | 1.19 s | 1.26 s |
| | 2.11 m | 1.76 m | 1.98 m | 29[b] | 1.20 s | 1.16 s | 1.17 s |
| 12 | 1.86 m | 1.49 m | 1.59 m | 30[b] | 1.44 s | 1.24 s | 1.27 s |
| | 2.11 m | | 1.74 m | COOMe | — | 3.78 s | — |
| | | | | OAc | 2.00 s | 2.04 s | 2.04 s |
| | | | | | 2.06 s | | 2.15 s |

$\delta$ Values in $CDCl_3$. Values in parentheses are coupling constants (Hz). *a*) $^1$H–$^1$H Correlation spectra were measured. *b*) Assignments were confirmed by NOE experiments. *c*) Long-range coupling with 18-$H_3$ was observed in $^1$H–$^1$H COSY.

Table II. $^{13}$C-NMR Spectral Data for Mahonin (**1**), Secomahoganin (**2**), and 6$\alpha$-Acetoxygedunin (**3**) from *Swietenia mahagoni*

| $^{13}$C | Compd. | | | $^{13}$C | Compd. | | |
|---|---|---|---|---|---|---|---|
| | **1**[a] | **2**[a] | **3**[a] | | **1**[a] | **2**[a] | **3**[a] |
| 1 | 155.81 (d) | 151.76 (d) | 156.17 (d) | 16 | 204.60 (s) | 166.56 (s) | 167.12 (s) |
| 2 | 126.67 (d) | 126.44 (d) | 126.67 (d) | 17 | 60.91 (d) | 78.35 (d) | 78.14 (d) |
| 3 | 203.99 (s) | 202.90 (s) | 204.08 (s) | 20 | 118.30 (s) | 120.00 (s) | 120.37 (s) |
| 4 | 44.94 (s) | 45.29 (s) | 44.99 (s) | 21 | 141.72 (d) | 141.04 (d) | 141.25 (d) |
| 5 | 36.93 (d) | 48.07 (d) | 38.45 (d) | 22 | 111.09 (d) | 110.00 (d) | 109.86 (d) |
| 6 | 62.29 (d) | 62.78 (t) | 69.67 (d) | 23 | 142.83 (d) | 143.09 (d) | 143.15 (d) |
| 7 | 73.39 (d) | 175.36 (s) | 72.64 (d) | 18 | 26.74 (q) | 19.53 (q) | 17.91 (q) |
| 8 | 44.74 (s) | 50.71 (s) | 43.12 (s) | 19 | 20.75 (q) | 17.85 (q) | 21.44 (q) |
| 9 | 47.99 (d) | 43.15 (d) | 47.86 (d) | 28 | 31.65 (q) | 24.44 (q) | 31.71 (q) |
| 10 | 40.81 (s) | 43.44 (s) | 40.63 (s) | 29 | 20.46 (q) | 23.31 (q) | 20.31 (q) |
| 11 | 15.80 (t) | 32.36 (t) | 15.07 (t) | 30 | 25.73 (q) | 15.45 (q) | 18.17 (q) |
| 12 | 30.14 (t) | 22.10 (t) | 25.92 (t) | $COO\underline{C}H_3$ | — | 53.14 (q) | — |
| 13 | 47.83 (s) | 37.96 (s) | 38.81 (s) | 6-$O\underline{C}OCH_3$ | 170.17 (s) | 170.69 (s) | 170.12 (s) |
| 14 | 190.66 (s) | 68.17 (s) | 47.86 (s) | 6-$OCO\underline{C}H_3$ | 21.28 (q) | 21.20 (q) | 21.00 (q) |
| 15 | 123.57 (d) | 51.47 (d) | 56.27 (d) | 7-$O\underline{C}OCH_3$ | 169.58 (s) | — | 170.05 (s) |
| | | | | 7-$OCO\underline{C}H_3$ | 20.81 (q) | — | 21.26 (q) |

$\delta$ Values in $CDCl_3$. The multiplicities of carbon signals are indicated as s, d, t, and q. *a*) $^1$H–$^{13}$C and $^1$H–$^{13}$C long-range COSY spectra were measured.

long-range COSY[7] (Fig. 1) of **1** in order to confirm the assumed structure (**1**). As expected, the $^{13}C$-signals at $\delta$ 204.60 (C-16) and 203.99 (C-3) showed long-range correlations with the $^{1}H$-signals at $\delta$ 3.43 (17-H) and at $\delta$ 1.20 (29-$H_3$), 1.28 (28-$H_3$), and 7.12 (1-H), respectively. Also, the $^{13}C$-signals at $\delta$ 190.66 (C-14), 47.83 (C-13), and 40.81 (C-10) were correlated with the $^{1}H$-signals at $\delta$ 1.03 (18-$H_3$) and 1.44 (30-$H_3$), at $\delta$ 1.03 (18-$H_3$), 3.43 (17-H), and 5.88 (15-H), and at $\delta$ 1.25 (19-$H_3$), 2.54 (5-H), and 5.97 (2-H), respectively. There were other significant $^{1}H$–$^{13}C$ long-range correlations observed, some of which are shown by arrows in the formula in Fig. 1.

Thus the planar structure of mahonin was concluded to be as shown by the formula **1**.

The relative stereochemistry was elucidated on the basis of the coupling constants of each proton (Table I) and the

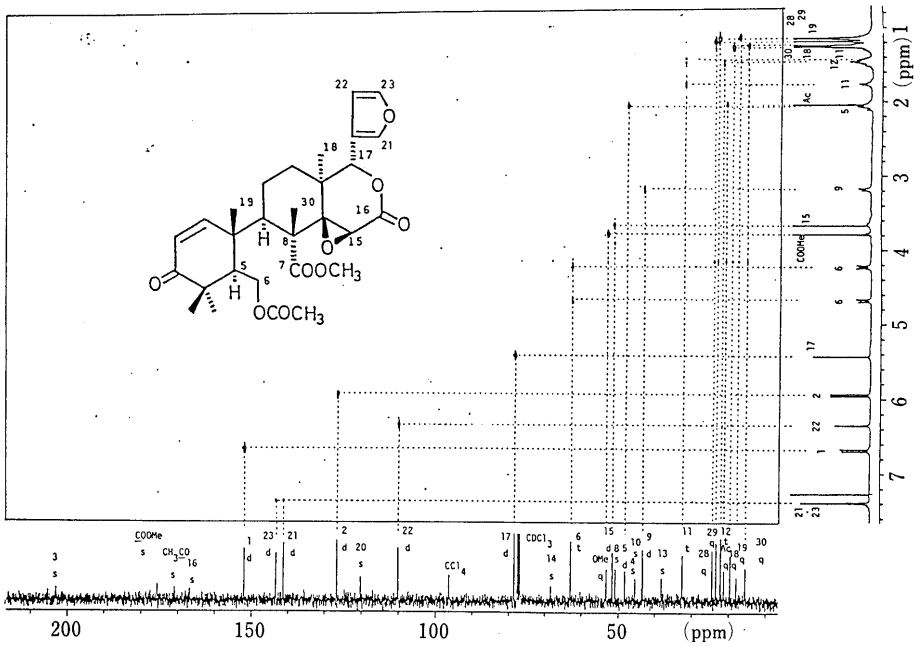


Fig. 3. Contour Map of the $^{1}H$–$^{13}C$ COSY Spectrum of Secomahoganin (**2**)

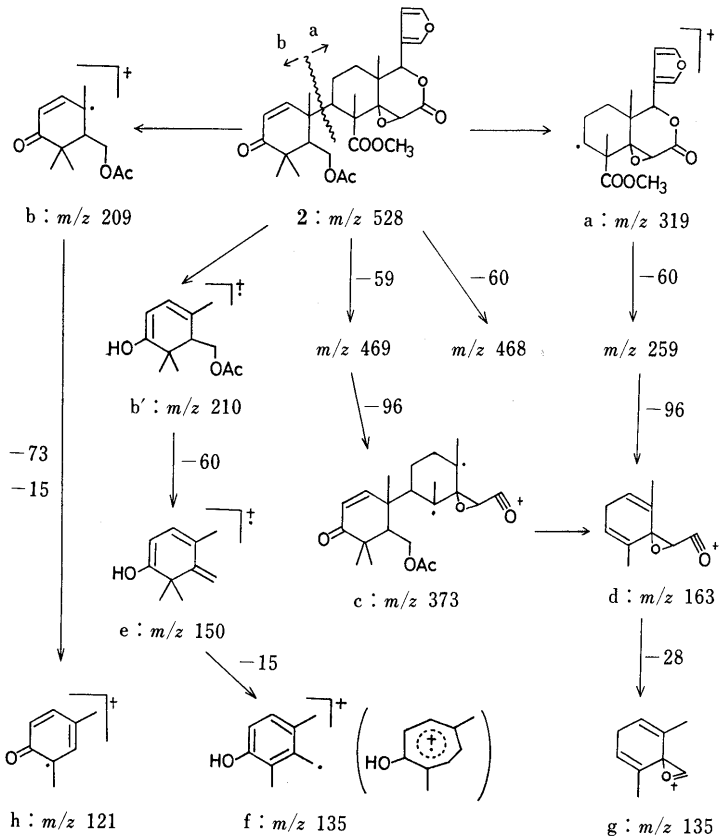


Chart 2

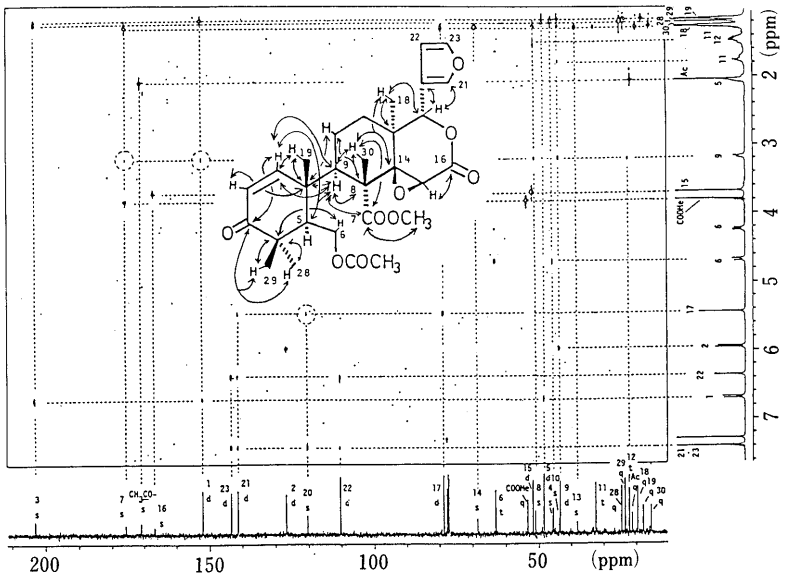


Fig. 4. Contour Map of the $^{1}H$–$^{13}C$ Long-Range COSY Spectrum of Secomahoganin (**2**) in $CDCl_3$ ($J_{CH}=10$ Hz)

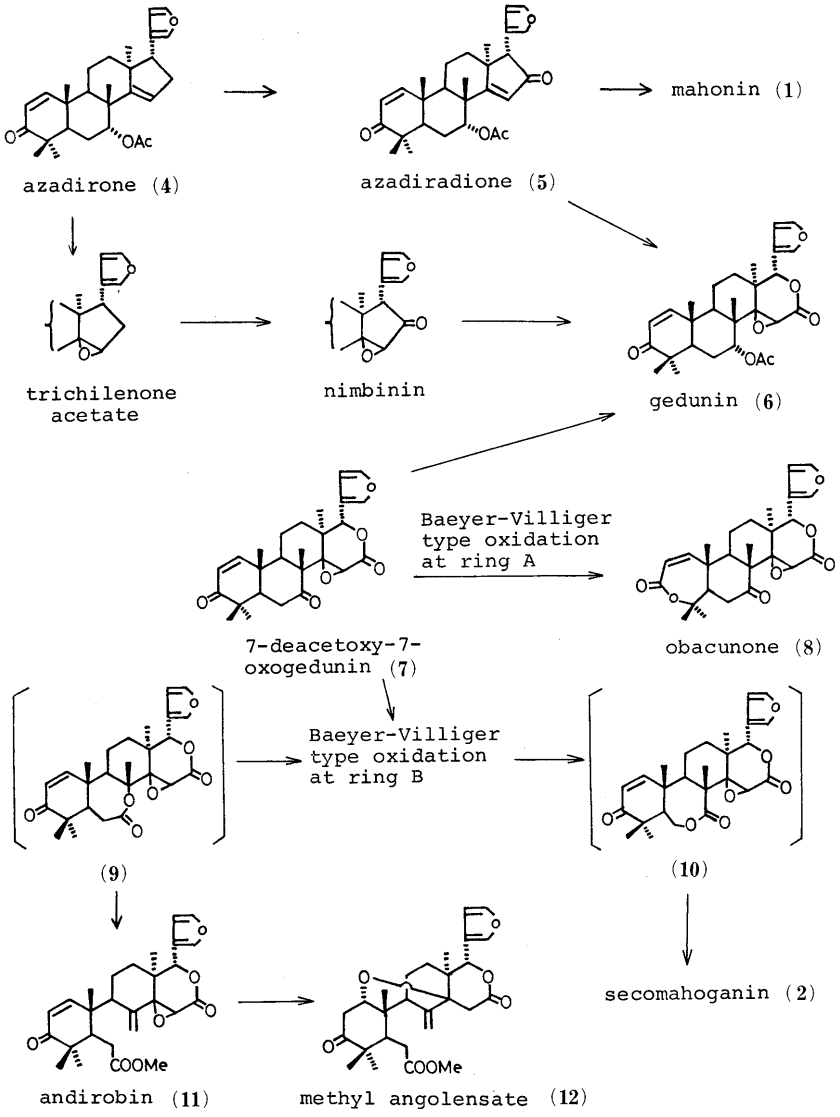


Chart 3

result of nuclear Overhauser effect (NOE) experiments. As shown in Fig. 2, irradiation at 18-$H_3$ and 19-$H_3$ caused an increase of the signal intensity of the 7-acetyl methyl, 9-, 21-, and 22-protons and the 29-, 30-, 6-, and 1-protons, respectively, and irradiation at the 28-$H_3$ and 29-$H_3$ enhanced the signal intensity of the 29-, 6-acetyl methyl, and 5-protons and the 19-, 28-, and 6-protons, respectively. Also, irradiation at the 30-$H_3$ gave NOE enhancement of the 19-, 6-, 7-, and 15-protons. Therefore the structure of mahonin was proved to be **1**,[8] in which ring C may have a boat conformation. This compound (**1**) may be biosynthesized from azadirone (**4**)[9] through azadiradione (**5**)[9] (Chart 3).

Secomahoganin (**2**) was obtained as a colorless oil, $[\alpha]_D$ $-9.5°$ ($CHCl_3$), and has the molecular formula $C_{29}H_{36}O_9$ as determined by MS and high-resolution MS. Its UV spectrum showed absorption bands at 233 nm (log $\varepsilon$: 4.20) and 285 nm (log $\varepsilon$: 2.99) and the IR spectrum exhibited absorptions attributable to a lactone (1740 $cm^{-1}$), an ester (1720 $cm^{-1}$), an $\alpha,\beta$-unsaturated ketone (1680 $cm^{-1}$), and a furan ring (1500 and 880 $cm^{-1}$). The $^1H$- and $^{13}C$-NMR spectra of **2**, analyzed with the aid of $^1H$–$^1H$ and $^1H$–$^{13}C$ COSY (Fig. 3), indicated the presence of a ketone ($\delta_C$ 202.90), an olefin group ($\delta_H$ 5.95 and 6.68; $\delta_C$ 126.44 and 151.76), an epoxy-lactone ($\delta_H$ 3.67 and 5.43; $\delta_C$ 51.47, 78.35, 166.56, and 68.17), a furan ($\delta_H$ 7.39, 6.35, and 7.39; $\delta_C$ 120.00, 141.04, 110.00, and 143.09), an acetoxyl-bearing methylene ($\delta_H$ 4.23 and 4.68; $\delta_C$ 62.78), an acetyl ($\delta_H$ 2.04; $\delta_C$ 170.69 and 21.20), a methyl ester ($\delta_H$ 3.78; $\delta_C$ 175.36 and 53.14), five *tert*-methyl groups ($\delta_H$ 1.14, 1.16, 1.19, 1.24, and 1.27; $\delta_C$ 17.85, 23.31, 24.44, 15.45, and 19.53), and four quaternary $sp^3$ carbons ($\delta_C$ 45.29, 50.71, 43.44, and 37.96) (Tables I and II).

These data led us to deduce that the structure of secomahoganin might be **2**. This was confirmed by the $^1H$–$^{13}C$ long-range COSY spectrum, which is reproduced in Fig. 4. As expected, the carbon atoms corresponding to the signals at $\delta$ 202.90 (C-3) and at $\delta$ 175.36 (C-7) were correlated with the protons corresponding to the signals at $\delta$ 1.16 (29-$H_3$), 1.19 (28-$H_3$), and 6.68 (1-H) and at $\delta$ 1.24 (30-$H_3$), 3.18 (9-H) and 3.78 ($COOCH_3$), respectively. Similarly, quaternary carbons corresponding to the signals at $\delta$ 45.29 (C-4), 50.71 (C-8), 43.44 (C-10), 37.96 (C-13), and 68.17 (C-14) could be correlated with the protons indicated by arrows in the formula in Fig. 4. Some of the significant $^1H$–$^{13}C$ long-range correlations observed are also illustrated by arrows. These data confirmed that the gross structure of this tetranortriterpenoid is represented by the formula **2**. In accordance with this conclusion, the MS of **2** revealed fragment ion peaks at *m/z* 469, 468, 373 (c), 319 (a), 259, 210 (b′), 209 (b), 163 (d), 150 (e), 135 (f and g), and 121 (h), which may be interpreted by the fragmentations shown in Chart 2. As expected, most characteristic was the fission at the $C_9$–$C_{10}$ bond without or with a hydrogen transfer, giving ions a, b, and b′. Another characteristic fragmentation of **2** was the elimination of furfuraldehyde,[10] which occurred after elimination of a carboxymethyl radical to yield ion c. Elimination of methyl formate and furfuraldehyde from ion a gave rise to ion d, which may also be formed from ion c. Ions b, b′, and d underwent further fragmentations to yield ions e, f, g, h, *etc.*

The relative stereochemistry of **2** was determined on the basis of the coupling constants of each proton and the result of NOE experiments. As shown in Fig. 5, irradiation at 19-$H_3$ and 29-$H_3$ enhanced the signal intensity of the 30-$H_3$, ester methyl, 6-, and 1-protons and the 6-proton, respectively, and irradiation at 28-$H_3$ and 30-$H_3$ enhanced the signal intensity of the 5-proton and the 19-, 15-, and 1-protons, respectively. Also, irradiation at 18-$H_3$ gave an NOE enhancement of the 9-, 15-, 22-, and 21-protons.

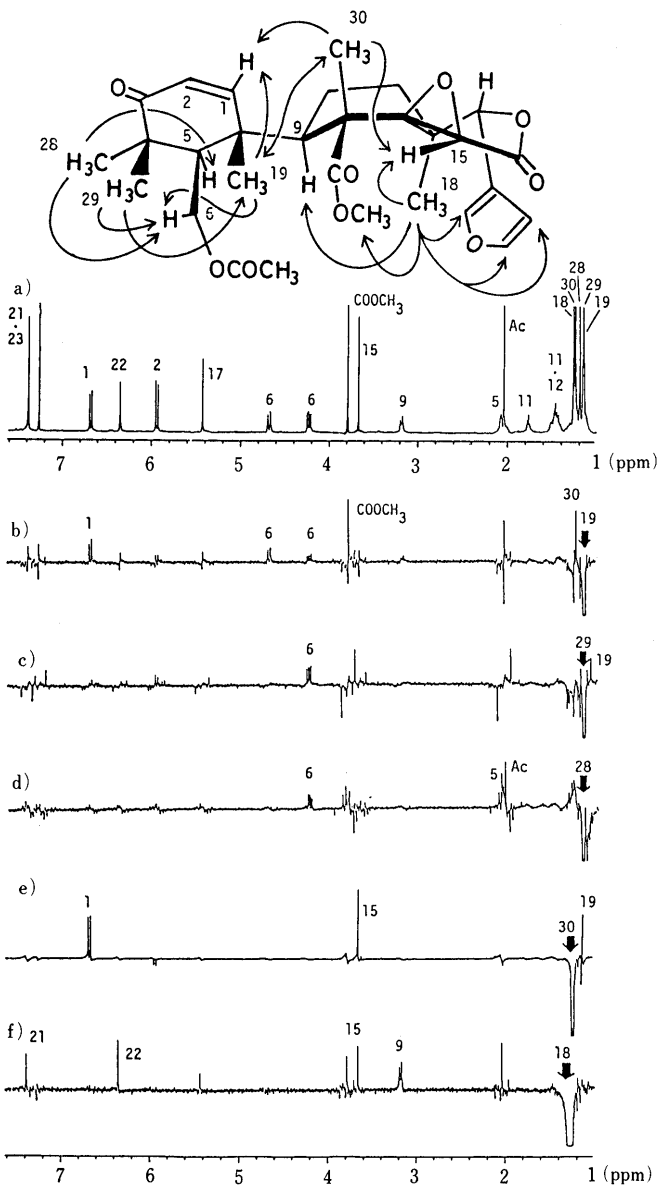


Fig. 5. $^1H$-NMR (Normal and NOE) Spectra of Secomahoganin (**2**)

a) Normal spectrum. b—f) NOE difference spectra on irradiation at $\delta$ 1.14, 1.16, 1.19, 1.24, and 1.27, respectively.

On the basis of these findings, the stereostructure of secomahoganin was determined to be as represented by the formula **2**, in which ring C has a skew-boat conformation.

Secomahoganin (**2**) is the first example of a tetranortriterpenoid formed by oxidative cleavage of the $C_{(6)}$–$C_{(7)}$ bond in the normal tetranortriterpene nucleus and is an interesting compound from a biogenetic viewpoint. As shown in Chart 3, a possible biosynthetic precursor of **2** is 7-deacetoxy-7-oxogedunin (**7**),[11] which may be synthesized from azadirone-type compounds[5,9] and co-

exists with **2** in the seeds of *S. mahagoni*.[3] Baeyer–Villiger type oxidation of **7** at the A-ring would produce an obacunone-type compound, while that at the B-ring would give lactones **9**[12] and **10**.[13] Further biotransformation of **9** would afford andirobin (**11**)[14] and methyl angolensate (**12**),[15] and **10** would give secomahoganin (**2**).

The absolute configuration and the anti-PAF (platelet-activating factor) activity of the above compounds are currently under investigation.

## Experimental

Melting points were determined with a Kofler-type apparatus and are uncorrected. Optical rotations were measured in chloroform solution on a JASCO DIP-4 automatic polarimeter at 20—22 °C. UV spectra were taken with a Shimadzu 202 UV spectrometer in EtOH solutions and IR spectra were taken with a JASCO IRA-2 spectrometer in chloroform solution. $^1$H- and $^{13}$C-NMR spectra were taken on a JEOL GX-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard, and chemical shifts are recorded in $\delta$ values. $^1$H–$^1$H COSY, $^1$H–$^{13}$C COSY, and $^1$H–$^{13}$C long-range COSY were measured under the same conditions as described in a previous paper.[3] MS and high-resolution MS were obtained with a JEOL JMS-D 300 spectrometer (ionization voltage, 70 eV; accelerating voltage, 3 kV) using a direct inlet system. Column chromatography was done with Mallinkrodt silica gel. Preparative thin-layer chromatography (TLC) was carried out on Merck Kieselgel $GF_{254}$ plates and the plates were examined under UV light. Extraction of substances from silica gel was done MeOH–$CH_2Cl_2$ (1 : 9 or 3 : 7) and solutions were concentrated *in vacuo*. TLC analyses were done on Merck Kieselgel $GF_{254}$ plates; the developed plates were examined under UV light.

**Isolation and Properties of Tetranortriterpenoids from the Cotyledons of *Swietenia mahagoni*** Details of the extraction and isolation of tetranortriterpenoids from the cotyledon part (700 g) of seeds (1.8 kg) of *Swietenia mahagoni* were described in our previous paper[3]; *viz.*, a portion (100 g) of the oily fraction of the ether extract was separated by a combination of silica gel column chromatography and preparative TLC to give mahonin (**1**) (5.3 mg) and secomahoganin (**2**) (10.5 mg) together with other tetranortriterpenoids.

Mahonin (**1**): Colorless needles (from AcOEt–isopropyl ether), mp 148—150 °C, $[\alpha]_D$ +10.7° ($c$=0.83). UV $\lambda_{max}$ nm (log $\varepsilon$): 232 (4.04), 280 (3.31). IR $\nu_{max}$ cm$^{-1}$: 1740, 1700, 1670, 1500, 880. $^1$H- and $^{13}$C-NMR: Tables I and II. MS $m/z$ (%): 508 ($M^+$) (100), 493 ($M^+-15$) (25), 389 ($M^+-60-59$) (9), 340 (11), 315 (11). High-resolution MS $m/z$: Found 508.2469, Calcd for $C_{30}H_{36}O_7$ ($M^+$) 508.2461; Found 493.2266, Calcd for $C_{29}H_{33}O_7$ 493.2227; Found 389.2133, Calcd for $C_{26}H_{29}O_3$ 389.2117.

Secomahoganin (**2**): Colorless oil, $[\alpha]_D$ −9.5° ($c$=1.0). UV $\lambda_{max}$ nm (log $\varepsilon$): 233 (4.20), 285 (2.99). IR $\nu_{max}$ cm$^{-1}$: 1740, 1720, 1680, 1500, 880. $^1$H- and $^{13}$C-NMR: Tables I and II. MS $m/z$ (%): 528 ($M^+$) (29), 469 (5), 468 (10), 373 (c) (12), 319 (a) (29), 259 (10), 210 (b′) (20), 209 (b) (15), 163 (d) (18), 150 (e) (100), 135 (f and g) (39), 121 (h) (37). High-resolution MS $m/z$: Found 528.2338, Calcd for $C_{29}H_{36}O_9$ ($M^+$) 528.2358; Found 469.2203, Calcd for $C_{27}H_{33}O_7$ 469.2225; Found 468.2132, Calcd for $C_{27}H_{32}O_7$ 468.2148; Found 373.2044, Calcd for $C_{22}H_{29}O_5$ 373.2016; Found 319.1197, Calcd for $C_{17}H_{19}O_6$ 319.1182; Found 259.0970, Calcd for $C_{15}H_{15}O_2$ 295.0991; Found 210.1237, Calcd for $C_{12}H_{18}O_3$ 210.1255; Found 209.1172, Calcd for $C_{12}H_{17}O_3$ 209.1177; Found 163.0762, Calcd for $C_{10}H_{11}O_2$ 163.0759; Found 150.1015, Calcd for $C_{10}H_{14}O$ 150.1043; Found 135.0796, Calcd for $C_9H_{11}O$ 135.0809; Found 121.0673, Calcd for $C_8H_9O$ 121.0653.

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