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MAHONIN AND SECOMAHOGANIN, NEW TETRANORTRITERPENOIDS FROM SWIETENIA MAHOGANI (L.) JACQ

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Two new tetranortriterpenoids, mahonin and secomahoganin, have been isolated from the cotyledons of Swietenia mahogani and their structures have been determined by means of 2-D NMR spectroscopy.

KEYWORDS Swietenia mahogani; mahonin; secomahoganin; tetranortriterpenoid; 2-D NMR

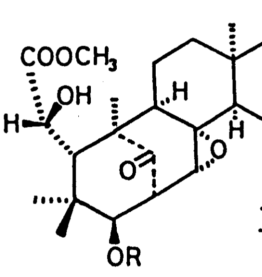
In a preceding communication,1) we reported the isolation and structure determination of three new tetranortriterpenoids having an antagonistic effect on PAF2) (platelet activating factor), swietemahonin A (1) and E (2), and 3-acetylswietenolide, from the cotyledons of Swietenia mahogani (L.) JACQ.3) In continuing investigation of the oily fraction of the ether extract, we isolated two new tetranortriterpenoids, named mahonin (3) and secomahoganin (4). In this paper we describe the structures of 3 and 4.

Mahonin (3), colorless needles, mp 148 - 150°C, $[\alpha]_D$ +10.7° ($CHCl_3$), has the molecular formula $C_{30}H_{36}O_7$ (M^+ 508.2469, calcd. 508.2461) and showed IR absorptions at 1740 (ester), 1700, 1670 (α,β-unsaturated ketone), and 880 cm^{-1} (furan).

The ^1H-NMR spectrum of 3 exhibited signals due to a furan (δ 7.48, 6.26, and 7.43), two α,β-unsaturated ketone (δ 7.12 and 5.97, each 1H, d, J = 10 Hz; 5.88 1H, s), two acetyl groups (δ 2.00 and 2.06), and two acetoxy-bearing methines (δ 5.48 and 5.57) along with five tert-methyl signals (δ 1.03, 1.25, 1.28, 1.20, and 1.44) (Table I). The ^{13}C-NMR spectrum of 3, analyzed with the aid of ^1H-^{13}C COSY, indicated the presence of two carbonyls (δ 203.99 and 204.60), a furan (δ 118.30, 141.72, 111.09, and 142.83), two acetyls (δ 170.17, 169.58, 21.28, and 20.81), two acetoxy-bearing methines (δ 62.29 and 73.39), and four olefine carbons (δ 155.81, 126.67, 190.66, and 123.57) along with five tert-methyls (δ 26.74, 20.75, 31.65, 20.46, and 25.73) (Table I).

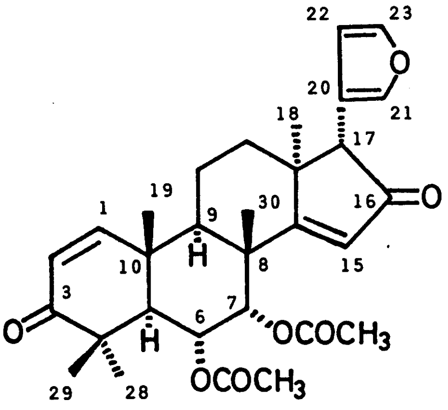
The above data led us to surmise that the structure of mahonin might be 3.

So we measured the ^1H-^{13}C long-range COSY4) spectrum of 3 to clarify the structure. As expected, the ^{13}C-signals at δ 204.60 (C-16) and at δ 203.99 (C-3) showed long-range correlations with the ^1H-signals at δ 3.43 (17-H) and at δ 1.20 (29-H_3), 1.28 (28-H_3), and 7.12 (1-H), respectively. Also, the ^{13}C-signals at δ 190.66



1: $R=\underset{O}{C}CH_2CH_3$

2: $R=\underset{O}{C}\text{-}\overset{CH_3CH_3}{C=CH}$



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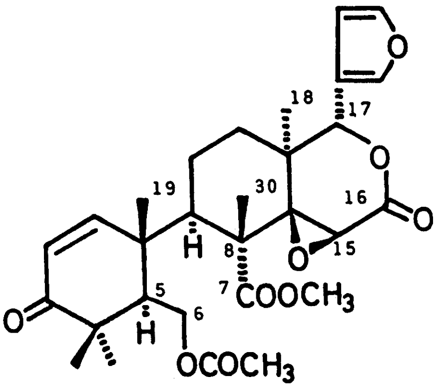
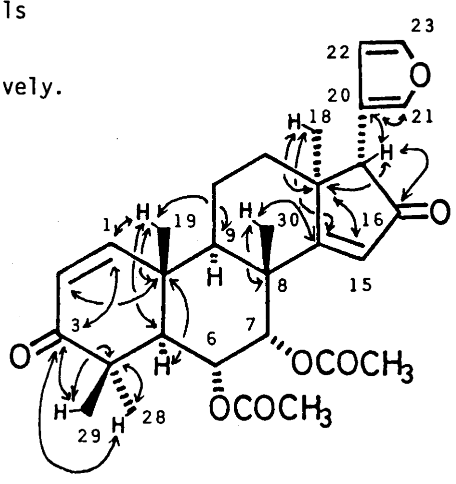


4

(C-14), 47.83 (C-13), and 40.81 (C-10) were correlated with the ^{1}H-signals at δ 1.03 (18-H_3) and 1.44 (30-H_3), at δ 1.03 (18-H_3), 3.43 (17-H), and 5.88 (15-H), and at δ 1.25 (19-H_3), 2.54 (5-H), and 5.97 (2-H), respectively.

Thus the planar structure of mahonin was assigned to the formula 3a, in which some of other significant long-range correlations observed are also shown here by arrows.



3a

The relative stereochemistry was elucidated on the basis of the coupling constants of each proton and the results of NOE experiments. Irradiation at the 18-H_3 and 29-H_3 enhanced the signal intensity of the 7-acetyl methyl, 9-, 22-, and 21-protons and the 19-, 28-, and 6-protons, respectively, and irradiation at the 19-H_3 and 28-H_3 enhanced the signal intensity of the 29-, 30-, 6-, and 1-protons and the 29- and 5-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 determined to be 3.

Secomahoganin (4), colorless oil, $[\alpha]_D$ -9.5° ($CHCl_3$), has the molecular formula $C_{29}H_{36}O_9$ (M^+ 528.2338, calcd. 528.2358) and its IR spectrum showed the presence of lactone (1740 cm^{-1}), ester (1720 cm^{-1}), α,β-unsaturated ketone (1680 cm^{-1}), and furan (1500 and 880 cm^{-1}). The ^{1}H and ^{13}C NMR and ^{1}H-^{1}H and ^{1}H-^{13}C COSY of 4 indicated the presence of a ketone (δ_C 202.90), an olefinic group (δ_H 5.95 and 6.68; δ_C 126.44 and 151.76), an epoxy-lactone (δ_H 3.67 and 5.43; δ_C 51.47, 78.35, 166.56, and 68.17), a furan (δ_H 7.39, 6.35, and 7.39; δ_C 120.00, 141.04, 110.00, and 143.09), an acetoxy-bearing methylene (δ_H 4.23 and 4.68; δ_C 62.78), an acetyl (δ_H 2.04; δ_C 170.69 and 21.20), a methyl ester (δ_H 3.78; δ_C 175.36 and 53.14), five *tert*-methyl groups (δ_H 1.14, 1.16, 1.19, 1.24, and 1.27; δ_C 17.85, 23.31, 24.44, 15.45, and 19.53), and four quaternary sp^3 carbons (δ_C 45.29, 50.71, 43.44, and 37.96) (Table I).

These data led us to surmise that the structure of secomahoganin might be 4.

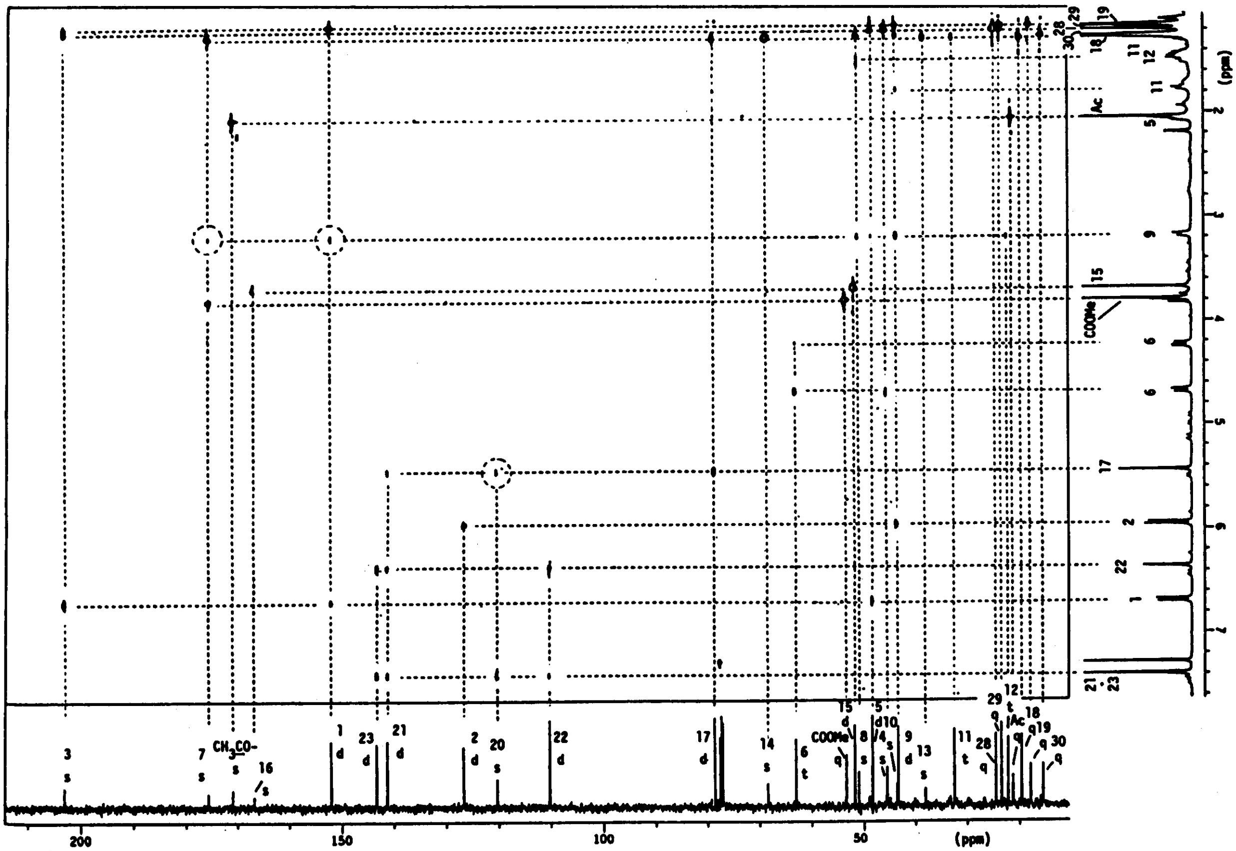


Fig. 1. ^{1}H-^{13}C Long-Range COSY Spectrum of Secomahoganin (4) in $CDCl_3$

Table I. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR Spectra of Mahonin (3) and Secomahoganin (4) in $CDCl_3$

	Mahonin (3)		Secomahoganin (4)	
Position	δ H	δ C	δ H	δ C
1	7.12 d (10)	155.81 (d)	6.68 d (10.5)	151.76 (d)
2	5.97 d (10)	126.67 (d)	5.95 d (10.5)	126.44 (d)
3	—	203.99 (s)	—	202.90 (s)
4	—	44.94 (s)	—	45.29 (s)
5	2.54 d (12.5)	36.93 (d)	2.07 dd (6.5,3.5)	48.07 (d)
6	5.48 dd (12.5,2.5)	62.29 (d)	4.23 dd (12,6.5) 4.68 dd (12,3.5)	62.78 (t)
7	5.57 d (2.5)	73.39 (d)	—	175.36 (s)
8	—	44.74 (s)	—	50.71 (s)
9	2.53 m	47.99 (d)	3.18 m	43.15 (d)
10	—	40.81 (s)	—	43.44 (s)
11	1.86 m 2.11 m	15.80 (t)	1.44 m 1.76 m	32.36 (t)
12	1.86 m 2.11 m	30.14 (t)	1.49 m	22.10 (t)
13	—	47.83 (s)	—	37.96 (s)
14	—	190.66 (s)	—	68.17 (s)
15	5.88 s	123.57 (d)	3.67 s	51.47 (d)
16	—	204.60 (s)	—	166.56 (s)
17	3.43 s	60.91 (d)	5.43 s	78.35 (d)
20	—	118.30 (s)	—	120.00 (s)
21	7.48 dd (1.8,0.8)	141.72 (d)	7.39 dd (1.8,0.8)	141.04 (d)
22	6.26 dd (1.8,0.8)	111.09 (d)	6.35 dd (1.8,0.8)	110.00 (d)
23	7.43 t (1.8)	142.83 (d)	7.39 t (1.8)	143.09 (d)
18[a]	1.03 s	26.74 (q)	1.27 s	19.53 (q)
19[a]	1.25 s	20.75 (q)	1.14 s	17.85 (q)
28[a]	1.28 s	31.65 (q)	1.19 s	24.44 (q)
29[a]	1.20 s	20.46 (q)	1.16 s	23.31 (q)
30[a]	1.44 s	25.73 (q)	1.24 s	15.45 (q)
$\mathrm{COOC\underline{H}_3}$	—	—	3.78 s	—
$\mathrm{COO\underline{C}H_3}$	—	—	—	53.14 (q)
$\mathrm{6\text{-}OCOC\underline{H}_3}$	2.06 s	—	2.04 s	—
$\mathrm{6\text{-}OCO\underline{C}H_3}$	—	21.28 (q)	—	21.20 (q)
$\mathrm{6\text{-}O\underline{C}OCH_3}$	—	170.17 (s)	—	170.69 (s)
$\mathrm{7\text{-}OCOC\underline{H}_3}$	2.00 s	—	—	—
$\mathrm{7\text{-}OCO\underline{C}H_3}$	—	20.81 (q)	—	—
$\mathrm{7\text{-}O\underline{C}OCH_3}$	—	169.58 (s)	—	—

δ Values in ppm. Values in parentheses are coupling constants (Hz). The ^{1}H-^{1}H, ^{1}H-^{13}C, and ^{1}H-^{13}C long-range correlation spectra were measured. The multiplicities of carbon signals were determined by the DEPT method, and are indicated as (s), (d), (t), and (q). a) Assignments were confirmed by NOE experiments.

Next, we applied the ^{1}H-^{13}C long-range COSY of 4 in order to confirm the assumed structure (4). As shown in Fig. 1, the carbon atoms corresponding to the signals at δ 202.90 (C-3) and at δ 175.36 (C-7) are correlated with the protons corresponding to the signals at δ 1.16 (29-H_3), 1.19 (28-H_3), and 6.68 (1-H) and at δ 1.24 (30-H_3) and 3.78 ($\mathrm{COOC\underline{H}_3}$), respectively. Similarly, quaternary carbons corresponding to the signals at δ 45.29 (C-4), 50.71 (C-8), 43.44 (C-10), 37.96 (C-13), and 68.19 (C-14) can be correlated with the protons indicated by arrows in the formula (Fig. 1). Also, some of significant ^{1}H-^{13}C long-range correlations observed are illustrated by arrows. These data show that the gross structure of this compound is represented by the formula 4.

The relative stereochemistry of 4 was determined on the basis of the coupling constants of each proton and the results of NOE experiments. Irradiation at the 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 the 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 the 18-H_3 gave NOE enhancement of the 9-, 15-, 22-, and 21-protons.

On the basis of these findings, the structure of secomahoganin was determined to be as represented by the formula 4.

Secomahoganin (4) is the first example of a tetranortriterpenoid[5)] formed by oxidative cleavage of the $C_{(6)}$-$C_{(7)}$ bond in the normal tetranortriterpene nucleus. This compound is of interest from a biogenetic viewpoint. The absolute configurations and the anti-PAF activities of the above compounds are currently under investigation.

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