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The Structure of a New Antifeeding Meliacarpinin from Chines *Melia azedarach* L.

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A new azadirachtin related antifeedant, 1-deoxy-3-tigloyl-11-methoxymeliacarpinin, was isolated from the root bark of Chinese *Melia azedarach* L. It inhibited completely the feeding of the larvae of *S. exigua* (Boisduval) at the concentration of 3 μg/cm^2 by the leaf disk method.

Melia azedarach L. (Meliaceae), the Chinaberry or Persian lilac tree, has long been recognized as a medicinal and insecticidal plant.1) One of the constituents isolated from *M. azedarach* is azadirachtin,2) a highly potent limonoid insect antifeedant3) and ecdysis inhibitor.4) By insect bioassay-guided fractionation, we have isolated a new tetranortriterpenoid structurally related to azadirachtin, with equipotent antifeedant activity, from the ethereal extract of the root bark of Chinese *M. azedarach* collected at Guangzhou in China. Herein we report the structure of this new antifeedant, designated as 1-deoxy-3-tigloyl-11-methoxymeliacarpinin (**1**).

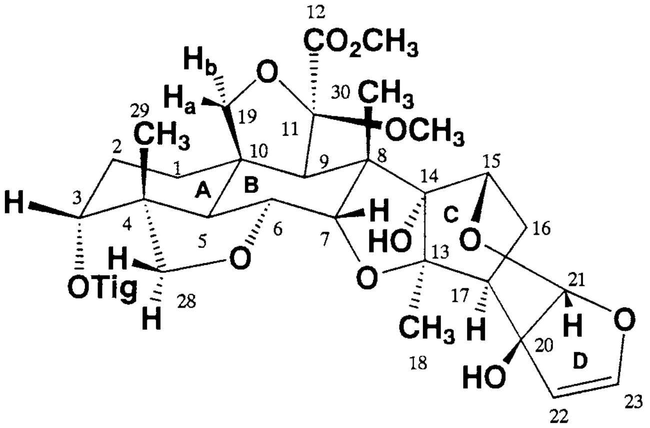
During the investigation of limonoid antifeedants from Meliaceae plants, we got **1** (0.8 mg) along with several intact apo-euphol limonoids5) with a 14,15-epoxide and a 19/29 lactol bridge from the root bark (1.5 kg). Compound **1** exhibited the following spectral data; $[\alpha]_D^{23}$ -6.7°(c 0.06, MeOH); IR(KBr): 3600-3300, 1740, 1710, 1655 and 1625 cm^{-1}; UV(MeOH): 270 (ε 1500) and 213 nm (ε 4500); CD(MeOH): $\Delta\varepsilon_{233}$ +13 and $\Delta\varepsilon_{209}$ -45; ^{1}H NMR: Table 1;

^{13}C NMR: Table 2; SIMS: m/z 633 $(M+1)^+$, corresponding to molecular formula $C_{33}H_{44}O_{12}$. ^{13}C NMR (DEPT spectrum) and ^{1}H NMR (at 27° and 45°C) data indicated that **1** contained 7 CH_3, 5 CH_2, 11 CH, 10 carbons (2 alkoxycarbonyl) not bonded to hydrogen and 2 protons due to OH groups. Furthermore, the NMR spectral data suggested that the structure of **1** was similar to that of 1-tigloyl-3-acetyl-11-methoxyazadirachtinin (**2**),6) isolated from *M. azadirachta indica*. Especially, the chemical shifts for protons attached to carbons 7, 15 to 18 and 21 to 23 in **1** including 11-OMe, $-CO_2Me$, tigloyl and two OH groups were almost identical to the corresponding shifts in **2** except for the following. The signals corresponding to an additional 4β-methyl and a tigloyl groups were present instead of 3α-OAc and 4β-CO_2CH_3, respectively. These data and the NOE enhancements (Fig. 1) suggested the stereochemistry of the B, C and D rings in **1** to be same with that of **2**.

The fact that the 4β-methoxycarbonyl group in **2** was displaced by methyl in **1** was deduced from the chemical shifts of 3β-, 6β- and 28β-H. The high shifts of δ5.00, 3.90 and 3.52 compared to those (δ5.48, 4.39 and 4.03) of **2** could be attributed to the removal of the anisotropic effect of the 29-carbonyl group. The presence of the 4β-Me group was also supported from a long range coupling with 28α-H at δ3.56 and a NOE between 29-H and 19-Ha.

On the other hand, the substitution pattern around the A-ring, namely, that **1** has only tigloyloxy group at 3α, was deduced from the fact that a W-type long range coupling was observed between 1α-H and 19-Ha, and irradiation of 5'-H (2'-Me) of tigloyl at δ1.85 enhanced the signal due to 3β-H at δ5.00, which also showed a W-type long range coupling with 1β-H at δ1.59. From these results, structural formula **1** was deduced for 1-deoxy-3-tigloyl-11-methoxymeliacarpinin. This is the second isolation of azadirachtin related tetranortriterpenoids from *M. azedarach* L.7)

The compound **1** showed a strong antifeedant activity at the concentration of 3 μg/cm^2 against the larvae of *Spodoptera exigua* Hübner (Boisduval), voracious Japanese pest insect, by conventional leaf disk method.8)



1: 1-deoxy-3-tigloyl-11-methoxymeliacarpinin
2: 1α-OTig, 3α-OAc, 4β-CO_2CH_3

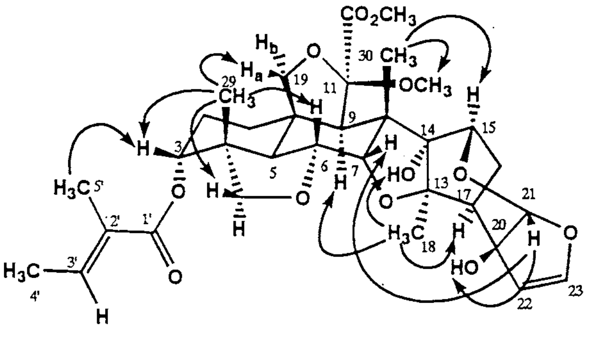


Fig. 1. Selected NOE connectivities for **1**.

Table 1. ^1H NMR Data ($CDCl_3$) for Compounds **1** and **2**

H	**1** δ Mult (J/Hz)	**2** δ Mult (J/Hz)
1α	1.38 br ddd (14.0, 14.0, 4.5)	-
1β	1.59 br d (14.0)	4.81 dd (3.1, 2.9)
2α	2.18 m	2.28 ddd (16.7, 2.9, 2.3)
2β	1.87 m	2.13 ddd (16.7, 2.9, 2.3)
3β	5.00 br t (2.8)	5.48 dd (3.3, 2.4)
5	2.73 d (12.8)	3.16 d (12.7)
6β	3.90 dd (12.9, 3.0)	4.39 dd (12.7, 3.2)
7β	4.52 d (2.9)	4.53 d (3.2)
9	3.16 s	3.56 s
15	4.12 br s	4.13 m
16a	2.20 m	2.15 m
16b	1.88 m	1.85 m
17	2.16 m	2.12 m
18	1.50 s	1.50 s
19a	4.06 br d (8.6)	4.21 d (9.7)
19b	3.96 d (8.8)	3.73 d (9.7)
21	5.63 s	5.64 s
22	4.88 d (2.9)	4.88 d (2.9)
23	6.38 d (2.9)	6.39 d (2.9)
28α	3.56 br d (7.7)	3.66 d (8.8)
28β	3.52 d (7.7)	4.03 d (8.8)
29	0.97 s	-
30	1.53 s	1.57 s
14-OH	4.20 s	4.33 s
20-OH	6.15 s	6.07 s
11-OMe	3.42 s	3.37 s
12-OMe	3.81 s	3.72 s
29-OMe	-	3.77 s
Ac	-	1.99 s
tigloyl		
3'	6.88 qq (7.0, 1.5)	6.93 qq (7.0, 1.5)
4'	1.83 dq (7.3, 1.1)	1.81 dq (7.0, 1.1)
5'	1.85 dq (1.5, 1.1)	1.85 dq (1.5, 1.1)

Table 2. ^{13}C NMR Data ($CDCl_3$) for **1** and **2**

C	**1** δ Mult	**2** δ Mult	C	**1** δ Mult	**2** δ Mult
1	24.9 t	70.3 d	20	86.2 s	86.4 s
2	33.5 t	30.2 t	21	109.4 d	109.4 d
3	70.7 d	67.0 d	22	108.0 d	108.2 d
4	42.7 s	52.9 s	23	146.0 d	146.1 d
5	39.7 d	36.3 d	28	76.8 t	no data
6	71.0 d	71.9 d	29	18.4 q	173.3 s
7	84.3 d	82.7 d	30	17.2 q	17.6 q
8	51.0 s	51.5 s	COO*Me*	52.9 q	52.9 q
9	54.8 d	47.9 d		-	53.7 q
10	49.5 s	49.8 s	11-OMe	52.3 q	52.5 q
11	106.7 s	107.3 s	MeCOO	-	169.7 s
12	170.1 s	170.1 s	*Me*COO	-	21.1 q
13	94.8 s	95.1 s	Tigloyl		
14	93.0 s	93.3 s	1'	167.0 s	166.8 s
15	81.1 d	81.4 d	2'	128.5 s	128.8 s
16	29.8 t	29.6 t	3'	138.1 d	138.2 d
17	51.3 d	50.8 d	4'	14.5 q	14.2 q
18	26.3 q	26.7 q	5'	12.1 q	12.1 q
19	71.0 t	70.4 t			

Although the activity may be weaker than that of azadirachtin, it is apparently stronger than those (6-15 μg/cm^2) of the second class limonoids[9)] such as trichilins[10)] with a 14,15-epoxide and a 19/29 lactol bridge.

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