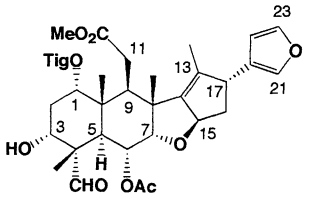
Salannal, a New Limonoid from *Melia azedarach* Linn

Munehiro Nakatani, Ruo Chun Huang,† Hiroaki Okamura, Tetsuo Iwagawa, and Kenjiro Tadera†
Department of Chemistry, Faculty of Science, Kagoshima University, Kagoshima 890
†*Department of Biochemical Science and Technology, Faculty of Agriculture, Kagoshima University, Kagoshima 890*

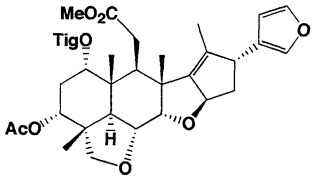
(Received July 3, 1995)

A new limonoid of biogenetic interest, salannal, was isolated along with salannin and nimbolinin B from the root of *M. azedarach* L. and the structure was elucidated by spectroscopic means.

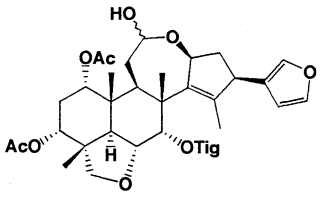
M. azedarach is a native of Persia, India and China, but naturalized in a number of continents including Africa, Australia and Americas. Thus, the constituents have been studied in many regions and various types of limonoids have been isolated; i.e., 19/29 bridged acetals, ring C-seco limonoids, azadirachtin-type meliacarpinins and degraded limonoids, etc. In the previous papers, we have reported the isolation and structures of new 19/29 bridged acetals, trichilins[1] and azedarachins,[2,3] and two new limonoids related to azadirachtins,[4] 1-deoxy-3-tigloyl-11-methoxy[5] and 1-cinnamoyl-3-acetyl-11-methoxymeliacarpinins,[6] as insect antifeedants from the bark of the Chinese and Okinawan plants.



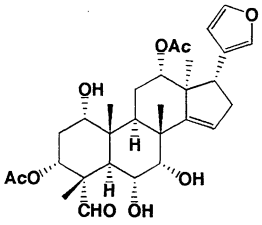
1



2



3



4

In our continuous study on the limonoids from the Chinese plant collectd at Guangzhou, we isolated a new limonoid **1**, named salannal, along with two congeners, salannin (**2**)[7] and nimbolinin B (**3**),[8] which were related to a hypothetical precursor of meriacarpinin class limonoids. This new compound **1** is a key compound together with sendanal (**4**),[9] isolated from the Japanese plant, biogenetically linking two classes of meliacane and nimbin.

Salannal (**1**; 0.7 mg), $[\alpha]_D^{20}$ +67° (MeOH), $C_{34}H_{44}O_{10}$ positive FAB-MS: m/z 613 $[M+H]^+$, was isolated along with salannin (**2**, 3.5 mg) and nimbolinin B (**3**; 1 mg) from the ether extract of the dried root bark (375 g) by flash chromatography on SiO_2 followed by careful use of normal and reversed phase HPLC. The ^1H NMR spectra at 27° (Table 1) and 45°C showed

Table 1. ^1H NMR data of salannal (**1**)

H	1	H	1
1	5.07 t (2.9)	19	0.97 s
2	2.03 m	21	7.25 m
	2.21 m	22	6.29 br s
3	3.75 dt (8.8, 2.6)	23	7.33 t (1.7)
5	3.68 d (12.1)	28	9.73 s
6	5.26 dd (12.1, 2.9)	29	1.08 s
7	4.03 d (2.6)	30	1.41 s
9	2.84 dd (8.4, 3.0)	CO_2Me	3.23 s
11	2.25 dd (15.7, 3.3)	Ac	1.98 s
	2.32 dd (15.7, 8.4)	OH	2.72 d (8.8)
15	5.48 br t (7.6)	Tig	
16	2.10 m	2'- Me	1.94 dq (1.5, 1.0)
	2.25 m	3'	6.94 qq (7.1, 1.5)
17	3.63 br d (7.8)	3'- Me	1.86 dq (7.1, 1.0)
18	1.65 br d (1.5)		

Measured in $CDCl_3$ at 400 MHz.

the presence of three tertiary and one olefinic methyls, one carbomethoxy and a formyl groups, and a 3-furyl moiety along with each one tigloyl, acetyl and hydroxyl groups. A comparison of the data with those of **2**, **3** and sendanal (**4**), and decoupling and NOE experiments strongly suggested that **1** was a salannin type ring-C cleaved limonoid with a 4α-formyl group, and allowed us to deduce the structure **1**. In particular, the abnormal high and low field shifts of 11-CO_2Me and 5α-H signals, respectively, in the spectrum of **1** clarified the presence of the 1α-tigloyloxy and 4α-formyl groups in **1**.

All of the limonoids isolated by us from *M. azedarach* L. showed antifeedant activities[1-5] against the larvae of Voisduval insects, *Spodoptera eridania* and *S. exigua* Hübner, by a conventional leaf disk method.[10] As the compounds **2** and **3** were also active at 1000 and 500 ppm, respectively, the activity of **1** was expected, but it had decomposed during structural studies before the test.

The authors would like to thank Mr. M. Nakayama, Nippon Roche Research Center, for MS measurement. We are also grateful to Mr. K. Takezaki, Kagoshima Prefectural Agricultural Experiment Station, for the supply of the insects.

References

1 M. Nakatani, R.C. Huang, H. Okamura, H. Naoki, and T. Iwagawa, *Phytochemistry*, **36**, 39 (1994).
2 R.C. Huang, H. Okamura, T. Iwagawa, and M.Nakatani, *Bull. Chem. Soc. Jpn.*, **69**, 2468 (1994).
3 R. C. Huang, H. Okamura, T. Iwagawa, K. Tadera, and M. Nakatani, *Phytochemistry*, **38**, 593 (1995).

4 W. Kraus, M. Bokel, A. Bruhn, R. Cramer, I. Klaiber, A. Klenk, G. Nagl, H. Põhnl, H. Sadlo, and B.Vogler, *Tetrahedron*, **43**, 2817 (1987).
5 M. Nakatani, R.C Huang, H.Okamura, and T. Iwagawa, *Chem. Lett.*, **1993**, 2125.
6 M. Nakatani, S. Arikawa, H. Okamura, and T. Iwagawa, *Heterocycles,* **38**, 327 (1994).
7 R. Henderson, R. McCrindle, A. Melera, and K. H. Overton, *Tetrahedron*, **24**, 1525 (1968).
8 W. Kraus and M. Bokel, *Chem. Ber.*, **114**, 267 (1981).
9 M. Ochi, H. Kotsuki, and T. Tokoroyama, *Chem. Lett.*, **1978**, 621.
10 K. wada and K. Munakata, *J. Agr. Food Chem.*, **17**, 471 (1968).