

A LIMONOID FROM *TURRAEA FLORIBUNDA*

BALDWIN TORTO, AHMED HASSANALI, EDWARD NYANDAT and MICHAEL D. BENTLEY\*

International Centre of Insect Physiology and Ecology, P.O. Box 30772, Nairobi, Kenya; \*Department of Chemistry,  
 University of Maine, Orono, ME 04469, U.S.A.

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**Key Word Index**—*Turraea floribunda*; Meliaceae; limonoids; nortriterpenoids.

**Abstract**—A novel limonoid of the havanensin class with six ester functions has been isolated from the root bark of *Turraea floribunda* and characterized by spectroscopic methods as 11 $\beta$ -acetoxy-3,7-diacetyl-4 $\alpha$ -carbomethoxy-12 $\alpha$ -isobutyryloxy-28-nor-1-tigloyl-havanensin.

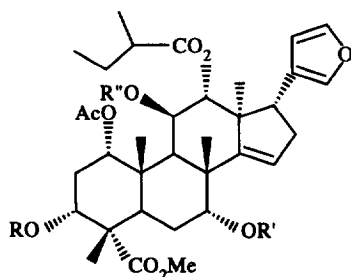
## INTRODUCTION

The seeds of *Turraea floribunda* have been reported to produce limonoids of the prieurianin class with 11 $\alpha$ ,12 $\alpha$ -substitution [1]. The rootbark of the plant, on the other hand, produces limonoids of the havanensin class with 11 $\beta$ ,12 $\alpha$ -substitution [2, 3]. In a previous paper [3] we reported the isolation from the root bark of four new havanensin-type limonoids (1–4) with a 14, 15 double bond. We have further examined fractions of the methanolic extract of the root bark and herein

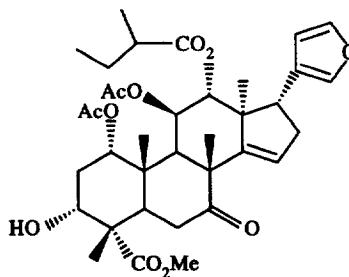
describe the isolation of a related novel limonoid, 11 $\beta$ -acetoxy-3,7-diacetyl-4 $\alpha$ -carbomethoxy-12 $\alpha$ -isobutyryloxy-28-nor-1-tigloyl-havanensin.

## RESULTS AND DISCUSSION

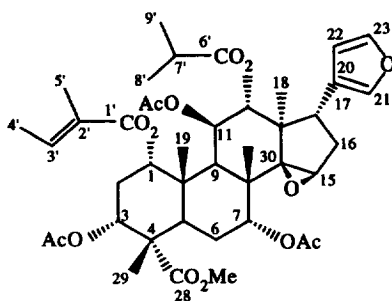
Extraction of the air-dried root bark of *T. floribunda* with methanol yielded an oil which was partitioned between chloroform and water. Chromatography of the chloroform fraction yielded a new limonoid (5). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Table 1) were consistent



- 1 R = H, R' = Ac, R'' = Ac  
 2 R = H, R' = H, R'' = H  
 3 R = H, R' = H, R'' = Ac



4



5

Table 1.  $^1\text{H}^*$  and  $^{13}\text{C}^\dagger$  NMR spectral data for limonoid [5]

Proton	$^1\text{H}$ NMR assignments	Carbon	$^{13}\text{C}$ NMR assignments
	$\delta$ (ppm), Multiplicity ( $J$ , Hz)		$\delta$ (ppm)
1	4.98, <i>t</i> (3.0)	1	74.22(1) $\ddagger$
2 $\alpha$	2.34, <i>m</i>	2	25.04(2)
2 $\beta$	2.16, <i>m</i>		
3	4.67, <i>t</i> (3.0)	3	72.44(1)
		4	40.79(0)
5	3.13, <i>dd</i> (10.6, 1.8)	5	40.23(1)
6	1.82–2.20, <i>m</i>	6	24.46(2)
7	4.71, <i>m</i>	7	73.72(1)
		8	49.02(0)
9	3.41, <i>d</i> (3.9)	9	40.54(1)
		10	40.79(0)
11	5.17, <i>t</i> (3.6)	11	74.39(1)
12	4.89, <i>d</i> (3.5)	12	79.16(1)
		13	49.74(0)
		14	73.89(0)
15	3.62, <i>s</i>	15	63.37(1)
16 $\alpha$	2.04, <i>m</i>	16	32.74(2)
16 $\beta$	2.36, <i>m</i>		
17	2.79, <i>br d</i> (9.4)	17	34.45(1)
18	1.09, <i>s</i>	18	16.86(3)
19	1.25, <i>s</i>	19	18.15(3)
		20	128.49(0)
21	7.07, <i>m</i>	21	140.47(1)
22	6.42, <i>m</i>	22	112.37(1)
23	7.28, <i>m</i>	23	142.30(1)
29	1.19, <i>s</i>	28	176.21(0) $\S$
30	1.34, <i>s</i>	29	18.92(3)
		1'	173.87(0) $\S$
		2'	128.14(0)
3'	6.85, <i>qq</i> (7, 1.5)	3'	137.72(1)
4'	1.76, <i>dq</i> (7.2, 1.1)	4'	16.86(3)
5'	1.78, <i>dq</i> (1.5, 1.1)	5'	16.86(3)
		6'	165.63(0)
7'	2.59, <i>m</i>	7'	33.52(1)
8'	1.20, <i>d</i> (7.0)	8'	14.91(3)
9'	1.22, <i>d</i> (7.0)	9'	11.85(3)
Ac(3-)	2.15, <i>s</i>	Ac(Me)	21.63(3)
Ac(7-)	2.06, <i>s</i>	Ac(Me)	21.39(3)
Ac(11-)	1.95, <i>s</i>	Ac(Me)	21.14(3)
		Ac(CO)	168.96(0) $\S$
		Ac(CO)	169.19(0) $\S$
		Ac(CO)	169.68(0) $\S$
COOMe	3.49, <i>s</i>	COOMe	51.99(3)

\*Recorded at 200 MHz in  $\text{CDCl}_3$ . $\dagger$ Recorded at 100.57 MHz in  $\text{CDCl}_3$ . $\ddagger$ The numbers in parentheses indicate number of attached protons as determined by APT. $\S$ Assignments with this superscript in same column may be reversed.

with the assignment of this compound to the havanensin group of limonoids related to those reported earlier from this plant with a 14,15-epoxide [2].

Compound **5** had a molecular formula of  $\text{C}_{42}\text{H}_{56}\text{O}_{14}$  (FAB HR-mass spectrometry). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra indicated the presence of a  $\beta$ -substituted furan, an epoxide, a carbomethoxyl group, three acetate functions, a tiglate and a 2-methylpropanoate residue and four quaternary methyls. The mass spectrum displayed fragment peaks corresponding to loss of acetic acid and C-4 and C-5 carboxylic acids. The  $^1\text{H}$  NMR

spectrum showed a proton singlet ( $\delta$  3.62) attributable to H-15, and  $^{13}\text{C}$  NMR signals ( $\delta$  73.89 and 63.37) were consistent with an epoxide at C-14 and C-15 [2, 4, 5]. The  $^1\text{H}$  COSY correlations were indicative of ester substitutions at C-1, C-3, C-7, C-11 and C-12. The COSY correlations of H-1 with H-2 and of H-3 with H-2 established the 1,3-substitution pattern of the A-ring. NOESY correlation of the H-1 triplet (3.0 Hz) with 19-Me indicated an  $\alpha$ -stereochemistry for the C-1 ester. Similarly, the stereochemistry of the C-3 and C-7 esters were deduced to be  $\alpha$  from the splitting pattern

of H-3 (*t*, 3.0 Hz) and H-7 (*m*, 3.0 Hz), respectively, and from NOESY correlations between H-3 and the 29-Me and of H-7 with the 30-Me and H-15. NOESY correlations between H-17 and H-12 and between H-9 and H-11 demonstrated the  $\alpha$ -configurations of the 12-ester and the  $\beta$ -configuration of the 11-ester, respectively.

The 2-methylpropanoate was placed at C-12 on the basis of NOESY correlations between 21-H and 18-Me and between 21-H and the methyl signal complex of the 2-methylpropanoate. The tiglate was placed at C-1 on the basis of the NOESY correlation between 2 $\alpha$ -H and the tiglate vinyl proton. Inspection of a model confirmed the close proximities of these groups in each case. The remaining three acetates, therefore, were located at C-3, C-7 and C-11. The relative stereochemistry of **5** is the same as that of the epoxides reported previously by Taylor and co-workers [2].

#### EXPERIMENTAL

**Plant material.** The root bark of *T. floribunda* was collected from Kwale National Park in the Longomagadi Forest in Kenya in May 1989. The plant was identified by Mr S. G. Mathenge (Department of Botany Herbarium, University of Nairobi) and a voucher specimen (89/401) is deposited in that department.

**Extraction and isolation.** Extraction and isolation of the limonoid employed the procedure described previously for the root bark of *T. floribunda* [3]. Briefly, a portion of the oil (22 g) obtained from the MeOH extract of the air-dried, powdered rootbark (0.9 kg) was partitioned between H<sub>2</sub>O and CHCl<sub>3</sub>. The CHCl<sub>3</sub> phase

was evapd and the residue chromatographed on silica gel (230–400 mesh) using a hexane–EtOAc gradient. Further fractionation by CC on silica gel using 10% Me<sub>2</sub>CO–toluene followed by prep. TLC on silica gel (toluene–EtOAc, 2:1) gave pure **5** (15 mg) as needles from hexane–EtOAc.

**Compound 5.** Mp 204–205°; FAB HR-MS: *m/z*: 784.3674, [M + Li]<sup>+</sup> calc. for C<sub>42</sub>H<sub>56</sub>O<sub>14</sub>Li 784.3670; EIMS *m/z* (rel. int.): 784 (5) [M]<sup>+</sup>, 724 (64) [M – HOAc]<sup>+</sup>, 696 (18) [M – C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>]<sup>+</sup>, 636 (48) [M – (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> + HOAc)]<sup>+</sup>, 576 (60) [M – (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> + 2HOAc)]<sup>+</sup>, 516 (18) [M – (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> + 3HOAc)]<sup>+</sup> and 416 (100) [M – (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> + 3HOAc + C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>)]<sup>+</sup>; <sup>1</sup>H NMR and <sup>13</sup>C NMR: Table 1.

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