

## Note

### A new lactone from aerial parts of *Tiliacora acuminata*

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A new lactone 4-hydroxy-3-[heptadeca-5'( $\varepsilon$ ),11'( $\varepsilon$ )-dienyl]-5-nonadecadihydrofuran-2(3H)-one has been isolated from the aerial parts of both male and female plants of *Tiliacora acuminata*. Its structure has been determined by spectroscopic methods and chemical reactions.

**Keywords:** *Tiliacora acuminata*, Lactone

The genus, *Tiliacora* (Tamil: *Kodaparuvavalli*) is a large, evergreen and woody climber shrub belonging to Menispermaceae. *Tiliacora acuminata* (Lam.) Miers, is typically dioecious with separate male and female plant and a valuable medicinal species. Its other names are *Cocculus acuminatus* and *Tiliacora racemosa*. Its long and flexible branches are used for thatching and weaving basket<sup>1</sup>. This plant has been used as an ingredient in many of the Ayurvedic preparations and regarded as an antidote for snake bite<sup>2</sup>. The diphenylbisbenzyl isoquinoline alkaloids tiliacorine, tiliacorinine, nortiliacorinine A, tiliarine and tiliamosine were isolated from the ethanolic extract of its roots<sup>3,4</sup>. The two alkaloids tiliaresine<sup>5</sup> and (+)N-methyl-tiliomasine<sup>6</sup> were isolated from its leaves. Earlier, an oil, acuminatide was isolated from the seeds<sup>7</sup>. In this communication is reported the isolation and characterization of a new lactone from the chloroform extract of the aerial parts of *Tiliacora acuminata*.

### Results and Discussion

The dried aerial parts of the female plant of *Tiliacora acuminata* was extracted using Soxhlet with chloroform for 8 hr. The extract was concentrated under reduced pressure and column chromatographed over silica gel. It was eluted with

hexane followed by chloroform-ethanol (9:1). The chloroform-ethanol fraction gave one compound and it was purified on preparative TLC. The compound was recrystallised from chloroform and obtained as pale yellow crystals. It was highly soluble in chloroform, diethylether, benzene and hot 10% sodium hydroxide solution. It decolourised Baeyer's reagent indicating unsaturation in the molecule and gave a positive hydroxamic test indicating the presence of lactone ring<sup>8a,b</sup>. Formation of red coloured spots developed on chromatographic plates with 1% methanolic resorcinol-5% phosphoric acid (1:1) (Ref. 9) and vaniline-H<sub>2</sub>SO<sub>4</sub> (Ref. 10) supported presence of lactone ring in it.

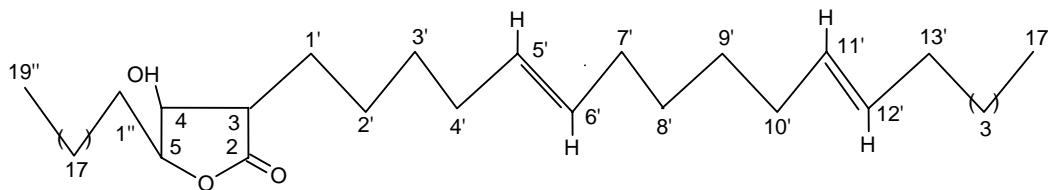
The M<sup>+</sup> peak in its mass spectrum at *m/z* 603.6 suggested a molecular formula C<sub>40</sub>H<sub>74</sub>O<sub>3</sub>. The carbon-hydrogen analysis also indicated that there are 40 carbons and 74 hydrogens. The UV-Vis spectral absorption at 200 and 210 nm indicated the presence of lactone ring<sup>11</sup>. The IR absorption at 1728 cm<sup>-1</sup> showed the presence of carbonyl group in the same lactone ring<sup>12</sup>. Other IR absorption bands which appeared are 2922 and 2852 cm<sup>-1</sup> (-CH<sub>2</sub>- str), 1663 cm<sup>-1</sup> (non-conjugated double bond), 1123 cm<sup>-1</sup> (C-OH str) and 671 cm<sup>-1</sup> (disubstituted alkene)<sup>13</sup>.

In the <sup>1</sup>H NMR spectrum (**Table I**) the signals at  $\delta$  2.3 (*td*, *J* = 12.5, 9 Hz), 4.15 (*dd*, 8.4, 8.2 Hz, 1 H, H-4) and 4.3 (*dd*, *J* = 10, 6 Hz, 1 H, H-5) agreed for the presence of lactone ring with one hydroxyl at the C-4 position. The <sup>13</sup>C NMR peaks at  $\delta$  173.1 strongly favoured the presence of carbonyl group and other prominent peaks at  $\delta$  69, 89.6 and 91.5 confirmed the existence of a lactone ring. The above spectral values are almost similar to those of the lactone ring present in acetogenins from *Porcelia macrocarpa*<sup>14</sup>.

The protons present in alkene carbon were observed as a multiplet at  $\delta$  5.1 to 5.4 (4H, H-5', H-6', H-11', H-12') and the corresponding carbons in <sup>13</sup>C NMR were at  $\delta$  127.9, 128.1, 129.7 and 130.2. The protons adjacent to carbon-carbon double bond were coupled with nearby methylene and alkene protons and appeared at  $\delta$  2.05 as a triplet of doublet with *J* values 12 and 9 Hz.

The remaining methylene protons showed peaks at  $\delta$  1.3 and 1.6 and appeared as broad singlets (38 H, H-

**Table** —  $^1\text{H}$  and  $^{13}\text{C}$  NMR characterization data of compound 1



Carbon number*	<sup>1</sup> H NMR ( $\delta$ ppm)	<sup>13</sup> C NMR ( $\delta$ ppm)
2	–	173.1
3	2.3 <i>td</i> (12.5, 9 Hz)	69
4	4.15 <i>dd</i> (8.4, 8.2 Hz)	89.6
5	4.3 <i>dd</i> (10, 6 Hz)	91.5
1'-3', 8'-9', 14', 1"	1.6 <i>brs</i>	34.2, 33.3, 31.9, 31.5
4', 7', 10', 13'	2.05 <i>td</i> (12.9 Hz)	33.6, 34
5'-6', 11'-12'	5.1-5.4 <i>m</i>	127.9, 128.1, 129.7, 130.2
15', 16', 2"-18"	1.3 <i>brs</i>	29.6, 29.3, 29.1, 28.3, 27.2, 24.8, 22.6
17', 19"	0.9 <i>t</i>	14, 16
–OH	2.8 <i>s</i>	–
CDCl <sub>3</sub> peak	7.2	76.6, 76.9, 77.3

\*Numbering as shown in structure of compound **1**  
 $(CDCl_3, ^1H: 400\text{ MHz}, ^{13}C: 100\text{ MHz})$ , *J* values are in parentheses

15', 16', 2"-18" and 14H, H-1'-3', 8'-9', 14', 1"). The triplet peak centered at  $\delta$  0.9 was due to the presence of methyl protons.

The configuration of the double bond in the long chain alkane moiety presumed to be *trans* ( $\delta$  33.6, 34) based on the chemical shifts of the adjacent carbons in the  $^{13}\text{C}$  NMR data. Usually the signals of carbons next to double bond in the case of *trans* configuration appeared at  $\delta$  32-34 in the  $^{13}\text{C}$  NMR spectroscopy<sup>15,16</sup>.

The analysis of mass spectrum revealed the presence of long alkane structure, lactone ring and a chain containing carbon-carbon double bond. The  $m/z$  values at 196, 212, 224 and 267 favoured the presence of long chain alkane structure containing 19 carbon atoms attached to the lactone ring at the fifth position. The prominent peak at  $m/z$  114 corresponded to the lactone moiety with the molecular formula  $C_5H_6O_3$ . The other fragment ions  $m/z$  170 and 149 displayed the position of double bond between C-5' and C-6' and C-11' and C-12' respectively.

The reaction with periodic acid in the presence of ruthenium chloride yielded three products hexanoic acid, adipic acid and lactone type carboxylic acids confirming the suggested molecular structure of compound **1**.

The compound isolated from male plant of *T. acuminata* using the same procedure of isolation as in female plant showed similar analytical data namely melting point, solubility, aliphatic nature, unsaturation, tests related to lactone ring, reaction with acetic anhydride and periodic acid test.

## Experimental Section

Melting points were determined using Toshiniwal capillary melting point apparatus and are uncorrected. The UV-Vis and IR spectra were taken in Varian-Cary and Brucker IF6-66V FT-IR spectrometers respectively. The solvent used for UV-Vis spectroscopic study was methanol. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded in AMX 400 instrument and the frequencies used were 400 MHz and 100 MHz respectively.

## Extraction and isolation

The aerial parts of male and female plants of *T. acuminata* were collected separately at the river bank of Cauvery, Tiruchirappalli and the Voucher specimens were deposited with Rapinat Herbarium, St. Joseph's College, Tiruchirappalli. Plant materials were air dried for twenty days.

About 500 g of the aerial parts of the female plant were extracted using Soxhlet extractor with chloroform for 8 hr. The procedure was repeated three times. Finally, the extracts were combined, concentrated under reduced pressure and the residue was subjected to column chromatography. It was eluted by hexane and chloroform-ethanol (9:1). The chloroform-ethanol fraction afforded one compound and it was further purified by preparative TLC. The homogeneity was checked on TLC in solvent systems of varying polarity.

The procedure adopted for the extraction of a compound from female plant is repeated with the male plant of *Tiliacora acuminata*. A compound from chloroform-ethanol fraction was analysed separately and correlated.

#### Compound (female plant)

$C_{40}H_{74}O_3$ : Anal. C, 79.703; H, 12.439%. m.p. 48°C,  $R_f$  = 0.82;  $[\alpha]_{28}^{2980\text{ nm}}$  +36.2° (CHCl<sub>3</sub>). Reaction with acetic anhydride<sup>17</sup> yielded an oily compound and its optical rotation was +30.6° indicating the presence of hydroxyl group. Reaction with periodic acid<sup>18,19</sup> in the presence of ruthenium chloride gave adipic acid (m.p. 152°C, Lit. m.p. 151°C) (Ref.20), hexanoic acid (b.p. >150°C, Lit. b.p. 205°C) and lactone carboxylic acid. Anal. C, 71.8; H, 11.10%.

#### Compound (male plant)

m.p. 49°C;  $R_f$  = 0.8;  $[\alpha]_{28}^{2980\text{ nm}}$  +36.4° (CHCl<sub>3</sub>). Anal. C, 79.502; H, 12.673%. It gave colour reactions and gave positive response with periodic acid and acetic anhydride tests. Reaction with periodic acid in the presence of ruthenium chloride yielded three carboxylic acids, Hexanoic acid. Anal. C, 62.1; H,

10.4%. Hexanedioic acid. Anal. C, 49.3; H, 6.80%. Lactone carboxylic acid. Anal. C, 71.85; H, 11.2%.

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