

Two new lactones and a sesquiterpenoid from the fruits of *Terminalia catappa*

Ranajit K Sutradhar*, Abdullah Al Masum

Abstract—Two new δ -lactones (1-2) along with a sesquiterpenoid 3 have been isolated from the chloroform extract of the fruits of *Terminalia catappa*. The structures of the isolated compounds were established by chemical and spectroscopic methods including IR, ^1H NMR, and ^{13}C NMR and Mass spectroscopy. The originality of this study lies in the fact that the lactones and terpenoid were reported for the first time from the fruits of *Terminalia catappa*

Keywords— *Terminalia catappa*, combretaceae, isolation, characterization, lactone, terpenoid

I. Introduction

Terminalia catappa is one of the important medicinal plants of Bangladesh. It belongs to the family Combretaceae and genus *Terminalia*. Locally it is known as Katbadam. The leaves, barks and fruits of *Terminalia catappa* are used as folk medicine at the southeastern region of Bangladesh [1]. The leaves and barks of *Terminalia catappa* have been reported as anti-cancer and hepato protective as well as anti-inflammatory, hepatitis and anti-diabetic [2,3,4,5,6]. The fruits are used in the treatment of leprosy and headaches [7]. Earlier phytochemical investigations showed the presence of different classes of compounds e.g. steroids [8,9], glycosides [10,11], flavonoids [12] in the genus *Terminalia* and the species *Terminalia catappa* showed the presence of terpenoids [13,14], flavonoids [15] along with ellagic acid, gallagic acid [16]. In continuation our studies on medicinal plants we isolate two new δ lactones (1-2) along with a sesquiterpenoid (3) from the CHCl_3 extract of the fruits of *Terminalia catappa*. In this paper, we report the isolation and structure elucidation of two new δ lactones (1-2) and a sesquiterpenoid (3).

II. Results and Discussion

The air dried powder (5 kg) of the fruits of *Terminalia catappa* was successively extracted with CHCl_3 (3 \times 72 h) and MeOH (3 \times 72 h) respectively. On removal of solvent, the CHCl_3 extract gave a deep green Mass 67 g and the MeOH extract gave a brown Mass 85 g. Fractionation and purification of CHCl_3 extract by chromatographic method afforded two new compounds 1 and 2 along with a sesquiterpenoid 3.

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Compound 1 (500 mg) was a white amorphous solid, m.p. 156-157°C. Compound 1 did not show any color test for steroid and terpenoid [17]. The IR spectrum of compound 1 showed a broad absorption band at 3340 cm^{-1} indicated the presence of hydroxyl function (OH) and an intense absorption band at 1730 cm^{-1} for carbonyl function (C=O) in the molecule. The ^{13}C NMR spectrum of compound 1 showed the presence of 17 carbons in the molecule (Table I). Its mass spectrum exhibited a molecular ion peak at m/z 280 consistent with the molecular formula of $\text{C}_{17}\text{H}_{28}\text{O}_3$ indicating a molecular weight of 280. The DEPT spectrum of 1 revealed the presence of six methylene carbons at δ 130.9 (C7), 128.8 (C8), 38.8 (C5), 30.0 (C1'), 14.1 (C2') and 11.0 (C6') and three methine carbons at δ 68.2 (C6), 31.0 (C3') and 68.2 (C4'). Two multiples at δ 7.69 and 7.52 in the ^1H NMR spectrum are attributed two sets of methylene protons attached to C7 and C8 respectively. Other four methylene protons attached to C5, C1', C2' and C6' appeared at δ 2.18 d, 1.57 m, 1.39 m and 1.38 m respectively. Three methine protons attached to C6, C3' and C4' appeared at δ 4.20 m, 2.18 m and 4.20 m respectively. The ^1H NMR spectrum of compound 1 showed four sets of methyl protons ($4\times\text{CH}_3$) absorptions as singlet at δ .91. The ^1H NMR absorption along with the carbon content of the molecule suggests the presence of a side chain as $-\text{CH}_2-\text{CH}_2-\text{CH}-(\text{CH}_3)-\text{CH}(\text{OH})-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{CH}_3$ is attached to the nucleus. The connectivity of the side chain to the nucleus with C6 can be explained by the HMBC and COSY correlations of compound 1. The important HMBC and COSY correlations are presented in Fig 1. Prominent mass peaks of compound 1 at m/z 280, 279, 262, 167, 149 (base peak), 113 can be explained nicely on the basis of the structure 1. Thus on the basis of IR, ^1H NMR, ^{13}C NMR, 2D COSY, HMBC and mass spectral data, the compound 1 is characterized as 6(4'-hydroxy-3',5',5'-trimethylheptyl)-3,4-dimethylenetetrahydro-2H-pyran-2-one and is a δ lactone and being reported for the first time in the present study.

Compound 2 (2.1g) was a white amorphous solid, m.p. 166-167°C. The IR spectrum of compound 2 showed a broad absorption band at 3340 cm^{-1} indicated the presence of hydroxyl function (OH) and an intense absorption band at 1730 cm^{-1} for carbonyl function (C=O) in the molecule. The ^{13}C NMR spectrum of compound 2 showed the presence of 17 carbons in the molecule (Table 1). Its mass spectrum exhibited a molecular ion peak at m/z 280 corresponding to the molecular formula of $\text{C}_{17}\text{H}_{28}\text{O}_3$. The ^{13}C NMR and the ^1H NMR spectra are also consistent with this formula. Compound 2 showed ^{13}C NMR and ^1H NMR spectra, which are very similar to those of compound 1 excepting the signals at carbons C5, C3', C4' and C5'. On the basis of the above spectral data structure 2 may be suggested for the compound 2. Compound 2 is thus characterized as 6-(5'-hydroxy-4', 4'-dimethylhexyl)-5, 5-dimethyl-3, 4-dimethylenetetrahydro-2H-pyran-2-one. It is also a δ lactone and being reported for the first time.

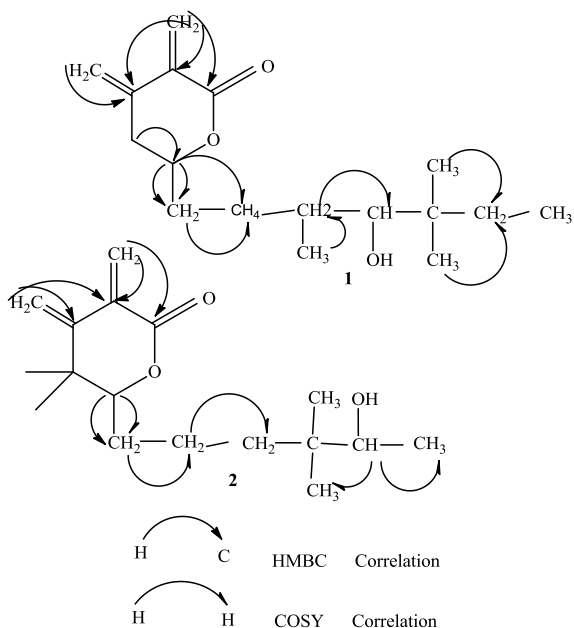


Fig.1. Important HMBC and COSY correlations of compounds **1** and **2**.

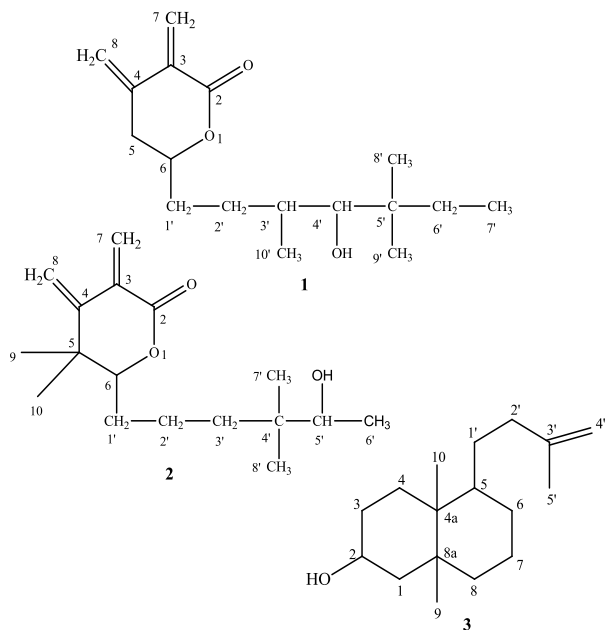


Fig. 2. Structure of compounds **1**, **2** and **3**.

TABLE I. ^{13}C NMR DATA OF COMPOUNDS 1, 2 AND 3 (100 MHz, CDCl_3)

Carbon No	Compounds		
	Compd. 1, ^{13}C , δ	Compd. 2, ^{13}C , δ	Compd. 3, ^{13}C , δ
1			29.9
2	167.8	167.8	63.5
3	132.5	132.5	29.7
4	130.9	130.9	29.4
4a			33.9
5	38.8	30.4	32.0
6	68.2	68.2	25.7
7	130.9	130.9	25.7
8	128.8	128.8	29.1
8a			33.0
9		23.8	22.7
10		23.0	21.1
1'	30.0	38.8	14.2
2'	14.1	14.1	24.7
3'	31.0	11.0	130.2
4'	68.2	30.4	130.1
5'	29.7	68.2	27.9
6'	11.0	23.8	
7'	23.0	29.7	
8'	23.8	29.0	
9'	23.8		
10'	29.0		

Compound **3** (50 mg) was a brown crystalline solid, m.p. 122-124°C. The compound gave Salkowski and Lieberman Burchard reactions for steroid and terpenoid [17]. The IR spectrum of compound **3** showed a broad absorption peak for O-H stretching at 3452 cm^{-1} . ^{13}C NMR spectrum of **3** showed the presence of 17 carbon atoms in the molecule (Table 1). The mass spectrum of **3** showed the molecular ion peak at m/z 250 and is consistent with the molecular formula $\text{C}_{17}\text{H}_{30}\text{O}$. The number of protons and carbons as suggested by NMR spectra of compound **3** are also in agreement with the molecular formula. ^1H NMR spectrum of compound **3** showed two olefinic protons at δ 5.32 and three sets methyl proton ($3 \times \text{CH}_3$) absorption as a broad singlet at δ .86 while the methyl proton attached to $\text{C}5'$ appeared at δ 1.60. ^{13}C NMR spectrum of compound **3** revealed the presence of 17 carbon atoms in the molecule. Presence of nine methylene carbons in the compound **3** was confirmed from the ^{13}C DEPT spectrum. Chemical shifts of all protons and carbons are given in the Table 1. The mass fragments of compound **3** at m/z 250 (M^+), 165, 124, 109 and 58 (base peak) also support the proposed structure **3** of the compound **3**. Compound **3** is thus characterized as 4a, 8a dimethyl-5 (3'- methyl-but-3'- enyl) decahydro-naphthalen-2-ol.

III. Experimental

The IR spectra were recorded on a Shimadzu FTIR Model 8400 spectrometer. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker BPX-200 spectrometer operating at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR

spectra. The chemical shift values are reported as parts per million (ppm) relative to tetramethylsilane. The Mass spectra were recorded on JEOL, THE Accu TOF GCv instrument. Column chromatography was performed using silica gel, Merck (100-200 mesh).

A. Plant material

The fruits of *Terminalia catappa* were collected from the EPZ region of the district of Chittagong situated in the southeastern region of Bangladesh. For the experimental purpose only the matured, fresh fruits were collected during the month of January 2016. The plant was identified in Chittagong University Herbarium (CUH) by Prof. Dr. Kamrul Huda and a voucher specimen (Acc. No. 19-04) was deposited at CUH.

B. Extraction and isolation

The air-dried powder (5 kg) of *Terminalia catappa* was successively extracted with CHCl_3 (3×72 h) and MeOH (3×72 h) respectively. On removal of the solvent, the CHCl_3 extract gave a deep green Mass CE (67.0 g), the MeOH extract gave a brown Mass ME (85.0 g).

Mass CE (20.0 g) was dissolved in minimum quantity of CHCl_3 and adsorbed onto silica gel and finally recovered in the powder form for application into the column. The dry powder was then placed over a column (90 cm × 8 cm) of silica gel made in $n\text{-C}_6\text{H}_{14}$. The elution was carried out with the solvent system $n\text{-C}_6\text{H}_{14}$: EtOAc (35:1). Portion of about 5 ml volume were collected at regular intervals. The eluents from the test tubes were monitored by TLC and the eluents of the tubes having identical spots were pooled together to give four fractions (A, B, C, D). Fraction A being the void volume did not show any spot on TLC. Fraction B on drying under reduced pressure gave a white amorphous solid mass (500 mg). It gave a single spot with R_f value 0.88 in $n\text{-C}_6\text{H}_{14}$: EtOAc (35 :1) solvent system and was named as compound 1.

Fraction C on drying under reduced pressure gave an amorphous white solid mass (2.1 g). It was less soluble in $n\text{-C}_6\text{H}_{14}$ but soluble in CHCl_3 and EtOAc. It gave a single spot with R_f value 0.69 in $n\text{-C}_6\text{H}_{14}$: EtOAc (35 : 1) solvent system and was named as compound 2.

On purification by repeated crystallization from the solvent system $n\text{-C}_6\text{H}_{14}$:DCM (3:1), fraction D gave a crystalline brown solid Mass (50.0 mg) and was named as compound 3. It gave a single spot with R_f value 0.75 in $n\text{-C}_6\text{H}_{14}$: EtOAc (10:1) solvent system.

Compound 1: white amorphous solid (500 mg); IR: ν_{max} (KBr) cm^{-1} : 1730 (C=O), 1040 (C-O), 1460, 1490 (C=C), 3340 (O-H). $^1\text{H-NMR}$ (CDCl_3) δ : 2.18 (2H, d, H-5), 4.04 (1H, m, H-6), 7.69 (2H, m, H-7), 7.52 (2H, m, H-8), 1.57 (2H, m, H-1'), 1.39 (2H, m, H-2'), 2.18 (1H, m, H-3'), 4.20 (1H, m, H-4'), 1.38 (2H, m, H-6'), 0.91 (3H, s, H-7'), 0.91 (3H, s, H-8'), 0.91 (3H, s, H-9'), 0.91 (3H, s, H-10'). $^{13}\text{C NMR}$ (CDCl_3) δ : Table 1: EIMS m/z: 280 [M+], 279, 262, 167, 149.

Compound 2: white amorphous solid (2.1g); IR: ν_{max} (KBr) cm^{-1} : 1730 (C=O), 1040 (C-O), 1460, 1490 (C=C), 3340 cm^{-1} (O-H). $^1\text{H NMR}$ (CDCl_3) δ : 4.20 (1H, m, H-6), 7.70 (2H, m, H-7), 7.51 (2H, m, H-8), 1.33 (3H, s, H-9), 1.33 (3H, s, H-10), 1.54 (2H, m, H-1'), 1.41 (2H, m, H-2'),

1.40 (2H, m, H-3'), 4.22 (1H, m, H-5'), 1.31 (3H, s, H-6'), 0.91 (3H, s, H-7'), 0.91 (3H, s, H-8'). $^{13}\text{C-NMR}$ (CDCl_3) δ : Table 1: EIMS m/z: 280 [M+], 279, 262, 167, 149.

Compound 3: brown crystalline solid (50 mg); IR: ν_{max} (KBr) 3452 cm^{-1} (O-H) and 1630 cm^{-1} (C=C). $^1\text{H NMR}$ (CDCl_3) δ : 2.16 (2H, H-1), 3.63 (1H, H-2), 2.16 (2H, H-3), 1.24 (2H, H-4), 1.60 (1H, H-5), 1.24 (2H, H-6), 1.24 (2H, H-7), 1.24 (2H, H-8), 0.86 (3H, H-9), 0.86 (3H, H-10), 1.60 (2H, H-1') 2.33 (2H, H-2') 5.3 (2H, H-4') 1.60 (3H, H-5'). $^{13}\text{C NMR}$ (CDCl_3) δ : Table 1: EIMS m/z: 250 [M+], 165, 124, 109, 58.

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