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## Two new Xanthones from *Garcinia chapelierii*: Chapexanthone A; chapexanthone B

Volaso Herilalaina Victorine Rabeloson, Léa Herilala Rasoanaivo, Anne Wadouachi, Rivoarison Randrianasolo, Hans Christoph Krebs and Amelie Raharisololalao

**Abstract**

From the stem bark hexanic extract of *Garcinia chapelierii*, chapexanthone A, B were isolated using combinations of column and thin-layer chromatographic methods. Their structures were elucidated by NMR spectroscopic methods, mainly 1D and 2D NMR.

**Keywords:** *Garcinia chapelierii*, Clusiaceae, Xanthones, Chapexanthone A, Chapexanthone B.

**1. Introduction**

*Garcinia chapelierii* is an endemic plant of Madagascar. The decoction of steam with leaves of *Garcinia chapelierii* is used to treat yellow fever, irritations on the skin, stomachache and also toothache. Extensive phytochemical studies have shown that *Garcinia* species are rich in a variety of oxygenated and prenylated xanthones [2]. Some of these exhibit a wide range of biological and pharmacological activities [3, 6]: antifungal [4, 7], anti-thrombotic, vasorelaxant, aggregation inhibitory platelet [8], anti-HIV [5, 9] and antimalarial [10].

According to available literature, no phytochemical research work has been carried out on this plant. Further investigation on the hexanic extract of the bark of the *Garcinia chapelierii* has resulted in the isolation of two xanthones. This paper describes structural elucidation of xanthones isolated from this plant.

**2. Materials and Methods**

**2.1 General:**

1D (1H, 13C, DEPT) and 2D (HSQC, HMBC) NMR spectra were measured on Varian Unity 400 and Varian Innova 500 spectrometers. Chemical shifts are shown in  $\delta$  values (ppm) with tetramethylsilane (TMS) as internal standard. HREIMS were determined on VG ZAB 2SEQ mass spectrometer. Column chromatography (CC) was carried out on silica gel F254 (Merck) in glass blades. Thin layer chromatography (TLC) was performed on precoated Si Gel plates (Merck Kiesel gel 60GF254) and detection wavelength (254 and 365 nm) was used.

**2.2. Plant material:**

*Garcinia chapelierii* H.Perr. (Clusiaceae) was collected in July 2012 in Farafangana Manombo, Vatovavy Fitovinany's Region Madagascar and was identified by botanists at the Parc National Botanic and Zoologique Tsimbazaza, Antananarivo, Madagascar where a voucher specimen has been deposited in the Herbarium.

**2.3 Extraction and isolation:**

The stem bark of *Garcinia chapelierii* were dried ground, reduced on powder. The powder was macerated successively with hexane, ethyl acetate and MeOH. The solvents were evaporated under reduced pressure to obtain crude residue: green, green and red solid gum (1.3 g; 7.75g; 12.45 g).

The hexanic extract was subjected to column chromatography (silicagel, 2x60 cm) and was eluted with a gradient profile of hexane and acetone to give 95 main fractions.

The fractions 5-6 were obtained after 100 mL and the fractions 7-8 were obtained after 120 mL and after elution with hexane and acetone (95:5).

The purification of fractions 5-6 and the 7-8 were carried out by column chromatography on Sephadex LH-20 with CDC13-MeOH (80:20).

### 3. Result and Discussion: Reported in tables 1 and 2

The dried and ground stem bark of *Garcinia chapelierii* collected from Farafangana (Madagascar) was extracted with n hexanes, ethyl acetate and methanol. The hexanic was repeatedly chromatographed over Si gel and Sephadex LH-20 to gives 2 xanthones (1-2)

Xanthon A, chapexanthone A (1) was obtained as a yellow powder. Its molecular formula C<sub>28</sub>H<sub>36</sub>O<sub>7</sub> was deduced by HREIMS mass spectroscopy (m/z 484.25).

The <sup>1</sup>H NMR spectrum shows five aromatic protons, one of which couple ortho at δ 7.28 ppm (H-5) and 7.87 (H-6), one of which couple meta at δ 7.28 ppm (H-5) and at δ 7.06 ppm (H-7), at δ 6.64 ppm (H-2) and (H-4) and implying that the compound 1 is tri-O-substituted xanthone.

In addition to the <sup>1</sup>H NMR spectra show the presence of protons in the region of the aliphatic protons, indicating the presence of a linear chain, showed signal in the 0.7-3.90 ppm range. The presence of long chain moiety in the molecule was indicated by the peaks in the region of weak field.

The <sup>13</sup>C Broadband spectra showed 28 carbon atom signals indicating 13 correspond to the carbon atoms of skeleton xanthone there is no symmetry in the molecule. The presence of linear chain was indicated by fifteen peaks between 8 and 80 ppm.

The <sup>13</sup>C Broadband spectra showed too five shielded aromatic methine groups at δ 104.09 ppm (C-4); δ 107.12 ppm (C-2); 119.83(C-5); δ 114.57 ppm (C-8) and δ 125.11 ppm (C-6) respectively.

Among the eight quaternary carbon atom signals noted in the HSQC spectra, three corresponded to O-linked aromatic carbon atom δ 154.65 ppm (C-7); δ 162.01 ppm (C-3) and δ 165.00 ppm (C-1), while the peak at 183.29 ppm indicated the presence of carbonyl function C=O group assigned to C-9 [1].

The signal at δ 207.32 ppm is attributed to the carbon at position C-8'. The remaining signals correspond to the carbons of the methyl, methylene and methine confirms the presence of a linear chain.

The 2D NMR experiments clearly showed that there were three aromatics protons on the A-ring. The substitute pattern of B-ring was clearly indicated by one singlet at δ 6.64 ppm (H-2) and (H-4) because the two protons are isochronous. According to the HMBC correlation the proton H-2 at δ 6.64 ppm correlates with the carbon atoms at δ 107.12 ppm (C-2) and δ 162.01 ppm (C-3). Moreover, the 7-dihydroxylation pattern of A-ring was confirmed by the reciprocal shielding of C-7 at δ 154.65 ppm. The signal at δ 3.80 ppm in <sup>1</sup>H NMR and δ 56.40 ppm in <sup>13</sup>C Broadband spectra suggested the presence of alcohol function (-CH<sub>2</sub>OH).

Finally, the cross peaks noted in the HMBC experiment between H-2' δ 2.42 ppm and the carbon atoms δ 104.09 ppm (C-4), δ 162.01 ppm (C-3) indicated unambiguously the linkage between the chain linear moiety and the xanthone part.

Thus xanthone 1 was identified to 1, 7-dihydroxy-3-O-[(1',3',4',5',6',7'-hexamethyloctanal) (2''hydroxymethylene)] xanthone named chapexanthone A.

Xanthon 2, chapexanthone B was obtained as a yellow needles and its molecular formula was assigned as C<sub>18</sub>H<sub>18</sub>O<sub>6</sub> by the molecular ion peak at m/z 327.0911 in the HREIMS. NMR data suggested that 2 also had a xanthone skeleton. A comparison of the <sup>1</sup>H and <sup>13</sup>C NMR data of 2 with those of 1 revealed that the difference was the substituent at C-3. The linear chain in 1 replaced by the δ 78.84 ppm (C-1'), δ 55.50 ppm (C-2') and δ 60.32 ppm (C-3') in 2. Therefore, chapexanthone B can be assigned as 1, 7-dihydroxy-3-O-[(1', 2'-dimethylpropan-3'-ol)] xanthone. Data NMR of compound 2 and 1 is given respectively in table 1 and table 2.

Table 1: <sup>1</sup>H and <sup>13</sup>C NMR spectral data for compound 1

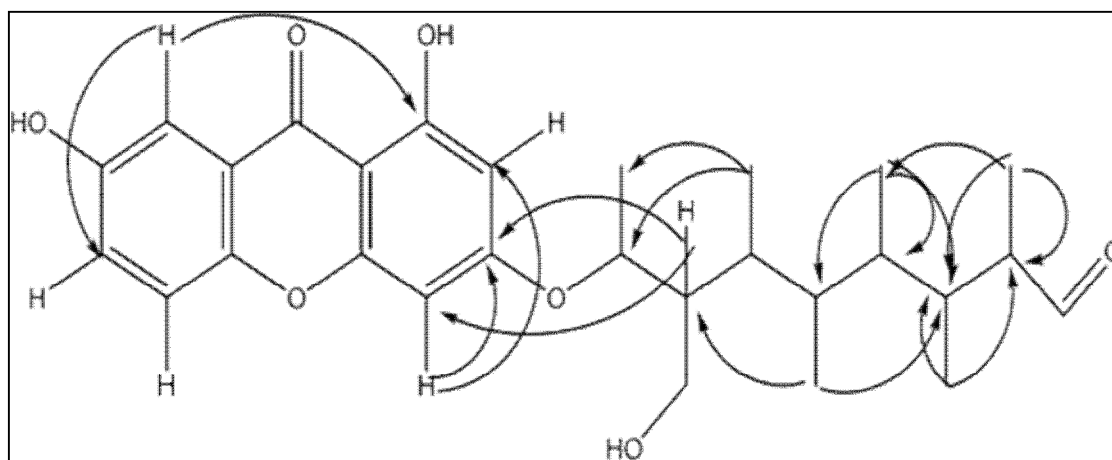
Position	<sup>1</sup> H	<sup>13</sup> C
1	-	165.00
2	6.64 (s)	107.12
3	-	162.01
4	6.64 (s)	104.09
4a	-	156.58
4b	-	141.05
5	7.28 (s)	121.47
6	7.87 (d, 9.3Hz)	128.12
7	-	152.95
8	7.06 (d, 9.3Hz)	114.57
8a	-	109.25
8b	-	123.22
9	-	183.29
1'	3.90 (d)	71.81
2'	2.39 (d)	55.55
3'	1.28 (s)	29.70
4'	0.72 (s)	50.80
5'	0.70 (s)	42.50
6'	0.90 (s)	31.38
7'	2.23 (s)	51.26
8'	12.87 (s)	207.32
1'-CH <sub>3</sub>	1.28(s)	21.19
2''-CH <sub>2</sub> OH	3.80, 3.90 (s)	60.33
3'-CH <sub>3</sub>	1.60 (s)	20.55
4'-CH <sub>3</sub>	1.03 (s)	12.47
5'-CH <sub>3</sub>	0.99 (s)	18.80
6'-CH <sub>3</sub>	0.85 (s)	9.60
7'-CH <sub>3</sub>	0.83(s)	8.46

<sup>a</sup> Assignments were confirmed by 2D experiments

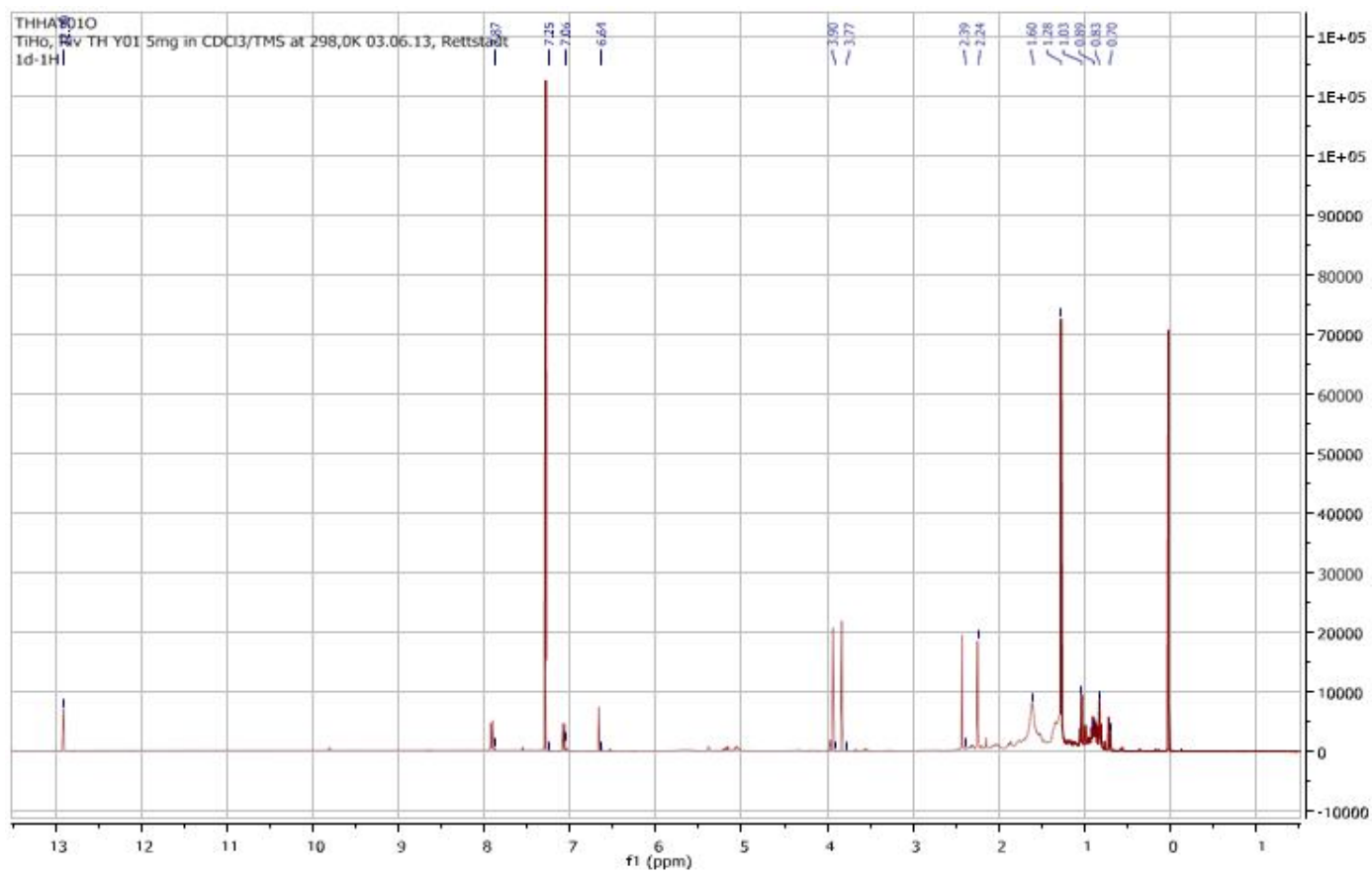
Table 2: <sup>1</sup>H and <sup>13</sup>C NMR spectral data for compound 2a

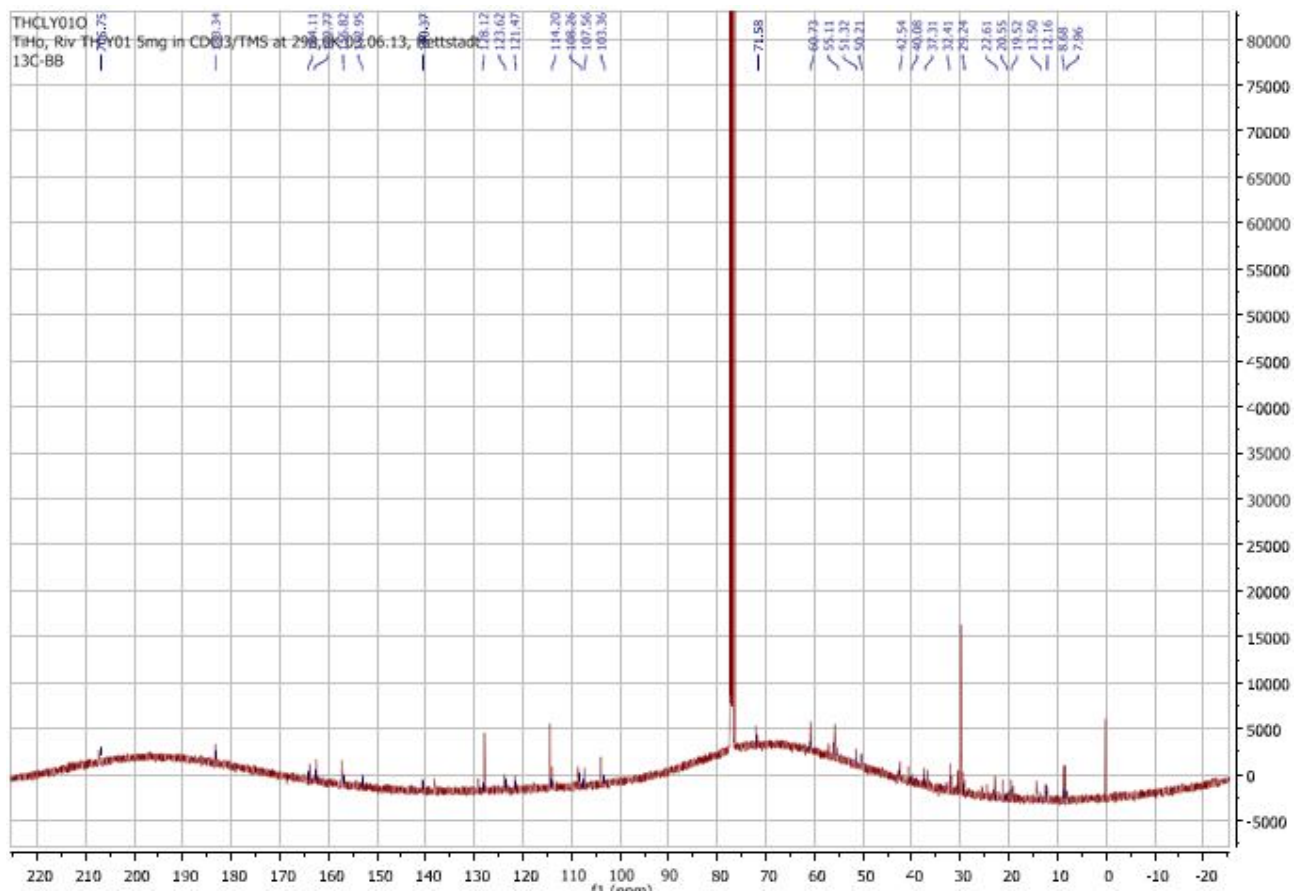
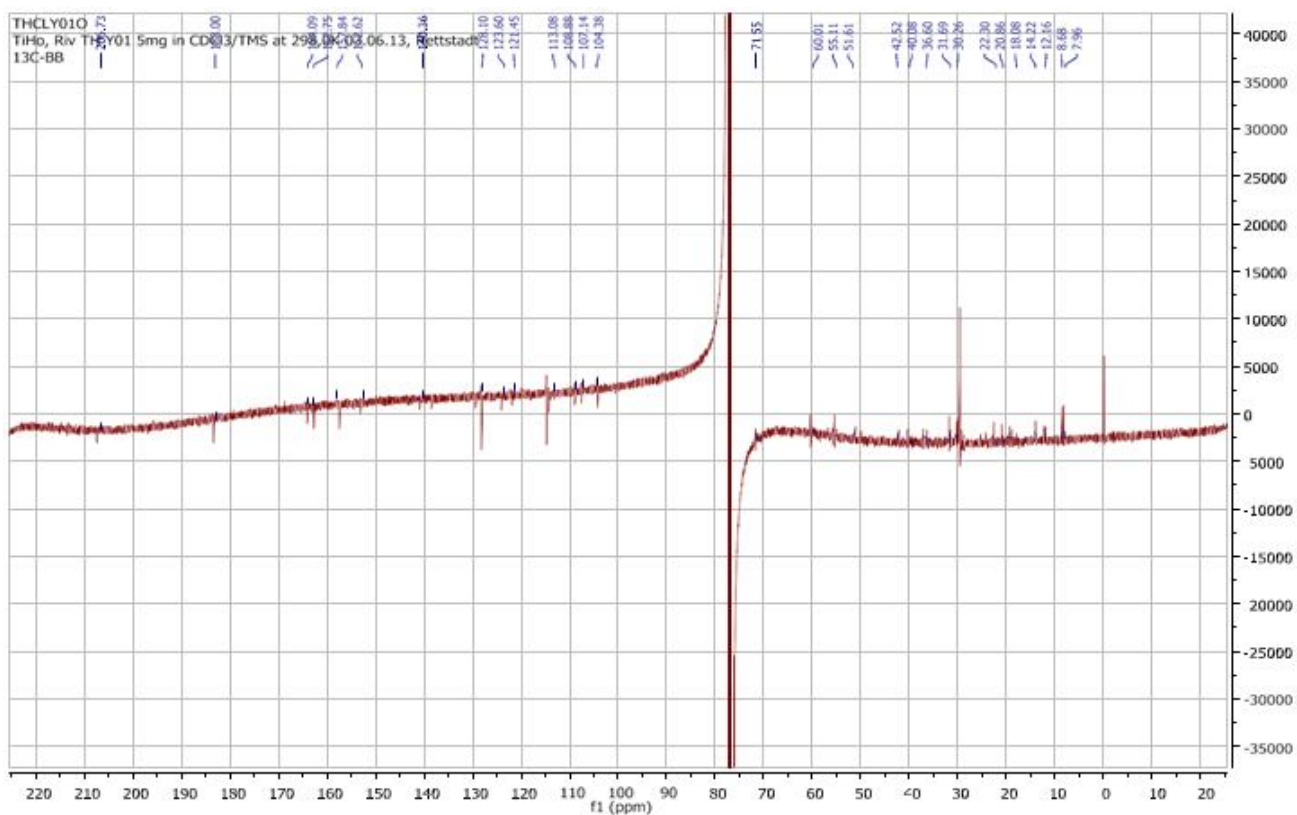
Position	<sup>1</sup> H	<sup>13</sup> C
1	-	163.77
2	6.79 (s)	106.12
3	-	162.79
4	6.97 (s)	103.66
4a	-	162.37
4b	-	152.62
5	7.14 (d, 2.6 Hz)	115.20
6	8.06 (s)	128.11
7	-	156.41
8	8.26 (d, 9.3Hz)	113.07
8a	-	108.89
8b	-	122.58
9	-	182.99
1'	3.87 (d)	78.84
2'	2.50 (t)	55.50
3'	3.87 ; 3.76 (d)	60.32
1'-CH <sub>3</sub>	2.11 (s)	8.68
2'-CH <sub>3</sub>	2.35 (s)	8.96

<sup>a</sup> Experiments were carried out at 500 MHz for <sup>1</sup>H and 400 MHz for <sup>13</sup>C CDCL<sub>3</sub>



**Fig 1:** Long-range heteronuclear correlation observed for 1 (chapexanthone A)





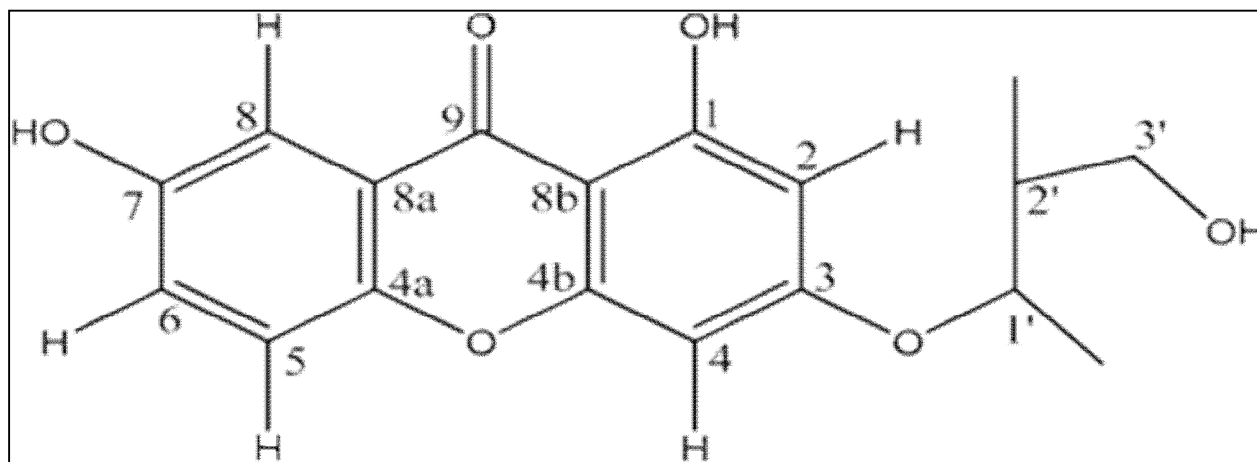
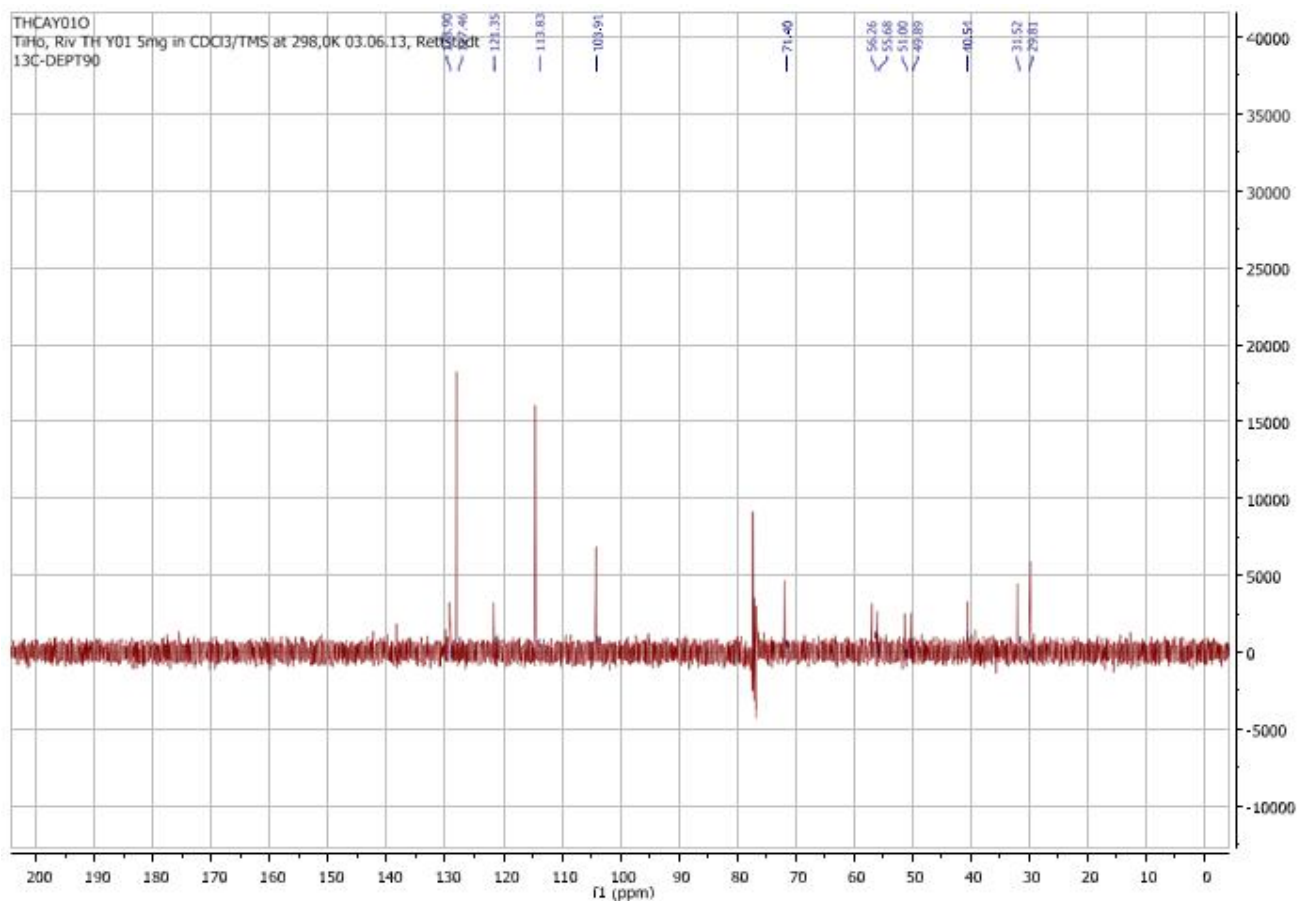
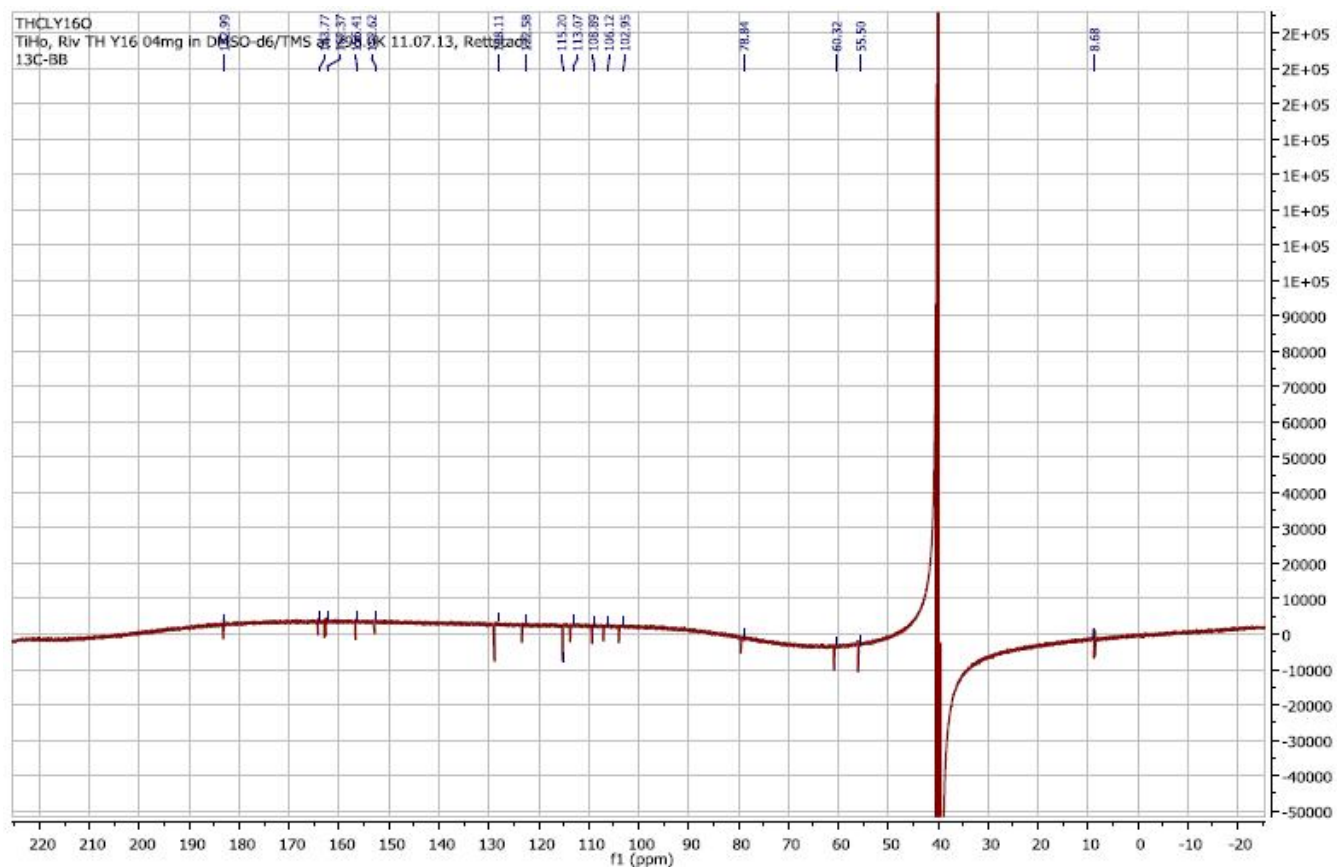
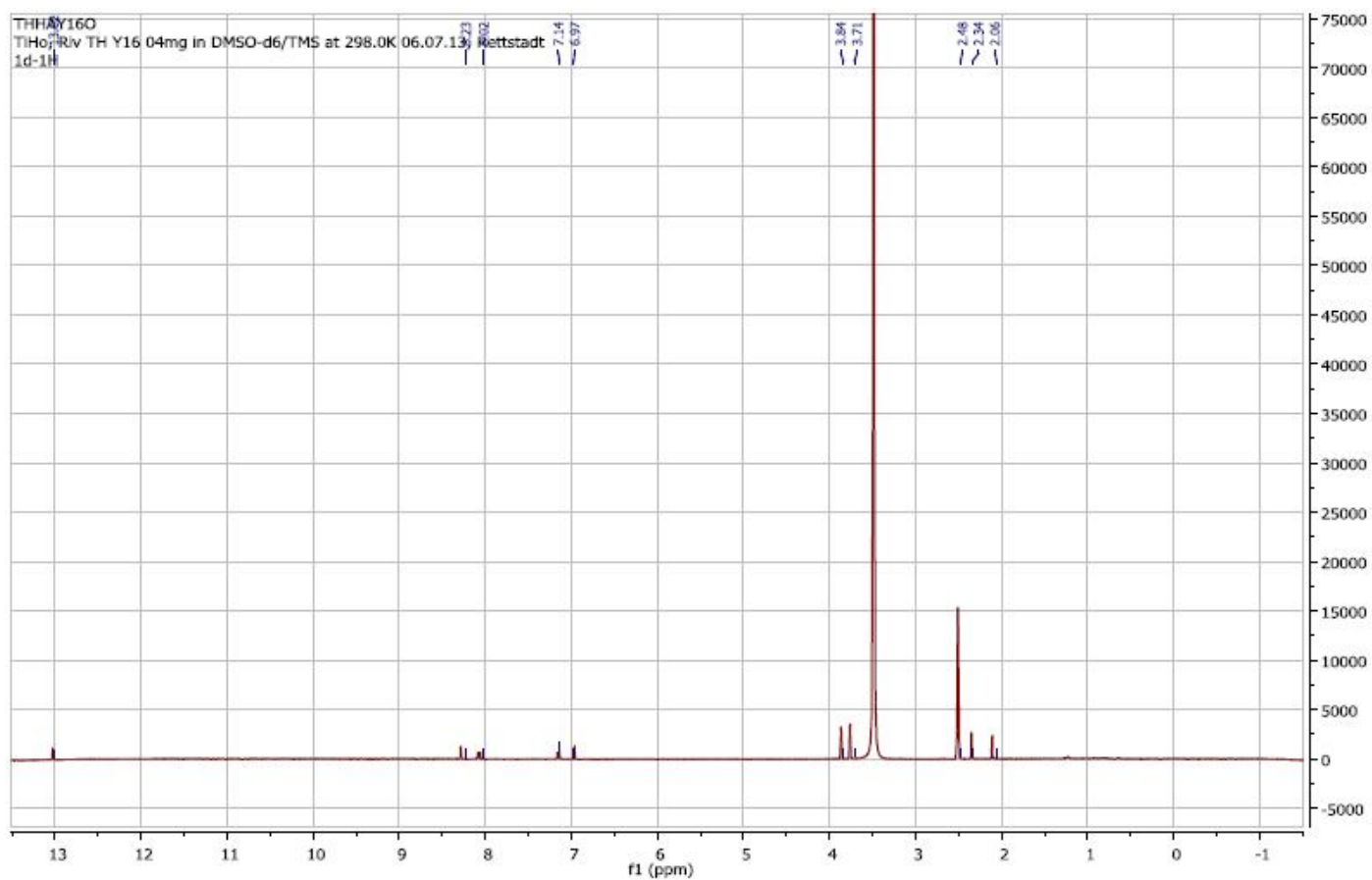
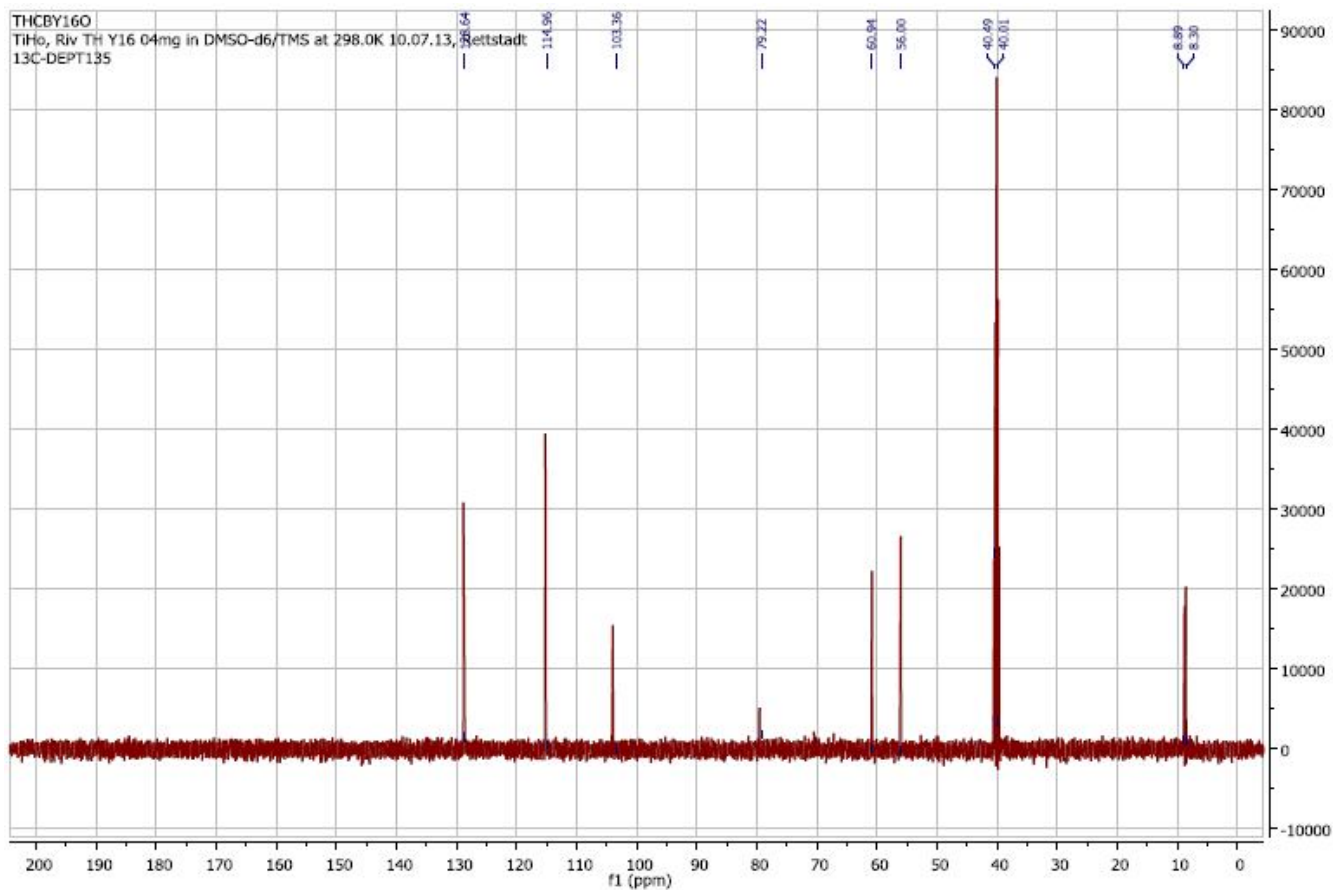
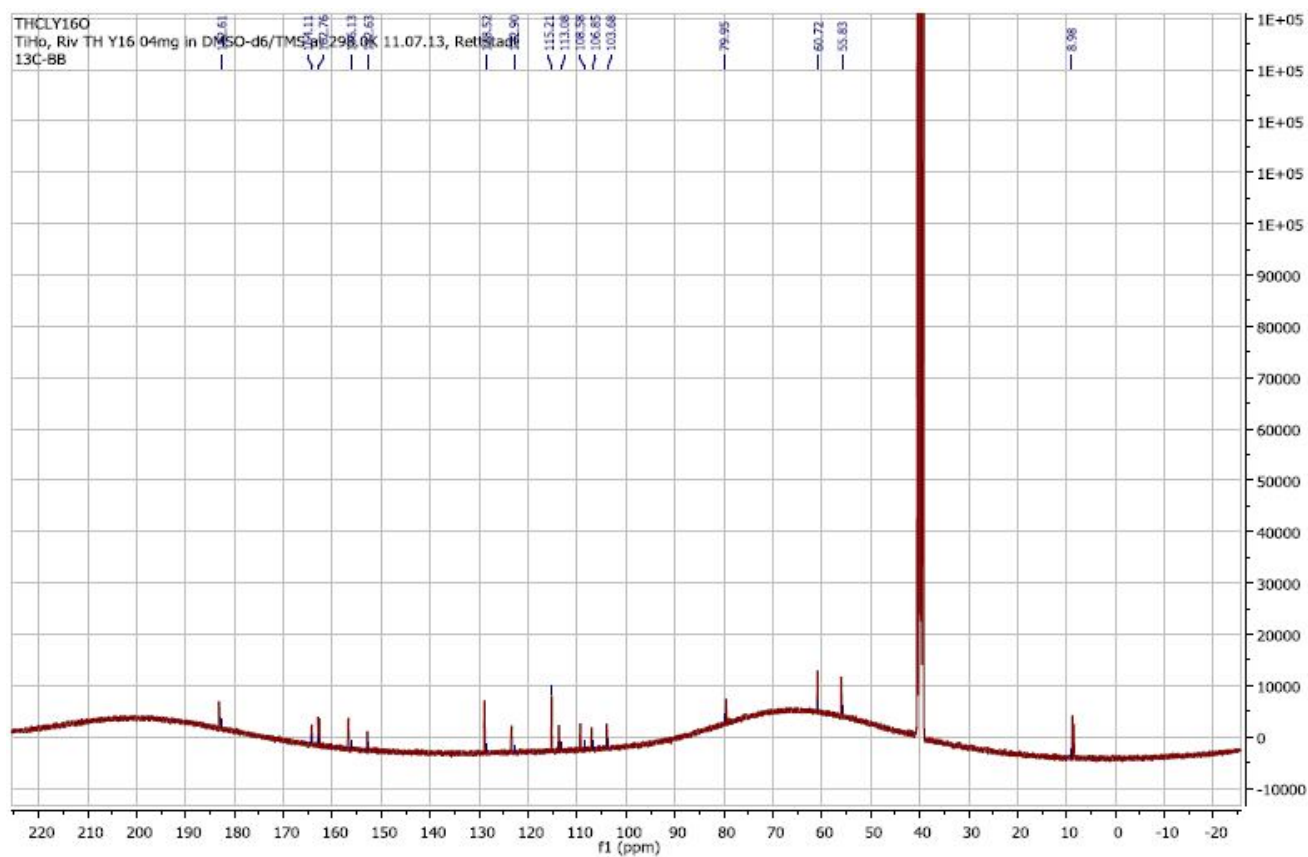
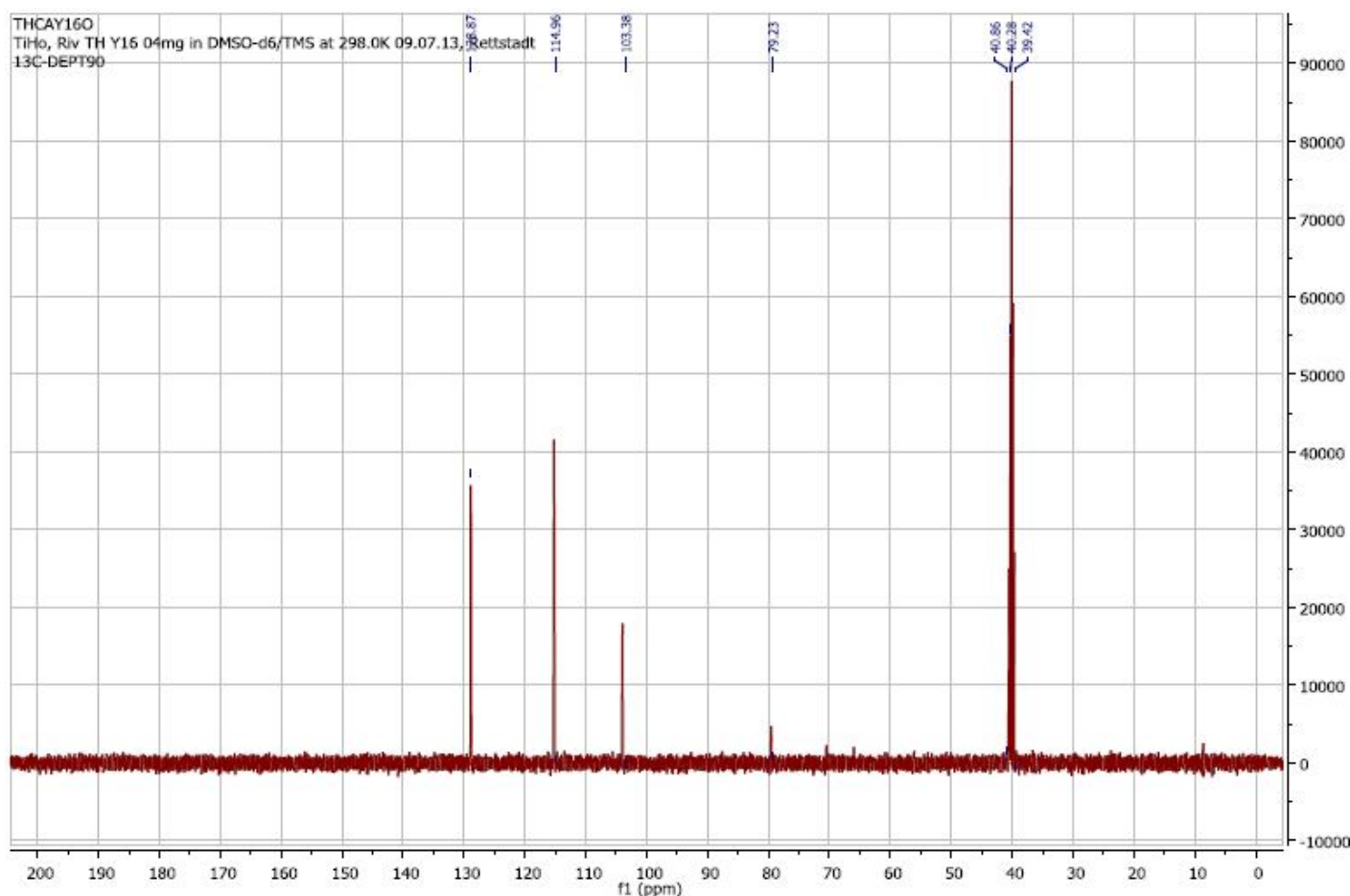


Fig 2: Structure of chapexanthone B









#### 4. Conclusion

Two new xanthones: chapexanthone A and chapexanthone B were isolated from the hexanic extract from the steam bark of *Garcinia chapelieri*. The structures of the isolated new compounds were identified as chapexanthone A and B on the basis of spectroscopic methods. The complete  $^1\text{H}$  and Broadband NMR spectral assignments of the one isolated compounds were made based on HSQC, HMBC spectroscopic data.

#### 5. Acknowledgement

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