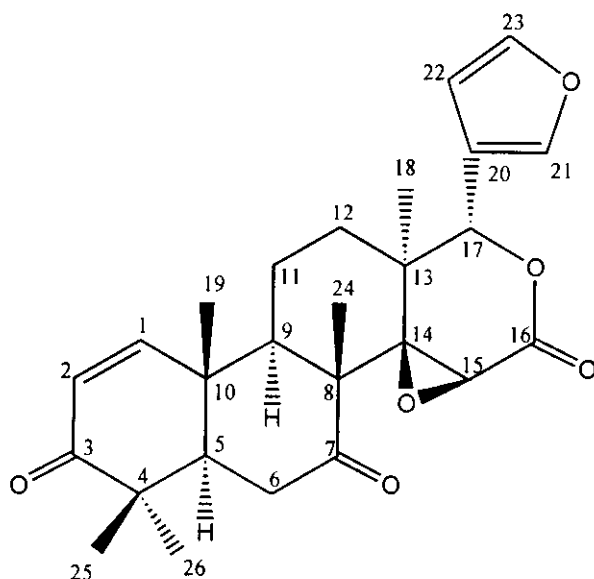


### 3 RESULTS AND DISCUSSION

#### 3.1 *Structural elucidation of compounds from the seeds of X.granatum*

The crude hexane extract from the seeds of *X. granatum* was subjected to chromatography and/or crystallization to give six limonoids [7-oxogedunin (XC1), xylocensin K (XC2) and 6-acetoxycedrodorin (XC3), methyl angolensate (XH1), xylocensin P (XH2) and xylocensin O (XH3)]. The crude dichloromethane extract, upon chromatographic separation, yielded one new triterpenoid [22-hydroxy piscidinol A (XC5)], a known triterpenoid [hispidol B (XC4)], together with a mixture of two steroids [stigmasterol (1) and  $\beta$ -sitosterol (2) (XC6)] and four limonoids previously isolated from the crude hexane extract [7-oxogedunin (XC1), xylocensin K (XC2), 6-acetoxycedrodorin (XC3) and methyl angolensate (XH1)]. Their structures were determined using 1D and 2D NMR spectroscopic data. All carbons were assigned by  $^{13}\text{C}$  NMR, HMQC and HMBC data. The chemical shifts were determined using 1D  $^1\text{H}$  NMR and  $^1\text{H}$ - $^1\text{H}$  COSY spectroscopic data. In addition, the structures of XC1, XC2 and XC4 were confirmed by X-ray diffraction.

### 3.1.1 Compound XC1



Compound **XC1** was isolated as a colorless solid mp = 263-265 °C,  $[\alpha]_D^{26} = -41^\circ$  ( $c = 1.22$ ,  $\text{CHCl}_3$ ). The mass spectrum of this compound (see **Fig. 14**) showed the molecular ion peak at 438  $m/z$ , corresponding to a molecular formula  $\text{C}_{26}\text{H}_{30}\text{O}_6$ . The UV spectrum (see **Fig. 5**) showed maximum absorption band ( $\lambda_{\text{max}}$ ) at 225 nm indicating the presence of  $\alpha,\beta$ -unsaturated carbonyl moiety in the molecule. The IR spectrum (see **Fig. 6**) showed the strong absorption bands at 1741  $\text{cm}^{-1}$ , 1709  $\text{cm}^{-1}$  and 1670  $\text{cm}^{-1}$  corresponding to a C=O stretching of lactone, C=O stretching of ketone and C=O stretching of  $\alpha,\beta$ -unsaturated carbonyl group, respectively. The presence of three carbonyl carbons at  $\delta$  208.15, 203.22 and 166.83 ppm from  $^{13}\text{C}$  NMR spectrum supported the above conclusion.

The  $^{13}\text{C}$  NMR spectrum of compound **XC1** (see **Table 7**, **Fig. 9**) recorded in  $\text{CDCl}_3$  showed 26 signals for 26 carbons. Analysis of DEPT-90° and DEPT-135° (see **Table 4**, **Fig. 10**) indicated the existence of five methyl carbons ( $\delta$  26.99, 20.93, 20.66, 19.82 and 17.40), three methylene carbons ( $\delta$  36.72, 32.20 and 14.20), nine methine carbons ( $\delta$  155.91, 143.13, 141.05, 126.46, 109.80, 78.02, 54.61, 53.66 and 47.64) and nine quaternary carbons ( $\delta$  208.17, 203.24, 166.85, 120.22, 65.62, 53.44, 45.24, 39.63 and 37.76). These chemical shifts were different from the values reported

45.24, 39.63 and 37.76). These chemical shifts were different from the values reported C-5 ( $\delta$  47.6), C-9 ( $\delta$  53.7), C-21 ( $\delta$  143.1) and C-23 ( $\delta$  141.0) (Taylor, *et al.*, 1974). COSY and HMQC confirmed chemical shifts of C-5 ( $\delta$  54.59), C-9 ( $\delta$  47.62), C-21 ( $\delta$  141.03) and C-23 ( $\delta$  143.11) as newly assigned values.

The  $^1\text{H}$  NMR spectrum of compound **XC1** (see **Table 7**, **Fig. 7**), with the characteristic peaks of furan nucleus as shown at  $\delta$  7.42 (1H, *br d*,  $J = 0.6$  Hz), 7.40 (1H, *t*,  $J = 1.8$  Hz) and 6.36 (1H, *dd*,  $J = 1.8, 0.6$  Hz) were assigned to H-21, H-23 and H-22, respectively. Two signals of olefinic protons resonated at  $\delta$  7.10 (1H, *d*,  $J = 10.2$  Hz) and 5.93 (1H, *d*,  $J = 10.2$  Hz). The signals at  $\delta$  5.47 (1H, *s*) and 3.88 (1H, *s*) could be assigned for methine protons which attached to a carbon adjacent to an oxygen atom at C-17 (78.00) and C-15 (53.64), respectively (Powell, 1966).

The structure of compound **XC1** was deduced from its  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectral data (see **Table 7**, **Fig. 8** and **9**) together with the results of  $^1\text{H}$ - $^1\text{H}$  COSY (see **Table 5**, **Fig. 10**), HMQC (**Fig. 11**) and HMBC (see **Table 6**, **Fig. 12**). The correlation peaks in the HMBC spectrum (see **Table 6**, **Fig. 12**) between H-17 ( $\delta$  5.47) and the carbon at  $\delta$  141.03 (C-21), 120.20 (C-20), 109.78 (C-22), 65.60 (C-14), 37.74 (C-13) and 32.18 (C-12) confirmed the position of the furanyl group at C-17 position. The carbon signals at  $\delta$  166.83 (C-16), 65.60 (C-14) and 53.64 (C-8) showed the correlation peaks with the H-15 ( $\delta$  3.88). The carbon signals at  $\delta$  208.15 (C-7), 53.42 (C-8), 47.62 (C-9) and 65.60 (C-14) showed the correlation peaks with the Me-24 ( $\delta$  1.22), confirming the position of the carbonyl group at C-7. The carbon signals at  $\delta$  203.22 (C-3), 54.59 (C-9), 47.62 (C-5) and 39.61 (C-10) showed the correlation peaks with the H-1 ( $\delta$  7.10), confirming the  $\alpha,\beta$ -unsaturated ketone. From NOESY experiment (**Fig. 13**), H-5 ( $\delta$  2.18) showed cross peak with H-6a ( $\delta$  2.93) and Me-26 ( $\delta$  1.14); H-9 ( $\delta$  2.21) showed cross peak with H-1 ( $\delta$  7.10) and Me-18 ( $\delta$  1.14); Me-19 ( $\delta$  1.36) showed cross peak with Me-24 ( $\delta$  1.22) and Me-25 ( $\delta$  1.16); H-17 ( $\delta$  5.47) did not showed cross peak with H-15 ( $\delta$  3.88) and Me-18 ( $\delta$  1.14). Thus, these

observations confirmed that H-5, H-9, H-15, Me-18 and Me-26 were on the same side and opposite side to H-17, Me-19, Me-24 and Me-25.

Compound **XC1** was identified as 7-oxogedunin which was the compound previously isolated from various genera of the Meliaceae family, such as the timber of *Cedrela odorata* (Powell, 1966), the bark of *Carapa procera* (Taylor, 1974) and the timber of *Xylocarpus moluccensis* (Mulholland and Taylor, 1992). The structure of compound **XC1** was support by X-ray diffraction (see **Table 56-58, Fig. 2**).

**Table 4**  $^{13}\text{C}$  and DEPT spectral data of compound **XC1**

$\delta_c$	DEPT-90°	DEPT-135°	Type of Carbon
208.17			C
203.24			C
166.85			C
155.91	155.91	155.91	CH
143.13	143.13	143.13	CH
141.05	141.05	141.05	CH
126.46	126.46	126.46	CH
120.22			C
109.80	109.80	109.80	CH
78.02	78.02	78.02	CH
65.62			C
54.61	54.61	54.61	CH
53.66	53.66	53.66	CH
53.44			C
47.64	47.64	47.64	CH

Table 4 (Continued)

$\delta_c$	DEPT-90°	DEPT-135°	Type of Carbon
45.24			C
39.63			C
37.76			C
36.72		36.72	CH <sub>2</sub>
32.20		32.20	CH <sub>2</sub>
26.99		26.99	CH <sub>3</sub>
20.93		20.93	CH <sub>3</sub>
20.66		20.66	CH <sub>3</sub>
19.82		19.82	CH <sub>3</sub>
17.40		17.40	CH <sub>3</sub>
17.20		17.20	CH <sub>2</sub>

Table 5 300 MHz COSY correlation of some protons of compound XC1

$\delta_H$ (ppm)	Proton Correlation with $\delta_H$ (ppm)
H-23 (7.40)	H-22 (6.36)
H-22 (6.36)	H-17 (5.47)
H-21 (7.42)	H-17 (5.47)
H-1 (7.10)	H-2 (5.93)
H-6a (2.93)	H-6b (2.41), H-5 (2.18)
H-6b (2.41)	H-5 (2.18)
H-9 (2.21)	H-11b (1.85)
H-11a (2.05)	H-12a (1.90), H-11b (1.85), H-12b (1.45)
H-12a (1.90)	H-11b (1.85), H-12b (1.45)
H-11b (1.85)	H-12b (1.45)

Table 6 Major HMBC correlation of compound XC1

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
1	7.10 (1H, <i>d</i> , $J = 10.2$ Hz)	C-3 (203.22), C-5 (54.59), C-9 (47.62) and C-10 (39.61)
2	5.93 (1H, <i>d</i> , $J = 10.2$ Hz)	C-4 (45.22) and C-10 (39.61)
5	2.18 (1H, <i>dd</i> , $J = 14.4, 3.0$ Hz)	C-1 (155.89), C-4 (45.22), C-6 (36.70), C-7 (208.15), C-9 (47.62), C-10 (39.61), C-19 (20.64), C-25 (26.97) and C-26 (19.80)
6a	2.93 (1H, <i>t</i> , $J = 14.4$ Hz)	C-4 (45.22), C-7 (208.15), C-8 (53.42) and C-10 (39.61)
6b	2.41 (1H, <i>dd</i> , $J = 14.4, 3.0$ Hz)	
9	2.21 (1H, <i>br d</i> , $J = 9.9$ Hz)	C-12 (32.18) and C-19 (20.64)
11	2.05 (1H, <i>m</i> ), 1.85 (1H, <i>m</i> )	-
12	1.90 (1H, <i>m</i> ), 1.45 (1H, <i>m</i> )	-
15	3.88 (1H, <i>s</i> )	C-8 (53.42), C-14 (65.60) and C-16 (166.83)
17	5.47 (1H, <i>s</i> )	C-12 (32.18), C-13 (37.74), C-14 (65.60), C-18 (20.91), C-20 (120.20), C-21 (141.03) and C-22 (109.78)
18	1.14 (3H, <i>s</i> )	C-12 (32.18), C-13 (37.74), C-14 (65.60) and C-17 (78.00)
19	1.36 (3H, <i>s</i> )	C-1 (155.89), C-5 (54.59), C-9 (47.62) and C-10 (39.61)
21	7.42 (1H, <i>dd</i> , $J = 1.8, 0.6$ Hz)	C-22 (109.78) and C-23 (143.11)
22	6.36 (1H, <i>dd</i> , $J = 1.8, 0.6$ Hz)	C-20 (120.20), C-21 (141.03) and C-23 (143.11)
23	7.40 (1H, <i>t</i> , $J = 1.8$ Hz)	C-20 (120.20) and C-21 (141.03)

Table 6 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
24	1.22 (3H, <i>s</i> )	C-7 (208.15), C-8 (53.42), C-9 (47.62) and C-14 (65.60)
25	1.16 (3H, <i>s</i> )	C-3 (203.22), C-4 (45.22), C-5 (54.59) and C-26 (19.80)
26	1.14 (3H, <i>s</i> )	C-3 (203.22), C-4 (45.22), C-5 (54.59) and C-25 (26.97)

\* Chemical shift was assigned by HMQC

Table 7  $^1\text{H}$  and  $^{13}\text{C}$  spectral data of compound XC1

position	$\delta_{\text{C}}^{\#}$ (ppm)		$\delta_{\text{H}}$ (ppm)
1	155.89	=CH	7.10 (1H, <i>d</i> , $J = 10.2$ Hz)
2	126.44	=CH	5.93 (1H, <i>d</i> , $J = 10.2$ Hz)
3	203.22	C=O	-
4	45.22	C	-
5	54.59	CH	2.18 (1H, <i>dd</i> , $J = 14.4, 3.0$ Hz)
6	36.70	CH <sub>2</sub>	2.93 (1H, <i>t</i> , $J = 14.4$ Hz) 2.41 (1H, <i>dd</i> , $J = 14.4, 3.0$ Hz)
7	208.15	C=O	-
8	53.42	C	-
9	47.62	CH	2.21 (1H, <i>br d</i> , $J = 9.9$ Hz)
10	39.61	C	-
11*	17.18	CH <sub>2</sub>	2.05 (1H, <i>m</i> ), 1.85 (1H, <i>m</i> )
12*	32.18	CH <sub>2</sub>	1.90 (1H, <i>m</i> ), 1.45 (1H, <i>m</i> )

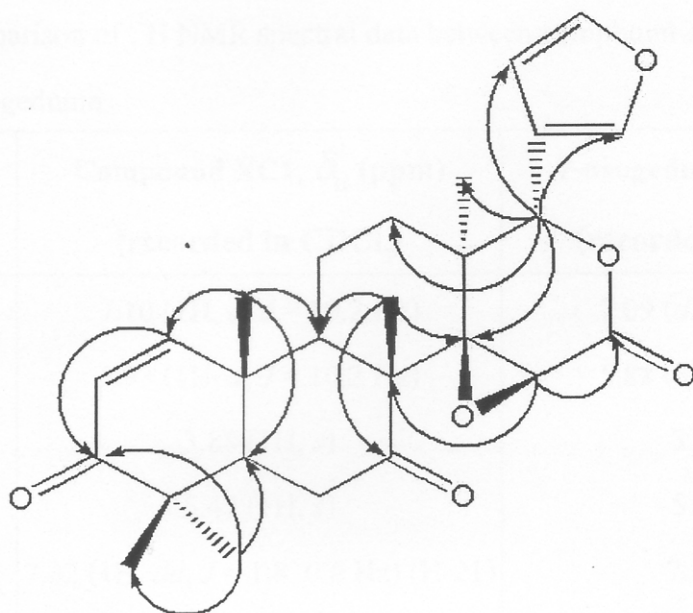
Table 7 (Continued)

position	$\delta_C^{\#}$ (ppm)		$\delta_H$ (ppm)
13	37.74	C	-
14	65.60	C-O	-
15	53.64	HC-O	3.88 (1H, <i>s</i> )
16	166.83	O-C=O	-
17	78.00	HC-O	5.47 (1H, <i>s</i> )
18	20.91	CH <sub>3</sub>	1.14 (3H, <i>s</i> )
19	20.64	CH <sub>3</sub>	1.36 (3H, <i>s</i> )
20	120.20	=C	-
21	141.03	=CH	7.42 (1H, <i>dd</i> , <i>J</i> = 1.8, 0.6 Hz)
22	109.78	=CH	6.36 (1H, <i>dd</i> , <i>J</i> = 1.8, 0.6 Hz)
23	143.11	=CH	7.40 (1H, <i>t</i> , <i>J</i> = 1.8 Hz)
24	17.38	CH <sub>3</sub>	1.22 (3H, <i>s</i> )
25	26.97	CH <sub>3</sub>	1.16 (3H, <i>s</i> )
26	19.80	CH <sub>3</sub>	1.14 (3H, <i>s</i> )

\* Chemical shift was assigned by HMQC.

# Carbon type deduced from DEPT experiment.





Selected HMBC correlation of compound XC1

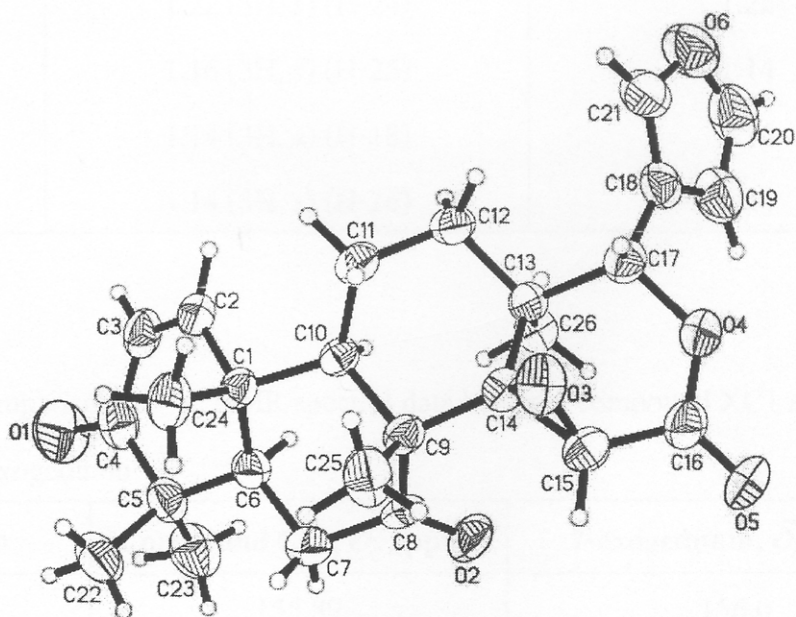


Figure 2 X-ray ORTEP diagram of compound XC1

**Table 8** Comparison of  $^1\text{H}$  NMR spectral data between compound XC1 and 7-oxogedunin

Position	Compound XC1, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )	7-oxogedunin, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )
1	7.10 (1H, <i>d</i> , $J = 10.2$ Hz)	7.09 ( <i>d</i> , $J = 10$ Hz)
2	5.93 (1H, <i>d</i> , $J = 10.2$ Hz)	5.88 ( <i>d</i> , $J = 10$ Hz)
15	3.88 (1H, <i>s</i> )	3.85 ( <i>s</i> )
17	5.47 (1H, <i>s</i> )	5.44 ( <i>s</i> )
$\alpha$ -furan	7.42 (1H, <i>dd</i> , $J = 1.8, 0.6$ Hz) (H-21) 7.40 (1H, <i>t</i> , $J = 1.8$ Hz) (H-23)	7.37 ( <i>m</i> )
$\beta$ -furan	6.36 (1H, <i>dd</i> , $J = 1.8, 0.6$ Hz) (H-22)	6.34 ( <i>m</i> )
methyl groups	1.36 (3H, <i>s</i> ) (H-19) 1.22 (3H, <i>s</i> ) (H-24) 1.16 (3H, <i>s</i> ) (H-25) 1.14 (3H, <i>s</i> ) (H-18) 1.14 (3H, <i>s</i> ) (H-26)	1.35 1.22 1.14 1.14 1.14

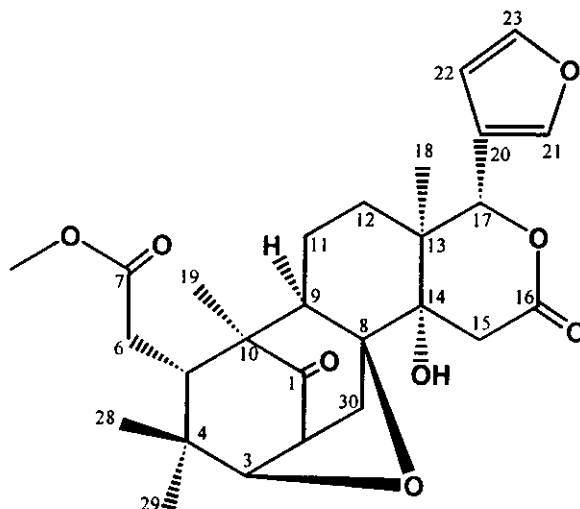
**Table 9** Comparison of  $^{13}\text{C}$  NMR spectral data between compound XC1 and 7-oxogedunin

Position	Compound Cx1, $\delta_{\text{C}}$ (ppm)	7-oxogedunin, $\delta_{\text{C}}$ (ppm)
1	155.89	156.0
2	126.44	126.3
3	203.22	203.2
4	45.22	45.2
5	54.59	47.6

Table 9 (Continued)

Position	Compound Cx1, $\delta_c$ (ppm)	7-oxogedunin, $\delta_c$ (ppm)
6	36.70	36.7
7	208.15	208.3
8	53.42	53.4
9	47.62	53.7
10	39.61	40.0
11	17.18	17.1
12	32.18	32.1
13	37.74	37.7
14	65.60	65.7
15	53.64	54.5
16	166.83	166.9
17	78.00	78.0
20	120.20	120.3
21	141.03	143.1
22	109.78	109.8
23	143.11	141.0
methyl groups	26.97 (C-25)	27.0
	20.91 (C-18)	20.9
	20.64 (C-19)	20.7
	19.80 (C-26)	19.7
	17.38 (C-24)	17.4

### 3.1.2 Compound XC2



Compound **XC2** was obtained as a colorless solid mp = 234-236 °C,  $[\alpha]_D^{26} = -40^\circ$  ( $c = 1.31$ ,  $\text{CHCl}_3$ ). The mass spectrum of this compound (see **Fig. 23**) showed the molecular ion peak at  $m/z$  486, thus this compound had molecular formula  $\text{C}_{27}\text{H}_{34}\text{O}_8$ . The UV spectrum (**Fig. 15**) showed maximum absorption band ( $\lambda_{\text{max}}$ ) at 212 nm. The IR spectrum (**Fig. 16**) showed absorption bands at 3452, 1724, 1721 and 1716  $\text{cm}^{-1}$  corresponding to a hydroxy group and three carbonyl groups, respectively. The presence of one carbonyl carbon of ketone at  $\delta$  215.31 and two carbonyl carbons of ester at  $\delta$  174.33 and 170.74 from  $^{13}\text{C}$  NMR spectrum supported the above conclusion.

The  $^{13}\text{C}$  NMR spectrum (see **Table 13**, **Fig. 18**) showed 27 signals for 27 carbon atoms. Analysis of the DEPT-90° and DEPT-135° (see **Table 10**, **Fig. 19**) spectra of this compound suggested the presence of five methyl carbons ( $\delta$  51.94, 28.08, 20.11, 16.91 and 16.16), five methylene carbons ( $\delta$  42.57, 36.96, 32.66, 28.74 and 17.95), eight methine carbons ( $\delta$  143.01, 140.84, 110.00, 91.41, 76.77, 52.14, 49.05 and 43.03) and nine signals for quaternary carbons ( $\delta$  215.31, 174.33, 170.74, 120.73, 85.53, 74.25, 51.11, 40.06 and 37.18). These chemical shifts were different from the values reported C-4 ( $\delta$  39.90), C-8 ( $\delta$  74.07 or 76.66), C-13 ( $\delta$  37.05), C-17 ( $\delta$  85.41), C-18 ( $\delta$  19.97), C-21 ( $\delta$  142.89), C-23 ( $\delta$  140.70) and C-29 ( $\delta$  16.03)

(Kokpol, *et al.*, 1996). HMQC and HMBC confirmed chemical shifts of C-4, C-8, C-13, C-17, C-18 and C-29 at  $\delta$  37.18, 85.53, 40.06, 76.77, 16.16 and 20.11, respectively and COSY and HMQC confirmed chemical shifts of C-21 and C-23 at 140.84 and 143.01 as newly assigned values.

The  $^1\text{H}$  NMR spectral data (see **Table 13**, **Fig. 17**) recorded in  $\text{CDCl}_3$  was a typical of limonoid. The characteristic peaks of furan nucleus as shown at  $\delta$  7.55 (1H, *br s*), 7.45 (1H, *br s*) and 6.47 (1H, *br s*) were assigned to H-21, H-23 and H-22, respectively. The signals at  $\delta$  6.27 (1H, *s*, H-17) could be assigned for a methine proton attached to a carbon adjacent to an oxygen atom and a furan ring. The signals at  $\delta$  3.10 (1H, *d*,  $J = 18.0$  Hz, H-15a) and 2.56 (1H, *d*,  $J = 18.0$  Hz, H-15b) were shown as a doublet with geminal coupling (Kokpol, *et al.*, 1996). The chemical shifts of H-18 and H-29 were assigned at  $\delta$  0.98 (3H, *s*) and  $\delta$  0.66 (3H, *s*), respectively. These chemical shifts were different from the values reported of H-18,  $\delta$  0.67 (3H, *s*) and H-29,  $\delta$  0.98 (3H, *s*) (Kokpol, *et al.*, 1996). HMBC confirmed chemical shifts of H-18 and H-29 at  $\delta$  0.98 (3H, *s*) and  $\delta$  0.66 (3H, *s*) as newly assigned values.

The structure of compound **XC2** was deduced from its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data (see **Table 13**, **Fig. 17** and **18**) together with the results of  $^1\text{H}$ - $^1\text{H}$  COSY (see **Table 11**, **Fig. 19**), HMQC (**Fig. 21**) and HMBC (see **Table 13**, **Fig. 22**). The correlation peaks in the HMBC spectrum (see **Table 13**, **Fig. 22**) between H-17 ( $\delta$  6.27) and the carbon at  $\delta$  140.84 (C-21), 120.73 (C-20), 110.00 (C-22), 74.25 (C-14), 40.06 (C-13), 28.74 (C-12) and 16.16 (C-18) confirmed the position of the furanyl group at C-17 position. The carbon signals at  $\delta$  170.74 (C-16), 85.53 (C-8), 74.25 (C-14) and 40.06 (C-13) showed the correlation peaks with the H-15a ( $\delta$  3.10), confirming the position of the carbonyl group at C-16. The carbon signals at  $\delta$  215.31 (C-1), 174.33 (C-7), 52.14 (C-9), 37.18 (C-4), 32.66 (C-6), 28.08 (C-28) and 20.11 (C-29) showed the correlation peaks with the H-5 ( $\delta$  3.07) and The carbon signals at  $\delta$  215.31 (C-1), 49.05 (C-2), 43.03 (C-5), 28.08 (C-28) and 20.11 (C-29) showed the

correlation peaks with H-3 ( $\delta$  4.20), confirming the position of the carbonyl group at C-1 and C-7. Thus, compound **XC2** was identified as xyloccensin K which was previously isolated from the fruits of *X. granatum* (Kokpol, *et al.*, 1996). The relative stereo structure of this compound was supported by X-ray diffraction, ring A is in a twist boat conformation, ring C is a relatively undistorted chair and ring D is a half-chair with C-13 and C-14 displaced from the mean plane of the other atoms. Ring B in both cases is a distorted chair, with the distortion being more pronounced in **XC2**, presumably as a direct result of the constraints of the C-3/C-8 linkage. The tetrahydrofuran ring of this compound is a slightly distorted  $\beta$ -envelope with the C-30 methylene grouping lying outside the approximate plane of the other four atoms (see **Table 59-61, Fig. 3**).

**Table 10**  $^{13}\text{C}$  and DEPT spectral data of compound **XC2**

$\delta_c$	DEPT-90°	DEPT-135°	Type of Carbon
215.31			C
174.33			C
170.74			C
143.01	143.01	143.01	CH
140.84	140.84	140.84	CH
120.73			C
110.00	110.0	110.00	CH
91.41	091.41	91.41	CH
85.53			C
76.77	76.77	76.77	CH
74.25			C

Table 10 (Continued)

$\delta_c$	DEPT-90°	DEPT-135°	Type of Carbon
52.14	52.14	52.14	CH
51.94		51.94	CH <sub>3</sub>
51.11			C
49.05	49.05	49.05	CH
43.03	43.03	43.03	CH
42.57		42.57	CH <sub>2</sub>
40.06			C
37.18			C
36.96		36.96	CH <sub>2</sub>
32.66		32.66	CH <sub>2</sub>
28.74		28.74	CH <sub>2</sub>
28.08		28.08	CH <sub>3</sub>
20.11		20.11	CH <sub>3</sub>
17.95		17.95	CH <sub>2</sub>
16.91		16.91	CH <sub>3</sub>
16.16		16.16	CH <sub>3</sub>

Table 11 300 MHz COSY correlation of some protons of compound XC2

$\delta_H$ (ppm)	Proton Correlation with $\delta_H$ (ppm)
H-23 (7.45)	H-22 (6.47)
H-3 (4.20)	H-2 (2.94)
H-15a (3.10)	H-15b (2.56)
H-5 (3.07)	H-6a (2.19)

Table 11 (Continued)

$\delta_{\text{H}}$ (ppm)	Proton Correlation with $\delta_{\text{H}}$ (ppm)
H-2 (2.94)	H-30a (2.52)
H-30a (2.52)	H-30b (2.05)
H-11a (2.03)	H-12b (1.48)
H-12a (1.72)	H-12b (1.48)

Table 12 Major HMBC correlation of compound XC2

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
2	2.94 (1H, <i>t</i> , $J = 6.0$ Hz)	C-1 (215.31), C-3 (91.41), C-4 (37.18), C-8 (85.53), C-10 (51.11) and C-30 (42.57)
3	4.20 (1H, <i>d</i> , $J = 5.7$ Hz)	C-1 (215.31), C-2 (49.05), C-5 (43.03), C-28 (28.08) and C-29 (20.11)
5	3.07 (1H, <i>m</i> )	C-1 (215.31), C-4 (37.18), C-6 (32.66), C-7 (174.33), C-9 (52.14), C-28 (28.08) and C-29 (20.11)
6*	2.15 (2H, <i>m</i> )	C-5 (43.03), C-7 (174.33) and C-10 (51.11)
7'	3.70 (3H, <i>s</i> )	C-7 (174.33)
9*	1.96 (1H, <i>m</i> )	C-1 (215.31), C-5 (43.03), C-10 (51.11) and C-11 (17.95)
11a*	2.03 (1H, <i>m</i> )	C-9 (52.14) and C-10 (51.11)
11b*	1.45 (1H, <i>m</i> )	C-9 (52.14)
12a	1.72 (1H, <i>td</i> , $J = 13.8, 13.8, 4.5$ Hz)	C-13 (40.06) and C-17 (76.77)
12b	1.48 (1H, <i>m</i> )	C-9 (52.14) and C-14 (74.25)



Table 12 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
15a	3.10 (1H, <i>d</i> , $J = 18.0$ Hz)	C-8 (85.53), C-13 (40.06), C-14 (74.25) and C-16 (170.74)
15b	2.56 (1H, <i>d</i> , $J = 18.0$ Hz)	C-8 (85.53), C-14 (74.25) and C-16 (170.74)
17	6.27 (1H, <i>s</i> )	C-12 (28.74), C-13 (40.06), C-14 (74.25), C-18 (16.16), C-20 (120.73), C-21 (140.84) and C-22 (110.00)
18	0.98 (3H, <i>s</i> )	C-12 (28.74), C-13 (40.06), C-14 (74.25) and C-17 (76.77)
19	0.92 (3H, <i>s</i> )	C-1 (215.31), C-5 (43.03), C-9 (52.14) and C-10 (51.11)
21	7.55 (1H, <i>br s</i> )	C-20 (120.73), C-22 (110.00) and C-23 (143.01)
22	6.47 (1H, <i>br s</i> )	C-20 (120.73), C-21 (140.84) and C-23 (143.01)
23	7.45 (1H, <i>br s</i> )	C-20 (120.73), C-21 (140.84) and C-22 (110.00)
28 <sup>a</sup>	1.10 (3H, <i>s</i> )	C-3 (91.41), C-4 (37.18), C-5 (43.03) and C-29 (20.11)
29 <sup>a</sup>	0.66 (3H, <i>s</i> )	C-3 (91.41), C-4 (37.18), C-5 (43.03) and C-28 (28.08)
30a*	2.52 (1H, <i>dd</i> , $J = 12.3, 6.6$ Hz)	C-1 (215.31), C-2 (49.05), C-9 (52.14) and C-14 (74.25)
30b*	2.05 (1H, <i>m</i> )	C-1 (215.31) and C-3 (91.41)

<sup>a</sup> Assignment with the same superscripts may be interchanged.

\* Chemical shift was assigned by HMQC

Table 13  $^1\text{H}$  and  $^{13}\text{C}$  spectral data of compound XC2

position	$\delta_{\text{C}}^{\#}$ (ppm)		$\delta_{\text{H}}$ (ppm)
1	215.31	C=O	-
2	49.05	CH	2.94 (1H, <i>t</i> , $J = 6.0$ Hz)
3	91.41	O-CH	4.20 (1H, <i>d</i> , $J = 5.7$ Hz)
4	37.18	C	-
5	43.03	CH	3.07 (1H, <i>m</i> )
6*	32.66	CH <sub>2</sub>	2.15 (2H, <i>m</i> )
7	174.33	O-C=O	-
7'	51.94	O-CH <sub>3</sub>	3.70 (3H, <i>s</i> )
8	85.53	O-C	-
9*	52.14	CH	1.96 (1H, <i>m</i> )
10	51.11	C	-
11*	17.95	CH <sub>2</sub>	2.03 (1H, <i>m</i> ), 1.45 (1H, <i>m</i> )
12	28.74	CH <sub>2</sub>	1.72 (1H, <i>td</i> , $J = 13.8, 13.8, 4.5$ Hz), 1.48 (1H, <i>m</i> )
13	40.06	C	-
14	74.25	O-C	-
15	36.96	CH <sub>2</sub>	3.10 (1H, <i>d</i> , $J = 18.0$ Hz), 2.56 (1H, <i>d</i> , $J = 18.0$ Hz)
16	170.74	O-C=O	-
17	76.77	O-CH	6.27 (1H, <i>s</i> )
18	16.16	CH <sub>3</sub>	0.98 (3H, <i>s</i> )
19	16.91	CH <sub>3</sub>	0.92 (3H, <i>s</i> )
20	120.73	=C	-
21	140.84	=CH	7.55 (1H, <i>br s</i> )

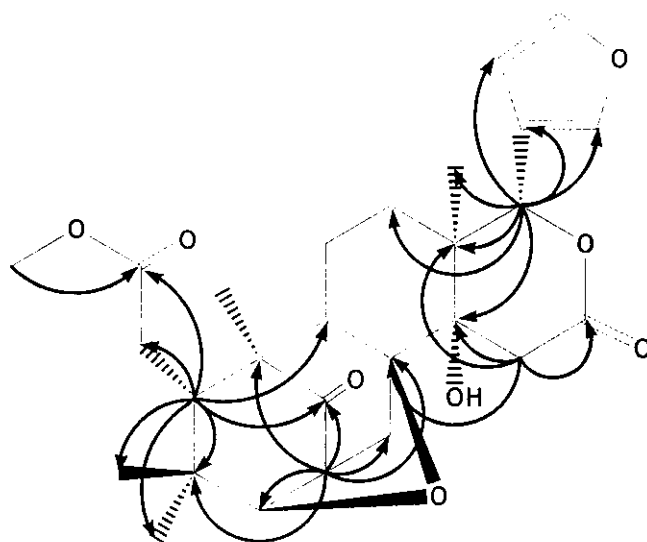
Table 13 (Continued)

position	$\delta_C^{\#}$ (ppm)		$\delta_H$ (ppm)
22	110.00	=CH	6.47 (1H, <i>br s</i> )
23	143.01	=CH	7.45 (1H, <i>br s</i> )
28 <sup>a</sup>	28.08	CH <sub>3</sub>	1.10 (3H, <i>s</i> )
29 <sup>a</sup>	20.11	CH <sub>3</sub>	0.66 (3H, <i>s</i> )
30*	42.57	CH <sub>2</sub>	2.52 (1H, <i>dd</i> , $J = 12.3, 6.6$ Hz), 2.05 (1H, <i>m</i> )

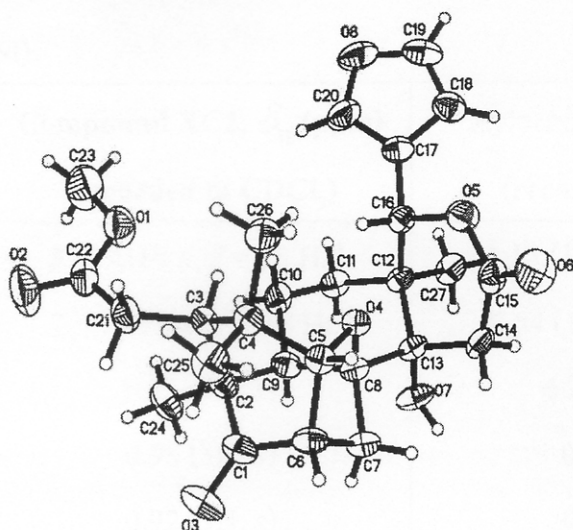
<sup>a</sup> Assignment with the same superscripts may be interchanged.

\* Chemical shift was assigned by HMQC.

<sup>#</sup> Carbon type deduced from DEPT experiment.



Selected HMBC correlation of compound XC2



**Figure 3** X-ray ORTEP diagram of compound XC2

**Table 14** Comparison of  $^1\text{H}$  NMR spectral data between compound XC2 and xylocensin K

Position	Compound XC2, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )	Xylocensin K, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )
2	2.94 (1H, <i>t</i> , $J = 6.0$ Hz)	2.96 (1H, <i>dd</i> , $J = 6, 6$ Hz)
3	4.20 (1H, <i>d</i> , $J = 5.7$ Hz)	4.22 (1H, <i>d</i> , $J = 6$ Hz)
5	3.07 (1H, <i>m</i> )	3.08 (1H, <i>dd</i> , $J = 11, 2$ Hz)
6	2.15 (2H, <i>m</i> )	2.24 (1H, <i>dd</i> , $J = 17, 11$ Hz), 2.14 (1H, <i>dd</i> , $J = 17, 2$ Hz)
7'	3.70 (3H, <i>s</i> )	3.70 (3H, <i>s</i> )
9	1.96 (1H, <i>m</i> )	1.97 (1H, <i>dd</i> , $J = 12.5, 5$ Hz)
11	2.03 (1H, <i>m</i> ), 1.45 (1H, <i>m</i> )	2.10 (1H, <i>m</i> ), 1.46 (1H, <i>m</i> )
12	1.72 (1H, <i>td</i> , $J = 13.8, 13.8, 4.5$ Hz), 1.48 (1H, <i>m</i> )	1.70 (1H, <i>ddd</i> , $J = 14, 14, 4$ Hz), 1.50 (1H, <i>ddd</i> , $J = 14, 1.5, 1.5$ Hz)

Table 14 (Continued)

Position	Compound XC2, $\delta_{\text{H}}$ (ppm) (recorded in CDCl <sub>3</sub> )	Xylocensin K, $\delta_{\text{H}}$ (ppm) (recorded in CDCl <sub>3</sub> )
15	3.10 (1H, <i>d</i> , $J = 18$ Hz), 2.56 (1H, <i>d</i> , $J = 18$ Hz)	3.13 (1H, <i>d</i> , $J = 17$ Hz), 2.54 (1H, <i>d</i> , $J = 17$ Hz)
17	6.27 (1H, <i>s</i> )	6.28 (1H, <i>br s</i> )
18	0.98 (3H, <i>s</i> )	0.67 (3H, <i>s</i> )
19	0.92 (3H, <i>s</i> )	0.94 (3H, <i>s</i> )
21	7.55 (1H, <i>br s</i> )	7.45 (1H, <i>dd</i> , $J = 2, 2$ Hz)
22	6.47 (1H, <i>br s</i> )	6.49 (1H, <i>br d</i> , $J = 2$ Hz)
23	7.45 (1H, <i>br s</i> )	7.56 (1H, <i>br s</i> )
28	1.10 (3H, <i>s</i> )	1.03 (3H, <i>s</i> )
29	0.66 (3H, <i>s</i> )	0.98 (3H, <i>s</i> )
30	2.52 (1H, <i>dd</i> , $J = 12.3, 6.6$ Hz), 2.05 (1H, <i>m</i> )	2.52 (1H, <i>dd</i> , $J = 12, 7$ Hz), 2.04 (1H, <i>d</i> , $J = 12$ Hz)

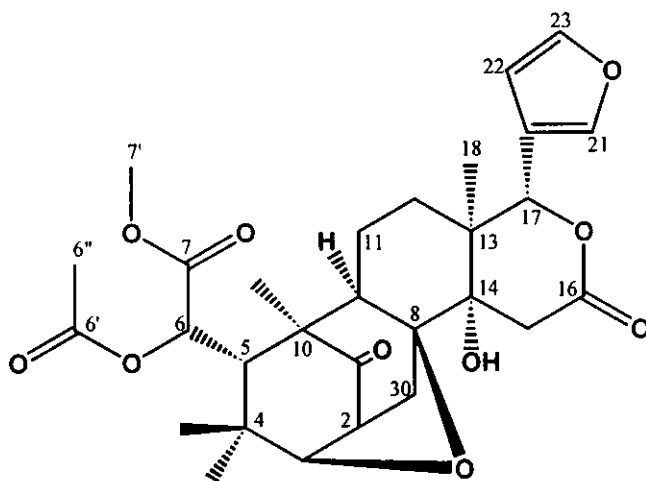
Table 15 Comparison of <sup>13</sup>C NMR spectral data between compound XC2 and xylocensin K

Position	Compound XC2, $\delta_{\text{C}}$ (ppm)	Xylocensin K, $\delta_{\text{C}}$ (ppm)
1	215.31	215.21
2	49.05	48.91
3	91.41	91.27
4	37.18	39.90
5	43.03	42.90

Table 15 (Continued)

Position	Compound XC2, $\delta_c$ (ppm)	Xylocensin K, $\delta_c$ (ppm)
6	32.66	32.52
7	174.33	174.19
7'	51.94	51.81
8	85.53	74.07 or 76.66
9	52.14	51.98
10	51.11	50.97
11	17.95	17.81
12	28.74	28.58
13	40.06	37.05
14	74.25	74.07 or 76.66
15	36.96	36.76
16	170.74	170.71
17	76.77	85.41
18	16.16	19.97
19	16.91	16.78
20	120.73	120.60
21	140.84	142.89
22	110.00	109.87
23	143.01	140.70
28	28.08	27.94
29	20.11	16.03
30	42.57	42.44

### 3.1.3 Compound XC3



Compound **XC3** was obtained as a colorless oil,  $[\alpha]_D^{26} = -46^\circ$  ( $c = 0.96$ ,  $\text{CHCl}_3$ ). The UV spectrum showed maximum absorption bands ( $\lambda_{\text{max}}$ ) at 210 nm (see **Fig. 24**). The IR spectrum showed absorption bands at 3460, 1745, 1739, 1732 and  $1716 \text{ cm}^{-1}$  corresponding to a hydroxy group and four carbonyl groups, respectively (see **Fig. 25**). The presence of one carbonyl carbon of ketone at  $\delta$  212.98 and three carbonyl carbons of ester at  $\delta$  170.17, 170.04 and 169.74 from  $^{13}\text{C}$  NMR spectrum supported the above conclusion.

The complete analysis of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of compound **XC3** (see **Table 19**, **Fig. 26** and **27**) were assigned with information provided from  $^1\text{H}$ - $^1\text{H}$  COSY (see **Table 17**, **Fig. 29**),  $^1\text{H}$ - $^{13}\text{C}$  correlation (HMOC) (**Fig. 30**) and  $^1\text{H}$ - $^{13}\text{C}$  correlation by long-range coupling (HMBC) (see **Table 18**, **Fig. 31**), along with comparison of  $^1\text{H}$  NMR spectral data to compound **XC2** (see **Table 13**, **Fig. 17**). The  $^{13}\text{C}$  NMR (see **Table 19**, **Fig. 26**) spectrum of compound **XC3** recorded in  $\text{CDCl}_3$  showed 29 signals for 29 carbon atoms. Analysis of the DEPT- $90^\circ$  and DEPT- $135^\circ$  spectra of this compound (see **Table 16**, **Fig. 28**) suggested the presence of six methyl carbons ( $\delta$  52.42, 29.73, 21.36, 20.66, 18.12 and 16.21), four methylene carbons ( $\delta$  42.83, 37.34, 28.86 and 18.23), nine methine carbons ( $\delta$  143.23, 140.75, 109.91,

92.89, 76.33, 71.99, 52.96, 48.92 and 47.03) and ten quaternary carbons ( $\delta$  212.98, 170.17, 170.04, 169.74, 120.77, 85.08, 74.53, 50.76, 40.17 and 38.25).

Compound **XC3**, a derivative of compound **XC2**, showed similar characteristic bands in IR and UV spectrum with those of **XC2**. Comparison of the  $^1\text{H}$  NMR spectral data (see **Table 13** and **19**) of the two compounds revealed close structural similarity. The two compounds differed in H-6 which was methylene proton in **XC2** but oxymethine proton in **XC3**. The H-6  $^1\text{H}$  NMR chemical shift of **XC2** and **XC3** were shown at  $\delta$  2.19 (1H, *m*), 2.03 (1H, *m*) and  $\delta$  5.08 (1H, *d*,  $J = 2.7$  Hz), respectively. An additional signal of acetoxy proton (H-6'') in **XC3** was shown as  $\delta$  2.07 (3H, *s*) which was not observed in compound **XC2**.

The HMBC correlation of compound **XC3** (see **Table 18**, **Fig. 31**) showed the same correlation with compound **XC2** (see **Table 12**), except the proton signals at H-6 ( $\delta$  5.08, 1H, *d*,  $J = 2.7$  Hz) and H-6'' ( $\delta$  2.07 (3H, *s*). The proton signal of H-6 gave correlation peaks with C-4 (38.25), C-5 (47.03), C-6' (170.04), C-7 (170.17) and C-10 (50.76) while H-6'' gave correlation peaks with carbonyl group (C-6', 170.04), thus confirming the position of the acetoxy group at C-6. Compound **XC3** was identified as 6-acetoxycedrodorin which was the compound previously isolated from the leaves of *Cedrela odorata* (Veitch, *et al.*, 1999)

**Table 16**  $^{13}\text{C}$  and DEPT spectral data of compound **XC3**

$\delta_{\text{C}}$	DEPT-90°	DEPT-135°	Type of Carbon
212.98			C
170.17			C
170.04			C
169.74			C



Table 16 (Continued)

$\delta_c$	DEPT-90°	DEPT-135°	Type of Carbon
143.23	143.23	143.23	CH
140.75	140.75	140.75	CH
120.77			C
109.91	109.91	109.91	CH
92.89	92.89	92.89	CH
85.08			C
76.33	76.33	76.33	CH
74.53			C
71.99	71.99	71.99	CH
52.96	52.96	52.96	CH
52.42		52.42	CH <sub>3</sub>
50.76			C
48.92	48.92	48.92	CH
47.03	47.03	47.03	CH
42.83		42.83	CH <sub>2</sub>
40.17			C
38.25			C
37.34		37.34	CH <sub>2</sub>
29.73		29.73	CH <sub>3</sub>
28.86		28.86	CH <sub>2</sub>
21.36		21.36	CH <sub>3</sub>
20.66		20.66	CH <sub>3</sub>
18.23		18.23	CH <sub>2</sub>
18.12		18.12	CH <sub>3</sub>
16.21		16.21	CH <sub>3</sub>

**Table 17** 300 MHz COSY correlation of some protons of compound XC3

$\delta_{\text{H}}$ (ppm)	Proton Correlation with $\delta_{\text{H}}$ (ppm)
H-23 (7.47)	H-22 (6.45)
H-6 (5.08)	H-5 (3.02)
H-3 (4.06)	H-2 (3.04)
H-15a (3.15)	H-15b (2.52)
H-2 (3.04)	H-30a (2.54)
H-30a (2.54)	H-30b (2.07)
H-11a (1.92)	H-12a (1.75), H-11b (1.55) and H-12b (1.53)
H-12a (1.75)	H-11b (1.55) and H-12b (1.53)

**Table 18** Major HMBC correlation of compound XC3

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
2	3.04 (1H, <i>t</i> , $J = 6.0$ Hz)	C-1 (212.98), C-3 (92.89), C-4 (38.25), C-8 (85.08), C-10 (50.76) and C-30 (42.83)
3	4.06 (1H, <i>d</i> , $J = 6.0$ Hz)	C-1 (212.98), C-2 (48.92), C-5 (47.03), C-28 (21.36) and C-29 (29.73)
5	3.02 (1H, <i>d</i> , $J = 2.7$ Hz)	C-1 (212.98), C-4 (38.25), C-6 (71.99), C-9 (52.96), C-10 (50.76), C-28 (21.36) and C-29 (29.73)
6	5.08 (1H, <i>d</i> , $J = 2.7$ Hz)	C-4 (38.25), C-5 (47.03), C-6' (170.04), C-7 (170.17) and C-10 (50.76)
6''	2.13 (3H, <i>s</i> )	C-6' (170.04)
7'	3.78 (3H, <i>s</i> )	C-7 (170.17)

Table 18 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
9	2.04 (1H, <i>dd</i> , $J = 11.4, 4.2$ Hz)	C-5 (47.03), C-10 (50.76) and C-11 (18.23)
11a*	1.92 (1H, <i>m</i> )	C-12 (28.86)
11b*	1.55 (1H, <i>m</i> )	C-8 (85.08), C-12 (28.86) and C-13 (40.17)
12a*	1.75 (1H, <i>m</i> )	C-11 (18.23), C-13 (40.17), C-17 (76.33) and C-18 (16.21)
12b*	1.53 (1H, <i>m</i> )	C-9 (52.96), C-11 (18.23), C-13 (40.17), C-14 (74.53) and C-17 (76.33)
15a	3.15 (1H, <i>d</i> , $J = 18.0$ Hz)	} C-8 (85.08), C-14 (74.53), C-13 (40.17) and C-16 (169.74)
15b	2.52 (1H, <i>d</i> , $J = 18.0$ Hz)	
17	6.21 (1H, <i>s</i> )	C-12 (28.86), C-13 (40.17), C-14 (74.53), C-18 (16.21), C-20 (120.77), C-21 (140.75) and C-22 (109.91)
18	1.00 (3H, <i>s</i> )	C-12 (28.86), C-13 (40.17), C-14 (74.53) and C-17 (76.33)
19	1.05 (3H, <i>s</i> )	C-1 (212.98), C-5 (47.03), C-6 (71.99), C-8 (85.08), C-9 (52.96) and C-10 (50.76)
21	7.49 (1H, <i>dd</i> , $J = 1.8, 0.9$ Hz)	C-20 (120.77), C-22 (109.91) and C-23 (143.23)
22	6.45 (1H, <i>dd</i> , $J = 1.8, 0.9$ Hz)	C-17 (76.33), C-20 (120.77), C-21 (140.75) and C-23 (143.23)
23	7.47 (1H, <i>t</i> , $J = 1.8$ Hz)	C-20 (120.77), C-21 (140.75) and C-22 (109.91)
28 <sup>a</sup>	0.99 (3H, <i>s</i> )	C-3 (92.89), C-4 (38.25), C-5 (47.03) and C-29 (29.73)

Table 18 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
29 <sup>a</sup>	1.05 (3H, <i>s</i> )	C-3 (92.89), C-4 (38.25), C-5 (47.03) and C-28 (21.36)
30a	2.54 (1H, <i>dd</i> , $J = 12.3, 6.6$ Hz)	C-1 (212.98), C-2 (48.92), C-8 (85.08), C-9 (52.96) and C-14 (74.53)
30b	2.07 (1H, <i>d</i> , $J = 12.3$ Hz)	C-1 (212.98), C-2 (48.92), C-3 (92.89) and C-9 (52.96)

<sup>a</sup> Assignment with the same superscripts may be interchanged.

\* Chemical shift was assigned by HMQC

Table 19 <sup>1</sup>H and <sup>13</sup>C spectral data of compound XC3

position	$\delta_{\text{C}}^{\#}$ (ppm)		$\delta_{\text{H}}$ (ppm)
1	212.98	C=O	-
2	48.92	CH	3.04 (1H, <i>t</i> , $J = 6.0$ Hz)
3	92.89	O-CH	4.06 (1H, <i>d</i> , $J = 6.0$ Hz)
4	38.25	C	-
5	47.03	CH	3.02 (1H, <i>d</i> , $J = 2.7$ Hz)
6	71.99	O-CH	5.08 (1H, <i>d</i> , $J = 2.7$ Hz)
6'	170.04	O-C=O	-
6''	20.66	CH <sub>3</sub>	2.13 (3H, <i>s</i> )
7	170.17	O-C=O	-
7'	52.42	O-CH <sub>3</sub>	3.78 (3H, <i>s</i> )
8	85.08	O-C	-

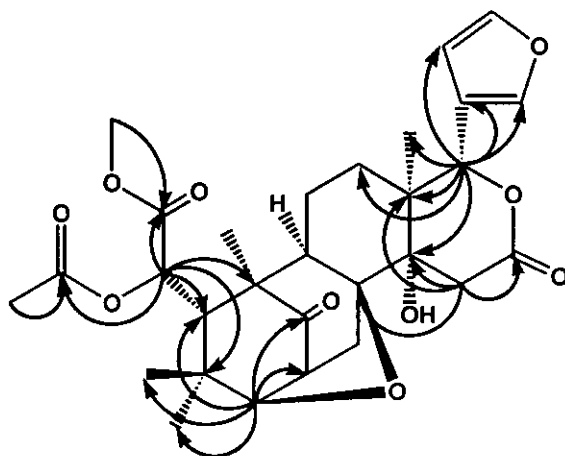
Table 19 (Continued)

position	$\delta_C^{\#}$ (ppm)		$\delta_H$ (ppm)
9	52.96	CH	2.04 (1H, <i>dd</i> , $J = 11.4, 4.2$ Hz)
10	50.76	C	-
11*	18.23	CH <sub>2</sub>	1.92 (1H, <i>m</i> ), 1.55 (1H, <i>m</i> )
12*	28.86	CH <sub>2</sub>	1.75 (1H, <i>m</i> ), 1.53 (1H, <i>m</i> )
13	40.17	C	-
14	74.53	O-C	-
15	37.34	CH <sub>2</sub>	3.15 (1H, <i>d</i> , $J = 18.0$ Hz), 2.52 (1H, <i>d</i> , $J = 18.0$ Hz)
16	169.74	O-C=O	-
17	76.33	O-CH	6.21 (1H, <i>s</i> )
18	16.21	CH <sub>3</sub>	1.00 (3H, <i>s</i> )
19	18.12	CH <sub>3</sub>	1.05 (3H, <i>s</i> )
20	120.77	=C	-
21	140.75	=CH	7.49 (1H, <i>dd</i> , $J = 1.8, 0.9$ Hz)
22	109.91	=CH	6.45 (1H, <i>dd</i> , $J = 1.8, 0.9$ Hz)
23	143.23	=CH	7.47 (1H, <i>t</i> , $J = 1.8$ Hz)
28 <sup>a</sup>	21.36	CH <sub>3</sub>	0.99 (3H, <i>s</i> )
29 <sup>a</sup>	29.73	CH <sub>3</sub>	1.05 (3H, <i>s</i> )
30	42.83	CH <sub>2</sub>	2.54 (1H, <i>dd</i> , $J = 12.3, 6.6$ Hz), 2.07 (1H, <i>d</i> , $J = 12.3$ Hz)

<sup>a</sup> Assignment with the same superscripts may be interchanged.

\* Chemical shift was assigned by HMQC.

# Carbon type deduced from DEPT experiment.



Selected HMBC correlation of compound XC3

**Table 20** Comparison of  $^1\text{H}$  NMR spectral data between compound XC3 and 6-acetoxycedrodorin

Position	Compound XC3, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )	6-Acetoxycedrodorin, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )
2	3.04 (1H, <i>t</i> , $J = 6.0$ Hz)	2.95 (1H, <i>m</i> )
3	4.06 (1H, <i>d</i> , $J = 6.0$ Hz)	3.98 (1H, <i>d</i> , $J = 5.8$ Hz)
5	3.02 (1H, <i>d</i> , $J = 2.7$ Hz)	2.95 (1H, <i>m</i> )
6	5.08 (1H, <i>d</i> , $J = 2.7$ Hz)	4.99 (1H, <i>d</i> , $J = 2.6$ Hz)
6''	2.13 (3H, <i>s</i> )	2.03 (1H, <i>s</i> )
7'	3.78 (3H, <i>s</i> )	3.73 (1H, <i>s</i> )
9	2.04 (1H, <i>dd</i> , $J = 11.4, 4.2$ Hz)	2.05 (1H, <i>dd</i> , $J = 11.8, 4.6$ Hz)
11	1.92 (1H, <i>m</i> ), 1.55 (1H, <i>m</i> )	1.74 (1H, <i>m</i> ), 1.48 (1H, <i>m</i> )
12	1.75 (1H, <i>m</i> ), 1.53 (1H, <i>m</i> )	1.69 (1H, <i>m</i> ), 1.26 (1H, <i>m</i> )
15	3.15 (1H, <i>d</i> , $J = 18.0$ Hz), 2.52 (1H, <i>d</i> , $J = 18.0$ Hz)	2.96 (1H, <i>d</i> , $J = 18$ Hz), 2.50 (1H, <i>d</i> , $J = 18$ Hz)
17	6.21 (1H, <i>s</i> )	6.07 (1H, <i>s</i> )

Table 20 (Continued)

Position	Compound XC3, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )	6-Acetoxycedrodorin, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )
18	1.00 (3H, <i>s</i> )	0.89 (3H, <i>s</i> )
19	1.05 (3H, <i>s</i> )	0.93 (3H, <i>s</i> )
21	7.49 (1H, <i>dd</i> , $J = 1.8, 0.9$ Hz)	7.65 (1H, <i>m</i> )
22	6.45 (1H, <i>dd</i> , $J = 1.8, 0.9$ Hz)	6.49 (1H, <i>dd</i> , $J = 1.6, 0.6$ Hz)
23	7.47 (1H, <i>t</i> , $J = 1.8$ Hz)	7.73 (1H, <i>t</i> , $J = 1.6$ Hz)
28	0.99 (3H, <i>s</i> )	0.88 (3H, <i>s</i> )
29	1.05 (3H, <i>s</i> )	0.97 (3H, <i>s</i> )
30	2.54 (1H, <i>dd</i> , $J = 12.3, 6.6$ Hz), 2.07 (1H, <i>d</i> , $J = 12.3$ Hz)	2.59 (1H, <i>dd</i> , $J = 12.6, 6.8$ Hz), 1.86 (1H, <i>d</i> , $J = 12.6$ Hz)

Table 21 Comparison of  $^{13}\text{C}$  NMR spectral data between compound XC3 and 6-acetoxycedrodorin

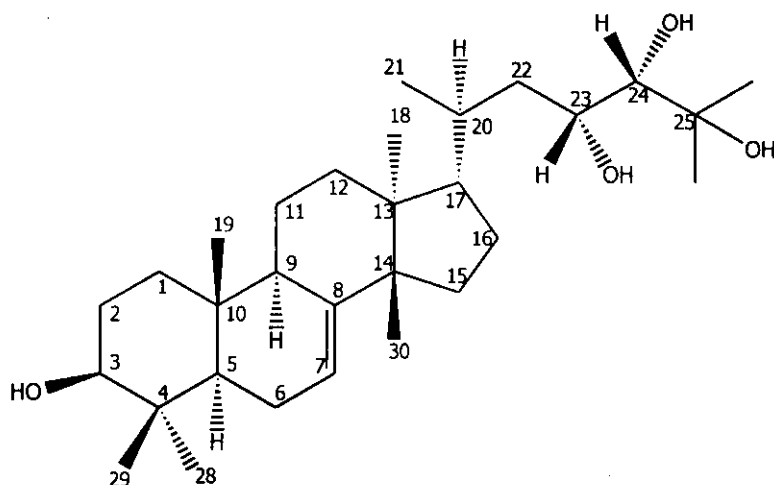
Position	Compound XC3, $\delta_{\text{C}}$ (ppm)	6-Acetoxycedrodorin, $\delta_{\text{C}}$ (ppm)
1	212.98	212.7
2	48.92	48.3
3	92.89	92.0
4	38.25	37.6
5	47.03	46.4
6	71.99	71.6
6'	170.04	169.2
6''	20.66	20.2
7	170.17	169.9

**Table 21** (Continued)

<b>Position</b>	<b>Compound XC3, <math>\delta_C</math> (ppm)</b>	<b>6-Acetoxycedrodorin, <math>\delta_C</math> (ppm)</b>
7'	52.42	52.2
8	85.08	85.3
9	52.96	52.2
10	50.76	50.1
11	18.23	17.6
12	28.86	28.5
13	40.17	39.7
14	74.53	73.0
15	37.34	36.1
16	169.74	169.3
17	76.33	75.3
18	16.21	16.1
19	18.12	17.5
20	120.77	121.1
21	140.75	140.5
22	109.91	110.0
23	143.23	143.5
28	21.36	20.7
29	29.73	29.1
30	42.83	42.6



### 3.1.4 Compound XC4



Compound **XC4** was obtained as a colorless solid mp = 246-248 °C,  $[\alpha]_D^{26} = -47^\circ$  ( $c = 0.068$ , acetone), this compound showed the characteristic of a triterpene by giving a purple spot with vanillin sulfuric acid reagent. Its IR spectrum (**Fig. 32**) showed the presence of hydroxy group at  $3321\text{ cm}^{-1}$

The  $^{13}\text{C}$  NMR spectrum (see **Table 25**, **Fig. 34**) showed 29 signals for 30 carbon atoms. Analysis of the DEPT- $90^\circ$  and DEPT- $135^\circ$  (see **Table 22**, **Fig. 35**) spectra of this compound suggested the presence of eight methyl carbons ( $\delta$  26.30, 25.67, 25.29, 20.39, 17.44, 13.49 and 11.55), eight methylene carbons ( $\delta$  39.32, 35.60, 32.31, 32.18, 26.66, 26.13, 22.30 and 16.41), eight methine carbons ( $\delta$  116.28, 76.21, 73.77, 67.19, 52.16, 49.01, 47.22 and 31.88) and six signals for quaternary carbons ( $\delta$  143.98, 71.77, 49.47, 41.83, 37.30 and 33.19).

The  $^1\text{H}$  NMR spectral data (see **Table 25**, **Fig. 33**) recorded in  $\text{DMSO-}d_6$  and  $\text{CDCl}_3$ , displayed the characteristic peaks of triterpene, as one methyl *doublet* at  $\delta$  0.90 (3H, *d*,  $J = 6.3$  Hz) and seven methyl *singlets* at  $\delta$  1.21, 1.20, 1.09, 0.96, 0.92, 0.80, 0.80 and 0.72. An olefinic proton and an oxymethine proton were resonated at 5.23 (1H, *br s*) and 3.09 (1H, *dd*,  $J = 9.0, 5.1$  Hz), respectively, which could be assigned to the position C-7 (116.28) and C-3 (76.21), respectively.

The structure of compound **XC4** was deduced from its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data (see **Table 25**, **Fig. 33** and **34**) together with the results of  $^1\text{H}$ - $^1\text{H}$  COSY (see **Table 23**, **Fig. 36**), HMQC (**Fig. 37**) and HMBC (see **Table 24**, **Fig. 38**). The correlation peaks in the HMBC spectrum (see **Table 24**, **Fig. 39**) between Me-28 ( $\delta$  0.92) and the carbon at  $\delta$  76.21 (C-3), 52.16 (C-5) and 20.39 (C-29) confirmed the position of the hydroxy group at C-3 position. The carbon signals at  $\delta$  143.98 (C-8), 41.83 (C-13) and 49.47 (C-14) showed the correlation peaks with the Me-30 ( $\delta$  0.96), confirming the position of the carbon  $\text{sp}^2$  at C-8. The compound **XC4** was identified as hispidol B which was first isolated from the leaves of *Trichilia hispida* Penning. (Meliaceae) (Jolad, *et al.*, 1981). The stereochemistry of compound **XC4** has been confirmed as (3*S*, 23*R*, 24*S*)-tirucall-7-ene-3,23,24,25-tetrol by means of a single-crystal X-ray diffraction study (see **Table 62-64**, **Fig. 4**). The presence of the 20*S* tirucallane rather than the 20*R* euphane skeleton was assumed on biogenetic grounds as the former occurred widely in the Meliaceae while the latter appeared to be confined to *Melia* species. The stereochemistry of compound **XC4** at C-23 and C-24 has previously been discussed in relation to spectroscopic data and their comparison with those of allied compounds. Thus, Jolad, *et al.* proposed that the stereochemistry was 23*R*, 24*S* because of the zero coupling constant between H-23 and H-24 (Bhandari, *et al.*, 1988).

**Table 22**  $^{13}\text{C}$  and DEPT spectral data of compound **XC4**

$\delta_{\text{C}}$	DEPT-90°	DEPT-135°	Type of Carbon
143.98			C
116.28	116.28	116.28	CH
76.21	76.21	76.21	CH
73.77	73.77	73.77	CH
71.77			C

Table 22 (Continued)

$\delta_c$	DEPT-90°	DEPT-135°	Type of Carbon
67.19	67.19	67.19	CH
52.16	52.16	52.16	CH
49.47			C
49.01	49.01	49.01	CH
47.22	47.22	47.22	CH
41.83			C
39.33		39.33	CH <sub>2</sub>
37.30			C
35.60		35.60	CH <sub>2</sub>
33.19			C
32.31		32.31	CH <sub>2</sub>
32.18		32.18	CH <sub>2</sub>
31.88	31.88	31.88	CH
26.66		26.66	CH <sub>2</sub>
26.30		26.30	CH <sub>3</sub>
26.13		26.13	CH <sub>2</sub>
25.67		25.67	CH <sub>3</sub>
25.29		25.29	CH <sub>3</sub>
25.29		25.29	CH <sub>3</sub>
22.30		22.30	CH <sub>2</sub>
20.39		20.39	CH <sub>3</sub>
17.44		17.44	CH <sub>3</sub>
16.41		16.41	CH <sub>2</sub>
13.49		13.49	CH <sub>3</sub>
11.55		11.55	CH <sub>3</sub>

**Table 23** 300 MHz COSY correlation of some protons of compound XC4

$\delta_{\text{H}}$ (ppm)	Proton Correlation with $\delta_{\text{H}}$ (ppm)
H-7 (5.23)	H-6 (2.01)
H-23 (3.97)	H-22a (1.82) and H-22b (1.09)
H-3 (3.09)	H-2 (1.58)
H-9 (2.17)	H-11 (1.52)
H-6 (2.01)	H-5 (1.46)

**Table 24** Major HMBC correlation of compound XC4

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
1*	1.38 (2H, <i>m</i> )	-
2*	1.58 (2H, <i>m</i> )	-
3	3.09 (1H, <i>dd</i> , $J = 9.9, 5.4$ Hz)	C-28 (26.30) and C-29 (13.49)
5*	1.46 (1H, <i>m</i> )	-
6*	2.12 (1H, <i>m</i> ), 1.91 (1H, <i>m</i> )	-
7	5.23 (1H, <i>br s</i> )	-
9*	2.17 (1H, <i>m</i> )	-
11*	1.52 (2H, <i>m</i> )	-
12*	1.51 (2H, <i>m</i> )	-
15*	1.63 (2H, <i>m</i> )	-
16*	1.51 (2H, <i>m</i> )	-
17*	1.27 (1H, <i>m</i> )	C-12 (32.31) and C-15 (35.60)
18	0.72 (3H, <i>s</i> )	C-12 (32.31) and C-17 (49.01)
19	0.80 (3H, <i>s</i> )	C-1 (32.18) and C-5 (52.16)
20*	1.83 (1H, <i>m</i> )	-

Table 24 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
21	0.90 (3H, <i>d</i> , $J = 6.3$ Hz)	C-17 (49.01) and C-22 (39.33)
22*	1.82 (1H, <i>m</i> ), 1.09 (1H, <i>m</i> )	-
23	3.97 (1H, <i>dd</i> , $J = 9.0, 4.5$ Hz)	-
24	3.04 (1H, <i>s</i> )	C-22 (39.33), C-26 (25.29) and C-27 (25.29)
26 <sup>a</sup>	1.20 (3H, <i>s</i> )	C-24 (73.77), C-25 (71.77) and C-27 (25.29)
27 <sup>a</sup>	1.21 (3H, <i>s</i> )	C-24 (73.77), C-25 (71.77) and C-26 (25.29)
28	0.92 (3H, <i>s</i> )	C-3 (76.21), C-5 (52.16) and C-29 (13.49)
29	0.80 (3H, <i>s</i> )	C-3 (76.21), C-5 (52.16) and C-28 (26.30)
30	0.96 (3H, <i>s</i> )	C-8 (143.98), C-13 (41.83) and C-14 (49.47)

<sup>a</sup> Assignment with the same superscripts may be interchanged.

\* Chemical shift was assigned by HMQC.

Table 25 <sup>1</sup>H and <sup>13</sup>C spectral data of compound XC4

position	$\delta_{\text{C}}$ (ppm)		$\delta_{\text{H}}$ (ppm)
1*	32.18	CH <sub>2</sub>	1.38 (2H, <i>m</i> )
2*	26.13	CH <sub>2</sub>	1.58 (2H, <i>m</i> )
3	76.21	O-CH	3.09 (1H, <i>dd</i> , $J = 9.0, 5.1$ Hz)
4	37.30	C	-
5*	52.16	CH	1.46 (1H, <i>m</i> )
6*	22.30	CH <sub>2</sub>	2.12 (1H, <i>m</i> ), 1.91 (1H, <i>m</i> )
7	116.28	=CH	5.23 (1H, <i>br s</i> )
8	143.98	=C	-
9*	47.22	CH	2.17 (1H, <i>m</i> )

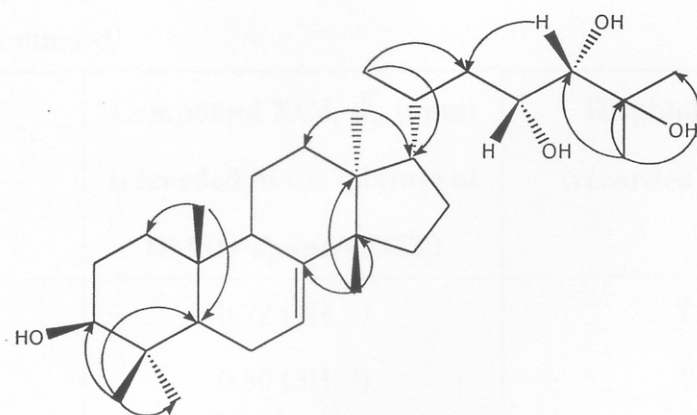
Table 25 (Continued)

position	$\delta_C^{\#}$ (ppm)		$\delta_H$ (ppm)
10	33.19	C	-
11*	16.41	CH <sub>2</sub>	1.52 (2H, <i>m</i> )
12*	32.31	CH <sub>2</sub>	1.51 (2H, <i>m</i> )
13	41.83	C	-
14	49.47	C	-
15*	35.60	CH <sub>2</sub>	1.63 (2H, <i>m</i> )
16*	26.66	CH <sub>2</sub>	1.51 (2H, <i>m</i> )
17*	49.01	CH	1.27 (1H, <i>m</i> )
18	11.55	CH <sub>3</sub>	0.72 (3H, <i>s</i> )
19	20.39	CH <sub>3</sub>	0.80 (3H, <i>s</i> )
20*	31.88	CH	1.83 (1H, <i>m</i> )
21	17.44	CH <sub>3</sub>	0.90 (3H, <i>d</i> , <i>J</i> = 6.3 Hz)
22*	39.33	CH <sub>2</sub>	1.82 (1H, <i>m</i> ), 1.09 (1H, <i>m</i> )
23	67.19	O-CH	3.97 (1H, <i>dd</i> , <i>J</i> = 9.0, 4.5 Hz)
24	73.77	O-CH	3.04 (1H, <i>s</i> )
25	71.77	O-C	-
26	25.29	CH <sub>3</sub>	1.20 (3H, <i>s</i> ) <sup>a</sup>
27	25.29	CH <sub>3</sub>	1.21 (3H, <i>s</i> ) <sup>a</sup>
28	26.30	CH <sub>3</sub>	0.92 (3H, <i>s</i> )
29	13.49	CH <sub>3</sub>	0.80 (3H, <i>s</i> )
30	25.67	CH <sub>3</sub>	0.96 (3H, <i>s</i> )

<sup>a</sup> Assignment with the same superscripts may be interchanged.

\* Chemical shift was assigned by HMQC.

<sup>#</sup> Carbon type deduced from DEPT experiment.



Selected HMBC correlation of compound XC4

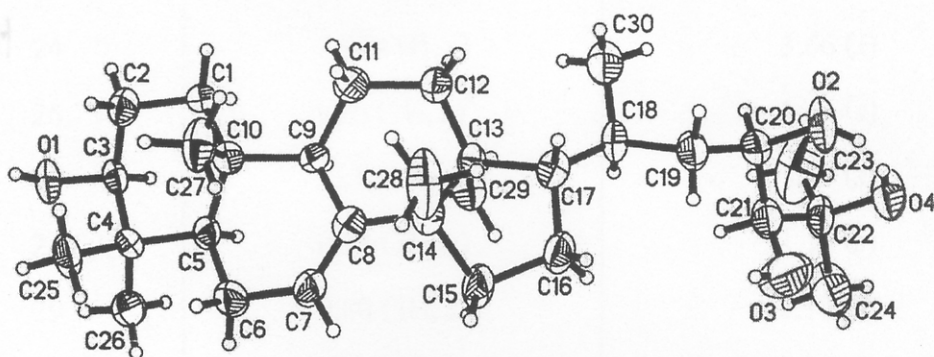


Figure 4 X-ray ORTEP diagram of compound XC4

**Table 26** Comparison of  $^1\text{H}$  NMR spectral data between compound XC4 and hispidol B

Position	Compound XC4, $\delta_{\text{H}}$ (ppm) (recorded in the mixture of DMSO- $d_6$ and $\text{CDCl}_3$ )	Hispidol B, $\delta_{\text{H}}$ (ppm) (recorded in pyridine- $d_5$ )
3	3.09 (1H, <i>dd</i> , $J = 9.0, 5.1$ Hz)	3.48 ( <i>dd</i> , $J = 11.0, 5.1$ Hz)
6	2.12 (1H, <i>m</i> ), 1.91 (1H, <i>m</i> )	1.86 ( <i>m</i> ), 2.07 ( <i>m</i> )
7	5.23 (1H, <i>br s</i> )	5.33 ( <i>m</i> )

Table 26 (Continued)

Position	Compound XC4, $\delta_{\text{H}}$ (ppm) (recorded in the mixture of DMSO- $d_6$ and $\text{CDCl}_3$ )	Hispidol B, $\delta_{\text{H}}$ (ppm) (recorded in pyridine- $d_5$ )
18	0.72 (3H, <i>s</i> )	0.83 ( <i>s</i> )
19	0.80 (3H, <i>s</i> )	0.90 ( <i>s</i> )
21	0.90 (3H, <i>d</i> , $J = 6.3$ Hz)	1.14 ( <i>d</i> , $J = 5.9$ Hz)
22	1.82 (1H, <i>m</i> ), 1.09 (1H, <i>m</i> )	2.33 ( <i>dd</i> , $J = 11.0, 9.2$ Hz)
23	3.97 (1H, <i>dd</i> , $J = 9.0, 4.5$ Hz)	4.57 ( <i>m</i> )
24	3.04 (1H, <i>s</i> )	3.66 ( <i>s</i> )
26	1.20 (3H, <i>s</i> ) <sup>a</sup>	1.61 ( <i>s</i> )
27	1.21 (3H, <i>s</i> ) <sup>a</sup>	1.63 ( <i>s</i> )
28	0.92 (3H, <i>s</i> )	1.17 ( <i>s</i> )
29	0.80 (3H, <i>s</i> )	1.12 ( <i>s</i> )
30	0.96 (3H, <i>s</i> )	1.02 ( <i>s</i> )

Table 27 Comparison of  $^{13}\text{C}$  NMR spectral data between compound XC4 and hispidol B

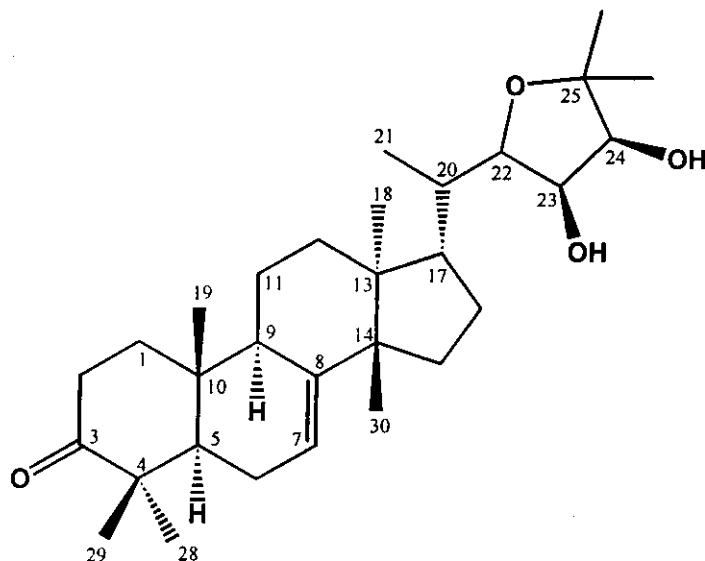
Position	Compound XC4, $\delta_{\text{C}}$ (ppm)	Hispidol B, $\delta_{\text{C}}$ (ppm)
1	32.18	37.6
2	26.13	28.6
3	76.21	78.3
4	37.30	39.5
5	52.16	51.2
6	22.30	24.4



Table 27 (Continued)

Position	Compound XC4, $\delta_C$ (ppm)	Hispidol B, $\delta_C$ (ppm)
7	116.28	118.5
8	143.98	146.1
9	47.22	49.3
10	33.19	35.2
11	16.41	18.4
12	32.31	34.3
13	41.83	43.8
14	49.47	51.4
15	35.60	34.3
16	26.66	28.6
17	49.01	54.4
18	11.55	13.5
19	20.39	22.1
20	31.88	34.3
21	17.44	19.6
22	39.33	42.3
23	67.19	69.5
24	73.77	76.8
25	71.77	73.8
26	25.29	27.2
27	25.29	27.8
28	26.30	28.3
29	13.49	15.5
30	25.67	27.4

### 3.1.5 Compound XC5



Compound **XC5** was obtained as a colorless oil,  $[\alpha]_D^{26} = -75^\circ$  ( $c = 0.035$ ,  $\text{CHCl}_3$ ). The IR spectrum showed absorption bands at  $3426\text{ cm}^{-1}$  and  $1704\text{ cm}^{-1}$  corresponding to a hydroxy group and carbonyl group, respectively (see **Fig. 39**). The presence of one carbonyl carbon of ketone at  $\delta$  217.43 from  $^{13}\text{C}$  NMR spectrum supported the above conclusion.

The complete analysis of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of compound **XC5** (see **Table 31**, **Fig. 40** and **41**) were assigned with information provided from  $^1\text{H}$ - $^1\text{H}$  COSY (see **Table 28**, **Fig. 43**), HMQC (**Fig. 44**) and HMBC (see **Table 30**, **Fig. 45**). The  $^{13}\text{C}$  NMR (see **Table 31**, **Fig. 41**) spectrum of compound **XC5** recorded in  $\text{CDCl}_3$  showed 29 signals for 30 carbon atoms. The DEPT- $90^\circ$  and DEPT- $135^\circ$  (see **Table 28**, **Fig. 42**) indicating the existence of eight methyl carbons ( $\delta$  27.86, 27.86, 24.71, 22.03, 21.76, 21.48, 12.97 and 12.58), seven methylene carbons ( $\delta$  38.76, 35.13, 34.24, 33.69, 27.93, 24.54 and 18.47), eight methine carbons ( $\delta$  117.96, 83.88, 77.52, 73.05, 52.59, 49.46, 48.71 and 37.70) and seven quaternary carbons ( $\delta$  217.43, 146.14, 81.12, 51.38, 48.08, 43.70 and 35.21).

Compound **XC5** was a derivative of compound **XC4**. Comparison of the  $^1\text{H}$  NMR spectral data (see **Table 31** and **25**) of the two compounds revealed close

structural similarity. The two compounds differed in H-22 which was methylene proton in **XC4** but oxymethine proton in **XC5**. The H-22  $^1\text{H}$  NMR chemical shift of **XC4** and **XC5** were shown at  $\delta$  1.82 (1H, *m*), 1.09 (1H, *m*) and  $\delta$  3.83 (1H, *dd*,  $J = 6.3, 0.9$  Hz), respectively. An additional signal of oxymethine proton (H-3) in **XC4** was shown as  $\delta$  3.09 (1H, *dd*,  $J = 9.0, 5.1$  Hz) which was not observed in compound **XC5**.

The HMBC correlation of compound **XC5** (see **Table 30**, **Fig. 45**) showed the same correlation with compound **XC4** (see **Table 24**), the proton signal of H-22 ( $\delta$  3.83, 1H, *dd*,  $J = 6.3, 0.9$  Hz) gave correlation peaks with C-17 (49.46), C-20 (37.70), C-21 (12.58) and C-23 (73.05), confirming the position of the oxymethine proton at C-22. The carbon signals at  $\delta$  217.43 (C-3), 52.59 (C-5), 48.08 (C-4) and 24.71 (C-28) showed the correlation peaks with the Me-29 ( $\delta$  1.12), thus confirming the position of the carbonyl group at C-3. From NOESY experiment (**Fig. 46**), H-5 ( $\delta$  1.73) showed cross peak with H-9 ( $\delta$  2.30) and Me-28 ( $\delta$  1.04); H-2a ( $\delta$  2.76) showed cross peak with Me-19 (1.01) and Me-29 ( $\delta$  1.12); H-17 ( $\delta$  1.88) showed cross peak with Me-30 ( $\delta$  1.04). Thus, this observation confirmed that H-2a, H-7, Me-19, Me-29 and Me-30 were on the same side and opposite side to H-5, H-9 and Me-28. H-23 ( $\delta$  3.98) showed cross peak with Me-18 ( $\delta$  0.82), Me-21 ( $\delta$  0.85), H-22 ( $\delta$  3.83) and H-24 ( $\delta$  3.66); H-24 ( $\delta$  3.66) showed cross peak with Me-18 ( $\delta$  0.82), Me-21 ( $\delta$  0.85), Me-26 ( $\delta$  1.22), H-27 ( $\delta$  1.22), H-22 ( $\delta$  3.83) and H-24 ( $\delta$  3.66). Thus, this observation confirmed that Me-18, H-23 and H-24 were on the same side.

Thus, compound **XC5** was identified as odoratone which was previously isolated from the seed kernels of *Azadirachta indica* (Luo, *et al.*, 2000).

**Table 28**  $^{13}\text{C}$  and DEPT spectral data of compound XC5

$\delta_{\text{C}}$	DEPT-90°	DEPT-135°	Type of Carbon
217.43			C
146.14			C
117.96	117.96	117.96	CH
83.88	83.88	83.88	CH
81.12			C
77.52	77.52	77.52	CH
73.05	73.05	73.05	CH
52.59	52.59	52.59	CH
51.38			C
49.46	49.46	49.46	CH
48.71	48.71	48.71	CH
48.08			C
43.70			C
38.76		38.76	CH <sub>2</sub>
37.70	37.70	37.70	CH
35.21			C
35.13		35.13	CH <sub>2</sub>
34.24		34.24	CH <sub>2</sub>
33.69		33.69	CH <sub>2</sub>
27.93		27.93	CH <sub>2</sub>
27.86		27.86	CH <sub>3</sub>
27.86		27.86	CH <sub>3</sub>
24.71		24.71	CH <sub>3</sub>
24.54		24.54	CH <sub>2</sub>
22.03		22.03	CH <sub>3</sub>

**Table 28** (Continued)

$\delta_c$	DEPT-90°	DEPT-135°	Type of Carbon
21.76		21.76	CH <sub>3</sub>
21.48		21.48	CH <sub>3</sub>
18.47		18.47	CH <sub>2</sub>
12.97		12.97	CH <sub>3</sub>
12.58		12.58	CH <sub>3</sub>

**Table 29** 300 MHz COSY correlation of some protons of compound XC5

$\delta_H$ (ppm)	Proton Correlation with $\delta_H$ (ppm)
H-7 (5.31)	H-6a (2.14), H-6b (2.08)
H-23 (3.98)	H-22 (3.83), H-24 (3.66)
H-22 (3.83)	H-20 (1.66)
H-2a (2.76)	H-2b (2.25), H-1a (2.01), H-1b (1.46)
H-2b (2.25)	H-1b (1.46)
H-6a (2.14)	H-5 (1.73)
H-6b (2.08)	H-5 (1.73)
H-1a (2.01)	H-1b (1.46)
H-12a (1.88)	H-12b (1.63), H-11 (1.60)
H-12b (1.63)	H-11 (1.60)
H-20 (1.66)	H-21 (0.85)

**Table 30** Major HMBC correlation of compound XC5

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
1a*	2.01 (1H, <i>m</i> )	C-2 (35.13), C-3 (217.43), C-5 (52.59), C-10 (35.21) and C-19 (12.97)
1b*	1.46 (1H, <i>m</i> )	C-2 (35.13), C-9 (48.71), C-10 (35.21) and C-19 (12.97)
2a	2.76 (1H, <i>td</i> , $J = 14.1, 5.4$ Hz)	} C-1 (38.76), C-3 (217.43) and C-10 (35.21)
2b	2.25 (1H, <i>s</i> , $J = 14.1, 3.6$ Hz)	
5*	1.73 (1H, <i>m</i> )	C-4 (48.08), C-6 (24.54), C-10 (35.21), C-19 (12.97), C-28 (24.71) and C-29 (21.76)
6a*	2.14 (1H, <i>m</i> )	C-5 (52.59), C-7 (117.96) and C-8 (146.14)
6b*	2.08 (1H, <i>m</i> )	C-4 (48.08), C-5 (52.59), C-7 (117.96), C-8 (146.14) and C-10 (35.21)
7	5.31 (1H, <i>dd</i> , $J = 6.0, 3.0$ Hz)	C-5 (52.59), C-6 (24.54), C-9 (48.71) and C-14 (51.38)
9*	2.30 (1H, <i>m</i> )	C-1 (38.76), C-8 (146.14), C-10 (35.21) and C-12 (33.69)
11*	1.60 (2H, <i>m</i> )	C-8 (146.14), C-9 (48.71), C-12 (33.69) and C-13 (43.70)
12a*	1.88 (1H, <i>m</i> )	} C-9 (48.71), C-11 (18.47), C-13 (43.70), C-17 (49.46) and C-18 (22.03)
12b*	1.63 (1H, <i>m</i> )	
15a*	1.58 (1H, <i>m</i> )	C-14 (51.38), C-16 (27.93), C-17 (49.46) and C-30 (27.86)
15b*	1.51 (1H, <i>m</i> )	C-8 (146.14), C-14 (51.38), C-16 (27.93), C-17 (49.46) and C-30 (27.86)
16a*	2.06 (1H, <i>m</i> )	C-13 (43.70), C-15 (34.24) and C-17 (49.46)

Table 30 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
16b*	1.39 (1H, <i>m</i> )	C-14 (51.38), C-15 (34.24), C-17 (49.46) and C-20 (37.70)
17*	1.88 (1H, <i>m</i> )	C-13 (43.70), C-16 (27.93), C-18 (22.03) and C-20 (37.70)
18	0.82 (3H, <i>s</i> )	C-12 (33.69), C-13 (43.70), C-14 (51.38) and C-17 (49.46)
19	1.01 (3H, <i>s</i> )	C-1 (38.76), C-5 (52.59), C-9 (48.71) and C-10 (35.21)
20*	1.66 (1H, <i>m</i> )	C-17 (49.46), C-21 (12.58) and C-22 (83.88)
21	0.85 (3H, <i>d</i> , $J = 6.6$ Hz)	C-17 (49.46), C-20 (37.70) and C-22 (83.88)
22	3.83 (1H, <i>dd</i> , $J = 6.3, 0.9$ Hz)	C-17 (49.46), C-20 (37.70), C-21 (12.58) and C-23 (73.05)
23	3.98 (1H, <i>t</i> , $J = 6.3$ Hz)	C-20 (37.70) and C-25 (81.12)
24	3.66 (1H, <i>d</i> , $J = 6.3$ Hz)	C-22 (83.88), C-23 (73.05), C-25 (81.12), C-26 (21.48) and C-27 (27.86)
26	1.22 (3H, <i>s</i> )	C-24 (77.52), C-25 (81.12) and C-27 (27.86)
27	1.22 (3H, <i>s</i> )	C-24 (77.52), C-25 (81.12) and C-26 (21.48)
28	1.04 (3H, <i>s</i> )	C-3 (217.43), C-4 (48.08), C-5 (52.59) and C-29 (21.76)
29	1.12 (3H, <i>s</i> )	C-3 (217.43), C-4 (48.08), C-5 (52.59) and C-28 (24.71)
30	1.04 (3H, <i>s</i> )	C-8 (146.14), C-13 (43.70), C-14 (51.38) and C-15 (34.24)

\* chemical shifts deduced from HMQC

Table 31  $^1\text{H}$  and  $^{13}\text{C}$  spectral data of compound XC5

position	$\delta_{\text{C}}^{\#}$ (ppm)		$\delta_{\text{H}}$ (ppm)
1*	38.76	$\text{CH}_2$	2.01 (1H, <i>m</i> ), 1.46 (1H, <i>m</i> )
2	35.13	$\text{CH}_2$	2.76 (1H, <i>td</i> , $J = 14.1, 5.4$ Hz), 2.25 (1H, <i>dt</i> , $J = 14.1, 3.6$ Hz)
3	217.43	C=O	-
4	48.08	C	-
5*	52.59	CH	1.73 (1H, <i>m</i> )
6*	24.54	$\text{CH}_2$	2.14 (1H, <i>m</i> ), 2.08 (1H, <i>m</i> )
7	117.96	=CH	5.31 (1H, <i>dd</i> , $J = 6.0, 3.0$ Hz)
8	146.14	=C	-
9*	48.71	CH	2.30 (1H, <i>m</i> )
10	35.21	C	-
11*	18.47	$\text{CH}_2$	1.60 (2H, <i>m</i> )
12*	33.69	$\text{CH}_2$	1.88 (1H, <i>m</i> ), 1.63 (1H, <i>m</i> )
13	43.70	C	-
14	51.38	C	-
15*	34.24	$\text{CH}_2$	1.58 (1H, <i>m</i> ), 1.51 (1H, <i>m</i> )
16*	27.93	$\text{CH}_2$	2.06 (1H, <i>m</i> ), 1.39 (1H, <i>m</i> )
17*	49.46	CH	1.88 (1H, <i>m</i> )
18	22.03	$\text{CH}_3$	0.82 (3H, <i>s</i> )
19	12.97	$\text{CH}_3$	1.01 (3H, <i>s</i> )
20*	37.70	CH	1.66 (1H, <i>m</i> )
21	12.58	$\text{CH}_3$	0.85 (3H, <i>d</i> , $J = 6.6$ Hz)
22	83.88	O-CH	3.83 (1H, <i>dd</i> , $J = 6.3, 0.9$ Hz)
23	73.05	O-CH	3.98 (1H, <i>t</i> , $J = 6.3$ Hz)

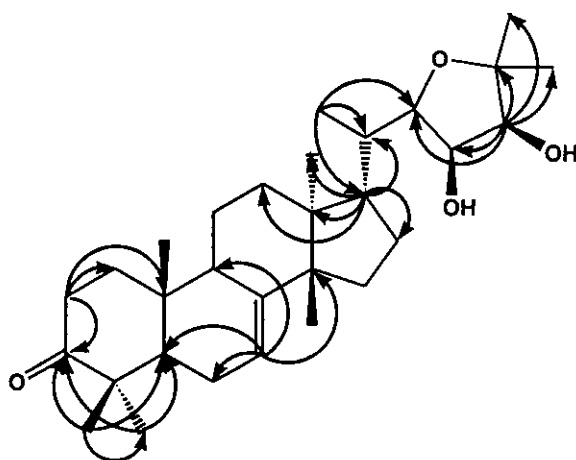


Table 31 (Continued)

position	$\delta_C^{\#}$ (ppm)		$\delta_H$ (ppm)
24	77.52	O-CH	3.66 (1H, <i>d</i> , <i>J</i> = 6.3 Hz)
25	81.12	O-C	-
26	21.48	CH <sub>3</sub>	1.22 (3H, <i>s</i> )
27	27.86	CH <sub>3</sub>	1.22 (3H, <i>s</i> )
28	24.71	CH <sub>3</sub>	1.04 (3H, <i>s</i> )
29	21.76	CH <sub>3</sub>	1.12 (3H, <i>s</i> )
30	27.86	CH <sub>3</sub>	1.04 (3H, <i>s</i> )

<sup>#</sup> Carbon type deduced from DEPT experiment.

\* Chemical shifts deduced from HMQC



Selected HMBC correlation of XC5

Table 32 Comparison of <sup>1</sup>H NMR spectral data between compound XC5 and odoratone

Position	Compound XC5, $\delta_H$ (ppm) (recorded in CDCl <sub>3</sub> )	Odoratone, $\delta_H$ (ppm) (recorded in CDCl <sub>3</sub> )
7	5.31 (1H, <i>dd</i> , <i>J</i> = 6.0, 3.0 Hz)	5.27 (1H, <i>d</i> , <i>J</i> = 3.0 Hz)

Table 32 (Continued)

Position	Compound XC5, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )	Odoratone, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )
17	1.88 (1H, <i>m</i> )	2.72 (1H, <i>dt</i> , $J = 14.5, 5.5$ Hz)-17
21	0.85 (3H, <i>d</i> , $J = 6.6$ Hz)	0.81 (3H, <i>d</i> , $J = 6.6$ Hz)
22	3.83 (1H, <i>dd</i> , $J = 6.3, 0.9$ Hz)	3.79 (1H, <i>d</i> , $J = 6.4$ Hz)-22
23	3.98 (1H, <i>t</i> , $J = 6.3$ Hz)	3.94 (1H, <i>dd</i> , $J = 6.4, 6.3$ Hz)-23
24	3.66 (1H, <i>d</i> , $J = 6.3$ Hz)	3.62 (1H, <i>d</i> , $J = 6.3$ Hz)-24
Me	0.82 (3H, <i>s</i> ) (H-18)	0.79 (3H, <i>s</i> )
	1.01 (3H, <i>s</i> ) (H-19)	0.97 (3H, <i>s</i> )
	1.04 (3H, <i>s</i> ) (H-28)	1.01 (3H, <i>s</i> )
	1.04 (3H, <i>s</i> ) (H-30)	1.01 (3H, <i>s</i> )
	1.12 (3H, <i>s</i> ) (H-29)	1.08 (3H, <i>s</i> )
	1.22 (3H, <i>s</i> ) (H-26)	1.19 (3H, <i>s</i> )
	1.22 (3H, <i>s</i> ) (H-27)	1.19 (3H, <i>s</i> )

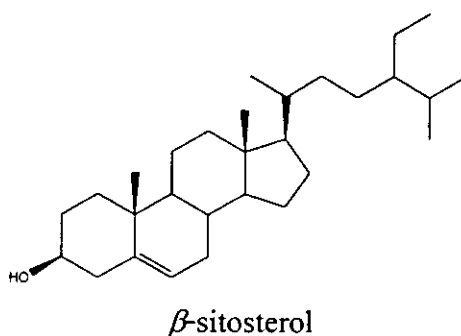
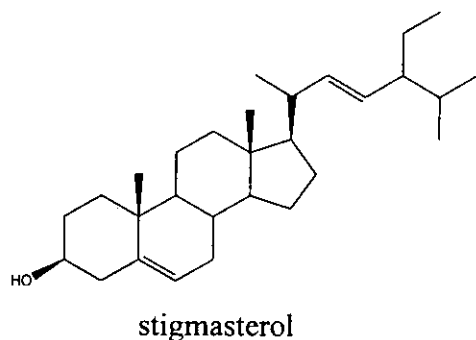
Table 33 Comparison of  $^{13}\text{C}$  NMR spectral data between compound XC5 and odoratone

Position	Compound XC5, $\delta_{\text{C}}$ (ppm)	Odoratone, $\delta_{\text{C}}$ (ppm)
1	38.76	33.6
2	35.13	38.6
3	217.43	210.2
4	48.08	47.9
5	52.59	49.4
6	24.54	24.4

Table 33 (Continued)

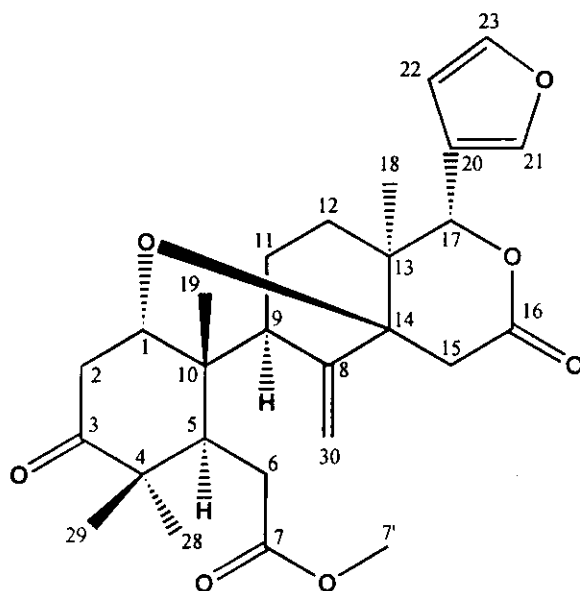
Position	Compound XC5, $\delta_C$ (ppm)	Odoratone, $\delta_C$ (ppm)
7	117.96	117.8
8	146.14	146.0
9	48.71	48.6
10	35.21	35.1
11	18.47	18.4
12	33.69	34.1
13	43.70	43.6
14	51.38	51.2
15	34.24	34.6
16	27.93	27.1
17	49.46	52.5
18	22.03	12.4
19	12.97	21.3
20	37.70	37.5
21	12.58	12.8
22	83.88	83.8
23	73.05	77.5
24	77.52	72.9
25	81.12	80.9
26	21.48	27.7
27	27.86	27.7
28	24.71	24.6
29	21.76	21.8
30	27.86	21.6

### 3.1.6 Compound XC6



Compound **XC6** was obtained as a white solid mp = 138-140 °C. The IR spectrum (see **Fig. 47**) exhibited an absorption band at 3442  $\text{cm}^{-1}$  for a hydroxyl group. The  $^1\text{H}$  NMR spectrum (see **Fig. 48**) showed characteristic signals of olefinic protons of stigmasterol and  $\beta$ -sitosterol  $\delta_{\text{H}}$  5.36 (2H, *d*,  $J = 5.4$  Hz), 5.16 (1H, *dd*,  $J = 15.3, 8.4$  Hz) and 5.02 (1H, *dd*,  $J = 15.3, 8.4$  Hz). The ratio of integration of olefinic protons at  $\delta_{\text{H}}$  5.02, 5.16 for stigmasterol and 5.36 for both compounds was 1:1:2, suggesting that **XC6** was a mixture of stigmasterol and  $\beta$ -sitosterol in a ratio of 1:1.

### 3.1.7 Compound XH1



Compound **XH1** was isolated as a colorless oil,  $[\alpha]_D^{26} = -44^\circ$  ( $c = 0.02$ ,  $\text{CHCl}_3$ ). The mass spectrum of this compound (see **Fig. 58**) showed the molecular ion peak at  $m/z$  471, corresponding to a molecular formula  $\text{C}_{27}\text{H}_{34}\text{O}_7$ . The UV spectrum (see **Fig. 49**) showed maximum absorption band ( $\lambda_{\text{max}}$ ) at 209 nm. The IR spectrum of **XH1** (**Fig. 50**) exhibited carbonyl ( $1735$ ,  $1730$  and  $1718 \text{ cm}^{-1}$ ) absorptions. The presence of three carbonyl carbons at  $\delta$  212.88, 173.88 and 170.15 ppm from  $^{13}\text{C}$  NMR spectrum supported the above conclusion.

The  $^{13}\text{C}$  NMR spectrum of compound **XH1** (see **Table 37**, **Fig. 52**) recorded in  $\text{CDCl}_3$  showed 27 signals for 27 carbons. Analysis of DEPT- $90^\circ$  and DEPT- $135^\circ$  (see **Table 34**, **Fig. 53**) indicated the existence of five methyl carbons ( $\delta$  52.09, 25.85, 21.63, 21.47 and 13.74), six methylene carbons ( $\delta$  111.55, 39.42, 33.77, 32.67, 29.29 and 23.73), seven methine carbons ( $\delta$  142.75, 140.77, 109.92, 79.60, 77.21, 49.88 and 42.91) and nine quaternary carbons ( $\delta$  212.88, 173.88, 170.15, 145.76, 120.81, 80.20, 48.05, 44.02 and 41.43).

The  $^1\text{H}$  NMR spectrum of compound **XH1** (see **Table 37**, **Fig. 51**), with the characteristic peaks of furan nucleus as shown at  $\delta$  7.44 (1H, *br s*), 7.39 (1H, *t*,  $J = 1.8$  Hz) and 6.37 (1H, *dd*,  $J = 1.8, 0.9$  Hz) were assigned to H-21, H-23 and H-22, respectively. Two signals of olefinic protons resonated at  $\delta$  5.16 (1H, *s*) and 4.90 (1H, *s*). The signals at  $\delta$  5.65 (1H, *s*) and 3.53 (1H, *dd*,  $J = 6.3, 3.9$  Hz) could be assigned for methine protons which attached to a carbon adjacent to an oxygen atom at C-17 (79.60) and C-1 (77.21), respectively.

The structure of compound **XH1** was deduced from its  $^{13}\text{C}$  and  $^1\text{H}$  spectral data (see **Table 37**, **Fig. 52** and **51**) together with the results of  $^1\text{H}$ - $^1\text{H}$  COSY (see **Table 35**, **Fig. 54**), HMQC (**Fig. 55**) and HMBC (see **Table 36**, **Fig. 56**). The correlation peaks in the HMBC spectrum (see **Table 36**, **Fig. 56**) between H-17 ( $\delta$  5.65) and the carbon signals at  $\delta$  140.77 (C-21), 120.81 (C-20), 109.92 (C-22), 41.43 (C-13), 29.29 (C-12) and 13.74 (C-18) confirmed the position of the furanyl group at C-17 position. The carbon signals at  $\delta$  170.15 (C-16), 145.76 (C-8) and 80.20 (C-14) showed the correlation peaks with H-15 ( $\delta$  2.92 and 2.58). The carbon signals at  $\delta$  C-1 (77.21), C-3 (212.88), C-4 (48.05), C-6 (32.64), C-7 (173.88), C-9 (49.88), C-10 (44.02), C-28 (25.85) and C-29 (21.47) showed the correlation peaks with H-5 ( $\delta$  2.88), confirming the carbonyl group at C-3 and C-7.

Compound **XH1** was identified as methyl angolensate which was the compound previously isolated from various genera of the Meliaceae family, such as the heartwood of *Khaya grandifoliola* (Connolly, *et al.*, 1967), the stem bark of *Khaya senegalensis* (Abdelgaleil, *et al.*, 2001) and the seed of *Neobeguea mahafalensis* (Naidoo, *et al.*, 2003).

**Table 34**  $^{13}\text{C}$  and DEPT spectral data of compound XH1

$\delta_c$	DEPT-90°	DEPT-135°	Type of Carbon
212.88			C
173.88			C
170.15			C
145.76			C
142.75	142.75	142.75	CH
140.77	140.77	140.77	CH
120.81			C
111.55		111.55	CH <sub>2</sub>
109.92	109.92	109.92	CH
80.20			C
79.60	79.60	79.60	CH
77.21	77.21	77.21	CH
52.09		52.09	CH <sub>3</sub>
49.88	49.88	49.88	CH
48.05			C
44.02			C
42.91	42.91	42.91	CH
41.43			C
39.42		39.42	CH <sub>2</sub>
33.77		33.77	CH <sub>2</sub>
32.67		32.67	CH <sub>2</sub>
29.29		29.29	CH <sub>2</sub>
25.85		25.85	CH <sub>3</sub>
23.73		23.73	CH <sub>2</sub>
21.63		21.63	CH <sub>3</sub>

**Table 34** (Continued)

$\delta_C$	DEPT-90°	DEPT-135°	Type of Carbon
21.47		21.47	CH <sub>3</sub>
13.74		13.74	CH <sub>3</sub>

**Table 35** 300 MHz COSY correlation of some protons of compound XH1

$\delta_H$ (ppm)	Proton Correlation with $\delta_H$ (ppm)
H-23 (7.39)	H-22 (6.37)
H-1 (3.53)	H-2a (2.90) and H-2b (2.50)
H-15a (2.92)	H-15b (2.58)
H-2a (2.90)	H-2b (2.50)
H-5 (2.88)	H-6a (2.63)
H-6a (2.63)	H-6b (2.26)
H-11a (2.20)	H-11b (1.58)
H-12a (1.90)	H-12b (1.22)

**Table 36** Major HMBC correlation of compound XH1

position	$\delta_H$ (ppm)	$\delta_C$ (ppm)
1	3.53 (1H, <i>dd</i> , <i>J</i> = 6.3, 3.9 Hz)	C-2 (39.42), C-3 (212.88), C-5 (42.91), C-14 (80.20) and C-19 (21.63)
2a	2.90 (1H, <i>dd</i> , <i>J</i> = 14.1, 6.3 Hz)	C-1 (77.21), C-3 (212.88), C-4 (48.05) and C-10 (44.02)
2b	2.50 (1H, <i>dd</i> , <i>J</i> = 14.1, 3.9 Hz)	C-1 (77.21), C-3 (212.88) and C-10 (44.02)



Table 36 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
5*	2.88 (1H, <i>m</i> )	C-1 (77.21), C-3 (212.88), C-4 (48.05), C-6 (32.64), C-7 (173.88), C-9 (49.88), C-10 (44.02), C-28 (25.85) and C-29 (21.47)
6a*	2.63 (1H, <i>m</i> )	} C-4 (48.05), C-5 (42.91), C-7 (173.88) and C-10 (44.02)
6b*	2.26 (1H, <i>m</i> )	
7'	3.72 (3H, <i>s</i> )	C-7 (173.88)
9*	2.18 (1H, <i>m</i> )	C-1 (77.21), C-8 (145.76), C-10 (44.02), C-11 (23.73), C-12 (29.29), C-14 (80.20), C-19 (21.63) and C-30 (111.55)
11a*	2.20 (1H, <i>m</i> )	C-8 (145.76), C-10 (44.02), C-12 (29.29) and C-13 (41.43)
11b*	1.58 (1H, <i>m</i> )	C-10 (44.02) and C-12 (29.29)
12a*	1.90 (1H, <i>m</i> )	C-13 (41.43), C-17 (79.60) and C-18 (13.74)
12b*	1.22 (1H, <i>m</i> )	C-9 (49.88), C-13 (41.43), C-17 (76.60) and C-18 (13.74)
15a	2.92 (1H, <i>d</i> , $J = 18.0$ Hz)	} C-8 (145.76), C-14 (80.20) and C-16 (170.15)
15b	2.58 (1H, <i>d</i> , $J = 18.0$ Hz)	
17	5.65 (1H, <i>s</i> )	C-12 (29.29), C-13 (41.43), C-18 (13.74), C-20 (120.81), C-21 (140.77) and C-22 (109.92)
18	0.87 (3H, <i>s</i> )	C-12 (29.29), C-13 (41.43), C-14 (80.20) and C-17 (79.60)
19	0.95 (3H, <i>s</i> )	C-1 (77.21), C-5 (42.91), C-9 (49.88) and C-10 (44.02)

Table 36 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
21	7.44 (1H, <i>br s</i> )	C-20 (120.81), C-22 (109.92) and C-23 (142.75)
22	6.37 (1H, <i>dd</i> , $J = 1.8, 0.9$ Hz)	C-20 (120.81), C-21 (140.77) and C-23 (142.75)
23	7.39 (1H, <i>t</i> , $J = 1.8$ Hz)	C-20 (120.81), C-21 (140.77) and C-22 (109.92)
28	1.05 (3H, <i>s</i> )	C-3 (212.88), C-4 (48.05), C-5 (42.91) and C-29 (21.47)
29	1.20 (3H, <i>s</i> )	C-3 (212.88), C-4 (48.05), C-5 (42.91) and C-28 (25.85)
30a	5.16 (1H, <i>s</i> )	} C-8 (145.76), C-9 (49.88) and C-14 (80.20)
30b	4.90 (1H, <i>s</i> )	

\* Chemical shift was assigned by HMQC.

Table 37  $^1\text{H}$  and  $^{13}\text{C}$  spectral data of compound XH1

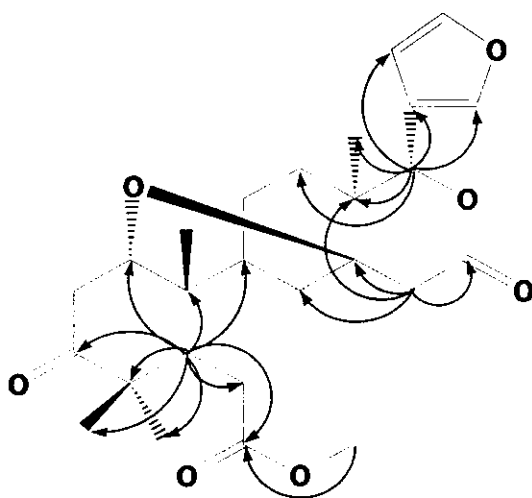
position	$\delta_{\text{C}}^{\#}$ (ppm)		$\delta_{\text{H}}$ (ppm)
1	77.21	O-CH	3.53 (1H, <i>dd</i> , $J = 6.3, 3.9$ Hz)
2	39.42	CH <sub>2</sub>	2.90 (1H, <i>dd</i> , $J = 14.1, 6.3$ Hz), 2.50 (1H, <i>dd</i> , $J = 14.1, 3.9$ Hz)
3	212.88	C=O	-
4	48.05	C	-
5*	42.91	CH	2.88 (1H, <i>m</i> )
6*	32.67	CH <sub>2</sub>	2.63 (1H, <i>m</i> ), 2.26 (1H, <i>m</i> )

Table 37 (Continued)

position	$\delta_C^{\#}$ (ppm)		$\delta_H$ (ppm)
7	173.88	O-C=O	-
7'	52.09	O-CH <sub>3</sub>	3.72 (3H, <i>s</i> )
8	145.76	=C	-
9*	49.88	CH	2.18 (1H, <i>m</i> )
10	44.02	C	-
11*	23.73	CH <sub>2</sub>	2.20 (1H, <i>m</i> ), 1.58 (1H, <i>m</i> )
12*	29.29	CH <sub>2</sub>	1.90 (1H, <i>m</i> ), 1.22 (1H, <i>m</i> )
13	41.43	C	-
14	80.20	O-C	-
15	33.77	CH <sub>2</sub>	2.92 (1H, <i>d</i> , <i>J</i> = 18.0 Hz), 2.58 (1H, <i>d</i> , <i>J</i> = 18.0 Hz)
16	170.15	O-C=O	-
17	79.60	O-CH	5.65 (1H, <i>s</i> )
18	13.74	CH <sub>3</sub>	0.87 (3H, <i>s</i> )
19	21.63	CH <sub>3</sub>	0.95 (3H, <i>s</i> )
20	120.81	=C	-
21	140.77	=CH	7.44 (1H, <i>br s</i> )
22	109.92	=CH	6.37 (1H, <i>dd</i> , <i>J</i> = 1.8, 0.9 Hz)
23	142.75	=CH	7.39 (1H, <i>t</i> , <i>J</i> = 1.8 Hz)
28	25.85	CH <sub>3</sub>	1.05 (3H, <i>s</i> )
29	21.47	CH <sub>3</sub>	1.20 (3H, <i>s</i> )
30	111.55	=CH <sub>2</sub>	5.16 (1H, <i>s</i> ), 4.90 (1H, <i>s</i> )

<sup>#</sup> Carbon type deduced from DEPT experiment

\* Chemical shift was assigned by HMQC



Selected HMBC correlation of compound XH1

**Table 38** Comparison of  $^1\text{H}$  NMR spectral data between compound XH1 and methyl 6-hydroxyangolensate

Position	Compound XH1, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )	Methyl 6-hydroxyangolensate, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )
1	3.53 (1H, <i>dd</i> , $J = 6.3, 3.9$ Hz)	3.57 (1H, <i>dd</i> , $J = 5.6, 2.7$ Hz)
2	2.90 (1H, <i>dd</i> , $J = 14.1, 6.3$ Hz), 2.50 (1H, <i>dd</i> , $J = 14.1, 3.9$ Hz)	3.10 (1H, <i>dd</i> , $J = 14.2, 5.6$ Hz), 2.34 (1H, <i>dd</i> , $J = 14.2, 2.7$ Hz)
5*	2.88 (1H, <i>m</i> )	2.75 (1H, <i>s</i> )
6*	2.63 (1H, <i>m</i> ), 2.26 (1H, <i>m</i> )	4.42 (1H, <i>d</i> , $J = 2.0$ Hz)
7'	3.72 (3H, <i>s</i> )	3.84 (3H, <i>s</i> )
9*	2.18 (1H, <i>m</i> )	2.34 (1H, <i>dd</i> , $J = 14.2, 2.7$ Hz)
11*	2.20 (1H, <i>m</i> ), 1.58 (1H, <i>m</i> )	2.20 (1H, <i>m</i> ), 1.57 (1H, <i>m</i> )
12*	1.90 (1H, <i>m</i> ), 1.22 (1H, <i>m</i> )	1.03 (1H, <i>m</i> ), 1.73 (1H, <i>m</i> )
15	2.92 (1H, <i>d</i> , $J = 18.0$ Hz), 2.58 (1H, <i>d</i> , $J = 18.0$ Hz)	2.90 (1H, <i>d</i> , $J = 18.1$ Hz), 2.58 (1H, <i>d</i> , $J = 18.1$ Hz)

Table 38 (Continued)

Position	Compound XH1, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )	Methyl 6-hydroxyangolensate, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )
17	5.65 (1H, <i>s</i> )	5.63 (1H, <i>s</i> )
18	0.87 (3H, <i>s</i> )	0.88 (3H, <i>s</i> )
19	0.95 (3H, <i>s</i> )	1.39 (3H, <i>s</i> )
21	7.44 (1H, <i>br s</i> )	7.42 (1H, <i>br s</i> )
22	6.37 (1H, <i>dd</i> , $J = 1.8, 0.9$ Hz)	6.36 (1H, <i>dd</i> , $J = 1.7, 0.8$ Hz)
23	7.39 (1H, <i>t</i> , $J = 1.8$ Hz)	7.38 (1H, <i>t</i> , $J = 1.7$ Hz)
28	1.05 (3H, <i>s</i> )	1.06 (3H, <i>s</i> )
29	1.20 (3H, <i>s</i> )	1.46 (3H, <i>s</i> )
30	5.16 (1H, <i>s</i> ), 4.90 (1H, <i>s</i> )	5.19 (1H, <i>s</i> ), 4.91 (1H, <i>s</i> )

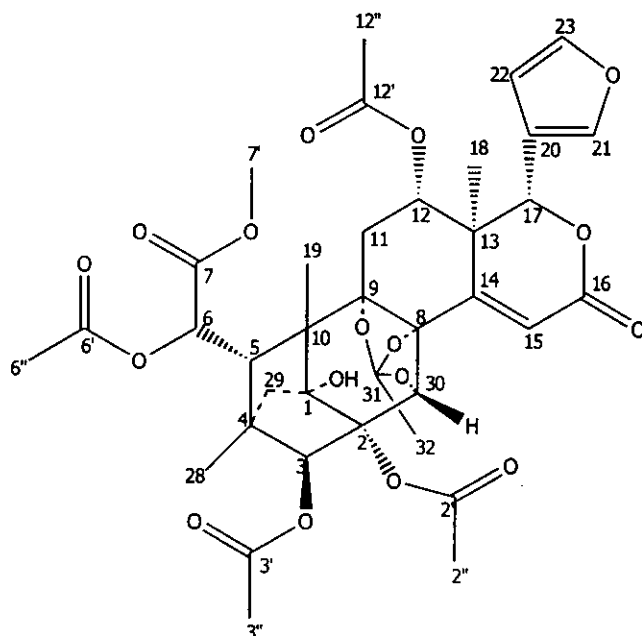
Table 39 Comparison of  $^{13}\text{C}$  NMR spectral data between compound XH1 and methyl angolensate

Position	Compound Hx1, $\delta_{\text{C}}$ (ppm)	Methyl angolensate, $\delta_{\text{C}}$ (ppm)
1	77.21	77.2
2	39.42	39.4
3	212.88	213.0
4	48.05	48.0
5	42.91	42.9
6	32.67	32.7
7	173.88	173.9
7'	52.09	52.1
8	145.76	145.8

Table 39 (Continued)

Position	Compound Hx1, $\delta_c$ (ppm)	Methyl angolensate, $\delta_c$ (ppm)
9	49.88	50.0
10	44.02	44.0
11	23.73	23.7
12	29.29	29.3
13	41.43	41.5
14	80.20	80.2
15	33.77	33.8
16	170.15	170.0
17	79.60	79.6
18	13.74	13.8
19	21.63	21.6
20	120.81	120.8
21	140.77	140.8
22	109.92	109.9
23	142.75	142.6
28	25.85	25.9
29	21.47	21.5
30	111.55	111.5

### 3.1.8 Compound XH2



Compound **XH2** was isolated as a colorless oil,  $[\alpha]_D^{26} = -40$  ( $c = 0.01$ , acetone).

The mass spectrum of this compound (see **Fig. 68**) showed the molecular ion peak at  $(M+H)^+$   $m/z$  759.2469, corresponding to a molecular formula  $C_{37}H_{42}O_{17}$ . The UV spectrum (see **Fig. 59**) showed maximum absorption band ( $\lambda_{max}$ ) at 216 nm supporting the  $\alpha, \beta$ -unsaturated carbonyl moiety in the molecule. The IR spectrum (see **Fig. 60**) showed the strong absorption bands at 3555, 1761, 1738, 1733 and 1728  $cm^{-1}$  corresponding to a hydroxy group and carbonyl group, respectively. The presence of six carbonyl carbons at  $\delta$  171.66, 170.51, 170.39, 169.17, 168.94 and 163.36 ppm from  $^{13}C$  NMR spectrum supported the above conclusion.

The  $^{13}C$  NMR spectrum of compound **XH2** (see **Table 43, Fig. 62**) recorded in  $CDCl_3$  showed 36 signals for 37 carbons. Analysis of DEPT-90° and DEPT-135° (see **Table 40, Fig. 63**) indicated the existence of nine methyl carbons ( $\delta$  53.30, 21.78, 21.60, 20.88, 19.75, 16.33, 16.33, 15.26 and 14.34), two methylene carbons ( $\delta$  40.72 and 32.36), ten methine carbons ( $\delta$  143.00, 142.01, 124.11, 110.16, 85.15, 78.92, 73.96, 71.11, 68.41 and 44.63) and sixteen quaternary carbons ( $\delta$  171.66, 170.51,

170.39, 169.17, 168.94, 163.36, 152.62, 120.91, 119.58, 86.05, 84.06, 83.63, 83.49, 48.75, 44.47 and 42.87).

The  $^1\text{H}$  NMR spectrum of compound **XH2** (see **Table 43**, **Fig. 61**), with the characteristic peaks of furan nucleus as shown at  $\delta$  7.45 (1H, *br s*), 7.41 (1H, *br s*), 6.56 (1H, *br s*) were assigned to H-21, H-23 and H-22, respectively. The signal of olefinic protons resonated at  $\delta$  6.61 (1H, *s*) were assigned to H-15. The signals at  $\delta$  6.31 (1H, *br s*), 5.91 (1H, *s*), 5.35 (1H, *s*), 5.21 (1H, *s*) and 4.94 (1H, *dd*,  $J = 14.1, 3.9$  Hz) could be assigned for methine protons which attached to a carbon adjacent to an oxygen atom at C-6 (71.11), C-17 (78.92), C-30 (73.96), C-3 (85.15) and C-12 (68.41), respectively.

The structure of compound **XH2** was deduced from its  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectral data (see **Table 43**, **Fig. 62** and **61**) together with the results of  $^1\text{H}$ - $^1\text{H}$  COSY (see **Table 40**, **Fig. 64**), HMQC (**Fig. 65**) and HMBC (see **Table 42**, **Fig. 66**). The correlation peaks in the HMBC spectrum (see **Table 42**, **Fig. 66**) between H-17 ( $\delta$  5.91) and the carbon at  $\delta$  C-16 (163.36), C-14 (152.62), C-21 (142.01), C-20 (120.91), C-22 (110.16), C-12 (68.41), C-13 (42.87) and C-18 (14.34) confirmed the position of the furanyl group at C-17 position. The carbon signals at  $\delta$  C-8 (83.49), C-12 (68.41), C-13 (42.87), C-14 (152.62), C-16 (163.36) and C-18 (14.34) showed the correlation peaks with the H-15 ( $\delta$  6.61), confirming the  $\alpha,\beta$ -unsaturated lactone. The carbon signals at  $\delta$  C-11 (32.36), C-12' (170.39), C-13 (42.87), C-17 (78.92) and C-18 (14.34) showed the correlation peaks with H-12 ( $\delta$  4.94) and the carbon signal at  $\delta$  C-12' (170.39) showed the correlation peaks with H-12'' ( $\delta$  1.56), confirming the position of the acetyl group at C-12. The carbon signals at  $\delta$  C-1 (84.06), C-8 (83.49), C-9 (86.05), C-14 (152.62) and C-31 (119.58) showed the correlation peaks with H-30 ( $\delta$  5.35). The carbon signal at  $\delta$  C-2' (170.51) showed the correlation peaks with H-2'' ( $\delta$  2.18). The carbon signals at  $\delta$  C-2 (83.63), C-3' (168.94), C-5 (44.63), C-28 (15.26), C-29 (40.72) and C-30 (73.96) showed the correlation peaks with the H-3 ( $\delta$



5.21) and the carbon signal at  $\delta$  C-3' (168.94) showed the correlation peaks with the H-3'' ( $\delta$  2.07), confirming the position of the acetyl group at C-3. The carbon signals at  $\delta$  C-4 (44.47), C-6' (169.17), C-7 (171.66) and C-10 (48.75) showed the correlation peaks with the H-6 ( $\delta$  6.31), the carbon signals at  $\delta$  C-6 (71.11) and C-6' (169.17) showed the correlation peaks with the H-6'' ( $\delta$  2.21), the carbon signal at C-7 (171.66) showed the correlation peaks with the H-7' ( $\delta$  3.74) confirming the position of the acetyl group at C-6 and methoxy at C-7 which attached to a carbon adjacent to an oxygen atom at C-6. From NOESY experiment (Fig. 67), H-3 ( $\delta$  5.21) showed cross peak with Me-28 ( $\delta$  0.92) and H-29b ( $\delta$  1.76); H-5 ( $\delta$  2.47) showed cross peak with H-3 ( $\delta$  5.21), H-6 ( $\delta$  6.31), H-12 ( $\delta$  4.94), H-15 ( $\delta$  6.61), H-17 ( $\delta$  5.91), Me-19 ( $\delta$  1.31) and Me-28 ( $\delta$  0.92); H-12 ( $\delta$  4.94) showed cross peak with H-5 ( $\delta$  2.47), H-6 ( $\delta$  6.31), H-11a ( $\delta$  2.35), H-11b ( $\delta$  2.00) and H-17 ( $\delta$  5.91); H-17 ( $\delta$  5.91) showed cross peak with H-5 ( $\delta$  2.47), H-12 ( $\delta$  4.94), H-21 ( $\delta$  7.45) and H-22 ( $\delta$  6.56); H-15 ( $\delta$  6.61) showed cross peak with H-30 ( $\delta$  5.35); H-30 ( $\delta$  5.35) showed cross peak with H-15 ( $\delta$  6.61). Thus, this observation confirming that H-3, H-5, H-12 and H-17 are on the same side and opposite side to both H-15 and H-30. Compound XH2 was identified as xylocensin P which was the compound previously isolated from the stem bark of *X. granatum*. (Wu, *et al.*, 2004)

**Table 40**  $^{13}\text{C}$  and DEPT spectral data of compound XH2

$\delta_{\text{C}}$	DEPT-90°	DEPT-135°	Type of Carbon
171.66			C
170.51			C
170.39			C
169.17			C

Table 40 (Continued)

$\delta_c$	DEPT-90°	DEPT-135°	Type of Carbon
168.94			C
163.36			C
152.62			C
143.00	143.00	143.00	CH
142.01	142.01	142.01	CH
124.11	124.11	124.00	CH
120.91			C
119.58			C
110.16	110.16	110.16	CH
86.05			C
85.15	85.15	85.15	CH
84.06			C
83.63			C
83.49			C
78.92	78.92	78.92	CH
73.96	73.96	73.96	CH
71.11	71.11	71.11	CH
68.41	68.41	68.41	CH
53.30		53.30	CH <sub>3</sub>
48.75			C
44.63	44.63	44.63	CH
44.47			C
42.87			C
40.72		40.72	CH <sub>2</sub>
32.36		32.36	CH <sub>2</sub>

**Table 40** (Continued)

$\delta_c$	DEPT-90°	DEPT-135°	Type of Carbon
21.78		21.78	CH <sub>3</sub>
21.60		21.60	CH <sub>3</sub>
20.88		20.88	CH <sub>3</sub>
19.75		19.75	CH <sub>3</sub>
16.33		16.33	CH <sub>3</sub>
16.33		16.33	CH <sub>3</sub>
15.26		15.26	CH <sub>3</sub>
14.34		14.34	CH <sub>3</sub>

**Table 41** 300 MHz COSY correlation of some protons of compound XH2

$\delta_H$ (ppm)	Proton Correlation with $\delta_H$ (ppm)
H-23 (7.41)	H-22 (6.56)
H-6 (6.31)	H-5 (2.47)
H-12 (4.94)	H-11a (2.35), H-11b (1.98)
H-11a (2.35)	H-11b (1.98)
H-29a (2.24)	H-29b (1.74)

**Table 42** Major HMBC correlation of compound XH2

position	$\delta_H$ (ppm)	$\delta_c$ (ppm)
2''	2.18 (3H, <i>s</i> )	C-2' (170.51)
3	5.21 (1H, <i>s</i> )	C-2 (83.63), C-3' (168.94), C-5 (44.63), C-28 (15.26), C-29 (40.72) and C-30 (73.96)
3''	2.07 (3H, <i>s</i> )	C-3' (168.94)

Table 42 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
5	2.47 (1H, <i>br s</i> )	C-1 (84.06), C-3 (85.15), C-4 (44.47), C-7 (171.66), C-9 (86.05), C-10 (48.75), C-19 (16.33) and C-29 (40.72)
6	6.31 (1H, <i>br s</i> )	C-4 (44.47), C-6' (169.17), C-7 (171.66) and C-10 (48.75)
6''	2.21 (3H, <i>s</i> )	C-6 (71.11) and C-6' (169.17)
7'	3.74 (3H, <i>s</i> )	C-7 (171.66)
11a	2.35 (1H, <i>dd</i> , $J = 14.1, 3.9$ Hz)	C-8 (83.49), C-9 (86.05), C-10 (48.75), C-12 (68.41) and C-13 (42.87)
11b	2.00 (1H, <i>t</i> , $J = 14.1$ Hz)	C-9 (86.05), C-10 (48.75), C-12 (68.41) and C-13 (42.87)
12	4.94 (1H, <i>dd</i> , $J = 14.1, 3.9$ Hz)	C-11 (32.36), C-12' (170.39), C-13 (42.87), C-17 (78.92) and C-18 (14.34)
12''	1.56 (3H, <i>s</i> )	C-12' (170.39)
15	6.61 (1H, <i>s</i> )	C-8 (83.49), C-12 (68.41), C-13 (42.87), C-14 (152.62), C-16 (163.36) and C-18 (14.34)
17	5.91 (1H, <i>s</i> )	C-12 (68.41), C-13 (42.87), C-14 (152.62), C-16 (163.36), C-18 (14.34), C-20 (120.91), C-21 (142.01) and C-22 (110.16)
18	1.59 (3H, <i>s</i> )	C-12 (68.41), C-13 (42.87), C-14 (152.62) and C-17 (78.92)
19	1.31 (3H, <i>s</i> )	C-1 (84.06), C-5 (44.63), C-9 (86.05) and C-10 (48.75)

Table 42 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
21	7.45 (1H, <i>br s</i> )	C-20 (120.91), C-22 (110.16) and C-23 (143.00)
22	6.56 (1H, <i>br s</i> )	C-20 (120.91), C-21 (142.01) and C-23 (143.00)
23	7.41 (1H, <i>br s</i> )	C-20 (120.91), C-21 (142.01) and C-22 (110.16)
28	0.92 (3H, <i>s</i> )	C-3 (85.15), C-5 (44.63) and C-29 (40.72)
29a	2.24 (1H, <i>d</i> , $J = 11.1$ Hz)	C-1 (84.06), C-2 (83.63), C-3 (85.15), C-4 (44.47), C-5 (44.63) and C-10 (48.75)
29b	1.76 (1H, <i>d</i> , $J = 11.1$ Hz)	
30	5.35 (1H, <i>s</i> )	C-1 (84.06), C-8 (83.49), C-9 (86.05), C-14 (152.62) and C-31 (119.58)
32	1.70 (3H, <i>s</i> )	C-31 (119.58)

Table 43  $^1\text{H}$  and  $^{13}\text{C}$  spectral data of compound XH2

position	$\delta_{\text{C}}^{\#}$ (ppm)		$\delta_{\text{H}}$ (ppm)
1 <sup>a</sup>	84.06	O-C	-
2 <sup>a</sup>	83.63	O-C	-
2'	170.51	O-C=O	-
2''	21.78	CH <sub>3</sub>	2.18 (3H, <i>s</i> )
3	85.15	O-CH	5.21 (1H, <i>s</i> )
3'	168.94	O-C=O	-
3''	21.60	CH <sub>3</sub>	2.07 (3H, <i>s</i> )
4	44.47	C	-

Table 43 (Continued)

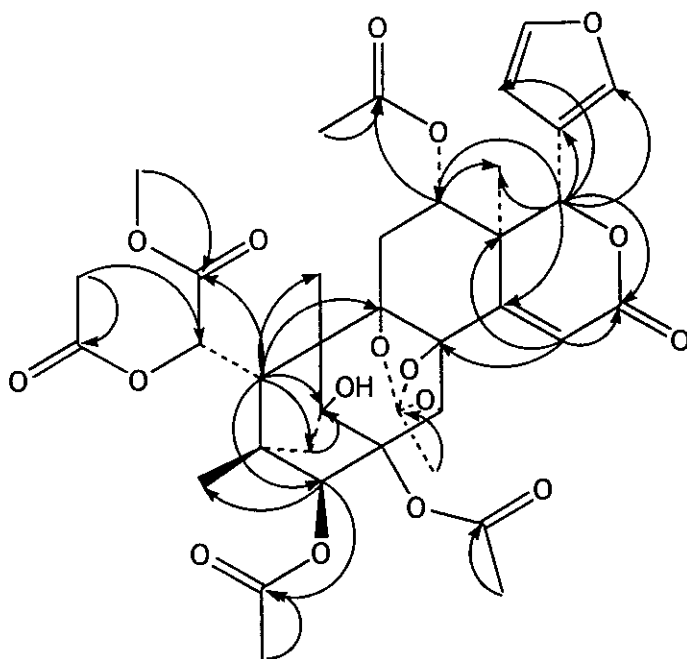
position	$\delta_C^*$ (ppm)		$\delta_H$ (ppm)
5	44.63	CH	2.47 (1H, <i>br s</i> )
6	71.11	O-CH	6.31 (1H, <i>br s</i> )
6'	169.17	O-C=O	-
6''	20.88	CH <sub>3</sub>	2.21 (3H, <i>s</i> )
7	171.66	O-C=O	-
7'	53.30	OCH <sub>3</sub>	3.74 (3H, <i>s</i> )
8	83.49	O-C	-
9	86.05	O-C	-
10	48.75	C	-
11	32.36	CH <sub>2</sub>	2.35 (1H, <i>dd</i> , $J = 14.1, 3.9$ Hz), 2.00 (1H, <i>t</i> , $J = 14.1$ Hz)
12	68.41	O-CH	4.94 (1H, <i>dd</i> , $J = 14.1, 3.9$ Hz)
12'	170.39	O-C=O	-
12''	19.75	CH <sub>3</sub>	1.56 (3H, <i>s</i> )
13	42.87	C	-
14	152.62	=C	-
15	124.11	=CH	6.61 (1H, <i>s</i> )
16	163.36	O-C=O	-
17	78.92	O-CH	5.91 (1H, <i>s</i> )
18	14.34	CH <sub>3</sub>	1.59 (3H, <i>s</i> )
19	16.33	CH <sub>3</sub>	1.31 (3H, <i>s</i> )
20	120.91	=C	-
21	142.01	=CH	7.45 (1H, <i>br s</i> )
22	110.16	=CH	6.56 (1H, <i>br s</i> )

Table 43 (Continued)

position	$\delta_C^{\#}$ (ppm)		$\delta_H$ (ppm)
23	143.00	=CH	7.41 (1H, <i>br s</i> )
28	15.26	CH <sub>3</sub>	0.92 (3H, <i>s</i> )
29	40.72	CH <sub>2</sub>	2.24 (1H, <i>d</i> , $J = 11.1$ Hz), 1.76 (1H, <i>d</i> , $J = 11.1$ Hz)
30	73.96	CH	5.35 (1H, <i>s</i> )
31	119.58	(O) <sub>3</sub> C	-
32	16.33	CH <sub>3</sub>	1.70 (3H, <i>s</i> )

<sup>a</sup> Assignment with the same superscripts maybe interchanged

<sup>#</sup> Carbon type deduced from DEPT experiment.



Selected HMBC correlation of compound XH2

**Table 44** Comparison of  $^1\text{H}$  NMR spectral data between compound XH2 and xyloccensin P

Position	Compound XH2, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )	Xyloccensin P, $\delta_{\text{H}}$ (ppm) (recorded in acetone- $d_6$ )
2''	2.18 (3H, <i>s</i> )	2.09 ( <i>s</i> )
3	5.21 (1H, <i>s</i> )	5.21 ( <i>s</i> )
3''	2.07 (3H, <i>s</i> )	1.99 ( <i>s</i> )
5	2.47 (1H, <i>br s</i> )	2.48 ( <i>br s</i> )
6	6.31 (1H, <i>br s</i> )	6.22 ( <i>br s</i> )
6''	2.21 (3H, <i>s</i> )	2.22 ( <i>s</i> )
7'	3.74 (3H, <i>s</i> )	3.80 ( <i>s</i> )
11	2.35 (1H, <i>dd</i> , $J = 14.1, 3.9$ Hz), 2.00 (1H, <i>t</i> , $J = 14.1$ Hz)	2.35 ( <i>dd</i> , $J = 14.0, 4.0$ Hz) 2.01 <sup>a</sup>
12	4.94 (1H, <i>dd</i> , $J = 14.1, 3.9$ Hz)	5.02 ( <i>dd</i> , $J = 13.5, 4.5$ Hz)
12''	1.56 (3H, <i>s</i> )	1.52 ( <i>s</i> )
15	6.61 (1H, <i>s</i> )	6.54 ( <i>s</i> )
17	5.91 (1H, <i>s</i> )	5.89 ( <i>s</i> )
18	1.59 (3H, <i>s</i> )	1.59 ( <i>s</i> )
19	1.31 (3H, <i>s</i> )	1.31 ( <i>s</i> )
21	7.45 (1H, <i>br s</i> )	7.54 ( <i>br s</i> )
22	6.56 (1H, <i>br s</i> )	6.65 ( <i>dd</i> , $J = 2.0, 1.0$ Hz)
23	7.41 (1H, <i>br s</i> )	7.62 ( <i>br s</i> )
28	0.92 (3H, <i>s</i> )	0.91 ( <i>s</i> )
29	2.24 (1H, <i>d</i> , $J = 11.1$ Hz), 1.76 (1H, <i>d</i> , $J = 11.1$ Hz)	2.26 ( <i>d</i> , $J = 11.0$ Hz) 1.81 ( <i>dd</i> , $J = 11.0, 1.0$ Hz)
30	5.35 (1H, <i>s</i> )	5.38 ( <i>s</i> )



**Table 44** (Continued)

Position	Compound XH2, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )	Xylocensin P, $\delta_{\text{H}}$ (ppm) (recorded in acetone- $d_6$ )
32	1.70 (3H, <i>s</i> )	1.71 ( <i>s</i> )

<sup>a</sup> no multiplicity assigned due to overlapped by the solvent of acetone- $d_6$ .

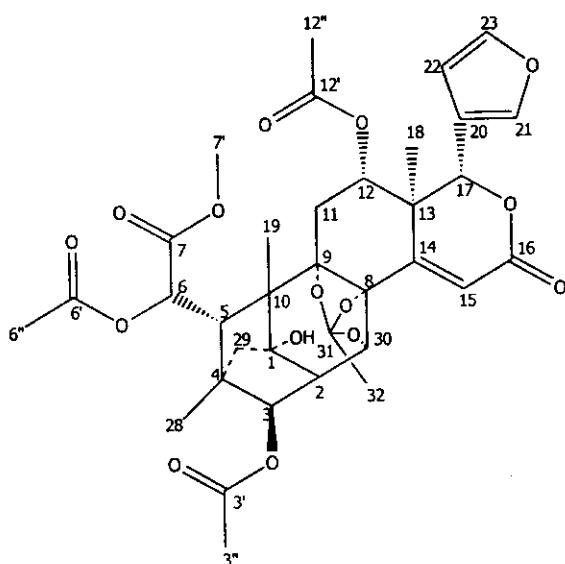
**Table 45** Comparison of  $^{13}\text{C}$  NMR spectral data between compound XH2 and xylocensin P

Position	Compound XC2, $\delta_{\text{C}}$ (ppm)	Xylocensin P, $\delta_{\text{C}}$ (ppm)
1	84.06	84.6
2	83.63	84.3
2'	170.51	168.8
2''	21.78	21.6
3	85.15	86.2
3'	168.94	170.9
3''	21.60	21.8
4	44.47	45.4
5	44.63	45.5
6	71.11	71.8
6'	169.17	169.3
6''	20.88	21.0
7	171.66	172.7
7'	53.30	53.7
8	83.49	84.9
9	86.05	87.8

Table 45 (Continued)

Position	Compound XC2, $\delta_C$ (ppm)	Xylococcin P, $\delta_C$ (ppm)
10	48.75	49.7
11	32.36	33.2
12	68.41	69.0
12'	170.39	170.2
12''	19.75	19.8
13	42.87	43.7
14	152.62	153.8
15	124.11	124.8
16	163.36	163.6
17	78.92	79.6
18	14.34	15.0
19	16.33	16.4
20	120.91	122.3
21	142.01	142.8
22	110.16	111.1
23	143.00	144.4
28	15.26	15.9
29	40.72	41.5
30	73.96	74.8
31	119.58	120.5
32	16.33	16.6

### 3.1.9 Compound HX3



Compound **XH3** was isolated as a colorless oil,  $[\alpha]_D^{26} = -35^\circ$  ( $c = 0.02$ , acetone). The mass spectrum of this compound (see **Fig. 78**) showed the molecular ion peak at  $(M+H)^+$   $m/z$  701, corresponding to a molecular formula  $C_{35}H_{40}O_{15}$ . The UV spectrum (see **Fig. 69**) showed maximum absorption band ( $\lambda_{max}$ ) at 217 nm supporting the  $\alpha,\beta$  - unsaturated carbonyl moiety in the molecule. The IR spectrum (see **Fig. 70**) showed the strong absorption bands at 3481, 1736 and 1729  $cm^{-1}$  corresponding to a hydroxy group and carbonyl groups, respectively. The presence of five carbonyl carbons at  $\delta$  171.84, 170.61, 170.46, 169.29 and 163.54 ppm from  $^{13}C$  NMR spectrum supported the above conclusion.

The complete analysis of  $^1H$  and  $^{13}C$  NMR spectral data of compound **XH3** (see **Table 49**, **Fig. 71** and **72**) were assigned with information provided from  $^1H$ - $^1H$  COSY (see **Table 47**, **Fig. 74**),  $^1H$ - $^{13}C$  correlation (HMQC) (**Fig. 75**) and  $^1H$ - $^{13}C$  correlation by long-range coupling (HMBC) (see **Table 48**, **Fig. 76**), along with comparison of  $^1H$  NMR spectral data to compound **XH3** (see **Table 49**). The  $^{13}C$  NMR (see **Table 49**, **Fig. 72**) spectrum of compound **XH3** recorded in  $CDCl_3$  showed 35 signals for 35 carbon atoms. Analysis of the DEPT-90 $^\circ$  and DEPT-135 $^\circ$  spectra of

this compound (see **Table 46, Fig. 73**) suggested the presence of eight methyl carbons ( $\delta$  53.28, 21.77, 20.95, 19.84, 16.54, 16.32, 15.56 and 14.37), two methylene carbons ( $\delta$  43.86 and 32.23), eleven methine carbons ( $\delta$  143.06, 142.08, 123.18, 110.22, 78.95, 78.17, 74.47, 71.40, 68.50, 45.42 and 44.60) and fourteen quaternary carbons ( $\delta$  171.84, 170.61, 170.46, 169.29, 163.54, 153.84, 121.00, 119.71, 86.92, 81.93, 81.72, 48.72, 45.85 and 42.92).

Compound **XH3**, a derivative of compound **XH2**, showed similar characteristic bands in IR and UV spectrum with those of **XH2**. Comparison of the  $^1\text{H}$  NMR spectral data (see **Table 50**) of the two compounds revealed close structural similarity. The two compounds differed in C-2 which was quaternary carbon in **XH2** but methine carbon in **XH3**. The H-2  $^1\text{H}$  NMR chemical shift of **XH3** was shown at  $\delta$  4.95 (1H, *dd*,  $J = 13.8, 4.2$  Hz). An additional signal of acetoxy proton (H-2'') in **XH2** was shown as  $\delta$  2.18 (3H, *s*) which was not observed in compound **XH3**.

The HMBC correlation of compound **XH3** (see **Table 48, Fig. 76**) showed the same correlation with compound **XH2** (see **Table 42**), except the proton signal at H-2  $\delta$  4.95 (1H, *dd*,  $J = 13.8, 4.2$  Hz). The proton signal of H-2 gave correlation peaks with C-1 (81.93), C-3 (78.17), C-4 (45.85), C-8 (81.72), C-10 (48.72) and C-30 (74.47), thus confirming the position of proton at C-2. From NOESY experiment (**Fig. 77**), **XH3** showed similar cross peaks with those of **XH2**, except the proton signals at H-2 ( $\delta$  3.16) showed cross peak with H-3 ( $\delta$  5.24), H-29b ( $\delta$  1.49) and H-30 ( $\delta$  4.64); H-3 ( $\delta$  5.24) showed cross peak with H-2 ( $\delta$  3.16), Me-28 ( $\delta$  0.94) and H-29b ( $\delta$  1.49); H-5 ( $\delta$  2.58) showed cross peak with H-6 ( $\delta$  6.33), H-12 ( $\delta$  4.95) and H-17 ( $\delta$  5.96); H-12 ( $\delta$  4.95) showed cross peak with H-3'' ( $\delta$  2.04), H-5 ( $\delta$  2.58), H-6 ( $\delta$  6.33), H-11a ( $\delta$  2.35) and H-17 ( $\delta$  5.96); H-17 ( $\delta$  5.96) showed cross peak with H-5 ( $\delta$  2.58), H-12 ( $\delta$  4.95), H-21 ( $\delta$  7.45) and H-22 ( $\delta$  6.56); H-15 ( $\delta$  6.32) showed cross peak with H-30 ( $\delta$  4.64) and H-30 ( $\delta$  4.64) showed cross peak with H-15 ( $\delta$

6.32) Thus, this observation confirming that H-5, H-12 and H-17 are on the same side and opposite side to both H-2, H-3, H-15 and H-30. Compound XH3 was identified as xylocensin O which was the compound previously isolated from the stem bark of *X. granatum*. (Wu, *et al.*,2004)

**Table 46**  $^{13}\text{C}$  and DEPT spectral data of compound XH3

$\delta_{\text{C}}$	DEPT-90°	DEPT-135°	Type of Carbon
171.84			C
170.61			C
170.46			C
169.29			C
163.54			C
153.84			C
143.06	143.06	143.06	CH
142.08	142.08	142.08	CH
123.18	123.18	123.18	CH
121.00			C
119.71			C
110.22	110.22	110.22	CH
86.92			C
81.92			C
81.72			C
78.95	78.95	78.95	CH
78.17	78.17	78.17	CH
74.47	74.47	74.47	CH
71.40	71.40	71.40	CH

Table 46 (Continued)

$\delta_c$	DEPT-90°	DEPT-135°	Type of Carbon
68.50	68.50	68.50	CH
53.28		53.28	CH <sub>3</sub>
48.72			C
45.85			C
45.42	45.42	45.42	CH
44.60	44.60	44.60	CH
43.86		43.86	CH <sub>2</sub>
42.92			C
32.23		32.23	CH <sub>2</sub>
21.77		21.77	CH <sub>3</sub>
20.95		20.95	CH <sub>3</sub>
19.84		19.84	CH <sub>3</sub>
16.54		16.54	CH <sub>3</sub>
16.32		16.32	CH <sub>3</sub>
15.56		15.56	CH <sub>3</sub>
14.37		14.37	CH <sub>3</sub>

Table 47 300 MHz COSY correlation of some protons of compound XH3

$\delta_H$ (ppm)	Proton Correlation with $\delta_H$ (ppm)
H-23 (7.40)	H-22 (6.56)
H-6 (6.33)	H-5 (2.58)
H-3 (5.24)	H-2 (3.16)
H-12 (4.95)	H-11a (2.35), H-11b (2.03)

Table 47 (Continued)

$\delta_{\text{H}}$ (ppm)	Proton Correlation with $\delta_{\text{H}}$ (ppm)
H-30 (4.64)	H-2 (3.16)
H-11a (2.35)	H-11b (2.03)
H-29a (2.26)	H-29b (1.49)

Table 48 Major HMBC correlation of compound XH3

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
2	3.16 (1H, <i>dd</i> , $J = 12.0, 3.9$ Hz)	C-1 (81.93), C-3 (78.17), C-4 (45.85), C-8 (81.72), C-10 (48.72) and C-30 (74.47)
3	5.24 (1H, <i>d</i> , $J = 12.0$ Hz)	C-2 (44.60), C-3' (170.61), C-5 (45.42), C-28 (15.56), C-29 (43.86) and C-30 (74.47)
3''	2.04 (3H, <i>s</i> )	C-3' (170.61)
5	2.58 (1H, <i>br s</i> )	C-1 (81.93), C-3 (78.17), C-4 (45.85), C-6 (71.40), C-7 (171.84), C-9 (86.92), C-10 (48.72), C-19 (16.32) and C-29 (43.86)
6	6.33 (1H, <i>br s</i> )	C-4 (45.85), C-5 (45.42), C-6' (169.29), C-7 (171.84) and C-10 (48.72)
6''	2.20 (3H, <i>s</i> )	C-6 (71.40) and C-6' (169.29)
7'	3.75 (3H, <i>s</i> )	C-7 (171.84)
11a	2.35 (1H, <i>dd</i> , $J = 13.8, 4.2$ Hz)	C-8 (81.72), C-9 (86.92), C-10 (48.72), C-12 (68.50) and C-13 (42.92)
11b	2.03 (1H, <i>t</i> , $J = 13.8$ Hz)	C-9 (86.92), C-10 (48.72), C-12 (68.50) and C-13 (42.92)

Table 48 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
12	4.95 (1H, <i>dd</i> , $J = 13.8, 4.2$ Hz)	C-12' (170.46), C-13 (42.92), C-17 (78.95) and C-18 (14.37)
12''	1.56 (3H, <i>s</i> )	C-12' (170.46)
15	6.32 (1H, <i>s</i> )	C-8 (81.72), C-13 (42.92), C-14 (153.84) and C-16 (163.54)
17	5.96 (1H, <i>s</i> )	C-12 (68.50), C-13 (42.92), C-14 (153.84), C-18 (14.37), C-20 (121.00), C-21 (142.08) and C-22 (110.22)
18	1.60 (3H, <i>s</i> )	C-12 (68.50), C-13 (42.92), C-14 (153.84) and C-17 (78.95)
19	1.26 (3H, <i>s</i> )	C-1 (81.93), C-5 (45.42), C-9 (86.92) and C-10 (48.72)
21	7.45 (1H, <i>br s</i> )	C-20 (121.00), C-22 (110.22) and C-23 (143.06)
22	6.56 (1H, <i>br d</i> , $J = 1.8$ Hz)	C-20 (121.00), C-21 (142.08) and C-23 (143.06)
23	7.40 (1H, <i>t</i> , $J = 1.8$ Hz)	C-20 (121.00), C-21 (142.08) and C-22 (110.22)
28	0.94 (3H, <i>s</i> )	C-3 (78.17), C-4 (45.85), C-5 (45.42) and C-29 (43.86)
29a	2.26 (1H, <i>d</i> , $J = 11.1$ Hz)	} C-1 (81.93), C-2 (44.60), C-3 (78.17), C-4 (45.85), C-5 (45.42) and C-10 (48.72)
29b	1.49 (1H, <i>d</i> , $J = 11.1$ Hz)	
30	4.64 (1H, <i>d</i> , $J = 3.9$ Hz)	C-1 (81.93), C-3 (78.17), C-8 (81.72), and C-9 (86.92)



Table 48 (Continued)

position	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)
32	1.69 (3H, <i>s</i> )	C-31 (119.71)

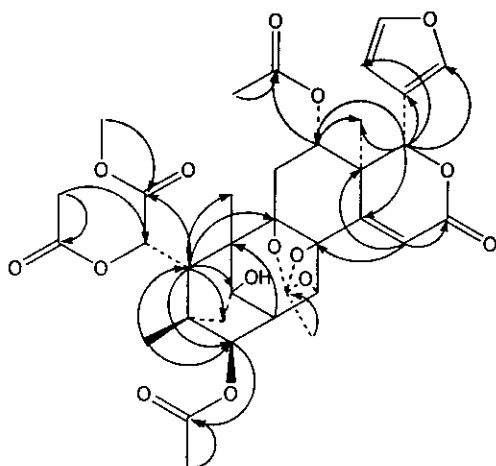
Table 49  $^1\text{H}$  and  $^{13}\text{C}$  spectral data of compound XH3

position	$\delta_{\text{C}}^{\#}$ (ppm)		$\delta_{\text{H}}$ (ppm)
1	81.93	C	-
2	44.60	CH	3.16 (1H, <i>dd</i> , $J = 12.0, 3.9$ Hz)
3	78.17	CH	5.24 (1H, <i>d</i> , $J = 12.0$ Hz)
3'	170.61	C	-
3''	21.77	CH <sub>3</sub>	2.04 (3H, <i>s</i> )
4	45.85	C	-
5	45.42	CH	2.58 (1H, <i>br s</i> )
6	71.40	CH	6.33 (1H, <i>br s</i> )
6'	169.29	C	-
6''	20.95	CH <sub>3</sub>	2.20 (3H, <i>s</i> )
7	171.84	C	-
7'	53.28	CH <sub>3</sub>	3.75 (3H, <i>s</i> )
8	81.72	C	-
9	86.92	C	-
10	48.72	C	-
11	32.23	CH <sub>2</sub>	2.35 (1H, <i>dd</i> , $J = 13.8, 4.2$ Hz), 2.03 (1H, <i>t</i> , $J = 13.8$ Hz)
12	68.50	CH	4.95 (1H, <i>dd</i> , $J = 13.8, 4.2$ Hz)
12'	170.46	C	-

Table 49 (Continued)

position	$\delta_C^{\#}$ (ppm)		$\delta_H$ (ppm)
12''	19.84	CH <sub>3</sub>	1.56 (3H, <i>s</i> )
13	42.92	C	-
14	153.84	C	-
15	123.18	CH	6.32 (1H, <i>s</i> )
16	163.54	C	-
17	78.95	CH	5.96 (1H, <i>s</i> )
18	14.37	CH <sub>3</sub>	1.60 (3H, <i>s</i> )
19	16.32	CH <sub>3</sub>	1.26 (3H, <i>s</i> )
20	121.00	C	-
21	142.08	CH	7.45 (1H, <i>br s</i> )
22	110.22	CH	6.56 (1H, <i>br d</i> , <i>J</i> = 1.8 Hz)
23	143.06	CH	7.40 (1H, <i>t</i> , <i>J</i> = 1.8 Hz)
28	15.56	CH <sub>3</sub>	0.94 (3H, <i>s</i> )
29	43.86	CH <sub>2</sub>	2.26 (1H, <i>d</i> , <i>J</i> = 11.1 Hz), 1.49 (1H, <i>d</i> , <i>J</i> = 11.1 Hz)
30	74.47	CH	4.64 (1H, <i>d</i> , <i>J</i> = 3.9 Hz)
31	119.71	C	-
32	16.54	CH <sub>3</sub>	1.69 (3H, <i>s</i> )

<sup>#</sup> Carbon type deduced from DEPT experiment.



Selected HMBC correlation of compound XH3

**Table 50** Comparison of  $^1\text{H}$  NMR spectral data between compound XH3 and xylocensins O

Position	Compound XH3, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )	Xylocensins O, $\delta_{\text{H}}$ (ppm) (recorded in $\text{Acetone-}d_6$ )
2	3.16 (1H, <i>dd</i> , $J = 12.0, 3.9$ Hz)	3.09 ( <i>dd</i> , $J = 12.0, 4.0$ Hz)
3	5.24 (1H, <i>d</i> , $J = 12.0$ Hz)	5.33 ( <i>d</i> , $J = 12.0$ Hz)
3''	2.04 (3H, <i>s</i> )	1.95 ( <i>s</i> )
5	2.58 (1H, <i>br s</i> )	2.61 ( <i>br s</i> )
6	6.33 (1H, <i>br s</i> )	6.24 ( <i>br s</i> )
6''	2.20 (3H, <i>s</i> )	2.21 ( <i>s</i> )
7'	3.75 (3H, <i>s</i> )	3.80 (3H, <i>s</i> )
11	2.35 (1H, <i>dd</i> , $J = 13.8, 4.2$ Hz), 2.03 (1H, <i>t</i> , $J = 13.8$ Hz)	2.34 ( <i>dd</i> , $J = 14.0, 4.0$ Hz), 2.04
12	4.95 (1H, <i>dd</i> , $J = 13.8, 4.2$ Hz)	4.99 ( <i>dd</i> , $J = 13.5, 4.5$ Hz)
12''	1.56 (3H, <i>s</i> )	1.52 ( <i>s</i> )
15	6.32 (1H, <i>s</i> )	6.67 ( <i>s</i> )
17	5.96 (1H, <i>s</i> )	5.92 ( <i>s</i> )

Table 50 (Continued)

Position	Compound XH3, $\delta_{\text{H}}$ (ppm) (recorded in $\text{CDCl}_3$ )	Xyloccensins O, $\delta_{\text{H}}$ (ppm) (recorded in $\text{Acetone-}d_6$ )
18	1.60 (3H, <i>s</i> )	1.60 ( <i>s</i> )
19	1.26 (3H, <i>s</i> )	1.23 ( <i>s</i> )
21	7.45 (1H, <i>br s</i> )	7.45 ( <i>br s</i> )
22	6.56 (1H, <i>br d</i> , $J = 1.8$ Hz)	6.64 ( <i>dd</i> , $J = 2.0, 1.0$ Hz)
23	7.40 (1H, <i>t</i> , $J = 1.8$ Hz)	7.62 ( <i>br s</i> )
28	0.94 (3H, <i>s</i> )	0.93 ( <i>s</i> )
29	2.26 (1H, <i>d</i> , $J = 11.1$ Hz), 1.49 (1H, <i>d</i> , $J = 11.1$ Hz)	2.25 ( <i>d</i> , $J = 10.5$ Hz), 1.49 ( <i>dd</i> , $J = 10.5, 1.5$ Hz)
30	4.64 (1H, <i>d</i> , $J = 3.9$ Hz)	4.97 ( <i>d</i> , $J = 4.0$ Hz)
32	1.69 (3H, <i>s</i> )	1.68 ( <i>s</i> )

Table 51 Comparison of  $^{13}\text{C}$  NMR spectral data between compound XH3 and xyloccensins O

Position	Compound XH3, $\delta_{\text{C}}$ (ppm)	Xyloccensins O, $\delta_{\text{C}}$ (ppm)
1	81.93	82.6
2	44.60	45.6
3	78.17	78.4
3'	170.61	170.5
3''	21.77	21.8
4	45.85	46.7
5	45.42	46.3
6	71.40	72.1

Table 51 (Continued)

Position	Compound XH3, $\delta_c$ (ppm)	Xylocensins O, $\delta_c$ (ppm)
6'	169.29	169.3
6''	20.95	21.0
7	171.84	172.8
7'	53.28	53.6
8	81.72	82.9
9	86.92	87.6
10	48.72	49.6
11	32.23	33.0
12	68.50	69.1
12'	170.46	170.2
12''	19.84	19.8
13	42.92	43.6
14	153.84	154.4
15	123.18	124.5
16	163.54	163.8
17	78.95	79.4
18	14.37	15.0
19	16.32	16.5
20	121.00	122.5
21	142.08	142.8
22	110.22	111.1
23	143.06	144.3
28	15.56	16.0
29	43.86	44.5

**Table 51** (Continued)

<b>Position</b>	<b>Compound XH3, <math>\delta_c</math> (ppm)</b>	<b>Xylocensins O, <math>\delta_c</math> (ppm)</b>
30	74.47	75.2
31	119.71	120.4
32	16.54	16.6

### **3.2 *Biological activities of the crude extract and the pure compounds from X. granatum***

The crude hexane extract and the pure compounds of the seeds exhibited weak activity against both antimicrobial and *Mycobacterium tuberculosis* H37Ra but showed no antimalarial and cytotoxic activity, while the crude dichloromethane extract exhibited anti-TB and antimalarial but no antimicrobial and cytotoxic activity. The crude methanol extract and compound **XC2** showed anti-TB.

**Table 52** Biological activity of antibacterial of the crude extract and the pure compounds from the seeds of *X. granatum*

Sample	SA		MRSA SK1		EC		PA	
	IZ	MIC	IZ	MIC	IZ	MIC	IZ	MIC
H	7,45	1024	7,75	1024	-	-	-	-
C	-	-	-	-	-	-	-	-
M	-	-	-	-	-	-	-	-
XC1		>128		>128				
XC2		>128		>128				
XC3		>128		>128				
XC4		>200		>200		>200		>200
XC5		>200		>200		>200		>200
XH1		>200		>200		>200		>200
XH2		>200		>200		>200		>200
XH3		>200		>200		>200		>200

SA = *Staphylococcus aureus* ATCC25923, MRSA = Methicillin – resistant *Staphylococcus aureus*, EC = *Escherichia coli*, PA = *Pseudomonas aeruginosa* ATCC27853, IZ = Inhibition zone (mm), MIC = Minimum inhibitory concentration (µg/ml), H = The hexane extract, C = The dichloromethane extract, M = The methanol extract



**Table 53** Biological activity of antiyeasts of the crude extract and the pure compounds from the seeds of *X. granatum*

Sample	CA		CA90028		TG90030		CN		CN90112		CN90113	
	IZ	MIC	IZ	MIC	IZ	MIC	IZ	MIC	IZ	MIC	IZ	MIC
H	6,15	>1024	6,15	>1024	6,1	>1024	6,15	>1024	6,25	>1024	6,15	>1024
C	-	-	-	-	-	-	-	-	-	-	-	-
M	-	-	-	-	-	-	-	-	-	-	-	-
XC1		>200		>200		>200		>200		>200		>200
XC2		>200		>200		>200		>200		>200		>200
XC3		>200		>200		>200		>200		>200		>200
XC4		>200		>200		>200		>200		>200		>200
XC5		>200		>200		>200		>200		>200		>200
XH1		>200		>200		>200		>200		>200		>200
XH2		>200		>200		>200		>200		>200		>200
XH3		>200		>200		>200		>200		>200		>200

CA = *Candida albicans* NCPF3153, CN = *Cryptococcus neoformans* clinical isolate, CN90112 = *Cryptococcus neoformans* ATCC90112

flucytosine – sensitive, CN90113 = *Cryptococcus neoformans* ATCC90113 flucytosine – resistant, IZ = Inhibition zone (mm), MIC = Minimum inhibitory concentration (µg/ml), H = The hexane extract, C = The dichloromethane extract, M = The methanol extract

**Table 54** Biological activity of antimicrobial of the reference for test the sample

Sample	Bacteria				Yeasts					
	SA	MRSA SK1	EC	PA	CA	CA90028	TG90030	CN	CN90112	CN90113
<b>Vancomycin</b> (30 µg/disc)	16.18	15.93								
<b>Gentamycin</b> (10 µg/disc)			18.18	17.53						
<b>Amphotericin B</b> (10 µg/disc)					15.45		21.38	18.65	13	10.9

SA = *Staphylococcus aureus* ATCC25923, MRSA = Methicillin – resistant *Staphylococcus aureus*, EC = *Escherichia coli*, PA = *Pseudomonas aeruginosa* ATCC27853, CA = *Candida albicans* NCPF3153, CN = *Cryptococcus neoformans* clinical isolate, CN90112 = *Cryptococcus neoformans* ATCC90112 flucytosine – sensitive, CN90113 = *Cryptococcus neoformans* ATCC90113 flucytosine – resistant, MIC = Minimum inhibitory concentration (µg/ml), H = The hexane extract, C = The dichloromethane extract, M = The methanol extract

**Table 55** Biological activity of antiyeasts of the crude extract and the pure compounds from the seeds of *X. granatum*

Sample	Anti-TB		Antimalarial		Cytotoxicity		
	Inactive/active	MIC, µg/ml	Inactive/active	ED <sub>50</sub>	KB	BC	NCI-H187
H	Active	25	Inactive		Inactive	Inactive	Inactive
C	Active	25	Active	6.6	Inactive	Inactive	Inactive
M	Active	200	Inactive		Inactive	Inactive	Inactive
XC1	Inactive	> 200	Inactive				
XC2	Active	100	Inactive				
XC3	Inactive	> 200	Inactive				

Anti-TB = *In vitro* antituberculous activity against *Mycobacterium tuberculosis* H37Ra, KB = Oral human epidermoid carcinoma, BC = Human breast cancer cells, NCI-H187 = Human small cells lung cancer, MIC = Minimum inhibitory concentration (µg/ml), EC<sub>50</sub> = 50% Effective concentration (µg/ml), H = The hexane extract, C = The dichloromethane extract, M = The methanol extract