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Two unusual rotenoid derivatives, 7a-*O*-methyl-12a-hydroxydeguelol and spiro-13-homo-13-oxaelliptone, from the seeds of *Derris trifoliata*

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Dedicated to Professor Ermias Dagne on the occasion of his 60th Birthday.

Abstract

The crude methanol extract of the seeds of *Derris trifoliata* showed potent and dose dependent larvicidal activity against the 2nd instar larvae of *Aedes aegypti*. From this extract two unusual rotenoid derivatives, a rotenoloid (named 7a-*O*-methyl-12a-hydroxydeguelol) and a spirohomooxarotenoid (named spiro-13-homo-13-oxaelliptone), were isolated and characterised. In addition a rare natural chromanone (6,7-dimethoxy-4-chromanone) and the known rotenoids rotenone, tephrosin and dehydrodeguelin were identified. The structures were assigned on the basis of spectroscopic evidence. The larvicidal activity of the crude extract is mainly due to rotenone.

Keywords: *Derris trifoliata*; Leguminosae; Seeds; Rotenoloid; Spirohomooxarotenoid; Rotenoids; 7a-*O*-methyl-12a-hydroxydeguelol; Spiro-13-homo-13-oxaelliptone; 6,7-Dimethoxy-4-chromanone; Mosquito; Larvicides; *Aedes aegypti*

1. Introduction

In the search for compounds with larvicidal and pesticidal activities from plants, the larvicidal activities of rotenoids isolated from the seeds of *Millettia dura* Dunn have been reported (Yenesew et al., 2003). Rotenoids are also known to occur in the genera *Derris*, *Lonchocarpus*, and *Tephrosia* of the family Leguminosae (Dewick, 1994).

In Kenya, the genus *Derris* is represented by *Derris trifoliata* Lour. From the stem of this plant, the presence of rotenoids with cancer chemopreventive properties has been reported (Ito et al., 2004). In a recent phytochemical investigation (Yenesew et al., 2005) of the roots of this plant, we have reported a modified rotenoid with an open ring-C (trivial name 7a-*O*-methyldeguelol), representing a new sub-class of isoflavonoids (the sub-class named rotenoloid). We have analyzed the seeds of this plant and report here the isolation and identification of a further two modified rotenoids (**1** and **2**) along with four known compounds.

2. Results and discussion

HR-MS of compound **1** established a molecular formula of $C_{24}H_{26}O_7$. Comparison of the ^1H and ^{13}C NMR

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Table 1
^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data of **1** and **2** in CD_2Cl_2 (*J* in Hz)

	1			**2**		
	^{1}H	^{13}C	HMBC (^2J, ^3J)	^{1}H	^{13}C	HMBC (^2J, ^3J)
1	6.44 *s*	110.7	C-2, -3, -4a, -12a	6.64 *s*	105.5	C-2, -3, -4a, -1a
1a		114.2			138.1	
2		144.6			146.7	
3		151.3			145.2	
4	6.47 *s*	101.6	C-1a, -2, -3, -4a	6.48 *s*	107.8	C-1a, -2, -3, -4a
4a		149.9			143.9	
6	4.26 *ddd* (3.2, 4.3, 10.8)	63.4		4.59 *ddd* (3.5, 5.5, 12.5)	65.6	C-4a, -12a
	4.14 *ddd* (2.2, 10.8, 12.1)			4.22 *ddd* (2.0, 10.0, 12.5)		C-4a, -12a
6a	2.42 *ddd* (4.4, 12.1, 14.2)	35.6	C-6	2.65 *ddd* (3.5, 10.0, 15.5)	35.4	C-12, -12a
	1.94 *ddd* (2.2, 3.2, 14.2)		C-12a	2.23 *ddd* (2.0, 5.5, 15.5)		C-12a
7a		156.4			166.3	
8		115.9			114.3	
9		157.6			162.5	
10	6.32 *dd* (0.7, 8.7)	112.1	C-8, -11a	7.33 *dd* (1.0, 8.5)	108.2	C-8, -11a
11	6.58 *d* (8.7)	130.5	C-7, -9, -10, -12	7.64 *d* (8.5)	120.9	C-7, -9, -12
11a		122.4			113.3	
12		203.1			194.4	
12a		74.8			105.1	
2′		77.2		7.72 *d* (2.5)	146.4	C-8, -9
3′	5.70 *d* (10.1)	131.3	C-2′, -8	6.95 *dd* (1.0, 2.5)	104.0	C-2′, -8, -9
4′	6.57 *dd* (0.7, 10.1)	116.5	C-2′			
2′-Me_2	1.42 *s*	28.2	C-2′, -3′			
	1.39 *s*	27.9	C-2′, -3′			
OMe-2	3.67 *s*	56.7	C-2	3.68 *s*	56.4	C-2
OMe-3	3.82 *s*	56.1	C-3	3.81 *s*	56.5	C-3
OMe-7a	3.74	63.3	C-7a			
OH-12a	5.10 *br s*					

(Table 1) spectra of **1** with those of 7a-*O*-methyldeguelol (**3**) indicated that it is a rotenoloid derivative (Yenesew et al., 2005). In fact, rings A, D and E were identical to that of **3**. In ring B, however, the methylene protons at C-6 and C-6a appeared as four sets of mutually coupled doublet of doublets (Table 1) which requires that C-12a is substituted by a hydroxyl group (δ 5.10 *br s* for OH-12a in ^{1}H and 74.8 for C-12a in ^{13}C NMR spectra). In the MS, the molecular ion peak at *m*/*z* 426 ($C_{24}H_{26}O_7$) and the fragment ions at *m*/*z* 217 ($C_{13}H_{13}O_3$) and 209 ($C_{11}H_{13}O_4$) are consistent with **1** being a 12a-hydroxy derivative of **3**. Hence this new compound was identified as 7a-*O*-methyl-12a-hydroxydeguelol (**1**). Compound **1** is levorotatory ($[\alpha]_D = -9.0°$) as 7a-*O*-methyldeguelol (**3**) suggesting the same configuration at C-12a. However, the absolute configuration at C-12a in these compounds remains to be determined. Compound **1** is an addition to the new sub-class of isoflavonoids named rotenoloids (Yenesew et al., 2005).

The ^{1}H and ^{13}C NMR (Table 1) spectra of compound **2** (molecular formula $C_{20}H_{16}O_7$) showed some features similar to those of 12a-hydroxyelliptone (**4**) (Ito et al., 2004). As in **4**, ring A contains two methoxyl groups at C-2 (δ_H 3.68 and δ_C 56.4) and C-3 (δ_H 3.81 and δ_C 56.5) with the *para*-oriented protons H-1 and H-4 appearing at δ 6.64 (*s*) and δ 6.48 (*s*), respectively. The placements of the two methoxyl groups at C-2 and C-3 was confirmed through HMBC correlation (Table 1) of the methoxyl protons, δ 3.68 and 3.81, with C-2 (δ 146.7) and C-3 (δ 145.2), respectively.

The ^{13}C NMR spectrum, however, displayed this ring to be tetra-oxygenated (instead of tri-oxygenation as in commonly found rotenoids such as **4**) viz. C-1a (δ 138.1), C-2 (146.7), C-3 (145.2) and C-4a (143.9). Such oxygenation pattern has been observed in the modified rotenoids 13-homo-13-oxa-6a,12a-dehydrorotenone (**5**) and 13-homo-13-oxa-6a,12a-dehydrodeguelin (**6**) (Fang and Casida, 1997; Wangenesteen et al., 2005). As in these compounds, ring B in **2** is also seven-membered with a second oxygen atom (O-13) bridging C-1a and C-12a.

In this ring, the ^{1}H NMR signals for the two protons at C-6 appeared as two sets of doublet of a double dou-