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Polyoxygenated cyclohexene derivatives from *Ellipeiopsis cherrevensis*

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Abstract

Aerial parts of *Ellipeiopsis cherrevensis* contained the polyoxygenated cyclohexenes zeylenol, ferrudiol and three analogs, ellipeiopsols A, B and C. The C-1 stereochemistry of ferrudiol has been revised.

Keywords: *Ellipeiopsis cherrevensis*; Annonaceae; Polyoxygenated cyclohexenes; Zeylenol; Ferrudiol; Ellipeiopsols A, B, C

1. Introduction

Ellipeiopsis cherrevensis (Pierre ex Finet et Gagn.) R. E. Fries (Annonaceae, subfamily Annonoideae, tribe Uvarieae) is one of only two species in the genus and is limited to Thailand and Cambodia. It has not been studied previously. The genus is closely related to the genus *Uvaria* species of which have furnished acetogenins (Cavé et al., 1997) and polyoxygenated cyclohexene derivatives (Thebtaranonth and Thebtaranonth, 1986; Nkunya et al., 1987; Parmar et al., 1994; Liao et al., 1996, 1997; Pan and Yu, 1995a,b, 1996; Pan et al., 1998; Zhou et al., 1998, 1999). Our study of the aerial parts has led to the isolation of zeylenol (**1a**, Jolad et al., 1981), its new 3-acetate analog **1b**, the new C-1 epi-derivatives **2a** and **3a** and ferrudiol (Schulte and Ganem, 1982; Schulte et al., 1982a) whose stereochemistry has been revised to **5a**.

2. Results and discussion

The MeOH extract of the aerial parts on concentration, precipitation of polar material from an EtOH–H_2O solution, extraction with $CHCl_3$ followed by column and thin layer chromatography of the nonpolar fraction afforded five polyoxygenated cyclohexene derivatives. The least polar substance was identified as zeylenol (**1a**, Jolad et al. 1981; Pan and Yu, 1995a) by ^1H and ^{13}C NMR spectrometry, HMBC, COSY and NOESY. A second substance was the new 3-acetate analog **1b** of zeylenol which we have named ellipeiopsol A. Chemical shifts and coupling constants, HMBC and the NOESY data (Table 1) showed that the acetate was on C-3, the benzoate on C-7 and that conformer A resembled the predominant conformer, with H-3 predominantly axial and H-6 predominantly equatorial.

A third constituent ellipeiopsol B was assigned structure **2a**, epimeric at C-1 and C-6 compared with **1a,b**, on the basis of the NMR spectral data (Table 2) and the formation of di- and triacetates **2b** and **2c** (Table 3). The locations of the acetate at C-3 and the benzoate at C-7 were clear from the chemical shifts of H-3 and H-7a,b and from HMBC, COSY and NOESY experiments while the chemical shifts and coupling constants

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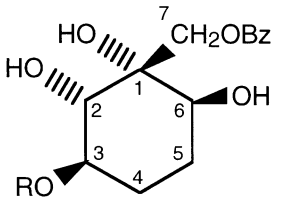

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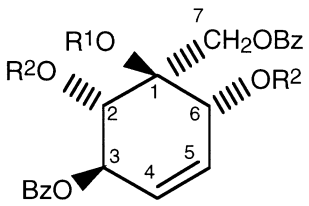
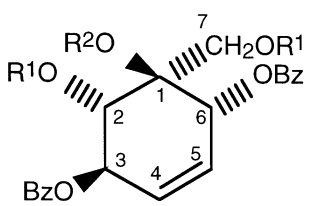
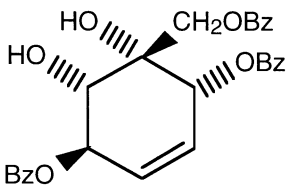
b R = Ac



2a R^1,R^2 = H
b R^1 = H, R^2 = Ac
c R^1,R^2 = Ac



3a R^1,R^2 = H
b R^1 = Ac, R^2 = H
c R^1,R^2 = Ac



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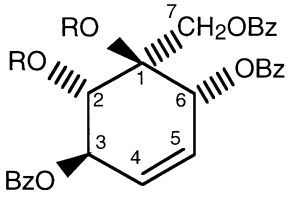
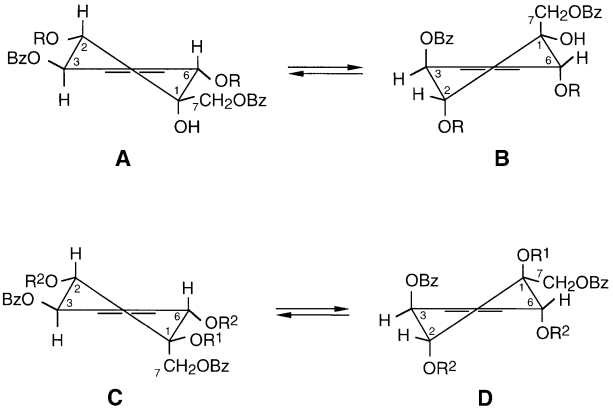


5a R = H
b R = Ac



A **B** **C** **D**

involving H-2 and H-4 indicated a stereochemistry at these centers similar to that of **1a** and **1b** but with a free hydroxyl on C-2. On the other hand the coupling constants involving H-5 and H-6 differed and the chemical shift of H-6 indicated the absence of an esterifying function on the C-6 hydroxyl which was now alpha orientated.

The remaining problem was the stereochemistry at C-1. Chemical shifts of H-7a,b differed somewhat from those reported for an isomer, ovarigranol G, which has the C-7 stereochemistry of **1a** and **1b** (Pan et al., 1998). In the NOESY spectrum the absence of a cross peak between H-7 and H-2, the latter clearly β-orientated in **2a** and triacetate **2c**, indicated that the stereochemistry at C-7 was inverted with a preference for conformation C (R^1, R^2 = H) because of the magnitude of $J_{2,3}$ (7.5 Hz) in **2a**. The difference in the stereochemistry at C-1 was also clearly manifested in the chemical shifts of C-2, C-6, both 1 ppm downfield from C-2 and C-6 in **1a,b**, and C-7, 3 ppm upfield from C-7 in **1a,b** (see also Table 7). The downfield shifts of C-2 and C-6 are negated in the case of the triacetate **2c** because of the effect produced by acylation of a neighboring hydroxyl. The coupling constants suggest that **2b** exists entirely in conformation C (R^1 = H, R^2 = Ac) while in **2c** conformation C (R^1 = H, R^2 = Ac) merely predominates. In both **2b** and **2c** the NOESY spectrum exhibited a cross peak between H-7 and H-3 as required by C.

A fourth substance, ellipeiopsol C (**3a**), was obviously closely related to **2a** with the same stereochemistry at C-1, C-2, C-3 and C-6 but with the benzoate at C-6 instead of at C-7 as shown by the ^{1}H and ^{13}C NMR data in Table 4. The signals of H-7a,b were now at considerably higher field while H-6 had moved downfield. The

Table 1
^{1}H (300 MHz) and ^{13}C NMR (75 MHz) data for compound **1b** ($CDCl_3$)

Position	δH	δC[a]	NOESY	COSY[b]	HMBC
1		75.70 *s*			
2	4.09 *d* (6)	70.47 *d*	H-3	H-3, 6,7a, b (5)	3
3	5.44 *m* (6, 2.5, 1.5)	73.33 *d*	H-2, 4	H-2, 4,7a, b (5)	2, 4, 5, AcCO
4	5.68 *dt* (10, 2.5)	126.66 *d*		H-3, 5	2, 3, 5, 6
5	5.91 *ddd* (10, 4, 2)	129.73 *d*	H-4, 6	H-4, 6,(3, 3, 7a, b)	1, 4
6	4.30 *brd* (4)	68.68 *d*	H-5, 7a, b	H-2, 5, 7a, b	1.4, 5
7a	4.74 *d* (12.2)	66.55 *t*	H-2	H-2, 3, 6, 7b (5)	1, 2, 6 ϕCO
7b	4.67 *d* (12.2)		H-2		
C=O		167.51 *s*			
1′		129.57 *s*			
2′, 6′	8.10 *dd* (8, 1)	129.73 *d*	H-2, 6,3′, 5′	H-3′, 5′	2′, 4′, 6′, ϕCO
3′, 5′	7.40 *dd* (8, 8)	128.46 *d*			1′, 3′, 5′, ϕCO
4′	7.55 *dd* (8, 1)	133.44 *d*	H-3′, 5′	H-3′, 5′	
3-Ac	1.99 *s* (3p)	171.77 *s*			
		21.03 *q*	AcCO		

[a] Assignments by HETCOR.
[b] Weak interactions in parentheses.

Table 2
^{1}H (300 MHz) and ^{13}C NMR (75 MHz) data for compound **2a** ($CDCl_3$)[a]

Position	δH	δC[a]	NOESY	COSY	HMBC
1		76.32 *s*			
2	4.13 *d* (7.5)	74.72 *d*	H-3 and/or H-5, H-6		1, 3,4, 7
3	5.80–5.83 *m*	73.98 *d*	H-2	H-2	1, 4,5, 3-CO
4	5.66 *dt* (10.3, 2.5)	124.89 *d*			
5	5.81 *dd* (10.3, 2.2)	132.25 *d*	H-2, 6	H-4	1, 4,5, 3-CO
6	4.46 *d* (2.2)	72.73 *d*	H-2, H-3 and/or H-5	H-5	4, 5
7a	4.77 *d* (12)	63.37 *t*	H-3 and/or H-5	H-7b	1, 2,6, ϕCO
7b	4.67 *d* (12)		H-2		
3-CO		166.58 *s*			
7-CO		167.67 *s*			
1′, 1′		129.47 *s*	H-2, 6,3′, 5′	H-3′, 5′	2′, 4′, 6′, ϕCO
2′, 6′2″, 6′	8.00 *dt* (8, 1.4)	129.75, 129.67*d*	H-2, 3,3′, 5′, 3″, 5″	H-3′, 5′, 3″, 5″	7′, 6′, 2,6, 4′, 4,3-CO, 7-CO
3′, 5′, 3″, 5″	7.36 *td* (8, 1.4)	128.39, 128.27 *d*			1′, 1, 3′, 3, 5, 3-CO, 7-CO
4′, 4″	7.49 *tt* (8, 1.4)	133.24, 133.13 *d*		H-3′, 5′, 3″, 5″	AcCO

[a] Assignments by HETCOR.

chemical shifts of C-1, C-2 and C-6 in **3a** exhibited the expected changes produced by acylation at C-6 and deacylation at C-7 while conversion to a diacetate **3b** and a triacetate **3c** mirrored the shifts observed in the conversion of **2a** to **2b** and **2c** (Tables 5 and 7). The ring coupling constants in the case of **3b** and **3c** indicate that the predominant if not exclusive conformations are C (R^1 = H, R^2, R^3 = Ac resp. R^1, R^2, R^3 = Ac with Ac on C-7) as also shown by strong cross peaks between H-3 and H-7 in the NOESY spectra.

The remaining substance was identical with ferrudiol based on the ^{1}H and ^{13}C NMR spectra (Table 5), mp and rotation for which structure **4** including the absolute configuration was derived twenty years ago on the basis of the ^{1}H NMR spectrum, formation of a tetra- and a pentabenzoate and CD measurements (Schulte et al. 1982a,b). The stereochemistry assigned to C-1 was based on the facile formation of a carbonate involving the hydroxyls on C-1 and C-2. Our own measurements, including the previously unrecorded ^{13}C NMR spectra, for ferrudiol and its new diacetate are listed in Table 6. Although interpretation of the NOESY spectra was difficult due to superposition of signals the existence of a cross peak between the H-3 and H-7 signals was evident, an observation which could only be explained by reversing the stereochemistry at C-1 as in formulas **5a** and **5b**, with conformation C (R^1, R^2 on C-2 = Ac, R^2 on C-6 = Bz) predominant. Moreover the chemical shifts of C-1, C-2, C-6 and C-7 were similar to those of **2a** and the shift changes on conversion of **5a** to **5b** closely parallel the shift changes which accompany the conversion of **2a** to **2c** as is evident from the compilation in Table 7; in fact the chemical shifts in the ^{13}C NMR spectra of **2c** and ferrudiol diacetate are very similar.

Structure **4** for ferrudiol was apparently based on the assumption that formation of a carbonate between the

Table 3
^{1}H (300 MHz) and ^{13}C NMR (75 MHz) data for compounds **2b** and **2c** ($CDCl_3$)[a]

2b 2c					
Position	δH (**2b**)	δC (**2b**)[a]	δH (**2c**)	δC (**2c**)[a]	NOESY
1		75.37 *s*		82.14 *s*	
2	5.67 *d* (8.8)	74.19 *d*	6.49 *d* (7.5)	70.14 *d*	
3	5.91 *ddd* (8.8, 5.8, 2.2)	71.28 *d*	5.90 *ddd* (7.5, 4.7, 2.4)	71.13 *d*	H-2,7a, b, 2́, 2, 6́, 6
4	6.00 *dt* (10.4, 2.2)	127.45 *d*	6.03 *dt* (10.5, 2.4)	126.76 *d*	
5	5.76 *dt* (10.4, 2.2)	128.39 *d*	6.03 *dt* (10.5, 2.4)	128.16 *d*	
6	5.70 *dd* (5.0, 2.4)	76.25 *d*	6.56 *dd* (5, 2.5)	68.88 *d*	
7a	4.70 *d* (12.3)	64.23 *t*	4.90 *d* (11.9)	60.97 *t*	H-2,3
7b	4.63 *d* (17.3)		4.71 *d* (11.9)		H-3
3-CO		165.96 *s*		165.91 s165.71 s	
7-CO		167.11 *s*			
1′,1″		129.38 *s*, 129.28 *s*		129.43 *s*, 129.29 *s*	
2′,6′,2″,6″	8.09 *d*, 8.07 *d* (8.2, 1.5)	129.79 *d*	8.00–8.07 *m*	129.79 *d*, 129.72 *d*	
3′,5′,3″,5″	7.42–7.49 *m*	128.59 *d*, 128.55 *d*	7.42–7.51 *m*	128.57 *d*, 128.29 *d*	
4′,4″	7.55–7.60 *m*	133.50 *d*, 133.46 *d*	7.55–7.62 *m*	128.57 *d*, 128.29 *d*	
2-Ac	1.90 *s* (3p)	20.61 *q*, 170.30*s*	2.01 *s* corresponds to 20.62 *q*		
6-Ac	2.08 *s* (3p)	20.92 *q*, 171.53 *s*	2.02 *s* corresponds to 21.98 *q*		
7-Ac			2.06 *s* corresponds to 20.79 *q*		

[a] Assignments by HETCOR and HMBC.

Table 4
^{1}H (300 MHz) and ^{13}C NMR (75 MHz) data for compound **3a** ($CDCl_3$)[a]

Position	δH	δC[a]	NOESY	COSY	HMBC
1		75.54 *s*			
2	4.19 *d* (8)	76.62 *d*	H-3	H-3	C-7
3	5.78 *m*	73.98 *d*			C−1C−2
4	5.82 *dt* (10, 5, 2.4)	127.18 *d*		H-5	
5	5.72 *dd* (10.5, 2.4)	128.47 *d*		H-4	C-1, 3,6
6	5.82 *m*	75.64 *d*			C-2.7
7a	4.17 *d* (12)	62.80 *t*		H-7	C-1, 2,6
7b	4.09 *d* (12)				C-1, 2,6
3-CO		166.17 *s*			
6-CO		166.61 *s*			
1′		129.49 *s*			
2′, 6′	8.02 *dd* (8, 1.4)	129.78 *s*	H-3′, 5′, 3″, 5″	H-3′, 5′, 3″, 5″	7-CO, C-2′, 6′, C-4′
3′, 5′	7.39 *tt* (8, 1.4)	128.44 *d*		H-3′, 5′, 3″, 5″	C-1′, C-1″, C-3′, 5′, C-3″, 5″
4′	7.53 *td* (8, 1.4)	133.28 *d*			
1″		129.36 *s*			
2″, 6″	8.00 *dd* (8)	129.72 *d*	H-3′, 5′, 3″, 5″, H-3	H-3′, 5′, 3″, 5″	3-CO, C-2″, 6″, C-4″
3″, 5″	7.39 *tt* (8, 1.4)	128.34 *d*			C-1′, C-1″, C-3′, 5′, C-3″, 5″
4″	7.53 *td* (8, 1.4)	133.39 *d*			

[a] Assignments by HETCOR.

hydroxyls at C-1 and C-2 of the cyclohexene ring required a *cis* relationship between the two hydroxyls. However, it has been relatively easy to construct a Dreiding model of the carbonate from **5a**. In the model the cyclohexene ring is a half-chair with the substituents at C-3 and C-6 quasi-equatorial, C-7 axial and the carbonate ring somewhat distorted and strained. The model of a carbonate is easier to form from the old structure, the carbonate ring being essentially planar, but the cyclohexene ring is a somewhat distorted boat with C-7 and the ester function on C-6 both axial and opposed and the ester on C-3 remaining equatorial.

3. Experimental

3.1. General experimental procedures

^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker AMC instrument operating at 300.13 and 75.47 MHz, respectively, EI mass spectra were measured on a Hitachi Perkin-Elmer RMU-6 M instrument. HRMS samples were run using +FAB ionization with Xe gas at 6 kV on a KRATUS CONCEPT III, 2 sector mass spectrometer. The accelerating voltage was 8 kV. Rotations were obtained on a

Polarotronic Universal Schmidt and Haensch polarimeter. Si gel for column chromatography was Si gel 60 (0.2–0.5 mm) Merck, for analytical and preparative TLS Si gel G-60 GF 254 Merck.

3.2. Plant material

Aerial/parts of *Ellipeiosis cherrevensis* (Pierre et Finet et Gagn.) R. E. Fries were collected in Sakon-Nakorn

Table 5
^{1}H (300 MHz) and ^{13}C NMR (75 MHz) data for compounds **3b** and **3c**

	3b		**3c**		
Position	δH	δC[a]	δH	δC[a]	NOESY
1		75.10 *s*		81.13 *s*	
2	5.69 *d* (8.5)	73.74 *d*	6.47 *d* (6.5)	69.70 *d*	H-7a,H-7b
3	5.78 *ddd* (8.5, 4.5, 2.2)	70.84 *d*	5.79 *ddd* (6.5, 4.5, 1.8)	70.71 *d*	H-2,H-6,H-7a,H-7b,2.01,2.02 *s*
4	6.02 *ddt* (10.5, 2.2)	127.64 *d*	6.04 *ddt* (10.3, 3, 1.8)	126.83 *d*	
5	5.78 *dt* (10.5, 2.2)	128.10 *d*	5.95 *ddd* (10.3, 1.8)	127.75 *d*	
6	5.88 *dd* (4.5, 2.2)	76.27 *d*	6.70 *dd* (3.2, 2)	68.50 *d*	
7a	4.60 *d* (11.8)	63.16 *t*	4.91 *d* (11.8)	60.42 *t*	H-2́,6́,2,6
7b	4.40 *d* (11.8)		4.40 *d* (11.8)		H-2́,6́,2,6
3-CO		165.91 *s*		165.86 *s*	
6-CO		166.92 *s*		165.71 *s*	
1′,1″		129.03 *s*, 129.22 *s*		129.31 *s*, 129.28 *s*	
2′,6′,2″,6″	8.07 *dd*, 8.03 *dd* (8.4, 1.1)	129.19 *d*, 129.80 *d*	8.01–8.07 *m*	129.80 *d*, 129.72 *d*	
3′,5′,3″,5″	7.43–7.51 *m*	128.59 *d*, 128.56 *d*	7.43–7.501 *m*	128.56 *d*, 128.52 *d*	
4′,4″	7.57–7.65 *m*	133.77 *d*, 133.49 *d*	7.57–7.61 *m*	135.53 *d*, 133.45 *d*	
2-OAc	2.09 *s*	20.79 *q*, 170.17 *s*	2.11 *s*	20.72 *q*, 169.23 *s*	
7-OAc	1.93 *s*	20.67 *q*, 171.19 *s*	2.02 *s*	20.79 *q*, 170.00 *s*	
1-OAc			2.01 *s*	22.03 *q*, 169.68 *s*	

[a] Assignments by HETCOR and HMBC.

Table 6
^{1}H (300 MHz) and ^{13}C NMR (75 MHz) data for compounds **5a** and **5b**

	5a			**5b**		
Position	δH	δC[a]	COSY	δH	δC[a]	NOESY
1		76.04 *s*			82.10 *s*	
2	4.31 *d* (8.5)	75.43 *d*	H-6	6.59 *d* (7)	70.08 *d*	
3	5.82–5.85 *m*	76.77 *d*	H-2	5.93 *dt* (10.3, 2.4)	71.13 *d*	H-2, 7a, b,2, 6,2, 6,2, 6
4	6.01 *dt* (10.2, 1.6)	127.91 *d*	H-5, 6	6.09 *dt* (10.3, 2.4)	126.93 *d*	
5	5.88 *dt* (10.2, 1.6)	128.30 *d*		5.97 *dt* (10.3, 2.4)	128.14 *d*	H-6
6	5.82–5.85 *m*	72.80 *d*		6.86 *dd* (5, 2.4)	69.10 *d*	
7a	4.83 *d* (12)	62.68 *t*	H-7b	5.06 *d* (11.8)	61.23 *t*	H-3
7b	4.75 *d* (12)			4.77 *d* (11.8)		H-3
3-CO		167.28 *s*			165.83 *s*	
6-CO		166.52 *s*			165.42 *s*	
7-CO		166.59 *s*			165.91 *s*	
1′		129.51 *s*			129.35 *d*	
2′, 6′	7.99 *dd* (8.5, 1.5)	129.85 *d*		7.99–8.05 *m*	129.82 *d*	
3′, 5′	7.47 *tt* (8, 1.5)	128.46 *d*	H-2′, H′, 6′, 2‴, 3‴, 5‴, 6‴	7.38–7.53 *m*	128.51 *d*	
4	7.60 *tt* (7.5, 1.5)	133.43 *d*	H-3′, 5′	7.53–7.61 *m*	133.49 *d*	
1″		129.34 *s*			129.32 *s*	
2″, 6″	8.10 *dd* (8.5, 1.5)	129.95 *d*	H-3″, 5″	7.99–8.05 *m*	129.73 *d*	
3″, 5″	7.34 *tt* (7.5, 1.5)	128.43 *d*		7.38–7.53 *m*	128.51 *d*	
4″	7.52 *tt* (7.5, 1.5)	133.13 *d*	H-3″, 5″, 3‴, 5‴	7.53–7.61 *m*	133.44 *d*	
1‴		128.88 *s*			129.16 *s*	
2‴, 6‴	7.91 *dd* (8.5, 1.5)	129.63 *d*	H-3‴, 5‴	7.99–8.05 *m*	129.73 *d*	
3‴, 5‴	7.32 *tt* (7.5, 1.5)	128.33 *d*		7.38–7.53 *m*	128.51 *d*	
4‴	7.47 *tt* (8, 1.5)	183.12 *d*		7.53–7.61 *m*	133.32 *d*	
1-OAc 2-OAc				{ 2.06 *s* { 2.03 *s*	{ 169.70, 22.07 *q* { 169.32, 20.72 *q*	

[a] Assignments by HETCOR and HMBC.

Province, Northeast Thailand, in August 1999. A voucher specimen CA-10-2542 was deposited in the herbarium of the Royal Forest Department, Bangkok, Thailand.

3.3. Extraction and isolation

Air dried whole aerial parts (400 g) were percolated by MeOH to exhaustion (3.5 l). Evaporation at reduced pressure furnished 35 g of crude extract which was dissolved in warm EtOH (700 ml) to which was added 750 ml of H_2O containing 27 mg of lead acetate and 8 ml of glacial acetic acid. The solution was kept in a dark chamber for 48 h and filtered, the filtrate was concentrated at reduced pressure to remove EtOH and extracted with $CHCl_3$ (4×300 ml). The combined $CHCl_3$ extracts were dried (Na_2SO_4) filtered and evaporated at reduced pressure to give a syrupy mass (4 g) which was applied to Si gel 60 (300 g) and eluted with petroleum ether–$CHCl_3$ and $CHCl_3$–Me_2O, 250 ml fractions being collected as follows: Frs. 1–40 (petrol–$CHCl_3$, 3:2), 41-80 (petrol–$CHCl_3$, 1:4) and 81–96 ($CHCl_3$–Me_2O, 9:1). Frs. 6–9 were combined and purified by TLC (Si gel, $CHCl_3$–petrol–EtOAc–HCO_2H, 8:1:1:0.1) to give ferrudiol (**5a**) (57 mg) and (32 mg) of a mixture. Frs 10–13 were combined and purified by TLC (Si gel, $CHCl_3$–petrol–EtOAc–HCO_2H, 8:1:1:0.1) to give more ferrudiol (42 mg) and 21 mg of the same mixture. Fr 41 was purified by TLC (Si gel, $CHCl_3$–Me_2O–HC_2OH, 8:2:0.1) to give **3a** (112 mg) and **2a** (38 mg). Fr 42 on TLC (Si gel, $CHCl_3$–MeOH–HCO_2H, 8:2:0.1) furnished more **3a** (41 mg), more **2a** (53 mg) and 53 mg of a mixture. Frs. 43 and 44 were combined and purified by TLC (Si gel, $CHCl_3$–Me_2O–HCO_2H, 8:2:0.1) to give zeylenol (**1a**, 186 mg) and 96 mg of the mixture from Fr. 42. Frs. 45–47 were combined and purified by TLC (Si gel, $CHCl_3$- Me_2O-HCO_2H, 8:2:0.1) to give more zeylenol (21 mg), 22 mg of the mixture from fr. 42, and **1b** (34 mg).

3.4. Zeylenol (*1a*)

White crystals, mp 137–140 °C ($CHCl_3$–petrol), $[\alpha]_b$ −113° ($CHCl_3$; c 1.35 g/100 ml) (lit Jolad et al., 1981, mp 144–145 °C, $[\alpha]_d$ −113°), + FAB MS (NBA): calc. for C_{21} $H_2O + H^+$: 385. Found: 385. The ^1H NMR spectrum corresponded to that reported in the literature (Pan and Yu, 1995b); the ^{13}C NMR spectrum corresponded to that reported earlier (Jolad et al., 1981); however, the values of δ C-2 and δ C-6 need to be interchanged as shown by HETCOR and HMBC.

3.5. Ellipeiopsol A (*1b*)

Yellowish gum, $[\alpha]_b$ +22.8° ($CHCl_3$, c = 1.27 g/100 ml); HRMS: +FAB 323.11305, $C_{16}H_{19}O_7$ requires 323.11308; ^1H NMR and ^{13}C NMR spectra in Table 1.

Table 7
Comparison of C-1, C-2, C-6 and C-7 frequencies ($CDCl_3$)

Compound	C-1	C-2	C-6	C-7
1a	75.79	70.62	68.79	66.53
1b	74.70	70.47	68.68	66.57
2a	76.32	74.72	72.73	63.37
2b	75.37	74.19	76.25	64.03
2c	82.14	70.14	68.88	60.97
3a	75.54	76.62	75.69	62.80
3b	75.10	73.74	76.27	63.16
3c	81.63	69.70	68.50	60.42
5a	76.04	75.43	72.80	62.68
5b	82.10	70.08	69.10	61.23

3.6. Ellipeiopsol B (*2a*)

Gum, $[\alpha]_b$ −139.7° ($CHCl_3$, c = 5.8 g/100 ml); HRMS +FAB 385.12877, $C_{21}H_{21}O_7$ requires 385.12873; ^1H NMR and ^{13}C NMR spectra in Table 2. Acetylation of 20 mg of **2a** with Ac_2O-pyridine overnight and work-up in the usual manner followed by purification of the crude product by TLC ($CHCl_3$–petrol–HCO_2H, 95:5: 0.1) afforded 11 mg of diacetate **2b** and 6 mg of triacetate **2c** as gums whose ^1H and ^{13}C NMR spectra are listed in Table 3; EI–MS of **2b**, *m/z* calc for $C_{25}H_{24}O9$, 468; found *m/z* (%) 468 (M^+, 12), 451 (7), 409 (32), 346 (55), 333 (40), 304 (16), 286 (93), 273 (11), 244 (85), 211 (6), 183 (10) 163 (30), 141 (11), 122 (12), 105 (100), 77 (27); EI–MS of **2c**, *m/z* calc. for $C_{27}H_{28}O_{10}$, 510; found m/z (%) 510 (M^+, 5), 466 (10), 389 (35), 348 (12), 286 (17), 244 (14), 226 (16), 164 (17), 122 (18), 105 (100), 77 (23).

3.7. Ellipeiopsol C (*3a*)

Gum, $[\alpha]_b$ −130° ($CHCl_3$, *c* = 1.10g/100 ml); HRMS +FAB 385.12868, $C_{21}H_{21}O_7$ requires 385.12873 ^1H NMR and ^{13}C NMR spectra in Table 4. Acetylation of 21 mg of **3a** with Ac_2O-pyridine overnight and work-up in the usual manner followed by purification of the crude product by TLC ($CHCl_3$–petrol–HCO_2H, 95:5: 0.1) afforded 10 mg of diacetate **3b** and 8 mg of triacetate **3c** as gums whose ^1H and ^{13}C NMR spectra are listed in Table 5; ; EI–MS of **3b**, *m/z* calc. for $C_{25}H_{24}O_9$, 468; found *m/z* (%) 468 (M^+, 6), 451 (8), 409 (5), 395 (8), 346 (5), 335 (4), 245 (20), 226 (7), 164 (10), 122 (12), 105 (100), 77 (30); EI–MS of **3c**, *m/z* calc. for $C_{27}H_{26}O_{10}$, 510 found *m/z* (%) 510 M^+, 12), 466 (12), 451 (7), 389 (10), 348 (20), 328 (12), 286 (8), 244 (5), 226 (77) 122 (6), 105 (100), 77 (21).

3.8. Ferrudiol (*5a*)

White crystals, mp 192–195°, ($CHCl_3$, petrol), $[\alpha]_b$ −156.9° ($CHCl_3$, 0.217 g/100 mg) −(lit Schulte et al., 1982, mp 191–192, [α]-141°) +FAB 489.15488, $C_{281}H_{25}O_8$

requires 489.15494, ^{1}H NMR and ^{13}C NMR spectra in Table 6. Acetylation of 25 mg with Ac_2O-pyridine overnight and work-up in the usual manner followed by purification of the crude product by TLC ($CHCl_3$–petrol-HCO_2H, 7525:0.1) afforded 19 mg of diacetate **5b** as a gum whose ^{1}H and ^{13}C NMR spectra are also listed in Table 6; ; EI–MS of **3b**, *m*/*z* calc. for $C_{32}H_{28}O_{10}$, 572; found 572 (M^+,7) 513 (12), 467 (10), 452 (7), 408 (5), 390 (7), 348 (15), 331 (15), 285 (21), 269 (17), 244 (16), 226 (32), 164 (21), 122 (35), 105 (100), 77 (30).

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