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neo-Clerodane diterpenoids from *Teucrium oliverianum* and structure revision of teucrolin E

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Abstract

The aerial parts of *Teucrium oliverianum* yielded two *neo*-clerodane diterpenoids, teucrolin F and G, together with the known teucrolin E. The previously proposed structure for teucrolin E was revised so that it contains a tetrahydrofuran ring instead of an oxetane ring. This was based on analysis of the NMR spectroscopic data of its diacetate, including its NOE spectra. In addition, the structural assignments of the new diterpenoids were based on ^{1}H and ^{13}C NMR spectroscopic studies, mainly 2D NMR experiments, including homonuclear and heteronuclear correlations.

Keywords: *Teucrium oliverianum*; Labiatae; Diterpenoids; *neo*-Clerodanes; Teucrolins E, F, G; 3β,6α-*O*-Diacetylteucrolin E; 2D NMR

1. Introduction

In previous communications (Al-Yahya et al., 1993, 1995), we described the structures of four C-3α-oxygenated *neo*-clerodane diterpenoids teucrolins A–D, together with the unusual C-10β-oxygenated diterpenoid teucrolin E. They were isolated from the aerial parts of *Teucrium oliverianum*, which is used in traditional Saudi medicine for the treatment of diabetes and is well known for its hypoglycemic activity (Al-Yahya, personal communication). Other investigators have reported on the isolation and structure elucidation of teucrolivins A–H (Bruno et al., 1991; De la Torre et al., 1991a,b) from the same source. However, the genus *Teucrium* is reputed for *neo*-clerodane and 19-*norneo*-clerodane diterpenoids (Piozzi, 1981; Piozzi et al., 1987), exhibiting various types of biological activities (Simmonds et al., 1989; Ulubelen et al., 2000).

In order to conclusively define the structure and stereochemistry of the minor diterpene teucrolin E (Al-Yahya et al., 1993, 1995), whose structure and partial stereochemistry (**1**) were solely based on comparing its NMR spectroscopic data with those of teucrolivin C (**2**), another collection from the same plant was reinvestigated. Besides isolating an additional supply of teucrolin E (**3**), two further *neo*-clerodane diterpene derivatives, namely teucrolins F (**4**) and G (**5**), were also obtained. The isolation and structure determination of the new isolates (**4** and **5**), and the structure revision of teucrolin E from **1** to **3**, are the subjects of this paper.

2. Results and discussion

The MeCN extract of *T. oliverianum* was subjected to silica gel flash-chromatography to give a number of fractions from which the diterpenes **3**–**5** were obtained (see Section 3). The isolation of additional amounts of teucrolin E (0.0026% yield), which was erroneously formulated as **1** (Al-Yahya et al., 1993, 1995), has now permitted the revision of its structure to **3**. Thus, on acetylation, teucrolin E afforded the corresponding 3β,6α-*O*-diacetylteucrolin E (**6**, $C_{26}H_{34}O_{10}$, δ 2.05, 2.0, each 3H, *s*), which eliminates structure **1** for teucrolin E. The ^{1}H and ^{13}C NMR spectral data (Tables 1 and 2) of **6** showed similarities to those of teusandrin F, isolated from *T. sandrasicum* (**7**) (De la Torre et al., 1997). The

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notable exceptions, though, are the absence of signals due to the C-4β,10β-oxetane ring and the C-9(12) lactone group, as well as the presence of C-3β acetoxy ($\delta_{C\text{-}3}$ 72.6, *d*), C-7 carbonyl ($\delta_{C\text{-}7}$ 207.5, *s*) and C-19 acetoxy ($\delta_{C\text{-}19}$ 61.8, *t*), groups. Hence, **6** displayed signals for a tertiary hydroxyl group at C-4 (ν_{max} 3400 cm^{-1}, $\delta_{C\text{-}4}$ 83.4, *s*), an oxymethylene group at C-18 (δ_H 3.86, 4.27; $\delta_{C\text{-}18}$ 70.0, *versus* δ_H 3.91, 4.06, $\delta_{C\text{-}18}$ 65.4 in **7**) (De la Torre et al., 1997) and a tertiary methyl group at C-9 (δ 0.89, 3H, *s*; δ_C 18.8, *q*). The lack of a downfield shift of the 18-CH_2O- protons in the ^1H NMR spectrum of 3-Ac (**6**) excluded structure **1** for teucrolin E, and suggested the presence of a tetrahydrofuran ring involving C-10 and C-18 positions in **3**.

Furthermore, the ^1H NMR spectrum of **6** showed the anticipated deshielding of both H-3 and H-6 to δ 5.06 (*ddd*, $J = 1.4$, 6.5, 9.1 Hz) and 5.69 (*s*), respectively, versus $\delta_{H\text{-}3}$ 3.97 (*br.dd*, $J = 5.6$, 9.2 Hz), $\delta_{H\text{-}6}$ 4.72 (*d*, $J = 1.4$ Hz) in **3**, which is hydroxylated at these positions. A 2D NMR ^1H-^1H COSY experiment showed long-range coupling between one of the oxymethylene protons at H-18A (δ 3.86, *dd*, $J = 1.4$, 8.8 Hz) and H-3α at δ 5.06 [in addition to its geminal coupling with the H-18B proton at δ 4.27 (*d*, $J = 8.8$ Hz)], that was further coupled to the methylene protons at δ 2.20 and 1.73 (H_2-2), thus establishing the system –O–CH_2–C(OH)–CH(OAc)–CH_2– in **6**.

The stereochemical assignment at C-4 was inferred from a 2D NMR ^1H–^1H NOESY experiment on **6**. It exhibited cross peaks between H-6, H-8 and H-18A protons (δ 5.69, 3.41 and 3.86, respectively), indicating that one H-18 proton is on the same side (β-face) of the ring as H-6 and H-8. In addition, correlation between the signals at δ 5.06 (H-3α) and 4.91 (H-19Bα) were also observed, as expected, in the NOESY spectrum. Thus, the NOESY cross peaks exhibited by H-18A and the long range coupling between H-18A and H-3α unambiguously established the β-axial configuration of C-18 in the *neo*-clerodane backbone of **6**. It is interesting to note that several *neo*-clerodane diterpenoids containing a tetrahydrofuran ring involving C-4, C-5, C-6 and C-18 or C-4, C-5, C-18 and C-19 have been isolated from *Teucrium* species (De la Torre et al., 1986; Savona et al., 1986; Simoes et al., 1989; Sexmero Cuadrado et al.,

Table 1
^1H NMR spectroscopic data and coupling constants for diterpenes **3**–**6**[a]

Proton	**3**[b]	**6**	**4**	**5**
	$CDCl_3$	CD_3OD	$(CD_3)_2CO$	(CD_3CN)
1	2.08–2.15 *m*	2.10 *m*	1.80 *m*[c]	1.94 *m*
	1.70–1.90 *m*	–	–	1.52 *m*
2	2.10 *m*	2.20 *m*	2.12 *m*	1.83 *m*
	1.88–1.98 *m*	1.73 *ddd* (3.2, 10.5, 13.0)	1.38 *m*	1.46 *m*
3	3.97 *brdd*	5.06 *ddd* (1.4, 6.5, 9.1)	3.98 *dd* (4.2, 11.3)	2.06 *m*[d]
	(5.6, 9.2)	–	–	0.95
6	4.72 *d* (1.4)	5.69 *s*	4.64 *br d* (9.0)	4.45 *dd* (1.0, 9.8)
7	–	–	3.53 *dd* (9.0, 10.7)	3.41 *t* (9.8, 9.8)
8	3.37 *q* (7.4)	3.41 *q* (6.7)	1.66 *qd* (6.6, 10.7)	1.59 *qd*[c]
10	–	–	1.82 *m*[c]	2.10 *rn*
11	2.34 *dd*	1.96 *ddt* (5.2, 12.5, 15.0)	1.60 *m*	2.22 *m*
	(5.8, 11.4)	1.54 *ddt* (4.0, 13.7, 15.0)	–	1.87 *m*[c]
	1.45–1.55 *m*			
12	2.90 *dd*	2.85 *dt* (5.2, 13.7)	2.34 *m*	4.72 *dd* (2.6, 8.3)
	(4.4, 13.6)	2.37 *dt* (4.0, 13.7)	–	–
14	6.26 *d* (1.0)	6.28 *d* (1.0)	6.38 *brs*	6.40 *m*
15	7.30 *d* (1.2)	7.36 *d* (1.6)	7.46 *t* (1.6)	7.4 *t* (1.7)
16	7.20 *d* (1.0)	7.26 *brs*	7.39 *brs*	7.39 *brt* (1.7)
17	1.08 *d* (7.4)	1.02 *d* (6.7)	1.02 *d* (6.6)	0.86 *d* (6.7)
18A	3.82 *dd*	3.86 *dd*	2.70 *d* (4.7)[e]	2.18 *d* (4.4)[e]
	(2.0, 9.4)	(1.4, 8.8)		
18B	4.37 *d* (9.4)	4.27 *d* (8.8)	2.94 *d* (4.7)[f]	2.98 *dd* (2.5[d], 4.4)[f]
19A	4.16 *d* (12.4)	4.10 *d* (12.2)	4.36 *brd* (12.0)	4.38 *brd* (12.1)
19B	4.35 *d* (12.4)	4.91 *d* (12.2)	4.69 *d* (12.0)	4.67 *d* (12.1)
20	0.74 *s*	0.89 *s*	0.80 *s*	0.70 *s*
OAc	2.04 *s*	2.05 *s*, 2.04 *s*, 2.00 *s*	2.05 *s*, 1.90 *s*	2.02 *s*, 1.91 *s*

[a] Spectra for **4**–**6** at 300 MHz; *J* values in Hz, in parentheses.
[b] Spectra for **3** at 200 MHz (Al-Yahya et al., 1993).
[c] Signals in the same vertical column are superimposed on each other, *J* unresolved.
[d] From H-18B and H-3α correlation observed in ^1H–^1H COSY spectrum.
[e] *exo*-Hydrogen with respect to ring B.
[f] *endo*-Hydrogen with respect to ring B.

1991; Rodriguez et al., 1994). However, teucrolin E (**3**) is the first to date be found as natural *neo*-clerodane diterpenoid with the unique C-4, C-5, C-10 and C-18 tetrahydrofuran ring.

During the course of isolation of **3**, teucrolin F (**4**) and G (**5**) were also obtained in 0.0013% and 0.002% yields, respectively. Both were analysed by CIMS for $C_{24}H_{34}O_8$; each contained two hydroxyl and two acetoxy groups (ν_{max} 3390, 1745, 1735 cm^{-1} for **4** and ν_{max} 3400, 1740, 1730 cm^{-1} for **5**) and a furan ring. Their furano *neo*-clerodane carbon skeletons were suggested based on their ^1H and ^{13}C NMR spectral data (Tables 1 and 2; Bruno et al., 1991; De la Torre et al., 1991a; Al-Yahya et al., 1993; Sattar et al., 1995). The ^1H NMR spectrum of teucrolin F (**4**) showed oxygenated protons at δ 3.98 (*dd, J* = 4.2, 11.3 Hz, $\delta_{C\text{-}3}$ 66.2), 3.53 (*dd, J* = 9.0 and 10.7 Hz; $\delta_{C\text{-}7}$ 71.6) and δ 4.64 (*d*, *J* = 9.0 Hz, $\delta_{C\text{-}6}$ 77.9), due to the presence of the C-3β- and C-7β-hydroxyl, and the C-6α-acetoxy groups, respectively. A 2D NMR COSY experiment showed that the signal at δ 3.53 (H-7) was coupled to the acetoxy proton at δ 4.64 (H-6) and a methine proton at δ 1.66 (H-8). The latter proton also showed coupling to a secondary methyl group at δ 1.02 (H-17), thus confirming the presence of the –CH(OAc)–CH(OH)–CH(Me)– system in **4**. In addition, the COSY spectrum suggested the presence of the system –CH(OH)–CH_2–CH_2–CH– that was confirmed by a 2D NMR ^1H-^{13}C HETCOR experiment.

The relative stereochemistry of teucrolin F, as depicted in **4**, was based on NOESY spectrum, coupling constant values and biogenetic correlation with teucrolivin D (**8**), isolated from *T. olivarianum* (De la Torre et al., 1991a). The NOESY analysis clearly showed that H-6 (δ 4.64) was correlated with H-8 (δ 1.66), suggesting that they are located on the same side (β-face) of the molecule. Comparison of the chemical shift and coupling constant values of H-6β and H-7α protons with those for teucrolivin D (**8**) (De la Torre et al., 1991a), clearly suggested that **4** contains the second -OAc and -OH substituents at C-6α and C-7β equatorial positions, respectively. Based on foregoing data this compound was formulated as **4**, and has been named teucrolin F.

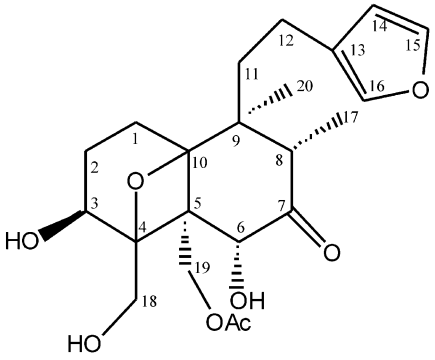
Comparison of the ^1H and ^{13}C NMR spectral data of teucrolin G (**5**, Tables 1 and 2) with those of its isomer **4** led to the conclusion that **5** contained the furano *neo*-clerodane skeletal backbone with the additional presence of a hydroxyl group at C-12 (δ 4.72, *dd, J* = 2.6, 8.3 Hz, δ_C 63.0), instead of the C-3 hydroxyl group as in **4**. The COSY experiment demonstrated the systems–CH(OAc)–CH(OH)–CH(Me)– for the base skeleton and –CH_2–CH(OH)– for the side chain of **5**, and was confirmed by a HETCOR experiment. In addition, the long-range COSY spectrum revealed correlation between H-6 (δ 4.45) and H-19B (δ 4.67), H-11 (δ 2.22) and Me-20 (δ 0.70), and C-19-OAc (δ 2.02) and H-19A (δ 4.38)/H-19B (δ 4.67). The ^{13}C NMR spectrum revealed the anticipated deshielding of C-11 and C-13 to δ_C 46.2 and 132.6, respectively (versus $\delta_{C\text{-}11}$ 39.4 and $\delta_{C\text{-}13}$ 126.1 for **4**) due to the presence of the C-12-hydroxyl group, and agrees with those previously reported for teucrolin B (**9**; $\delta_{C\text{-}11}$ 45.02 and $\delta_{C\text{-}13}$ 130.9), a related C-12 hydroxylated diterpenoid (Al-Yahya et al., 1993). Furthermore, the ^{13}C NMR spectroscopic data for C-1–C-3 and C-18 (δ_C 22.3, 25.3, 33.5 and 49.1, respectively) were in close agreement with those reported for 6,19-diacetylteumassilin (**10**) ($\delta_{C\text{-}1}$ 21.5, $\delta_{C\text{-}2}$ 24.8, $\delta_{C\text{-}3}$ 32.8 and $\delta_{C\text{-}18}$ 48.5) and its analogs (Savona et al., 1984). The strong deshielding of C-18 in **5** (δ_C 49.1) with respect to **4** (δ_C 43.1) is a consequence of the absence of C-3β hydroxyl group in **5** and thus the absence of a shielding γ-gauche effect which is present in **4**.

A NOESY spectrum of **5** revealed similar stereochemical (in *relative*) correlation between H-6 and H-8 to those observed for **4**. Since no NOESY correlation was observed between H-6 and H-7 or H-7 and H-8, while H-6 (δ 4.45) was clearly correlated with H-18B (δ 2.98), hence compound **5** should contain a C-7β-(hydroxyl) substituent. Furthermore, a similar study of the coupling constant values of **5** was in agreement with those observed for **4** and **8**, suggesting the -OAc and -OH

Table 2
^{13}C NMR spectral data for diterpenes **3**–**6**[a]

Carbon	**3**[b]	**6**	**4**	**5**
	$CDCl_3$	CD_3OD	$(CD_3)_2CO$	CD_3CN
1	27.3 (*t*)[c]	28.2 (*t*)	20.7 (*t*)	22.3 (*t*)
2	25.8 (*t*)	25.4 (*t*)	33.6 (*t*)	25.3 (*t*)
3	68.7 (*d*)	72.6 (*d*)	66.2 (*d*)	33.5 (*t*)
4	84.1(*s*)	83.4 (*s*)	68.5 (*s*)	66.1(*s*)
5	58.2 (*s*)	60.1(*s*)	46.6 (*s*)	46.8 (*s*)
6	75.0 (*d*)	76.5 (*d*)	77.9 (*d*)	78.0 (*d*)
7	210.9 (*s*)	207.5 (*s*)	71.6 (*d*)	71.9 (*d*)
8	43.8 (*d*)	45.3 (*d*)	42.3 (*d*)	42.7 (*d*)
9	48.3 (*s*)	48.0 (*s*)	39.9 (*s*)	40.7 (*s*)
10	90.1(*s*)	92.0 (*s*)	47.6 (d)	48.6(*d*)
11	38.7 (*t*)	40.5 (*t*)	39.4 (*t*)	46.2 (*t*)
12	21.1 (*t*)	22.2 (*t*)	18.4 (*t*)	63.0 (*d*)
13	125.3 (*s*)	127.2 (*s*)	126.1 (*s*)	132.6 (*s*)
14	110.6 (*d*)	111.8 (*d*)	111.8 (*d*)	109.7(*d*)
15	142.7 (*d*)	143.9 (*d*)	143.7 (*d*)	144.3 (*d*)
16	138.2 (*d*)	139.6 (*d*)	139.6 (*d*)	139.5 (*d*)
17	7.7 (*q*)	8.2 (*q*)	11.0 (*q*)	11.4 (*q*)
18	68.6 (*t*)	70.0 (*t*)	43.1 (*t*)	49.1(*t*)
19	61.7 (*t*)	61.8 (*t*)	63.6 (*t*)	63.6 (*t*)
20	18.6 (*q*)	18.8 (*q*)	18.7 (*q*)	18.8 (*q*)
OAc	169.7(*s*)	172.5, 171.6,	170.6, 169.9	171.5,170.8
	20.8(*q*)	171.5 (3x*s*)	(2x*s*)	(2x*s*)
		21.0, 20.8	21.3, 21.1	21.6, 21.4
		20.8 (3x*q*)	(2x*q*)	(2x*q*)

[a] Spectra for **4**–**6** recorded at 75 MHz.
[b] Spectra for **3** at 50 MHz (Al-Yahya et al., 1993).
[c] Multiplicities of the carbon signals were determined by APT/DEPTGL experiments. Assignments for **4**–**6** were aided by 2D NMR COSY and HETCOR experiments.



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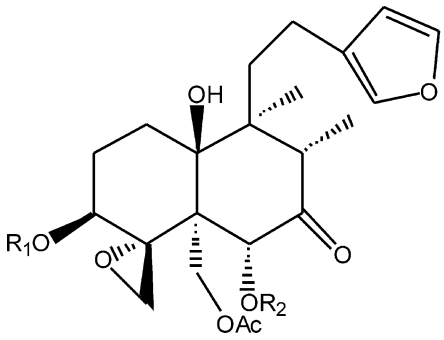

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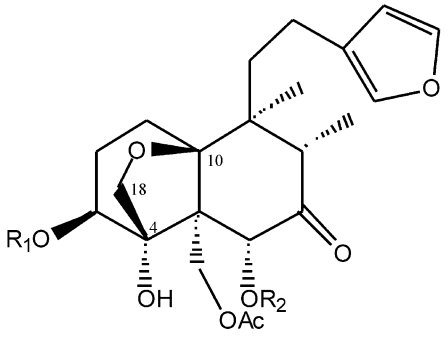
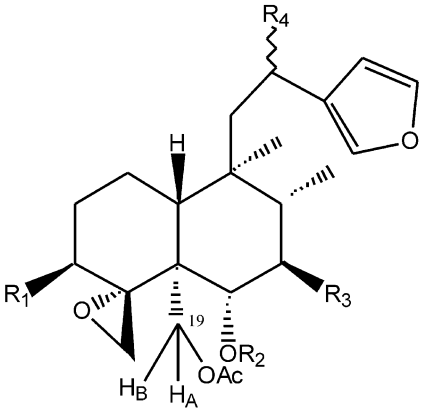
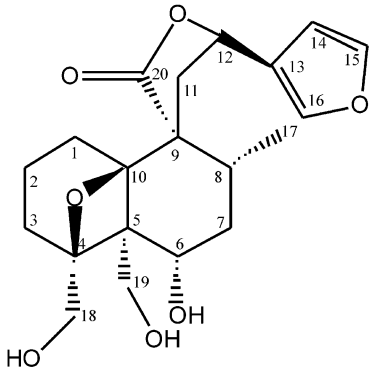


	R_1	R_2
3	H	H
6	Ac	Ac



	R_1	R_2	R_3	R_4
4	OH	Ac	OH	H
5	H	Ac	OH	OH
8	OAc	H	OAc	H
10	H	Ac	H	OH



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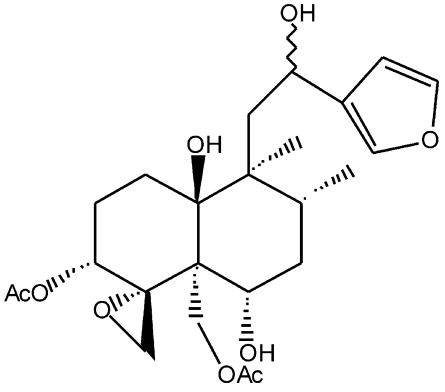

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groups at C-6α and C-7β- equatorial positions, respectively. Based on the foregoing data, structure **5** has been formulated as shown and named teucrolin G. Finally, teucrolin F (**4**) and G (**5**) appear to be structural analogs of the previously reported teucrolivin D (**8**) (De la Torre et al., 1991a), isolated from *T. oliverianum* of Saudi

Arabian origin, suggesting that they are derived from a common biogenetic precursor.

3. Experimental

3.1. General

Mp uncorr.; NMR: were aquired on a Varian VXR-300 or XL-300 instruments at 300 (^{1}H) and 75 MHz (^{13}C) using TMS as int. standard; Standard Varian/Brüker pulse programs were used for APT, DEPTGL, 2D NMR COSY, HETCOR and NOESY (for **3**) spectra; The 2D NMR long-range COSY and NOESY spectra (for **4** and **5**) were recorded on a Bruker Avance DRX-500 spectrometer; CIMS: were obtained by direct injection using a Finnigan 3300 MS, using methane as ionizing gas; Optical rotation measurements were taken on a Perkin-Elmer 241 MC polarimeter at 27 °C; TLC: silica gel 60 F254 plates; solvent: (a) 30%Me_2CO–$CHCl_3$ (b) Et_2O–CH_2Cl_2–MeOH (1:1:0.5); CC: flash-silica gel G (Merck, 40 μm); Centrifugal preparative TLC (CPTLC, using Chromatotron®, Harrison Research Inc. Model 7924): 1 or 4 mm silica gel P_{254} disks, at a N_2 flow rate of 3ml/min. The isolated compounds were visualized by observing under UV at 254 nm, followed by spraying using 1% vanillin-H_2SO_4 spray reagent and heated to 100 °C for 3 min.

3.2. Plant material

The aerial parts of *T. oliverianum* (Ging. ex Benth.) R.Br. (Labiatae) (Collenette, 1985; Migahid, 1989) were collected in Gassim, Saudi Arabia, in June 1993. A voucher specimen was kept at the herbarium of the Medicinal, Aromatic and Poisonous Plants Research Center (MAPPRC), College of Pharmacy, King Saud University, Riyadh, Saudi Arabia.

3.3. Extraction and isolation

The dried ground aerial parts (4 kg) were extracted by percolation with MeCN at room temp. and the extract was dried in vacuo (yield 125 g). The crude MeCN extract (100 g) was subjected to flash-CC over silica gel (5 kg) and eluted with petroleum ether (60–80 °C)–EtOAc (1:1) to afford 2 frs., as pale yellow solids, namely, fr. A (1.5 g) and fr. B (2.0 g). Fr. A (1.2 g) was subjected to additional chromatography (CPTLC, 4 mm silica gel P_{254} disk, solvent: 6% Me_2CO-$CHCl_3$) to yield **4** [80 mg, R_f 0.23 and 0.57, solvents (a) and (b), respectively], followed by **5** (50 mg, R_f 0.23 and 0.45). Fr. B (1.5 g), on the other hand, was purified by re-chromatography (CPTLC, 4 mm silica gel P_{254} disk) solvent: EtO_2–CH_2Cl_2–MeOH (2:8:0.5) to give teucrolin E (**3**; 100 mg, R_f 0.34, solvent B), followed by teucrolivin C (**2**, 500 mg, R_f 0.31, solvent B).

3.4. Teucrolin E (3β,4α,6α-trihydroxy-10β,18;15,16-diepoxy-7-oxo-19-acetoxy-neo-cleroda-13(16),14-diene) (*3*)

Colourless amorphous solid, mp 80–82°; $[\alpha]_D$ −37° (*c* 0.05, C_6H_6); Lit. (Al-Yahya et al., 1993) mp 78–79° and $[\alpha]_D$ −35.4° (C_6H_6). The identity of **3** was confirmed by direct comparison with an authentic sample of teucrolin E.

3.5. Acetylation of teucrolin E (*3*)

Compound **3** (75 mg) was dissolved in pyridine and treated with Ac_2O at room temp. for 24 h. Regular work-up gave crude **6** (70 mg), that was purified by chromatography (CPTLC, 1 mm silica gel P_{254} disk, solvent: Me_2CO–CH_2Cl_2, 0.2:9.8) to give 3β,6α-*O*-diacetylteucrolin E (3β,6α,19-triacetoxy-10β,18;15,16-diepoxy-4α-hydroxy-7-oxo-*neo*-cleroda-13(16),14-diene) (**6**) as gum (65 mg, R_f 0.62, solvent: 30% Me_2CO-$CHCl_3$); $[\alpha]_D$ −20.2° (*c* 0.03, C_6H_6); UV λ_{Max}^{MeOH} nm: 210 (log ε 4.35) and 270 br (log ε 2.83); IR ν_{Max}^{KBr} cm^{-1}: 3450 (OH), 1745, 1740–1735 br (3×OAc), 1720 (CO), 1500; ^{1}H and ^{13}C NMR: see Tables 1 and 2, respectively; CIMS *m*/*z* (rel. int.): 507 $[MH]^+[C_{26}H_{34}O_{10}.H]^+$ (30).

3.6. Teucrolin F (3β,7β-dihydroxy-4α,18;15,16-diepoxy-6α,19-diacetoxy-neo-cleroda-13(16), 14-diene) (*4*)

Colourless amorphous solid from Et_2O, mp 82–84°; $[\alpha]_D$ +13.2° (*c* 0.35, C_6H_6); UV λ_{Max}^{MeOH} nm: 210 (log ε 4.10) and 260 (log ε 2.38); IR ν_{Max}^{KBr} cm^{-1}: 3350 (OH), 1745, br (2×OAc), 1380, 1240, 1050; ^{1}H and ^{13}C NMR: see Tables 1 and 2, respectively; CIMS *m*/*z* (rel. int.): 451$[MH]^+$ $[C_{24}H_{34}O_8.H]^+$ (25).

3.7. Teucrolin G (7β,12-dihydroxy-4α,18;15,16-diepoxy-6α,19-diacetoxy-neo-cleroda-13(16), 14-diene) (*5*)

Pale yellow amorphous solid form Me_2CO–$CHCl_3$, mp 90–91°; $[\alpha]_D$ −18.4° (*c* 0.1, C_6H_6); UV λ_{Max}^{MeOH} nm: 210 (log ε 4.40); IR ν_{Max}^{KBr} cm^{-1}: 3400 (OH),1740, 1730 br (2xOAc); ^{1}H and ^{13}C NMR: see Tables 1 and 2, respectively; CIMS *m*/*z* (rel. int.): 451 $[MH]^+[C_{24}H_{34}O_8.H]^+$ (25).

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