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SIX DITERPENES FROM *VELLOZIA COMPACTA*

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Key Word Index—*Vellozia compacta*; Velloziaceae; Monocotyledoneae; pimarane-type diterpenes; structure elucidation.

Abstract—*Vellozia compacta* contains six new diterpenes of the pimarane type. Their structures were deduced on the basis of spectral data and chemical modification.

INTRODUCTION

The Velloziaceae constitute one of the most interesting plant families occurring in South America and Africa. The family contains *ca* 250 species of perennial herbs and shrubs, of which the genus *Vellozia* Vand. contains *ca* 140 species [1]. These plants are found in rocky regions on dry soil. They are ligneous, rooted superficially to the soil and they grow very slowly. In spite of their apparent fragility they attain a surprising longevity. This may be partly due to the terpenes which are present in large quantities in these plants and which might act as chemical defence against predators [2].

As part of our programme on systematic phytochemical investigation of Brazilian Velloziaceae, we wish to report on the study of *Vellozia compacta* Martius ex Schultes, a perennial species widely distributed in the State of Minas Gerais, Brazil.

RESULTS AND DISCUSSION

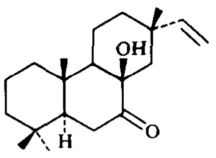
The hexane extract of roots, stem and leaf sheaths of *V. compacta* yielded a series of new diterpenes of the pimarane type besides compactone (**1**) and one diterpene with a cleisthantane skeleton (**2**). Substances **1** and **2** were discussed in our previous works [3, 4]. Characterization of the new pimarane type substances (**3**–**8**) is reported in this paper.

In accordance with their substitution pattern, the compounds listed can be divided into three groups.

Group I

The spectral data of compactol (**3**) suggested two hydroxyl, one vinyl and four tertiary methyl groups. This information, together with the molecular formula, $C_{20}H_{34}O_2$, obtained from the high resolution mass spectrum suggested that **3** could be a diterpenoid of the pimarane type, similar to those found in this family during our previous studies [3].

A carbinol methine signal at δ 3.24 (1H, *dd*, $J = 9$ and 5 Hz) accounted for a secondary hydroxyl group. The multiplicity of the signal of the C$\underline{H}$OH proton demonstrates that it is flanked by two hydrogens and, from its coupling constants, an axial orientation could be assigned to it. Consequently, the hydroxyl group is equatorial.



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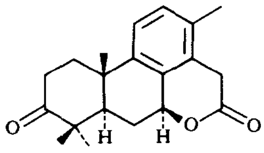

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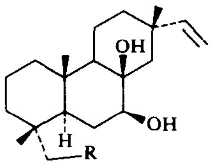
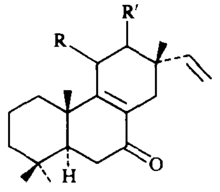
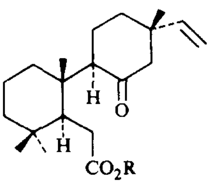


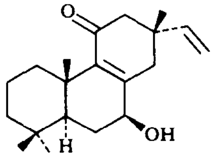
3 R = H
4 R = OH



5 R = H, H; R′ = β-OH
6 R = β-OH; R′ = H, H
7 R = O; R′ = H, H
8 R = O; R′ = β-OH
14 R = H, H; R′ = β-OAc
15 R = O; R′ = β-OAc



9 R = H
10 R = Me



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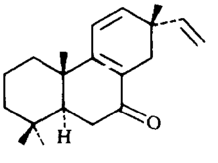

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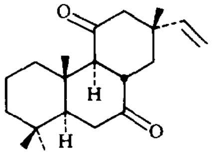

13

Oxidation of compound **3** with Jones' reagent afforded **9**. The IR spectrum of this compound showed a broad absorption in the region 3420–2950 cm^{-1} and a carbonyl band at 1730 cm^{-1}, strongly suggesting the presence of a carboxyl group. Chemical confirmation of this assumption was obtained by methylation (CH_2N_2) leading to **10**, which showed, in the IR, absorptions for two carbonyl groups (1740 and 1712 cm^{-1}). The mass spectrum of **10** presented the molecular ion at *m/z* 334 and an intense peak at *m/z* 138 resulting from McLafferty rearrangement involving the keto group and probably the hydrogen at C-5.

Similar results were obtained when **3** was oxidized by either PCC or PCD [5].

A confirmation of structure **3** by oxidation into compactone (**1**) failed. Reduction of **1** with sodium borohydride in methanol yielded an epimeric mixture of alcohols (2:1) in which compactol (**3**) was the one major isolated.

Compactotriol (**4**) was obtained as colourless prisms, and shown to have the formula $C_{20}H_{34}O_2$. The IR spectrum showed a broad peak at 3350 cm^{-1} (OH), it also exhibited a vinyl band at 905 cm^{-1}. The ^{1}H NMR spectrum in pyridine-*d*$_5$ was very similar to that of compactol (**3**) except for the presence of a pair of doublets centred at δ 3.10 (1H, $J = 11$ Hz) and 3.44 (1H, $J = 11$ Hz), due to the CH_2OH of C-18.

The ^{13}C NMR spectrum of **4** confirmed its structure with the carbon resonances being in agreement with a 7β,8β-dihydroxypimarane possessing a hydroxymethyl group at the C-18 equatorial position. This was deduced from the chemical shifts of Me-19 and C-5 (δ 18.2 and 46.0, respectively [6]).

Group II

The unsaturated compounds of this group comprise two α,β-unsaturated pimarane ketones. The molecular formula of 12β-hydroxy-7-oxopimar-8(9),15-dien (**5**), $C_{20}H_{30}O_2$, was determined by high resolution mass spectrometry. The IR spectrum revealed the presence of a conjugated ketone (1645 cm^{-1}), hydroxyl (3480 cm^{-1}) and vinyl (3080 and 910 cm^{-1}) groups. The UV confirmed the α,β-unsaturated carbonyl group [$\lambda_{\max}^{\text{EtOH}}$ 252 nm (log ε 4.15)].

The ^{1}H NMR spectrum, in deuterochloroform showed signals for four tertiary methyl groups (δ 0.90, 0.95, 0.99 and 1.14), one tertiary vinyl [5.05 (1H, *dd*, $J = 18$ and 1.5 Hz), 5.09 (1H, *dd*, $J = 10$ and 1.5 Hz) and 5.72 (1H, *dd*, $J = 18$ and 10 Hz)] group and one carbinolic proton δ 3.66 (1H, *t*, $J = 6$ Hz). The multiplicity of the carbinolic proton signal and the magnitude of its coupling constants suggested that the hydroxyl group is pseudo-equatorial. The stereochemistry of the hydroxyl at C-12 was confirmed by the high field position of the methyl group at C-17 (δ 19.8). The shielding was attributed to the strong γ-gauche effect of the hydroxyl group (Table 1) [7].

The UV, IR and ^{1}H NMR spectra of 11β-hydroxy-7-oxopimar-8(9),15-dien (**6**) were similar to those of **5**. A carbinol methine signal at δ 4.60 indicated a secondary hydroxyl group. The low yield position of the carbinolic proton of **6** suggested that the C$\underline{\text{H}}$OH proton might be allylic [8]. The interrelation between the secondary hydroxyl group and ethylenic linkage was derived by oxidation of **6** with PCC. The product, 7,11-dioxopimar-8(9),15-diene (**7**), exhibited, in the UV, an absorption at $\lambda_{\max}^{\text{EtOH}}$ 264 nm (log ε 3.93) for an enedione [9].

The stereochemistry of the hydroxyl group at C-11 was deduced from the ^{1}H NMR spectrum of **6** in deuteropyridine. The methyl group at C-20 suffered a downfield shift of δ 0.23 on changing from deuterochloroform to pyridine solution, which establishes its *syndiaxial* relationship with the hydroxyl group [10]. The A/B *trans* junction was determined by the positive Cotton effect for the n–π^* transition in the CD spectrum. (0.334 mg/ml in dioxane $[\theta] = +7.830$ at 326 nm).

Reduction of **7** (structure elucidation, see below) with sodium borohydride in methanol yielded the keto alcohol,

Table 1. ^{13}C NMR data for compounds **1** and **3**–**8** (25.2 MHz, $CDCl_3$, **1** and **4** C_5D_5N, TMS as int. standard)

C No.	**1**	**3**	**4**	**5**	**6**	**7**	**8**
1	39.8 *t*	39.4 *t*	39.6 *t*	35.6 *t*	35.3 *t*	35.2 *t*	35.4 *t*
2	18.6 *t*	18.4 *t*	18.4 *t*	18.3 *t*	18.5 *t*	18.5 *t*	18.4 *t*
3	42.0 *t*	41.9 *t*	35.9 *t*	40.1 *t*	41.0 *t*	40.8 *t*	40.8 *t*
4	33.8 *s*	33.1 *s*	37.9 *s*	32.9 *s*	33.2 *s*	32.8 *s*	33.0 *s*
5	56.2 *d*	53.1 *d*	46.0 *d*	49.9 *d*	51.0 *d*	49.7 *d*	49.6 *d*
6	35.3 *t*	27.2 *t*	27.3 *t*	35.1 *t*	35.0 *t*	35.0 *t*	34.7 *t*
7	190.9 *s*	78.2 *d*	77.7 *d*	199.8 *s*	201.6 *s*	200.4 *s*	200.6 *s*
8	76.5 *s*	74.1 *s*	74.0 *s*	128.0 *s*	130.2 *s*	141.5 *s*	141.3 *s*
9	59.1 *d*	55.7 *d*	56.0 *d*	163.3 *s*	163.4 *s*	154.9 *s*	153.2 *s*
10	37.7 *s*	36.9 *s*	37.0 *s*	39.3 *s*	40.1 *s*	39.0 *s*	38.9 *s*
11	17.1 *t*	16.8 *t*	17.4 *t*	30.9 *t*	67.1 *d*	201.6 *s*	202.0 *s*
12	38.3 *t*	37.8 *t*	38.6 *t*	70.1 *d*	44.8 *t*	50.5 *t*	79.3 *d*
13	36.7 *s*	36.0 *s*	36.7 *s*	39.3 *s*	35.3 *s*	37.8 *s*	46.0 *s*
14	43.0 *t*	47.1 *t*	47.7 *t*	30.7 *t*	34.1 *t*	34.8 *t*	37.4 *t*
15	151.7 *d*	151.2 *d*	152.3 *d*	144.0 *d*	144.5 *d*	144.5 *d*	143.7 *d*
16	108.7 *t*	108.5 *t*	108.3 *t*	112.9 *t*	111.6 *t*	112.3 *t*	113.3 *t*
17	24.9 *q*	24.3 *q*	24.7 *q*	19.8 *q*	28.1 *q*	26.4 *q*	18.2 *q*
18	33.0 *q*	33.4 *q*	71.1 *t*	32.2 *q*	32.8 *q*	32.8 *q*	32.6 *q*
19	21.3 *q*	21.6 *q*	18.2 *q*	21.1 *q*	21.6 *q*	21.2 *q*	21.1 *q*
20	15.5 *q*	15.5 *q*	16.6 *q*	17.6 *q*	19.0 *q*	17.3 *q*	15.6 *q*

11, which showed, in the IR, absorptions for hydroxyl (3390 cm^{-1}) and carbonyl (1653 cm^{-1}) groups. The ^{1}H NMR spectrum of **11** exhibits a pair of doublets centred at δ 4.13 (1H, $J = 9$ and 6 Hz).

Dehydration of **5** and **6** with TsOH/ΦH yielded the α,β,γ,δ-unsaturated carbonyl compound, **12**. The ^{1}H NMR spectrum of **12** showed signals for the olefinic protons of an AB system [δ 6.01 (1H, *d*, $J = 10$ Hz) and 6.27 (1H, *d*, $J = 10$ Hz)]. The UV spectrum of **12** contained a band at λ_{max}^{EtOH} 309 nm (log $\varepsilon = 3.85$) which confirmed an extended conjugation and, consequently, the position of the hydroxyl at C-12 in **5**.

Group III

The compounds of this group comprise two pimaranes with cross-conjugated CO–C=C–CO of the transoid type. The cross-conjugated compound 7,11-dioxopimar-8(9),15-diene, obtained through oxidation of **6**, was identical with the diketone, **7**, isolated from the plant.

The ^{13}C NMR spectrum of **7** showed a vinyl group, two keto groups at C-7 and C-11 and a double bond between C-8 and C-9 [δ 144.5 (*d*) and 112.3 (*t*) ($CH=CH_2$), 200.4 and 201.6 (two ketones C-7 and C-11) 154.9 (*s*, C-9) and 141.5 (*s*, C-8)] [11].

The ^{1}H NMR spectrum of **7** showed a pair of doublets centred at δ 2.38 and 2.82 ($J = 16$ Hz) for the hydrogens of C-14.

Reduction of the double bond between C-8 and C-9 with zinc–acetic acid confirmed the enedione system [12]. In the mass spectrum of the reduced compound **13** the most prominent peak is the one at *m/z* 137. This fragment is the product of a McLafferty rearrangement followed by the cleavage of the C-7–C-8 bond.

The last compound described in this paper is 12β-hydroxy-7,11-dioxopimar-8(9),15-dien (**8**). The molecular formula, $C_{20}H_{28}O_3$, was obtained from high resolution mass spectrometry.

The UV spectrum of **8** was similar to that of **7**. The IR spectrum showed one hydroxyl (3448 cm^{-1}) and two carbonyl groups (1668 and 1660 cm^{-1}).

The ^{1}H NMR spectrum of **8** showed a signal at δ 4.22 (1H, *d*, $J = 2$ Hz) for the carbinolic proton. The magnitude of the coupling constants suggested that the hydroxyl group is β-oriented, which allows an ω-type coupling with the hydrogen at C-14. The chemical shift of C-13 observed in the ^{13}C NMR spectrum (δ 46.0) is further evidence for the localization of the hydroxyl group at C-12.

Treatment of **8** with acetic anhydride in the presence of DMAP gave the acetate, **15**.

Reduction of **8** with zinc–acetic acid yielded **13**, identical in all aspects to the product obtained by the similar reaction with **7**.

The structure of **8** was confirmed by correlation of its acetate, **15**, obtained by treatment with acetic anhydride in the presence of DMAP, with compound **5** as described below. Thus, acetylation of **5** (acetic anhydride–DMAP) into **14** and subsequent *t*-butyl chromate oxidation furnished a compound identical with **15** by spectrophysical data.

EXPERIMENTAL

Mps uncorr. (Kofler apparatus); CC: Merck Si gel (0.05–0.20 mm); TLC: Merck Si gel H, G or $PF_{254+366}$.

Vellozia compacta was collected in the Serra do Cipó, State of Minas Gerais, Brazil. Stem, roots and leaf sheaths were cut into small pieces and extracted with hexane. The hexane soln was concd *in vacuo*. Crude extract (90 g) thus obtained was redissolved in $CHCl_3$ absorbed on 90 g Si gel 60 and, after evaporation of the solvent, placed on top of a column of 1 kg of the same absorbent. Elution was started with hexane and the polarity of the eluent increased gradually. Compounds were eluted in the following order, although in the first chromatographic fractionation the separations was not clear-cut, often requiring purification on smaller columns or by prep. TLC.

7,11-Dioxopimar-8(9),15-dien (**7**). White-yellow crystals from hexane, mp 88–89°, 0.2% yield of the dry plant. $[\alpha]_{24°}^{589} = +34.8$ (*c* 1.23); UV λ_{max}^{EtOH} nm: 264 (log $\varepsilon = 3.93$); IR ν_{max}^{KBr} cm^{-1}: 3020, 2940, 1670, 1450, 1200, 1000, 960 and 920; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.90 (3H, *s*), 0.94 (3H, *s*), 1.07 (3H, *s*), 1.32 (3H, *s*), 1.60 (1H, *dd*, $J = 12$, 5 Hz), 2.38 (1H, *d*, $J = 16$ Hz), 2.82 (1H, *d*, $J = 16$ Hz), 4.90 (1H, *dd*, $J = 17$, 1 Hz), 5.01 (1H, *dd*, $J = 11$, 1 Hz) and 5.74 (1H, *dd*, $J = 17$, 11 Hz); ^{13}C NMR: Table 1; MS *m/z* (rel. int.): 300 $[M]^+$ (98), 285 (27), 258 (100), 257 (35), 243 (32), 217 (24), 204 (28), 203 (29), 189 (25), 175 (19), 161 (24), 147 (20), 135 (23), 119 (18), 109 (38), 105 (32), 91 (53), 77 (35), 69 (38), 55 (54) and 41 (98). Found, *m/z* 300.2065 ($C_{20}H_{28}O_2$ requires 300.2082).

Reduction of enedione 7 *with powdered zinc.* To a soln of **7** (140 mg) in HOAc (8 ml) was added with stirring and heating powdered Zn (210 mg). After 6 hr the yellow colour of **7** had disappeared. The mixture was filtered and the filtrate diluted with H_2O and extracted with Et_2O. The washed and dried Et_2O extract was evaporated and the residue (98 mg) was recrystallized from a mixture of hexane and EtOAc to give **13** which had mp 156–158°. IR ν_{max}^{KBr} cm^{-1}: 1710, 1695, 1200 and 910; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.86 (3H, *s*), 0.90 (3H, *s*), 0.96 (3H, *s*), 1.36 (3H, *s*), 2.0 at 2.96 (7H, *m*), 4.85 (1H, *dd*, $J = 10$, 1.5 Hz), 4.95 (1H, *dd*, $J = 17$, 1.5 Hz) and 5.82 (1H, *dd*, $J = 17$, 10 Hz); MS *m/z* (rel. int.): 302 $[M]^+$ (26), 287 (4), 206 (3), 165 (7), 137 (100), 123 (18), 109 (11) and 95 (16).

Reduction of 7 *with sodium borohydride.* To a soln of **7** (110 mg) in MeOH (10 ml) was added $NaBH_4$ (30 mg). The reaction mixture was left for 20 min at room temp. and, by the usual work-up, gave **11** (101 mg); mp 141–142°. IR ν_{max}^{KBr} cm^{-1}: 3390, 1653, 1600 and 920; UV λ_{max}^{EtOH} 250 nm; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.88 (3H, *s*), 0.90 (3H, *s*), 1.10 (3H, *s*), 1.24 (3H, *s*), 2.0 at 2.8 (~ 5H, *m*), 4.13 (1H, *dd*, $J = 9$, 6 Hz), 4.87 (1H, *dd*, $J = 17$, 1.5 Hz), 4.97 (1H, *dd*, $J = 10$, 1.5 Hz) and 5.72 (1H, *dd*, $J = 17$, 10 Hz); MS *m/z* (rel. int.): 302 $[M]^+$ (54), 287 (17), 284 (24), 274 (27), 269 (31), 259 (28), 245 (28), 179 (72), 150 (62), 145 (42), 123 (37), 121 (43), 109 (100), 107 (40), 105 (34), 95 (44), 91 (40), 69 (70), 55 (68), 43 (67) and 41 (88).

12β-Hydroxy-7,11-dioxopimar-8,(9),15-dien (**8**). White-yellow crystals from hexane, mp 116–118°, 0.05% yield of the dry plant. UV λ_{max}^{EtOH} nm: 264 (log $\varepsilon = 3.94$); IR ν_{max}^{KBr} cm^{-1}: 3448, 1668, 1660, 1105, 1050 and 915; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.83 (3H, *s*), 0.92 (3H, *s*), 0.96 (3H, *s*), 1.4 (3H, *s*), 1.68 (1H, *dd*, $J = 12$, 4 Hz), 2.38 (1H, *d*, $J = 18$ Hz), 2.6 (1H, *m*), 2.82 (1H, *d*, $J = 18$ Hz), 4.22 (1H, *d*, $J = 2$ Hz), 5.16 (1H, *dd*, $J = 10$, 1 Hz), 5.18 (1H, *dd*, $J = 17$, 1 Hz) and 6.04 (1H, *dd*, $J = 17$, 10 Hz); ^{13}C NMR: Table 1. Found, *m/z* 316.2042 ($C_{20}H_{28}O_3$ requires 316.2031).

Reduction of 8 *with powdered zinc.* Reduction of **8** was carried out using the same procedure described for **7** to give **13**.

Acetylation of 8. Compound **8** was acetylated using the same procedure described for **6** above. Compound **15** was obtained as a yellow oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2940, 1746, 1686, 1667, 1250 and 910; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.96 (3H, *s*), 0.98 (6H, *s*), 1.4 (3H, *s*), 2.2 (3H, *s*), 5.08 at 5.34 (3H, *m*) and 5.9 (1H, *dd*, $J = 17$, 10 Hz).

Oxidation of 12β-*acetyl-7-oxopimar*-8(9),15-*dien* (**14**). To a soln of **14** (78 mg) in dry CCl_4 (10 ml) were added, under stirring, HOAc (4 ml), Ac_2O (2.2 ml) and *t*-butyl chromate (2.4 ml). The reaction medium was refluxed for 3 hr, after which the solvents were evaporated under red. pres. The product was extracted successively (twice) with a satd aq. soln of oxalic acid, $CHCl_3$ and H_2O. Evaporation of the $CHCl_3$ layer furnished **15** (76.2 mg, 95%) as a yellowish oil.

Compactone (**1**). White needles from hexane and EtOAc (5:1), mp 217–218°, 0.1% yield of the dry plant. CD (dioxane; *c* 4.5 $\times 10^{-4}$ g/ml): $[\theta]_{335}$ 0, $[\theta]_{320}$ −2252, $[\theta]_{307}$ −4188, $[\theta]_{285}$ −2207, $[\theta]_{260}$ 0; IR ν_{max}^{KBr} cm^{-1}: 3480, 1700, 1640, 980 and 910; ^1H NMR (100 MHz, C_5D_5N, TMS as int. standard): δ 0.86 (3H, *s*), 0.88 (3H, *s*), 1.19 (1H, *dd*, $J = 13, 3$ Hz), 1.30 (3H, *s*), 1.36 (3H, *s*), 1.62 (2H, *s*), 2.24 (1H, *dd*, $J = 12, 3$ Hz), 3.16 (1H, *dd*, $J = 13, 12$ Hz), 4.84 (1H, *dd*, $J = 10, 1.5$ Hz), 4.93 (1H, *dd*, $J = 17, 1.5$ Hz), 5.84 (1H, *dd*, $J = 17, 10$ Hz) and 6.22 (1H, *br s*, exchangable with D_2O); ^{13}C NMR: Table 1. MS *m/z* (rel. int.): 304 $[M]^+$ (100), 286 (18), 167 (20), 165 (24), 138 (52), 123 (56), 109 (28), 95 (35), 81 (34), 69 (40), 67 (30), 55 (38) and 41 (98).

Reduction of compactone (**1**) *with sodium borohydride.* Compactone (100 mg) was reduced with $NaBH_4$ in MeOH for 10 min at room temp., followed by the usual work-up to give two compounds which were chromatographed on prep. TLC (hexane–EtOAc, 9:1, developed × 3) to produce compactol (**3**) and its epimers in the proportion of 2:1.

Compactol (**3**). White crystals from hexane, mp 104–105°, 0.08% yield of the dry plant. $[\alpha]_{24^\circ}^{589}$ −3.5 (*c* 1.25); IR ν_{max}^{KBr} cm^{-1}: 3510, 2940, 1640, 1380, 1360, 1060, 990, 970 and 905; ^1H NMR (100 MHz, CCl_4, TMS as int. standard): δ 0.86 (3H, *s*), 0.88 (3H, *s*), 1.00 (3H, *s*), 1.22 (3H, *s*), 1.26 (2H, *s*), 2.4 (1H, *br s*, exchangable with D_2O), 3.24 (1H, *dd*, $J = 9, 5$ Hz), 4.75 (1H, *dd*, $J = 10, 1.5$ Hz), 4.82 (1H, *dd*, $J = 17, 1.5$ Hz) and 5.7 (1H, *dd*, $J = 17, 10$ Hz); ^{13}C NMR: Table 1; MS *m/z* (rel. int.): 306 $[M]^+$ (84), 291 (30), 288 (67), 285 (83), 273 (18), 236 (24), 207 (25), 206 (20), 182 (48), 164 (20), 163 (18). 123 (53), 121 (26), 109 (51), 107 (29), 95 (47), 93 (34), 81 (59), 79 (31), 69 (98), 67 (46), 55 (68), 43 (41) and 41 (100). Found, *m/z* 306.2482 ($C_{20}H_{34}O_2$ requires 306.2550).

Oxidation of compactol (**3**) *with Jones' reagent.* A soln of **3** (80 mg) in Me_2CO (12 ml) was allowed to stand with slight excess of Jones' reagent at room temp. for 10 min and usual work-up gave the keto acid, **9**, which was methylated with CH_2N_2 to produce a colourless oil **10** (82 mg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 1712, 1654, 990 and 910; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.85 (3H, *s*), 0.92 (3H, *s*), 0.98 (3H, *s*), 1.06 (3H, *s*), 3.68 (3H, *s*), 4.91 (1H, *d*, $J = 11$ Hz), 4.92 (1H, *d*, $J = 17$ Hz) and 5.78 (1H, *dd*, $J = 17, 11$ Hz); MS *m/z* (rel. int.): 334 $[M]^+$ (15), 303 (2), 287 (3), 249 (2), 231 (6), 197 (53), 181 (27), 165 (30), 138 (80), 123 (100), 109 (31), 95 (68) and 69 (63).

11β-*Hydroxy-7-oxopimar*-8(9),15-*dien* (**6**). White crystals from hexane and EtOAc (10:1), mp 164–165°, 0.9% yield of the dry plant. $[\alpha]_{24^\circ}^{589} = +75.4$ (*c* 1.43); UV λ_{max}^{EtOH} nm: 252 ($\log \varepsilon = 4.12$); IR ν_{max}^{KBr} cm^{-1}: 3330, 2920, 1650, 1620, 1260, 1020 and 910; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.88 (3H, *s*), 0.95 (3H, *s*), 1.08 (3H, *s*), 1.35 (3H, *s*), 1.6 (1H, *t*, $J = 9$ Hz), 2.0 (1H, *ddd*, $J = 12, 5, 2$ Hz), 2.47 (2H, *d*, $J = 9$ Hz), 4.6 (1H, $W_{1/2} = 16$ Hz), 4.85 (1H, *dd*, $J = 17, 1.5$ Hz), 4.92 (1H, *dd*, $J = 11, 1.5$ Hz) and 5.7 (1H, *dd*, $J = 17, 11$ Hz); (100 MHz, C_5D_5N): δ 0.82 (3H, *s*), 0.91 (3H, *s*), 1.16 (3H, *s*), 1.58 (3H, *s*), 1.74 (1H, *t*, $J = 9$ Hz), 2.2 (1H, *ddd*, $J = 12, 5, 2$ Hz), 2.64 (2H, *d*, $J = 9$ Hz), 2.9 (1H, *m*), 4.88 (1H, *m*), 4.98 (1H, *dd*, $J = 18, 2$ Hz), 5.00 (1H, *dd*, $J = 10, 2$ Hz), 5.85 (1H, *dd*, $J = 18, 10$ Hz) and 6.33 (1H, *d*, $J = 6$ Hz, exchangable with D_2O); ^{13}C NMR: Table 1; MS *m/z* (rel. int.): 302 $[M]^+$ (100), 287 (8), 260 (6), 259 (5), 245 (9), 205 (9), 179 (82), 164 (71), 135 (19), 121 (24), 109 (12), 107 (10), 105 (11), 91 (22), 69 (25), 55 (30) and 41 (54). Found, *m/z* 302.2212 ($C_{20}H_{30}O_2$ requires 302.2238).

Oxidation of **6** *with pyridinium chlorochromate.* PCC (90 mg) was added with stirring to a soln of **6** (100 mg) in dry CH_2Cl_2 (2 ml). After 2 hr, dry Et_2O (10 ml) was added and the supernatant decanted from a brown gum. The insoluble residue was washed thoroughly with dry Et_2O (3 × 5 ml) whereupon it gave a brown granular solid. The Et_2O solns were combined and filtered through a pad of Florisil. The solvent was removed at red. pres. and crystals of **7**, mp 86–88° (86 mg, 87%), were obtained.

Dehydration of **6**. Compound **6** (50 mg) was refluxed for 4 hr with ΦH (20 ml) and TsOH (10 mg). After cooling, the mixture was washed with 5% aq. $NaHCO_3$ (3 × 10 ml), H_2O (3 × 10 ml), dried and concd *in vacuo* to give a yellow oil, **12** (46 mg). UV λ_{max}^{EtOH} nm 309 ($\log \varepsilon = 3.85$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1655; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.90 (3H, *s*), 0.94 (3H, *s*), 1.11 (3H, *s*), 1.14 (3H, *s*), 2.25 (1H, *d*, $J = 17$ Hz), 2.27 (1H, *dd*, $J = 17, 4$ Hz), 2.57 (1H, *dd*, $J = 17, 7$ Hz), 2.61 (1H, *d*, $J = 17$ Hz), 4.92 (1H, *dd*, $J = 10, 2$ Hz), 4.94 (1H, *dd*, $J = 18, 2$ Hz), 5.72 (1H, *dd*, $J = 18, 10$ Hz), 6.01 (1H, *d*, $J = 10$ Hz) and 6.27 (1H, *d*, $J = 10$ Hz); MS *m/z* (rel. int.): 284 $[M]^+$ (3), 269 (3) and 160 (100).

12β-*Hydroxy-7-oxopimar*-8(9),15-*dien* (**5**). Colourless crystals from hexane and EtOAc (4:1), mp 155–156°, 0.8% yield of the dry plant. $[\alpha]_{24^\circ}^{589} = +26.3$ (*c* 1.48); UV λ_{max}^{EtOH} nm: 252 ($\log \varepsilon = 4.15$); IR ν_{max}^{KBr} cm^{-1}: 3480, 3080, 1645, 1614, 910 and 880; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard); δ 0.90 (3H, *s*), 0.95 (3H, *s*), 0.99 (3H, *s*), 1.14 (3H, *s*), 1.84 (1H, *s*, exchangable with D_2O), 3.66 (1H, *t*, $J = 6$ Hz), 5.05 (1H, *dd*, $J = 18, 1.5$ Hz), 5.09 (1H, *dd*, $J = 10, 1.5$ Hz) and 5.72 (1H, *d*, $J = 18, 10$ Hz); ^{13}C NMR: Table 1; MS *m/z* (rel. int.): 302 $[M]^+$ (55), 284 (28), 273 (30), 261 (45), 219 (25), 179 (90), 161 (68), 123 (29), 109 (36), 105 (32), 91 (46), 84 (44), 69 (45) and 41 (100). Found, *m/z* 302.2204 ($C_{20}H_{30}O_2$ requires 302.2238).

Dehydration of **5**. Compound **5** was dehydrated using the same procedure described for **6**, above, to give **12**.

Acetylation of **5**. Compound **5** (93.8 mg) was dissolved in Ac_2O (10 ml) and a catalytic amount of DMAP added. The mixture was left for 24 hr at room temp. and the usual work-up yielded **14** as a colourless oil (106 mg, 100%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740 and 1660; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.90 (3H, *s*), 0.94 (3H, *s*), 1.02 (3H, *s*), 1.06 (3H, *s*), 2.03 (3H, *s*), 4.88 (1H, *t*, $J = 5$ Hz), 4.99 (1H, *dd*, $J = 17, 1.5$ Hz), 5.03 (1H, *dd*, $J = 10, 1.5$ Hz) and 5.70 (1H, *dd*, $J = 17, 10$ Hz).

7a,8,10,11-*Tetrahydro*-3,8,8,11a-*tetramethyl-phenanthro*(10,1-*bc*) *pyran* 5(4H),9(7H)-*dione* (**2**). Colourless crystals from hexane and EtOAc (3:1), mp 177–178° in 0.1% yield of the dry plant. $[\alpha]_{24^\circ}^{589} = +43.8$ (*c* 0.74); UV λ_{max}^{EtOH} nm: 209 ($\log \varepsilon = 4.09$), 269 (2.72), and 278 (2.44); IR ν_{max}^{KBr} cm^{-1}: 2940, 1740, 1700, 1490, 1450, 1410, 1240, 1150, 1020 and 825; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 1.2 (3H, *s*), 1.22 (3H, *s*), 1.36 (3H, *s*), 2.3 (3H, *s*), 3.44 (1H, *d*, $J = 17$ Hz), 3.93 (1H, *d*, $J = 17$ Hz), 5.38 (1H, *t*, $J = 8$ Hz) and 7.16 (2H, *s*); ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS as int. standard): δ 37.0 (*t*, C-1), 34.4 (*t*, C-2), 215.2 (*s*, C-3), 47.0 (*s*, C-4), 47.8 (*d*, C-5), 26.1 (*t*, C-6), 76.8 (*d*, C-7), 123.8 (*s*, C-8), 144.0 (*s*, C-9), 37.4 (*s*, C-10), 123.8 (*d*, C-11), 130.8 (*d*, C-12), 132.5 (*s*, C-13), 129.1 (*s*, C-14), 33.8 (*t*, C-15), 170.9 (*s*, C-16), 18.4 (*q*, C-17), 24.5 (*q*, C-18), 21.7 (*q*, C-19) and 26.8 (*q*, C-20); MS *m/z* (rel. int.): 312 $[M]^+$ (93), 297 (18), 279 (11), 268 (100), 255 (80), 251 (88), 213 (33), 211 (39), 182 (32), 170 (42), 169 (61), 97 (54), 69 (34), 55 (28) and 41 (75). Found, *m/z* 312.1760 ($C_{20}H_{24}O_3$, requires 312.1719).

Compactotriol (**4**). White needles from hexane and EtOAc (2:1), mp 192–193°, 0.05% yield of the dry plant. IR ν_{max}^{KBr} cm^{-1}: 3350, 2940, 1640 and 905; ^1H NMR (100 MHz, C_5D_5N, TMS as int. standard): δ 0.8 (3H, *s*), 1.06 (3H, *s*), 1.22 (3H, *s*), 1.74 (2H, *s*), 3.1 (1H, *d*, $J = 11$ Hz), 3.39 (1H, *m*), 3.44 (1H, *d*, $J = 11$ Hz), 4.84 (1H, *dd*, $J = 17, 1.5$ Hz), 4.87 (1H, *dd*, $J = 10, 1.5$ Hz) and 5.74

(1H, *dd*, $J = 17, 10$ Hz); ^{13}C NMR: Table 1; MS *m/z* (rel. int.): 322 $[M]^+$ (8), 273 (4), 251 (5), 183 (3), 171 (6), 145 (5), 123 (8), 121 (9), 109 (8), 107 (10), 105 (9), 95 (10), 79 (12), 55 (22) and 31 (100). Found, *m/z* 322.2545 ($C_{20}H_{34}O_3$ requires 322.2499).

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