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DITERPENES WITH PIMARANE AND CLEISTANTHANE SKELETONS FROM *VELLOZIA PIRESIANA*

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Key Word Index—*Vellozia piresiana*; Velloziaceae; diterpenes; pimarane and cleistanthane type; structure elucidation.

Abstract—*Vellozia piresiana* contains β-sitosterol, stigmasterol, taraxerone, compactone, 7β,8β-dihydroxy-3-oxopimar-15-ene and three new diterpenes, one of the pimarane type and the other two with a cleistanthane skeleton. Their structures were deduced on the basis of spectral data and chemical modifications.

INTRODUCTION

As part of our systematic phytochemical investigation of Brazilian Velloziaceae, we wish to report on the study of *Vellozia piresiana* L. B. Smith, a perennial species widely distributed in the State of Minas Gerais, Brazil. The hexane extract of a sample of this plant collected on the Serra do Cipó, State of Minas Gerais, has been shown to have ichthyotoxic activity in *Lebistes reticulatus**.

RESULTS AND DISCUSSION

The hexane extract of roots, stem and leaf sheaths of *V. piresiana* afforded five known compounds: β-sitosterol and stigmasterol isolated as a mixture and identified by comparison with authentic samples, taraxerone (**1**) [1], compactone (**2**) [2], and 7β-8β-dihydroxy-3-oxopimar-15-ene (**4**) [3]. In addition three new diterpenes (**3**, **5** and **6**) were isolated and are reported in this paper. The diterpenes can be divided into two groups on the basis of their skeletons.

Group I (pimarane type)

The spectral data of diterpene **3** suggested the presence of one hydroxyl, one carbonyl, one vinyl and four tertiary methyl groups. This information, together with the molecular formula, $C_{20}H_{32}O_2$ (HRMS), suggested that **3** was a diterpenoid of the pimarane type, with a structure similar to **2**, a compound found in the same extract.

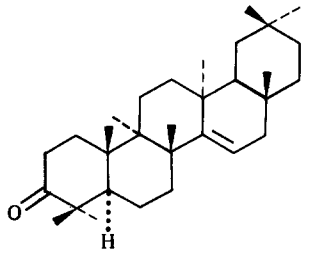
The absence of carbinolic protons in the ^{1}H NMR spectrum of **3** indicated that the hydroxyl group was tertiary. On the other hand, the ^{13}C NMR spectrum of **3** showed typical absorptions for a carbonyl group at C-3 i.e. singlets at δ 47.4 (C-4) and 217.2 (C-3) (Table 1). The position and stereochemistry of the hydroxyl group at C-8 was deduced from the ^{1}H NMR spectrum of **3** in deuteropyridine. The methyl groups C-17 and C-20 underwent downfield shifts of 0.15 and 0.25 ppm, respectively, on changing from deuterochloroform to pyridine solution a fact that establishes their *syndiaxial* relationship with the hydroxyl group [4]. The configuration of C-13 was confirmed by the chemical shift of Me-17 (δ 24.4), since it is known that axial methyl groups are usually more shielded than equatorial ones [5].

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

C	3	4
1	37.9	37.8
2	34.1	34.0
3	217.2	217.1
4	47.4	47.0
5	55.2	52.1
6	18.8	27.7
7	42.9	77.6
8	72.0	73.5
9	55.8	54.5
10	36.7	36.4
11	17.5	17.6
12	38.3	38.0
13	36.5	36.1
14	51.5	47.0
15	151.0	151.0
16	108.6	108.7
17	24.3	24.4
18	26.6	26.6
19	21.3	21.5
20	15.4	15.3

The other diterpene (**4**) of the pimarane type was obtained as colourless crystals, and had the formula $C_{20}H_{32}O_3$. The IR spectrum showed a broad absorption at 3370 (OH), a carbonyl absorption at 1690 cm^{-1} and a vinyl band at 900 cm^{-1}. The ^{1}H NMR spectra in deuterochloroform and -pyridine were similar to that of **3** except

*Assay performed by Dr A. Martins, Biology Section, NPPN-UFRJ.



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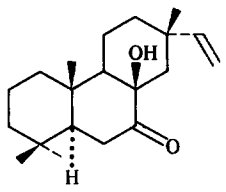

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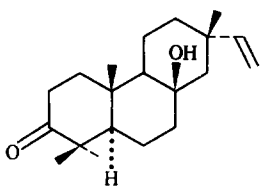

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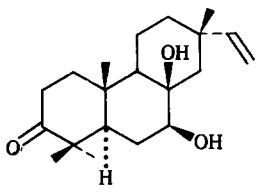

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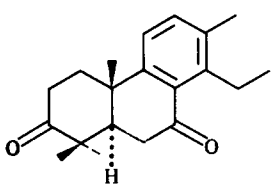

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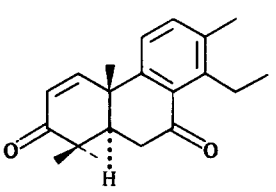

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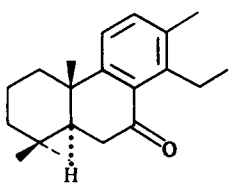

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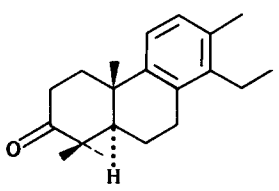

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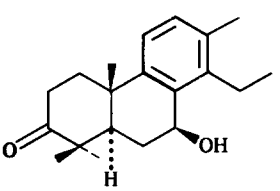

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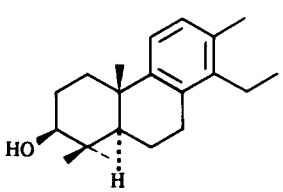

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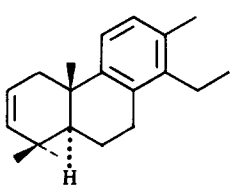

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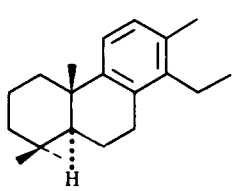

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for the presence of a carbinol methine signal at δ 3.36 (1H, *dd*, J = 10, 5 Hz) due to a secondary hydroxyl group. The multiplicity of the signal of the CHOH proton showed that it was flanked by two hydrogens. The coupling constants were in accord with the axial orientation of the carbinolic hydrogen. Consequently, the hydroxyl group was equatorial.

The ^{13}C NMR spectrum of **4** confirmed the proposed structure. Thus, the presence of an equatorial hydroxyl group at C-7 was ascertained from the chemical shifts of C-14 and C-6 (δ 47.0 and 27.7, respectively). The shielding effect on C-14 was determined by the strong *γ-gauche* effect of the hydroxyl group, the deshielding on C-6 being due to a β-effect of the same group [5] (Table 1). The positive Cotton effect for the n–π^* transition in the CD spectrum of **4** (8.2×10^{-2} g/ml in MeOH $[\theta] = +4487$ at 285 nm) was comparable with that observed in the case of β-amyrone, establishing the *trans* junction for ring A/B, the 8-hydroxyl group being in the β-orientation [6].

During the course of our work, **4** was isolated from *Bromelia pinguin* L. (Bromeliaceae) and its structure was deduced from X-ray spectroscopy [3].

Group II (cleistanthane type)

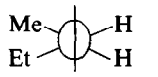
The two diterpenes (**5** and **6**) of this group were isolated as a mixture. The difference of two amu in the mass spectrum and two doublets at δ 6.12 (J = 11 Hz) and δ 7.45 (J = 11 Hz) in the ^{1}H NMR spectrum of the mixture showed that **5** and **6** differed only by the presence of a supplementary double bond in **6** which was in conjugation with a carbonyl group, as demonstrated by ^{13}C and ^{1}H NMR.

Catalytic reduction of the mixture (10% Pd–C, 40 psi, ethyl acetate) afforded a single substance, spectrally similar to **5**, confirming the structural pattern previously postulated for the two diterpenes. After several chromatographic trials, it was possible to obtain **5** as a pure substance, identical in all respects to the single compound previously obtained by catalytic hydrogenation. On the

other hand, in spite of exhaustive attempts, it was not possible by preparative TLC or column chromatography to isolate **6** as a pure compound, minor amounts of **5** remaining as an impurity.

The high-resolution mass spectrum of **5** indicated the molecular formula $C_{20}H_{26}O_2$. The IR spectrum showed absorptions for 'normal' (1700 cm^{-1}) and conjugated (1665 cm^{-1}) carbonyl groups and a tetrasubstituted aromatic ring (830 cm^{-1}). This was confirmed by the UV spectrum which exhibited absorptions at 218 ($\log\varepsilon$ = 4.09), 255 ($\log\varepsilon$ = 3.85) and 304 nm ($\log\varepsilon$ = 3.08). The ^{1}H NMR spectrum showed four C-methyl resonances (δ 1.12, 1.25, 1.41 and 2.37, this latter signal assigned to an aromatic methyl substituent), and two doublets for two aromatic protons *ortho* to each other at δ 7.07 (J = 8 Hz) and δ 7.3 (J = 8 Hz). The signals at δ 1.25 (3H, t, J = 7 Hz) and the complex pattern between δ 2.8 at 3.1 (2H, m) corresponded to an ethyl group attached to the aromatic nucleus. Double irradiation experiments demonstrated that these five protons were mutually spin coupled.

These data, in combination with comparative analysis of the proton noise decoupled and single frequence off resonance decoupled ^{13}C NMR spectra, allowed expansion of the partial structure to $(CO)_2$ $(C)_2$ (CH) $(CH_2)_3$



$(Me)_3$.

These results, together with biogenetic considerations and the previous isolation of cleistanthane diterpenoids from plants of this family [7, 8], supported structure **5**. The chemical shift of the angular methyl carbon (δ 21.3) also proved the A/B ring junction to be *trans* with a carbonyl group at C-3. The absolute configuration of **5** was deduced by chemical correlation with cleistantha-8, 11,13-trien-7-one (**7**), isolated from *Vellozia leptopetala* [9] and of known absolute stereochemistry.

Catalytic hydrogenation of **5** in the presence of 10% Pd–C at 62 psi in acetic acid gave compound **8**. However, when the reaction was run at 45 psi under otherwise identical experimental conditions, a mixture of **8** and **9** was obtained. The magnitude of the coupling constants for the carbinolic proton in the ^{1}H NMR spectrum of **9** indicates that the hydroxyl group has the equatorial (β) orientation. Reduction of ketone **8** with sodium borohydride in methanol afforded the alcohol **10** (IR: 3485 cm^{-1}). This, upon dehydration with $POCl_3$ in pyridine at room temperature furnished **11** (^{1}H NMR: δ 5.54, 2H, m). Catalytic reduction of olefin **11** in the presence of 10% Pd–C at 60 psi in ethyl acetate gave hydrocarbon **12**, previously obtained by hydrogenolysis of ketone **7** [9].

EXPERIMENTAL

Mps (Kofler apparatus): uncorr; ^{1}H NMR and ^{13}C NMR: TMS as int standard. TLC: Kieselgel 60 PF (Merck) the analytical chromatograms were examined under UV (λ_{254} nm) and by spraying a 0.2% soln of $Ce(SO_4)_2$ in 2 N H_2SO_4 followed by heating on a hot plate. CC: Kieselgel 60 (Merck, 70–230 mesh).

V. piresiana 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*. The crude extract (10 g) thus obtained was redissolved in $CHCl_3$, absorbed on 10 g silica gel 60 and after evaporation of the solvent, placed on top of a column of 200 g 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 were not clear-cut, often requiring purification on smaller columns or by prep. TLC.

Taraxerone (**1**). Colourless crystals from hexane, mp 233–235°, 1.85×10^{-3}% dry wt. IR ν_{max}^{KBr} cm^{-1}: 3040, 2930, 1710, 1470, 1455 and 1370; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int standard): δ 0.85 (3H, s), 0.95 (6H, s), 0.97 (3H, s), 1.08 (3H, s), 1.09 (6H, s), 1.16 (3H, s) and 5.58 (1H, dd, J = 8, 3 Hz); MS m/z (rel. int.): 424 $[M]^+$ (65), 409 (23), 300 (99), 285 (49), 205 (82), 204 (100), 201 (26), 189 (23), 133 (47), 123 (21), 121 (29), 119 (24), 109 (37), 107 (38), 105 (27), 95 (42), 81 (32), 69 (37) and 55 (38).

Compactone (**2**). White needles from hexane and EtOAc (5:1), mp 217–218°, 2.85×10^{-4}% dry wt. IR ν_{max}^{KBr} cm^{-1}. 3480, 1700, 1640, 980 and 910; ^{1}H 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) and 5.84 (1H, dd, J = 17, 10 Hz); 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).

8β-Hydroxy-3-oxopimar-15-ene (**3**). Colourless crystals from hexane, mp 157–158°, 5.0×10^{-4}% dry wt. IR ν_{max}^{KBr} cm^{-1} 3445, 2915, 2865, 1695, 1635, 1445, 1385, 1255, 1200, 1125, 990 and 910; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.98 (1H, d, J = 3 Hz), 1.1 (3H, s), 1.12 (3H, s), 1.13 (3H, s), 1.25 (3H, s), 1.37 (2H, s), 2.52 (2H, m), 4.84 (1H, dd, J = 10, 2 Hz), 4.89 (1H, dd, J = 17, 2 Hz) and 5.76 (1H, dd, J = 17, 10 Hz); (100 MHz, C_5D_5N, TMS as int. standard): δ 1.1 (3H, s), 1.18 (3H, s), 1.29 (3H, s), 1.48 (3H, s), 2.55 (2H, m), 4.83 (1H, dd, J = 10, 2 Hz), 4.92 (1H, dd, J = 17, 2 Hz) and 5.88 (1H, dd, J = 17, 10 Hz); ^{13}C NMR: Table 1; MS m/z (rel. int.): 304 $[M]^+$ (16), 289 (27), 286 (27), 271 (6), 261 (4), 235 (11), 201 (12), 193 (17), 109 (21), 107 (25), 95 (37), 81 (52), 79 (36), 69 (52), 67 (49), 55 (71), 43 (59) and 41 (100). Found, m/z 304.2405 ($C_{20}H_{32}O_2$ requires 304.2402).

8,11,13-Cleistanthatrien-3,7-dione (**5**). Colourless crystals from hexane, mp 99–100°, 1.14×10^{-2}% dry wt. $[\alpha]_{24°}^{589}$ −38.2 ($CHCl_3$; c 1.00); UV λ_{max}^{MeOH} nm ($\log\varepsilon$): 218 (4.09), 255 (3.85) and 304 (3.08); IR ν_{max}^{KBr} cm^{-1}. 2960, 2930, 2870, 1700, 1665, 1455, 1270, 1225, 1113 and 830, ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 1.12 (3H, s), 1.25 (3H, s), 1.25 (3H, t, J = 7 Hz), 1.41 (3H, s), 2.37 (3H, s), 2.8–3.1 (2H, m), 7.07 (1H, d, J = 8 Hz) and 7.3 (1H, d, J = 8 Hz); ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS as int standard): δ 38.1 (t, C-1), 34.4 (t, C-2), 214.0 (s, C-3), 47.2 (s, C-4), 48.5 (d, C-5), 37.5 (t, C-6), 200.0 (s, C-7), 130.4 (s, C-8), 151.9 (s, C-9), 37.7 (s, C-10), 120.6 (d, C-11), 134.7 (d, C-12), 135.7 (s, C-13), 144.4 (s, C-14), 23.6 (t, C-15), 14.4 (q, C-16), 19.1 (q, C-17), 24.4 (q, C-18), 22.6 (q, C-19) and 21.3 (q, C-20); MS m/z (rel. int.): 298 $[M]^+$ (62), 265 (28), 199 (32), 187 (32), 185 (31), 181 (25), 157 (32), 155 (26), 125 (73), 115 (64), 91 (35), 77 (36), 69 (29), 55 (35), 53 (25), 43 (86) and 41 (100). Found, m/z 300.2091 ($C_{20}H_{28}O_2$ requires 300.2089).

1,8,11,13-Cleistanthatetraen-3,7-dione (**6**). Yellowish oil. ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 1.17 (3H, s), 1.20 (3H, t, J = 7 Hz), 1.23 (3H, s), 1.40 (3H, s), 2.36 (3H, s), 2.44 to 3.12 (5H, m), 6.10 (1H, d, J = 11 Hz), 7.15 (1H, d, J = 8 Hz), 7.29 (1H, d, J = 8 Hz) and 7.43 (1H, d, J = 11 Hz); MS m/z (rel. int.). 296 $[M]^+$ (99), 281 (32), 263 (21), 201 (22), 200 (100), 199 (78), 185 (24), 165 (29), 141 (21), 128 (29), 125 (46), 116 (23), 91 (16), 83 (26) and 69 (35).

Hydrogenolysis of 8,11,13-cleistanthatrien-3,7-dione (**5**). Compound **5** (100 mg) in AcOH (6 ml) was treated at room temp with H_2 at 45 psi. After 4 hr, the catalyst was filtered off and washed with EtOAc. Evaporation of the filtrate under red. pres. furnished two compounds **8** and **9** which were separated by silica

gel 60 CC. Treatment of **5** under the same conditions as used above at 60 psi gave the compound **8** as the only product

8,11,13-*Cleistanthatrien-3-one* (**8**). Colourless crystals from hexane and EtOAc (8:1), mp 84–86°. UV λ_{max}^{MeOH} nm (log ε) 219 (3.85) and 267 (2.62); IR ν_{max}^{KBr} cm^{-1}. 2965, 2930, 2875, 1695, 1680, 1450, 1370, 1088 and 815; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int standard): δ 1.13 (3H, *t*, *J* = 7 Hz), 1.17 (3H, *s*), 1.19 (3H, *s*), 1.34 (3H, *s*), 2.32 (3H, *s*), 2.38–3.06 (6H, *m*) and 7.05 (2H, *s*); ^{13}C NMR (25.2 MHz, $CDCl_3$): δ 38.0 (*t*, C-1), 34.7 (*t*, C-2), 217.0 (*s*, C-3), 47.1 (*s*, C-4), 50.0 (*d*, C-5), 21.0 (*t*, C-6), 28.0 (*t*, C-7), 133.0 (*s*, C-8), 145.4 (*s*, C-9), 37.4 (*s*, C-10), 122.8 (*d*, C-11), 128.1 (*d*, C-12), 132.3 (*s*, C-13), 140.1 (*s*, C-14), 22.2 (*t*, C-15), 13.0 (*q*, C-16), 19.3 (*q*, C-17), 26.7 (*q*, C-18), 24.7 (*q*, C-19) and 20.3 (*q*, C-20), MS *m/z* (rel. int): 284 $[M]^+$ (56), 269 (100), 227 (58), 217 (20), 185 (37), 183 (23), 171 (28), 159 (32), 157 (35), 155 (24), 143 (28), 142 (26), 141 (31), 129 (25), 128 (30), 125 (39), 115 (21), 55 (25), 43 (29) and 41 (52).

7β-*Hydroxyl*-8,11,13-*cleistanthatrien*-3-*one* (**9**) Colourless crystals from hexane and EtOAc (5:1), mp 154–156°; UV λ_{max}^{MeOH} nm (log ε) 220 (3.85) and 267 (2.68); IR ν_{max}^{KBr} cm^{-1}. 3470, 2929, 2919, 2845, 1695, 1450, 1380, 1260, 1112, 996 and 815; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int standard): δ 1.15 (3H, *s*), 1.19 (3H, *s*), 1.21 (3H, *t*, *J* = 7 Hz), 1.51 (3H, *s*), 2.01 (1H, *dd*, *J* = 12, 7 Hz), 2.34 (3H, *s*), 2.4 to 3.12 (6H, *m*), 5.18 (1H, *dd*, *J* = 11, 7 Hz) and 7.05 (2H, *br*, *s*); ^{13}C NMR (25.2 MHz, $CDCl_3$): δ 38.4 (*t*, C-1), 34.7 (*t*, C-2), 215.7 (*s*, C-3), 47.2 (*s*, C-4), 48.8 (*d*, C-5), 31.4 (*t*, C-6), 67.7 (*d*, C-7), 134.8 (*s*, C-8), 147.0 (*s*, C-9), 37.5 (*s*, C-10), 121.7 (*d*, C-11), 130.2 (*d*, C-12), 134.6 (*s*, C-13), 142.5 (*s*, C-14), 23.0 (*t*, C-15), 14.7 (*q*, C-16), 19.2 (*q*, C-17), 25.3 (*q*, C-18), 23.6 (*q*, C-19) and 21.3 (*q*, C-20); MS *m/z* (rel int). 300 $[M]^+$ (25), 282 (100), 267 (24), 225 (36), 196 (26), 185 (23), 184 (21), 183 (48), 162 (43), 157 (22), 147 (23), 125 (27), 43 (34) and 41 (31).

Reduction of 8,11,13-*cleistanthatrien*-3-*one* (**8**) *with* $NaBH_4$ Compound **8** (200 mg) was reduced with $NaBH_4$ (40 mg) in MeOH (10 ml) for 20 min at room temp, followed by the usual work-up, to give **10** (180 mg); mp 118–120° UV λ_{max}^{MeOH} nm (log ε) 220 (3.84) and 271 (2.66); IR ν_{max}^{KBr} cm^{-1}. 3485, 2900, 2865, 1430, 1360, 1020, 995 and 805, ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int standard) δ 0.9 (3H, *s*), 1.08 (3H, *s*), 1.1 (3H, *t*, *J* = 7 Hz), 1.22 (3H, *s*), 1.59 (1H, *s* (*br*), exchangeable with D_2O), 2.3 (2H, *q*, *J* = 7 Hz), 2.83 (1H, *d*, *J* = 3 Hz), 2.94 (2H, *dd*, *J* = 5, 3 Hz), 3.29 (1H, *dd*, *J* = 8, 6 Hz) and 7.01 (2H, *s*), ^{13}C NMR (25.2 MHz, $CDCl_3$): δ 37.4 (*t*, C-1), 27.9 (*t*, C-2), 78.5 (*d*, C-3), 38.8 (*s*, C-4), 49.1 (*d*, C-5), 19.0 (*t*, C-6), 28.0 (*t*, C-7), 132.7 (*s*, C-8), 147.4 (*s*, C-9), 37.6 (*s*, C-10), 121.9 (*d*, C-11), 127.8 (*d*, C-12), 132.4 (*s*, C-13), 140.1 (*s*, C-14), 22.1 (*t*, C-15), 13.0 (*q*, C-16), 19.3 (*q*, C-17), 27.9 (*q*, C-18), 15.3 (*q*, C-19) and 25.0 (*q*, C-20), MS *m/z* (rel int). 286 $[M]^+$ (41), 271 (45), 253 (100), 199 (23), 185 (37), 183 (41), 171 (25), 159 (68), 157 (25), 143 (25), 119 (40), 117 (37), 57 (30), 55 (38), 43 (50) and 41 (66).

Dehydration of 8,11,13-*cleistanthatrien*-3β-*ol* (**10**). To a soln of **10** (35 mg) in C_5H_5N (3.5 ml) cooled to 0°, was added $POCl_3$ (2 ml). After 12 hr, H_2O (3 ml) was added and mixture extracted with CH_2Cl_2 (3 × 10 ml) The organic layer was washed with H_2O (2 × 10 ml), dried over Na_2SO_4, filtered and taken to dryness *in vacuo* The crude reaction mixture was purified by prep TLC (silica gel, hexane developed × 2) to give **11** (20 mg), mp 110–111° UV λ_{max}^{MeOH} nm (log ε): 220 (3.9) and 267 (2.63); IR ν_{max}^{KBr} cm^{-1}. 2965, 2935, 2875, 1455, 1430, 1370, 820 and 730; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int standard): δ 1.0 (3H, *s*), 1.05 (3H, *s*), 1.12 (3H, *t*, *J* = 7 Hz), 1.28 (3H, *s*), 2.3 (3H, *s*), 2.44 (2H, *d*, *J* = 6 Hz), 2.64 (2H, *q*, *J* = 7 Hz), 2.82 (2H, *m*), 5.54 (2H, *m*) and 7.04 (2H, *m*), ^{13}C NMR (25.2 MHz, $CDCl_3$). δ 40.3 (*t*, C-1), 123.4 *d*, C-2), 137.7 (*d*, C-3), 34.9 (*s*, C-4), 47.4 (*d*, C-5), 20.1 (*t*, C-6), 28.1 (*t*, C-7), 132.9 (*s*, C-8), 145.9 (*s*, C-9), 37.1 (*s*, C-10), 121.9 (*d*, C-11), 128.0 (*d*, C-12), 132.5 (*s*, C-13), 139.8 (*s*, C-14), 22.2 (*t*, C-15), 13.0 (*q*, C-16), 19.4 (*q*, C-17), 31.8 (*q*, C-18), 25.2 (*q*, C-19 and 22.3 (*q*, C-20), MS *m/z* (rel int.): 268 $[M]^+$ (25), 253 (25), 187 (20), 186 (100), 171 (23), 159 (27) and 157 (23)

Catalytic reduction of 2,8,11,13-*cleistanthatetraene* (**11**). A soln of **11** (30 mg) in EtOAc (8 ml) was hydrogenated over 10% Pd–C (3 mg) at 60 psi. After 3 hr, the mixture was filtered under red pres to yield a crystalline compound, **12**, (27 mg) identical with the hydrogenolysis product of 8,11,13-cleistanthatrien-7-one (**7**) Mp 58–59°

$$[\alpha]_{24°} = \frac{\begin{matrix}589 & 578 & 546 & 436 & 365\ nm\end{matrix}}{\begin{matrix}+41.0 & +42.6 & +48.3 & +80.1 & +121.6\end{matrix}} (CHCl_3,\ 1.00)$$

UV λ_{max}^{MeOH} nm (log ε) 226 (3.30) and 270 (2.16), IR ν_{max}^{KBr} cm^{-1}. 2875, 1455, 1350 and 820, ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int standard): δ 0.94 (3H, *s*), 0.97 (3H, *s*), 1.19 (3H, *t*, *J* = 7 Hz), 1.22 (3H, *s*), 2.30 (3H, *s*), 2.64 (2H, *q*, *J* = 7 Hz), 2.82 to 3.0 (1H, *m*), 6.97 (1H, *d*, *J* = 8 Hz) and 7.09 (1H, *d*, *J* = 8 Hz), ^{13}C NMR (25.2 MHz, $CDCl_3$): δ 39.3 (*t*, C-1), 19.3 (*t*, C-2), 41.6 (*t*, C-3), 33.2 (*s*, C-4), 49.7 (*d*, C-5), 19.4 (*t*, C-6), 27.6 (*t*, C-7), 132.5 (*s*, C-8), 148.1 (*s*, C-9), 37.8 (*s*, C-10), 121.8 (*d*, C-11), 127.7 (*d*, C-12), 134.9 (*s*, C-13), 140.1 (*s*, C-14), 22.1 (*t*, C-15), 13.0 (*q*, C-16), 19.3 (*q*, C-17), 33.2 (*q*, C-18), 21.6 (*q*, C-19) and 25.0 (*q*, C-20); MS *m/z* (rel int): 270 $[M]^+$ (33), 255 (72), 199 (24), 185 (47), 173 (56), 159 (100), 69 (35) and 41 (23).

7β,8β-*Dihydroxy*-3-*oxoimar*-15-*ene* (**4**). Colourless crystals from hexane and EtOAc (7.1), mp 149–150°, 9.3×10^{-4}% dry wt CD ($c\ 8.2 \times 10^{-2}$ g/ml, MeOH). $[\theta]_{285} + 4487$. IR ν_{max}^{KBr} cm^{-1}. 3370 (*br*), 2910, 2880, 2860, 1695, 1645, 1420, 1375, 1355, 1310, 1225, 1135, 1055, 980 and 900; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.9 (1H, *d*, *J* = 3 Hz), 1.08 (3H, *s*), 1.11 (3H, *s*), 1.13 (3H, *s*), 1.25 (3H, *s*), 1.85 (1H, *s* (*br*), exchangeable with D_2O), 2.52 (2H, *m*), 3.36 (1H, *dd*, *J* = 10, 5 Hz), 4.83 (1H, *dd*, *J* = 10, 1.5 Hz), 4.89 (1H, *dd*, *J* = 17, 1.5 Hz) and 5.76 (1H, *dd*, *J* = 17, 10 Hz), (100 MHz, C_5D_5N): δ 1.1 (3H, *s*), 1.18 (3H, *s*), 1.29 (3H, *s*), 1.48 (3H, *s*), 3.57 (1H, *dd*, *J* = 10, 5 Hz), 4.8–5.2 (2H, *m*) and 5.9 (1H, *dd*, *J* = 17, 10 Hz), ^{13}C NMR (25.2 MHz, $CDCl_3$): δ 37.8 (*t*, C-1), 34.0 (*t*, C-2), 217.1 (*s*, C-3), 47.0 (*s*, C-4), 52.1 (*d*, C-5), 27.7 (*t*, C-6), 77.6 (*d*, C-7), 73.5 (*s*, C-8), 54.9 (*d*, C-9), 36.4 (*s*, C-10), 17.6 (*t*, C-11), 38.0 (*t*, C-12), 36.1 (*s*, C-13), 47.0 (*t*, C-14), 151.0 (*d*, C-15), 108.7 (*t*, C-16), 24.4 (*q*, C-17), 26.6 (*q*, C-18), 21.5 (*q*, C-19) and 15.3 (*q*, C-20). MS *m/z* (rel. int.). 320 $[M]^+$ (28), 302 (100), 250 (21), 249 (52), 220 (25), 164 (22), 125 (30), 121 (32), 109 (31), 107 (33), 96 (22), 81 (52), 79 (32), 69 (40), 67 (48), 55 (55), 43 (56) and 41 (67) Found *m/z* 320. 2268 ($C_{20}H_{32}O_3$ requires 320.2350).

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