Diterpenes from *Vellozia bicolor*

Angelo C. Pinto*, Pedro P.S. Queiroz

Instituto de Química da Universidade Federal do Rio de Janeiro, Cidade Universitária, Centro de Tecnologia, Bloco A, 21910 Rio de Janeiro, RJ, Brasil.

and

Walmir S. Garcez

Depto. de Química, Universidade Federal de Mato Grosso do Sul P.O. Box 649, Campo Grande, MS, Brasil

Received: January 22, 1991; April 24, 1991

Vellozia bicolor contém novos diterpenos do tipo isopimarano. Suas estruturas foram deduzidas com base em seus dados espectrais e transformações químicas.

Vellozia bicolor contains new diterpenes of the isopimarane type. Their structures were deduced on the basis of spectral data and chemical modifications.

Key words: Vellozia bicolor, *Velloziaceae, isopimarane type diterpenes, structure elucidation.*

Introduction

The ethyl acetate extract of stem and leaf sheaths of *V.bicolor* yielded a series of new diterpenes of the isopimarane type, besides compactone (**9**), which was earlier isolated from *V.compacta*[1].

Results and Discussion

Mass spectrometry of the compounds isolated from *Vellozia bicolor* L.B. Smith indicated their diterpenoid constitution. These diterpenes contain the isopimarane skeleton as is clearly indicated by the IR bands at *ca* 980 and 910 cm^{-1}, by the signals for three methyl groups attached to quaternary carbon atoms with sp^3 hybridization associated with the signals for three olefinic protons at *ca* δ 5.70 (1H, dd, J 17 and 10 Hz), *ca* δ 4.85 (1H, dd, J 17 and 2 Hz) and *ca* δ 4.80 (1H, dd, J 10 and 2 Hz) and, in the case of ^{13}C NMR spectrum, by the absorption at *ca* 150.0 ppm and at *ca* 109.0 ppm, characteristics of a tertiary vinyl group. The junction of the rings are deduced to be *trans-transoid-trans*[2] based on ^{13}C NMR data (Table 1)[3].

Mass spectrometry indicated that (**1**) had the molecular formula $C_{20}H_{34}O_2$(M^+ 306). The ^1H NMR spectrum showed the presence of two doublets of an AB pattern at δ 4.00 and 3.59 (J 12 Hz) which moved downfield to δ 4.82 and δ 4.38 upon acetylation of (**1**) to (**1a**). These data when associated with a triplet at 63.6 ppm in the ^{13}C NMR spectrum indicated the presence of an hydroxymethylene group. The second oxygen atom belongs to a tertiary alcohol (^{13}C NMR: 70.4 ppm). The positions of the hydroxymethylene and tertiary hydroxyl groups were determined to be at C-20 and C-8, respectively, from the ^{13}C NMR chemical shifts of C-1, C-10 and C-14. The tertiary hydroxyl position at C-8 was determined from the chemical shift of C-14 (50.5 ppm) which must be flanked by two quaternary carbons in order to explain the strong deshielding effect. On the other hand, the hydroxymethylene group was localized at C-20 due to the upfield shift of C-1 through the γ-gauche interaction between this carbon atom and the hydroxyl at C-20 and by downfield shift of C-10 by a β-effect of the hydroxyl group. The oxidation generated the γ-lactone (**1b**) (νCO = 1752 cm^{-1}). The configuration at C-13 was deduced by chemical shift of Me-17 (24.4 ppm), since it is known that axial methyl groups are usually more shielded than equatorial ones[4].

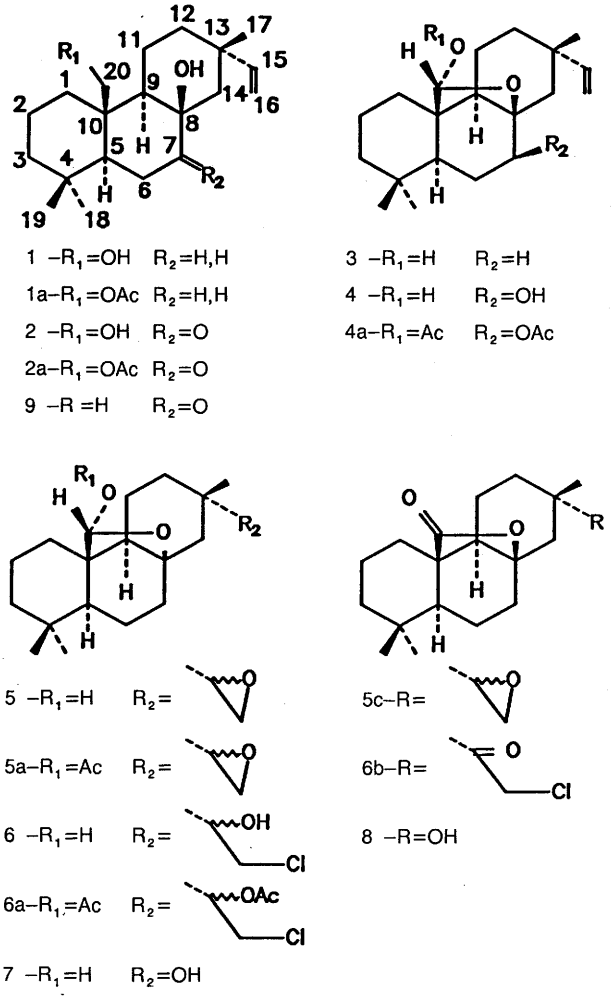
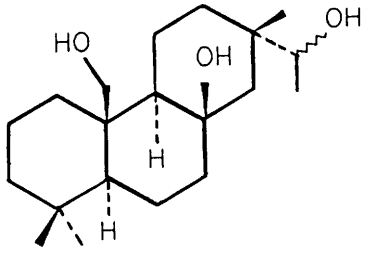


Figure 1

Table 1. *^{13}C NMR data (25,3 MHz)**

C/Compound	(1)[a]	(1a)[a]	(1b)[a]	(2)[a]	(2a)[a]	(3)[a]	(4)[b]	(4a)[a]	(5)[a]	(5a)[a]	(6)[a]	(8)[c]
1	37.1[d]	35.0	28.3	36.9	34.6	28.1	28.5	27.9	28.9	28.0	28.0	28.4
2	19.6[e]	18.7[d]	21.1	19.3	18.5	20.7[d]	20.1	19.5	19.8[d]	19.5[d]	20.6[d]	21.9[d]
3	42.3	41.9	41.7	41.8	41.5	42.0	42.1	41.5	41.9	41.7	41.9	41.7
4	33.3	33.2	33.8	33.8	33.6	33.7	33.6	33.6	33.6	33.5	33.6	33.7
5	56.5	56.5	50.0	55.2	55.1	51.2	42.1	48.7	51.1	51.1	51.1	50.0
6	18.5[e]	18.7[d]	18.5[d]	36.1	35.0	19.6[d]	31.3	26.9	19.6[d]	19.1[d]	19.6[d]	18.4[d]
7	43.5	43.5	36.9	211.3	210.2	40.3	77.7	78.6	40.0	39.5	40.3	36.7
8	70.4	72.0	82.1	75.3	76.6	82.1	84.1	84.2	82.0	83.3	82.2	83.3
9	58.2	57.2	54.3	59.3	59.3	53.9	51.9	51.0	53.7	53.0	53.8	54.0
10	40.8	40.0	50.5	41.6	40.1	50.3	49.8	50.0	50.4	50.7	50.5	50.6
11	17.4[e]	18.0[d]	19.4[d]	16.8	18.5	19.2[d]	19.4	18.4	18.5	18.0	18.6	21.1[d]
12	38.7[d]	38.8	34.2	37.9	38.4	35.5	35.9	34.7	30.1	30.0	31.4	38.9
13	36.6	36.5	35.0	36.3	36.2	35.5	35.6	34.7	32.7	31.5	37.0	68.4
14	50.5	51.4	42.3	40.5	42.1	42.9	39.5	37.9	40.8	40.2	40.3	46.3
15	151.7	151.4	150.1	150.7	150.6	151.3	152.2	150.6	61.1	61.0	80.5	
16	108.2	108.6	109.3	108.9	109.1	108.5	108.6	109.3	43.5	43.4	47.9	
17	24.4	24.1	22.8	24.7	24.5	22.7	23.2	21.9	20.6	20.4	18.6	27.3
18	33.6	33.9	32.0	32.9	33.3	32.7	32.7	32.5	32.7	32.5	32.7	32.0
19	21.6	21.8[e]	20.2	20.9	21.2	21.4	21.6	21.2	21.4	21.3	21.4	20.2
20	63.6	69.4	179.5	63.5	63.5	98.7	98.4	97.5	98.7	97.5	98.6	179.3
$COCH_3$		170.7			170.7			169.4		169.7		
$COCH_3$								170.6				
$COCH_3$		21.3[e]			21.5			21.1		21.1		
$COCH_3$								21.1				

* Chemical shifts are expressed in ppm from TMS;
Solvente: a) $CDCl_3$, b) Piridine-d5, c) CDCl3/drops of piridine-d5;
d,e) Values bearing the same superscript in one column may be reversed.



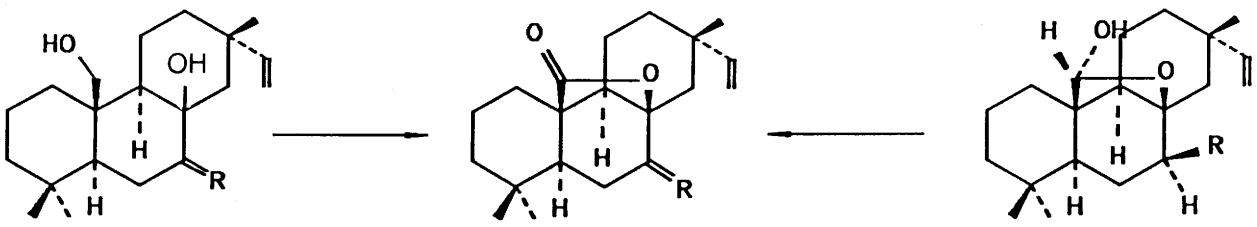
5b

Figure 2

Compound (**2**) showed a molecular ion $M^{+}\cdot$ at m/z 320 in accordance with the molecular formula $C_{20}H_{32}O_3$. The IR spectrum showed a broad band at 3190 cm^{-1} due to the hydroxyl and a carbonyl absorption at 1702 cm^{-1}. The ^1H NMR spectrum, in $CDCl_3$, was similar to that of (**1**) except for the presence of signals of the AMX pattern ($C\text{-}6_{ax}$, $C\text{-}6_{eq}$ and $C\text{-}5_{ax}$ hydrogens: δ 3.47 t, 14 Hz; 2.27, dd, J 14 and 2 Hz). The absence of the sp^3 methylene signal of C-14 at *ca* 50.0 ppm as in (**1**) suggests that C-7 is the site of the carbonyl group. This is confirmed by the deshielding effects observed at C-6 (17.6 ppm) and C-8 (4.9 ppm) and the shielding, resulting from a strong γ-gauche interaction, at C-14 whose signal appears at 40.5 ppm[5]. Acetylation of (**2**) with Ac_2O/DMAP afforded the monoacetylated derivate (**2a**), while oxidation with PCC yielded the γ-lactone (**2b**) (νCO = 1780 cm^{-1}).

Compound (**3**) showed a molecular ion $M^{+}\cdot$ at m/z 304 in accordance with the molecular formula $C_{20}H_{32}O_2$. The IR spectrum presented a band at 3310 cm^{-1} due to the hydroxyl group. The ^{13}C NMR spectrum exhibited a methine signal at 98.7 ppm indicating the hemiacetal function in (**3**), which was confirmed by the appearance of a singlet in the ^1H NMR spectrum at δ 5.50. Oxidation of (**3**) with PCC yielded the γ-lactone (**1b**) obtained from oxidation of (**1**). The configuration at C-20 was deduced by the chemical shift of C-1 which is shielded by 9.1 ppm, when

Scheme 1



1–R=H,H
2–R=O

1b–R=H,H
2b–R=O

3–R=H
4–R=OH

compared to (**1**), due to a strong γ-gauche interaction of its hydrogens with the hemiacetal hydroxyl. This was confirmed through a NOE experiment, which upon irradiation of the hydroxyl group at C-7 was defined from chetensity of the signal at δ 5.50 by about 35%.

Compound (**4**), $C_{20}H_{32}O_3$, showed ^1H NMR spectrum similar to that of (**3**), except for the presence of a carbinol methine signal at δ 3.30 (1H, dd, J 10 and 6 Hz) which accounted for a secondary hydroxyl group. The multiplicity of this signal demonstrated that the CHOH group was flanked by two hydrogens and, due to the value of its coupling constant, an axial orientation could be assigned to the carbinolic proton. Consequently, the hydroxyl was equatorial. The signal of the carbinolic proton moved downfield to δ 4.64 upon acetylation (**4a**). The localization of the hydroxyl group at C-7 was defined from chemmical shifts of C-6 and C-14 carbon atoms in the ^{13}C NMR spectrum. While C-6 is deshielded by the β effect, C-14 is shielded by the γ-effect (Table 1). This structure was confirmed through oxidation with PCC, which furnished the γ-lactone (**2b**), also obtained from oxidation of (**2**).

Compound (**5**), $C_{20}H_{32}O_3$, showed in the IR spectrum a band at 3440 cm^{-1} indicating an hydroxyl group. The ^1H and ^{13}C NMR spectra of (**5**) were similar to those of (**3**) except for the absence of vinyl group signal. Acetylation of (**5**) furnished (**5a**) ($C_{22}H_{34}O_4$), indicating the incorporation of only one acetate group. The IR spectrum of this compound did not show absorptions for hydroxyl group, demonstrating that the other oxygen atom belongs to an epoxide function, which was confirmed by ^{13}C NMR data (Table 1). Reduction of (**5**) with LAH afforded the triol (**5b**) (AB pattern C-20 H 3.98, 3.59, d, J 12 Hz; C-15 H 3.30, q, J 6 Hz). Upon treatment with MCPBA, compound (**3**) was converted to the γ-lactone epoxide (**5c**) (ν1750 cm^{-1}) which presented ^1H NMR signals at 2.68 and 2.66 (3H) corresponding to the hydrogens of oxirane ring (diasteroisomeric mixture).

Compound (**6**) showed the presence of hydroxyl functions (IR spectrum 3450 and 3250 cm^{-1}) which upon acetylation furnished a diacetate (**6a**) devoid of hydroxyl absorption in the IR spectrum. The observed molecular ion peaks at m/z 356 and 358 (proportion of 3:1) in the mass spectrum of (**6**) indicated the existence of a chlorine atom in its structure. The ^1H NMR spectrum of (**6**) exhibited signals belonging to three methyl groups (δ 1.12, 3H and 0.90, 6H), one hemiacetalic proton at δ 5.50 and the following signals at δ 3.80 (1H, dd, J 10 and 2 Hz), 3.51 (1H, t J 10 Hz) and 3.31 (1H, dd, J 10 and 2 Hz). These data indicated the occurrence of a chlorohydrin moiety at C-15, C-16 which was confirmed through the ^{13}C NMR spectrum (Table 1). Treatment of (**6**) with KOH/MeOH gave the epoxide (**5**) previously related, while oxidation with PCC afforded the γ-lactone-ketone (**6b**) (ν1760 and 1725 cm^{-1}).

As a consequence of the isolation of the chlorohydrin (**6**) together with the corresponding epoxide (**5**), it might be thought that (**6**) was an artefact of isolation as it is known that epoxides are very sensitive to acids and may incorporate Cl^- from the plant, silica gel or solvent, e.g. $CHCl_3$. However, in this case we have submitted the epoxide to the same work-up and the chlorohydrin was not detected, the epoxide being recovered.

Compound (**7**), $C_{18}H_{30}O_3$, showed ^1H and ^{13}C NMR spectra very similar with those of (**4**) except for the absence of the signals due to the vinyl group. The IR spectrum (ν3390 cm^{-1}) indicated the presence of hydroxyl group and the ^1H NMR spectrum demonstrated the presence of an hemiacetal group (δ 5.81, 1H, s) and also three methyl groups (δ 1.87, 3H, s and 0.90, 6H, s). These data suggest a structure of a (15,16)-bis-nor-isopimarane diterpene for (**7**) featuring an hydroxyl group at C-13 position. The axial orientation of the C-17 methyl was defined by the value of the signal of the ^1H NMR spectrum (δ 1.87) in C_5D_5N. This deshielding is attributed to an anisotropic effect due to the pyridine associaton with C-20 hydroxyl group, wich is positioned over the C-17 methyl.

Compound (**8**), $C_{18}C_{28}O_3$, showed the presence of hydroxyl and carbonyl groups (ν3340 and 1745 cm^{-1}), while the ^1H and ^{13}C NMR spectra indicated a similarity with compound (**2b**), except for the absence of a vinyl group. The C-17 methyl appeared at 27.3 ppm in the ^{13}C NMR spectrum, indicating an axial orientation[4]. Thus, the structure of (**8**) was characterized as a C-20, C-8-lactone-C-15(C-16)-bis-nor-isopimarane. Compound (**7**) was transformed into (**8**) by oxidation with PCC. The structure of the diterpenoid (**8**), and consequently of (**7**) were confirmed with the help of 'INADEQUATE' NMR experiments[6].

In addition to compounds (**1-8**), compound (**9**) (compactone), which was previously obtained from *V.compacta*[1], was also isolated from *V.bicolor*.

Experimental

Plant material - *V.bicolor* L.B. Smith was collected in Diamantina-MG, Brazil and identified by Dra. Nanuza L. de Menezes (Deptº de Botânica - Universidade de São Paulo - Brazil).

Isolation and separation - The dried plant (stems and leaf sheaths, 1.8 kg) were extracted with hexane followed by EtOAc. The later extract (67 g) was chromatographed (CC) on silica-gel 60 column (70-230 mesh) eluted with hex/EtOAc gradient. The fractions obtained were purified by crystallization and preparative TLC.

^1H NMR: 100 MHz; ^{13}C NMR: 25.3 MHz (TMS as int. standard).

Oxidation with PCC (general procedure)

The substrate was dissolved in dry CH_2Cl_2 and added to a suspension of PCC in CH_2Cl_2. The mixture was stirred at room temp. and monitored by TLC, being supplied with more PCC if necessary. When the reaction finished, dry Et_2O (*ca* 80 ml) was added and the mixture was stirred for 1-2 h. The supernatant layer was filtered through silica gel 60 and evaporated to dryness.

15-Isopimaren-8β, 20-diol (**1**) - CC: hex/EtOAc 9:1. Colourless needles (215 mg), m.p. 180-184°C (CCl_4).

$$[\alpha]^{25}_{max}\ \begin{matrix}-0.9 & -1.3 & -1.6 & -4.9\\ 589 & 578 & 546 & 436\end{matrix}\ (c0.86\ EtOH)$$

$$IR\nu^{KBr}_{max}\ 3160,\ 1645\ and\ 900\ cm^{-1}$$

MS m/z (rel. int.) 306,2646 $[M]^+$ (calc. for $C_{20}H_{34}O_2$: 306,2774), 288(17), 275(22). ^1H NMR ($CDCl_3$) δ 5.78 (1H, dd, J 17 and 10 Hz), 4.86 (1H, dd, J 17 and 2 Hz), 4.81 (1H, dd, J 10 and 2 Hz), 4.00 (1H, d, J 12 Hz), 3.59 (1H, d, J 12 Hz) - AB pattern, 1.30 (3H,s), 1.06 (3H,s) and 0.92 (3H,s). ^{13}C NMR - Table 1.

20-Acetoxy-15-isopimaren-8β-ol (**1a**) - Acetylation of (**1**) (68 mg) with Ac_2O/DMAP, 14 h, room temp., usual work up gave, after preparative TLC (hex/EtOAc 8:2), 65 mg (84%) of (**2b**) as a colourless oil; IR ν_{max}^{filme} 3470,1730 1640 and 900 cm^{-1}. MS m/z (rel.int.) 275(100), 270(24) and 257(25). ^1H NMR ($CDCl_3$) δ 5.75 (1H, dd, J 18 and 10 Hz), 4.87 (1H, dd, J 18 and 2 Hz), 4.83 (1H, dd, J 10 and 2 Hz), 4.82 (1H, d, J 12 Hz), 4.38 (1H, d, J 12 Hz) - AB pattern, 2.10 (3H,s), 1.24 (3H,s), 0.90 (3H,s) and 0.88 (3H,s).

15-Isopimaren-20,8-olide (**1b**) - Oxidation of (**1**) (59 mg), with PCC (82 mg), after 20 h, gave (**1c**) (50 mg, 86%). White solid, m.p. 180-184°C.

$[\alpha]_{max}^{25}$ -14.2 -14.9 -17.1 -31.1 (c0.94 EtOH)

589 578 546 436

IR ν_{max}^{KBr} 1752, 1640 and 930 cm^{-1}

MS m/z (rel. int.) 302 $[M]^+$ (**4**), 258(18), 256(16), 229(19), 216(81). ^1H NMR ($CDCl_3$) δ 5.79 (1H, dd, J 18 and 10 Hz), 4.84 (1H, dd, J 18 and 2 Hz), 4.81 (1H, dd, J 10 and 2 Hz), 1.10 (3H,s) and 0.92 (6H,s). ^{13}C NMR - Table 1.

8β,20-Dihydroxy-15-isopimaren-7-one (**2**) - CC: hex/EtOAc 85:15. Colourless crystals (158 mg), m.p. 156-158°C (hex/EtOAc).

$[\alpha]_{max}^{25}$ -73.9 -77.9 -91.3 -191.1 (c0.94 EtOH)

589 578 546 436

IR ν_{max}^{KBr} 3190, 1702, 1640 and 900 cm^{-1}

MS m/z (rel.int.) 320.2310 $[M]^+$ (Calc. for $C_{20}H_{32}O_3$: 320,2269), 302(18), 274(15), 261(57). ^1H NMR ($CDCl_3$) δ 5.79 (1H, dd, J 17 and 10 Hz), 4.92 (1H, dd, J 17 and 2 Hz), 4.84 (1H, dd, J 10 and 2 Hz), 4.10 (1H, d, J 12 Hz), 3.66 (1H, d, J 12 Hz) - AB pattern, 3.47 (1H, t, J 14 Hz), 2.27 (1H, dd, J 14 and 2 Hz), 1.24 (1H,s), 1.06 (3H,s) and 0.92 (3H,s). ^{13}C NMR - Table 1.

8β-Hydroxy-20-acetoxy-15-isopimaren-7-one (**2a**) - Acetylation of (**2**) (51 mg) with Ac_2O/DMAP, 12 h, 50°C, gave, after crystalization (hex/EtOAc), 2a (50 mg, 87%) as colourless crystals, m.p. 180-181°C. IR ν_{max}^{KBr} 3440, 1730, 1710 and 900 cm^{-1}. MS m/z (rel.int.) 362 $[M]^+$ (4), 344(2), 302(8), 289(36), 261(35). ^1H NMR ($CDCl_3$) δ 5.80 (1H, dd, J 18 and 10 Hz), 4.94 (1H, dd, J 18 and 2 Hz), 4.87 (1H, dd, J 10 and 2 Hz), 4.88 (1H, d, J 12 Hz), 4.56 (1H, d, J 12 Hz) - AB pattern, 2.98 (1H, t, J 14 Hz), 2.30 (1H, dd, J 14 and 2 Hz), 2.12 (3H,s), 1.26 (3H,s) and 0.97 (6H,s).

7-Oxo-15-isopimaren-20,8-olide (**2b**) - Oxidation of (**2**) (28 mg) with PCC (41 mg), after 15 h, gave (2b) (25 mg - 90%). Colourless crystals, m.p. 183°C (hex/EtOAc).

$[\alpha]_{max}^{25}$ -104.7 -110.0 -128.1 -253.9 (c0.75 EtOH)

589 578 546 436

IR ν_{max}^{KBr} 1780, 1730, 915 cm^{-1}

MS m/z (rel. int.) 316 $[M]^+$ (38), 298(13), 288(46), 272(22), 245(45). ^1H NMR ($CDCl_3$) δ 5.82 (1H, dd, J 18 and 10 Hz), 5.01 (1H, dd, J 18 and 2 Hz), 4.95 (1H, dd, J 10 and 2 Hz), 2.72 (1H, dd, J 16 and 12 Hz), 2.64 (1H, dd, J 16 and 6 Hz), 1.10 (3H,s), 0.96 (3H,s) and 0.91 (3H,s). ^{13}C NMR - Table 1.

8,20R-Epoxy-15-isopimaren-20R-ol (**3**) - CC: hex/EtOAc 9:1. Colourless crystals (207 mg), m.p. 151-154°C (hex/EtOAc).

$[\alpha]_{max}^{25}$ -53.9 -56.0 -63.3 -104.6 (c0.88 EtOH)

589 578 546 436

IR ν_{max}^{KBr} 3310, 1635 and 910 cm^{-1}

MS m/z (rel.int.) 304,2465 $[M]^+$ (calc for $C_{20}H_{32}O_2$: 304,2402) (100), 289(2), 286(4), 275(4), 258(17), 243(27). ^1H NMR ($CDCl_3$) δ 5.74 (1H, dd, J 18 and 11 Hz), 5.50 (1H,s), 4.87 (1H, dd, J 18 and 2 Hz), 4.81 (1H, dd, J 11 and 2 Hz), 4.00 (exchange with D2O), 1.20 (3H,s), 0.91 (3H,s) and 0.90 (3H,s). ^{13}C NMR - Table 1.

8,20R-Epoxy-15-isopimaren-7β-20R-diol (**4**) - CC: hex/EtOAc 8:2. Colourless Crystals (315 mg), m.p. 203°C (hex/EtOAc).

$[\alpha]_{max}^{25}$ -54.8 -56.7 -64.0 -105.0 (c0.96 EtOH)

589 578 546 436

IR ν_{max}^{KBr} 3450, 1640 and 925 cm^{-1}

MS m/z (rel. int.) 320,2354 $[M]^+$ (calc. for $C_{20}H_{32}O_3$: 320,2357) (100), 302(15), 274(12), 256(8), 245(15). ^1H NMR ($CDCl_3$/drops of C_5D_5N) δ 5.83 (1H, dd, J 17 and 10 Hz), 5.55 (1H,s), 4.93 (1H, dd, J 17 and 2 Hz), 4.84 (1H, dd, J 10 and 2 Hz), 3.50 (exchange with D2O), 3.30 (1H, dd, J 10 and 6 Hz), 2.2 (m), 1.28 (3H,s) and 0.90 (6H,s). ^1H NMR (C_5D_5N) δ 5.90 (1H, dd, J 17 and 10 Hz), 5.77 (1H,s), 5.00 (1H, dd, J 17 and 2 Hz), 4.88 (1H, dd, J 10 and 2 Hz), 3.50 (1H, dd, J 10 and 6 Hz), 1.48 (3H,s), 0.87 (3H,s) and 0.85 (3H,s). ^{13}C NMR -Table 1.

8,20R-Epoxy-7β,20R-diacetoxy-15-isopimaren (**4a**) - Acetylation of (**4**) (52 mg) with Ac_2O/DMAP, 16 h, room temp., and usual work up gave, after recrystallization, 60 mg of (**4a**) (91%) as colourless crystals, m.p. 201-202°C (hex/EtOAc).

IR ν_{max}^{KBr} 1735, 1635 and 970 cm^{-1}. MS m/z (rel.int.) 404 $[M]^+$ (43), 352(9), 344(13), 276(5) and 256(6). ^1H NMR ($CDCl_3$) δ 6.46 (1H,s), 5.79 (1H, dd, J 18 and 10 Hz), 4.93 (1H, dd, J 18 and 2 Hz), 4.88 (1H, dd, J 10 and 2 Hz), 4.64 (1H, dd, J 10 and 6 Hz), 2.10 (3H,s), 2.08 (3H,s), 1.00 (3H,s) and 0.92 (3H,s). ^{13}C NMR - Table 1.

Oxidation of (**4**) to (**2b**) - 35 mg of (**4**) were oxidized with PCC (28 mg), giving (**2b**) (29 mg, 82%) after 15 h [(m.p., [α], IR, ^1H NMR identical to (**2b**) obtained from (**2**)].

8,20R: 15ξ,16-Diepoxy-20R-isopimaranol (**5**) - CC: hex/EtOAc 85:15. Purified by recrystallization and preparative TLC (hex/EtOAc 8:2; 2x). Colourless crystals (200 mg), m.p. 138°C (hex/EtOAc).

$[\alpha]^{25}_{max}$ -54.4 -56.8 -64.5 -108.8 (c1.00 EtOH)
589 578 546 436

IR ν^{KBr}_{max} 3340, and 920 cm^{-1}

MS m/z (rel.int.) 320,2291 $[M]^+$ (calc. for $C_{20}H_{32}O_3$: 320,2231) (83), 302(2), 289(5), 259(9), 243(9). ^1H NMR ($CDCl_3$) δ 5.50 (1H,s), 2.66 (3H, broad s), 1.11 (3H,s) and 0.91 (6H,s). ^1H NMR ($CDCl_3$/drops of C_5D_5N) δ 5.56 (1H,s), 2.64 (3H,m), 1.20 (3H,s) and 0.88 (6H,s). ^{13}C NMR - Table 1.

8,20R: 15ξ,16-Diepoxy-20R-isopimaranolacetate (**5a**) - Acetylation of (**5**) (80 mg) with Ac_2O/DMAP, 12 h room temp., and usual work up, gave, after purification on preparative TLC (hex/EtOAc 85:15), 70 mg (77%) of (**5b**) (oil).

MS m/z (rel.int.) 362 $[M]^+$ (18), 320(12), 302(12), 302(9), 259(14), 231(6) and 216(10). ^1H NMR ($CDCl_3$) δ 6.36 (1H,s), 2.68 (3H,s), 2.08 (3H,s), 1.02 (3H,s), 0.97 (3H,s) and 0.89 (3H,s). ^{13}C NMR - Table 1.

8β,15ξ,20-Isopimaranetriol (**5b**) - To 61 mg of (**5**) in dried THF (15 ml) were added 121 mg of LAH. After 12 h at room temp. and magnetic stirring, the excess of LAH was consumed by 2N HCl. The reaction mixture was extracted with Et_2O (3x, 20 ml), affording, after drying(Na_2SO_4) and evaporation of the solvent, an oily mass. This was purified by preparative TLC (hex/EtOAc 1:1), resulting (**5b**) as a white solid (53 mg, 85%). ^1H NMR ($CDCl_3$) δ 3.98 (1H, d, J 12 Hz), 3.59 (1H, d, J 12 Hz) - AB pattern, 3.30 (1H, q, J 6 Hz), 1.10 (3H,s), 1.08 (3H, d, J 6 Hz), 1.01 (3H,s) and 0.90 (3H,s). Double irradiation experiments at δ 3.30 changed the signal at δ 1.08 into a singlet.

15,16-Epoxy-20,8-isopimaranolide (**5c**) - diastereoisomeric mixture in C-15 - MCPA (20 mg) was added to (**2**) (18 mg) in CH_2Cl_2 (30 ml). The reaction was monitored by TCL and more MCPA (20 and 10 mg) was necessary to consume (**2**) (48 h). The mixture was dissolved in $CHCl_3$ (20 ml), extracted with NaOH 1N (20 ml, 3x), washed with brine, dried (Na_2SO_4) and evaporated, affording (**5c**) (13 mg, 73%) as colourless crystals. IR ν^{KBr}_{max} 1750 cm^{-1}.

^1H NMR ($CDCl_3$) δ 2.68 and 2.66 (2nd order pattern, 3H), 1.27 (6H,s) and 0.90 (3H,s).

16-Chloro-8,20R-epoxy-15ξ,20-isopimaranediol (**6**) - CC: hex/EtOAc 85:15. Colourless crystals (265 mg), m.p. 162°C (hex/EtOAc).

$[\alpha]^{25}_{max}$ -36.9 -38.4 -43.1 -67.5 (c0.95 EtOH)
589 578 546 436

IR ν^{KBr}_{max} 3450, 3250 and 900 cm^{-1}

MS m/z (rel.int.) 358,2059 $[M + 2]^+$ (31), 356,2162 $[M]^+$ (100), (calc. for $C_{20}H_{33}O_3Cl$: 358,2031 and 356,2206, respectively), 320(18), 310(18), 295(10) and 231(61). ^1H NMR ($CDCl_3$) δ 5.50 (1H,s), 3.80 (1H, dd, J 10 and 1.5 Hz), 3.51 (1H, t, J 10 Hz), 3.31 (1H, dd, J 10 and 1.5 Hz), 1.12 (3H,s) and 0.90 (6H,s). ^{13}C NMR - Table 1.

16-Chloro-8,20R-epoxy-15ξ,20-isopimaranediol diacetate (**6a**) - Acetylation of (**6**) (36 mg) with Ac_2O/DMAP, 12 h, room temp., gave, after purification by preparative TLC, (hex/EtOAc 80:20; 2X) (**6a**) (29 mg, 65%) as a yellow solid.

IR ν^{KBr}_{max} 1725 cm^{-1}. ^1H NMR ($CDCl_3$3) δ 6.30 (1H,s), 4.84 (1H, dd, J 10 and 3 Hz), 3.72 (1H, dd, J 13 and 3 Hz), 3.55 (1H, dd, J 13 and 10 Hz), 2.12 (3H,s), 2.07 (3H,s), 1.06 (3H,s), 0.96 (3H,s) and 0.90 (3H,s).

16-Chloro-15-oxo-20,8-isopimaranolide (**6b**) - Oxidation of (**6**) (33 mg) with PCC (70 mg) gave after 24 h (**6b**) (24 mg, 74%), which was purified by preparative TLC (hex/EtOAc 80:20). Colourless crystals, m.p. 135°C.

IR ν^{KBr}_{max} cm^{-1} 1760, 1725 and 940 cm^{-1}; MS m/z (rel.int.) 275(34), 231(42), 230(26) and 229(100). ^1H NMR ($CDCl_3$) δ 4.22 (2H,s), 1.35 (3H,s) and 0.90 (6H,s).

Transformation of (**6**) in (**5**) - A solution of (**6**) (15 mg) in 2N KOH (5 ml) was stirred at room temp. for 2 h. The mixture was concentrated to *ca* 2 ml, diluted with $CHCl_3$ (20 ml) and extracted with water (20 ml, 2x).The organic layer was dried (Na_2SO_4) and evaporated, affording (**5**) as colourless crystals (12 mg, 89%): m.p., [α], ^1H NMR, IR and MS spectra.

8,20-Epoxy-15,16-bis-nor-isopimaran-13,20R-diol (**7**) - CC: hex/EtOAc 1:1. Amorphus white powder (96 mg).

IR ν^{KBr}_{max} 3390 and 910 cm^{-1}. MS m/z (rel.int.) 294 $[M]^+$ (36), 276(4), 230(6), 215(15), 161(51). ^1H NMR (C_5D_5N) δ 5.81 (1H,s), 5.50 (1H, exchange with D_2O), 1.87 (3H,s) and 0.90 (6H,s).

13-Hydroxy-15,16-bis-nor-isopimaran-20,8-olide (**8**) - CC: hex/EtOAc 75:25. Colourless crystals (1.5 g), m.p. 173°C (hex/EtOAc).

$[\alpha]^{25}_{max}$ -9.8 -9.9 -11.6 -22.1 (c0.96EtOH)
589 578 546 436

IR ν^{KBr}_{max} 3420, and 1745 cm^{-1}

MS m/z (rel.int.): 292,2028 $[M]^+$ (calc. for $C_{18}H_{28}O_3$: 292,2028) (3), 277(5), 274(2), 230(100), 215(28) and 161(56). ^1H NMR ($CDCl_3$) δ 1.30 (3H,s) and 0.90 (6H,s). ^1H NMR (C_5D_5N) δ 1.50 (3H,s), 0.97 (3H,s) and 0.84 (3H,s). ^{13}C NMR - Table 1.

Transformation of (**7**) into (**8**) - Oxidation of (**7**) (19 mg) with PCC (15 mg), gave (**8**) (15 mg, 80%) after 15 h (m.p., [α], IR, ^1H NMR and MS spectra).

8β-Hydroxy-15-isopimaren-7-one [*compactone*, (**9**)][1] - CC: hex/EtOAc 95:5. Colourless crystals (213 mg), m.p. 217°C (hex/EtOAc).

IR ν_{max}^{KBr} 3500, 1700, 1650 and 910 cm^{-1}. MS m/z (rel.int.) 304(100), 286(18) and 167(20). ^1H NMR (C_5D_5N) δ 6.22 (1H,s, exchange with D_2O), 5.84 (1H, dd, J 17 and 10 Hz), 4.93 (1H, dd, J 17 and 1.5 Hz), 4.84 (1H, dd, J 10 and 1.5 Hz), 3.16 (1H, dd, J 13 and 12 Hz), 2.24 (1H, dd, J 12 and 3 Hz), 1.36 (3H,s), 1.30 (3H,s), 0.88 (3H,s) and 0.80 (3H,s).

Acknowledgements

This work was supported by grants from FINEP, CNPq and CEPG-UFRJ and was performed at the Núcleo de Pesquisas de Produtos Naturais/UFRJ. The authors are indebted to Dra. Nanuza L. de Menezes (IB-USP) for identification of the plant.

References

1. A.C. Pinto, A.J.R. Silva, L.M.U. Mayer and R. Braz Fº, *Phytochemistry* **18**, 2036-2037 (1979).
2. J.W. Rowe, *The Common and Systematic Nomenclature of Cyclic Diterpenes* (U.S. Forest Products Laboratory, Madison, 1968).
3. A.C. Pinto, W.S. Garcez, R.S. Silva, L.M.M. Valente, E.M. Peixoto, P.P.S. Queiroz and A.L. Pereira, *J. Chem. Res.* (S), 154-155 (1982) and *J. Chem. Res.* (M) 1701-1709 (1982).
4. R. Beier, *Org. Mag. Res.* **11**, 586 (1978).
5. B. Dockerill, J.R. Hanson and M. Siverns, *Phytochemistry* **17**, 572-573 (1978).
6. A.C. Pinto, W.S. Garcez, W.E. Hull, A. Neszmelyi and G. Lukacs, *J. Chem. Soc., Chem. Commun.* 464-465 (1983).