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DITERPENES FROM *VELLOZIA PATENS*

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Key Word Index—*Vellozia patens*; Velloziaceae; isopimarene type diterpenes.

Abstract—Eight new diterpenes with isopimarane skeleton have been isolated from *Vellozia patens*. Their structures were elucidated by spectroscopic methods and by chemical transformations.

INTRODUCTION

From the ethyl acetate extracts of roots, stem and leaf sheaths of *Vellozia patens* L. B. Smith & Ayensu, we have isolated eight new diterpenes with the isopimarane skeleton (**4**, **6**, **8**, **10**, **16**, **17**, **19**, **23**), similar to those found in other species of this family during previous studies [1–4] (e.g. **1**–**3**). Four of them, which possess a hydroxyl group at C-14 (Group II), are uncommon in nature. The first members of this series were isolated from *Vellozia variabilis* [3]. The structures of these compounds have been elucidated on the basis of their spectral data, chemical transformations and comparison with known isopimaranes.

RESULTS AND DISCUSSION

Mass spectrometry of the isolated compounds indicated their diterpenoid composition. These diterpenes contain the isopimarane skeleton as is clearly indicated by: the singlet signals in the ^{1}H NMR spectra for three (**4**, **6**, **8**, **10**, **19** and **23**) or four (**16** and **17**) tertiary methyl groups bonded to sp^3 carbon atoms; the signals characteristic of a tertiary vinyl group; the IR bands at *ca* 1640, 980 and 915 cm^{-1}, and the ^{1}H NMR signals for the olefinic protons [an ABX pattern at *ca* δ4.8 (1H, *dd*, J_{gem} and J_{cis}), 5.0 (1H, *dd*, J_{gem} and J_{trans}) and 5.7 (1H, *dd*, J_{cis} and J_{trans}) and the ^{13}C NMR spectra signals at *ca* δ150 (*d*) and 110 (*t*)]. The ^{13}C NMR data also proved that these diterpenes are not of the rosane group [5].

Group I

The spectral data of **4** suggested two hydroxyl groups and an acetyl group. This information, together with the molecular formula, $C_{22}H_{36}O_4$, obtained from the HR mass spectrum, indicated that **4** is correlated with compactotriol (**3**) previously isolated from *Vellozia compacta* [4]. The main difference between these two diterpenes is the shielded AB pattern in the ^{1}H NMR spectrum at δ3.71 (1H, *d*, J=11 Hz) and 3.90 (1H, *d*, J=11.0 Hz), corresponding to the C-18 protons of compound **4**. Localization of the acetyl group at the C-18 equatorial position was deduced from the chemical shifts of C-18 and C-5, which were found to be in agreement with the proposed stereochemistry (Table 1).

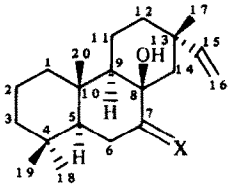
Some simple reactions have confirmed the proposed structure of **4**. The spectral data of its basic hydrolysis product were identical to those of compactotriol. Acetylation of **3** gave a mixture of the mono and diacetylated derivatives (3:1). The mono acetylated product, separated from the mixture, was identical with 18-acetoxy-15-isopimaren-7β,8-diol, isolated from the plant.

The HR mass spectrum indicated that **6** has the molecular formula $C_{20}H_{32}O_4$ ([M]$^+$ 336.2300). The IR absorption bands at 3500 and 1725 cm^{-1} show that one of the methyl groups of the pimarane skeleton of **1** had been oxidized to form carboxylic acid. The ^{13}C NMR

Table 1. ^{13}C NMR spectral data of *Vellozia patens* diterpenes ($CDCl_3$, TMS=0)*

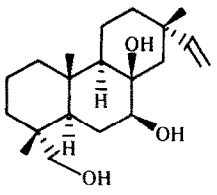
C	**4**	**6**	**8**	**10**	**16**	**17**	**19**
1	39.0	38.8	39.2	39.0	39.6	39.7	39.1
2	17.5	17.9	17.6	17.8	18.3	18.3	18.1
3	35.6	38.1	35.2	38.0	41.8	41.7	37.1
4	36.0	47.2	38.3	47.4	33.0	33.9	47.1
5	46.7	47.4	49.1	50.2	53.0	56.5	47.5
6	26.9	29.8	34.9	37.4	26.0	35.5	29.9
7	77.2	77.0	212.0	209.2	79.1	214.2	79.4
8	73.9	74.2	76.8	76.4	74.3	76.9	75.1
9	55.1	55.9	58.9	58.9	55.0	57.3	55.1
10	36.3	36.3	36.3	36.5	36.9	36.5	36.7
11	16.8	16.9	16.8	16.7	16.1	15.7	16.4
12	37.2	37.2	37.9	37.2	37.3	37.5	37.2
13	36.7	36.3	37.2	36.9	42.4	40.7	42.2
14	47.0	47.4	42.9	42.7	82.1	74.7	82.4
15	151.3	151.7	151.0	151.4	148.2	148.2	148.5
16	108.3	108.2	108.8	108.6	113.0	111.0	110.6
17	24.4	24.4	24.8	24.7	16.1	17.5	17.1
18	72.5	181.4	70.7	180.0	33.3	32.9	180.8
19	17.5	16.7	17.3	16.5	21.4	21.2	17.0
20	15.9	16.0	15.6	15.7	15.1	15.3	16.4
COMe	171.0						
COMe	21.0						

*Assignments aided by DEPT sequence and comparison with related compounds.



X

1 β-OH,H
2 O



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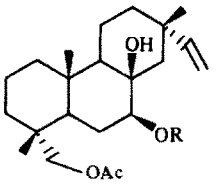
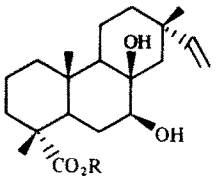


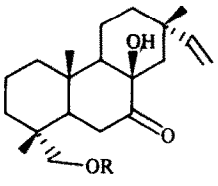
R

4 H
5 Ac



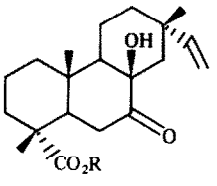
R

6 H
7 Me



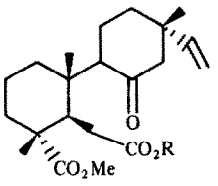
R

8 H
9 Ac



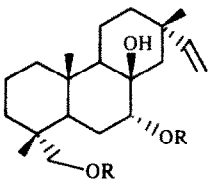
R

10 H
11 Me



R

12 H
13 Me



R

14 H
15 Ac

analysis showed a perfect correlation with other isopimarane diterpenes (Table 1) and led us to attribute the position of the carboxylic acid at C-18. The chemical shifts were assigned by referring the A ring to sandaracopimaradienic acid [6] and the B/C rings to **1** [4]. The carboxyl group at C-18 deshields C-4 (+14.1) and shields C-3 (−3.8), C-5 (−5.7) and C-19 (−4.9) when compared with compactol. Like other natural C-7 hydroxylated isopimaranes found in the Velloziaceae family, the hydroxyl group of **6** has a β-equatorial configuration, demonstrated by the C-7 proton coupling constants in the ^{1}H NMR spectrum (δ3.46, *dd*, $J_{ax,eq}$ = 4.5 and $J_{ax,ax}$ = 12.0 Hz). The structure was confirmed through reaction with diazomethane and the reduction of the methyl ester with $LiAlH_4$, yielding **3**.

The $[M]^+$ at *m/z* 320 in the EI mass spectrum of **8** indicated that this diterpene has the molecular formula $C_{20}H_{32}O_3$. The IR spectrum showed the presence of hydroxyl and carbonyl groups. The ^{1}H NMR spectrum ($CDCl_3$) showed signals of an ABX pattern at δ2.17 (1H, *dd*, $J_{eq,ax}$ = 3.0 and J_{gem} = 14.0 Hz) and 3.02 (1H, *dd*, $J_{ax,ax}$ = 13.0 and J_{gem} = 14.0 Hz) for the equatorial and axial C-6 hydrogens adjacent to the carbonyl group.

The effects of the carbonyl group at C-7 and the β-hydroxyl group at C-8, with a 1,3-diaxial interaction with H-6β, moved this signal downfield in a similar manner to the effects observed in **2** in relation to **1**. The carbonyl group at C-7 shields C-14 (−4.8) and deshields C-8 (+2.8) and C-6 (+7.6) when compared to **3**.

To confirm the proposed structure we obtained **8** through the oxidation of the C-7 hydroxyl group of **3**. Oxidation of **4** (Swern conditions) [7, 8] afforded **9** in high yield. Hydrolysis of **9** afforded **8**, identical with the natural product.

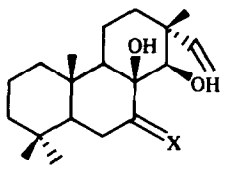
The molecular formula of **10**, $C_{20}H_{30}O_4$, was obtained by HR mass spectrometry ($[M]^+$ obs. 334.2149). The IR spectrum revealed the presence of hydroxyl (broad bands at 3540 and 3280 cm^{-1}) and carbonyl (1700 cm^{-1}) groups. The ^{1}H NMR data of **10** suggested that this diterpene is correlated with compactoic acid (**6**). Like the pair **8**/**3**, the difference between these two compounds is related to the carbonyl group at C-7. Like compactone, the ^{1}H NMR spectrum of **10**, in pyridine-d_5, showed signals of the CH–CH_2–C=O system at δ2.20 (1H, *dd*, $J_{eq,ax}$ = 3.0 and J_{gem} = 14.0 Hz) and 3.24 (1H, *dd*, $J_{ax,ax}$ = 13.0 and J_{gem} = 14.0 Hz). The axial hydrogen underwent a downfield shift of δ0.18 on changing from chloroform-*d* to pyridine-d_5 solution, establishing a *syn*-diaxial relationship with the hydroxyl group at C-8.

The reaction of **11** with Jones reagent furnished the same product (**12**) of oxidative cleavage observed in the reaction of **7** with the same reagent [9]. The reduction of the methyl ester of **11** with $NaBH_4$ in methanol yielded an epimeric mixture of diols. However, reduction of **11** with $LiAlH_4$ yielded only one product with OH-7α (epimeric compactotriol, **14**). The acetylated product of **14** (Ac_2O–DMAP; **15**) when compared with the corresponding compactotriol diacetate (**5**) shows the epimeric relationship of the two diterpenes. The C-7 hydrogen of **15** and the C-7 hydrogen of **5** appear in the ^{1}H NMR spectrum at δ4.62 (*dd*, $J_{eq,eq}$ = 3.0 and $J_{eq,ax}$ = 4.0 Hz) and 4.53 (*dd*, $J_{ax,eq}$ = 5.0 and $J_{ax,ax}$ = 11.0 Hz), respectively. The stereoselectivity of this reaction is due to the initial formation of an alkoxymetal hydride complex followed by an intramolecular hydride attack over the β face of the molecule.

The CD curve of **10** showed a negative Cotton effect ($[\theta]_{295}$ −4813); one may, thus, conclude that **10** is a diterpene of the normal series. Consequently, diterpenes **8**, **6** and **4** belong to the same series.

Group II

The ^{1}H NMR spectra of the compounds of this group were similar to those of the previous isopimarane diterpenes, except for the presence of a singlet signal in the δ3.3–3.8 range, consistent with a hydroxyl group in equatorial orientation at C-14. The most remarkable effects observed for these diterpenes are correlated with the hydroxyl functionalization of C-14. The stereochemistry of this hydroxyl group was determined by the high field position of C-17. The shielding was due to the strong γ-gauche effect of the hydroxyl group (Table 1) [10]. However, the chemical shift of C-12 was not affected, as

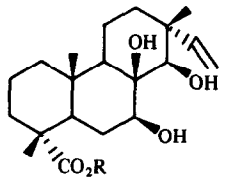


X

16 β-OH,H

17 O

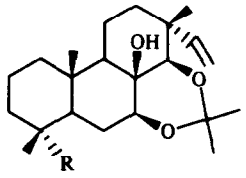
18 α-OH,H



R

19 H

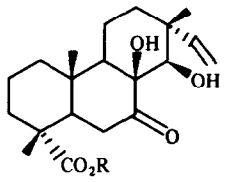
20 Me



R

21 Me

22 CO_2Me



R

23 H

24 Me

the equatorial orientation of the hydroxyl group at C-14 precludes the occurrence of a γ-gauche interaction with the hydrogens of this carbon. The mass spectra of the 14-hydroxy-7-oxo-isopimaranes of this group gave fragments at *m/z* $[M-98]^+$ due to loss of $C_6H_{10}O$ resulting from cleavage of the bonds between C-8/C-14 and C-11/C-12. The molecular formulae of **16**, **17** and **19** were determined to be $C_{20}H_{34}O_3$, $C_{20}H_{32}O_3$ and $C_{20}H_{32}O_5$ by HR mass spectrometry, respectively.

The ^{1}H NMR spectrum of **16** showed a signal at δ 3.64 (1H, *dd*, $J_{ax,eq}=6.0$ and $J_{ax,ax}=10.0$ Hz) for the hydrogen at C-7. It demonstrated that, like all the isopimarenes until now isolated from Velloziaceae, the hydroxyl group at C-7 has a β-equatorial configuration.

Treatment of **16** with acetone in the presence of drops of conc. HCl gave the acetonide (**21**). This same acetonide was obtained from **17** by reduction with $NaBH_4$ in methanol affording a mixture of C-7 epimeric triols (**16** and **18**). The major epimer was transformed into the acetonide through the same conditions used for **16**.

The ^{1}H NMR spectrum of the acid diterpene **19** was very similar to that of **16** except for the presence of only three methyl groups and by the presence of a carboxyl group absorption band in the IR spectrum. The localization of the carboxyl group at C-18 was deduced in the same way as that presented for diterpene **6** of Group I. Both **16** and the methyl ester derivative of **19** (**20**) were oxidized with Swern reagent to furnish **17** and **24**, respectively. The first compound was identical in all respects with the natural diterpene **17**. The diterpene **19** also formed an acetonide when it was treated with acetone in the presence of drops of conc. HCl.

Finally, the absolute configuration of **17**, and consequently of **16**, was deduced from the negative Cotton effect of its CD curve ($[\theta]_{297}$ −1018). As **19** was isolated from the same plant, it can be assumed that this diterpene has the same absolute configuration as that shown for **16** and **17**.

In spite of the minute amount of the acid **23** available, its structure was proposed by comparison of the spectral data of its methyl ester (**24**) with those of the synthetic product obtained by the Swern oxidation [7] of **20**.

EXPERIMENTAL

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

Vellozia patens L. B. Smith & Ayensu 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 EtOAc after preliminary extraction with hexane. The crude EtOAc extract (45 g) was chromatographed on a silica gel column (100 g). Elution was started with hexane and the polarity of the eluent gradually increased with EtOAc. The products were eluted in the following order: **17**, **16**, **8**, **4**, **10**, **6**, **23** and **19**. Further purification was carried out using smaller silica gel columns, by prep. TLC or by repeated recrystallizations.

18-Acetoxy-15-isopimaren-7β,8-diol (**4**). Crystals from hexane–EtOAc (23:2), mp 121°, 2.31% dry wt. $[\alpha]_D^{28}$ −3.0° (MeOH; *c* 0.917). IR ν_{max}^{KBr} cm^{-1}: 3500, 2950, 1725, 1635, 1375, 1260, 1040, 985 and 915; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.88 (3H, *s*), 1.05 (3H, *s*), 1.24 (3H, *s*), 2.07 (3H, *s*, H-22), 2.46 (1H, *sl*, changed with D_2O), 3.26 (1H, *dd*, $J_{ax,eq}=6.0$ and $J_{ax,ax}=9.0$ Hz, H-7), 3.71 (1H, *d*, $J_{gem}=11.0$ Hz, H-18), 3.90 (1H, *d*, $J_{gem}=11.0$ Hz, H-18), 4.79 (1H, *dd*, $J_{gem}=1.5$ and $J_{cis}=10.0$ Hz, H-16), 4.84 (1H, *dd*, $J_{gem}=1.5$ and $J_{trans}=18.0$ Hz, H-16) and 5.74 (1H, *dd*, $J_{cis}=10.0$ and $J_{trans}=18.0$ Hz, H-15); ^{13}C NMR: Table 1; EIMS (probe) 70 eV, *m/z* (rel. int.): 364 $[M]^+$ (22), 349 $[M-15]^+$ (60), 293 $[M-71]^+$ (65), 273 $[M-91]^+$ (50), 255 $[M-109]^+$ (40), 205 $[M-159]^+$ (61), 189 $[M-175]^+$ (79), 161 $[M-203]^+$ (59), 147 $[M-217]^+$ (55), 123 $[M-241]^+$ (81), 109 $[M-255]^+$ (100), 93 $[M-271]^+$ (71) and 81 $[M-283]^+$ (70). HRMS: found, *m/z* 364.2635 ($C_{22}H_{36}O_4$ requires 364.2613).

Hydrolysis of 18-acetoxy-15-isopimaren-7β,8-diol (**4**). Compound **4** (19.5 mg) was added to a 1% soln of KOH in EtOH (2 ml) and refluxed for 4 hr. After neutralization with HCl and extraction with $CHCl_3$ 18.9 mg (97.1%) of compactotriol (**3**) [4] was obtained.

Preparation of compound 4 from compactotriol (**3**). A soln of **3** (120 mg) in Ac_2O was left at room temp. for 12 hr. After the usual work-up and purification through prep. TLC 81.3 mg (60%) of a crystalline compound was isolated and identified as **4** [4], together with 30 mg (20%) of an oil identified as 7β,18-diacetoxy-15-isopimaren-8-ol (**5**) (data below) and 10 mg of substrate **3**. **5**: IR ν_{max}^{film} cm^{-1}: 3670, 2950, 1760, 1620, 1460, 1380, 1250, 915, 862 and 810; ^{1}H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ 0.87 (3H, *s*), 1.05 (3H, *s*), 1.23 (3H, *s*), 2.70 (3H, *s*), 2.90 (3H, *s*), 3.61 (1H, *d*, $J_{gem}=11.0$ Hz, H-18), 3.85 (1H, *d*, $J_{gem}=11$ Hz, H-18), 4.53 (1H, *dd*, $J_{ax,eq}=5.0$ and $J_{ax,ax}=11.0$ Hz, H-7), 4.80 (1H. *dd*, $J_{gem}=2.0$ and $J_{cis}=10.0$ Hz, H-16), 4.84 (1H, *dd*, $J_{gem}=2.0$ and $J_{trans}=18.0$ Hz, H-16) and 5.70 (1H, *dd*, $J_{cis}=10.0$ and $J_{trans}=18.0$ Hz, H-15).

7β,8-Dihydroxy-15-isopimaren-18-oic acid (**6**). Crystals from hexane–EtOAc (1:1), mp 180–181°, 1.24% dry wt. $[\alpha]_D^{28}$ +6.4° (MeOH; *c* 5.141). IR ν_{max}^{KBr} cm^{-1}: 3500, 2950, 1725, 1460, 1395, 1720, 1170, 1070, 998–983, 918 and 810; ^{1}H NMR (100 MHz, $CDCl_3$–pyridine-d_5, TMS an int. standard): δ 0.88 (1H, *dd*, *J* = 2.5 and 11.0 Hz), 1.10 (3H, *s*), 1.25 (3H, *s*), 1.27 (3H, *s*), 3.46 (1H, *dd*, $J_{ax,eq}=4.5$ and $J_{ax,ax}=12.0$ Hz, H-7), 4.74 (1H, *dd*, $J_{gem}=2.0$ and $J_{cis}=10.0$ Hz, H-16), 4.82 (1H, *dd*, $J_{gem}=2.0$ and $J_{trans}=18.0$ Hz, H-16) and 5.74 (1H, *dd*, $J_{cis}=10.0$ and $J_{trans}=18.0$ Hz, H-15); ^{13}C NMR: Table 1; EIMS (probe) 70 eV, *m/z* (rel. int.): 336 $[M]^+$ (28), 318 $[M-18]^+$ (39), 265 $[M-71]^+$ (56), 223 $[M-113]^+$ (45), 109 $[M-127]^+$ (63), 107 $[M-229]^+$ (83), 81 $[M-255]^+$ (68), 67 $[M-269]^+$ (45), 55 $[M-281]^+$ (65) and 43 $[M-293]^+$

(100). HRMS: found, *m/z* 336.2304 ($C_{20}H_{32}O_4$ requires 336.2300).

Methyl 7β,8-dihydroxy-15-isopimaren-18-oate (**7**). Treatment of the acid **6** with CH_2N_2 yielded crystals of **7**, mp 130–132°. IR ν_{max}^{KBr} cm^{-1}: 3500, 3380, 2950, 1740, 1640, 1240, 1090, 988–975 and 915; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ1.02 (3H, *s*), 1.21 (3H, *s*), 1.23 (3H, *s*), 1.74 (2H, *sl*, changed with D_2O), 3.36 (1H, *dd*, $J_{ax,eq}$ = 4.0 and $J_{ax,ax}$ = 12.0 Hz, H-7), 3.66 (3H, *s*, H-21), 4.81 (1H, *d*, J_{cis} = 10.0 Hz, H-16), 4.85 (1H, *d*, J_{trans} = 18.0 Hz, H-16) and 5.73 (1H, *dd*, J_{cis} = 10.0 and J_{trans} = 18.0 Hz, H-15); EIMS (probe) 70 eV, *m/z* (rel. int.): 350 $[M]^+$ (39), 332 $[M-18]^+$ (41), 278 $[M-72]^+$ (57), 257 $[M-93]^+$ (47), 123 $[M-227]^+$ (96), 109 $[M-241]^+$ (100), 81 $[M-269]^+$ (85) and 55 $[M-295]^+$ (98).

Reduction of **7** *with* $LiAlH_4$. To a soln of **7** (20 mg) in dioxane (5 ml) an excess of $LiAlH_4$ was added. After 4 hr at room temp., followed by the usual work-up, a crystalline compound was obtained (18.1 mg, 98.4%) and identified as compactotriol (**3**) [4].

8,18-Dihydroxy-15-isopimaren-7-one (**8**). Crystals from hexane, mp 190–191°, 0.03% dry wt. IR ν_{max}^{KBr} cm^{-1}: 3450, 2850, 1700, 1630, 990 and 905; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ0.83 (3H, *s*), 1.26 (6H, *s*), 2.17 (1H, *dd*, $J_{eq,ax}$ = 3.0 and J_{gem} = 14.0 Hz, H-6α), 3.02 (1H, *dd*, $J_{ax,ax}$ = 13.0 and J_{gem} = 14.0 Hz, H-6β), 3.06 (1H, *d*, J_{gem} = 12.0 Hz, H-18), 3.42 (1H, *d*, J_{gem} = 12.0 Hz, H-18), 3.64 (1H, *s*, OH), 4.22 (1H, *sl*, OH), 4.81 (1H, *dd*, J_{gem} = 1.5 and J_{cis} = 10.0 Hz, H-16), 4.88 (1H, *dd*, J_{gem} = 1.5 and J_{trans} = 18.0 Hz, H-16) and 5.72 (1H, *dd*, J_{cis} = 10.0 and J_{trans} = 18.0 Hz, H-15); ^{13}C NMR: Table 1; EIMS (probe) 70 eV, *m/z* (rel. int.): 320 $[M]^+$ (6), 302 $[M-18]^+$ (3), 215 $[M-105]^+$ (24), 189 $[M-131]^+$ (16), 165 $[M-155]^+$ (36), 149 $[M-171]^+$ (20), 138 $[M-182]^+$ (16), 139 $[M-181]^+$ (18), 123 $[M-197]^+$ (100), 121 $[M-199]^+$ (30), 109 $[M-211]^+$ (54), 107 $[M-213]^+$ (30), 95 $[M-225]^+$ (50) and 81 $[M-239]^+$ (48).

18-Acetoxy-8-hydroxy-15-isopimaren-7-one (**9**). Compound **4** (50 mg) was oxidized using the procedure described in ref. [7] (Swern conditions) yielding, after work-up and purification through prep. TLC, 41.4 mg (83%) of **9**. IR ν_{max}^{KBr} cm^{-1}: 3600–3200, 2900, 1740, 1710, 1650, 1450, 1420, 1250, 1160, 1080, 980, 920 and 850; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ0.91 (3H, *s*), 1.20 (3H, *s*), 1.22 (3H, *s*), 2.05 (3H, *s*), 2.10 (1H, *dd*, $J_{eq,ax}$ = 3.0 and J_{gem} = 14.0 Hz, H-6α), 2.98 (1H, *dd*, $J_{ax,ax}$ = 13.0 and J_{gem} = 14.0 Hz, H-6β), 3.59 (1H, *d*, J_{gem} = 12.0 Hz, H-18), 3.80 (1H, *d*, J_{gem} = 12.0 Hz, H-18), 4.80 (1H, *dd*, J_{gem} = 1.5 and J_{cis} = 11.0 Hz, H-16), 4.90 (1H, *dd*, J_{gem} = 1.5 and J_{trans} = 18.0 Hz, H-16) and 5.75 (1H, *dd*, J_{cis} = 11.0 and J_{trans} = 18.0 Hz, H-15); ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS as int. standard): δ15.4 (*q*, C-20), 16.6 (*t*, C-11), 17.1 (*q*, C-19), 17.4 (*q*, C-2), 20.9 (*q*, C-22), 24.6 (*q*, C-17), 34.8 (*t*, C-6), 35.6 (*t*, C-3), 36.1 (*s*, C-4), 36.9 (*s*, C-10), 37.2 (*s*, C-13), 37.6 (*t*, C-12), 38.9 (*t*, C-1), 43.1 (*t*, C-14), 49.8 (*d*, C-5), 58.3 (*d*, C-9), 71.8 (*t*, C-18), 76.9 (*s*, C-8), 109.1 (*t*, C-16), 150.5 (*d*, C-15), 170.9 (*s*, C-21) and 210.6 (*s*, C-7); EIMS (probe) 70 eV, *m/z* (rel. int.): 362 $[M]^+$ (8), 344 $[M-18]^+$ (24), 302 $[M-60]^+$ (14), 284 $[M-78]^+$ (26), 269 $[M-93]^+$ (24), 241 $[M-121]^+$ (25), 189 $[M-173]^+$ (23), 165 $[M-197]^+$ (43), 163 $[M-199]^+$ (18), 149 $[M-213]^+$ (36), 136 $[M-226]^+$ (40), 135 $[M-227]^+$ (25), 133 $[M-229]^+$ (29), 123 $[M-239]^+$ (88), 121 $[M-241]^+$ (64), 109 $[M-253]^+$ (63), 108 $[M-254]^+$ (20) and 81 $[M-281]^+$ (100).

Hydrolysis of compound **9**. Using the same procedure described for hydrolysis of **4**, we have obtained **8** (identical with the natural product) in 98% yield starting from **9**.

8β-Hydroxy-7-oxo-15-isopimaren-18-oic acid (**10**). Crystals from hexane–EtOAc (1:1), mp 225–228°, 0.71% dry wt. $[\alpha]_D^{28}$ −42.0° (MeOH; *c* 0.277). CD: $[\theta]_{270}$ −1532, $[\theta]_{295}$ −4813, $[\theta]_{310}$ −2738. IR ν_{max}^{KBr} cm^{-1}: 3540, 3280, 2998, 1700, 1440, 1375, 1240, 1165, 982, 908 and 819; ^1H NMR (100 MHz, $CDCl_3$–pyridine-d_5, TMS as int. standard): δ1.31 (9H, *sl*), 2.20 (1H, *dd*, $J_{ax,eq}$ = 3.0 and J_{gem} = 14.0 Hz, H-6α), 3.24 (1H, *dd*, $J_{ax,ax}$ = 13.0 and J_{gem} = 14.0 Hz, H-6β), 4.77 (1H, *dd*, J_{gem} = 2.0 and J_{cis} = 11.0 Hz, H-16), 4.86 (1H, *dd*, J_{gem} = 2.0 and J_{trans} = 17.0 Hz, H-16) and 5.73 (1H, *dd*, J_{cis} = 11.0 and J_{trans} = 17.0 Hz, H-15); ^{13}C NMR: Table 1; EIMS (probe) 70 eV, *m/z* (rel. int.): 334 $[M]^+$ (15), 316 $[M-18]^+$ (17), 291 $[M-43]^+$ (20), 277 $[M-57]^+$ (18), 273 $[M-61]^+$ (48), 218 $[M-116]^+$ (35), 165 $[M-169]^+$ (54), 183 $[M-151]^+$ (40), 123 $[M-211]^+$ (77), 109 $[M-225]^+$ (78), 95 $[M-239]^+$ (80), 69 $[M-265]^+$ (86) and 55 $[M-279]^+$ (100). HRMS: found, *m/z* 334.2149 ($C_{20}H_{30}O_4$ requires 334.2144).

Methyl 8-hydroxy-7-oxo-15-isopimaren-18-oate (**11**). Compound **10** was methylated with CH_2N_2 to yield a crystalline compound, **11**, mp 185–187°. IR ν_{max}^{KBr} cm^{-1}: 3500, 2990, 1710, 1380, 1245, 1180–1160, 985 and 915; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ1.08 (3H, *s*), 1.14 (6H, *s*), 2.01 (1H, *dd*, $J_{eq,ax}$ = 3.0 and J_{gem} = 13.0 Hz, H-6α), 3.06 (1H, *dd*, $J_{ax,ax}$ = 13.0 and J_{gem} = 14.0 Hz, H-6β), 3.66 (3H, *s*, H-21), 4.82 (1H, *dd*, J_{gem} = 2.0 and J_{cis} = 11.0 Hz, H-16), 4.90 (1H, *dd*, J_{gem} = 2.0 and J_{trans} = 17.0 Hz, H-16) and 5.72 (1H, *dd*, J_{cis} = 11.0 and J_{trans} = 17.0 Hz, H-15); EIMS (probe) 70 eV, *m/z* (rel. int.): 348 $[M]^+$ (4), 320 $[M-28]^+$ (9), 139 $[M-209]^+$ (38), 124 $[M-224]^+$ (100), 86 $[M-262]^+$ (47), 72 $[M-276]^+$ (55), 68 $[M-280]^+$ (66) and 53 $[M-295]^+$ (46).

8-Oxo-18-carbometoxi-7,8-seco-isopimaren-15-ene-7-oic acid (**12**). Compound **11** (106.0 mg) was oxidized using the procedure described in ref. [7] yielding crystals of **12**: (100%), mp 127–130°. IR ν_{max}^{KBr} cm^{-1}: 3430, 3000, 1750, 1700, 1240, 1180, 1160, 1008, 844 and 774; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ0.95 (3H, *s*), 1.10 (3H, *s*), 1.23 (3H, *s*), 2.81 (1H, *t*, *J* = 6.0 Hz, H-5), 3.65 (3H, *s*, H-21), 4.87 (1H, *dd*, J_{gem} = 1.5 and J_{cis} = 10.0 Hz, H-16), 4.89 (1H, *dd*, J_{gem} = 1.5 and J_{trans} = 17.0 Hz, H-16) and 5.77 (1H, *dd*, J_{cis} = 10.0 and J_{trans} = 17.0 Hz, H-15); ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS as int. standard): δ17.7 (*t*, C-2), 20.1 (*q*, C-20), 21.0 (*q*, C-19), 22.6 (*q*, C-17), 24.0 (*t*, C-11), 31.8 (*t*, C-6), 32.8 (*t*, C-12), 34.5 (*t*, C-3), 36.5 (*t*, C-1), 38.8 (*s*, C-10), 40.7 (*d*, C-5), 42.5 (*s*, C-13), 47.0 (*s*, C-4), 52.1 (*q*, C-21), 54.8 (*t*, C-14), 55.8 (*d*, C-9), 110.2 (*t*, C-16), 147.4 (*d*, C-15), 178.8 (*s*, C-18), 180.0 (*s*, C-7) and 210.1 (*s*, C-8); EIMS (probe) 70 eV, *m/z* (rel. int.): 364 $[M]^+$ (1), 227 $[M-137]^+$ (17), 181 $[M-183]^+$ (26), 167 $[M-197]^+$ (53), 107 $[M-257]^+$ (51), 95 $[M-269]^+$ (47), 67 $[M-297]^+$ (44), 55 $[M-309]^+$ (49), 43 $[M-321]^+$ (53) and 41 $[M-323]^+$ (100).

Dimethyl 8-oxo-7,8-seco-15-isopimaren-7,18-dioate (**13**). Treatment of **12** with CH_2N_2 yielded crystals of **13**, mp 108–110°. IR ν_{max}^{KBr} cm^{-1}: 2940, 1740, 1725, 1710, 1450, 1430, 1370, 990, 920 and 850; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ0.97 (3H, *s*), 1.07 (3H, *s*), 1.22 (3H, *s*), 2.86 (1H, *t*, *J* = 5.0 Hz), 3.66 (3H, *s*, H-21), 3.70 (3H, *s*, H-22), 4.92 (1H, *dd*, J_{gem} = 2.0 and J_{cis} = 10.0 Hz, H-16), 4.93 (1H, *dd*, J_{gem} = 2.0 and J_{trans} = 18.0 Hz, H-16) and 5.80 (1H, *dd*, J_{cis} = 10.0 and J_{trans} = 18.0 Hz, H-15). EIMS (probe) 70 eV, *m/z* (rel. int.): 378 $[M]^+$ (3), 347 $[M-31]^+$ (2), 328 $[M-50]^+$ (2), 319 $[M-59]^+$ (3), 304 $[M-74]^+$ (3), 273 $[M-105]^+$ (2), 241 $[M-137]^+$ (19), 209 $[M-169]^+$ (18), 195 $[M-183]^+$ (14), 181 $[M-197]^+$ (100), 165 $[M-213]^+$ (25), 149 $[M-229]^+$ (33), 121 $[M-257]^+$ (43), 107 $[M-271]^+$ (62) and 44 $[M-334]^+$ (60).

15-Isopimaren-7α,8,18-triol (**14**) *and 7α,18-diacetoxy-15-isopimaren-8-ol* (**15**). The methyl ester **11** (29 mg) was reduced with $LiAlH_4$ (37 mg) in Et_2O (5 ml) for 12 hr at room temp., to give an epimeric mixture of compactotriol (**3**) and its epimer as the major component (24.2 mg, 90.2%). The epimeric compactotriol (**14**), after purification (20 mg), was subjected to acetylation with Ac_2O with catalytic amounts of DMAP yielding a crystalline compound (**15**) (24.5 mg, 97.1%), mp 137–140°. IR ν_{max}^{KBr} cm^{-1}: 3470, 2940, 1740, 1220, 1038, 910 and 848; ^1H NMR (100 MHz,

$CDCl_3$, TMS as int. standard): δ0.85 (3H, *s*), 1.03 (3H, *s*), 1.22 (3H, *s*), 2.05 (3H, *s*, H-22), 2.07 (3H, *s*, H-24), 3.68 (2H, *sl*, OH), 4.62 (1H, *dd*, $J_{eq,eq}$ = 3.0 and $J_{eq,ax}$ = 4.0 Hz, H-7), 4.78 (1H, *dd*, J_{gem} = 1.5 and J_{cis} = 10.0 Hz, H-16), 4.82 (1H, *dd*, J_{gem} = 1.5 and J_{trans} = 18.0 Hz, H-16) and 5.70 (1H, *dd*, J_{cis} = 10.0 and J_{trans} = 18.0 Hz, H-15); EIMS (probe) 70 eV, *m/z* (rel. int.): 406 $[M]^+$ (5), 346 $[M-60]^+$ (33), 273 $[M-133]^+$ (85), 255 $[M-151]^+$ (88), 149 $[M-257]^+$ (72), 95 $[M-311]^+$ (75), 81 $[M-325]^+$ (95), 55 $[M-351]^+$ (88) and 43 $[M-363]^+$ (100).

15-*Isopimaren-7β*-8,14*β-triol* (**16**). Crystals from hexane–EtOAc (19:1), mp 125–127°, 0.058% dry wt. IR ν_{max}^{KBr} cm^{-1}: 3210, 2860, 1440, 1350, 1255, 1088, 1040, 965 and 910; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ0.86 (3H, *s*), 0.88 (3H, *s*), 1.02 (3H, *s*), 1.20 (3H, *s*), 2.64 (2H, *sl*, changed with D_2O), 3.30 (1H, *s*, H-14), 3.64 (1H, *dd*, $J_{ax,eq}$ = 6.0 and $J_{ax,ax}$ = 10.0 Hz, H-7), 5.10 (1H, *dd*, J_{gem} = 1.5 and J_{cis} = 10.0 Hz, H-16), 5.50 (1H, *dd*, J_{gem} = 1.5 and J_{trans} = 18.0 Hz, H-16) and 5.71 (1H, *dd*, J_{cis} = 10.0 and J_{trans} = 18.0 Hz, H-15); ^{13}C NMR: Table 1; EIMS (probe) 70 eV, *m/z* (rel. int.): 322 $[M]^+$ (8), 222 $[M-100]^+$ (6), 180 $[M-142]^+$ (4), 123 $[M-199]^+$ (18), 109 $[M-213]^+$ (13), 95 $[M-227]^+$ (17), 81 $[M-241]^+$ (44), 69 $[M-253]^+$ (35), 67 $[M-255]^+$ (35), 55 $[M-267]^+$ (48), 43 $[M-279]^+$ (60) and 41 $[M-281]^+$ (100). HRMS: found, *m/z* 322.2522 ($C_{20}H_{34}O_3$ requires 322.2508).

8,14*β-Dihydroxy*-15-*isopimaren*-7-*one* (**17**). Crystals from hexane, mp 156–158°, 0.064% dry wt. $[\alpha]_D^{28}$ +11.4° (MeOH; *c* 0.352). CD: $[\theta]_{270}$ −309.1, $[\theta]_{297}$ −1018.2, $[\theta]_{310}$ −709.1. IR ν_{max}^{KBr} cm^{-1}: 3560, 3380, 2998, 1725, 1440, 1380, 1080, 957 and 915; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ0.90 (3H, *s*), 0.92 (3H, *s*), 1.19 (3H, *s*), 1.22 (3H, *s*), 2.22 (1H, *dd*, $J_{eq,ax}$ = 3.0 and J_{gem} = 13.0 Hz, H-6α), 3.01 (1H, *dd*, J_{gem} = 13.0 and $J_{ax,ax}$ = 14.0 Hz, H-6β), 3.07 (1H, *sl*, changed with D_2O), 3.20 (1H, *sl*, changed with D_2O), 3.70 (1H, *s*, H-14), 4.97 (1H, *dd*, J_{gem} = 1.5 and J_{cis} = 10.0 Hz, H-16), 5.01 (1H, *dd*, J_{gem} = 1.5 and J_{trans} = 18.0 Hz, H-16) and 5.90 (1H, *dd*, J_{cis} = 10.0 and J_{trans} = 18.0 Hz, H-15); ^{13}C NMR: Table 1; EIMS (probe) 70 eV, *m/z* (rel. int.): 320 $[M]^+$ (77), 222 $[M-98]^+$ (73), 209 $[M-211]^+$ (42), 123 $[M-197]^+$ (100), 109 $[M-211]^+$ (79), 81 $[M-239]^+$ (78), 69 $[M-251]^+$ (86), 55 $[M-265]^+$ (80) and 41 $[M-279]^+$ (99). HRMS: found, *m/z* 320.2357 ($C_{20}H_{32}O_3$ requires 320.2351).

7*β*,8,14*β-Trihydroxy*-15-*isopimarene*-18-*oic acid* (**19**). Crystals from hexane–EtOAc (7:3), mp 191–193°, 0.9% dry wt. $[\alpha]_D^{28}$ +15.4° (MeOH; *c* 0.251). IR ν_{max}^{KBr} cm^{-1}: 3450, 2880, 1700, 1645, 1450, 1380, 1250, 980–961 and 915; ^1H NMR (100 MHz, $(CD_3)_2CO$–pyridine-d_5, TMS as int. standard): δ0.88 (1H, *dd*, *J* = 11.0 and 2.5 Hz, H-5), 1.15 (3H, *s*), 1.26 (3H, *s*), 1.29 (3H, *s*), 3.46 (1H, *s*, H-14), 3.76 (1H, *m*), 4.90 (1H, *dd*, J_{gem} = 2.0 and J_{cis} = 10.0 Hz, H-16), 5.10 (1H, *dd*, J_{gem} = 2.0 and J_{trans} = 18.0 Hz, H-16), 5.36 (4H, *sl*, exch. with D_2O) and 5.97 (1H, *dd*, J_{cis} = 10.0 and J_{trans} = 18.0 Hz, H-15); ^{13}C NMR: Table 1; EIMS (probe) 70 eV, *m/z* (rel. int.): 352 $[M]^+$ (4), 314 $[M-38]^+$ (11), 252 $[M-100]^+$ (9), 109 $[M-243]^+$ (25), 107 $[M-245]^+$ (30), 81 $[M-271]^+$ (41), 55 $[M-297]^+$ (60), 53 $[M-299]^+$ (37), 43 $[M-309]^+$ (56) and 41 $[M-311]^+$ (100). HRMS: found, *m/z* 352.2263 ($C_{20}H_{32}O_5$ requires 352.2250).

Methyl 7*β*,8,14*β-trihydroxy*-15-*isopimaren*-18-*oate* (**20**). Compound **19** was methylated with CH_2N_2 to yield crystals of **20**, mp 137–139°. IR ν_{max}^{KBr} cm^{-1}: 3450, 2994, 1710, 1640, 1440, 1380, 1248, 976–970–958 and 794; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ1.04 (3H, *s*), 1.20 (3H, *s*), 1.21 (3H, *s*), 2.63 (3H, *m*, exch. with D_2O), 3.29 (1H, *d*, *J* = 2.0 Hz, H-14), 3.65 (3H, *s*, H-21 + 1H, *m*), 5.40 (1H, *dd*, J_{gem} = 1.5 and J_{trans} = 18.0 Hz, H-16), 5.60 (1H, *dd*, J_{gem} = 1.5 and J_{cis} = 10.0 Hz, H-16) and 5.68 (1H, *dd*, J_{cis} = 10.0 and J_{trans} = 18.0 Hz, H-15); EIMS (probe) 70 eV, *m/z* (rel. int.): 366 $[M]^+$ (21), 193 $[M-173]^+$ (19), 123 $[M-243]^+$ (59), 109 $[M-257]^+$ (41), 81 $[M-285]^+$ (88), 79 $[M-287]^+$ (43) and 54 $[M-312]^+$ (100).

Preparation of the acetonide **21**. (i) *From* 15-*isopimaren*-7*β*,8,14*β-triol* (**16**). A soln of **16** (12 mg) in Me_2CO (2 ml) and 2 drops of conc. HCl was allowed to stand at room temp. for 12 hr. Usual work-up yielded **21** as crystals, mp 112–115° (11 mg, 81.5%). IR ν_{max}^{KBr} cm^{-1}: 3580, 3300, 2998, 1660, 1470, 1380, 1200, 1110, 1025, 988 and 879; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ0.90 (6H, *s*), 1.05 (3H, *s*), 1.18 (3H, *s*), 1.46 (3H, *s*, H-21), 1.48 (3H, *s*, H-22), 3.36 (1H, *s*, H-14), 3.56 (1H, *dd*, $J_{ax,eq}$ = 6.0 and $J_{ax,ax}$ = 10.0 Hz, H-7), 4.88 (1H, *dd*, J_{gem} = 1.5 and J_{cis} = 10.0 Hz, H-16), 4.94 (1H, *dd*, J_{gem} = 1.5 and J_{trans} = 18.0 Hz, H-16) and 5.78 (1H, *dd*, J_{cis} = 10.0 and J_{trans} = 18.0 Hz, H-15); EIMS (probe) 70 eV, *m/z* (rel. int.). 362 $[M]^+$ (5), 347 $[M-15]^+$ (30), 304 $[M-58]^+$ (36), 287 $[M-75]^+$ (44), 123 $[M-239]^+$ (85), 81 $[M-281]^+$ (92), 69 $[M-293]^+$ (100) and 55 $[M-307]^+$ (99).

(ii) *From* 8,14*β-dihydroxy*-15-*isopimaren*-7-*one* (**17**). Compound **17** (15 mg) was reduced with $NaBH_4$ in MeOH for 20 min at room temp., giving a mixture of the epimeric triols at C-7. The major product, purified by prep. TLC, was subjected to the same procedure described for **16** to give the acetonide **21** (9 mg, 60%).

Preparation of the acetonide **22**. Using the same procedure described for acetonide **21**, we obtained 27.8 mg (86.4%) of **22** from 20 mg of **20**. Crystals, mp 138–140°. IR ν_{max}^{KBr} cm^{-1}: 3450, 2998, 1740, 1450, 1380, 1250, 984, 915 and 885; ^1H NMR (100 MHz, $CDCl_3$, TMS as int. standard): δ1.08 (3H, *s*), 1.18 (3H, *s*), 1.23 (3H, *s*), 1.44 (3H, *s*, H-22), 1.46 (3H, *s*, H-23), 3.38 (1H, *s*, H-14), 3.56 (1H, *m*, H-7), 3.67 (3H, *s*, H-21), 4.87 (1H, *dd*, J_{gem} = 1.5 and J_{cis} = 10.0 Hz, H-16), 4.92 (1H, *dd*, J_{gem} = 1.5 and J_{trans} = 18.0 Hz, H-16) and 5.76 (1H, *dd*, J_{cis} = 10.0 and J_{trans} = 18.0 Hz, H-15); EIMS (probe) 70 eV, *m/z* (rel. int.): 406 $[M]^+$ (13), 392 $[M-14]^+$ (69), 349 $[M-57]^+$ (88), 322 $[M-84]^+$ (58), 152 $[M-254]^+$ (77), 107 $[M-299]^+$ (72), 95 $[M-311]^+$ (89), 81 $[M-325]^+$ (100), 55 $[M-351]^+$ (80) and 43 $[M-363]^+$ (63).

Methyl 7-*oxo*-8,14*β-dihydroxy*-15-*isopimaren*-18-*oate* (**24**). Compound **23** isolated from *V. patens* (0.01% dry wt) was methylated with CH_2N_2 to yield an oil. This compound was also obtained (6.0 mg) from **20** (8.0 mg) using the procedure described for the preparation of **9** (Swern oxidation). IR ν_{max}^{KBr} cm^{-1}: 3490, 2990, 1710, 1400, 1380, 1248, 1170, 980 and 910; ^1H NMR (200 MHz, $CDCl_3$, TMS as int. standard): δ1.09 (3H, *s*), 1.14 (3H, *s*), 1.18 (3H, *s*), 1.96 (1H, *dd*, $J_{eq,ax}$ = 2.2 and J_{gem} = 14.0 Hz, H-6α), 3.00 (1H, *t*, *J* = 14.0 Hz, H-6β), 3.14 (1H, *d*, *J* = 3.2 Hz, exch. with D_2O), 3.61 (3H, *s*), 3.64 (1H, *d*, *J* = 3.1 Hz, H-14), 4.93 (1H, *dd*, J_{gem} = 1.5 and J_{cis} = 10.7 Hz, H-16), 4.96 (1H, *dd*, J_{gem} = 1.5 and J_{trans} = 17.5 Hz, H-16) and 5.83 (1H, *dd*, J_{cis} = 10.7 and J_{trans} = 17.5 Hz, H-15); EIMS (probe) 70 eV, *m/z* (rel. int.): 364 $[M]^+$ (4), 289 $[M-75]^+$ (10), 266 $[M-98]^+$ (30), 230 $[M-134]^+$ (5), 207 $[M-157]^+$ (25), 181 $[M-183]^+$ (25), 123 $[M-241]^+$ (80) and 109 $[M-255]^+$ (100).

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