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# TERPENOIDS FROM LEAVES OF *JUNIPERUS THURIFERA*

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**Key Word Index**—*Juniperus thurifera*; Cupressaceae; diterpenoids; labdanes; pimaranes; abietanes; chemotaxonomy.

**Abstract**—Nineteen diterpenoids of the labdane, pimarane and abietane skeletons and four known sesquiterpenoids were isolated from *Juniperus thurifera* leaves. Thirteen of these diterpenoids are described for the first time as natural products. Their structures were elucidated principally by NMR techniques and chemical transformations.

## INTRODUCTION

Continuing our research on the composition of the *Juniperus* species growing in the Iberian Peninsula we have initiated the study of *Juniperus thurifera* leaves. In this communication we describe the isolation and structural determination of four sesquiterpenes and 18 diterpenes with labdane, pimarane and abietane skeletons. In previous papers we have described coumarins [1], phenylpropane derivatives [2], monoterpenes [3] and lignans [4, 5] isolated from this plant source.

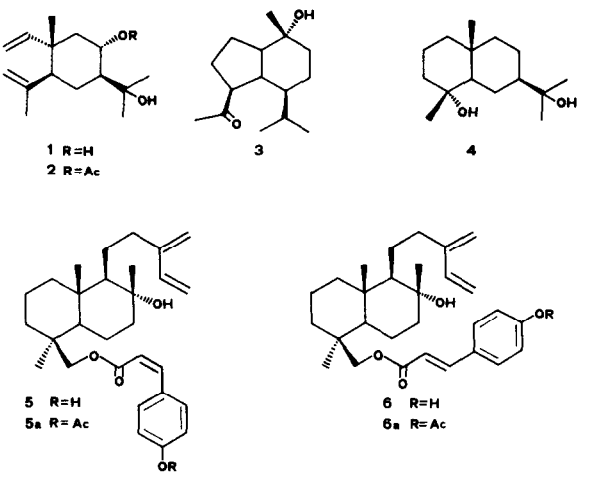
## RESULTS AND DISCUSSION

By repeated chromatographic separations of the insoluble fraction of a hexane extract several terpenoids were isolated, among them the sesquiterpenoids 8α,11-elemodiol (**1**), 8α-acetoxyelemol (**2**), oplopanone (**3**) and cryptomeridiol (**4**). Compounds **1–3** were identified by comparison with authentic samples and **4** by comparison of its spectroscopic properties with the data in the literature [6]. Sesquiterpenoids **1** and **3** have been isolated from berries of some *Juniperus* species [7, 8], and **2**, previously obtained by saponification of **1**, has been recently described as a component of the aerial parts of *Chenopodium graveolens* [9].

Among the isolated labdanes, agatadiol (**7**) [10], isoagatholal (**8**) [11] and labd-13*E*-en-8,15-diol (**13**)[12] have also been obtained from other species of *Juniperus*, while ribenol (**17**) [13, 14] is the first example of a diterpene belonging to the antipode series isolated from this genus. Tabacik *et al.* reported the presence of the labdane eperuendiol **13a** of the antipode series in *Juniperus phoenicea* extracts [15], but further studies carried out by our group have shown that this compound, displaying a specific rotation close to zero, coincides with labd-13*E*-en-8,15-diol (**13**) (unpublished observations). The remaining compounds are new natural products.

From the less polar fractions after acetylation two isomeric compounds **5** and **6** were isolated. Their spectroscopic properties suggest a labdane structure with a hydroxyl group at position 8, $\Delta^{13(16)}$ and $\Delta^{14}$ unsaturations and esterification with *cis* and *trans* *O*-acetyl-*p*-coumaric acids as can be deduced from the shift and coupling constants of the AB system of the double bond conjugated with the aromatic ring. The relative stereochemistry of the C-5, C-8, C-9 and C-10 carbons was assigned in accordance with other related labdanes [16]. The shift of the methyl at C-4 (27.5 ppm) indicates an equatorial disposition of the group [16] and as a consequence the *O*-acetylcoumaric ester must be at C-19. Once the relative stereochemistries are known absolute configurations are deduced from the positive sign of their molecular rotation as those of a labdane belonging to the normal series. As a result we assign for these two compounds the structures 8-hydroxy-labda-13(16),14-dien-19-yl *O*-acetyl-*Z*-coumarate (**5**) and *O*-acetyl-*E*-coumarate (**6**). Compound **6** was also obtained from another chromatographic fraction of the same extract.

Compound **9** is an oily compound whose IR spectrum shows absorptions of a primary hydroxyl, double bonds, acetate and aldehyde. Its $^1H$ and $^{13}C$ NMR spectra are very similar those of isoagatholal (**8**), with signals of two quaternary methyls, an axial aldehyde proton, a vinylidene and a Me–C(=CH–CH$_2$OH)– group [17]; the major difference observed in its NMR spectra corresponds

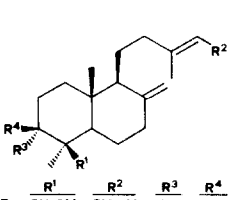


to signals belonging to a secondary axial acetate group whose geminal hydrogen atom absorbs as a triplet (*t*, $J = 2.8$ Hz) at 5.32 ppm and, consequently, it could be located at positions 1, 3 or 7 of the labdane nucleus. Attempted saponification of **9** afforded a hydroxy aldehyde whose $^1$H NMR spectrum shows the proton geminal to the secondary hydroxyl as a double doublet ($J = 11.3$, 4.6 Hz) centred at 3.80 ppm, indicating an inversion of the configuration in the carbon supporting the acetate. A 0.3 ppm shielding of the C-18 aldehyde signal in its $^1$H NMR spectrum and the strong shielding (11 ppm) of the C-19 methyl signal in the $^{13}$C NMR spectrum suggest their proximity to the carbon having the oxygenated function that correspondingly was located at C-3. The pyridine-induced shifts [18] only affecting the C-18 methyl (+0.26 ppm) and the aldehyde (+0.23 ppm) signals, are in agreement with the equatorial disposition of the OH group at C-3. The product, therefore, has the structure 3$\beta$-hydroxy-isoagatholal (**9a**) and the natural compound is 3$\alpha$-acetoxy-isoagatholal (**9**). Inversion of the configuration at C-3 was confirmed by acetylation of **9a**, affording 3$\beta$-acetoxy-15-*O*-acetyl-isoagatholal (**9b**) showing the resonance of the proton geminal to the acetate group as a double doublet ($J = 11.4$, 4.5 Hz) centred at 5 ppm.

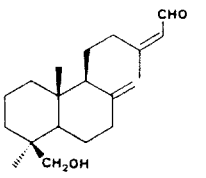
Compound **10** is a crystalline substance isolated from more polar fractions, whose IR spectrum displays absorption bands of primary and secondary hydroxyls, double bonds and aldehyde. Its $^1$H and $^{13}$C NMR spectra are very similar to those of **9**, with the signals of a hydroxy group instead of those an acetate as the only difference. Addition of trichloroacetylisocyanate allowed us to solve the crowded $^1$H NMR spectrum separating a triplet ($J = 3$ Hz) belonging to the proton geminal to the secondary hydroxyl group from the doublet of the allylic $-CH_2OH$ group. From these data we assigned the structure of 3$\beta$-hydroxy-isoagatholal for this compound. Acetylation yielded the diacetate **10a** which upon treatment with bases gave **9a**, correlating **10** with the natural compound **9.**

Compounds **11** and **12** are two isomeric substances whose mass spectra show $[M]^+$ at *m/z* 304, in accordance with the molecular formula $C_{20}H_{32}O_2$. In their IR spectra absorptions of primary alcohol, double bonds and conjugated aldehyde are observed. Their UV spectra display intense absorption at 240 nm. The $^1$H NMR spectrum of compound **11** has two quaternary methyls (0.66 and 0.97 ppm), a $-CH_2OH$ group (AB system, 3.38 and 3.75 ppm), an olefinic methylene and a $-CH_2-C(Me)=CH-CHO$ grouping, whose *E* configuration can be deduced from the shifts of the methyl (2.16 ppm in $^1$H NMR and 17.7 ppm in $^{13}$C NMR) and methylene (39.6 ppm) groups. These data and the remaining signals of the $^{13}$C NMR spectrum allow us to assign the structure of 19-hydroxylabda-8(17),13*E*-dien-15-al (**11**) for this compound, previously described as a transformation product from some diterpene acids [18a]. The other isomer (**12**) has as a major difference from **11** in the shift of the methyl (1.97 ppm in $^1$H NMR and 27.1 ppm in $^{13}$C NMR ) and methylene (31.3 ppm in $^{13}$C NMR) signals, which indicates a *Z* configuration for $\Delta^{13}$. Manganese dioxide oxidation of agatadiol gives both compounds as reaction products in agreement with the structures proposed for these natural products.

Another two isomeric compounds were isolated, whose mass spectra had $[M]^+$ at *m/z* 306 ($C_{20}H_{34}O_2$).



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| 7 | $CH_2OH$ | $CH_2OH$ | H | H |
| 8 | CHO | $CH_2OH$ | H | H |
| 9 | CHO | $CH_2OH$ | OAc | H |
| 9a | CHO | $CH_2OH$ | H | OH |
| 9b | CHO | $CH_2OAc$ | H | OAc |
| 10 | CHO | $CH_2OH$ | OH | H |
| 10a | CHO | $CH_2OAc$ | OAc | H |
| 11 | $CH_2OH$ | CHO | H | H |



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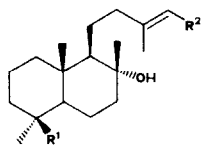
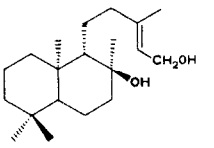


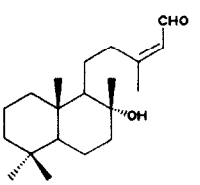
| | $R^1$ | $R^2$ |
|---|---|---|
| 13 | Me | $CH_2OH$ |
| 14 | CHO | $CH_2OH$ |
| 15 | Me | CHO |



13a

Their IR spectra are almost identical, displaying absorption bands of a tertiary alcohol, double bonds and a $\alpha,\beta$-unsaturated aldehyde, with UV absorption maxima at 242 nm. Their $^1$H NMR are also very similar showing signals of four methyls, one of them (1.16 ppm) geminal to hydroxyl group and a Me–C=CH–CHO grouping, with *E* configuration in one isomer and *Z* in the other, as can be deduced from the methyl shifts (2.18 and 2.00 ppm, respectively). The only differences in their $^{13}$C NMR spectra are the shifts of the methyl (25.2 and 17.8 ppm) and the methylene (36.4 and 45.1 ppm) bonded to a double bond, in agreement with the proposed configurations. These data prompted us to assign the structures *E* and *Z* 8-hydroxy-labd-13-en-15-al, **15** and **16** respectively, for both compounds, that were also obtained by PDC oxidation of **13.**

Compound **14** is the more polar of the terpenoids isolated from the *Juniperus* extract. Its IR spectrum shows absorptions of alcohol, aldehyde and trisubstituted double bonds. The signals on the $^1$H NMR spectrum could be assigned to three quaternary methyls (0.68, 1.02 and 1.17 ppm), two of them geminal with oxygenated functions, an axial aldehyde (9.26 ppm) and a Me–C=CH–$CH_2OH$ grouping, whose *E* configuration is deduced from the methyl shift (1.70 ppm). These spectroscopic data allow us to propose the structure 8,15-dihydroxy-labd-13*E*-en-19-al (**14**) for this compound.



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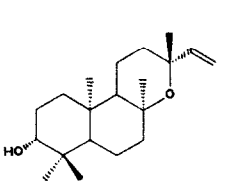

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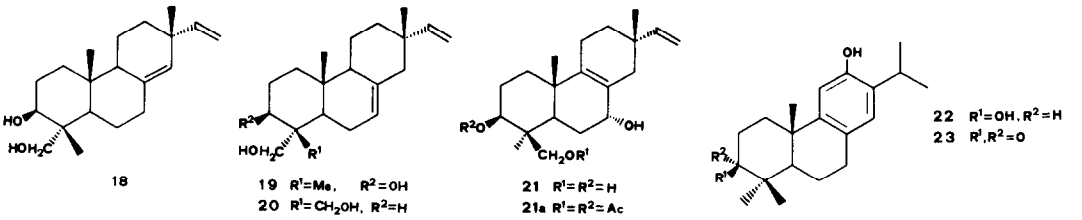


Four diterpenes (**18**–**21**) with a pimarane skeleton were also obtained and their isolation, having verified their close $R_f$ values, was achieved using the corresponding acetate derivatives. The IR spectrum of the first compound (**18**) shows absorption bands of primary and secondary hydroxyl groups and mono- and trisubstituted double bonds. The $^1$H NMR spectrum shows signals of three quaternary methyls, an equatorial $-CH_2OH$ group as an AB system (3.38 and 3.65 ppm, $J = 10.5$ Hz), a vinyl group as an ABX system (4.88, 4.90 and 5.76 ppm) and another two protons at 5.22 ppm (*s*) and 3.66 ppm (*dd*, $J = 10.0$, 4.2 Hz). The spectroscopic properties correspond to those of sandaracopimarol with an additional equatorial hydroxyl group at C-3, as could be deduced from the pyridine-induced shifts [18], the excision model and the preparation of the corresponding acetonide [19]. Although this compound has been isolated from *Xylia dolabriformis* [20] its spectroscopic properties have not been described previously. Also a related substance *ent*-pimara-8(14), 15-dien-3$\beta$, 18-diol has been described with opposite specific rotation [21].

The second substance (**19**), whose spectroscopic data are very similar to those of compound **18**, has the olefinic proton excision pattern model as the major difference, corresponding to a $\Delta^7$ unsaturation in a pimarane skeleton instead of a $\Delta^{8(14)}$ one. Accordingly a structure of isopimaradien-3$\beta$,18-diol (**19**) was assigned to this compound. In addition the location of the hydroxyl group at C-3 was confirmed by the formation of its acetonide.

The third compound with a pimarane skeleton (**20**) has an IR spectrum showing absorptions of mono- and trisubstituted double bonds and combined and free hydroxyl groups. Its $^1$H NMR has signals of two quaternary methyls, a vinyl group, a broad singlet assigned to the H-7 olefinic proton of an isopimarane, and two AB systems belonging to an equatorial $-CH_2OH$ (3.36 and 3.91 ppm) and an axial $-CH_2OH$ (3.86 and 4.06 ppm) group. Its $^{13}$C NMR shows two methyls and two hydroxymethyl (74.2 and 64.9 ppm) groups that, besides the other signals, agree with a structure of isopimaradien-18, 19-diol (**20**) for this compound. The existence of intramolecular hydrogen bonding, the pyridine-induced shifts in the $^1$H NMR spectrum and the formation of the corresponding acetonide support the structure proposed.

The final compound with a pimarane skeleton (**21**) was isolated after acetylation. It is an oily product whose IR spectrum shows absorption bands of acetate, secondary alcohol and double bonds. In its $^1$H NMR spectrum it displays signals of three quaternary methyls, two acetate groups, an ABX system of a vinyl group, a $-CH_2OAc$ group as an AB system and two geminal hydrogen atoms with oxygenated functions. From the chemical shifts of the $-CH_2OAc$ ($^1$H NMR: 3.33 and 4.77 ppm, $J = 11.6$ Hz. $^{13}$C NMR: 64.2 ppm) an axial disposition and a C-19 location was deduced for this grouping [22, 23]. The other acetate must be at the 3$\beta$-equatorial position according to the $^1$H NMR signal of the geminal hydrogen (4.89 ppm, *dd*, $J = 12.6$, 4.5 Hz) and the $^{13}$C NMR shift (83.1 ppm) for C-3, similar to those other pimaranes isolated from this plant or described in the literature [24]. These data and the presence of a tetrasubstituted double bond ($^{13}$C NMR: 145.2 and 122.7 ppm) and the allylic position of the hydroxyl group ($^1$H NMR: 4.17 ppm for the geminal hydrogen. $^{13}$C NMR: 83.1 ppm), in accordance with the data described for other $\Delta^8$ unsaturated pimaranes [25, 26], allow us to propose the structure of 3$\beta$,19-diacetoxy-7$\alpha$-hydroxypimara-8,15-dieno (**21a**) for this substance. Basic saponification yielded the natural product **21**, with the shieldings of a methyl group (0.78 ppm), the H-3 (3.66 ppm) and the H-19 AB system (3.43 and 3.75 ppm) and the absence of acetate signals as the major $^1$H NMR differences.

Finally, two previously reported [27] abietanes, hinokiol (**22**) and hinokione (**23**), were isolated, whose $^{13}$C NMR data are now reported.

## EXPERIMENTAL

*General.* MPs: uncorr. Optical rotations were measured in $CHCl_3$. UV spectra were recorded in EtOH; $\lambda_{max}$ values are expressed in nm. IR spectra were obtained in $CHCl_3$. $\nu_{max}$ values are expressed in cm$^{-1}$. $^1$H NMR (200.13 MHz) and $^{13}$C NMR (50.3 MHz) spectra were measured in $CDCl_3$ with TMS as int stdard; $\delta$ values are expressed in ppm. EIMS were obtained at 70 eV. *M/z* values followed by rel. int. (%) are stated. Flash chromatography was carried out on silica gel (Merck No. 9385).

*Plant material, extraction and isolation.* Material was collected in September 1981, at Prádena (Segovia, Spain). Voucher specimens are deposited in the Botany Department, Faculty of Biology, Salamanca (register number SALA No. 7193). Leaves (15 kg) were extracted with hexane and the resulting extract cooled at 0° overnight to give 615 g (34% of extract) of insol. fraction, which was successively defatted with MeOH and a satd soln of urea in MeOH and fractionated with 4% aq. NaOH. The neutral part (130g. 7.1%) was chromatographed over silica gel with hexane–EtOAc mixtures of increasing polarity, yielding (mg): **1** (1900), **2** (510), **3** (951), **4** (980), **5** (162), **6** (170), **7** (550), **8** (154), **9** (920), **10** (300), **11** (350), **12** (180), **13** (6500), **14** (120), **15** (101), **16** (110), **17** (1600), **18** (700), **19** (510), **20** (123), **21** (80), **22** (185), **23** (130).

8$\alpha$-*Acetoxy-elemol* (**2**). $^{13}$C NMR $\delta$ ppm (C assign) 17.6 (15), 21.7 (MeCO), 24.6 (12), 26.5 (13), 28.5 (14), 29.1 (6), 41.1 (10), 44.9 (9), 52.2 (5), 52.2 (7), 72.6 (11), 72.8 (8), 110.8 (8), 112.8 (2), 146.3 (4), 148.4 (1), 169.0 (MeCO).

8-*Hydroxy-labda*-13(16),14-*dien*-19-*yl* O-*acetyl*- cis-*coumarate* (**5a**). Colourless oil, $[\alpha]^{23}$ ($\lambda$) = +7.3° (589), +7.8° (578), +8.7° (546) EIMS: *m/z* 494 (1) 477 (1), 476 (1), 411 (3), 273 (10), 255 (23), 219 (10), 203 (11), 201 (7), 189 (21), 187 (11), 177 (11), 147 (100). IR $\nu_{max}$ 3610, 3090, 3040, 1765, 1720, 1640, 1600, 1510, 1240, 1180, 1160, 1010, 995, 940, 915, 860. $^1$H NMR (Table 1). $^{13}$C NMR (Table 2).

8-*Hydroxy-labda*-13 (16),14-*dien*-19-*yl* O-*acetil*-trans-*coumar*-

Table 1. $^1$H NMR (200 MHz) spectra of labdanes **6**, **6a**, **5a**, **14**, **15** and **16**

| H | 6 | 6a | 5a | 14 | 15 | 16 |
|---|---|---|---|---|---|---|
| 14 | 6.54 *dd* (17.5; 10.8) | 6.36 *dd* (17.5; 11.1) | 6.36 *dd* (17.5; 11.1) | 5.44 *t* (6.9) | 5.91 *d* (8.2) | 5.85 *d* (8.0) |
| 15 | 5.18 *d* (10.8) | 5.07 *d* (11.1) | 5.07 *d* (11.1) | 4.15 *d* (6.9) | 9.99 *d* (8.2) | 9.94 *d* (8.0) |
| | 5.62 *d* (17.5) | 5.31 *d* (17.5) | 5.31 *d* (17.5) | | | |
| 16 | 5.12 *br s* | 5.01 *br s* | 5.01 *br s* | 1.70 *s* | 2.18 *s* | 2.00 *s* |
| 17 | 1.31 *s* | 1.15 *s* | 1.13 *s* | 1.17 *s* | 1.16 *s* | 1.16 *s* |
| 18 | 1.09 *s* | 1.03 *s* | 0.90 *s* | 1.02 *s* | 0.88 *s* | 0.88 *s* |
| 19 | 4.21 *d* (11.1) | 4.02 *d* (11.1) | 3.92 *d* (11.1) | 9.26 *s* | 0.79 *s* | 0.79 *s* |
| | 4.58 *d* (11.1) | 4.31 *d* (11.1) | 4.20 *d* (11.1) | | | |
| 20 | 0.87 *s* | 0.85 *s* | 0.80 *s* | 0.68 *s* | 0.80 *s* | 0.79 *s* |
| 2′ | 6.73 *d* (15.9) | 6.39 *d* (16.0) | 5.95 *d* (12.6) | | | |
| 3′ | 8.04 *d* (15.9) | 7.64 *d* (16.0) | 6.90 *d* (12.6) | | | |
| 5′ | 7.67 *d* (8.5) | 7.55 *d* (8.6) | 7.63 *d* (8.7) | | | |
| 6′ | 7.20 *d* (8.5) | 7.12 *d* (8.6) | 7.07 *d* (8.7) | | | |
| 8′ | 7.20 *d* (8.5) | 7.12 *d* (8.6) | 7.07 *d* (8.7) | | | |
| 9′ | 7.67 *d* (8.5) | 7.55 *d* (8.6) | 7.63 *d* (8.7) | | | |
| AcO | | 2.31 *s* | 2.29 *s* | | | |

$CDCl_3$, TMS as internal standard, $\delta$ multiplicity ($J$ in Hz).

Table 2. $^{13}$C NMR (50.3 MHz) spectra of labdanes **6**, **6a**, **5a**, **14**, **15** and **16**

| C | 6* | 6a | 5a | 14 | 15 | 16 |
|---|---|---|---|---|---|---|
| 1 | 40.0 | 40.0 | 39.8 | 34.5 | 40.0 | 39.9 |
| 2 | 18.5 | 18.3 | 18.1 | 23.9 | 18.6 | 18.6 |
| 3 | 36.7 | 36.7 | 36.4 | 39.3 | 42.1 | 42.0 |
| 4 | 37.7 | 37.5 | 37.0 | 48.4 | 33.3 | 33.5 |
| 5 | 57.2 | 57.0 | 56.9 | 56.7 | 56.3 | 56.3 |
| 6 | 21.2 | 20.8 | 20.8 | 20.3 | 20.7 | 20.7 |
| 7 | 45.6 | 45.1 | 45.0 | 44.6 | 44.0 | 45.0 |
| 8 | 73.1 | 74.1 | 74.0 | 73.7 | 74.2 | 74.3 |
| 9 | 62.4 | 62.0 | 61.9 | 60.0 | 61.4 | 61.7 |
| 10 | 39.2 | 39.2 | 39.1 | 39.8 | 39.3 | 39.2 |
| 11 | 25.6 | 25.0 | 24.8 | 18.4 | 23.4 | 25.5 |
| 12 | 35.8 | 35.3 | 35.2 | 42.7 | 45.1 | 36.4 |
| 13 | 147.8 | 147.6 | 147.5 | 140.4 | 164.8 | 165.5 |
| 14 | 139.6 | 139.0 | 138.9 | 123.6 | 127.2 | 127.9 |
| 15 | 115.6 | 115.5 | 115.6 | 59.3 | 191.3 | 191.4 |
| 16 | 113.6 | 113.5 | 113.5 | 16.4 | 17.8 | 25.2 |
| 17 | 24.5 | 24.2 | 24.1 | 23.9 | 24.3 | 24.4 |
| 18 | 27.7 | 27.7 | 27.5 | 24.2 | 33.5 | 33.4 |
| 19 | 66.8 | 67.3 | 67.1 | 205.4 | 21.6 | 21.6 |
| 20 | 16.3 | 16.1 | 16.0 | 14.4 | 15.5 | 15.5 |
| 1′ | 167.6 | 167.0 | 166.4 | | | |
| 2′ | 115.5 | 118.1 | 120.1 | | | |
| 3′ | 145.2 | 143.5 | 142.0 | | | |
| 4′ | 134.5 | 132.4 | 132.7 | | | |
| 5′ | 130.7 | 129.2 | 131.1 | | | |
| 6′ | 116.9 | 122.2 | 121.3 | | | |
| 7′ | 161.5 | 152.4 | 151.2 | | | |
| 8′ | 116.9 | 122.2 | 121.3 | | | |
| 9′ | 130.7 | 132.4 | 131.1 | | | |
| AcO | | 21.1 | 21.1 | | | |
| $CO_2$ | | 168.9 | 169.0 | | | |

$CDCl_3$, *$C_5D_5N$, TMS as internal standard.

*ate* (**6a**). Colourless oil $[\alpha]^{23}$ ($\lambda$) = +2.1° (589), +2.3° (578), +2.6° (546) + 5.3° (436). CIMS ($NH_3$): *m/z* 528 (3), 511 (2), 494 (1), 477 (2), 476 (3), 468 (3), 418 (6), 416 (10), 361 (22), 360 (100), 341 (13), 340 (52), 280 (55), 252 (48). IR $\nu_{max}$ 3610, 3090, 1765, 1720, 1640, 1600, 1510, 1240, 995, 915. $^1$H NMR (Table 1). $^{13}$C NMR (Table 2).

*8-Hydroxy-labda-*13(16),14*-dien-*19*-yl* trans-*coumarate* (**6**). Colourless crystals (MeOH). mp 217°C. $[\alpha]^{23}$ ($\lambda$) = +5.8° (589), +6.1° (578), +7.1° (546), +14.7° (436). UV $\lambda_{max}$ 225 ($\varepsilon$ = 18 500), 313 ($\varepsilon$ = 9000). IR $\nu_{max}^{KBr}$ 3430, 1690, 1630, 1610, 1590, 1520, 995, 915. $^1$H NMR ($C_5D_5N$) (Table 1). $^{13}$C NMR ($C_5D_5N$) (Table 2).

*3α-Acetoxy-isoagatholal* (**9**). Colourless oil. $[\alpha]^{23}$ ($\lambda$) = −14.5° (589), −18.2° (546), −40.4° (436). IR $\nu_{max}$ 3620, 3080, 3030, 2740, 1730, 1650, 1610, 1240, 1050, 995, 895. $^1$H NMR (Table 3). $^{13}$C NMR (Table 4). **9** (110 mg) was treated with 10% ethanolic KOH at room temp. The reaction product (102 mg), was flash-chromatographed yielding 60 mg of *3β-hydroxy-isoagatholal* (**9a**) as colourless crystals ($CHCl_2$–hexane). mp 134° $[\alpha]^{23}$ ($\lambda$) = +22.3° (589), +23.6° (578), +26.5° (546), +42.7° (436). EIMS: *m/z* 320 (4), 305 (13), 302 (30), 207 (43), 284 (12), 275 (11), 273 (18), 269 (34), 255 (17), 241 (13), 213 (4), 201 (19), 161 (26), 41 (100). IR $\nu_{max}$ 3620, 3080, 3020, 2720, 1730, 1670, 1650, 1460, 1400, 1090, 1040, 1000, 900. $^1$H NMR (Table 3). $^{13}$C NMR (Table 4). Acetylation of **9a** (60 mg) ($Ac_2O$–pyridine) gave *3β,15-diacetoxy-isoagatholal* (**9b**) (70 mg), oily product, $[\alpha]^{23}$ ($\lambda$) = +20.3° (589), +21.3° (578), +24.5° (546), +45.0° (436). IR $\nu_{max}$ 3080, 3020, 2720, 1730, 1670, 1650, 1240, 950, 900. $^1$H NMR (Table 3). $^{13}$C NMR (Table 4).

*3α-Hydroxy-isoagatholal* (**10**). Colourless crystals ($CH_2Cl_2$–hexane) mp 129°, $[\alpha]^{23}$ ($\lambda$) = −0.7° (589), −1.1° (578), −1.8° (546), −5.9° (436). IR $\nu_{max}$ 3520, 3440, 3080, 3020, 2740, 1720, 1670, 1650, 1450, 1390, 1065, 1045, 905, 895. $^1$H NMR (Table 3). $^{13}$C NMR (Table 4). Acetylation of **10** (30 mg) ($Ac_2O$–pyridine, room temp.) gave 3α,15-diacetoxy-isoagatholal (**10a**) (33 mg), oil, IR: $\nu_{max}$ 3080, 3020, 2740, 1740, 1720, 1670, 1650, 1240, 905, 895. $^1$H NMR (table 3). $^{13}$C NMR (Table 4). Treatment of **10a** (20 mg) with 5% KOH–MeOH (0.5 ml) afforded 15 mg of reaction mixt. that after flash chromatography gave **9a** (5 mg).

*19-Hydroxylabda-*8(17),13*E-dien-*15*-al* (**11**). Colourless crystals mp 112° $[\alpha]^{23}$ ($\lambda$) = −26.8 (589), +28.0 (578), +31.6° (546). UV: 240 ($\varepsilon$ = 14 500). EIMS: *m/z* 304 (1), 289 (5), 287 (1), 286 (1), 273 (10), 261 (6), 255 (9), 221 (13), 203 (16), 189 (7), 187 (8), 81 (100). IR: $\nu_{max}$ 3640, 3080, 3020, 2780, 1670, 1640, 1630, 1025, 905, 870. $^1$H NMR (Table 3). $^{13}$C NMR (Table 4).

*19-Hydroxylabda-*8 (17),13*Z-dien-*15*-al* (**12**). Colourless crystals mp 115° $[\alpha]^{23}$ ($\lambda$) = +14.1 (589), +15.5° (578), +19.0°

Table 3. $^1$H NMR (200 MHz) spectra of labdanes **9**, **9a**, **9b**, **10**, **10a**, **11** and **12**

| H | 9 | 9a | 9b | 10 | 10a | 11 | 12 |
|---|---|---|---|---|---|---|---|
| 3 | 5.32 *t* (2.8) | 3.80 *dd* (11.3; 4.6) | 5.00 *dd* (11.4; 4.5) | 4.15 *t* (2.8) | 5.32 *t* (2.8) | — | — |
| 14 | 5.39 *t* (6.9) | 5.59 *t* (6.9) | 5.31 *t* (6.9) | 5.39 *t* (6.9) | 5.32 *t* (7.0) | 5.87 *d* (8.1) | 5.88 *d* (8.3) |
| 15 | 4.15 *d* (6.9) | 4.16 *d* (6.9) | 4.59 *d* (6.9) | 4.16 *d* (6.9) | 4.59 *d* (7.0) | 9.98 *d* (8.1) | 9.98 *d* (8.3) |
| 16 | 1.67 *bs* | 1.68 *bs* | 1.71 *bs* | 1.67 *s* | 1.70 *s* | 2.16 *bs* | 1.97 *bs* |
| 17 | 4.59 *bs* | 4.58 *bs* | 4.58 *bs* | 4.56 *bs* | 4.58 *bs* | 4.48 *bs* | 4.55 *bs* |
| | 4.92 *bs* | 4.88 *bs* | 4.88 *bs* | 4.88 *bs* | 4.92 *bs* | 4.85 *bs* | 4.89 *bs* |
| 18 | 1.02 *s* | 1.05 *bs* | 1.07 *s* | 1.12 *s* | 1.02 *s* | 0.98 *s* | 0.97 *s* |
| 19 | 9.68 *s* | 9.39 *s* | 9.28 *s* | 9.73 *s* | 9.69 *s* | 3.38 *d* (10.9) | 3.38 *d* (10.9) |
| | | | | | | 3.75 *d* (10.9) | 3.74 *d* (10.9) |
| 20 | 0.59 *s* | 0.74 *s* | 0.76 *s* | 0.59 *s* | 0.59 *s* | 0.66 *s* | 0.64 *s* |
| AcO-3 | 2.11 *s* | | 2.07 *s* | | 2.11 *s* | | |
| AcO-15 | | | 1.97 *s* | | 2.05 *s* | | |

$CDCl_3$, TMS as internal standard, $\delta$ multiplicity ($J$ in Hz).

Table 4. $^{13}$C NMR (50.3 MHz) spectra of labdanes **7**, **9**, **9a**, **10**, **11** and **12**

| C | 7 | 9 | 9a | 9b | 10 | 10a | 11 | 12 |
|---|---|---|---|---|---|---|---|---|
| 1 | 38.5 | 32.3 | 36.8 | 36.4 | 31.7 | 32.4 | 38.7 | 38.7 |
| 2 | 19.1 | 23.6 | 27.0 | 25.7 | 23.7 | 23.6 | 19.1 | 19.1 |
| 3 | 35.6 | 72.2 | 72.2 | 73.5 | 69.3 | 72.3 | 35.6 | 35.6 |
| 4 | 39.6 | 51.7 | 55.4 | 54.5 | 52.6 | 51.7 | 39.7 | 39.7 |
| 5 | 56.4 | 50.2 | 47.9 | 47.3 | 48.8 | 50.3 | 56.4 | 56.2 |
| 6 | 24.6 | 22.2 | 22.2 | 21.8 | 22.0 | 22.1 | 24.6 | 24.8 |
| 7 | 39.2 | 38.4 | 37.7 | 37.5 | 38.3 | 38.3 | 39.2 | 39.2 |
| 8 | 148.2 | 147.0 | 147.1 | 146.6 | 147.3 | 146.9 | 147.8 | 147.8 |
| 9 | 56.6 | 54.9 | 56.1 | 55.7 | 54.7 | 54.9 | 56.5 | 56.5 |
| 10 | 38.9 | 39.8 | 38.5 | 38.2 | 39.9 | 39.9 | 39.0 | 38.9 |
| 11 | 22.1 | 23.9 | 26.1 | 23.4 | 26.7 | 24.0 | 21.6 | 22.6 |
| 12 | 38.7 | 38.3 | 38.3 | 38.1 | 38.3 | 38.3 | 39.6 | 31.3 |
| 13 | 140.3 | 139.9 | 140.0 | 142.3 | 140.0 | 142.5 | 164.6 | 164.6 |
| 14 | 123.3 | 123.4 | 123.6 | 118.6 | 123.5 | 118.4 | 127.3 | 129.1 |
| 15 | 59.4 | 59.3 | 59.5 | 61.4 | 59.4 | 61.4 | 191.3 | 191.0 |
| 16 | 16.3 | 16.3 | 16.4 | 16.5 | 16.3 | 16.5 | 17.7 | 27.1 |
| 17 | 106.6 | 107.6 | 107.8 | 108.0 | 107.4 | 107.4 | 106.8 | 106.7 |
| 18 | 27.2 | 19.5 | 8.9 | 9.4 | 20.0 | 19.5 | 27.1 | 27.1 |
| 19 | 65.1 | 202.9 | 206.7 | 204.1 | 204.7 | 202.8 | 65.2 | 65.2 |
| 20 | 15.3 | 13.2 | 14.8 | 14.9 | 13.3 | 13.3 | 15.3 | 13.3 |
| AcO-3 | | 21.2 | | 21.0 | | 21.2 | | |
| $CO_2$-3 | | 170.2 | | 171.0 | | 170.0 | | |
| AcO-15 | | | | 20.9 | | 21.0 | | |
| $CO_2$-15 | | | | 170.2 | | 170.0 | | |

$CDCl_3$, TMS as internal standard.

(546). EIMS: *m/z* 304 (1), 289 (3), 273 (7), 261 (4), 255 (5), 221 (7), 203 (10), 189 (4), 187.4, 81 (100). IR: $\nu_{max}$ 3640, 3080, 3020, 2780, 1670, 1640, 1610, 1025, 905, 870. $^1$H NMR (Table 3). $^{13}$C NMR (Table 4). To 90 mg of **7** in 12 ml of $CHCl_3$, 800 mg of $MnO_2$ active were added; after 24 hr at room temp, 78 mg of reaction product were recovered which after chromatography ($AgNO_3$–silica gel 4:1) yielded **11** (50 mg) and **12** (15 mg).

8,15-*Dihydroxylabd*-13*E*-*en*-19-*al* (**14**). Colourless crystals ($CH_2Cl_2$–hexane) mp 134°. $[\alpha]^{23}$ ($\lambda$) = +17.8° (589), +18.6° (578), +21.5° (546), +38.7° (436). IR $\nu_{max}$ 3420, 2750, 1725, 1675, 1015, 815. $^1$H NMR (Table 1). $^{13}$C NMR (Table 2).

8-*Hydroxylabd*-13*E*-*en*-15-*al* (**15**). Colourless crystals, mp 105°. $[\alpha]^{23}$ ($\lambda$) = +12.1° (589), +12.8° (578), +15.1° (546), 30.3° (436). UV: $\lambda_{max}$ 218 ($\varepsilon$ = 12 600), 242 ($\varepsilon$ = 9800). EIMS: *m/z* 306 (4), 291 (3), 289 (2), 263 (3), 245 (11), 205 (5), 191 (10), 183 (3), 177 (10), 149 (3), 137 (16), 123 (18), 109 (28), 95 (29) 43 (100). IR 3610, 2760, 1675, 1630, 1160, 1110, 1085, 1070, 940, 910. $^1$H NMR (Table 1). $^{13}$C NMR (Table 2).

8-*Hydroxylabd*-13*Z*-*en*-15-*al* (**16**). Colourless crystals ($CH_2Cl_2$–hexane) mp (109°. $[\alpha]^{23}$ ($\lambda$) = +5.2° (589), +5.6 (578), +6.4° (546). UV: $\lambda_{max}$ 218 ($\varepsilon$ = 12 600), 242 ($\varepsilon$ = 9800). EIMS: *m/z* 306 (4), 291 (10), 289 (2), 288 (1), 279 (1), 263 (4), 245 (17), 205 (25), 189 (8), 177 (22), 161 (9), 159 (7), 149 (20), 137 (37), 43 (100). IR $\nu_{max}$ 3610, 2760, 1675, 1630, 1160, 1110, 1085, 1070, 940, 910. $^1$H NMR (Table 1). $^{13}$C NMR (Table 2). A stirred soln of *labd*-13*E*-*en*-8,15-*diol* (**13**) (120 mg) in $CH_2Cl_2$ (4 ml) was added to pyridinium dichromate (150 mg in 2 ml $CH_2Cl_2$). After 2 hr at room temp the reaction mixt was dil with 40 ml of $Et_2O$. By chromatography ($AgNO_3$–silica gel 4:1) 70 mg of **16** and 20 mg of **15** were obtained.

*Sandaracopimaradiene*-3$\beta$,18-*diol* (**18**). Colourless crystals ($C_6H_6$ mp 151°, $[\alpha]^{23}$ ($\lambda$) = −17.0° (589). −17.8° (578) −20.7°

Table 5. $^1$H NMR (200 MHz) spectra of pimaranes

| H | 18 | 18 Acetonide | 19 |
|---|---|---|---|
| 3 | 3.66 *dd* (10.0; 4.2) | 3.54 *dd* (11.3; 3.7) | 3.66 *dd* (10.1; 4.0) |
| 7 | ... | ... | 5.32 *s* |
| 14 | 5.22 *s* | 5.24 *s* | ... |
| 15 | 5.76 *dd* (17.4; 10.7) | 5.77 *dd* (17.3; 10.6) | 5.80 *dd* (17.5; 10.7) |
| 16 | 4.88 *dd* (10.7; 1.6) | 4.88 *dd* (10.6; 1.6) | 4.86 *dd* (10.7; 1.4) |
| | 4.90 *dd* (17.4; 1.6) | 4.90 *dd* (17.3; 1.6) | 4.92 *dd* (17.5; 1.4) |
| 17 | 0.84 *s* | 0.86 *s* | 0.86*s* |
| 18 | 3.38 *d* (10.5) | 3.45 *d* (10.6) | 3.38 *d* (10.4) |
| | 3.65 *d* (10.5) | 3.53 *d* (10.6) | 3.64 *d* (10.4) |
| 19 | 1.03 *s* | 1.09 *s* | 0.99 *s* |
| 20 | 0.90 *s* | 1.04 *s* | 0.91 *s* |
| Other | | | |
| | | Acetonide | |
| | | 1.42 *s* | |
| | | 1.45 *s* | |

$CDCl_3$, TMS as internal standard, $\delta$ multiplicity ($J$ in Hz).

Table 6. $^{13}$C NMR (50.3 MHz) spectra of pimaranes **18**, **18** acetonide **19**, **20** and **21a**

| C | 18 | 18 acetonide | 19 | 20 | 21a |
|---|---|---|---|---|---|
| 1 | 37.4 | 37.7 | 37.6 | 39.5 | 33.4 |
| 2 | 27.5 | 24.2 | 27.0 | 19.9 | 22.7 |
| 3 | 77.4 | 77.7 | 77.2 | 30.2 | 83.1 |
| 4 | 37.8 | 37.2 | 42.0 | 41.4 | 41.1 |
| 5 | 49.0 | 50.6 | 44.6 | 47.7 | 38.0 |
| 6 | 22.9 | 21.5 | 23.4 | 23.6 | 23.2 |
| 7 | 35.1 | 34.6 | 121.0 | 121.3 | 74.3 |
| 8 | 136.7 | 136.3 | 135.7 | 135.7 | 122.7 |
| 9 | 50.8 | 50.8 | 51.8 | 52.1 | 145.1 |
| 10 | 38.4 | 38.4 | 35.2 | 35.3 | 38.0 |
| 11 | 19.2 | 18.8 | 20.2 | 20.4 | 21.7 |
| 12 | 36.0 | 35.5 | 36.2 | 36.2 | 34.4 |
| 13 | 42.6 | 37.5 | 36.8 | 36.9 | 35.2 |
| 14 | 129.5 | 129.5 | 46.0 | 46.2 | 38.6 |
| 15 | 149.3 | 149.0 | 150.3 | 150.3 | 145.3 |
| 16 | 110.5 | 110.3 | 109.3 | 109.3 | 111.4 |
| 17 | 26.5 | 26.2 | 21.6 | 21.6 | 27.8 |
| 18 | 71.9 | 72.9 | 71.8 | 74.2 | 12.9 |
| 19 | 12.0 | 12.7 | 11.5 | 64.9 | 64.2 |
| 20 | 15.9 | 15.8 | 15.5 | 15.9 | 18.6 |
| Other | | Acetonide | | | Acetates |
| | | 19.4 | | AcO-3 | 21.2 |
| | | 30.0 | | $CO_2$-3 | 170.5 |
| | | 99.1 | | AcO-7 | 21.3 |
| | | | | $CO_2$-7 | 173.5 |

$CDCl_3$, TMS as internal standard.

(546) −40.0° (436). −75.5° (365). IR: $\nu_{max}$ 3610, 3490, 3090, 1640, 1045, 1000, 915, 870, 860. $^1$H NMR (Table 5). $^{13}$C NMR (Table 6). *Diacetate* (**18a**). Colourless crystals from $CH_2Cl_2$–hexane mp 127°. $[\alpha]^{23}$ ($\lambda$)= +23.0° (589). +24.0° (578) +26.5° (546) +37.1° (436), +38.4° (365). EIMS: *m/z* 388 (19), 373 (13), 328 (9), 268 (13), 255 (9), 253 (24), 239 (7), 187 (7), 159 (13), 157 (7), 145 (13), 133 (65), 132 (31), 131 (16), 119 (47), 105 (36), 43 (100). IR $\nu_{max}$ 3090, 1730, 1645, 1390, 1380, 1255, 1045, 990, 915. A soln of **18** (40 mg) in $Me_2CO$ (2 ml) with 2,2-dimethoxypropane (1 ml) and a small amount of trimethylsilyl chloride were allowed to react at room temp for 5 min yielding 45 mg of *sandaracopimaradiene-3β,18-diol acetonide* (**18b**). Colourless crystals (MeOH) mp 111°. $[\alpha]^{23}$ ($\lambda$)= −18.8° (589), −19.4° (578), −22.4° (546), −41.1° (436), −73.5° (365). IR $\nu_{max}$ 3080, 1645, 1390, 1380, 1200, 1170, 1010, 950, 920, 865. $^1$H NMR (Table 5). $^{13}$C NMR (Table 6).

*Isopimaradiene-3β,18-diol* (**19**). Colourless crystals ($C_6H_6$). mp 121°. $[\alpha]^{23}$ ($\lambda$)= −31.5° (589), −32.7° (578), −38.2° (546), −70.0° (436), −119.3° (365). EIMS: *m/z* 304 (22), 286 (20), 273 (21), 271 (46), 255 (64), 253 (46), 239 (20), 201 (21), 199 (27), 188 (31), 187 (70), 91 (100). IR: $\nu_{max}$ 3630, 3490, 3090, 1640, 1060, 1035, 995, 915. $^1$H NMR (Table 5). $^{13}$C NMR (Table 6). **19** (50 mg) treated as described for **18** gave 51 mg of *isopimaradiene-3β,18-diol acetonide*, colourless crystals (MeOH). mp 105°. $[\alpha]^{23}$ ($\lambda$)= −32.1° (589), −33.4° (578), −38.4° (546), −70.1° (436), −117.9° (365). IR: $\nu_{max}$ 3090, 1645, 1390, 1380, 1200, 1180, 1160, 1100, 950, 920, 860.

*Isopimaradiene-18,19-diol* (**20**). Colourless crystals ($C_6H_6$). mp 108°, $[\alpha]^{23}$ ($\lambda$)= −10.5° (589), −11.2° (578), −12.9° (546), −23.4° (436), −37.8° (365). EIMS: *m/z* 304 (31), 273 (59), 271 (25), 255 (71), 253 (23), 242 (38), 227 (12), 212 (18), 91 (100). IR 3620, 3440, 3080, 1645, 1025, 995, 915. $^1$H NMR (Table 5). $^{13}$C NMR (Table 6). **20** (30 mg) treated as described for **18** and **19** gave 32 mg of *isopimaradiene-18,19-diol acetonide*, colourless crystals (MeOH), mp 93°. $[\alpha]^{23}$ ($\lambda$)= −10.1° (589), −10.9° (578), −11.5° (546), −18.4° (436), −31.6° (365). IR $\nu_{max}$ 3080, 1645, 1390, 1380, 1200, 1170, 1110, 1000, 920, 860, 840.

*Isopimara-8,15-diene-3β,7α,19-triol* (**21**). Colourless crystals ($C_6H_6$) $^1$H NMR (Table 5).

*3β,19-Diacetoxy-isopimara-8,15-dien-7α-ol* (**21a**). Oil. $[\alpha]^{23}$ ($\lambda$) = +62.6° (589), +66.0° (578), +75.4° (546), +133.4° (436), +243.3° (365). IR: 3400, 1740, 1670, 1650, 1390, 1260, 1050, 1040, 930. $^1$H NMR (Table 5). $^{13}$C NMR (Table 6).

*Hinokiol* (**22**). Colourless crystals (MeOH). mp 230°, $[\alpha]^{23}$ ($\lambda$) = +62.6° (589), +75.8° (578), +86.9° (546), +153.5° (436), +250.1° (365). $^{13}$C NMR (DMSO-$d_6$) (Table 7)

*Hinokione* (**23**). Colourless crystals (MeOH). mp 190°C, $[\alpha]^{23}$ ($\lambda$)= +104.5° (589), +109.1° (578), +125.0° (546), +226.2° (436), +369.2° (365). UV $\lambda_{max}$ 212 ($\varepsilon$=6300), 236

**18**, **18** acetonide, **19**, **20**, **20** acetonide, **21** and **21a**

| **20** | **20** Acetonide | **21** | **21a** |
|---|---|---|---|
| — | — | 3.66 *dd* (10.7; 4.8) | 4.89 *dd* (12.6; 4.5) |
| 5.32 *s* | 5.30 *s* | 4.22 *m* | 4.17 *m* |
| — | — | — | — |
| 5.80 *dd* (17.5; 10.7) | 5.80 *dd* (17.5; 10.7) | 5.67 *dd* (17.6; 10.7) | 5.63 *dd* (17.5; 10.7) |
| 4.86 *dd* (10.7; 1.5) | 4.86 *dd* (10.7; 1.5) | 4.91 *dd* (10.7; 1.5) | 4.87 *dd* (10.7; 1.7) |
| 4.92 *dd* (17.5; 1.5) | 4.92 *dd* (17.5; 1.5) | 4.95 *dd* (17.6; 1.5) | 4.90 *dd* (17.5; 1.7) |
| 0.85 *s* | 0.86 *s* | 0.97 *s* | 0.96 *s* |
| 3.36 *d* (10.4) | 3.28 *d* (10.4) | 0.77 *s* | 0.99 *s* |
| 3.91 *d* (10.4) | 3.80 *d* (10.4) | | |
| 3.86 *d* (10.4) | 3.79 *d* (10.4) | 3.43 *d* (11.4) | 3.33 *d* (11.6) |
| 4.06 *d* (10.4) | 3.92 *d* (10.4) | 3.75 *d* (11.4) | 4.77 *d* (11.6) |
| 0.83 *s* | 0.76 *s* | 0.99 *s* | 0.89 *s* |
| | Acetonide | | Acetates |
| | 1.35 *s* | | 2.06 *s* |
| | 1.37 *s* | | 2.15 *s* |

Table 7. $^{13}C$ NMR (50.3 MHz) spectra of abietanes **22** and **23**

| C | 22* | 23† |
|---|---|---|
| 1 | 36.7 | 37.6 |
| 2 | 27.7 | 34.6 |
| 3 | 76.6 | 205.4 |
| 4 | 38.4 | 47.4 |
| 5 | 49.5 | 50.7 |
| 6 | 18.6 | 20.5 |
| 7 | 29.4 | 30.2 |
| 8 | 124.4 | 126.7 |
| 9 | 147.1 | 145.7 |
| 10 | 37.8 | 37.4 |
| 11 | 110.3 | 111.9 |
| 12 | 152.0 | 151.3 |
| 13 | 131.4 | 132.5 |
| 14 | 125.6 | 126.9 |
| 15 | 26.0 | 26.9 |
| 16 | 22.3 | 22.6 |
| 17 | 22.4 | 22.7 |
| 18 | 15.5 | 26.9 |
| 19 | 28.1 | 21.1 |
| 20 | 24.5 | 24.6 |

*DMSO-$d_6$, †$CDCl_3$, TMS as internal standard.

($\varepsilon = 5250$), 288 ($\varepsilon = 5350$). IR $\nu_{max}$ 3600, 3400, 1715, 1630, 1510, 1470. $^{13}C$ NMR (Table 7). To a stirred soln of **22** (15 mg) in $CH_2Cl_2$ (1 ml) pyridinium dichromate (25 mg) was added and left at room temp for 2 hr. After diln with $Et_2O$ (10 ml) and flash chromatography 10 mg of **23** were obtained.

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