

Di- and Triterpenoids from the Liverwort *Blepharidophyllum densifolium***

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Blepharidophyllum, Jungermanniales, Scapaniaceae, *ent*-kauranes, *ent*-pimaranes, Dammaranes

22 *ent*-kaurane and *ent*-pimarane type diterpenoids, ten of which are new, *ent*-19-acetoxy-kaur-16-en-15-one, *ent*-19-oxo-kaur-16-en-15-one, *ent*-11 α -acetoxy-20-oxo-kaur-16-en-15-one, *ent*-11 α -acetoxy-15-oxo-kaur-16-en-20-acid, *ent*-11 α -acetoxy-7 β -hydroxy-kaur-16-en-15-one, *ent*-11 α -acetoxy-19-hydroxy-kaur-16-en-15-one, *ent*-19-acetoxy-11 α -hydroxy-kaur-16-en-15-one, *ent*-11 α -acetoxy-6 β ,19-dihydroxy-kaur-16-en-15-one, *ent*-11 α -acetoxy-19-hydroxy-kauran-15-one and *ent*-19-acetoxy-11 α -hydroxy-kauran-15-one were isolated from the liverwort *Blepharidophyllum densifolium*. Furthermore three known triterpenoids cabraleadiol, cabraleadiolacetate and shoreic acid have been found. Their structures were established by NMR spectroscopy.

Introduction

Liverworts are known to be a rich source of terpenoid constituents (Asakawa, 1995; Zinsmeister *et al.*, 1991; Zinsmeister *et al.*, 1994). Since there has been no previous investigation on the South American liverwort *Blepharidophyllum densifolium*, we decided to analyse the constituents of this species, in order to find new natural products. This paper describes the isolation and characterisation of ten new *ent*-kauranes (**1–10**) along with eleven known compounds of this type of structure (**11–21**), an *ent*-pimarane type diterpenoid (**22**) and three known dammarane triterpenoids (**23–25**).

Result and Discussion

A combination of size exclusion chromatography, vacuum liquid chromatography and HPLC of the ether and the methanolic extract of the plant led to the isolation of the constituents discussed below.

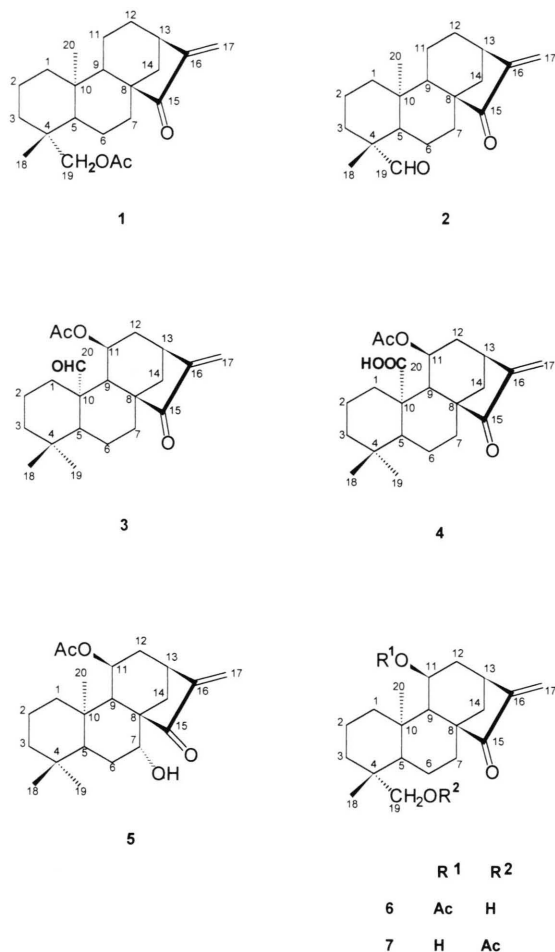
Compound **1**, C₂₂H₃₂O₃ (*m/z* 344.2, [M]⁺), was obtained as crystalline needles. The IR spectrum indicated the presence of an α,β -unsaturated carbonyl in a five membered ring (1727 cm⁻¹, 1645 cm⁻¹). The ¹H NMR spectrum showed signals for

two tertiary methyl groups (δ_H 0.95, 1.08), a deshielded proton at δ_H 3.03 (*brs*, H-13), two exomethylene protons (δ_H 5.92, *brs*; 5.23, *brs*), two protons of an oxygen carrying methylene group (δ_H 4.19, *d*, *J* = 11.0 Hz; 3.86, *d*, *J* = 11.0 Hz) and an acetoxy group (*s*, δ_H 2.03). The ¹³C NMR spectrum indicated the presence of 22 carbons (Table I), three methyls, eight methylenes, three methines, three quarternary carbons, two carbonyl carbons (δ_C 210.2, *s*; 171.2, *s*), one oxygenated methylene (δ_C 67.1, *t*) and two olefinic carbons (δ_C 149.6, *s*; 114.3, *t*). The above spectral data show that compound **1** is tetracarboyclic and consistent with an acetylated kaur-16-en-15-one structure. Since only three methyls are visible in the ¹H NMR spectrum an acetylation in position 18, 19 or 20 can be assumed. The location of the acetyl was determined by twodimensional NMR. A correlation between the protons of the methyl at C-20 and the oxygenated methylene indicates that the structure of **1** is *ent*-19-acetoxy-kaur-16-en-15-one. The assumption of an *ent*-kaurane can be deduced from the co-occurrence of the known *ent*-kauranes and from the sign of the specific rotation of **1** ($[\alpha]_D^{20} = -76^\circ$) since *ent*-kauranes in general have negative rotations.

Compound **2** with the molecular formula C₂₀H₂₈O₂ was obtained as crystalline needles. The IR and ¹H NMR spectra indicated a close relation to **1**. The NMR showed an additional signal of an

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aldehyde proton (δ_{H} 9.73, s) instead of the singlet of the methyl from an acetylic group. From this observation the location of an aldehyde in position 19 can be assumed, which corresponds with the detected mass of m/z 300, $[\text{M}]^+$. Therefore, the structure of **2** is represented as *ent*-19-oxo-kaur-16-en-15-one.

Compound **3** gave the molecular formula $\text{C}_{20}\text{H}_{30}\text{O}_4$. Comparison of its ^1H and ^{13}C NMR spectra with those of **2** displayed an additional singlet of an acetyl methyl at δ_{H} 1.80 corresponding to the ^{13}C NMR signal at δ_{C} 21.2. A secondary carbinole proton at δ_{H} 5.24 (t , $J = 3.2$ Hz) is visible in the spectrum. The low field shift of this signal indicates the acetylation of this alcohol. The location and the stereochemistry of the acetoxy group was determined by NOE experiments. Those revealed NOEs between H-11 and both H-1 α and

H-12 α . Thus, these results establish the acetoxy group as 11 α . NOE experiments also showed that the aldehyde at δ_{H} 10.34 must be attached to C-20. The above data indicate, that the structure of **3** is *ent*-11 α -acetoxy-20-oxo-kaur-16-en-15-one.

Compound **4** has the molecular formula $\text{C}_{22}\text{H}_{30}\text{O}_5$ (m/z 374, $[\text{M}]^+$). Its ^{13}C NMR data are similar to those of **3** except for the presence of a carboxylic acid (δ_{C} 181.4) instead of a C-20 aldehyde. This was proven by HMBC correlation between both H-5 and H-9 and C-20. On the basis of these results structure **4**, *ent*-11 α -acetoxy-15-oxo-kaur-16-en-20-acid, is assigned to this compound.

Compound **5** did not give a molecular ion on GC-mass spectrometry analysis. However, ^{13}C NMR and DEPT spectra revealed its molecular formula $\text{C}_{22}\text{H}_{32}\text{O}_4$. Comparison of the ^1H and ^{13}C NMR data with those of the compounds described above indicated that the structure is another acetylated *ent*-kaur-16-en-15-one with an additional hydroxyl group which is represented by a doublet of doublet (δ_{H} 4.08, $J = 12.0, 4.6$ Hz). The location and stereochemistry of the hydroxyl group was determined by NOE experiments revealing correlation between H-7 and both H-5 β and H-9 β . These results establish the hydroxyl group as 7 α . Therefore, the structure of **5** is represented as *ent*-11 α -acetoxy-7 β -hydroxy-kaur-16-en-15-one.

Compound **6** gave the molecular formula $\text{C}_{22}\text{H}_{32}\text{O}_4$ (m/z 360, $[\text{M}]^+$). Its ^1H NMR data are similar to those of **5** except for the occurrence of two doublets (δ_{H} 3.67, $J = 11.7$ Hz; 3.43, $J = 11.7$ Hz) instead of the H-7 doublet of doublet. This indicates the presence of an oxygenated methylene in position 18, 19 or 20. A NOE correlation between the methylene protons and the protons of the methyl at C-20 indicates that the structure of **6** is *ent*-11 α -acetoxy-19-hydroxy-kaur-16-en-15-one.

The CI-mass spectrometry of compound **7** displayed the same molecular ion (m/z 360, $[\text{M}]^+$) as that of **6**. The NMR data of both compounds are also very similar. In the ^1H NMR of **7** the doublets of the protons at C-19 are shifted to lower fields whereas the signal of H-11 shows a high field shift of 1.06 ppm. The above results reveal that **7** contains an acetylated hydroxyl group at C-19 and an unsubstituted alcohol at C-11. On the basis of these findings structure **7**, *ent*-19-acetoxy-11 α -hydroxy-kaur-16-en-15-one, is assigned to this compound.

Table I. ^{13}C NMR spectral data of compound **1–10**.

C	1	2	3	4	5	6	7	8	9	10
C-1	39.7 <i>t</i>	39.6 <i>t</i>	34.3 <i>t</i>	38.7 <i>t</i>	39.1 <i>t</i>	39.6 <i>t</i>	39.8 <i>t</i>	42.1 <i>t</i>	39.2 <i>t</i>	39.1 <i>t</i>
C-2	18.0 <i>t</i>	18.4 <i>t</i>	19.0 <i>t</i>	20.2 <i>t</i>	18.2 <i>t</i>	17.9 <i>t</i>	17.9 <i>t</i>	18.2 <i>t</i>	18.0 <i>t</i>	17.8 <i>t</i>
C-3	36.4 <i>t</i>	36.5 <i>t</i>	41.4 <i>t</i>	42.0 <i>t</i>	41.5 <i>t</i>	35.4 <i>t</i>	36.1 <i>t</i>	40.2 <i>t</i>	35.2 <i>t</i>	36.1 <i>t</i>
C-4	37.1 <i>s</i>	37.9 <i>s</i>	33.8 <i>s</i>	34.1 <i>s</i>	33.3 <i>s</i>	38.8 <i>s</i>	37.0 <i>s</i>	39.1 <i>s</i>	38.2 <i>s</i>	37.1 <i>s</i>
C-5	55.9 <i>d</i>	56.0 <i>d</i>	54.5 <i>d</i>	55.8 <i>d</i>	52.5 <i>d</i>	55.7 <i>d</i>	55.7 <i>d</i>	56.4 <i>d</i>	55.5 <i>d</i>	55.7 <i>d</i>
C-6	18.2 <i>t</i>	18.8 <i>t</i>	17.8 <i>t</i>	18.5 <i>t</i>	27.5 <i>t</i>	18.3 <i>t</i>	18.6 <i>t</i>	64.7 <i>d</i>	18.7 <i>t</i>	18.7 <i>t</i>
C-7	34.0 <i>t</i>	33.7 <i>t</i>	33.0 <i>t</i>	33.3 <i>t</i>	71.1 <i>d</i>	33.9 <i>t</i>	33.9 <i>t</i>	39.8 <i>t</i>	34.8 <i>t</i>	34.7 <i>t</i>
C-8	52.5 <i>s</i>	51.4 <i>s</i>	50.4 <i>s</i>	50.5 <i>s</i>	56.7 <i>s</i>	50.6 <i>s</i>	50.4 <i>s</i>	48.8 <i>s</i>	50.9 <i>s</i>	50.9 <i>s</i>
C-9	52.8 <i>d</i>	52.3 <i>d</i>	60.7 <i>d</i>	57.3 <i>d</i>	59.2 <i>d</i>	59.9 <i>d</i>	64.2 <i>d</i>	59.9 <i>d</i>	59.0 <i>d</i>	63.9 <i>d</i>
C-10	40.0 <i>s</i>	39.9 <i>s</i>	53.4 <i>s</i>	48.0 <i>s</i>	38.8 <i>s</i>	38.8 <i>s</i>	38.6 <i>s</i>	38.7 <i>s</i>	38.3 <i>s</i>	38.2 <i>s</i>
C-11	18.9 <i>t</i>	20.0 <i>t</i>	67.6 <i>d</i>	67.9 <i>d</i>	68.0 <i>d</i>	68.3 <i>d</i>	66.0 <i>d</i>	68.5 <i>d</i>	67.2 <i>d</i>	65.0 <i>d</i>
C-12	32.4 <i>t</i>	32.1 <i>t</i>	35.7 <i>t</i>	36.5 <i>t</i>	39.9 <i>t</i>	38.6 <i>t</i>	41.3 <i>t</i>	38.3 <i>t</i>	31.5 <i>t</i>	33.2 <i>t</i>
C-13	38.2 <i>d</i>	38.1 <i>d</i>	36.8 <i>d</i>	36.4 <i>d</i>	36.3 <i>d</i>	36.7 <i>d</i>	36.8 <i>d</i>	37.1 <i>d</i>	34.3 <i>d</i>	34.7 <i>d</i>
C-14	36.6 <i>t</i>	37.1 <i>t</i>	38.6 <i>t</i>	35.0 <i>t</i>	27.8 <i>t</i>	36.3 <i>t</i>	36.5 <i>t</i>	37.7 <i>t</i>	36.9 <i>t</i>	37.0 <i>t</i>
C-15	210.2 <i>s</i>	210.1 <i>s</i>	207.4 <i>s</i>	209.1 <i>s</i>	209.2 <i>s</i>	208.8 <i>s</i>	209.4 <i>s</i>	209.4 <i>s</i>	222.0 <i>s</i>	223.8 <i>s</i>
C-16	149.6 <i>s</i>	149.5 <i>s</i>	149.8 <i>s</i>	149.9 <i>s</i>	149.9 <i>s</i>	150.0 <i>s</i>	150.1 <i>s</i>	149.6 <i>s</i>	48.9 <i>d</i>	49.4 <i>d</i>
C-17	114.3 <i>t</i>	114.6 <i>t</i>	113.2 <i>t</i>	113.1 <i>t</i>	113.4 <i>t</i>	113.1 <i>t</i>	113.0 <i>t</i>	113.0 <i>t</i>	10.4 <i>q</i>	11.1 <i>q</i>
C-18	27.5 <i>q</i>	28.6 <i>q</i>	32.0 <i>q</i>	33.0 <i>q</i>	33.6 <i>q</i>	27.1 <i>q</i>	27.5 <i>q</i>	27.9 <i>q</i>	26.7 <i>q</i>	27.4 <i>q</i>
C-19	67.1 <i>t</i>	n. d.	20.8 <i>q</i>	22.2 <i>q</i>	21.5 <i>q</i>	65.5 <i>t</i>	66.9 <i>t</i>	68.2 <i>t</i>	65.5 <i>t</i>	66.9 <i>t</i>
C-20	18.0 <i>q</i>	15.4 <i>q</i>	206.6 <i>d</i>	180.1 <i>s</i>	18.1 <i>q</i>	18.2 <i>q</i>	17.9 <i>q</i>	18.8 <i>q s</i>	18.4 <i>q</i>	17.9 <i>q</i>
C-21	171.2 <i>s</i>		169.1 <i>s</i>	169.3 <i>s</i>	169.4 <i>s</i>	169.4 <i>s</i>	171.3 <i>s</i>	169.3 <i>s</i>	169.9 <i>s</i>	171.3 <i>s</i>
C-22	20.9 <i>q</i>		21.2 <i>q</i>	21.4 <i>q</i>	21.5 <i>q</i>	21.4 <i>q</i>	21.0 <i>q</i>	21.3 <i>q</i>	21.2 <i>q</i>	21.5 <i>q</i>

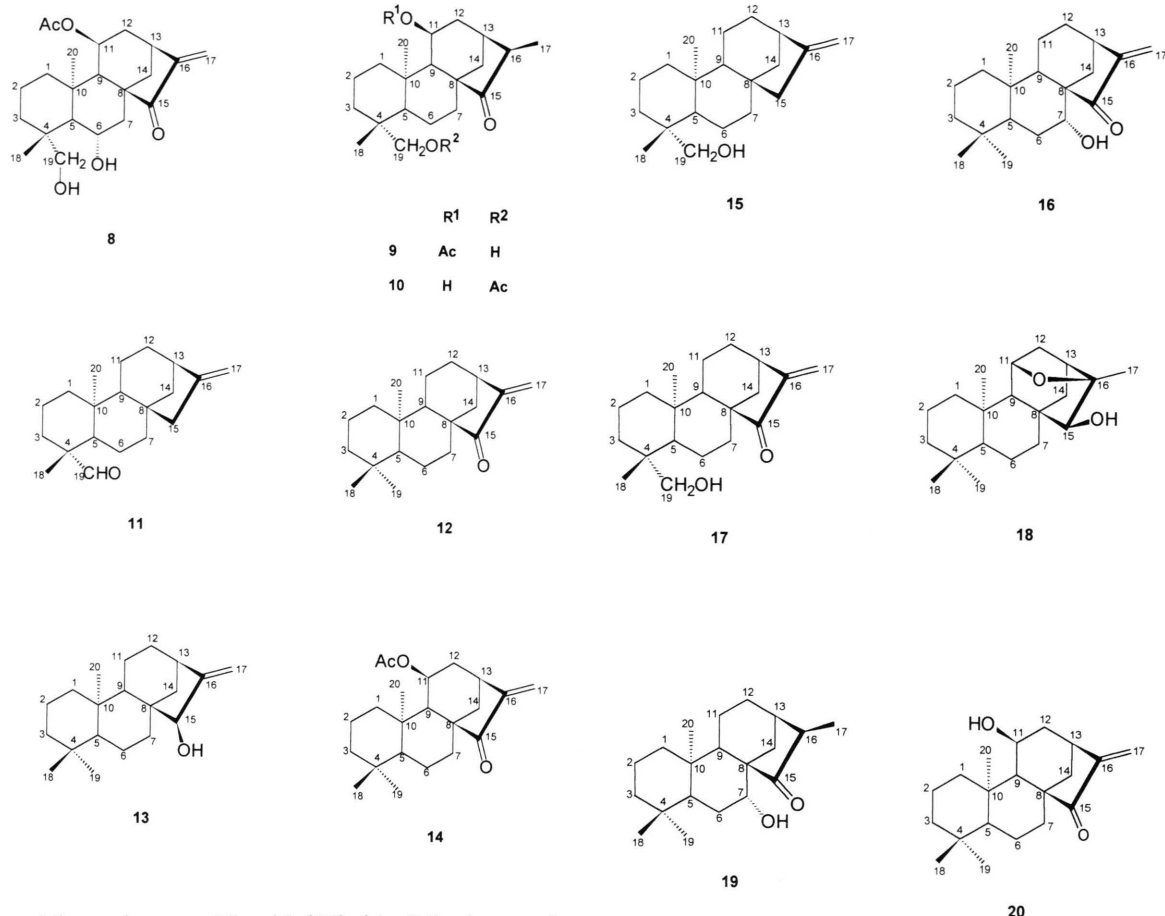
The molecular formula of compound **8** was established as $\text{C}_{22}\text{H}_{32}\text{O}_5$ (m/z 376, $[\text{M}]^+$). Its ^1H NMR data are similar to those of **6** but in the spectrum of **8** an additional broad singlet of another hydroxyl group can be observed at δ_{H} 4.38. In order to elucidate the location of this oxygenated methine HMBC experiments had been done which indicated correlation between the methine proton and C-10 and C-8. For this reason the alcohol must be located in position 6. Its stereochemistry was determined by NOE. The above results reveal that **8** is *ent*-11 α -acetoxy-6 β ,19-dihydroxy-kaur-16-en-15-one.

Compound **9** was obtained as colourless needles with a molecular formula of $\text{C}_{22}\text{H}_{34}\text{O}_4$ as calculated from the CI mass spectrum (m/z 362, $[\text{M}]^+$). On comparison of the ^1H NMR data of the compounds described above with the data of **9** it is obvious that the singlets of the olefinic protons are missing. Instead a doublet of a secondary methyl (δ_{H} 1.14, $J = 7.3$ Hz) is visible in the spectrum corresponding to a ^{13}C NMR signal at δ_{C} 10.6. This signal can be assigned to a methyl at C-16. Thus, compound **9** is consistent with a kauran-15-one structure. Based on its chemical shift and multiplicity a doublet at δ_{H} 5.03 ($J = 6.0$ Hz) could be assigned to a proton of an acetylated methine in 11 α . The shifts of two doublets at δ_{H} 3.66 ($J =$

11.0 Hz) and δ_{H} 3.42 ($J = 11.0$ Hz) are almost identical with the signals of the methylene protons in position 19 of compound **6**. The above data indicate that the structure of **9** is *ent*-11 α -acetoxy-19-hydroxy-kauran-15-one.

The last new diterpenoid from *B. densifolium*, **10**, gave the molecular formula $\text{C}_{22}\text{H}_{34}\text{O}_4$ (m/z 362, $[\text{M}]^+$). The ^1H NMR spectra of **10** and **9** are very similar. From the shifts of the doublet of H-11 (δ_{H} 3.90, $J = 5.8$ Hz) and of the two doublets of the protons at C-19 (δ_{H} 4.14, $J = 11.2$ Hz; δ_{H} 3.93, $J = 11.2$ Hz) can be deduced that the location of the acetylation of compound **10** has changed from 11 to 19. For these reasons the structure of **10** is *ent*-19-acetoxy-11 α -hydroxy-kauran-15-one.

The previously known *ent*-19-oxo-kaur-16-en (**11**) (Piozzi *et al.*, 1971), *ent*-kaur-16-en-15-one (**12**) (Langenbahn *et al.*, 1993), *ent*-15 α -hydroxy-kaur-16-en (**13**) (Langenbahn *et al.*, 1993), *ent*-11 α -acetoxy-kaur-16-en-15-one (**14**) (Fujita and Ochiai, 1978), *ent*-19-hydroxy-kaur-16-en (**15**) (Gonzales *et al.*, 1980), *ent*-7 β -hydroxy-kaur-16-en-15-one (**16**) (Buchanan *et al.*, 1996), *ent*-19-hydroxy-kaur-16-en-15-one (**17**) (Boaventura *et al.*, 1994), *ent*-11,16-epoxy-15 α -hydroxy-kauran (**18**) (Benes *et al.*, 1977), *ent*-7 β -hydroxy-kauran-15-one (**19**) (Buchanan *et al.*, 1996), *ent*-11 α -hydroxy-kaur-16-en-15-one (**20**) (Nagashima *et al.*, 1990),



ent-15-oxo-kauran-19-acid (**21**) (de Oliveira *et al.*, 1995), *ent*-3 β -hydroxy-pimara-8(14),15-diene (**22**) (Ansell *et al.*, 1993) together with the triterpenoids cabraleadiol (**23**) (Hisham *et al.*, 1996), cabraleadiolacetate (**24**) (Waterman and Ampofo, 1985) and shoreic acid (**25**) (Govindachari *et al.*, 1994) were also isolated from *B. densifolium* and identified by comparison of their spectroscopic data with published results.

Experimental

Solvents used for spectral measurements

CDCl₃ [¹H NMR: 400 MHz; ¹³C NMR: 100 MHz for 1D, 500 MHz and 125 MHz for 2D techniques, respectively. Chemical shifts are given in β values (ppm) from TMS], CHCl₃ (optical rotation).

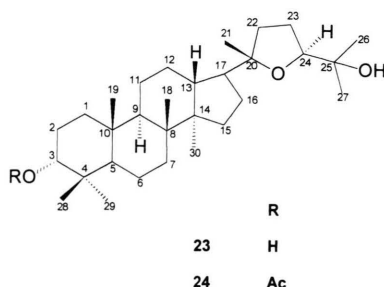
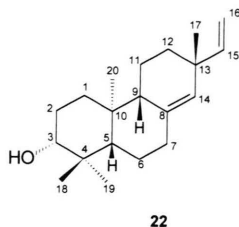
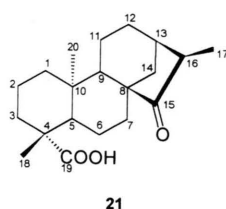
Plant material

Blepharidophyllum densifolium (Hook.) Ångstr. was collected in Tierra del Fuego, south of Paso

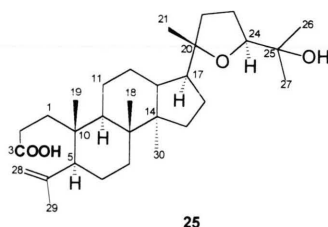
Garibaldi, Argentina, in March 1997 by Prof. Dr. R. Mues and identified by Dr. U. Drehwald, Göttingen. A voucher specimen is deposited at the Botanical Institute of the Universität des Saarlandes (Herbarium SAAR, No. 5692).

Extraction and isolation

The extraction scheme followed standard procedures of our group (Bungert *et al.*, 1998; Cullmann *et al.*, 1993; Adam and Becker, 1994). Powdered air dried plant material (400 g) was subsequently extracted with Et₂O and MeOH. The Et₂O extract (13.9 g) was chromatographed on Sephadex LH-20 (150 $\times$ 2.5 cm i.d.) with MeOH-CH₂Cl₂ (1:1) as eluent to give two fractions (B 1 and B 2). Fraction B 2 (7.5 g) was separated by VLC (Silica gel 15 μ m, 60 mm $\times$ 35 mm i.d., step-wise with an *n*-hexane-EtOAc gradient) and gave the fractions B 2-1 (1.5–2% EtOAc, 707 mg), B 2-2 (2–4% EtOAc, 777 mg), B 2-3 (4–12%



24 Ac



EtOAc, 1249 mg), B 2–4 (12–20% EtOAc, 966 mg), B 2–5 (20–40% EtOAc, 823 mg) and B 2–6 (40–80% EtOAc, 845 mg). These fractions were further purified by HPLC (5 μ m, 4 $\times$ 250) on silica gel, diol-modified silica gel and cyano-modified silica gel to give the following constituents in order of increasing polarity: **11** (Si 60, n-hexane-EtOAc 99.5:0.5) (3.0 mg), **12** (Si 60, n-hexane-EtOAc 99.5:0.5) (10.0 mg), **1** (Si 60, n-hexane-EtOAc 97.5:2.5) (12.4 mg), **14** (Si 60, n-hexane-EtOAc 97.5:2.5) (14.3 mg), **2** (Si 60, n-hexane-EtOAc 97.5:2.5) (1.2 mg), **13** (Si 60, n-hexane-EtOAc 97:3) (5.0 mg), **22** (Si 60, n-hexane-EtOAc 93:7) (1.8 mg), **15** (Si 60, n-hexane-EtOAc 93:7) (19.0 mg), **3** (Si 60, n-hexane-EtOAc 93:7) (21.0 mg), **24** (Si 60, n-hexane-EtOAc 92:8) (5.8 mg), **16** (CN, n-hexane-EtOAc 93:7) (8.4 mg), **17** (Diol, n-hexane-EtOAc 95:5) (4.5 mg), **18** (Si 60, n-hexane-EtOAc 84:16) (11.4 mg), **19** (Si 60, n-hexane-EtOAc 84:16) (6.4 mg), **23** (Si 60, n-hexane-EtOAc 84:16) (3.1 mg), **20** (Si 60, n-hexane-EtOAc 84:16) (5.4 mg), **21** (Si 60, n-hexane-

EtOAc 84:16) (3.3 mg), **4** (Diol, n-hexane-EtOAc 90:10) (6.2 mg), **25** (Si 60, n-hexane-EtOAc 82:18) (8.5 mg), **10** (Si 60, n-hexane-EtOAc 75:25) (2.5 mg), **5** (Si 60, n-hexane-EtOAc 70:30) (6.4 mg), **6** (Diol, n-hexane-EtOAc 85:15) (8.6 mg), **9** (Si 60, n-hexane-EtOAc 65:35) (1.8 mg) and **7** (Si 60, n-hexane-EtOAc 60:40) (4.4 mg). The methanol soluble extract was distributed between EtOAc and H₂O. The organic layer was evapd *in vacuo* and also chromatographed via Sephadex LH-20 with MeOH-CH₂Cl₂ (4:1) as eluent to give the two fractions BE-1 and BE-2. The VLC (Diol, 15 μ m, 60 mm $\times$ 35 mm i. d., step-wise with an n-hexane-EtOAc gradient) of BE-2 (6.21 g) afforded fraction BE-2.3 (25–40% EtOAc, 156 mg). A HPLC purification (5 μ m, 4 $\times$ 250) on CN modified silica gel gave compound **8** (CN, n-hexane-EtOAc 79:21) (25.4 mg).

ent-19-acetoxy-kaur-16-en-15-one (**1**)

[α]_D²⁰ –76° (CHCl₃); EI-MS *m/z* (rel. int.): 344.2 [M]⁺ (22), 284(13), 271(24), 269(12), 173(15), 161(20), 148(39), 136(51), 131(23), 123(88), 119(45), 107(78), 95(53), 91(100); IR $\nu_{\max}^{KBr}$ cm⁻¹: 2980, 1727, 1645; ¹H-NMR (CDCl₃) δ_H 5.92 (1H, *brs*, H-17A), 5.23 (1H, *brs*, H-17B), 4.19 (1H, *d*, *J* = 11.0 Hz, H-19A), 3.86 (1H, *d*, *J* = 11.0 Hz, H-19B), 3.03 (1H, *brs*, H-13), 2.35 (1H, *d*, *J* = 11.9 Hz, H-11), 2.03 (3H, *s*, H-22), 1.89 (1H, *brd*, *J* = 13.0 Hz, H-1 α), 1.08 (3H, *s*, H-20), 0.95 (3H, *s*, H-18); ¹³C-NMR (CDCl₃): Table I

ent-19-oxo-kaur-16-en-15-one (**2**)

[α]_D²⁰ –98° (CHCl₃); EI-MS *m/z* (rel. int.): 300.3 [M]⁺ (16), 271(13), 173(11), 161(15), 149(26), 133(25), 119(31), 107(45), 95(37), 91(100); IR $\nu_{\max}^{KBr}$ cm⁻¹: 2980, 1727, 1645; ¹H-NMR (CDCl₃) δ_H 9.73 (1H, *s*, H-19), 5.93 (1H, *brs*, H-17A), 5.24 (1H, *brs*, H-17B), 3.03 (1H, *brs*, H-13), 2.36 (1H, *d*, *J* = 11.9 Hz, H-14 α), 1.79 (1H, *brd*, *J* = 13.0 Hz, H-1 α), 1.00 (3H, *s*, H-20), 0.92 (3H, *s*, H-18); ¹³C-NMR (CDCl₃): Table I

ent-11 α -acetoxy-20-oxo-kaur-16-en-15-one (**3**)

[α]_D²⁰ –86° (CHCl₃); EI-MS *m/z* (rel. int.): 330.3 [M-CO]⁺ (0.8), 314(1.4), 296(2.7), 269(7), 253(6), 217(7), 160(14), 145(10), 133(13), 126(20), 111(55), 91(34), 69(31), 43(100); IR $\nu_{\max}^{KBr}$ cm⁻¹: 2980, 1727; ¹H-NMR (CDCl₃) δ_H 10.34 (1H, *s*, H-20), 5.83 (1H, *s*, H-17A), 5.18 (1H, *s*, H-17B), 5.24 (1H, *t*, *J* = 3.2 Hz, H-11), 2.98 (1H, *brs*, H-13), 2.67 (1H, *d*, *J* = 13.6 Hz, H-14 α), 1.80 (3H, *s*, H-22), 0.93

(3H, *s*, H-18), 0.75 (3H, *s*, H-19); ^{13}C -NMR (CDCl_3): Table I

ent-11 α -acetoxy-15-oxo kaur-16-en-20-acid (4)

$[a]_{\text{D}}^{20} -43^\circ$ (CHCl_3); EI-MS m/z (rel. int.): 374.3 $[\text{M}]^+(32)$, 318(28), 300(96), 285(51), 270(32), 241(15), 169(21), 151(100), 131(19), 123(51), 109(55), 91(79); IR $\nu_{\text{max}}^{\text{KBr}} \text{ cm}^{-1}$: 2980, 1727; ^1H -NMR (CDCl_3) δ_{H} 5.83 (1H, *s*, H-17A), 5.18 (1H, *s*, H-17B), 5.38 (1H, *brs*, H-11), 2.87 (1H, *d*, $J = 3.2$ Hz, H-12), 2.68 (1H, *brd*, $J = 13.0$ Hz, H-1 α), 2.49 (1H, *d*, $J = 12.5$ Hz, H-14 α), 1.80 (3H, *s*, H-22), 0.88 (3H, *s*, H-18), 0.78 (3H, *s*, H-19); ^{13}C -NMR (CDCl_3): Table I

ent-11 α -acetoxy-7 β -hydroxy-kaur-16-en-15-one (5)

$[a]_{\text{D}}^{20} -86^\circ$ (CHCl_3); CI-MS m/z (rel. int.): 300.0 $[\text{M}+\text{H}-\text{C}_2\text{H}_3\text{O}-\text{H}_2\text{O}]^+(24)$, 282(20), 175(64), 149(31), 134(20), 123(63), 176(27), 109(58), 91(56), 69(100); IR $\nu_{\text{max}}^{\text{KBr}} \text{ cm}^{-1}$: 3450, 2980, 1727; ^1H -NMR (CDCl_3) δ_{H} 5.88 (1H, *s*, H-17A), 5.22 (1H, *s*, H-17B), 5.10 (1H, *d*, $J = 4.8$ Hz, H-11), 4.08 (1H, *dd*, $J = 11.9, 4.5$ Hz, H-7), 3.07 (1H, *s*, H-13), 1.82 (3H, *s*, H-22), 1.05 (3H, *s*, H-20), 0.88 (3H, *s*, H-18), 0.81 (3H, *s*, H-19); ^{13}C -NMR (CDCl_3): Table I

ent-11 α -acetoxy-19-hydroxy-kaur-16-en-15-one (6)

$[a]_{\text{D}}^{20} -101^\circ$ (CHCl_3); CI-MS m/z (rel. int.): 361.0 $[\text{M}+\text{H}]^+(5)$, 329(14), 301(100), 283(20), 169(14), 141(20), 119(22), 91(69), 69(27); IR $\nu_{\text{max}}^{\text{KBr}} \text{ cm}^{-1}$: 3450, 2980, 1727, 1650; ^1H -NMR (CDCl_3) δ_{H} 5.85 (1H, *s*, H-17A), 5.19 (1H, *s*, H-17B), 5.09 (1H, *d*, $J = 5.0$ Hz, H-11), 3.68 (1H, *d*, $J = 11.0$, H-19A), 3.43 (1H, *d*, $J = 11.0$, H-19B), 3.01 (1H, *s*, H-13), 2.35 (1H, *s*, H-14), 1.82 (3H, *s*, H-22), 1.75 (1H, *d*, $J = 13.8$ Hz, H-1 α), 1.02 (3H, *s*, H-20), 0.96 (3H, *s*, H-18); ^{13}C -NMR (CDCl_3): Table I

ent-19-acetoxy-11 α -hydroxy-kaur-16-en-15-one (7)

$[a]_{\text{D}}^{20} -110^\circ$ (CHCl_3); CI-MS m/z (rel. int.): 361.0 $[\text{M}+\text{H}]^+(1)$, 333(1), 301(5), 283(50), 205(3), 91(44), 73(100); IR $\nu_{\text{max}}^{\text{KBr}} \text{ cm}^{-1}$: 3450, 2980, 1727,

1650; ^1H -NMR (CDCl_3) δ_{H} 5.84 (1H, *s*, H-17A), 5.24 (1H, *s*, H-17B), 4.16 (1H, *d*, $J = 11.0$, H-19A), 4.02 (1H, *d*, $J = 4.4$ Hz, H-11), 3.84 (1H, *d*, $J = 11.0$, H-19B), 2.03 (3H, *s*, H-22), 1.00 (3H, *s*, H-20), 0.96 (3H, *s*, H-18); ^{13}C -NMR (CDCl_3): Table I

ent-11 α -acetoxy-6 β ,19-dihydroxy-kaur-16-en-15-one (8)

$[a]_{\text{D}}^{20} -66^\circ$ (CHCl_3); EI-MS m/z (rel. int.): 376.0 $[\text{M}]^+(16)$, 357(17), 316(23), 299(32), 281(18), 253(30), 197(16), 91(100); IR $\nu_{\text{max}}^{\text{KBr}} \text{ cm}^{-1}$: 3450, 2980, 1727, 1650; ^1H -NMR (CDCl_3) δ_{H} 5.84 (1H, *s*, H-17A), 5.21 (1H, *s*, H-17B), 5.12 (1H, *d*, $J = 4.5$ Hz, H-11), 4.38 (1H, *brs*, H-6), 4.17 (1H, *d*, $J = 11.4$ Hz, H-19A), 3.16 (1H, *d*, $J = 11.4$, H-19B), 3.01 (1H, *brs*, H-13), 1.81 (3H, *s*, H-22), 1.42 (3H, *s*, H-20), 1.01 (3H, *s*, H-18); ^{13}C -NMR (CDCl_3): Table I

ent-11 α -acetoxy-19-hydroxy-kauran-15-one (9)

$[a]_{\text{D}}^{20} -91^\circ$ (CHCl_3); EI-MS m/z (rel. int.): 362.0 $[\text{M}]^+(9)$, 331(16), 319(2), 302(47), 285(12), 271(100), 259(35), 123(33), 91(29); IR $\nu_{\text{max}}^{\text{KBr}} \text{ cm}^{-1}$: 3450, 2980, 1727; ^1H -NMR (CDCl_3) δ_{H} 5.03 (1H, *d*, $J = 5.9$ Hz, H-11), 3.66 (1H, *d*, $J = 11.0$ Hz, H-19A), 3.43 (1H, *d*, $J = 11.0$, H-19B), 1.92 (3H, *s*, H-22), 1.14 (1H, *d*, H-17), 0.99 (3H, *s*, H-20), 0.94 (3H, *s*, H-18); ^{13}C -NMR (CDCl_3): Table I

ent-19-acetoxy-11 α -hydroxy-kauran-15-one (10)

$[a]_{\text{D}}^{20} -83^\circ$ (CHCl_3); EI-MS m/z (rel. int.): 362.0 $[\text{M}]^+(4)$, 345(5), 317(4), 303(15), 285(41), 271(3), 123(7), 91(65), 73(100); IR $\nu_{\text{max}}^{\text{KBr}} \text{ cm}^{-1}$: 3450, 2980, 1727; ^1H -NMR (CDCl_3) δ_{H} 4.15 (1H, *d*, $J = 11.0$ Hz, H-19A), 3.90 (1H, *d*, $J = 5.8$ Hz, H-11), 3.84 (1H, *d*, $J = 11.0$, H-19B), 2.03 (3H, *s*, H-22), 0.97 (1H, *d*, H-20), 0.94 (3H, *s*, H-18); ^{13}C -NMR (CDCl_3): Table I

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