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DITERPENES FROM *BACCHARIS* SPECIES*

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Key Word Index—*Baccharis minutiflora*; *B. alaternoides*; Compositae; diterpenes; *ent*-kaurane derivatives; homoditerpenes; clerodanes.

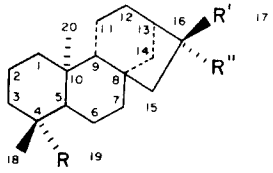
Abstract—The aerial parts of *Baccharis minutiflora* afforded in addition to known compounds eight new *ent*-kaurane derivatives, one being a homo kaurane, while the aerial parts of *B. alaternoides* gave two pairs of epimeric clerodane derivatives, which, however, had to be modified chemically before they could be separated. The stereochemistry of these diterpenes could not be elucidated with certainty.

In a continuation of our chemical investigations of the large genus *Baccharis* (tribe Astereae), we have now studied the constituents of *B. minutiflora* Mart. The aerial parts afforded germacrene D, lupeol, methyl betulinate, the *ent*-kaurane derivatives **1–5**, **10** [1], **14** [2], **17** [3], **18** [3], **21** [4] and nine further compounds, their structures being **6**, **7**, **9**, **11**, **13**, **15**, **16**, **19** and **20**. The ^{1}H NMR data of **6** (Table 1) and the molecular formula as well as the fragmentation pattern indicated the presence of a kauranal. The chemical shifts of the methyl signals showed that the aldehyde group had to be placed at C-16. The α-orientation was deduced from the chemical shifts of H-13 and H-14, which were deshielded by the carbonyl group. This was further confirmed by the Eu(fod)$_3$-induced shifts, which could only be explained by an α-orientated carbonyl group at C-16. Consequently, the ^{1}H NMR data of **8**, obtained from the natural acid by addition of diazomethane, were similar, while those of **9** differed from the data of **6** as one Me group was replaced by CH_2OH. The stereochemistry at C-4 was deduced by comparing the chemical shifts of H-19 and H-20 with those of similar compounds with known stereochemistry. **11**, molecular formula $C_{21}H_{34}O_2$, was a homoditerpene, the structure of which followed from the ^{1}H NMR data (Table 2) and from the ^{1}H NMR data of the diol **12** obtained by sodium boronate reduction, which clearly indicated the presence of an acetyl group. As the typical signal of H-13 was shifted downfield, as in the spectra of **8** and **9**, the position of the acetyl group was at C-16, and one of the H-14 and H-15 signals was at a lower field as in the spectra of **8** and **9**, the stereochemistry at C-16 should be the same as in **8** and **9**. The position of the hydroxyl group clearly followed from the chemical shifts of the corresponding doublets. The ^{1}H NMR data of **13**, molecular formula $C_{20}H_{30}O_2$, showed that a dialdehyde was present. While the α-orientation of the C-16 aldehyde group was deduced from the shifts of H-13 and H-14 and by comparison of the ^{1}H NMR data with those of **10** and **11**, the orientation of C-4 aldehyde group followed from the chemical shifts of the methyl singlets, which were compared with those of the C-4 epimeric *ent*-kaurenic acids. The ^{1}H NMR data of **15** and **16** (Table 1) were in part close to those of **17** and **18** [3], especially the chemical shifts of the epoxide protons which were the same as those of **17** and **18**, indicating the presence of 16α, 17-epoxides. **15** was identical with the main product of epoxidation of *ent*-kaurene. The axial orientation of the CH_2OH group in **16** was deduced from the corresponding ^{1}H NMR data. The molecular formula of **19** indicated the presence of an *ent*-kaurene with an unusual oxygen function while the fragment *m/z* 257 ($C_{19}H_{29}$) showed that all three oxygen atoms were placed in one group. The nature of this function followed from the ^{1}H NMR data (Table 1). In addition to a singlet at δ 8.32, typical for a formyl proton, an AB-quartet centred at δ 4.98 indicated the presence of a OCH_2O group. All the data, therefore, were in agreement with structure **19**. Saponification consequently afforded **4**. As all known kaurane derivatives present in this plant were *ent*-kauranes, **6–8** most likely belong to the same series.

The structure of **20** followed from the molecular formula and the ^{1}H NMR data (Table 1), which were close to those of **21**, while the chemical shifts of the methyl signals were similar to those of *ent*-kaurene. The roots gave lupeol, **3** and its 15α-isovaleryloxy derivative.

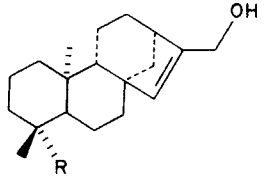
A re-investigation of the aerial parts of *B. alaternoides* HBK afforded in addition to the flavanones isolated previously [5], the flavone **29** [6], *Baccharis* oxide, α-pinene, germacrene D, eugenol methyl ether and a complex mixture of polar diterpenic acids, which, even after conversion to their Me esters, could not be separated completely. However, saponification and reaction with MeOH afforded the epimeric cyclic

*Part 381 in the series "Naturally Occurring Terpene Derivatives". For Part 380 see Bohlmann F., Jakupovic, J., Schuster, A., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 161.



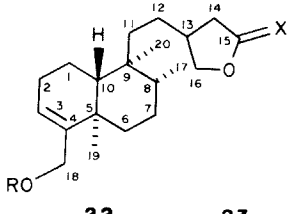
	1	2	3	4	5	6	7
R	Me	CHO	CO_2H	CH_2OH	Me	Me	Me
R' } R'' }	$=CH_2$	$=CH_2$	$=CH_2$	$=CH_2$	Me	H	H
					OH	CHO	CO_2H

	8	9	10	11	12	13	14	15	16	17	18	19
R	Me	CH_2OH	CH_2OH	CH_2OH	CH_2OH	CHO	CO_2H	Me	CH_2OH	CHO	CO_2H	CH_2OCH_2OCHO
R'	H	H	H	H	H	H	H					$=CH_2$
R''	CO_2Me	CHO	CO_2H	COMe	CH(OH)Me	CHO	CH_2OH					

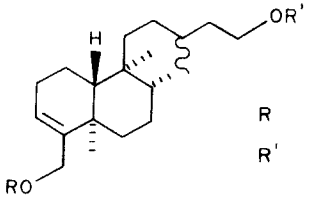


20 R=Me

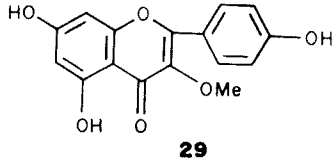
21 R=CH_2OH



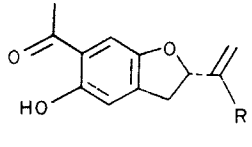
	22	23	24	25	26
R	$COCH_2CO_2H$	$COCH_2CO_2Me$	$COCH_2CO_2Me$	H	Ac
X	H, OH	H, OH	=O	H, OMe	H, OMe



	27	28
R	$COCH_2CO_2H$	Ac
R'	H	Ac



29



30 R=CHO

31 R=CH_2OAc

Table 1. ^{1}H NMR spectral data of compounds **6**, **8**, **9**, **11**, **12**, **13**, **15**, **16**, **19** and **20** (400 MHz, $CDCl_3$, TMS as int. standard)

	6	Δ*	**8**	**9**	**11**†	**12**‡	**13**	**15**	**16**	**19**‖	**20**
H-13	2.83 *br*	0.14	2.45 *br*	2.54 *br*	2.40 *br*	2.27 *br*	2.54 *br*	§	§	2.63 *br*	2.54 *br*
H-14	1.89 *d*(*br*)	0.07	1.88 *d*(*br*)	1.85 *d*(*br*)	1.83 *d*(*br*)	§	1.87 *d*(*br*)	§	§	§	§
H-15	1.71 *dd*	0.18	1.64 *dd*	1.72 *dd*	1.70 *dd*	§	1.77 *dd*	2.04 *dd*	2.01 *dd*	§	5.35 *s*(*br*)
H-16	2.56 *dd*(*br*)	0.21	2.61 *dd*(*br*)	2.57 *dd*(*br*)	2.73 *dd*(*br*)	§	2.61 *dd*(*br*)	§	§	§	—
H-17	9.64 *d*	0.15	—	9.64 *d*	—	3.40 *dq*	9.67 *d*	2.87 *d*	2.89 *d*	4.79 *s*(*br*)	4.18 *d*
H-17′			—		—			2.80 *d*	2.79 *d*	4.73 *s*(*br*)	
H-18	0.98 *s*	0.03	0.97 *s*	0.97 *s*	0.97 *s*	0.97 *s*	0.98 *s*	1.02 *s*	1.02 *s*	1.00 *s*	1.02 *s*
H-19	0.83 *s*	0.02	0.83 *s*	3.73 *d* 3.43 *d*(*br*)	3.73 *d* 3.42 *d*(*br*)	3.73 *d* 3.43 *d*(*br*)	9.60 *d*	0.84 *s*	3.74 *s* 3.45 *d*(*br*)	3.73 *d* 3.42 *d*(*br*)	0.84 *s*
H-20	0.78 *s*	0.02	0.78 *s*	0.94 *s*	0.95 *s*	0.94 *s*	0.84 *s*	0.80 *s*	0.95 *s*	0.98 *s*	0.78 *s*
OMe	—	—	3.65 *s*	—	—	—	—	—	—	—	—

*Δ values after addition of $Eu(fod)_3$. †H-21 2.14 *s*. ‡H-21 1.12 *d*. §Obscured multiplets. ‖OCH_2OCHO 4.98 AB*q*, 8.32 *s*.

J (Hz): Compounds **6**, **8**, **9**, **11**, **12** and **13**: 14,14′ = 12; 15,15′ = 13.5; 15,16 = 5.5; 15′,16 = 8.5; 16,17 = 1.8; compound **9**: 19,19′ = 11; compound **13**: 18,19 = 1.2; compound **11**: 19,19′ = 11; compound **12**: 19,19′ = 11; 16,17 = 9; 17,21 = 6; compounds **15/16**: 15,15′ = 12; 15,16 = 2; 17,17′ = 5; compounds **16/19**: 19,19′ = 11; compound **20**: 16,17 = 1.5.

Table 2. ^{1}H NMR spectral data of compounds **23**, **24**, **25**, **26** and **28** (400 MHz, $CDCl_3$, TMS as int. standard)

	23	**24**	**25** ($CDCl_3$)			**25** ($CDCl_3$–C_6D_6, 2:1)				**26**		**28**
H-3	5.59 *s*(*br*)	5.59 *t*(*br*)	5.55 *s*(*br*)			5.39 *s*(*br*)				5.56 *s*(*br*)		5.58 *t*(*br*)
H-13		2.44 *m*	2.28 *m*	2.03 *m*		2.15 *m*				2.27 *m*		2.05 *m*
H-14		2.65 *dd*	1.53 *m*			1.36 *m*				1.5 *m*		2.05 *m*
H-14′		2.14 *dd*	2.28 *m*			1.90 *m*				2.03 *m*		
H-15	4.03 *m*	—	4.99 *dd*	4.97 *d*(*br*)	4.87 *dd*		4.85 *d*(*br*)	4.99 *dd*			4.97 *d*(*br*)	4.09 *m*
H-16′	3.69 *m*	4.43	3.44 *dd*	3.41 *dd*		3.33 *dd*		3.43 *dd*			3.41 *dd*	0.90 *d*
H-16′			4.05 *dd*	3.96 *dd*	3.96 *dd*		3.87 *dd*	4.04 *dd*			3.95 *dd*	
H-17	0.80 *d*(*br*)	0.78 *d*(*br*)	0.77 *d*		0.69 *d*		0.68 *d*			0.79 *d*		0.78 *d*
H-18	4.58 *s*(*br*)	4.58 *s*(*br*)	4.07 *s*(*br*)			3.91 *s*(*br*)				4.52 *d*(*br*)		4.54 *d*(*br*)
H-18′										4.46 *d*(*br*)		4.48 *d*(*br*)
H-19	1.06 *s*	1.04 *s*	1.05 *s*			0.94 *s*				1.04 *s*		1.05 *s*
H-20	0.73 *s*	0.71 *s*	0.69 *s*			0.60 *s*				0.69 *s*		0.70 *s*
H-2′	3.40 *s*	3.38 *s*	—	—	—		—			—		—
OMe	3.75 *s*	3.74 *s*	3.39 *s*	3.31 *s*	3.22 *s*		3.20 *s*	3.33 *s*			3.31 *s*	—
OAc	—	—	—	—	—		—			2.05 *s*		2.06 *s*
												2.04 *s*

J (Hz): 8,17 ~ 6; compound **24**: 2,3 = 3; 13,14 = 8; 13,14′ = 8; 14,14′ = 17; 13,16 = 7.5; 16,16′ = 9; compounds **25** and **26**: 13,16 = 16,16′ = 7.5; 14,15 = 5.5; 14′,15 = 2.5; compounds **26** and **28**: 18,18′ = 13; compound **28**: 2,3 = 3; 13,16 = 6.

acetals **25**, as was deduced from the ^{1}H NMR spectra (Table 2), though only a partial separation of the epimers was possible. Acetylation gave the epimeric acetates **26**, while oxidation of the crude methyl esters gave a single γ-lactone, the malonate **24**. The ^{1}H NMR data (Table 2) showed that a malonate residue was at C-18 of a clerodane with a saturated lactone moiety at C-12, as all signals were close to those of similar diterpenes [7]. The presence of a *trans*-clerodane was deduced from the chemical shifts of the signals of the methyl groups. Careful comparison of several compounds of this type showed that in *cis*-clerodanes a remarkable downfield shift of H-19 (*ca* 0.1 ppm) can be observed on esterification of the C-18 hydroxyl group [8], probably due to the nearly in plane orientation of the oxygen function and C-19, which is not the case in *trans*-clerodanes. Therefore, as in the case of **25** and **26** and in other *trans*-clerodanes no such effect was visible. Furthermore, the H-19 signal is at a lower field in *cis*- than in *trans*-clerodanes. Consequently, the natural compounds most probably were the epimeric lactols **22**. No assignment of the stereochemistry at C-13 was possible. Saponification and acetylation of the crude acids also afforded the diacetate **28** as followed from the ^{1}H NMR data (Table 2), if compared with those of similar diterpenes [7]; therefore most probably **27** was also a natural diterpene, as the corresponding signals of the methyl ester of **27** were present in the spectrum of the crude ester mixture. Again the stereochemistry at C-13 could not be assigned. The absolute configuration of the clerodanes was not determined. However, they are probably *ent*-clerodanes, as most diterpenes from *Baccharis* have this stereochemistry. We have also isolated **22** from the aerial parts of *B. polyphylla* Gardn. The roots of *B. alaternoides* afforded *Lachnophyllum* ester, *Matricaria* ester, *Baccharis* oxide and the acetophenone derivatives **30** and **31** [9] with the unusual substitution pattern typical for *Baccharis* species.

EXPERIMENTAL

The air-dried plant material was extracted with Et_2O–petrol (1 : 2) and the resulting extracts were separated first by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic material.

Baccharis minutiflora (*voucher RMK* 8396). The roots (50 g) afforded 12 mg lupeol, 8 mg **3** and 7 mg 15α-isovaleroyloxy-*ent*-kaurenic acid, while the aerial parts (100 g) gave 3 mg germacrene D, 5 mg lupeol, 4 mg methyl betunilate, 12 mg **1**, 35 mg **2**, 18 mg **3**, 215 mg **4**, 5 mg **5**, 30 mg **6** (Et_2O–petrol, 1 : 10), 1 mg **7** (isolated as methyl ester), 19 mg **9** (Et_2O–petrol, 1 : 1), 1 mg **10** (isolated as methyl ester), 3 mg **11** (Et_2O–petrol, 1 : 1), 20 mg **13** (Et_2O–petrol, 1 : 3), 2 mg **14** (isolated as methyl ester), 35 mg **15** (Et_2O–petrol, 1 : 20), 6 mg **16** (Et_2O–petrol, 1 : 1), 24 mg **17**, 4 mg **18**, 1.5 mg **19** (Et_2O–petrol, 1 : 10), 6 mg **20** (Et_2O–petrol, 1 : 1) and 1 mg **21**.

Baccharis alaternoides (*voucher RMK* 7749). The aerial parts (300 g) gave in addition to the flavanones isolated previously, 300 mg α-pinene, 4 mg germacrene D, 10 mg *Baccharis* oxide, 15 mg eugenol methyl ether, 300 mg of a mixture of **22** and **27** (Et_2O–MeOH, 20 : 1). To 100 mg of the mixture in Et_2O, CH_2N_2 was added. TLC (Et_2O–petrol, 3 : 1) afforded a mixture of **23** and the ester of **27** (*ca* 4 : 1), which could not be separated. 30 mg of this mixture were stirred for 12 hr with 30 mg pyridine chlorochromate. TLC (Et_2O–petrol, 3 : 1) gave 10 mg **24**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785 (γ-lactone), 1755, 1740 (CO_2R); MS *m/z* (rel. int.): 302.225 $[M-RCO_2H]^+$(11)($C_{20}H_{20}O$), 287 $[302-Me]^+$(8), 189 $[C_{14}H_{21}]^+$(100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-12 \quad -13 \quad -15 \quad -24} (c = 0.4,\ CHCl_3).$$

To 100 mg of the crude acids in 2 ml MeOH, 100 mg KOH in 0.5 ml H_2O were added. After heating for 10 min at 70°, the cooled mixture was acidified with dil. H_2SO_4. TLC (Et_2O) afforded 30 mg **25** (epimers, 1 : 1) and 15 mg of a diol, which on acetylation (Ac_2O, 30 min 70°) gave 15 mg **28**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1240 (OAc); MS *m/z* (rel. int.): 392.293 $[M]^+$(2)($C_{24}H_{40}O_4$), 332 $[M-AcOH]^+$(31), 273 $[332-OAc]^+$(2), 189 $[C_{14}H_{21}]^+$(100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-18 \quad -19 \quad -21 \quad -37} (c = 1.0,\ CHCl_3).$$

The epimeric alcohols **25** on acetylation (Ac_2O, 30 min, 70°) gave after TLC (Et_2O–petrol, 1 : 3) the epimeric acetates **26**, which could not be separated completely, but enriched fractions were obtained. Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1240 (OAc); ^{1}H NMR see Table 2. The roots (150 g) afforded 1 mg *Lachnophyllum* ester, 0.3 mg *Matricaria* ester, 100 mg *Baccharis* oxide, 1 mg **30** and 1 mg **31**.

16β-H-Ent-*kauran*-17-*al* (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2700, 1720 (CHO); MS *m/z* (rel. int.): 288.245 $[M]^+$(18)($C_{20}H_{32}O$), 273 $[M-Me]^+$(44), 231 $[M-C_3H_5O]^+$(34), 123 $[C_9H_{15}]^+$(100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-71 \quad -74 \quad -85 \quad -152} (c = 1.06,\ CHCl_3).$$

Methyl-16β-H-ent-*kauran*-17-*oate* (**8**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (CO_2R); MS *m/z* (rel. int.): 318.256 $[M]^+$(33)($C_{21}H_{34}O_2$), 303 $[M-Me]^+$(53), 287 $[M-OMe]^+$(6), 243 $[303-HCO_2Me]^+$(13), 123 $[C_9H_{15}]^+$(100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-56 \quad -60 \quad -71 \quad -117} (c = 1.0,\ CHCl_3).$$

19-*Hydroxy*-16β-H-ent-*kauran*-17-*al* (**9**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 2700, 1720 (CHO); MS *m/z* (rel. int.): 304.240 $[M]^+$(1)($C_{20}H_{32}O_2$), 273 $[M-CH_2OH]^+$(100), 123 $[C_9H_{15}]^+$(60).

16α - *Acetyl* - 19 - *hydroxy* - 16 - *desmethyl* - ent - *kaurane* (**11**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH), 1710 (C=O); MS *m/z* (rel. int.): 318.256 $[M]^+$(2)($C_{21}H_{34}O_2$), 300 $[M-H_2O]^+$(5), 287 $[M-CH_2OH]^+$(82), 275 $[M-COMe]^+$(20), 123 $[C_9H_{15}]^+$(81), 81 $[C_6H_9]^+$(100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-59 \quad -60 \quad -71 \quad -125} (c = 0.12,\ CHCl_3).$$

3 mg **11** were reduced in MeOH with 10 mg $NaBH_4$. TLC (Et_2O) afforded 2.5 mg **12**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH); MS *m/z* (rel. int.): 320 $[M]^+$(0.3) 302 $[M-H_2O]^+$(1), 289 $[M-CH_2OH]^+$(23), 271 $[289-H_2O]^+$(14), 57 (100).

16β-H-ent-*kauran*-17,19-*dial* (**13**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2700, 1720 (CHO); MS *m/z* (rel. int.): 302.225 $[M]^+$(10), 273 $[M-CHO]^+$(100), 245 $[273-CO]^+$(42), 123 $[C_9H_{15}]^+$(91);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-63 \quad -65 \quad -73 \quad -120} (c = 0.74, CHCl_3).$$

16α,17-*Epoxy*-ent-*kaurane* (**15**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}; 1460, 1390, 1372, 980, 960, 910; MS *m/z* (rel. int.): 288.245 $[M]^+$(35)($C_{20}H_{32}O$), 273 $[M-Me]^+$(52), 123 $[C_9H_{15}]^+$(100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-51 \quad -53 \quad -60 \quad -99} (c = 1.2, CHCl_3).$$

16α,17-*Epoxy*-ent-*kauran*-19-*ol* (**16**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}; 3620 (OH); MS *m/z* (rel. int.): 304.240 $[M]^+$(3) ($C_{20}H_{32}O_2$), 273 $[M-CH_2OH]^+$(58), 255 $[273-H_2O]^+$(31), 123 $[C_9H_{15}]^+$(100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-34 \quad -35 \quad -40 \quad -65} (c = 0.3, CHCl_3).$$

19-*Formyloxymethylenoxy*-ent-*kaurene* (**19**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (CO_2R); MS *m/z* (rel. int.); 346.251 $[M]^+$(0.5)($C_{22}H_{34}O_3$), 316 $[M-CH_2O]^+$(22), 301 $[316-Me]^+$(20), 273 $[301-CO]^+$(33), 257 $[M-CH_2OCH_2OCHO]^+$(93), 123 $[C_9H_{15}]^+$(100); CIMS (isobutane): 347 $[M+1]^+$(6), 271 $[M-OCH_2OCHO]^+$(70), 161 (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-62 \quad -64 \quad -77 \quad -126} (c = 0.12, CHCl_3).$$

1.5 mg **19** on hydrolysis with KOH/MeOH afforded 1 mg **4**, identical with the natural compound.

17-*Hydroxy*-ent-*kaur*-15-*ene* (**20**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 288.245 $[M]^+$(31) ($C_{20}H_{32}O$), 273 $[M-Me]^+$(42), 123 $[C_9H_{15}]^+$(58), 55 (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-19 \quad -20 \quad -24 \quad -37} (c = 0.26, CHCl_3).$$

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