Phytochemistry, Vol 28, No. 10, pp. 2745–2751, 1989
Printed in Great Britain

0031–9422/89 $3.00 + 0.00

PLATYCARPHOL AND OTHER KAURENE DERIVATIVES FROM *PLATYCARPHA CARLINOIDES*

C. ZDERO and F. BOHLMANN

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, F R G

(*Received* 3 *January* 1989)

Key Word Index—*Platycarpha carlinoides*; Compositae; diterpenes, *ent*-kaurene derivatives, norditerpenes, glycosides; glucopyranoside; allopyranoside

Abstract—The extract of the aerial parts of *Platycarpha carlinoides* gave, in addition to some known compounds, 10 *ent*-kaurenes including two glycosides, one being an allopyranoside, and three norkaurene derivatives. The structures were elucidated by high field ^{1}H NMR techniques and a few chemical transformations. The doubtful position of the genus *Platycarpha* is discussed again following the new chemical findings.

INTRODUCTION

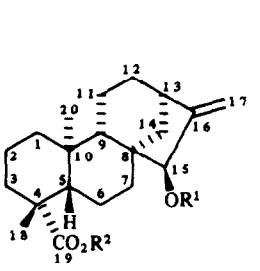
The small South African genus *Platycarpha* [syn. *Cynara* and *Stobaea* (sect. of Berkheya)] with only three species grows in saline spots. They are stemless perennials with radical leaves, numerous spreading like a star on the ground, petiolate and pinnately divided. Flower heads are numerous, densely crowded, covering the crown of the root The corymb is purple and much white wool is about the insertion of the leaves. The name is derived from the Greek words for the flat scale. The genus has been placed in several different tribes of the Compositae. W H. Harvey [1] added it next to *Corymbium* in the Vernonieae, while O. Hoffmann [2] has taken it as a genus of the Arctotideae. However, he mentioned a relationship to Mutisieae which was supported by E. Stix [3] on the basis of its pollenmorphology. However, later the same arguments led to the proposal that the genus should be a member of the Cynareae [4, 5], while in a treatment of the latter tribe just *Platycarpha* was again transferred to Arctotideae [6]. Finally, it should be mentioned that even a relationship to *Lasthenia* (tribe Heliantheae) was proposed by the nature of the isolated flavanoids [7]. The chemical investigation of one species gave in addition to thiophenacetylenes, typical for *Berkheya*, some germacranolides [8]. These findings could be taken as an indication that the genus is an intermediate between Arctotideae and Cynareae. To obtain a clearer picture, we have now studied a further species from Namibia, *P carlinoides* Oliver et Hiern. The results are presented in this paper.

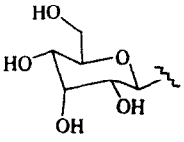
RESULTS AND DISCUSSION

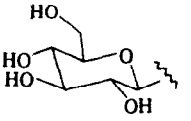
The extract of the aerial parts of *P. carlinoides* gave the *ent*-kaurene derivatives **1**, **2**, **3a** and **4**–**10**, the norkaurenes **13**–**15**, the thiophene derivative **16** [9], *ent*-16β-hydroxykaurane-19-oic acid [10] and the germacranolide **17** [8].

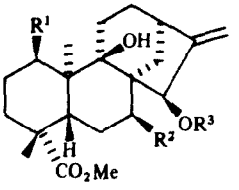
The acid **1** could not be obtained pure. After acetylation and esterification with diazomethane **1a**Ac was obtained in crystalline form. HRMS led to the molecular formula $C_{35}H_{50}O_{12}$. This was in agreement with the ^{13}C NMR spectrum (Table 1) which showed 35 signals, five carbonyl, two olefinic and eight oxygen-bearing carbons. In agreement with the ^{1}H NMR spectrum (Table 2), therefore, the presence of a tetraacetate of a diterpene glycoside with a carbomethoxy group was very likely. More detailed inspection of the ^{1}H NMR spectrum showed that the data required an *ent*-kaurenic acid derivative as followed from the typical signals for H-13, H-17, H-18 and H-20 A proton with a broadened triplet at δ3.79 was coupled with H-17. Accordingly, an oxygen function was at C-15. Comparison of the couplings with those of related 15α-and β-substituted kaurene derivatives showed that the configuration was the same as in a corresponding diterpene from a *Stevia* species [10] while the 15-epimers displayed a broadened singlet [11]. As, except for the carbomethoxy, no further signal for an oxygen function at the carbon skeleton of the diterpene was visible the sugar moiety had to be placed at C-15. The fragmentation pattern in the MS of **1a**Ac also supported the absence of further functions. In addition to the prominent peak *m/z* 331 ($C_{14}H_{19}O_9$, sugar moiety) a fragment at *m/z* 314 ($C_{21}H_{30}O_2$) was obviously due to loss of the sugar part. Fragments at *m/z* 299 $[314-Me]^+$ and 255 $[314-CO_2Me]^+$ supported this assumption The fragmentation pattern of the sugar ion *m/z* 331 is typical for tetraacetates of pyranosides [*m/z* 271 (6), 211 (6), 169 (100), 127 (16) 109 (43)]. The nature of the sugar moiety followed from the ^{1}H NMR signals and spin decouplings especially in deuteriobenzene as in deuteriochloroform some signals were overlapped The obtained sequence required a pyranoside which is epimeric at C-3 of a β-glucopyranoside tetraacetate. Accordingly, $J_{2,3}$ and $J_{3,4}$ were small. This configuration indicated the presence of an allopyranoside which seems to be very rare. The sugar itself has been reported from an *Ochromas malhamensis* culture [12]. The ^{1}H NMR couplings agree with the reported ones [13].

Compound **2** also had to be acetylated to get a pure sample. Though the highest fragment was *m/z* 648 ($C_{34}H_{48}O_{12}$) the molecular formula of **2**Ac was

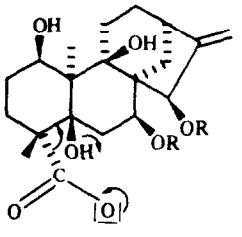


1 R^1 =  , R^2 = H

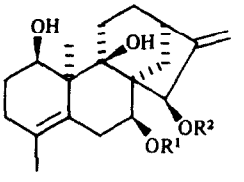
2 R^1 = H, R^2 = 



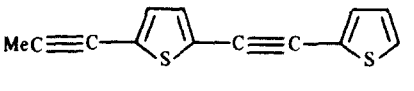
	3	4	5	6	7	8	9	10	11
R^1	OH	OEA*	OEA	OEA	OEA	OEA	OEA	OEA	OH
R^2	H	OEA	OH	OAc	OAc	OiBu	OiVal	Prop	OH
R^3	H	H	H	H	Ac	Ac	Ac	Ac	H



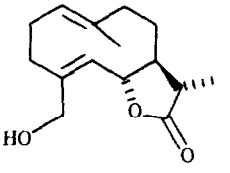
12



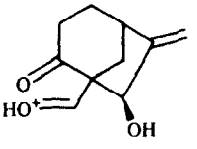
	13	14	15
R^1	H	Ac	H
R^2	H	H	Ac



16



17



18 (*m/z* 181)

1a methyl ester, **1** Ac tetraacetate, **3a** free acid, **2** Ac pentaacetate
*OEA = epoxyangelate

$C_{36}H_{50}O_{13}$ as *m/z* 630 was obviously due to loss of acetic acid and therefore *m/z* 648 to loss of ketene This assumption was established by the ^{13}C NMR spectrum (Table 1) which required 36 carbons. Again the fragmentation ion at *m/z* 331 and the subsequent fragments at *m/z* 271, 211, 169, 127 and 109 were attributable to a pyranoside tetraacetate. The ^1H NMR spectrum (Table 2) clearly showed that the latter was a β-glucopyranoside tetraacetate as followed from the characteristic couplings. Furthermore, again an *ent*-kaurene derivative with an oxygen function at C-15 followed from the coupling of the corresponding proton (δ5 12 *br t*) with H-17 and the

Table 1 ^{13}C NMR spectral data of **1a**Ac, **2**Ac, **3**, **7**, **8** and **13** (100.6 MHz, $CDCl_3$, δ-values)

C	**1a**Ac*	**2**Ac†	**3**	**7**‡	**8**§	**13**
1	40 5 *t*	40 5 *t*	72.8 *d*	72 2 *d*	72 0 *d*	73 5 *d*
2	19 3 *t*	19.0 *t*	30 4 *t*	31 7 *t*	31 2 *t*	30 4 *t*
3	37 9 *t*	37.7 *t*	35 0 *t*	31 6 *t*	31 1 *t*	31 7 *t*
4	43 7 *s*	44 1 *s*	44 0 *s*	43 7 *s*	43 4 *s*	125 4 *s*
5	56.0 *d*	56 4 *d*	43 7 *d*	38 9 *d*	38 4 *d*	133 3 *s*
6	22 0 *t*	21 3 *t*	21 4 *t*	26.9 *t*	26 8 *t*	27 1 *t*
7	38 1 *t*	39.3 *t*	30 4 *t*	79 9 *d*	79 4 *d*	79 5 *d*
8	45 9 *s*	46 0 *s*	48 5 *s*	51 4 *s*	51 3 *s*	50 3 *s*
9	46 2 *d*	46 8 *d*	83 1 *s*	80 4 *s*	80 2 *s*	85 8 *s*
10	39 1 *s*	38 8 *s*	46 1 *s*	47.6 *s*	47 4 *s*	47 4 *s*
11	17.9 *t*	17 9 *t*	28.2 *t*	27 3 *t*	26.3 *t*	27.4 *t*
12	33.6 *t*	33 3 *t*	33 5 *t*	34 0 *t*	34 3 *t*	33 9 *t*
13	40 7 *d*	40 5 *d*	38 9 *d*	38 9 *d*	38 6 *d*	38 8 *d*
14	36 5 *t*	36 4 *t*	35 9 *t*	35.7 *t*	36 0 *t*	34.4 *t*
15	90 4 *d*	81 5 *d*	85.7 *d*	82 6 *d*	82 8 *d*	85.4 *d*
16	156 7 *s*	153.5 *s*	156.0 *s*	151.9 *s*	150 9 *s*	154 0 *s*
17	105 1 *t*	106 2 *t*	104 7 *t*	105.7 *t*	106 3 *t*	106 1 *t*
18	28 5 *q*	28 7 *q*	28 7 *q*	28 6 *q*	28 6 *q*	25 6 *q*
19	177 2 *s*	175 6 *s*	178 2 *s*	177 3 *s*	177 7 *s*	—
20	15 7 *q*	16 1 *q*	17 6 *q*	17.8 *q*	17 7 *q*	20 0 *q*
OAc	20 1 *q*	21 1 *q*	—	20.9 *q*	168.6 *s*	—
	20 0 *q*	20.7 *q* (2×)		20 8 *q*	21.2 *q*	
	20 0 *q*	20.6 *q* (2×)		169 2 *s*		
	19 8 *q*	169 6 *s*		168 7 *s*		
	171 3 *s*	169 0 *s*				
	170 5 *s*	168 3 *s*				
	170 1 *s*	168 0 *s*				
	169 4 *s*					
	169 1 *s*					
OMe	50 5 *q*	—	51 3 *q*	51 1 *q*	51 5 *q*	—

*Glycoside 100 4 *d*, 70 4 *d*, 69 4 *d*, 69 0 *d*, 66 7 *d*, 62 3 *t*
†Glucoside 91.1 *d*, 70 4 *d*, 69 4 *d*, 69.0 *d*, 66 7 *d*, 62 3 *t*
‡Epang 168 9, 59 9 *s*, 59 7 d, 14.3 *q*, 19 79.
§Epang 168 8 *s*, 59.8 *s*, 59 9 *d*, 13 9 *q*, 19.5 *q*, *t*Bu 175 7 *s*, 34 3 *q*, 19 3 *q*, 18 1 *q*.

Table 2 ^1H NMR spectral data of **1a**Ac and **2**Ac (400 MHz, δ-values)

H	**1a**Ac (C_6D_6)	**2**Ac ($CDCl_3$)	Pyranoside H	**1a**Ac (C_6D_6)	**2**Ac ($CDCl_3$)
3	2 38 *br d*	2 12 *br d*	1	5 05 *d*	5 72 *d*
3′	1 00 *dt*	1 00 *dt*	2	5 30 *dd*	5 19 *t*
7	2 22 *dt*	*	3	5.99 *t*	5 23 *t*
7′	1 33 *dt*	*	4	4.99 *dd*	5 12 *t*
13	2 61 *br s*	2.64 *br s*	5	4 04 *ddd*	3 79 *ddd*
14	2 04 *d*	*	6_1	4 36 *dd*	4 27 *dd*
15	3.79 *t*	5 12 *t*	6_2	4 23 *dd*	4.01 *dd*
17	5.31 *br s*	4 91 *br d*	OAc	1 79 s (6*H*)	2 14 *s*
17′	5 06 *br s*	4.85 *br s*		1 77 *s*	2 05 *s*
18	1 30 *s*	1 15 *s*		1.64 s	2 01 *s*
20	0 96 *s*	0 82 *s*			1 99 *s*
OMe	3 43 *s*	—			

*Obscured
J[Hz] 2,3′ = 3,3′ = 13, 2′,3′ = 4, compound **1a**Ac 14,14′ = 12, 15,17 = 15,17′ = 2, pyranoside 1,2 = 8, 2,3 = 3,4 = 3, 4,5 = 10, $5,6_1 = 5\,5$, $5,6_2 = 2\,5$, $6_1,6_2 = 12$, compound **2**Ac 15,17 = 2, pyranoside. 1,2 = 8, 2,3 = 3,4 = 4,5 ~ 9, $5,6_1 = 5,6_2 = 2$, $6_1 6_2 = 12$

typical signals of the diterpene part The chemical shift of H-15 and an additional acetate methyl singlet as well as the downfield shifted doublet of the H-1′ proton required an *ent*-kaurenic acid esterified with the β-glucopyranoside and a 15α-acetoxy group

The ^{1}H NMR spectra of **3–10** (Table 3) showed that these compounds also were *ent*-kaurene derivatives differing in the nature of the oxygen functions The main compound was the methyl ester **7**, which was crystallized from an ether–petrol mixture. The mass spectrum gave no clear molecular formula as the highest fragment corresponded to $C_{26}H_{36}O_7$ while the ^{13}C NMR spectrum (Table 1) required 30 carbons, four being due to carbonyl, seven to oxygen-bearing and two to olefinic carbons Furthermore, the ^{1}H NMR data required the presence of a diacetate with a methyl ester and an epoxy angelate residue Therefore, the highest MS fragment was due to loss of acetic acid and ketene. This was also supported by further typical fragments (*m/z* 442 $[M-2\times HOAc]^+$, 404 $[M-$ketene, EpangOH$]^+$ 386 $[M-HOAc,$ EpangOH$]^+$ and 326 $[386-HOAc]^+$). The ^{1}H NMR spectrum and spin decoupling showed that axial orientated ester groups were at C-1, C-7 and C-15 of a methyl *ent*-kaur-16-en-19-oate The presence of a 9-hydroxy group was deduced from the ^{13}C NMR spectrum which showed a singlet at δ80.4 The downfield shift of the signals of C-8 and C-10, if compared with those of *ent*-kaurenic acid, supported this assumption This and the relative position of the ester groups were established by COLOC experiments in deuteriobenzene after assigning the carbon signals by 2D techniques. Long range couplings between OH and C-8 required a 9-hydroxy group. The couplings between the carbonyl of the epoxyangelate, H-1 and the methyl at C-2 of the ester group, between the acetate carbonyl, H-15 and the acetate methyl at δ1.83, between the second acetate carbonyl, H-7 and the second acetate methyl as well as between the carbomethoxy carbonyl, H-5, H-18 and OMe established the positions of the oxygen functions

The position of the ester groups in the kaurene derivative **8** was determined by INEPT experiments again after assigning the carbon signals by 2D techniques. In this case the epoxyangelate carbonyl could be connected with H-1 and the methyl at C-2 of the ester, the isobutyrate carbonyl with H-7 and the isobutyrate methyl, the acetate carbonyl with H-15 and the acetate methyl and the carbomethoxy group with H-5, H-3 and OMe There seems to be no clear advantage to the use of either one of the two applied methods of establishing the position of different oxygen functions

The structures of **4–6**, **9** and **10** clearly followed from the ^{1}H NMR spectra (Table 3) if the data were compared with those of **8** The nature of the ester groups could be deduced from the typical signals For comparison the ester **7** was saponified affording the tetrol **11**.

The only *ent*-kaurene derivative which was isolated as the free acid was **3a** The ^{1}H NMR spectrum of the methyl ester **3** (Table 3) indicated that this compound had one less oxygen function. Spin decoupling showed that no function was at C-7 Accordingly, a new threefold doublet at δ2 39 was visible which had to be due to the axial H-7. The ^{13}C NMR spectrum (Table 1) indicated that again a hydroxy group was at C-9 (δ83.1 *s*) and chemical shifts of δ21 4 (C-7), 72 8 *d* and 85.7 *d* required that the remaining hydroxy groups were at C-1 and C-15. These assignments were also deduced from the spin decoupling results.

The highest fragment in the MS of **13** corresponds to $C_{19}H_{26}O_3$ followed by those due to the sequential loss of three molecules of water (*m/z* 284, 266, 248) Inspection of the ^{13}C NMR spectrum (Table 1), however, indicated that four oxygen-bearing carbons were present Thus the molecular formula was $C_{19}H_{28}O_4$ in agreement with a nor-diterpene with four rings and two double bonds. The nature of the latter bonds followed from the ^{1}H NMR spectrum (Table 4) which showed signals for exomethylene protons (H-17) and for an olefinic methyl group (δ1 77 *br s*) As no further olefinic proton signal was visible, a ditertiary double was present its position was deduced from the observed homoallylic coupling of H-18 with H-6 which itself could be assigned from its coupling with H-7 (δ3 68 *t*) Further spin decouplings allowed the placement of two further secondary hydroxy groups at C-1 and C-15. Accordingly, the substitution pattern as well as the stereochemistry were the same as in the esters **4–10** except for the situation at C-4 and C-5 The assignments and the configuration were supported by the observed NOE's [H-13 with H-14 (3%), H-14′ (5%), H-17 (3%) and H-12 (4%), H-15 with H-7 (4%), H-20 with H-1 (10%), H-14′ with H-15 (3%) and H-7 (2%), H-11 with H-20 (6%) and H-7 with H-15 (10%)]. The tetrol **13** we have named platycarphol. Most likely, it was biogenetically formed via the pentahydroxyacid **12** by fragmentation as shown in the Scheme

The ^{1}H NMR spectra of **14** and **15** (Table 4) showed that the 7- and 15-*O*-acetates, respectively, were present Accordingly, in the spectrum of **14** the H-7 signal and in that of **15** the H-15 signal was shifted downfield if compared with the shift in the spectrum of **13.** The configuration of the chiral centres in the acetate **14** also was established by the NOE's in deuteriobenzene [H-7 with H-14 (5%), H-15 with H-7 (10%) and H-14′ (6%), H-1 with H-20 (8%), H-11 (6%)]

The mass spectroscopical behaviour in this series is a good indication of the presence of kaurene derivatives with oxygen functions at C-7 and C-9 which leads to the splitting of the 6 7 and the 9.10 bonds As an example, the MS of the ester **13** may be discussed The fragment *m/z* 181 ($C_{10}H_{13}O_3$) most likely is best represented by **18** Loss of water leads to the base peak *m/z* 163 ($C_{10}H_{11}O_2$) followed by elimination of CO (*m/z* 135)

The additional results on the chemistry of the genus *Platycarpha* support the proposed position between the Arctotideae and Cynareae by the occurrence of thiophenes like **16** and germacranolides. The high concentration and the degree of variation in the diterpenes in *P. carlinoides* may indicate a relationship to *Atractylis* (tribe Cynareae, subtribe Carlineae) where norkaurene derivatives and their glycosides are present [14] though in these compounds a 4-methyl group is missing The proposed relationship to *Corymbium* may be supported by the co-occurrence of diterpenes [15] which, however, excludes a placement of these two genera in the Vernonieae where so far no diterpenes or thiophenes like **16** have been isolated. The latter have so far only been reported from *Berkheya* species [16] which also contain germacranolides [17] It is, therefore, interesting that *P. glomerata* has been placed in Berkheya sect *Stobaea* [1], where, however, no diterpenes have been isolated.

EXPERIMENTAL

The air-dried aerial parts (400 g, collected in March 1988, Uis Pass, SW of Windhoek, Namibia, voucher 88/26, deposited in the SW Herbarium at Windhoek) were extracted and worked-up as

Table 3 ^{1}H NMR spectral data of compounds **3–11** (400 MHz, $CDCl_3$, δ-values)

H	3	4	5	6	7	C_6D_6†	8‡	9§	10‖	11	multiplicity
1	4 15	5 32	5 34	5 31	5.45	5 57	5 46	5 45	5.46	4 10	*br t*
5	2.31	2.60	2.62	2.60	2 61	2.81	2 61	2.62	2 61	2.51	*dd*
7	2 39 *dt* 1.91 *br d*	5 11	3.79	5.13	4.84	4 95	4 83	4 85	4 87	3 71	*t*
13	2.68	2.72	2.70	2 70	2 72	2 24	2,71	2.71	2 72	2.69	*br q*
14	2 15	1 95	2 05	1 90	2.13	1.53	2 13	2.10	*	*	*d*
14′	1.13 *br dd*	1.30 *m*	1 18 *br dd*	1.32 *m*	1 37 *m*	0 65 *ddd*	1,24 *br dd*	*	*	*	
15	4.02	4.22	4 33	4.19	5.55	5,71	5 55	5.55	5 56	4.48	*t*
17	5 11	5.17	5.20	5.15	4 78	4 99	4,76	4.76	4,77	5.20	*br s*
17′	5.03	4 97	5 00	4.95	5.07	4,85	5 06	5 06	5 07	5.05	*br d*
18	1 25	1 22	1 31	1.25	1 20	1 22	1,18	1.18	1,19	1.26	*s*
20	0 93	1.06	1.03	1.05	1.01	0 75	1 02	1.01	1 02	0 91	*s*
OAc	—	—	—	2 16	2.13	1 83	2,11	2.12	2,12	—	s
					2.01	1 80					*s*
OMe	3.65	3.68	3.67	3 67	3.66	3,32	3 65	3.65	3 66	3.65	s
OCOR	—	3 10 *q*	3 06 *q*	3.09 *q*	3.02 *q*	2,73 *q*	2 37 *qq*	2.12 *m*	2 26 *q*	—	
		3.08 *q*	1 35 *d*	1.38 *d*	1.36 *d*	1,37 *d*	1,21 *d*	1.00 *d*	1 17 *t*		
		1 39 *q*	1 53 *s*	1.55 *s*	1.55 *s*	1 53 *s*	1,16 *d*	0 98 *d*			
		1.38 *d*									
		1 53 *s*									
		1.66 *s*									

*Obscured

†H-2 2.45, 1 45 *m*, H-3 2 17 *br d*, 1 78 *dt*, H-6 2 57 *dt*, 2 10 *ddd*, H-11 2 42 *br dd*, 1.82 *m*, H-12 1 45, 1 30 *m*

‡Epang 2 99 *q*, 1.37 *d*, 1 53 *s*

§Epang 3.01 *q*, 1 37 *d*, 1 53 *s*

‖Epang 3 01 *q*, 1 37 *d*, 155 *s*

J[Hz]. 1,2 = 1,2′ = 2 5; 2,3′ = 13, 2′,3′ = 4, 3,3′ = 14, 5,6 = 2 5; 5,6′ = 13; 6,7 = 6′,7 = 3; 11,11′ = 14, 11,12 = 5, 12,13 = 12′,13 = 13,14′ ~ 3, 12,14′ = 13,17 ~ 1, 14,14′ = 12, 15,17′ = 15,17′ ~ 2 5, Epang 3,4 = 5.5, *i*Bu 2,3 = 2,4 = 7, *i*Val. 3,4 = 3,5 = 7; Prop 2,3 = 7 5

Table 4 ^{1}H NMR spectral data of compounds **13–15** (400 MHz, $CDCl_3$, δ-values)

H	13	14	C_6D_6	15
1	4 11 *br s*	4 11 *br s*	4 43 *br s*	4 10 *br s*
2	1 83 *m*	*	1 78 *m*	*
2′	1 71 *m*	*	1 65 *m*	*
3	2.50 *m*	2 55 *m*	2 66 *br dd*	2 51 *m*
3′	1 80 *m*	*	1 65 *m*	*
6	2 95 *dd*	2 91 *dd*	2 85 *dd*	2 92 *dd*
6′	2 31 *br d*	2 35 *br d*	2 07 *br d*	2 30 *br d*
7	3 68 *t*	5 14 *t*	5 19 *t*	3 66 *t*
11	*	*	2 32 *ddd*	*
11′	*	*	1 92 *ddd*	*
12	*	*	1 52 *m*	*
12′	*	*	1 45 *m*	*
13	2 75 *br s*	2 77 *br s*	2 41 *br q*	2 78 *br s*
14	2 01 *d*	2 05 *d*	1 50 *d*	2 19 *d*
14′	1 23 *ddd*	1 38 *ddd*	0 89 *ddd*	1 36 *ddd*
15	4 47 *t*	4 27 *t*	4.00 *br d*	5 69 *t*
17	5 22 *br s*	5 18 *br s*	5 47 *ddd*	5.04 *dd*
17′	5 07 *br d*	5 01 *br d*	5 02 *ddd*	4 91 *dd*
18	1 77 *br s*	1.70 *br s*	1 60 *br s*	1 75 *br s*
20	1 24 *s*	1 28 *s*	0 88 *s*	1 28 *s*
OAc	—	2 11 *s*	1 78 *s*	2 14 *s*

*Obscured

J[Hz] 2,3 = 12, 3,3′ = 18, 6,6′ = 16, 6,7 = 6′,7 = 3 5, 11,11′ = 15, 11,12 = 2, 11,12′ = 5, 12,13 = 12′,13 = 13,14 ~ 3, 14,14′ = 12, 13,17 = 13,17′ = 14′,17 = 14′,17′ ~ 1, 15.17 = 15′,17 ~ 2

reported previously [18] CC gave four fractions [(1) Et_2O–petrol, 1 19, (2) Et_2O–petrol, 1 1, (3) Et_2O and (4) Et_2O–MeOH, 9 1] Fraction 1 gave by TLC 15 mg **16** Fraction 2 was separated first by medium pressure CC (silica gel, ϕ 30–60 μ) to give five combined fractions (2/1–2/5, Et_2O petrol, 1 1–Et_2O) Fraction 2/1 gave by HPLC (MeOH–H_2O, 4 1, always RP 8, flow rate, 3 ml/min) 4 mg **10** (R_t 8 3 min), 20 mg **8** (R_t 10 3 min) and 20 mg **9** (R_t 14 3 min) Fraction 2/2 gave 60 mg **7** and fraction 2/3 by HPLC (MeOH–H_2O, 7 3) 20 mg **15** (R_t 8 2 min), 20 mg **6** (R_t 9 3 min) and 2 mg **4** (R_t 12 1 min) HPLC of fraction 2/4 (MeOH–H_2O, 7 3) gave 2 mg **17** (R_t 3 3 min), 4 mg *ent*-16β-hydroxykauran-19-oic acid (R_t 6 2 min), 20 mg **14** (R_t 8.0 min) and 4 mg **5** (R_t 8 5 min) Fraction 2/5 gave by crystallization 40 mg **13** HPLC of fraction 3 (MeOH–H_2O, 13 7) afforded 5 mg **3** (R_t 6.5 min) and 20 mg **13** (R_t 13 2 min) Fraction 4 showed in the ^{1}H NMR spectrum no acetate or methoxy signals Acetylation (DMAP/Ac_2O, $CHCl_3$, 2 hr, 70°) and addition of CH_2N_2 gave a mixture which was separated by HPLC (MeOH–H_2O, 9 1) to give 150 mg **2Ac** (R_t 8 8 min) and 150 mg **1aAc** (R_t 10 3 min) Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material

ent-15α-*Hydroxykaur*-16-*en*-19-*oic acid*-β-D-*allopyranoside* (**1**) Acetylation and esterification (s a) gave **1aAc**, colourless crystals, mp 184°, IR $\nu_{max}^{CCl_4}$, cm^{-1} 1765 (OAc), 1735 (CO_2R), MS *m/z* (rel int.). 662 330 [M]$^+$, (0 9) (calc for $C_{35}H_{50}O_{12}$ 662 330), 602 (0 2), 542 (0 2), 482 (0 2), 422 (0 1), 331 [sugar part]$^+$ (88), 271 (6), 211 (6), 169 (211 – ketene]$^+$ (100), 109 (43), $[\alpha]_D^{24}$ – 64 ($CHCl_3$, *c* 0 4)

β-D-*Glucopyranosyl*-*ent*-15α-*acetoxykaur*-16-*en*-19-*oate* (**2**) Isolated as its pentaacete **2Ac**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1765 (OAc), MS *m/z* (rel int.) 648 315 [M – ketene]$^+$ (0 2) (calc for $C_{34}H_{48}O_{12}$ 648 315), 630 [M – HOAc]$^+$ (0 1), 331 [sugar part]$^+$ (28), 271 (8), 211 (5), 169 [211 – ketene]$^+$ (100), 109 (61), $[\alpha]_D^{24}$ – 56 ($CHCl_3$, *c* 3 44)

ent-1α,9α,15α-*Trihydroxykaur*-16-*en*-19-*oic acid* (**3a**) Colourless gum, ^{1}H NMR ($CDCl_3$/CD_3OD) δ5 05 (*br t*, H-1), 2 62 (*br s*, H-13), 2 13 (*d*, H-14), 1 08 (*ddd*, H-14′), 3 91 (*t*, H-15), 5 07 and 4 97 (*br d*, H-17), 1 24 (*s*, H-18) 0 98 (*s*, H-20), (*J* [Hz] 1,2 = 15,17 ~ 2, 14,14′ = 13, 13,14 = 5, 12,14′ = 1) Esterification gave **3**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3400 (OH), 1735 (CO_2R), MS *m/z* (rel int) 346 214 [M – H_2O]$^+$ (3) (calc for $C_{21}H_{30}O_4$ 346 214), 328 (4), 269 [328 – CO_2Me]$^+$ (12), 155 (40), 91 (100)

Methyl-ent-1α,7α-di[2-*methyl*-2,3-*epoxybutyryloxy*]-9α,15α-*dihydroxykaur*-16-*en*-19-*oate* (**4**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3520 (OH), 1730 (CO_2R), MS *m/z* (rel int) 558 283 [M – H_2O]$^+$ (1) (calc for $C_{31}H_{42}O_9$ 558 283), 460 [M – RCO_2H]$^+$ (2 7), 242 (2 2), 344 [460 – RCO_2H]$^+$ (81), 326 [344 – H_2O]$^+$ (84), 267 [326 – CO_2Me]$^+$ (100), 119 (66), 107 (87)

Methyl-ent-1α-[2-*methyl*-2,3-*epoxybutyryloxy*]-7α,9α,15α-*trihydroxykaur*-16-*en*-19-*oate* (**5**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3480 (OH), 1735 (CO_2R), MS *m/z* (rel int) 460 246 [M – H_2O]$^+$ (0 5) (calc for $C_{26}H_{36}O_7$ 460 246), 362 [M – RCO_2H]$^+$ (5 5), 344 [362 – H_2O]$^+$ (12), 326 [344 – H_2O]$^+$ (9), 267 [326 – CO_2Me]$^+$ (62), 182 (56), 123 (68), 107 (100)

Methyl-ent-7α-*acetoxy*-1α-[2-*methyl*-2,3-*epoxybutyryloxy*]-9α,15α-*dihydroxykaur*-16-*en*-19-*oate* (**6**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3530 (OH), 1750 (OAc), 1735 (CO_2R), MS *m/z* (rel int) 502 257 [M – H_2O]$^+$ (0 5) (calc for $C_{28}H_{38}O_8$ 502 257), 460 [M – HOAc]$^+$ (2), 442 (1 8), 404 [M – RCO_2H]$^+$ (2.2), 344 [404 – HOAc]$^+$ (100), 326 (42), 267 [326 – CO_2Me]$^+$ (61), 119 (46), 107 (68)

Methyl-*ent*-7α,15α-*diacetoxy*-1α-[2-*methyl*-2,3-*epoxybutyryloxy*]-9α-*hydroxykaur*-16-*en*-19-*oate* (**7**) Colourless crystals, mp 198°, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3590 (OH), 1740 (CO_2R), *m/z* (rel int) 460.246 [M – HOAc, ketene]$^+$ (1) (calc for $C_{26}H_{36}O_7$ 460 246), 442 [M – 2 × HOAc]$^+$ (0 4), 386 [M – HOAc, – RCO_2H]$^+$ (8), 326 [386 – HOAc]$^+$ (66), 267 [326 – CO_2Me]$^+$ (68), 119 (92), 107 (100), $[\alpha]_D^{24}$ + 13 ($CHCl_3$, *c* 0 56) Saponification (MeOH, H_2O, KOH, 10 min, 70°) gave **11**, colourless crystals, mp 105°, MS *m/z* (rel int) 362 209 [M]$^+$ (5) (calc for $C_{21}H_{30}O_5$ 362 209), 344 (18), 326 (8), 183 (76), 163 (66), 144 (100), 107 (92)

Methyl-*ent*-15α-acetoxy-1α-[2-*methyl*-2,3-*epoxybutyryloxy*]-7α-isobutyryloxy-9α-*hydroxykaur*-16-*en*-19-*oate* (**8**) Colourless crystals, mp 198°, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3580 (OH), 1735 (CO_2R), MS *m/z* (rel int) 530 288 [M – HOAc]$^+$ (0 5) (calc for $C_{32}H_{42}O_8$ 530 288), 474 [M – EpangOH]$^+$ (0 3), 442 [530 – *i*BuOH]$^+$ (1 5), 414 [530 – EpangOH]$^+$ (2), 386 [474 – *i*BuOH]$^+$ (15), 326 [386 – HOAc]$^+$ (100), 267 [326 – CO_2Me]$^+$ (88), 161 (51), 119 (78), 107 (87), $[\alpha]_D^{24}$ + 11 ($CHCl_3$, *c* 0 34)

Methyl-ent-15α-*acetoxy*-1α-[2-*methyl*-2,3-*epoxybutyryloxy*]-9α-*hydroxy*-7α-*isovaleryloxykaur*-16-*en*-19-*oate* (**9**) Colourless crystals, mp 155°, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1730 (CO_2R), MS *m/z* (rel int) 544 303 [M – HOAc]$^+$ (0 4) (calc for $C_{33}H_{44}O_8$ 544 303), 488 [M – EpangOH]$^+$ (0 6) 442 [544 – *i*ValOH]$^+$ (1 5), 386 [488 – *i*ValOH]$^+$ (24), 326 [386 – HOAc]$^+$ (100), 267 (83), 181 (15), 163 (30), 119 (66), 107 (78), 85 (C_4H_9CO)$^+$ (40), 57 (85 – CO)$^+$ (94), $[\alpha]_D^{24}$ + 9 ($CHCl_3$, *c* 0 59)

Methyl-ent-15α-*acetoxy*-1α-[2-*methyl*-2,3-*epoxybutyryloxy*]-9α-*hydroxy*-7α-*propionyloxykaur*-16-*en*-19-*oate* (**10**) Colourless crystals, mp 136°, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3580 (OH), 1735 (CO_2R), MS *m/z* (rel int) 460 246 [M – EpangOH]$^+$ (1 4) (calc for $C_{26}H_{36}O_7$ 460 246), 386 [460 – PropOH]$^+$ (14), 326 [386 – HOAc]$^+$ (100), 267 (77), 119 (75), 107 (78), 57 [C_3H_5O]$^+$ (70)

Platycarphol (**13**) Colourless crystals, mp 157°, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3450 (OH), MS *m/z* (rel int) 302 188 [M – H_2O]$^+$ (11) (calc for $C_{19}H_{26}O_3$: 302 188), 284 (9), 266 (10), 181 [$C_{10}H_{13}O_3$]$^+$ (66), 163 [$C_{10}H_{11}O_2$]$^+$ (100), 135 (36), 122 (43), 107 (42), $[\alpha]_D^{24}$ – 120 ($CHCl_3$, *c* 0 31)

Platycarphol-7-O-*acetate* (**14**) Colourless crystals, mp 182°, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3420 (OH), 1740 (OAc), MS *m/z* (rel int) 344 199

$[M-H_2O]^+$ (8) (calc for $C_{21}H_{28}O_4$: 344.199), 302 $[M-HOAc]^+$ (2), 284 (12), 266 (9), 181 (18), 163 (50), 135 (17) 61 (100).

Platycarphol-15-O-*acetate* (**15**). Colourless crystals, mp. 199°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3420 (OH), 1735 (OAc), MS *m/z* (rel. int.): 344.199 $[M-H_2O]^+$ (12) (calc for $C_{21}H_{28}O_4$. 344.199), 328 (8), 181 (28), 163 (100), 135 (27), 91 (79), 83 (85), 55 (80)

REFERENCES

1. Harvey, W. H. in *Flora Capensis*, p 54. Dublin.
2. Hoffmann, O. (1899) in *Die naturlichen Pflanzenfamilien* (Engler, A. and Prantl, K., eds). Verlag W Engelmann, Leipzig.
3. Stix, E (1960) *Granopalynol* **2**, 41.
4. Robinson, H and Bratell, R. D. (1973) *Phytologia* **26**, 78.
5. Hilliard, O M. (1977) *Compositae in Natal*, p 1. Pietermaritzburg, Univ of Natal Press
6. Dittrich, M. (1977) in *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds). Academic Press, London.
7. Bohm, B. A., Saleh, N A. M. and Ornduff, R. (1974) *Am. J. Botany* **61**, 551.
8. Bohlmann, F and Zdero, C. (1977) *Phytochemistry* **16**, 1832.
9. Bohlmann, F. and Zdero, C. (1972) *Chem. Ber.* **105**, 1245.
10. Herz, W and Sharma, R. (1976) *J. Org. Chem.* **41**, 1021.
11. Bohlmann, F., Jakupovic, J , Schuster, A., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 2317.
12. Kauss, H (1965) *Pflanzenphysiol.* **53**, 58.
13. De Bruyn, A., Anteunis, M. and van Beeumen, J. (1977) *Bull. Soc. Chim. Belg.* **86**, 259.
14. Danieli, B., Bombardelli, E., Bonati, A. and Gabetta, B. (1974) *Phytochemistry* **11**, 3501.
15. Zdero, C and Bohlmann, F (1988) *Phytochemistry* **27**, 227.
16. Bohlmann, F , Burkhardt, T and Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London.
17. Bohlmann, F , Mohammadi, D. and Jakupovic, J. (1984) *Planta Med.* 192.
18. Bohlmann, F., Zdero, C , King, R. M and Robinson, H. (1984) *Phytochemistry* **23**, 1979.