EXPERIMENTAL

Cultivation. L. lepideus FPRL 7B (Forest Products Research Laboratory, Princes Risborough, U.K.) was cultivated on a defined synthetic medium containing glucose (2%), *iso*-leucine (0.15%), and mineral salts [3] for 90 days.

Identification of sesquiterpene hydrocarbons. The volatile metabolites were obtained by circulation steam distillation [8] in pentane. The hydrocarbon fraction was separated from the more polar components by modified dry-CC [4]. The identification resulted from GC/MS data by comparison with lit. data [5], and retention time comparison of R_I values, and comparison with commercial essential oils of well-known composition (e.g. copaiva balsam), respectively. Preparation of single components for IR by prep. TLC is described in ref. [3]; IR spectral data were compared with lit. data [7]. GC conditions are described in [9], using additionally capillary columns (Carbowax 20 M) of different lengths, and a computing integrator.

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SESQUITERPENES AND NORSESQUITERPENES FROM *PECHUEL-LOESCHEA LEIBNITZIAE**

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Key Word Index—*Pechuel-Loeschea leibnitziae*; Compositae; Inuleae; sesquiterpenes; guaiene derivative; norsequiterpenes; guaianolide.

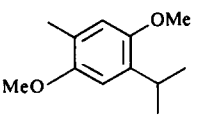
Abstract—The aerial parts of *Pechuel-Loeschea leibnitziae* afforded, in addition to thymohydroquinone dimethyl ether, sitosterol and stigmasterol, xerantholide and its probable precursor, the 11,13-dihydro derivative methyl pechueloate and two norsequiterpenes, probably formed by degradation of the corresponding sesquiterpene acid. Two eudesmane derivatives were also isolated. The chemotaxonomy of *Pechuel-Loeschea* is discussed briefly.

INTRODUCTION

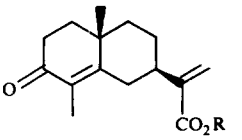
The monotypic genus *Pechuel-Loeschea* has not been investigated chemically. This genus was included in *Pluchea* [1], but was later maintained to be a separate genus [2, 3]. It was of interest, therefore, to see whether the chemistry supports a separation from *Pluchea* or not.

RESULTS AND DISCUSSION

The roots of *P.-L. leibnitziae* (Kuntze) O. Hoffm. gave only thymohydroquinone dimethyl ether (**1**).



1



2a R = H

2b R = Me

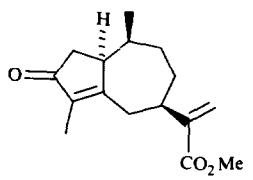
Whilst the aerial parts afforded it as the main compound, stigmasterol, sitosterol, the acid **2a** [4], the corresponding methyl ester **2b** and the isomeric ester **3** were also produced. The structure of compound **3** followed from the ^{1}H NMR data (Table 1). The

*Part 424 in the series "Naturally Occurring Terpene Derivatives". For Part 423 see Bohlmann, F., Jakupovic, J. and Vogel, W. (1982) *Phytochemistry* **21**, 1153.

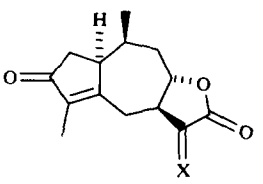
Table 1. ^{1}H NMR spectral data of compounds **3**, **6** and **7** (400 MHz, TMS as int. standard)

	3	6	7
H-1	3.18 *ddd(br)*	3.26 *ddd(br)*	2.96 *ddd(br)*
H-2α	2.59 *ddd*	2.60 *dd*	2.41 *dd*
H-2β	2.06 *d(br)*	2.17 *dd*	2.03 *dd*
H-6α	2.82 *dd(br)*	2.73 *t(br)*	2.78 *dddd(br)*
H-6β	2.44 *dd(br)*		2.25 *dd(br)*
H-7α	2.91 *dd(br)*	2.80 *dddd*	1.31 *m*
H-7β		2.43 *dddd*	
H-8	1.63 *m*	—	3.90 *dddd*
H-8′		—	
H-9α	1.78 *m*	2.82 *dd*	1.38 *ddd*
H-9β		2.52 *ddd*	1.53 *d(br)*
H-10	2.13 *dddq*	2.33 *dddq*	2.15 *dddq*
H-13	6.20 s	—	—
H-13′	5.62 *s*	—	—
H-14	0.65 *d*	0.71 *d*	1.10 *d*
H-15	1.63 *d*	1.72 *dd*	1.70 *d*
OMe	3.77 *s*	—	—

J(Hz): Compound **3**: 1,2α = 7; 1,2β ~ 1; 1,10 ~ 3; 1,15 = 2; 2α,2β = 19; 2α,10 = 1; 6α,6β = 19; 6α,7 ~ 1.5; 6β,7 = 12; 6α,8α ~ 1; 7,8α ~ 1.5; 7.8β = 12; 9α,10 = 9β,10 ~ 3; 10,14 = 7; compound **6**: 1,2α = 7; 1,2β = 2; 1,10 ~ 7; 2α,2β = 18; 6α,6β = 14; 6β,15 = 10,15 = 2; 6,7 = 6.5; 7,7′ = 13; 7β,9β = 1; 9,9′ = 13.5; 9α,10 = 6.5; 9β,10 = 4; 10,14 = 7; compound **7**: 1,2α = 6; 1,2β = 3.5; 1,10 = 7; 6,6β = 14; 6α,7α = 7; 6α,7β = 2; 6β,7α = 12; 6β,7β ~ 2; 7α,8β = 10; 7β,8β = 3.5; 7β,9β = 1; 8β,9α = 10; 8β,9β = 3.5; 9α,9β = 14; 9α,10 ~ 6; 9β,10 = 3.5; 10,14 = 7.

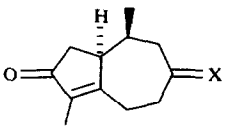


3



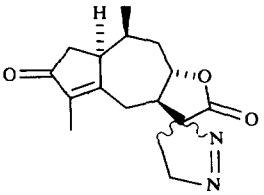
4 X = CH_2

5 X = α-Me, H



6 X = O

7 X = α-OH, H



8 11α − CH_2

9 11β − CH_2

presence of an ester group, already indicated by the mass spectrum, followed from the methoxyl signal, while the methylene protons (H-13) showed signals

Table 2. ^{1}H NMR spectral data of compounds **4**, **5**, **8** and **9** (400 MHz, $CDCl_3$ TMS as int. standard)

	4	5	8	9
H-1	3.20 *dddd*	3.13 *dddd*	3.13 *dddd*	3.26 *dddd*
H-2α	2.66 *ddd*	2.63 *ddd*	2.65 *ddd*	2.68 *ddd*
H-2β	2.13 *d(br)*	2.09 *d(br)*	2.12 *d(br)*	2.11 *d(br)*
H-6α	3.15 *d(br)*	2.98 *d(br)*	2.35 *d(br)*	2.43 *d(br)*
H-6β	2.49 *dd(br)*	2.38 *m*	2.63 *m*	2.35 *m*
H-7	3.05 *ddddd*	2.08 *m*		3.62 *ddd*
H-8	4.14 *ddd*	4.15 *ddd*	5.18 *ddd*	4.15 *ddd*
H-9α	1.95 *ddd*	1.82 *ddd*	1.94 *ddd*	2.05 *ddd*
H-9β	2.43 *m*	2.38 *m**	2.61 *ddd*	2.53 *ddd*
H-10	2.32 *dddq*	2.27 *dddq*	2.33 *m*	2.35 *m*
H-11	—	2.38 *m**	—	—
H-13	6.30 *d*	1.29 *d*	2.31 *ddd*	1.91 *ddd*
H-13′	5.61 *d*		1.50 *ddd*	1.80 *ddd*
H-14	0.76 *d*	0.75 *d*	0.82 *d*	0.76 *d*
H-15	1.75 *ddd*	1.71 *ddd*	1.64*ddd*	1.65 *ddd*
H-16	—	—	4.91 *ddd*	4.87 *ddd*
H-16′	—	—	4.68 *ddd*	4.77 *ddd*

*In C_6D_6 H-11 *dq* 1.65 (*J* = 11, 7), H-9 1.96 *ddd* (*J* = 13, 3.5, 3.5).

J(Hz): Compound **5**: 1, 2α = 7; 1, 2β ~ 1; 1, 10 ~ 7; 1, 15 = 6, 15 ~ 1.5; 2α, 2β = 19; 6α, 6β = 19; 6α, 7 ~ 3; 6β, 7 = 10; 7, 8 = 9.5; 7, 11 = 11; 8, 9α = 12; 8, 9β = 3.5; 9α, 9β = 13; 9α, 10 = 3.5; 9β, 10 = 4; 10, 14 = 11, 13 = 7; compounds **8** and **9**: 1, 2α ~ 7; 1, 2β ~ 1; 1, 10 ~ 7; 2α, 2β = 6α, 6β = 19; 6α, 7 = 3; 6β, 7 = 12; 7, 8 = 10; 8, 9α = 12; 8, 9β ~ 2; 9α, 9β = 13; 9α, 10 = 3.5; 9β, 10 = 4; 10, 14 = 7; 13, 13′ = 13; 13, 16 = 4.5; 13, 16′ = 9; 13′, 16 = 9; 13′, 16′ = 7; 16, 16′ = 17.

with the typical chemical shifts and very few allylic couplings. The position of the second oxygen function, a conjugated keto group, could also be deduced from the spectral data. The proton which displayed a broadened three-fold doublet at δ 3.18 was coupled with the olefinic methyl group, with two downfield proton signals, obviously those α- to the keto group, and with a proton which was further coupled with the secondary methyl group (0.65 *d*). These observations clearly indicated the presence of a guaiene derivative with a 3-keto group and a 4,5-double bond. Further spin decoupling showed that the side-chain was, as usual, equatorially orientated at C-7, while the β-orientation of the 10-methyl group followed from the couplings. Therefore, compound **3** was the precursor of xerantholide (**4**). Two further compounds, the diketone **6** and the keto alcohol **7**, showed in part similar ^{1}H NMR spectral data (Table 1). Oxidation of **7** afforded **6**. Accordingly, both had the same carbon skeleton and identical stereochemistry. The α-orientation of the hydroxyl group in **7** followed from the couplings, while its position was assigned by spin decoupling, which further showed that the conjugated keto group had the same position as in **3**. Compounds **6** and **7** were degradation products of **3**. The latter we have given the name methyl pechueloate. In addition we have named **6** norpechuelone and **7** norpechuelol.

Two sesquiterpene lactones were also isolated, although the guaianolides **4** and **5**, could not be

separated completely. Addition of diazomethane gave the pyrazolines **8** and **9**, which were easily separated from **5**. Compound **4** was the known guaianolide xerantholide[5]. Its structure and stereochemistry clearly followed from the ^{1}H NMR spectral data of **4** and the derivatives **8** and **9** (Table 2). Furthermore **5** had already been prepared from **4**, though no stereochemistry was assigned[5]. These data were very similar to previous results[5]. Spin decoupling showed that the 11-methyl group was α-orientated since $J_{7,11}$ was 11 Hz. The presence of an 8,12-*trans*-lactone followed from the chemical shift of H-8 and the couplings observed and the fact that **5** was prepared from **4**. The relative stereochemistry of the pyrazolines **8** and **9** followed from the chemical shifts of H-7 and H-8. In the spectrum of **8** and **9**, H-8 and H-7 respectively were deshielded by an azo group. This further supported the proposed *trans*-stereochemistry of the lactone ring.

The compounds isolated from *Pechuel-Loeschea* species clearly support the separation from *Pluchea*. So far nine species of this genus have been investigated chemically, most of them affording thiophene acetylenes and eudesmane derivatives of the cuauthemone type[6–9]. The main compound **1**, however, is also present in *Pluchea* species[9], but is a widespread compound, having been isolated from widely differing genera.

EXPERIMENTAL

The air-dried plant material, collected in February 1981 in Transvaal (voucher 81/53 deposited in the Herbarium of the Botanic Research Institute, Pretoria) was extracted with Et_2O–petrol (1 : 3) and the resulting extracts were separated first by CC (Si gel) and further by repeated TLC (Si gel). The roots (150 g) gave 300 mg **1** and the aerial parts (290 g) 30 mg sitosterol, 30 mg stigmasterol, 200 mg **1**, 8 mg **2a**, 8 mg **2b**, 13 mg **3** (Et_2O–petrol, 1 : 3), mixture of 20 mg **4** and 8 mg **5** (Et_2O–CH_2Cl_2, 1 : 5, not fully separated; **5** was obtained pure after transformation of **4** to **8** and **9** by addition of CH_2N_2 in Et_2O), 2 mg **6** (Et_2O–CH_2Cl_2, 1 : 5) and 14 mg **7** (Et_2O–CH_2Cl_2, 1 : 4).

Methyl pechueloate (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1715, 1640 (C=CCO$_2$R, O=C–C=C); MS *m/z* (rel. int.): 262.157 [M]$^+$ (87) ($C_{16}H_{22}O_3$), 247 [M – Me]$^+$ (100), 230 [M – MeOH]$^+$ (69), 215 [230 – Me]$^+$ (27), 187 [215 – CO]$^+$ (25), 176 [M – H$_2$C=CCO$_2$Me]$^+$ (61), 161 [176 – Me]$^+$ (30);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+24 \quad +26 \quad +45 \quad +63} \ (CHCl_3;\ c\ 0.4).$$

11β,13-*Dihydroxerantholide* (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1795 (γ-lactone), 1710, 1650 (C=CC=C); MS *m/z* (rel. int.): 248.141 [M]$^+$ (82) ($C_{15}H_{18}O_3$), 233 [M – Me]$^+$ (6), 220 [M – CO]$^+$ (8), 161 (65), 133 (51), 91 (71), 79 (100);

$$[\alpha]_{24°}^{\lambda} = \frac{578 \quad 546 \quad 436\,nm}{+4 \quad +5 \quad +226} \ (CHCl_3;\ c\ 0.8).$$

Pyrazoline derivative (**8**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1790 (γ-lactone), 1710 (C=CC=O); MS *m/z* (rel. int.): 260.141 [M – N$_2$]$^+$ (25) ($C_{16}H_{20}O_3$), 245 [260 – Me]$^+$ (10), 217 [245 – CO]$^+$ (5), 161 (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+192 \quad +190 \quad +167 \quad -95} \ (CHCl_3;\ c\ 0.1).$$

Pyrazoline derivative (**9**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1782 (γ-lactone), 1702 (C=CC=O); MS *m/z* (rel. int.): 288 [M]$^+$ 260.141 [M – N$_2$]$^+$ (63), 245 [260 – Me]$^+$ (12), 161 (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+8 \quad +11 \quad +16 \quad +53} \ (CHCl_3;\ c\ 0.1).$$

(**8** and **9** were crystalline compounds, but owing to the small amounts produced no exact mp can be given).

Norpechuelone (**6**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1710 (C=O); 1710, 1645 (C=CC=O); MS *m/z* (rel. int.): 192.115 [M]$^+$ (48) ($C_{12}H_{16}O_2$), 177 [M – Me]$^+$ (14), 149 [177 – CO]$^+$ (10), 122 [M – C_4H_6O]$^+$ (100); $[\alpha]_D$ = + 10 ($CHCl_3$; *c* 0.2).

Norpechuelol (**7**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1700, 1640 (C=CC=O); MS *m/z* (rel. int.): 194, 131 [M]$^+$ (8) ($C_{12}H_{18}O_2$), 176 [M – H_2O]$^+$ (100), 161 [176 – Me]$^+$ (39), 148 [176 – CO]$^+$ (45), 147 [176 – CHO]$^+$ (45); $[\alpha]_D$ = + 14 ($CHCl_3$; *c* 1.4). 6 mg **7** in 1 ml CH_2Cl_2 was stirred for 30 min with 10 mg pyridine dichromate. TLC afforded 3 mg **6**, identical with the natural diketone.

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