as zexbrevin by comparison with an authentic sample [7], (mp, mmp, IR, ^{1}H NMR, MS, co-TLC) and 200 mg of a mixture of caleine E (**1**) and caleine F (**2**).

A second collection of *C. zacatechichi* from the same locality (May 1982) gave, after chromatographic separation, 25 mg of yellow crystals, mp 170–172°, identified as 5-hydroxy-7,4'-dimethyl flavone, by comparison with an authentic sample [5] (mp, mmp, IR, ^{1}H NMR, MS, co-TLC) and 200 mg of a mixture of caleine E (**1**) and caleine F (**2**).

HPLC analysis. Solvent: EtOAc isopropyl ether–hexene (3:3:4) column: micropack Si10, detector: refraction index, flow rate: 230 ml/hr, retention time: caleine F (**2**) 9 min 90%, caleine E (**1**) 7.2 min 10%.

Isolation of caleine F (**2**). A sample of 60 mg of the above mixture was dissolved in 2 ml of THF to which 0.1 ml of propanethiol and 2 ml of buffer pH 9.2 (borate) were added. After 18 hr at room temp. the reaction mixture was diluted with 5 ml of buffer soln. Usual work up [11] gave 70 mg of a mixture of adducts. The mixture was separated by prep. TLC (Me_2CO–$CHCl_3$ 1:1) yielding 20 mg of the adduct of **1** and 18 mg of the adduct of **2**. Each adduct was dissolved in 10 ml of EtOAc to which 30 g of silica gel were added. After refluxing the suspensions for 18 hr, 10 mg of **1** and 5 mg of **2** were obtained. Caleine F (**2**) shows mp 141–143°, IR ν_{max} cm^{-1}: 3470, 1765, 1715, 1695, 1645. MS *m/z* (rel. int.): 362 (0.7), 344 (0.3), 83 (100), 55.1 (39.8). $C_{20}H_{26}O_6$ requires M^+ at *m/z* 362.

Reduction of **1**. A sample of 100 mg of caleine E (**1**) was dissolved in 2.5 ml soln of 0.4 M of $CeCl_3 \cdot 6H_2O$ and then treated with 11.4 mg of $NaBH_4$ at 0°. After 15 min it was quenched with a sat. soln. of NaCl. Usual work up [10] gave 22 mg of **5**, IR ν_{max} cm^{-1}: 3460, 1760, 1710, 1660.

Acknowledgements—The authors thank Dr. P. Joseph-Nathan for his critical review of the manuscript and Messrs A. Toscano, H. Bojórquez, L. Velasco, J. Cárdenas and R. Villena for technical assistance.

REFERENCES

1. Quijano, L., Calderón, J. and Rios, T. (1977) *Rev. Latinoam. Quim.* **8**, 90.
2. Nash, D. L. (1976) Calea (in Fl. Guatemala) Fiedana, Bot 24 (XII), 215.
3. Quijano, L., Romo de Vivar, A. and Ríos, T. (1979) *Phytochemistry* **18**, 1745.
4. Herz, W. and Kuwar, N. (1980) *Phytochemistry* **19**, 593.
5. Guerrero, C., Silva, M., Maldonado, E. and Martinez, M. (1978) *Rev. Latinoam. Quim.* **9**, 71.
6. Delgado, G., Romo de Vivar, A. and Herz, W. (1982) *Phytochemistry* **21**, 1305.
7. Romo de Vivar, A., Guerrero, C., Diaz, E., Ortega, A. (1970) *Tetrahedron* **26**, 1657.
8. Machand, P. S. and Blount, J. F. (1978) *J. Org. Chem.* **43**, 4352.
9. Borges del Castillo, J., Maera-Ferrero, M. T., Rodriguez-Luis, F., Rodriguez-Ubis, J. C. and Vázquez-Bueno, P. (1984) *Rev. Latinoam. Quim.* **15**, 96.
10. Luche, J. L., Rodriguez-Hahn, L. and Crabbé, P. (1978) *J. Chem. Soc. Chem. Commun.* 601.
11. Kupchan, M. S., Giacobhe, T. J. and Krull, I. S. (1970) *Tetrahedron Letters* 2859.
12. Salmón, M., Penieres, G., Miranda, R. and Alvarez, C. (1981) *J. Heterocyclic Chem.* **18**, 1475.

Phytochemistry, Vol. 26, No. 7, pp. 2106–2107, 1987.
Printed in Great Britain.

0031-9422/87 $3.00 + 0.00

KAURENE DERIVATIVES FROM *ALEPIDEA AMATYNSIA*

ABDOLHOSSEIN RUSTAIYAN and ABDULFAZL S. SADJADI*

Department of Chemistry, Shahid Beheshty University, Tehran, Iran; *Department of Chemistry, University of Technology and Engineering, Tehran, Iran

(*Revised received* 5 *November* 1986)

Key Word Index—*Alepidea amatynsia*; Umbelliferae; diterpenes; kaurene derivatives.

Abstract—*Alepidea amatynsia* afforded several known diterpenes, *ent*-16-kauren-19-oic acid, its 9(11)-dehydro derivative, *ent*-16-kauren-12-on-19-oic acid, wedelia *seco*-kaurenolide and a further *seco*-diterpene. The structure of the latter was established by ^{1}H NMR spectroscopy.

INTRODUCTION

The small South African genus *Alepidea* (Umbelliferae, subfamily Saniculoideae, tribe Saniculeae) so far has not been studied chemically. Careful separation of the extracts of the roots and the aerial parts of *A. amatynsia* Eck. et Leyh. each yielded *ent*-16-kauren-19-oic acid, its 9(11)-dehydro derivative, the corresponding 12-keto derivative [1], wedelia *seco*-kaurenolide **1** [2] and a further diterpene, the 3β-acetoxy derivative **2**. The structure of **2** followed from the molecular formula and from the ^{1}H NMR and ^{13}C NMR spectral data which were in part very similar to those of **1** [2] (Table 1). The presence of an acetoxy group at C-3 was deduced from the downfield shift of the C-2, C-3 and C-4 signals and the shielding effect at C-5, while the couplings of H-3 indicated a β-orientation of the oxygen function. An α-acetoxy group

Table 1. ^{1}H NMR and ^{13}C NMR spectral data of 1 and 2 (CDCl$_3$, TMS as internal standard)

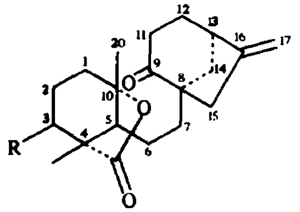
	1*	2*		1†	2†
H-2		1.91 *m*	C-1	37.0 *t*	33.5 *t*
H-3		4.90 *br d*	C-2	19.8 *t*	25.5 *t*
H-11	2.36 *m*	2.37 *m*	C-3	33.7 *t*	73.1 *d*
H-11′	2.26 *dd*	2.28 *dd*	C-4	48.5 *s*	52.5 *s*
H-13	2.87 *br s*	2.87 *br s*	C-5	56.1 *d*	48.6 *d*
H-15	2.46 *br d*	2.46 *br d*	C-6	22.1 *t*	21.6 *t*
H-15′	2.32 *br d*	2.37 *br d*	C-7	36.8 *t*	33.8 *t*
H-17	5.06 *br s*	5.06 *br s*	C-8	57.1 *s*	56.9 *s*
H-17′	4.97 *br s*	4.97 *br s*	C-9	212.8 *s*	213.0 *s*
H-18	1.20 *s*	1.19 *s*	C-10	84.9 *s*	85.4 *s*
H-20	1.48 *s*	1.52 *s*	C-11	43.6 *t*	43.5 *t*
OAc	—	2.11 *s*	C-12	33.1 *t*	32.7 *t*
			C-13	42.3 *d*	42.2 *d*
			C-14	36.0 *t*	35.9 *t*
			C-15	42.0 *t*	41.9 *t*
			C-16	152.2 *s*	152.0 *s*
			C-17	106.9 *t*	107.0 *t*
			C-18	22.1 *q*	21.8 *q*
			C-19	130.2 *s*	178.0 *s*
			C-20	18.1 *q*	15.4 *q*

*^{1}H NMR, 400 MHz.

†^{13}C NMR, 67.92 MHz.

J (Hz): 2,3 = 4; 11,11′ = 17; 11,12 = 6; 15,15′ = 17.

will require a large coupling of 2α,3β as there is no reason for the presence of a boat conformation. Spin decoupling allowed the assignment of several ^{1}H NMR signals though many were overlapped multiplets. The fragmentation pattern in the mass spectrum also supported the structure, elimination of acetic acid, the loss of CO$_2$ and formation of a strong C$_9$H$_{11}$O fragment, obviously a result of splitting the C-7/C-8-bond agreed with the presence of a 9(11)-*seco*-kaurane structure with a ditertiary lactone group. The absolute configuration could not be determined. However, the isolated kaurenic acid was identical with *ent*-kaurenic acid and the proposed configuration was very likely. The presence of kaurene derivatives in a member of Umbelliferae again supports the relationship of the family to the Compositae [3]. Only a few diterpenes are reported from the Umbelliferae, but this family so far has not been investigated on a wide scale.



1 R = H
2 R = OAc

EXPERIMENTAL

The air dried material of *Alepidea amatynsia* Eck. et Leyh. (120 g) was collected in Natal in February 1977 (voucher 77/40, deposited in the Herbarium of the Department of Botany, University of Natal) and extracted with Et$_2$O–petrol (1:2). The resulting extracts after removal of saturated hydrocarbons by treatment with MeOH were separated by CC (silica gel) and repeated TLC (silica gel). Known compounds were identified by comparing their 400 MHz ^{1}H NMR spectra with those of authentic material, which are present in the collection of the Institute of Organic Chemistry, Technical University of Berlin. The roots (200 g) afforded 10 mg *ent*-16-kauren-19-oic acid and 5 mg of its 9(11)-dehydro derivative (Et$_2$O-petrol, 1:9), 37 mg **1** (Et$_2$O–petrol, 2:3, R_f 0.40) and 7 mg **2** (Et$_2$O–petrol, 2:3, R_f 0.35), while the aerial parts (120 g) gave 10 mg *ent*-16-kauren-19-oic acid and 5 mg of its 9(11)-dehydro derivative, 8 mg of *ent*-12-oxo-9(11),16-kauradien-19-oic acid, 12 mg **1** and 3 mg **2**.

3β-Acetoxywedelia-seco-kaurenolide (**2**). Colourless crystals, mp 120° (petrol); IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1770 (γ-lactone), 1740 (COOR), 1710 (C = O), 3075, 1660 (C = CH$_2$); MS *m/z* (rel. int.). 374.209 $[M]^+$ (4) (calc. for C$_{22}$H$_{30}$O$_5$: 374.209), 356 $[M - H_2O]^+$ (6), 330 $[M - CO_2]^+$ (12), 314 $[M - CH_3COOH]^+$ (24), 296 $[314 - H_2O]^+$ (44), 270 $[314 - CO_2]^+$ (32), 155 $[C_9H_{11}O]^+$ (78), 55 (100);

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\ \mathrm{nm}}{-25 \quad -25 \quad -31 \quad -71}\ \mathrm{CHCl_3};\ c\,0.1.$$

Acknowledgements—A. R. thanks Prof. Dr. O. Hilliard for her help during plant collection and Prof. Dr. F. Bohlmann, Technical University of Berlin, for providing the opportunity to work in his Institute and for helpful discussions.

REFERENCES

1. Bohlmann, F., Suding, H., Cuatrecasas, J., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19**, 267.
2. Bohlmann, F., Ziesche, J., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 751.
3. Mabry, T. J. and Bohlmann, F. in *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds) p. 1097. Academic Press, London.