Phytochemistry, Vol. 25, No. 4, pp. 949–950, 1986.
Printed in Great Britain.

0031-9422/86 $3.00 + 0.00

4-EPIPLUCHEINOL, A SESQUITERPENE FROM *PLUCHEA ARGUTA*

VIQAR UDDIN AHMAD and KANIZ FIZZA

H.E.J. Research Institute of Chemistry, University of Karachi, Karachi-32, Pakistan

(*Revised received* 8 *October* 1985)

Key Word Index—*Pluchea arguta*; Compositae; eudesmane derivative; sesquiterpene.

Abstract—From the whole plant of *Pluchea arguta* a new eudesmane sesquiterpene was isolated and identified as 4-epiplucheinol.

INTRODUCTION

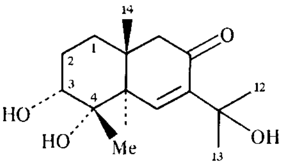
Pluchea arguta Boiss. (syn. *Conyza audentophylla* Boiss.) grows as a common weed in Sind and other parts of Pakistan. No work on its chemical constituents has been reported so far although other species of the genus *Pluchea* have been examined chemically [1–12]. In view of the medicinal properties [13] of the plants belonging to this genus, a chemical investigation of *P. arguta* was undertaken.

As a result of this work, triacontanol, lupeol, lupeol acetate and a new eudesmane sesquiterpene, 4-epiplucheinol (**1**), were isolated from *P. arguta*. The structure of the last named compound was elucidated by spectroscopic methods.

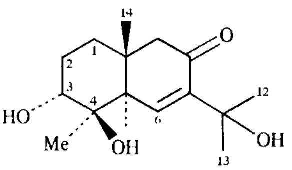
RESULTS AND DISCUSSION

The fast atom bombardment (FAB) mass spectrum of **1** contains an $[M+H]^+$ peak at *m/z* 269 corresponding to the molecular formula $C_{15}H_{24}O_4$. In the EI mass spectrum, the $[M]^+$ peak is absent but there is an $[M-Me]^+$ peak at *m/z* 253. The rest of the important peaks at *m/z* 235 (base peak) 217, 193, 175, 149 and 123 are identical to those reported [1] for plucheinol (**2**), a sesquiterpene isolated from *Pluchea* species, although the intensity of the peaks are somewhat different. The UV absorption maximum at 243 nm indicates the presence of an α,β-unsaturated ketone in **1**. The IR spectrum contains peaks at 3450 and 3340 (OH) and 1674 and 1645 cm^{-1} (α,β-unsaturated ketone). The ^1H NMR spectrum (300 MHz) is very similar to that of plucheinol [1, 2] but there are some differences. Thus compound **1** shows four methyl singlets at δ0.92, 1.18, 1.41 and 1.42 due to methyl groups attached to C-10, C-4, C-11 and C-11 respectively. There is a narrow triplet at δ3.67 ($J = 2.7$ Hz) characteristic of the proton geminal to α hydroxyl group at C-3. A doublet at δ7.03 ($J = 2.19$ Hz) is assigned to the olefinic H at C-6. Unlike plucheinol, the signal of these two protons attached to C-9 is not a broad singlet [2], but rather an AB quartet centred at δ2.29 ppm ($J_{AB} = 15.7$ Hz, $\delta_A - \delta_B = 18.5$ Hz).

The broad band and DEPT ^{13}C NMR spectra of **1** were very useful in elucidating the structure of the compound. As Table 1 shows, the signal of C-4 is shifted upfield by 3.3 ppm in **1** as compared to plucheinol. The chemical shift of C-2 is also affected because the hydroxyl group in plucheinol (**2**) is near to C-2 whereas this is not the case in



2 Plucheinol



1 4 - Epi - plucheinol

Table 1. ^{13}C NMR data of plucheinol (**2**) [2] and compound **1** ($CDCl_3$, δ)

C	Plucheinol (**2**)	Compound **1**
1	31.93	32.00
2	25.10	25.85
3	73.44*	73.39
4	75.43*	72.10
5	48.91	49.02
6	143.21	143.57
7	145.42	144.86
8	201.34	201.53
9	57.73	57.79
10	39.20	39.25
11	71.98	72.00
12	29.28	29.38
13	28.82	28.86
14	17.71	17.76
15	22.36	22.38

*Assignments revised by us on the basis of DEPT experiment.

1. This finding indicates that **1** is stereoisomeric with plucheinol (**2**) at C-4. This conclusion is supported by the fact that although plucheinol forms an acetonide at room temperature in the presence of *p*-toluenesulphonic acid [2], **1** does not. Thus both hydroxyl groups at C-3 and C-4 are axial.

EXPERIMENTAL

Mps: uncorr; UV: MeOH; IR: KBr; ^{1}H NMR (300.13 MHz) and ^{13}C NMR (75.43 MHz): $CDCl_3$; EI and FABMS: Finnigan MAT 312 double focussing mass spectrometer coupled with PDP 11/34 computer system.

Extraction and isolation. The plant (8 kg) was soaked and homogenized (Ultraturrax) in hexane. The residue obtained on evaporation of the hexane was chromatographed on a silica gel column with hexane, hexane–$CHCl_3$, $CHCl_3$, $CHCl_3$–EtOAc, EtOAc, EtOAc–MeOH and finally with MeOH.

Triacontanol and lupeol acetate were eluted from the column with hexane, and lupeol with hexane–$CHCl_3$ (9:1). These compounds were identified from their mass and ^{13}C NMR spectra [14], and also through mmps and co-TLC with authentic samples.

4-*Epi-plucheinol* was eluted with $CHCl_3$–EtOAc (7:3), crystallized from C_6H_6, mp 80°; $[\alpha]_D$ 50° ($CHCl_3$); UV λ_{max}^{MeOH} 243 nm; IR ν_{max}^{KBr} cm^{-1}: 3450–3340 (OH), 1674, 1645 (α,β-unsatd ketone); ^{1}H NMR: see Results and Discussion. ^{13}C NMR: See Table 1. FABMS m/z: 307 $[M+K]^+$, 291 $[M+Na]^+$, 269 $[M+H]^+$, 251 $[M+H-H_2O]^+$, 232 $[M-2H_2O]^+$; EIMS m/z (rel. int.): 253 $[M-Me]^+$ (38), 235 (100), 217 (12), 193 (14), 175 (10), 149 (74), 132 (12), 123 (16), 109 (22), 95 (14), 83 (14), 77 (12), 55 (12).

REFERENCES

1. Chiang, M. T., Bittner, M., Silva, M., Watson, W. H. and Sammes, G. P. (1979) *Phytochemistry* **18**, 2033.
2. Arriaga, F. J. and Borges-del-Castillo, J. (1985) *Planta Med.* 290.
3. Bohlmann, F. and Mahanta, P. K. (1978) *Phytochemistry* **17**, 1189.
4. Bohlmann, F. and Grenz, M. (1969) *Tetrahedron Letters* 5111.
5. Bohlmann, F. and Zdero, C. (1976) *Chem. Ber.* **109**, 2653.
6. Nakanishi, K., Crouch, R., Miura, I., Dominguez, X. A., Zamudio, A. and Villarreal, R. (1974) *J. Am. Chem. Soc.* **96**, 609.
7. Bohlmann, F., Zeische, J., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19**, 969.
8. Domingues, X. R., Franco, R., Cano, G., Villareal, R., Bapuji, M. and Bohlmann, F. (1981) *Phytochemistry* **20**, 2297.
9. Mukhopadhyay, S. and Cordell, G. A. (1983) *J. Nat. Prod.* **46**, 671.
10. Omar, A. A., Sarg, T. M., Khafagy, S. M., Ibrahim, Y. E., Zdero, C. and Bohlmann, F. (1983) *Phytochemistry* **22**, 779.
11. Arriaga-Giner, F. J., Borges-Del-Castillo, J., Manresa-Ferrero, M. T., Vazquez-Bueno, P., Rodriguez-Luis, F. and Valdes-Iraheta, S. (1983) *Phytochemistry* **22**, 1767.
12. Bohlmann, F., Metwally, M. A. and Jakupovic, J. (1984) *Phytochemistry* **23**, 1975.
13. Chopra, R. N., Nayar, S. L. and Chopra, I. C. (1956) *Glossary of Indian Medicinal Plants.* CSIR, New Delhi.
14. Wenkert, E., Baddeley, G., Burfill, I. R. and Moreno, L. N. (1978) *Org. Magn. Reson.* **11**, 337.