Phytochemistry, 1980, Vol. 19, pp. 2235–2236. © Pergamon Press Ltd. Printed in England. 0031-9422/80/1001-2235 $02.00/0

CHEMOTAXONOMY OF THE GENUS *PLAGIOCHEILUS**

FERDINAND BOHLMANN†, HAROLD ROBINSON‡ and ROBERT M. KING‡

†Institute for Organic Chemistry, Technical University, D-1000 Berlin 12, West Germany; ‡Smithsonian Institution, Washington, DC 20560, U.S.A.

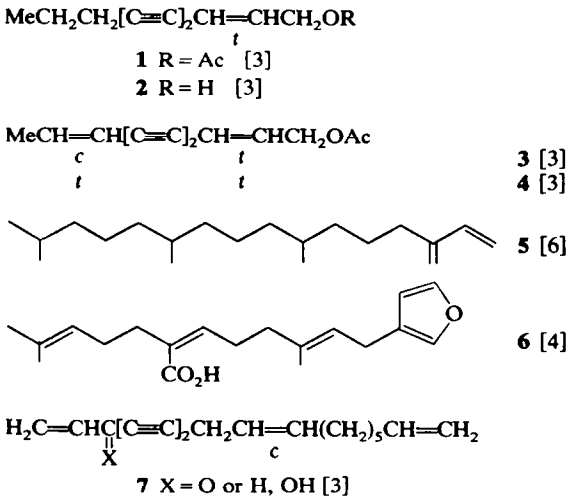
(*Received* 21 *September* 1979)

Key Word Index—*Plagiocheilus prostratus*; Compositae; C_{10}-acetylenes; furanoditerpene; tribal classification.

The position of the South American genus *Plagiocheilus* is doubtful [1]. Earlier it was placed in the tribe Anthemideae; however, its relationship to the Astereae also seems to be obvious and the genus therefore has been placed more recently in the Astereae [2]. Furthermore, its affinities with the 'Cotuleae' and *Centipeda* have also been indicated [1]. While the chemistry of several species of the genus *Cotula* has been reasonably well investigated, only one species of *Centipeda* has been studied. Nothing is known about the constituents of *Plagiocheilus*; we therefore have investigated *P. prostratus* Benth.

The roots contain a mixture of acetates, which only could be separated after repeated TLC. Finally three acetates were obtained. The UV and ^{1}H NMR data clearly show that the compounds are the known diynene **1** [3] and the isomeric endiynenes **3** and **4** [4] (see Experimental). Though **4** could not be obtained pure, the position of the ^{1}H NMR signal of the methyl group clearly shows that the 8,9-double bond has the *trans*-configuration (in the *cis*-isomer **3**, this methyl is deshielded by the diyne). The aerial parts afforded, in addition to linoleic and linolenic acid, neophytadiene (**5**), **1** and **3** again as well as traces of the alcohol **2** [3] and a diterpene, which proved to be identical to centipedic acid (**6**), previously isolated from *Centipeda orbicularis* [4]. The ^{1}H NMR spectrum was completely identical to that of this acid.

The isolation of **1–4** indicates that *Plagiocheilus* indeed must be at least closely related to the Astereae as these compounds are typically found in many members of this tribe [3]. The diterpene **6**, so far only found in a *Centipeda* species, which contains further diterpenes typical for Astereae [4], also supports the placement of *Plagiocheilus* in the Astereae. *Centipeda*, on the other hand, shows relationships to the Astereae on the basis of the pollen-grain structure [5] and therefore should be preferably placed in this tribe too. The very similar C_{17}-acetylenes in *Centipeda* [4] and *Cotula* [3], which are found both in Astereae and Anthemideae [3], could be an indication that the *Cotula* group [1] may be a link between these two tribes, while *Plagiocheilus* and *Centipeda* might be better positioned in the Astereae.



EXPERIMENTAL

The air-dried plant material, collected in Ecuador (voucher RMK 7786) was ground and extracted with Et_2O–petrol (1:2). The extracts were separated first by CC (Si gel, act. grade II) and further by repeated TLC (Si gel, GF 254). Roots (30 g) afforded 5 mg **1** [^{1}H NMR ($CDCl_3$, 270 MHz): 4.61 (*dd*, J = 6.3, 1.5 Hz, 1-H), 6.27 (*dt*, J = 15, 6.3 Hz, 2-H), 5.77 (*d*(*br*), J = 15 Hz, 3-H), 2.31 (*t*(*br*), J = 7 Hz, 8-H), 1.58 (*tq*, J = 7, 7 Hz, 9-H), 1.00 (*t*, J = 7 Hz, 10-H)], 10 mg **3** [^{1}H NMR($CDCl_3$): 4.64 (*dd*, J = 6.3, 1.5 Hz, 1-H), 6.31 (*dt*, J = 15, 6.3 Hz, 2-H), 5.85 (*d*(*br*), J = 15 Hz, 3-H), 5.57 (*d*(*br*), J = 10 Hz, 8-H), 6.18 (*dq*, J = 10, 6.5 Hz, 9-H), 1.93 (*dd*, J = 6.5, 1.5 Hz, 10-H) and 1 mg **4** [3], while 70 g aerial parts yielded 20 mg **5**, 10 mg **1**, 2 mg **2**, 1 mg **3**, 200 mg linolic and linolenic acid (2:1) and 15 mg **6** [4], IR and ^{1}H NMR spectra identical with those of authentic material.

Acknowledgement—We thank the Deutsche Forschungsgemeinschaft for financial support.

REFERENCES

1. Heywood, V. H. and Humphries, C. J. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds). pp. 855, 871. Academic Press, London.
2. Grau, J. (1977) *The Biology and Chemistry of the Compositae*, p. 555. Academic Press, London.

*Part 270 in the series "Naturally Occurring Terpene Derivatives". For Part 269 see Bohlmann, F. and Eickeler, E. (1980) *Chem. Ber.* **113**, 1189.

3. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London.
4. Bohlmann, F. and Mahanta, P. K. (1977) *Phytochemistry* **18,** 1067.
5. Skvarla, J., Turner, B. L., Patel, V. C. and Tomb, A. S. (1977) In *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.). Academic Press, London.
6. Whigth, H. E., Jr., Burton, W. W. and Berry, R. C., Jr. (1959) *Arch. Biochem. Biophys.* **82,** 107.