



Pergamon

Biochemical Systematics and Ecology 31 (2003) 107–109

www.elsevier.com/locate/biochemsysseco

biochemical
systematics
and ecology

A piptocarphin and other constituents of *Lepidaploa myriocephala*

Susana Borkosky ^a, Alicia Bardón ^a, César A.N. Catalán ^a,
Thomas E. Gedris ^b, Werner Herz ^{b,*}

^a Instituto de Química Orgánica, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, Ayacucho 491, S. M. de Tucumán, Argentina

^b Department of Chemistry and Biochemistry, The Florida State University, Tallahassee, FL 32306-4390, USA

Received 16 January 2002; accepted 19 March 2002

Keywords: *Lepidaploa myriocephala*; Vernoniinae; Vernoniaeae; Asteraceae; Sesquiterpene lactone; Piptocarphin; Triterpenes

1. Subject and source

Aerial parts of *Lepidaploa myriocephala* (DC.) H. Robinson were collected at the flowering stage in October 1992 in Buena Vista, Bolivia. A voucher specimen (Lil No. 597 307) is on deposit in the herbarium of the Fundación Miguel Lillo, Tucumán.

2. Previous work

Earlier work on *Lepidaploa* species, a segregate of the *Lepidaploa* complex of western hemisphere *Vernonia* species (Robinson, 1990, 1994, 1995, 1999) has been reviewed (Alvares Valdés et al., 1998). A study not cited in the earlier paper dealt with *Lepidaploa leptoclada* (Sch. Bip.) H. Robinson (as *Vernonia moaensis* Alain and *V. acuña* Budesinsky et al. (1994). Sesquiterpene lactones of the glaucolide, goyazensolide (piptocarphin) and cadinanolide type are common, although germacra-dienolides, guaianolides and occasionally eudesmanolides have also been found.

* Corresponding author. Tel.: +1-850-644-2774; fax: +1-850-644-8281.

E-mail address: jdulin@chem.fsu.edu (W. Herz).

3. Present study

In the course of our study of Vernoniinae of northern Argentina and adjacent regions (Borkosky et al., 1997, and references therein) we examined *Lepidaploa myriocephala* (DC.) H. Robinson (old synonym *Vernonia myriocephala* DC.), a species found in Bolivia and Peru (Robinson, 1999). Air-dried flowers and leaves (419 g) were extracted with EtOAc (2×1.5 l) free of HOAc at room temperature for 4 days with shaking to give 15 g (3.6%) of crude extract which was suspended in EtOH (129 ml) at 55°C, diluted with warm H₂O (97 ml) and extracted successively with hexane (2×150 ml) and CH₂Cl₂ (150 ml). Evaporation of the CH₂Cl₂ extract in vacuo furnished 1.95 g of residue which was chromatographed on Si gel (60 g) using CHCl₃ containing increasing amounts of EtOAc (0–100%), three frs. being collected (I to III). The IR spectrum of fr. II (74 mg) exhibited a strong band at 1760 cm⁻¹ characteristic of α,β -unsaturated γ -lactones. HPLC using a Phenomenex C 18 column (5 μ m, 250×10 mm i.d., MeOH–H₂O 4:3, 2 ml min⁻¹) gave 0.9 mg of **1** (R_t 12 min measured from the solvent peak) which we previously reported from *L. remotiflora* (Alvares Valdés et al., 1998). The substance was identified by ¹H NMR spectroscopy (500 MHz, CDCl₃), MS and comparison with spectra in our files. Evaporation of the hexane extract in vacuo furnished 13 g of residue which was chromatographed on Si gel (390 g) using hexane and increasing amounts of EtOAc (0–100%), six frs. (I–VII) being collected. A 63 mg portion of fr. III (219 mg) was processed by HPLC using the Phenomenex column (MeOH, 2 ml min⁻¹) to give 2.3 mg of lupenone (R_t 42 min), 3.5 mg of β -amyronone (R_t 58 min) and 8.8 mg of a mixture containing mainly β -amyronone (R_t 70 min). Fr. VI (270 mg) on HPLC using a Beckman Ultrasphere column (5 μ m, 250×10 mm i.d., MeOH–H₂O 9:1, 2.3 ml min⁻¹) gave 10.6 mg of palmitic acid (R_t 50 min), 4.2 mg of a mixture of unsaturated acids (C₁₈–C₂₄, R_t 60 min) and 2.0 mg of stearic acid (R_t 69 min). The remaining fractions contained unresolved mixtures.

4. Chemotaxonomic significance

Although the small amount of sesquiterpene lactone detected in our collection of *L. myriocephala* was surprising, the type of lactone found was consistent with previous work on the *Lepidaploa* complex. Triterpenes, mainly lupeol and lupeol acetates, have previously been reported from *Lepidaploa* species, but lupenone and β -amyronone are new.

Acknowledgements

Work in Tucumán was supported by grants from the Consejo Nacional de Investigaciones Científicas y Técnicas de Argentina (CONICET) and Consejo de Investigaciones de la Universidad Nacional de Tucumán (CIUNT).

References

- Alvares Valdés, D., Bardón, A., Catalán, C.A.N., Gedris, T.E., Herz, W., 1998. *Biochem. Syst. Ecol.* 26, 685.
- Borkosky, S., Bardón, A., Catalán, C.A.N., Díaz, J.G., Herz, W., 1997. *Phytochemistry* 44, 465.
- Budesinsky, M., Perez Souto, N., Holub, M., 1994. *Coll. Czechoslov. Chem. Commun.* 59, 913.
- Robinson, H., 1990. *Proc. Biol. Soc. Wash.* 103, 464.
- Robinson, H., 1994. *Phytologia* 76, 27.
- Robinson, H., 1995. *Phytologia* 78, 384.
- Robinson, H., 1999, *Smithsonian Contributions to Botany*, No. 89.