Chemical constituents of *Packera coahuilensis* and *Packera bellidifolia*

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1. Subject and source

Until now only six out of the 51 species which constitute the genus *Packera* (Weber and Löve, 1981) had been studied chemically (Pettit et al., 1980; Bohlmann et al., 1981; McCoy et al., 1983; Zalkow et al., 1988; Pérez et al., 1991; Bah et al., 1994). In order to contribute to the chemistry of the genus, we decided to study *Packera coahuilensis* (Grenm.) C. Jeffrey (MEXU 781268) and *Packera bellidifolia* (HBK) Weber and Löve (MEXU 781267), collected in Coahuila, October 1996, and in Oaxaca, June 1997. Voucher specimens are deposited at the Herbarium del Instituto de Biología, UNAM.

2. Previous work

The six *Packera* species already studied contained pyrrolizidine alkaloids (PAs), eremophilanes and acetic acid derivatives as the main secondary metabolites. This
paper reports the phytochemical study of *P. coahuilensis* and *P. bellidifolia*, which to our knowledge have not been studied previously.

3. Present study

Dried and ground aerial parts (322.3 g) of *P. coahuilensis* were extracted with MeOH until the extract gave a negative Dragendorff test. The solvent was evaporated to one-tenth of its volume; acidified with 2.5% aq. H$_2$SO$_4$ (to pH 1), stirred overnight with Zn powder (32.0 g) at room temperature and filtered. The acidic filtrate was washed with CHCl$_3$, basified with aq. NH$_3$ (to pH 10), and extracted with CHCl$_3$. The organic solution dried over Na$_2$SO$_4$, was concentrated to yield 4.56 g of alkaloidal extract. This was submitted to consecutive CCs on silica gel (60 GF$_{254}$ Merck, 1 : 15) eluting with CHCl$_3$–MeOH 19 : 1, to give retrorsine (1, 60.1 mg), mp 209–211° (Segall and Dallas, 1983), senecionine (2, 89.4 mg), mp 235–7° (Segall and Dallas, 1983), and retrorsine hydrochloride (1•HCl, 14.0 mg). The less polar fractions were combined and purified by CC eluted with hexane-EtOAc 9 : 1 affording methyl p-hydroxyphenyl acetate (3, 413.0 mg) as colorless oil (Dictionary of Natural Products, 1999), and methyl 1-hydroxy-4-oxocyclohexyl acetate (4, 441.0 mg) as colorless oil (Bohlmann et al., 1981). Roots (102.0 g) analyzed following the above-mentioned procedure gave 485.6 mg of alkaloidal extract, which after purification by CC afforded 1 (41.0 mg),
2 (63.2 mg), 3 (24.1 mg), and 4 (70.8 mg). The aerial parts (234.0 g) of *P. bellidifolia* worked up by the usual procedure, gave before the NH$_3$ treatment a non-alkaloidal oily residue. This residue was successively extracted with CHCl$_3$ and MeOH giving 1.3 and 6.0 g of the respective extracts. The CHCl$_3$ residue (1.3 g) gave 3 (744.9 mg) after a CC eluted with hexane EtOAc 4 : 1. The MeOH residue (6.0 g) gave by CC 3 (1.305 g), jacaranone (5, 65.0 mg) as white crystals, mp 78–93°C (Ogura et al., 1976; Bohlmann et al., 1981), and p-hydroxyphenyl acetic acid (6, 94.0 mg) as white crystals, mp 152–4°C (Dictionary of Natural Products, 1999). The aqueous phase basified and extracted as described for *P. coahuilensis*, afforded 2.19 g of alkaloidal extract. Successive CCs of the latter eluting with hexane-Me$_2$CO 4 : 1, 17 : 3, CHCl$_3$, CHCl$_3$–MeOH 49 : 1, and 24 : 1, afforded 3 (863.1 mg), 4 (185.5 mg), 5 (29.6 mg), and anisic acid (7, 13.9 mg) as white crystals, mp 179–181°C (Dictionary of Natural Products, 1999). Roots (260.0 g) of *P. bellidifolia* worked up as described for its aerial parts gave 1.8 g of alkaloidal residue and 1.4 g of non-alkaloidal residue. Both were analyzed by HPLC, Waters Delta Prep 4000 chromatograph equipped with an UV–VIS Model 486 detector set at 223 nm. An IB-SIL 5 PHENYL column (15 cm × 4.6 mm) was used. Mobil phase was CH$_3$CN–H$_2$O 1 : 9 during 5 min, changed to 1 : 3 at 8 min, and held 14 min. A flowrate of 1 ml/min was used. The yield of metabolites in each residue (alkaloidal and non alkaloidal) was: 31.8% and 6.2% of 3, 32.3% and 24.8% of 4, 1.7% and 0.2% of 5, 0.5% and 0.07% of 7. Compound 6 (0.8%) was only detected in the non-alkaloidal residue. Compound 2 was identified by comparison with an authentic sample. Compounds 1, 3–7 were identified by comparison of their spectral data with those reported in the literature. Compound 1zHCl was converted to the free alkaloid 1, by treatment with aq. NaOH.

4. Chemotaxonomic significance

*P. coahuilensis* gave the PAs retrorsine (1) and sepicionine (2), previously found in other species of *Packera* (McCoy et al., 1983; Zalkow et al., 1988; Bah et al., 1994) and *Senecio* (Segall and Dallas, 1983). Both species afforded the acetic acid derivatives 3–7. Compound 4 and jacaranone (5) had been previously isolated from *P. fendleri* (Pettit et al., 1980), *P. clevelandii* (Bohlmann et al., 1981), *P. anonyama* (Gelbaum et al., 1982) and from some species of *Senecio* (Mericli et al., 1989). Although MeOH extract of *P. bellidifolia* gave a positive Dragendorff test, no PA was isolated, and only the acetic acid derivatives 3–7 were obtained. This is in agreement with the results described earlier on the Dragendorff test (Svendsen and Verpoorte, 1983), which gave false positives with carboxylic acid and phenolic compounds.

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