

EXPERIMENTAL

Analysis and identification were performed on a Hewlett-Packard *gs/ms* system complete with data bank (Hewlett-Packard 5700-5980A-5933A). Gas chromatographic separation was performed using a WCOT Emulphor ON 870 column, 50m×0.32mm i.d. Gas flow (helium) 1.8 ml/min, temperature 90-230° at 2°/min. The detectors FID and TCD were operated simultaneously with 1:100 split ratio. Mass spectra were measured every 0.6 s over the *m/z* 34-420 range utilizing an ionizing voltage of 70 eV.

PREPARATION OF THE ESSENTIAL OIL.—The above-ground parts of *H. dissectum* were collected in June 1980, near and to the west of Ulan Batar. The herbarium item No. 6122 is deposited in the Botanical Institute of the Mongolian Academy of Sciences, Ulan Batar. The air-dried material (8 kg) was steam distilled in the conventional manner, affording 10 g of a light yellow, fluid essential oil with d_{20}^{20} 0.9770, n_D^{20} 1.4814, and $[\alpha]^{20}_D -7.6^\circ$.

HYDROCARBON FRACTION.—The essential oil (5 g) was chromatographed on silica gel (500 g) deactivated by addition of 11% of H₂O. Elution with light petroleum gave the hydrocarbon fraction (1.2 g).

ACKNOWLEDGMENTS

Thanks are due to Dr. T.C. Sanchir (Botanical Institute, Ulan Batar, Mongolia) for the identification of the plant material.

LITERATURE CITED

1. R.I. Shokova, T.F. Fedosova, G.A. Syrtanova, and V.M. Yakovleva, *Izv. Akad. Nauk Kaz SSR, Ser. Biol.*, **11** (5), 6 (1973); *Chem. Abstr.*, **80**, 130 529 s (1974).
2. L.M. Belenovskaya, V.S. Sinitskii, and H. Tumbaa, *Khim. Prir. Soedin.*, 574 (1977); *Chem. Abstr.*, **87**, 164 242 c (1977).
3. L.E. Gusak and L.K. Safina, *Tr. Inst. Bot. Akad. Nauk Kaz. SSR*, **35**, 145 (1976); *Chem. Abstr.*, **86**, 68 378 k (1977).
4. L.S. Kozovka, *Vopr. Pitan.*, 76 (1976).
5. K.G. Tkachenko, *Rastit. Resurs.*, **18**, 83 (1982); *Chem. Abstr.*, **96**, 139 664 v (1982).
6. A.A. Dzhaparidze, *Maslo-zbir. Prom.*, (2), 31 (1981); *Chem. Abstr.*, **94**, 145 163 f (1981).
7. R. Hegnauer, "Chemotaxonomie der Pflanzen," Vol. 6, Basel, Birkhäuser Verlag, 1973, p. 622.

Received 7 November 1984

COUMARINS FROM *ERYNGIUM ILICIFOLIUM*

MARIANO PINAR* and MARIANO P. GALAN

Instituto de Química Orgánica General, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

Eryngium ilicifolium Lam. (Umbelliferae) is an annual herb endemic on the Iberian Peninsula. This plant was studied previously, and only kaempferol (1) was detected. The genus *Eryngium* is poor in coumarins.

An Et₂O extract of the plant, chromatographed on silica gel with CHCl₃, afforded a fraction which on thin layer chromatograms gave only a single spot. The ¹H-nmr spectrum revealed a mixture of three components with characteristic signals for an angelate [δ 5.98 (1H, qq), 1.88 (3H, dq), and 1.67 (3H, d)], a tiglate (δ 6.52 (1H, qq), 1.67 (3H, dq), and 1.64 (3H, d)], and a senecioate [δ 5.56 (1H, qq), 2.10 (3H, d), and 1.86 (3H, d)], all esterified with marmesin. These assignments are unequivocal because the three components of the mixture are in different proportions: tiglate ca. 50%, angelate 17%, and senecioate 33%. The methanolic saponification of the fraction afforded (+)-marmesin. Therefore, the three coumarins are deltoin (2), prantschimgin (2), and (+)-marmesin tiglate; the last was previously found in its racemic form (2).

EXPERIMENTAL

PLANT MATERIAL.—Whole plants (roots and aerial parts) were collected in June 1980, in Ronda (Málaga, Spain). A voucher specimen (MA 84813) was deposited in the Herbarium of the Royal Botanic Garden of Madrid.

EXTRACTION AND SEPARATION.—Dried and finely powdered whole plants (600 g) were extracted with Et₂O in a Soxhlet apparatus. The extract was chromatographed on silica gel (containing 15% H₂O); elution with CHCl₃ yielded a single spot (tlc) fraction (0.055 g). ¹H-nmr (360 MHz, CDCl₃) double resonance experiments confirmed the chemical shifts stated above. The methanolic saponification of the fraction, worked up by usual procedures (3), gave (+)-marmesin mp 186-187°, [α]²⁰_D 28.5° (c=0.40, CHCl₃), which was identical by mmp, ir, ¹H-nmr, and ms data and co-chromatography with an authentic sample. The angelic acid (part of it becomes isomerized to tiglic acid), tiglic acid, and senecioic acid were subsequently isolated over silica gel plates impregnated with ammoniacal AgNO₃ as previously described (4).

Full details of the isolation and identification are available on request to the senior author.

ACKNOWLEDGMENTS

The authors thank Dr. M. Rico and Dr. J. Santoro (Instituto de Estructura de la Materia, CSIC, Madrid) for recording the ¹H-nmr spectra and Dr. J. Borja (Botany Department, Faculty of Pharmacy, University of Madrid) for the identification of the plant material.

LITERATURE CITED

1. R.K. Crowden, J.B. Harborne, and V.H. Heywood, *Phytochemistry*, **8**, 1963 (1969).
2. R.D.H. Murray, *Progress in the Chemistry of Organic Natural Products*, **35**, 199 (1978).
3. J. Lemmich, E. Lemmich, and B.E. Nielsen, *Acta. Chem. Scand.*, **19**, 1810 (1965).
4. S.P. Dutta and A.K. Barna, *J. Chromatogr.*, **29**, 263 (1967).

Received 26 November 1984

STUDIES ON CHILEAN LICHENS, VIII.¹ DEPSIDONES FROM *PSOROMA* SPECIES

MARISA PIOVANO, MARIA I. GARRIDO, VICENTE GAMBARO, JUAN A. GARBARINO*

*Departamento de Química, Facultad de Ciencia, Universidad Federico Santa María,
Castilla 110-V, Valparaíso, Chile*

and WANDA QUILHOT

*Escuela de Química y Farmacia, Facultad de Medicina, Universidad de Valparaíso,
Casilla 92-V, Valparaíso, Chile*

Species of the lichen genus *Psoroma* (Pannariaceae) are characterized by the tendency to accumulate chlorinated depsidones biogenetically related to β-orcinol. The presence of vicanicin and norvicanicin from *Psoroma sphinctrinum* (2) and isovicanicin from *Psoroma atrophylum*, have been reported (3); vicanicin was also isolated from *Psoroma leprolomun* (4), pannarin from *Psoroma diuretzi* (5) and dechloropannarin from *Psoroma caesium* (3). Recently, allorhizin was isolated from *Psoroma allorhizum* (3).

We wish to report here the results on research on the depsidones of four *Psoroma* species (Table 1).

TABLE 1. Depsidones from the Genus *Psoroma*

<i>Psoroma</i> Species		Compounds (%)	References
<i>P. dimorphum</i> Malme	vicanicin	0.2	4
	diploicin	0.01	6
	pannarin	0.01	
<i>P. pallidum</i> (Mont.) Nyl.	pannarin	2.0	7
	vicanicin	0.01	
	dechloropannarin	0.20	3
<i>P. pulchrum</i> Malme	vicanicin	0.53	
	pannarin	0.20	
<i>P. reticulatum</i> (Hue.) Zahlbr.	pannarin	0.19	

¹For Part VII, see Chamy *et al.* (1).