COMPOSITION OF THE ESSENTIAL OIL FROM *HERACLEUM DISSECTUM*

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Heracleum dissectum Ledeb. (Umbelliferae) is a perennial sturdy plant widespread in East Asia. In Mongolia, it occurs mainly in mountainous regions where it is used as an edible plant, for example, in the preparation of salads as a substitute for cucumbers. The fruits and roots are used in traditional Tibetan medicine (the "bru-nag" drug). Currently, the plant is being used as fodder and for silaging (1). In common with other species of *Heracleum*, the presence of coumarins in the roots (2) and the fruits of the plant (3) have been recorded. Also, a high content of vitamin C has been reported (4).

The essential oils from fruits of *Heracleum* species have attracted considerable attention (5-7). However, the presence of essential oil in *H. dissectum* has not been previously reported and, therefore, nothing is known about its composition despite the fact that the plant has been used for medical purposes. The present paper refers to the acquisition of the essential oil, the fractionation and the identification of the individual components.

Steam distillation of dry parts of the plant yielded 0.1% (based on dry weight) essential oil. Preliminary separation by column chromatography gave 24% hydrocarbons, mainly monoterpenes of low molecular weight. By combination of gc and computer assisted mass spectral analysis, it was possible to isolate 64 components. The identification of the individual components was achieved with the aid of various computer interpretative techniques as well as by separate interpretation of some mass spectra.

The computer techniques included a comparison of unknown spectra with a collection of 25,000 authentic mass spectra and plots of relative intensities of significant masses ("mass chromatograms") either to reveal structural isomers of compounds or to detect some minor components hidden by other constituents in an incompletely separated gas chromatographic peak.

The main components of the essential oil were α-pinene, myrcene, kessan, humulene, β-phellandrene, kessanyl acetate, limonene, linalol, β-*cis*-ocimene, and kessyl acetate (Table 1).

TABLE 1. Glc/Ms Analysis of Essential Oil of *Heracleum dissectum*

Peak No.	Component	Relative Concentration	Source of identification
1	α-Pinene	22.17	Rt[a], ms[b]
2	Camphene	1.51	Rt, ms
3	β-Pinene	1.31	Rt, ms
4	Sabinene	2.33	Rt, ms
5	Carene-3	0.55	Rt, ms
6	Myrcene	10.91	Rt, ms
7	*p*-Menthadiene-1(7)-8	tr.[c]	ms
8	*trans*-2-Hexenal	tr.	Rt, ms
9	iso-Butyl isovalerate	tr.	Rt, ms
10	*n*-Amyl butyrate	tr.	Rt, ms
11	Limonene	2.82	Rt, ms
12	β-Phellandrene	5.51	Rt, ms
13	β-*trans*-Ocimene	1.33	Rt, ms
14	β-*cis*-Ocimene	2.34	Rt, ms
15	*p*-Cymene	1.54	Rt, ms
16	Methylhexyl ketone	tr.	Rt, ms

TABLE 1. *Continued*

Peak No.	Component	Relative Concentration	Source of identification
17	iso-Amyl butyrate	1.30	Rt, ms
18	iso-Amyl iso-valerate	1.32	Rt, ms
19	iso-Amyl valerate	0.44	Rt, ms
20	6-Methyl-5-hepten-2-one	tr.	Rt, ms
21	*cis*-3-Hexenol	tr.	Rt, ms
22	Butyl tiglate	tr.	Rt, ms
23	Allyl valerate	tr.	Rt, ms
24	Octen-1-ol-3-acetate	tr.	Rt, ms
25	Pentenyl butyrate	tr.	Rt, ms
26	Pentenyl isovalerate	0.55	Rt, ms
27	Perillen	tr.	Rt, ms
28	Pentenyl valerate	0.34	Rt, ms
29	*trans*-Linalol oxide	tr.	Rt, ms
30	*cis*-Linalol oxide	tr.	Rt, ms
31	Ocimene epoxide I	tr.	Rt, ms
32	Amyl tiglate	tr.	Rt, ms
33	Ocimene epoxide II	tr.	Rt, ms
34	Amyl caproate	0.29	Rt, ms
35	3-Hexenyl valerate	tr.	Rt, ms
36	Heptyl valerate	tr.	Rt, ms
37	Linalol	2.36	Rt, ms
38	α-Copaene	0.34	Rt, ms
39	Amyl heptoate	0.55	Rt, ms
40	Bourbonene	0.55	Rt, ms
41	Octyl butyrate	tr.	Rt, ms
42	iso-Bornyl acetate	1.58	Rt, ms
43	Terpinene-1-ol-4	0.35	Rt, ms
44	Pentenyl caproate	0.20	Rt, ms
45	Pentadecane	0.05	ms
46	γ-Cadinene	0.15	ms
47	Caryophyllene	0.17	Rt, ms
48	Cryptone	0.32	Rt, ms
49	iso-Bornyl propionate	0.11	Rt, ms
50	Octyl valerate	tr.	Rt, ms
51	α-Terpineol	tr.	Rt, ms
52	Humulene	8.33	ms
53	Germacrene D	0.43	ms
54	iso-Bornyl butyrate	0.27	Rt, ms
55	α-Muurolene	0.10	ms
56	Bisabolene	0.62	ms
57	α-Farnesene	tr.	ms
58	Kessan	8.79	ms
59	α-Bisabolol	0.16	ms
60	Kessyl acetate	2.03	ms
61	Nerolidol	1.72	Rt, ms
62	Elemol	tr.	Rt, ms
63	Kessanyl acetate	3.19	ms
64	Cadinol isomer	tr.	ms

[a]Rt=Retention time
[b]ms=Mass spectrum
[c]tr.=traces

The composition of this oil is characterized by the presence of valerianic esters in substantial percentage. Similarly, the presence of kessan and its derivatives is very prominent. The overall ratio of these constituents indicates that the composition of this essential oil resembles that obtained from the root of Japanese Valerian (*Valeriana officinalis*).

EXPERIMENTAL

Analysis and identification were performed on a Hewllet-Packard gs/ms system complete with data bank (Hewllet-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}_4 0.9770, n^{20}_D 1.4814, and $[\alpha]^{20}_D$ −7.6°.

HYDROCARBON FRACTION.—The essential oil (5 g) was chromatographed on silica gel (500 g) deactivated by addition of 11% of H_2O. 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.

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Received 7 November 1984

COUMARINS FROM *ERYNGIUM ILICIFOLIUM*

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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 Et_2O extract of the plant, chromatographed on silica gel with $CHCl_3$, afforded a fraction which on thin layer chromatograms gave only a single spot. The ^{1}H-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 esterfied 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.