

Studies Related to Naturally-Occuring Acetylene Compounds

VI. The Essential Oils of Some Species of *Erigeron*

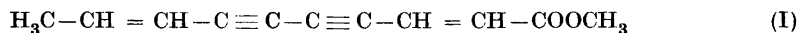
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In connection with our investigations on the highly unsaturated derivatives of methyl caprate, so far only found in some *Compositae* plants, our attention was directed to some *Erigeron* oils. The only commercially available *Erigeron*- or fleabane-oil from *Erigeron canadense* L. = marestalk, horseweed, or butterweed is officinal in U. S. A. The only known components of *Erigeron canadense* oil are *d*-limonene which accounts for the major part of the oil, and *rac.* α -terpineol¹.

The crude marestalk oils are remarkable in that their refractive indices $n_D^{20} = 1.499-1.506$ are appreciably higher, than the corresponding constants for the two main known constituents (Limonene; $n_D^{20} = 1.4750$, α -Terpineol: $n_D^{20} = 1.4826$). Sometimes these oils were noticed to deposit crystals in the cold².

Through Magnus, Mabee & Reynard Inc. we obtained a sample of "genuine" marestalk oil distilled in the 1947 season. The sample showed $n_D^{20} = 1.4893$, a value that is amongst the lowest recorded in literature. No crystallisation took place at -16° . The U. V.-absorption spectrum of the oil, however, was in close agreement with that of matricaria ester (I), the spectrographically estimated concentration in the crude oil being about 0.2 %.



The matricaria ester is predominantly hypophasic (73 %) between petroleum ether and 90 % methanol. By means of four consecutive partitions between these solvents we obtained an epiphasic portion (85 % of the oil) practically devoid of longwave U. V.-absorption, and a hypophasic portion consisting of terpineol, a volatile carbonyl compound of unknown structure, and the compound with the matricaria ester spectrum. On distillation at

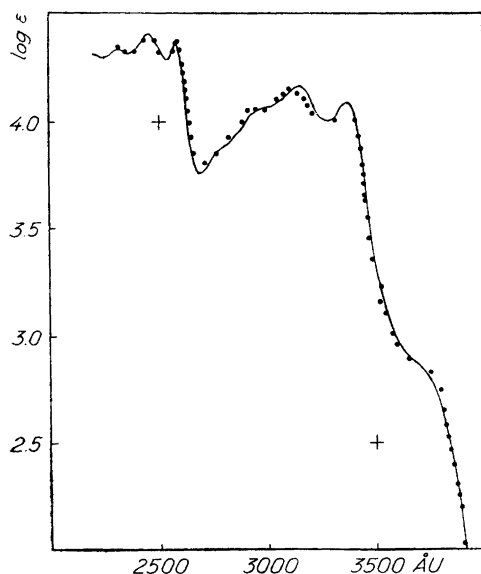


Fig. 1. Ultraviolet absorption of matricaria ester in hexane.

— R. T. Holman and N. A. Sørensen⁴.
 ••• Matricaria ester from *Erigeron canadense* L.
 ($\epsilon = \frac{\log I_0/I}{c \cdot d}$, c in mol/l, d in cm)

0.5—1 mm Hg the carbonyl compound passed over at 57—58°, then at 75—90° a fraction which solidified on cooling. Recrystallization from petroleum ether gave colourless needles m. p. 32.2—32.5°, raised on admixture with matricaria ester from *Matricaria inodora* L. to 33°. Since the crystals from *Erigeron canadense* were colourless, whereas matricaria ester from scentless mayweed is slightly straw yellow, even after repeated recrystallization, Debye-Scherrer diagrams were taken and confirmed the identity. The reason for this difference in colour is a small contamination of matricaria ester from scentless mayweed by its hexahydro compound ("Composit-cumulen I") which is yellow³. After chromatographic purification on deactivated alumina the matricaria ester from scentless mayweed also crystallized in colourless needles. When colourless, matricaria ester is remarkably more stable to oxidation in air than the original substance. Preliminary measurements by Dr. Ralph T. Holman (Department of Biochemistry and Nutrition, College Station, Texas) showed a rate of oxidation of only 1/10 of that of the original substance. The amount of impurity, "Composit-cumulen I", is very small. In Fig. 1 the drawn curve shows the spectrum of matricaria ester from scentless mayweed according to Holman and Sørensen⁴, and the dotted curve our measurements on the pure ester from fleabane oil.

The occurrence of matricaria ester in the 1947 sample of marestalk oil was thus definitely established. The small yield, and the description in American periodicals of the fleabane oil industry⁵:

“The plant is never cultivated, but when it grows very abundantly in a field in the mint or wormwood growing section the “crop” is likely to be bought for a few dollars by somebody who owns a still and the oil distilled from it. The buyer harvests it with a binder or mower —.”

gave rise to the postulate that the isolated matricaria ester might originate by contamination of the raw material of marestail with the widely distributed weed, scentless mayweed. In fact about 0.4 % of scentless mayweed in the starting weed material would be sufficient to give the observed quantity of matricaria ester in the marestail oil.

Through the courtesy of Dr. Ralph T. Holman, we obtained a sample of marestail seeds from Texas, and, in the summer of 1949 tried to cultivate some marestail in Trondheim. The plants did not flower, possibly because of the extremely bad summer, or because *E. canadense* L. is a short day plant. The leaves and stems were distilled and gave a good yield of essential oil, which, however, was spectroscopically devoid of matricaria ester.

Because of the lack of marestail flowers we decided to try flowers of some other *Erigeron* species. *Erigeron boreale* (Vierh.) Simm. is a small calciferous plant of scattered occurrence in Norwegian mountains. In Fagerlidalen, Trollheimen, there are some good localities which gave us 160 g of air dry flowers. These yielded 0.25 g of essential oil, which crystallized in the cold. The U. V. spectrogram of the crude oil was identical with that of matricaria ester and corresponded to a concentration of 51 % of the latter in the crude essential oil. Recrystallization from petroleum ether gave colourless crystals, m. p. 32.2—32.5°.

The ability of the genus *Erigeron* to synthesise matricaria ester was thus definitely established and the high content of matricaria ester in the *E. boreale* oil suggested an investigation of the other available Norwegian *Erigeron* species. In southern Norway these are *E. acre* L., *E. politum* Fr. and *E. uniflorum* L. and although these 3 *Erigeron* species are practically odourless, the flowers as well as the non floral parts gave good yields of essential oils.

The essential oil from *E. politum* Fr. solidified at room temperature. U. V. spectrograms of the crude flower oil gave a perfect curve for matricaria ester and indicated a concentration of 83 % of matricaria ester in the crude oil. The essential oil from the non floral parts showed the same behaviour and, in addition, the somewhat astonishing concentration of 100 % of matricaria ester as determined spectrographically. A single crystallization from petroleum gave colourless crystals m. p., and mixed m. p. with matricaria ester, 33°.

Since the crude essential oil from *E. acre* L. flowers — and also the oil from the non floral parts — partly solidified at room temperature, we expected matricaria ester to be a general component of *Erigeron* oils. The U. V.-spectrograms,

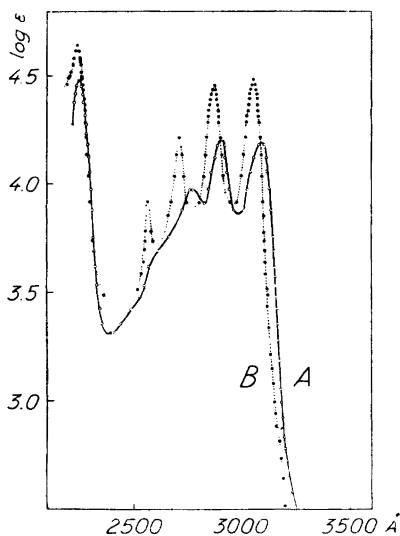


Fig. 2. Ultraviolet absorption of lachnophyllum ester in hexane.

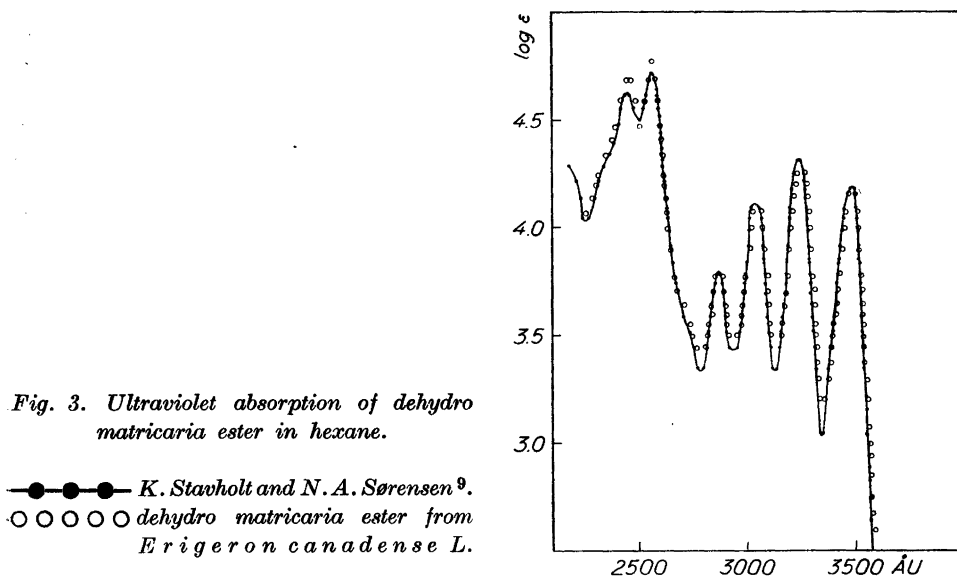
A: —○—○—○— *cis* lachnophyllum ester from *Erigeron acre* L.
 B: ···●···●···●··· *trans* lachnophyllum ester; Bruun, Haug and Sørensen⁷.

however, revealed the occurrence of another polyene chromophore with one less double bond. Crystallization from petroleum ether or diluted ethanol gave quite colourless needles m. p. 32°. The elementary composition was $C_{11}H_{12}O_2$, that is dihydro matricaria ester. A dihydro matricaria ester with m. p. 32.6—32.8° was isolated in 1935 from the compositae plant *Lachnophyllum gossypinum*, Bge, by the Russian chemists Wiljams, Smirnow and Goljmow⁶. They proved the constitution to be the *cis* form of II, — for which the name *lachnophyllum* ester is proposed



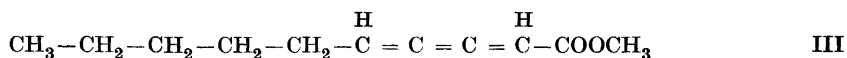
The U. V. spectrum of the pure *cis*-lachnophyllum ester from *Erigeron acre* L. is given in Fig. 2, together with the spectrum of *trans*-lachnophyllum ester synthesized a short time ago by Bruun, Haug and Sørensen⁷. It will be seen that the two spectra are very similar. The difference is in agreement with experience in the polyene series⁸, in that the synthetic *trans* compound shows the most pronounced fine structure. The maxima of the natural *cis* compound, however, occur at about 40 Å longer wave lengths, whereas *cis* compounds in general absorb at shorter wavelengths than the corresponding *trans* isomers⁸.

We have not been able to find any report on *cis*-lachnophyllum ester since the interesting paper of the discoverers⁶. The concentration of lachnophyllum ester in the flower oil of *E. acre* L. is 81%, in the essential oil from the non floral parts close to 100%.



The difference in composition of the essential oils of *E. acre* L. and *E. politum* Fr. may be of some botanical interest. *E. politum* Fr. has for a long time been treated as only a subspecies of *E. acre*; *E. acre* subsp. *elongatus* Ledeb. being its botanical synonym.

Erigeron uniflorum L. is a close botanical relative to *E. boreale* (Vierh.) Simm. The whole plant of *E. uniflorum* yielded 1.5 % of essential oil. The U. V.-spectrum of this oil was rather more complex than the previously investigated *Erigeron* oils. Strong absorption started at longer wave lengths than with matricaria ester, the first definite maximum at 3 360 Å corresponded with the first maximum of matricaria ester; then followed with appreciably higher intensities, the maxima at 3 080, 2 915 and 2 240 Å characteristic of *cis*-lachnophyllum ester. Chromatography led to the ready isolation of a yellow compound with the properties of the hexahydro-matricaria ester, III, ("Composit cumulen I"), isolated from scentless mayweed³.



We have not yet found convenient chromatographic procedures for separating *cis*-lachnophyllum ester and matricaria ester. Both are absorbed on slightly activated alumina, 30 % benzene-petroleum ether does not elute either of them and 70 % benzene-petroleum ether elutes both. The matricaria ester was concentrated in the last fractions, but we have only succeeded in a perfect

separation, after recrystallization, of the main component, the *cis*-lachnophyllum ester. The matricaria ester from the mother liquors still remained impure.

Some investigations on other plants, belonging to the family *Compositae*, this summer have revealed that enynes of this class may occur preferentially in the root. Accordingly, a preliminary study of the essential oil of marestail root was carried out using the rest of our Texas culture which had hibernated in a window culture. The U. V.-spectrum of the marestail root oil exhibited not less than 6 prominent maxima between 3 470 and 2 560 Å. Of these 6 maxima, 5 belonged to dehydro matricaria ester, to date the most highly unsaturated member of this series, isolated a short time ago from the root oil of common mugwort (*Artemisia vulgaris* L.). By crystallization from petroleum ether the dehydro matricaria ester was isolated in a pure condition, m. p. 112.5—112.7°. The spectral measurements are given in Fig. 3, together with the curve for the original dehydro matricaria ester⁹.

The remaining peak in the U. V.-spectrum of marestail root oil lies at 2 690 Å and stands out with a remarkable sharpness. This peak has so far been observed only in one compound, the "Centaur X" which Löfgren¹⁰ has demonstrated to be a component of some species of the composite genus *Centaurea*. As shown in the fifth communication of this series⁹ "Centaur X" is also a component of the mugwort root oil. Its structure is still obscure.

All the 5 species of *Erigeron* so far investigated contain enyne-derivatives of methyl caprate. The results are summarized in Table 1.

It is of course to be expected that the known enynes will prove to be widely spread amongst *Erigeron* species and many foreign *Erigeron* species are at present under cultivation to give some general indication of the occurrence of enynes in this genus which contains more than 150 good species. Botanically the genus *Erigeron* is closely related to *Lachnophyllum*, which provided the first compound of elucidated structure in this series. The rela-

Table 1. Enyne components of the investigated *Erigeron* oils.

Compound isolated	Fleabane species				
	<i>E. acre</i> L.	<i>E. boreale</i> Simm.	<i>E. canadense</i> L.	<i>E. polatum</i> Fr.	<i>E. uniflorum</i> L.
Lachnophyllum ester	+				+
Matricaria ester		+	+	+	+
Dehydro matricaria ester			+		
"Composite cumulene I"					+
"Centaur X"			+		

tionship to *Matricaria* and *Artemisia* is, however, very remote. An account of our investigations on essential oils from different compositae genera will appear later.

EXPERIMENTAL

Erigeron canadense L. 100 mls of essential oil of *Erigeron canadense* L. (Magnus, Mabee & Reynard Inc.) in 300 mls of petroleum ether was given 4 consecutive extractions with 90 % methanol, the methanol phase being re-extracted with one third of its volume of petroleum ether. The combined epiphasic portion from 505 mls of marestail oil amounted to 440 mls, i. e. 87 %. This epiphasic fraction was devoid of long wave U. V.-absorption.

The hypophasic fraction (68 g) was distilled at 0.5–1 mm. At 57–58° there distilled a fraction with very penetrating mint-like odour. By condensation with phenylhydrazine *p*-sulphonic acid and regeneration with steam in acid solution this forerun fraction gave a liquid carbonyl compound showing an inflexion by 3250 Å ($\log \epsilon = \text{ca. } 1.5$) followed, at 2300 Å, by a maximum with $\log \epsilon = \text{ca. } 3.6$.

The fraction distilling between 75° and 90° (ca. 1 g.) solidified on cooling. The crude material melted at 18° and after several crystallisations from petroleum ether, formed colourless needles, m. p. 31.5°, raised on admixture with matricaria ester to 33°. U. V.-absorption spectrum: Fig. 1, dotted curve.

Essential oil from marestail leaves and stems. 4 kg of fresh material gave about 2 % of essential oil on steam distillation. This oil was devoid of long wave U. V.-absorption.

Essential oil from marestail roots. 121 gs of 1 ½ year old marestail root gave 0.2 g of essential oil on steam distillation. The oil partially crystallized in the cooler. The crude oil showed the following sharp maxima in the ultra violet.

λ	3 473	3 235	3 040	2 865	2 690	2 560	Å
$\log \epsilon$	3.41	3.55	3.35	3.16	3.54	3.98	

(The extinction coefficients are calculated on a molecular weight of 172 for dehydro matricaria ester.) Recrystallisation from petroleum ether gave slightly yellow needles m. p. 112.5–112.7 corr. U. V.-absorption: Fig. 3, dotted curve.

Erigeron boreale (Vierh.) Simm. The material was collected on August 28th, 1949 in Fagerlidalen, Storlidalen, Trollheimen. The flowers were dried at room temperature in shadow and then weighed 160 g. On steam distillation they yielded 0.25 g of essential oil which crystallized immediately on cooling. The U. V.-absorption spectrum in hexane solution showed main maxima at 3 375 Å ($\log \epsilon = 3.75$), 3 110 Å ($\log \epsilon = 3.9$) and 2 580 Å ($\log \epsilon = 4.15$). The position of these main maxima and the shape of the curve are in excellent agreement with matricaria ester at a calculated concentration of 51 %. Crystallization from petroleum ether gave colourless crystals of m. p. 32.2–32.5°, having U. V.-absorption curve identical with that of matricaria ester.

Erigeron polatum Fr. The material was collected on August 17th, 1950 in Vinstradalen, Oppdal. The flowers were separated from the non-flowering parts, and both were dried in shadow at room temperature; dry flowers 45 g; plant residue 137 g. Steam distillation of the flowers: yield 0.13 g of essential oil; from the plant residue 0.55 g. Both oils solidified at room temperature. The U. V.-absorption curves of both oils were in complete agree-

ment with that of matricaria ester; flower oil concentration, 83 %; concentration in the oil from the non floral parts 100 % of matricaria ester.

Erigeron acre L. Through the kind assistance of Mrs. Helene Sørensen we obtained 85 gs of air dry flowers and 200 g of air dry material of the non-flowering parts of *Erigeron acre* L collected in mid-July, 1950, at Lykkja, Hemsedal. Steam distillation gave 0.20 g of flower oil and 0.30 g of oil from the non floral parts. Both oils solidified at 0°. Although the oils were transparent at higher wave-lengths, intense absorption commenced abruptly at about 3 200 Å and continued to shorter wave-lengths with sharp maxima as follows:

	λ	3 100	2 916	2 750	2 250
flowers:	log ϵ	4.11	4.03	3.89	4.37
	λ	3 088	2 911	2 770	2 240
non floral parts:	log ϵ	4.20	4.16	3.98	4.55

Both oils gave colourless needles, m. p. 32° C, after one crystallization from petroleum ether.

$C_{11}H_{12}O_2$ (176.1)	Calc.	C = 74.98	H = 6.88
	Found	» = 74.8	» = 7.20

U. V.-spectrum of the pure substance Fig. 2, curve A.

Erigeron uniflorum L. The material was collected below Ryphuskollen, Oppdal, on August 19th, 1950, and brought fresh to the laboratory for steam distillation. The whole plant material (= 214 gs) was distilled in one batch, yielding 0.32 g of essential oil. The crude oil was slightly yellow, and its U. V.-absorption started even in the violet region with appreciable absorption in the range 3 800—4 000 Å, where matricaria ester is transparent. The long wave maximum of matricaria ester at 3 375 Å occurred (log ϵ = 3.53), then followed the three main maxima of the lachnophyllum ester:

λ	3 080	2 915	2 240
log ϵ	4.21	4.20	4.57

Chromatography of the crude oil in petroleum ether solution on slightly deactivated alumina gave a yellow zone at the top of the column and the petroleum ether filtrate was devoid of long wave U. V.-absorption. Elution with a 30 % benzene-petroleum ether mixture removed only small amounts of compounds, also devoid of polyenyne spectra. On elution with a 70 % benzene-petroleum ether mixture, both *cis*-lachnophyllum and matricaria ester were removed. The ratio of the two esters was 10 in the first fractions of 100 mls of the 70 % benzene-petrol eluate, but decreased to 4, 4 and 3.2 in the following fractions. The weights of unsaturated methyl caprate derivatives were 71, 85, 32.6, 4.7 and 0.5 mg. The first two fractions were united, the solvent removed, and the residue recrystallized once from petroleum ether, then from dilute ethanol until the U. V.-spectrum showed it to be free of matricaria ester. The m. p. of the resulting colourless needles was 32° C, and the U. V.-absorption curve was identical with that of *cis*-lachnophyllum ester from *Erigeron acre* L.

The chromatogram was then eluted with 96 % ethanol, the lipoids transferred to ether, and distilled at 10⁻⁴ mm Hg. At 52—54° C (air bath temperature) there distilled 15 mgs of yellow oil with a penetrating odour. The U. V.-spectrum of this oil agreed with that

recorded for the hexahydro-matricaria ester³ ("Composite cumulene I"). As the value of $\log \epsilon$ was about 0.08 units low throughout the entire spectrum, the fraction should contain about 17 % of a transparent impurity. The small amount did not allow any further purification.

SUMMARY

The essential oils of the following species of the genus *Erigeron* have been investigated for their content of enyne derivatives of methyl caprate: *E. acre* L., *E. boreale* (Vierh.) Simm., *E. canadense* L., *E. polatum* Fr. and *E. uniflorum* L. All these fleabanes contain enynes. Lachnophyllum ester, matricaria ester and dehydro matricaria ester were isolated in pure condition: Hexahydro matricaria ester ("Composit cumulen I") and "Centaur X" was detected spectrographically. The distribution of the enynes among the investigated fleabanes is summarized in Table 1.

REFERENCES

1. Gildemeister E., and Hoffmann, Fr. *Die ätherischen Öle*, III Miltitz (1931) pp. 954—955; Foote, P. A., and Mathews, A. W. *J. Am. Pharm. Ass.* **28** (1939) 1030.
2. Rabak, F. *Pharm. Review* **23** (1905) 81; **24** (1906) 326. *Chem. Zentr.* (1905 I) 1323, (1907 I) 165.
3. Sörensen, N. A., and Stavholt, K. *Acta Chem. Scand.* **4** (1950) 1080.
4. Holman, R. T., and Sörensen, N. A. *Acta Chem. Scand.* **4** (1950) 416.
5. Sievers, A. F. *Economic Botany* **1** (1947) 156.
6. Wiljams, W. W., Smirnow, V. S., and Goljmov, V. P. *J. Gen. Chem. (U. S. S. R.)* **5** (1935) 1195.
7. Bruun, T., Haug, C. M., and Sörensen, N. A. *Acta Chem. Scand.* **4** (1950) 850.
8. Smakula, A., and Wassermann, A. *Z. physik. Chem.* **A 155** (1931) 353; Kuhn, R., and Winterstein, A. *Ber.* **65** (1932) 646, **66** (1933) 209; Kuhn, R., and Hoffer, M. *Ibid.* **65** (1932) 651; Pauling, L. *Fortschr. Chem. organ. Naturstoffe* **3** (1939) 203; Zechmeister, L., and Pauling, L., *et. al. J. Am. Chem. Soc.* **65** (1943) 1940.
9. Stavholt, K., and Sörensen, N. A. *Acta Chem. Scand.* **4** (1950) 1567.
10. Löfgren, N. *Acta Chem. Scand.* **3** (1949) 82.

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