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Studies Related to Naturally Occurring Acetylene Compounds. XI. Further Investigations on the Composition of Essential Oils from the Genus *Erigeron*

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Some years ago Sörensen and Stavholt [1] described in this journal investigations of 5 essential oils of fleabanes *(Erigeron) viz. E. acris* L., *E. borealis* Simm., *E. canadensis* L., *E. politus* Fr. and *E. uniflorus* L. The main constituents of these oils were matricaria ester (I) and lachnophyllum ester (II).

$$CH_3-CH=CH-C\equiv C-C\equiv C-CH=CH-COOCH_3 \quad (I)$$

$$CH_3-CH_2-CH_2-C\equiv C-C\equiv C-CH=CH-COOCH_3 \quad (II)$$

With the object of establishing whether these acetylenic compounds were characteristic of the genus *Erigeron*, we have in the past years tried to investigate as many fleabane oils as possible. As only the oil of *E. canadensis* L. is commercially available all had to be prepared from cultivations of foreign *Erigeron*-species in Tröndelagen and we are greatly indepted to Mr. Jens Roll-Hansen, curator of Statens Forsöksgaard Kvithamar and to his skilled staff for the great work laid down by them in the cultivation of most of our material. In the season 1951 and 52 some additional *Erigerons* were cultivated at *Norges Tekniske Högskole*, Trondheim.

All of the hitherto investigated 32 fleabanes turned out to contain acetylenic compounds. All but one did contain either matricaria (I) or lachnophyllum (II) ester or, more commonly, mixtures of these two compounds. The relative proportions were estimated spectroscopically. The results are summarised in Table 1.

Since earlier investigations had shown [2] that the oils from the roots of some plants belonging to the *Compositae* differed remarkably from the oils from the rest of the plant, the plants have mostly been divided into three parts: flowers, stem + leaves and root. This division is of course not a sharp one, the phyllaries for example may in some species be rather herbaceous, further the

Table 1. Acetylenic Compounds in the Genus Erigeron.

Section and Species:	Relative Concentrations Matricaria Ester: Lachnophyllum E		
	Flowers	Leaves	Roots
Section *Euerigeron* A.Gr.			
1. *E. aurantiacus* Rgl.	100 : 0	100 : 0	48 : 52
2. *E. candidus* Widder	100 : 0	100 : 0	42 : 58
3. *E. Coulterii*, Porter et Coult.	100 : 0	27 : 73	100 : 0
4. *E. compositus* Pursh, var. *glabratus* Macoun	43 : 57	42 : 58	39 : 61
5. *E. compositus* Pursh, var. *typicus* Payson f. *discoideus*	35 : 65	34 : 66	44 : 56
6. *E. compositus* Pursh. var. *discoideus* A. Gray	56 : 44	54 : 46	44 : 56
7. *E. elatior* Greene	100 : 0	100 : 0	56 : 44
8. *E. eriocephalus* J. Vahl	whole plant 18 : 82		
9. *E. glabellus* Nutt.	100 : 0	100 : 0	100 : 0
10. *E. glaucus* Ker.	100 : 0	53 : 47	17 : 83
11. *E. nematophyllus* Rydb.	70 : 30	65 : 35	28 : 72
12. *E. polymorphus* Scop.	61 : 39	50 : 50	100 : 0
13. *E. speciosus* D.C.	100 : 0	100 : 0	100 : 0
14. *E. superbus* Greene ex Rydb.	80 : 20	69 : 31	62 : 38
15. *E. subtrinervis* L.	100 : 0	100 : 0	100 : 0
16. *E. uniflorus* L.s.s.	2 : 98	2 : 98	45 : 55
Section *Olygotrichium* Cronq.			
17. *E. flagellaris* A.Gr.	whole plant 10 : 90		
18. *E. philadelphicus* L.	100 : 0	100 : 0	100 : 0
Section *Phalacroloma* Cronq.			
19. *E. annus* Pers.	8 : 92	31 : 69	48 : 52
20. *E. strigosus* var. *Beyrichii* (Fische & Mey) A.Gr.	55 : 45	50 : 50	53 : 47
21. *E. strigosus* var. *typicus* Cronq.	11 : 89	17 : 83	56 : 54
Section *Trimorphaea* Cass.			
22. *E. acris* L. var. *brachycephalum* H. Lindb.	20 : 80	16 : 84	16 : 84
23. *E. atticus* Vill.	100 : 0	100 : 0	59 : 41
24. *E. borealis* Vierh. et Simm.	100 : 0	—	—
25. *E. droebachiensis* O. F. Müll.	8 : 92	11 : 89	11 : 89
26. *E. eriocephalus* Regel et Smalh.	4 : 96	7 : 93	24 : 76
27. *E. Mairei* Braun-Blanquet	60 : 40	60 : 40	47 : 53
28. *E. politus* Fr.	56 : 44	70 : 30	59 : 41
Section *Caenotus* Nutt.			
29. *E. canadensis* L.s.s.	48.6 : 51.4	56 : 44	100 : 0
» subsp?	100 : 0	100 : 0	—
30. *E. montevidensis* Baker	5 : 95	33 : 67	100 : 0
31. *E. linifolius* L.	62 : 38	56 : 44	42 : 58
Section *Conyzastrum* Boiss.			
32. *E. khorassanicus* Boiss	—	—	Matricarianol!

division between stem and root had to be done rather arbitrarily. Sometimes the proportions between the two esters are rather remarkably constant through the whole plant (see Nos. 4—6 *E. compositus* and No. 13 and No. 15 *E. speciosus* and *E. subtrinervis*). In other cases, as will be seen from Table 1, the propor-

tions may vary considerably and in both directions (see for example No. 10 *E. glaucus* and No. 30 *E. montevidensis*).

No regularity has been found between these variations and the botanical subdivision of the genus *Erigeron*. O. Hoffmann [3] in 1897 divided the genus *Erigeron* into 5 sections *viz.*:

Sections of Hoffmann	Further sections of Cronquist
I *Oritrophium*	
II *Leptostelma*	
III *Euerigeron*	*Olygotrichium*, *Phalacroloma*, *Wyomingia*, *Pycnophyllum*
IV *Trimorphaea*	
V *Caenotus*	

Cronquist [4], who recently revised the North-American species of *Erigeron*, transferred section V *Caenotus* to the genus *Conyza* and further introduced 4 new sections into the section *Euerigeron* of Hoffmann.

Of the altogether 32 *Erigerons* investigated on the presence of acetylenic compounds none belongs to the sections I and II of Hoffmann, 7 belongs to section *Trimorphaea*, 3 to section *Caenotus* and 21 to the large section *Euerigeron*. Of these 21 some 18 belongs to the section *Euerigeron* in the narrower sense given to it by Cronquist, 2 belongs to his section *Olygotrichium* and 3 to his section *Phalacroloma*, whereas no representative has been available in his sections *Wyomingia* and *Pycnophyllum*.

There has been obtained one example of the section *Conyzastrum* of E. Boissier [5] *viz. E. khorassanicus* Boiss. This section of Boissier is not treated either by Hoffmann or by Cronquist. We understand that some modern botanists refer this section to the genus *Conyza*, whereas others are of the opinion that this section botanically belongs to *Erigeron*. The essential oil of *E. khorassanicus* differs fundamentally from that of the 31 other fleabanes investigated by us. The essential oil from the flowers and the green parts of the plant was spectroscopically devoid of acetylenic compounds. In fact the U.V.-spectra had only a "stepout" at short wave-lengths and no selective absorption. The essential oil from the root showed a characteristic selective absorption in U.V., but none of the observed maxima did agree with either matricaria or lachnophyllum ester. The maxima observed coincide with those of matricarianol (III) = deca-diene-2 : 8-diyne-4 : 6-ol-1. This alcohol was synthesized in 1951

$$CH_3-CH=CH-C\equiv C-C\equiv C-CH=CH-CH_2OH \qquad \text{(III)}$$

by Bruun *et al.*[6] in both the 2-*trans*-8-*trans* (m.p. 104°) and the 2-*trans*-8-*cis* (liq.) modifications. In 1951 Dagny Holme [7] isolated for the first time a liquid compound with the U.V.-spectrum of matricarianol from the root of *Aster tripoleum* L. Recently Holme *et al.*[8] firstly isolated the acetate of 2-*trans*-8-*trans* matricarianol from the leaves and roots of *Grindelia arenicola*, and later the same alcohol from *G. stricta*.

2-*trans*-8-*trans* Matricarianol synt.[6]	λ_{max},	3 122	2 930	2 765	2 615	2 300	ÅU
2-*trans*-8-*cis*- » »	»	3 132	2 938	2 755	2 612	2 320	»
Oil from root of *Erigeron khorassanicus*	»	3 130	2 940	2 785	2 620	2 290	»

So far only 7 species of *Aster* have been investigated in this laboratory, and of these only *A. tripoleum* has given pure *trans-trans*-matricarianol after saponification; the acid moiety of the ester is still unknown. All the 7 species of *Aster* so far investigated are lacking acetylenic compounds in the flowers and herbaceous parts; if present, the acetylenic compounds do occur in the root exactly as in *Erigeron khorassanicus*. It is hoped that it will be possible later on to obtain some further representatives of the section *Conyzastrum* as well as some real *Conyza* species, which might establish the chemical boundaries between the botanically somewhat overlapping genera *Aster-Erigeron-Conyza*.

It is remarkable that the 3 representatives of the section *Caenotus* investigated by us all behave chemically as real *Erigerons*. This section *Caenotus*, the members of which are found in North- and South-America, no doubt morphologically approaches *Conyza*, and for that reason was transferred to this genus by Cronquist. This view is opposed by their chemistry which indicates that they are real *Erigerons*.

It is hoped that a further investigation of some of the most intermediate representatives may introduce distinct chemical boundaries and so give some hints to the genesis of these genera. The indications furnished by the results of the present investigation are obviously not in accordance with the view of most botanists [4,9] *viz.* that *Conyza* is derived from *Erigeron*, whereas *Erigeron* and *Aster* are parallel groups.

Artificial mixtures of equal parts of matricaria and lachnophyllum esters are liquid at ordinary temperature and difficult to separate. If any component is dominating M : L $< 30 : 70$ or M : L $> 70 : 30$ the main component can easily be isolated in pure condition by crystallisations from ethanol-water or petroleum ether. If the liquid 2-*trans*-8-*cis*-matricaria ester is present, as in some *Amellus* oils [10], the isolation of the pure components is very troublesome. With the exception of *E. compositus* we have encountered no difficulties in the isolation of the crystalline esters and so we have no indications for the presence of 2-*trans*-8-*cis* matricaria ester in fleabane oils. As will be seen from the experimental part some of the commonly cultivated *Erigerons* (as *E. speciosus* and *E. strigosus*) are excellent sources of matricaria and lachnophyllum esters.

EXPERIMENTAL

Section *Euerigeron* A. Gr.

1. *Erigeron aurantiacus* Rgl. Seed samples: *Hortus Universitatis Lousonnensis, Botanischer Garten München-Nymphenburg, Botaniska Trädgården*, Lund, Sweden. Cultivated Kvithamar 1950/51.

	kg	Essential oil ‰	ME / LE
Flowers	1.0	2.6	100 : 0
Leaves	6.7	0.5	100 : 0
Roots	0.9	3.6	48 : 52

The essential oils from the flowers and from the leaves solidified spontaneously, m.p. of the crude matricaria ester 33°.

2. *Erigeron candidus* Widder. Seed sample: *Hortus Universitatis Lousonnensis*. Cultivated Kvithamar 1950/51.

	g	Essential oil ‰	ME / LE
Flowers	34	2.5	100 : 0
Leaves	166	0.9	100 : 0
Roots	30	7.4	42 : 58

The oils from the flowers and from the leaves solidified in the cold, m.p. of the crude matricaria ester 34° and 32° C.

3. *Erigeron Coulterii*, Porter et Coult. Seed sample: *Hortus Botanicus Hauniensis*. Cultivated Kvithamar 1950/51.

	g	Essential oil ‰	% ME	% LE
Flowers, air-dried	305	1.8	30	—
Leaves, » »	1180	0.76	7	19.3
Roots, » »	220	6.7	81	—

4. *Erigeron compositus* var. *glabratus* Macoun. Four different cultivations have been separately investigated. Seed sample: a) *Botanischer Garten München-Nymphenburg*, b) *Hortus botanicus Hauniensis*, c) *Botaniska Trädgården*, Lund, Sweden, d) *Botanischer Garten der Universität Graz*. All cultivations at Kvithamar 1950/51.

	g	Essential Oil ‰	ME / LE
a) Flowers	33	2.3	45 : 55
Leaves	234	7.5	44 : 56
Roots	23	4.5	46 : 54
b) Flowers	36	2.4	44 : 56
Leaves	360	8.3	44 : 56
Roots	33	1.7	33 : 67
c) Flowers	43	2.0	42 : 58
Leaves	390	4.4	43 : 57
Roots	63	1.4	36 : 64
d) Flowers	8	1.9	39 : 61
Leaves	200	3.9	37 : 63
Roots	15	1.2	41 : 59

The variations in the composition of the oils from different cultivations and from different parts of the plant are rather small. All these oils remain liquid at −15° and the isolation of crystalline matricaria ester succeeded only after several recrystallisations at −30°.

5. *Erigeron compositus* var. *typicus* Payson f. *discoideus*. Seed sample: *Hortus Universitatis Lousonnensis*. Cultivated Kvithamar 1950/51.

	g	Essential oil ‰	ME / LE
Flowers	29	1.9	35 : 65
Leaves	200	2.3	34 : 66
Roots	25	1.4	44 : 56

These oils remained liquid at −15°, compare 4.

6. *Erigeron compositus* var. *discoideus* A. Gray. Seed sample: a) *Hortus botanicus Hauniensis*. Cultivated Kvithamar 1950/51.

	g	Essential oil ‰	ME / LE
Flowers	33	2.7	50 : 50
Leaves	535	6.2	52 : 48
Roots	84	1.5	43 . 57

The essential oils remained liquid at −15°.

b) *Royal Botanic Gardens, Edinburgh,* cultivated Trondheim 1951.

	g	Essential oil ‰	% ME	% LE
Flowers	132	0.9	46	27
Leaves	380	1.7	40	30
Roots	30	2.0	35	44

7. *Erigeron elatior* Greene. Seed sample: *Hortus Universitatis Lousonnensis,* Cultivated Kvithamar 1950/51.

	g	Essential oil ‰	ME / LE
Flowers	37	0.5	100 : 0
Leaves	135	0.75	100 : 0
Roots	200	1.8	56 : 44

8. *Erigeron eriocephalus* J. Vahl see *E. uniflorus* L. No. 16.

9. *Erigeron glabellus* Nutt. Cultivations were carried out at Kvithamar on 4 different seed samples: a) *Botanischer Garten München-Nymphenburg,* b) *Hortus Botanicus Bergianus,* Stockholm, c) 75 = ? and d) *Hortus Universitatis Lousonnensis.* a) b) and c) gave essential oils which in all parts of the plant contained only matricaria ester as chromophoric substance. All oils solidified and afforded pure matricaria ester after one crystallisation.

	kg	Essential oil ‰	% ME	% LE
d) Flowers	1.51	0.40	13	26
Leaves	4.65	0.09	14	9
Roots	0.98	0.92	77	—

The essential oil from the root of d) gave a high yield of crystalline matricaria ester, m.p. crude 33° undepressed by authentic matricaria ester. Whether sample d) is somewhat mixed up botanically through hybridisation or there really are variations in the composition of *E. glabellus* oils has not been investigated further.

10. *Erigeron glaucus* Ker. Seed sample: *Hortus Botanicus Hauniensis.* Cultivated Kvithamar 1950/51.

	g	Essential oil ‰	ME / LE
Flowers	720	2	100 : 0
Leaves	4000	1.4	53 : 47
Roots	260	1.9	17 : 83

The oil from the flowers solidified at room temperature and a single crystallisation from petroleum ether furnished pure matricaria ester. The oil from the leaves deposited from petroleum ether solution crystalls which after one recrystallisation also was pure matricaria ester. The essential oil from the roots was diluted with a little 96 % alcohol and the crystalls which separated at 0° recrystallised from alcohol. M.p. and mixed m.p. with lachnophyllum ester 31°.

11. *Erigeron nematophyllus* Rydb. Seed sample: *Hortus Universitatis Lousonnensis,* cultivated Kvithamar 1950/52.

	g	Essential oil ‰	% ME	% LE
Flowers	15	2.5	70	30
Leaves	160	5.7	41	22
Roots	8	5.4	22	65

12. *Erigeron polymorphus* Scop. Seed sample: a) *Royal Botanic Gardens, Kew.* Cultivated Kvithamar 1950/51.

	g	Essential oil ‰	% ME	% LE
Flowers air-dried	350	1.1	11	7
Leaves » »	1400	0.5	4	4
Roots » »	225	3.2	66	—

b) From a seed sample marked with the name of *E. uniflorus (Bot. Garten München-Nymphenburg)* developed genuine *E. polymorphus* (Kvithamar 1950/51). The whole plant, 740 g, was distilled without separation, essential oil 1.4 ‰, the U.V. curve of the oil was indistinguishable from the prototype of matricaria ester. The oil solidified at room temperature and afforded matricaria ester m.p. 33° after one single crystallisation from petroleum ether.

13. *Erigeron speciosus* D.C. Seed samples: a) *Royal Botanic Gardens, Kew*, b) *Botanischer Garten der Universität Graz*, c) *Botaniska Trädgården*, Lund, Sweden, d) *Botanischer Garten München-Nymphenburg*, all four cultivated at Kvithamar 1950/51. As with most of the *E. glabellus* samples all parts of the four cultivations of *E. speciosus* gave oils which contained only the matricaria ester and in high percentage. One single crystallisation afforded pure matricaria ester.

14. *Erigeron superbus* Greene ex Rydb. The seed sample originated from the *Royal Botanic Gardens, Kew*, and was named *E. macranthus* without author designation. The plant which developed was the most splendid fleabane in our cultivations and as far as can be decided from the scanty comparison material available the plant must be *E. superbus* Greene ex Rydb.≡ *E. macranthus* subsp. *mirus* A. Nels. Cultivated Trondheim 1951/52.

	g	Essential oil ‰	% ME	% LE
Flowers	178	0.69	80	20
Leaves	700	0.20	55	25
Roots	210	2.5	58	35.5

15. *Erigeron subtrinervis* L. Seed samples: a) and b) *Botanischer Garten München-Nymphenburg* (under two other, obviously false, designations) c) *Botanicus Lovaniensis* d) *Hortus Universitatis Lousonnensis*, all cultivated at Kvithamar 1950/51. With a) b) and c) the concentrations were not estimated, all U.V.-spectrograms of the crude oils from all parts of the plant were identical with that of matricaria ester; with d) the content of matricaria ester was estimated.

	kg	Essential oil ‰	% ME
Flowers	1.1	0.18	19
Leaves	3.5	0.11	5
Roots	0.93	1.5	83

All the essential oils from the *E. subtrinervis* samples solidified at zero degree and gave pure matricaria ester after one single crystallisation.

16. *E. uniflorus* L.

In our first paper on the composition of the essential oils of *Erigeron* species [1] the results were given of an investigation of the species *E. uniflorus* L. collected in the Dovre region of Southern Norway. Mr. J. Lid, curator of the Botanical Museum at the University of Oslo had the kindness to direct our attention to the fact that two main types of *E. uniflorus* occurs in the Norwegian mountains, the one agreeing with *E. uniflorus* L.s.s., the other identical with the plant described by J. Vahl in Flora Danica [11] as *E. eriocephalus*. A study of the two descriptions revealed that the material reported on in our first paper was in all probability a mixture of *E. uniflorus* s.s. and *E. eriocephalus* J. Vahl. Some botanical excursions confirmed the view of Mr. Lid. When *E. boreale* Vierh. & Simm. is absent, there is mostly no difficulty in keeping the two types apart. *E. eriocephalus*, which reaches the highest altitudes available in southern Norwegian mountains, retain the curved spreading phyllaries with woolly-villous hairs when cultivated at sea level in Trondheim.

E. uniflorus s. s. with adpressed phyllaries are in the mountains mostly somewhat hairy on the lower parts of the phyllaries, practically glabrous at lower altitudes. From a seed sample named *E. Schleicheri* (without author designation) a fleabane developed in our garden which obviously had nothing to do with either *E. Schleicheri* Moritz ≡ *E. alpinus* L. var. *intermedius* (Schleicher) Gremli or with *E. Schleicheri* Gremli ≡ *E. glandulosus* Hegetschev, but turned out to be a nearly glabrous form of *E. uniflorus*. With this type and another sample from seeds from Hortus Universitatis Lousonnensis and a char-

acteristic collection of *E. eriocephalus* J. Vahl from Vinstradalen, Opdal, Sör-Tröndelag, a reinvestigation of the essential oils was carried out.

8. *E. eriocephalus* J. Vahl.

The air-dried material weighed 4 g which furnished 14 mg essential oil, that is 3.5 ‰. ME = 11.7 %, LE = 52.7 %.

16. *E. uniflorus* L.s.s. a) Seed sample: *Botanicka Zahrada University Karlovy*, Praha, cultivated Trondheim 1951.

	g	Essential oil ‰	% ME	% LE
Flowers	1.7	3.5	1.2	57.5
Leaves	91	2.1	2.0	98
Roots	23	4.4	44	55

Only the U.V.-spectrum of the oil from the root extends into visible light and so the origin of "Compositcumulene I" is the root of *E. uniflorus* L. Recalculated on the whole plant the relation is: LE : ME = 5.1 whereas *E. eriocephalus* J. Vahl gives 4.5. The two types thus cannot be separated chemically.

b) Seed sample: *Hortus Universitatis Lousonnensis*, cultivated Kvithamar 1950/51. Whole plant 105 g, essential oil 4.0 ‰, ME : LE = 11 : 89.

The oil solidified in the cold; from an alcoholic solution pure lachnophyllum ester crystallised immediately, m.p. 31.2° undepressed by authentic lachophyllum ester.

Section *Olygotrichium* Cronq.

17. *Erigeron flagellaris* A. Gr. Seed sample: *Botanischer Garten München-Nymphenburg*. Cultivated Kvithamar 1950. The whole plant distilled with steam. U.V.-spectrum of the essential oil gave ME : LE = 10 : 90; pure lachnophyllum ester was obtained by repeated crystallisations from 96 % alcohol.

18. *Erigeron philadelphicus* L. Seed sample: *Botanischer Garten München-Nymphenburg*, cultivated Kvithamar 1950/51.

	kg	Essential oil ‰	% ME
Flowers	0.98	0.25	37
Leaves	3.8	0.08	11.5
Roots	0.69	1.4	93

All three U.V.-curves were within the limits of the experimental errors identical with that of matricaria ester. The oil from the root solidified and gave pure matricaria ester after one crystallisation from petroleum ether.

Section *Phalacromola* Cronq.

19. *Erigeron annus* Pers. Seed sample: *Hortus Botanicus Bergianus*. Cultivated Kvithamar 1950/51.

	kg	Essential oil ‰	% ME	% LE
Flowers	1.5	3.5	6	66
Leaves	3.5	0.20	1.7	3.8
Roots	0.78	0.33	32	35

The oil from the flowers deposited white crystals from alcohol, m.p. 31°, mixed m.p. with lachnophyllum ester 31.5°, test with a 1 : 1 mixture with matricaria ester: liquid at 20°.

20. *Erigeron strigosus* var. *Beyrichii* (Fisch & Mey) A. Gr. Seed sample: *Jardin Botanique Rouan*. Cultivated Kvithamar 1950/51.

	g	Essential oil ‰	% ME	% LE
Flowers, air-dried	97	1.4	3.6	3
Leaves » »	700	0.5	4.0	4
Roots » »	8	0.05	20	18

21. *Erigeron strigosus* var. *typicus* Cronquist. Seed samples: a) *Hortus Botanicus Bergianus*, Stockholm. b) *Royal Botanic Gardens*, Kew; both cultivated Kvithamar 1950/51.

	kg	Essential oil ‰	% ME	% LE
a) Flowers	3.25	1.5	7.5	75
Leaves	3.5	0.31	4.2	23
Roots	0.92	0.88	18.5	22
b) Flowers	2.3	1.9	5	34
Leaves	3.6	0.38	8	34.5
Roots	1.0	0.76	56	29

The oils from the flowers solidified in the cold and gave pure lachnophyllum ester after some crystallisations from alcohol.

Section *Trimorphaea* Cass.

22. *Erigeron acris* L. var. *brachycephalus* H. Lindb. *Erigeron acris* L.s.s. was reported on in our first paper on fleabane oils and turned out to contain large amounts of oil, rich in lachnophyllum ester. Mr. Knut Stokke, Drammen, had the kindness to send us an air-dried sample of a fleabane found by him in the vicinity of Kragerö, Southern Norway, and supposed by the discoverer to be *E. politus* Fr. Since three different strains of *E. politus* Fr. had given very consistent results (cf. Ref. No. 28) — dominance of matricaria ester in all parts of the plant — whereas the *Erigeron* of Mr. Stokke chemically comes very close to the investigated strains of *E. acris* L. a redetermination was demanded, the more so since *E. politus* Fr. has a rather sharp southern limit in the mountains of Torpa, some 200 km north of Kragerö. The only alternative seems to be the subspecies *brachycephalus*, described by the Finnish botanist Harald Lindberg. This subspecies has been ignored in Norwegian flora and no distinguishing marks between *E. politus* Fr. and *E. acris* var. *brachycephalus* H. Lindberg have been worked out.

	g	Essential oil ‰	% ME	% LE
Flowers, air-dried	110	0.7	2	7.8
Leaves, stems and roots	260	0.16	10	53

Both oils solidified in the cold and gave pure lachnophyllum ester from ethanol solution.

23. *Erigeron atticus* Vill. Seed samples: a) *Botanischer Garten München-Nymphenburg*, b) *Hortus Universitatis Lousonnensis*. Cultivated Kvithamar 1950/51.

	kg	Essential oil ‰	% ME	% LE
Flowers	3.07	0.57	26	—
Leaves	4.2	0.25	20	—
Roots	1.22	0.35	56	39

The oils from flowers and leaves solidified at room temperature and furnished pure matricaria ester from petroleum ether solution.

24. *Erigeron borealis* Vierh. et Simm. data taken from [1], only the flowers were collected.

25. *Erigeron droebachiensis* O. F. Müll. In 1782 Flora Danica described in Fasciculus XV, Tab. DCCCLXXIV a fleabane discovered by O. F. Müller in the vicinity of the village of Dröbak as in many respects so different from *E. acris* L.s.s. that it ought to be given the rank of a species. Norwegian floras have, however, either included *E. droebachiensis* into *E. acris* or they have only given it the rank of a subspecies under *E. acris*.

In contrast to Norwegian botanists their American colleagues have upheld the distinction between these two species, which of course is confirmed by the fact that *E. acris* L.s.s. does not occur in U.S.A., whereas *E. droebachiensis* O. F. Müller is regarded as

synonymous to *E. acris* var. *asteroides* (Andrz. ex Bess) DC, which is widely spread in Northern U.S.A.[4].

Through the most kind assistance of Professor Dr. T. Braarud, Oslo, and Mr. Knut Stokke, we had the opportunity to inspect this species in the original locality and to obtain good samples for chemical investigations. In our opinion the morphological differences between *E. droebachiensis* and *E. acris* s.s. are considerable, and there did not seem to exist intermediate types. *E. acris* s.s. occurs in the immediate surroundings in its typical form.

	g	Essential oil ‰	% ME	% LE
Flowers	110	0.7	4.0	49
Leaves & Roots	260	1.6	9	75

Pure lachnophyllum ester was obtained from both oils by crystallisation from alcohol.

26. *Erigeron eriocephalus* Regel et Smalh. In 1877 the cited authors described a fleabane from Turkestan and gave it the designation "*eriocephalus*", obviously overlooking the older work of J. Vahl, which already had occupied this name. The plant of Regel and Schmalhans belongs to the *E. acris* group. Seed sample *Hortus Botanicus Hauniensis.* cultivated Kvithamar 1950/51.

	g	Essential oil ‰	% ME	% LE
Flowers air-dried	200	1.9	2	42.5
Leaves » »	700	0.7	2.5	32
Roots » »	32	1.7	17	54.5

The oils from flowers and leaves solidified in the cold and afforded pure lachnophyllum ester after crystallisations from ethanol.

27. *Erigeron Mairei* Braun-Blanquet. Seed sample: *Botanicka Zahrada.* Cultivated at N.T.H. 1951/52.

	g	Essential oil ‰	% ME	% LE
Flowers	126	1.5	44	30
Leaves	380	1.1	60	40
Roots	120	2.7	47	53

28. *Erigeron politus* Fr. was mentioned in our first paper. The material originated from Vinstradalen, Dovre and was separated into flowers and non-floral parts. The essential oil from both gave U.V. curves nearly identical with that of matricaria ester. Two cultivations have been carried out at Kvithamar 1950/51. Seed samples: a) *Hortus Botanicus Bergianus*, Stockholm, b) *Hortus Universitatis Lousonnensis.*

	g	Essential oil ‰	ME / LE
a) Flowers	190	2.5	50 : 50
Leaves	820	1.3	70 : 30
Roots	154	6.3	60 : 40
b) Flowers	750	1.8	62 : 38
Leaves	820	1.3	71 : 29
Roots	154	6.3	58 : 42

All essential oils solidified in the cold and gave pure matricaria ester from petroleum ether solution.

Section *Caenotus* Nutt.

29. *Erigeron canadensis* L. This widespread weed was first investigated through a sample of the commercially available essential oil which, besides large amounts of terpene hydrocarbons, contained small amounts of matricaria ester (0.2 %). Owing to the danger of contamination with oils from other plants in the distilled material we further tried to

cultivate *E. canadensis* from a seed sample from Texas. This plant did not flower in Trondheim; the stem and leaves gave an oil devoid of selective absorption. From the oil of the root was isolated a dehydromatricaria ester m.p. 112.5°, also found in the oil from the root of *Artemisia vulgaris* [2]. The constitution of this dehydromatricaria ester might be that of the 2-*cis* isomer of

$$H_3C-C\equiv C-C\equiv C-C\equiv C-CH=CH-COOCH_3$$

These deviating results gave rise to an investigation of other samples of this plant. Cultivations at Kvithamar 1950 from two different seed samples were unsuccessfull as the plant would not flower and all died during the winter 1950/51 in accordance with the general habit of *E. canadensis* to be annual.

Further cultivations at Trondheim were also unsuccessfull until it was discovered that *E. canadensis* is a short day plant, readily developing flowers in Trondheim, when kept in darkness for 10 hours a day. Further one quite different strain occurring wild near Oslo has been investigated.

a) *E. canadensis* s.s. Seed sample: *Hortus Botanicus Hauniensis.* Cultivated Trondheim 1952 with a 14 hour night.

	g	Essential oil ‰	% ME	% LE
Flowers	65.5	1.7	48.6	51.4
Leaves	611	1.0	45	35
Roots	180	1.1	90	—

b) *E. canadensis* subsp.? On "Kadettangen" in Sandvika near Oslo there has for many years existed a colony of a small species of *Erigeron*, by Norwegian botanists determined to be *E. canadensis* L. The tiny plant, which to an amateur botanist looks very different from most drawings of *E. canadensis* and all the specimens seen in culture or in exsiccata, was collected August 1951 and air-dried. On our refusal to accept this species as *E. canadensis* the plant has been carefully inspected by Dr. Carl Blom, Gothenburg and Johs. Lid, Oslo, who both assure us that the plant is really *E. canadensis* L. We are indebted to both of them for the solicitude with which this question has been settled.

	g	Essential oil ‰	% ME	% LE
Flowers air-dried	14	3.1	64	—
Leaves » »	30	0.84	65	—

Both oils solidified in the cold and furnished pure matricaria ester from petroleum ether.

The roots, which only weighed 9 g, were extracted with acetone to look for the presence of the somewhat thermolabile dehydro ester m.p. 112.5°. The acetone extract was evaporated at room temperature in a vacuum (185 mg) and showed only a very weak U.V.-absorption. Distillation at 0.001 mm afforded 2.2 mg distillate with the U.V.-curve of pure matricaria ester, content 12 %.

The two investigated strains of *E. canadensis* do not agree in the composition of the essential oils, and since most of the investigated different strains of other fleabanes have agreed remarkably well, we do still suppose that a study of the microspecies of *E. canadensis* would be desireable.

What is much more important is that both of the two strains investigated this time have a composition of the essential oil in accordance with the general picture arrived at for real fleabane oils, whereas the non-flowering Texas-plant investigated 1950 has so far found no chemical relatives. The leaves of that plant reminded very much of those of *E. canadensis;* the stem was more slender and somewhat woody and in one respect it really showed a deviation not met with any other of our cultivations of *E. canadensis;* the Texas plant developed subterraneous runners. We are trying to obtain new seed samples of this plant, because the occurence of dehydromatricaria ester m.p. 112.5° in the roots makes a safe botanical determination desireable.

30. *Erigeron montevidensis* Baker. Seed sample: *Hortus Botanicus Hauniensis.* Cultivated Trondheim 1951 in hothouse.

	g	Essential oil ‰	% ME	% LE
Flowers	9.5	6.8	2	35
Leaves	1 630	2.4	13	27
Roots	300	3.5	78	—

The oil from the flowers furnished pure lachnophyllum ester, the oil from the roots pure matricaria ester.

31. *Erigeron linifolius* L. Seed sample: *Hortus Botanicus Hauniensis.* Cultivated Trondheim 1952 in hothouse.

	g	Essential oil ‰	% ME	% LE
Flowers	153	1.6	57	34.5
Leaves	3 770	0.4	45.5	35
Roots	870	0.2	42	58

Section *Conyzastrum* Boiss.

32. *Erigeron khorassanicus* Boiss. Seed sample: *Hortus Botanicus Hauniensis.* Cultivated in hothouse, Trondheim 1951/52.

	g	Essential oil ‰	% ME	% LE
Flowers	28.5	0.8	—	—
Leaves	190	0.2	—	—
Roots	105	0.5	—	—

All maxima of the oil from the roots were in agreement with those of matricarianol (III). The concentration calculated as free alcohol from the 4 most long-waved maxima was 43, 41, 40, 40, mean 41 %. The amount of essential oil was too small to allow an isolation of the chromophore.

SUMMARY

The essential oil of some further 27 species of the genus *Erigeron* have been investigated as to their content of acetylenic compounds. With the exception of one species *(E. khorassanicus)* belonging to the section *Conyzastrum* of Boissier — which seems to contain matricarianol — all the other fleabane oils contained the matricaria ester (I) or the lachnophyllum ester (II), both mostly in varying mixtures. Since the only exception belongs to a section, which by the botanists has been placed now in *Conyza*, now in *Erigeron*, it seems likely to conclude that all true *Erigerons* shall have the acetylenic esters I or II in all parts of the plant. It is remarkable that the investigated members of Section *Caenotus* Nutt. chemically behave as true *Erigerons*. Modern botanists have been inclined to transfer the whole section *Caenotus* to *Conyza*.

We are greatly indebted to Professor Dr. K. Fægri, the Botanical Department, University of Bergen and the Botanical Garden of the University of Copenhagen, who most kindly have furnished the seed samples. Some university garden samples gave rise to numerous cultivations of plants with quite false names. We are utmostly grateful to Mr. Olav Gjærevoll, curator of the botanical Museum in Trondheim for the valuable assistance he has rendered with the redeterminations of the plants. Grants from *Norges Almenvitenskapelige Forskningsråd*, which have made it possible to carry through these investigations, are gratefully acknowledged.

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