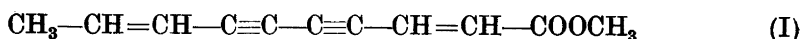


**Studies Related to Naturally Occurring Acetylene
Compounds. XIV. The Occurrence of 2-*trans* : 8-*trans*
Deca-2 : 8-diene-4 : 6-diyne-1-ol = *trans* : *trans*-
Matricarianol in Nature**

DAGNY HOLME and NILS ANDREAS SÖRENSEN

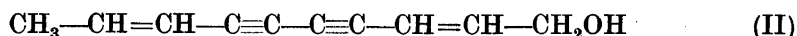
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The 2-*cis*:8-*cis* matricaria ester (I) is so far the acetylenic compound, which seems to be of most general occurrence in essential oils from plants be-



longing to the family of the *Compositae*. Table 1 summarises the results of our investigations so far concerning the occurrence of (I) in nature.

In this table ordinary types denote that (I) has been isolated in a pure state, small types that (I) because of the small amounts present has been made probable only through U.V.-spectrography. In the tribus VII = *Anthemideae*, where this ester was first found, its occurrence seems restricted to the small sub-genus *Tripleurospermum*, separated from *Matricaria* some 100 years ago on pure botanical indications¹. Table 1 demonstrates, however, that a lot of genera in the tribus III = *Astereae* contain (I), mostly in large quantities. Besides (I), its α,β -dihydro derivative also occurs in this tribus². During our investigation of some further members of this tribus, deviating results were obtained. One of us (D.H.)³ in 1951 demonstrated that the root of *Aster tripoleum* L. contained a chromophore, resembling very much that of the two isomers (2-*trans* : 8-*trans* and 2-*trans* : 8-*cis*) of deca-2 : 8-diene-4 : 6-diyne-1-ol (II), synthesized by Bruun *et al.*⁴ as intermediates in their syntheses of some stereoisomers of (I), and for this reason were named "matricarianols".



Aster tripoleum L. is the only common wild *Aster* of Norway. This rather tall plant contains only small amounts of essential oil in all parts of the plant. The oils from the flowers and the leaves are — to judge from the U.V.-spectra of the crude oils — quite devoid of acetylenic compounds. The root, which is surprisingly small, contains very little oil but definitely with an acetylenic

Table I.

The Occurrence of 2-cis:8-cis *Matricaria Ester* in the 13 tribes of the *Compositae* Family.

I	II	III	
<i>Vernoniae</i> (not investigated)	<i>Eupatorieae</i>	<i>Astereae</i>	
		<i>Amellus strigosus</i> (flowers and leaves) <i>Aster mongolicus</i> (root) » <i>lautureanus</i> (root) <i>Aster Novae Angliae</i> (root) <i>Brachycome iberidifolia</i> (flowers) <i>Erigeron</i> 19 species (all parts) <i>Erigeron</i> 10 species (all parts) <i>Felicia amelloides</i> (all parts) » <i>fragilis</i> » » » <i>rotundifolia</i> » » <i>Grindelia arenicola</i> (root) <i>Solidago virga aurea</i> (root) <i>Townsendia Parryi</i> (all parts)	
IV	V	VI	
<i>Inuleae</i> <i>Ammobium alatum</i> (leaves)	<i>Heliantheae</i> —	<i>Helenieae</i> <i>Gaillardia aristata</i> (leaves)	
VII	VIII	IX	
<i>Anthemideae</i> <i>Matricaria caucasicum</i> » <i>inodora</i> » <i>oreades</i>	<i>Senecioeae</i> —	<i>Calenduleae</i> <i>Dimorphotheca aurantiacus</i> (flower)	
X	XI	XII	XIII
<i>Arctotideae</i> —	<i>Cynareae</i> <i>Saussurea alpina</i> (all parts)	<i>Mutisieae</i> (not investigated)	<i>Cichorieae</i> —

chromophore but in a low concentration and so one of the main difficulties in this work has been to procure enough starting material. We are greatly indebted to Mrs. Helene Sørensen and Mrs. J. Stene Sørensen for their kind assistance on this point.

Because of the small amounts of acetylenic compounds present in *Aster tripoleum* L. this work extended over several years. In the meantime two species of *Grindelia* viz. *arenicola* f. *trichophora* Steyermark and *stricta* D.C., of which Dr. Philip A. Munz, Rancho Santa Ana Botanic Gardens, had most kindly sent us seed samples, had been cultivated at Norges Tekniske Høgskole, Trondheim.

Grindelia arenicola did not flower the first year at N.T.H. Most of the plants were distilled without flowers, because we did not trust the plants to stand the winter climate of Trondheim. Both the leaves and the root of *Grindelia arenicola* were rich in oil (1.8%), and the crude oil showed an U.V.-spectrum in general agreement with the matricarianols (see Fig. 1), contents

~ 50—70 % calculated as free alcohol. After high vacuum distillation the extinction coefficients had changed very little. Analysis agreed with a substance $C_{12}H_{12}O_2$, corresponding to the acetate of a matricarianol. The ester structure was confirmed through strong infra red maxima at 1745 and 1230 cm^{-1} , characteristic of an ester of acetic acid. Catalytic hydrogenation furnished *n*-decyl-acetate identical in m.p., mixed m.p. and infra-red spectrum with synthetic *n*-decyl-acetate.

Thus only the configuration at the double bonds remained to be established. Saponification under cautious conditions afforded immediately a solid alcohol, the m.p. of which could not be raised above 93° by recrystallisation. After further purification by chromatography, this crude matricarianol was esterified with 3:5-dinitro-benzoyl chloride in pyridine and the ester purified by recrystallisation from acetone-petroleum ether. The 3:5-dinitrobenzoate then melted at 126—128° undepressed by an authentic sample of synthetic 3:5-dinitrobenzoate of 2-*trans* : 8-*trans*-matricarianol. Dr. H. Sörum had the kindness to take Debye Scherrer diagrams of these two dinitrobenzoates. The diagrams were completely identical.

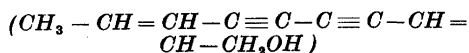
The reason for the low m.p. of the crude matricarianol might be the presence of some *cis*-isomer. Thus in the infrared spectrum of the native acetate there occurred the characteristic 720 cm^{-1} band of the *cis*-double bond. Pure 2-*trans* : 8-*trans*-matricarianol was devoid of selective absorption in this region.

As described in the experimental part the isolation of 2-*trans* : 8-*trans*-matricarianol then was successful also from *Grindelia stricta* (leaves and root) and from the root of *Aster tripoleum*, where this chromophore was first discovered. In these cases also the primary compound was an ester. The amounts and purity of the oils did not allow the preparation of the original esters in a pure state, and therefore nothing is known about the acid moiety.

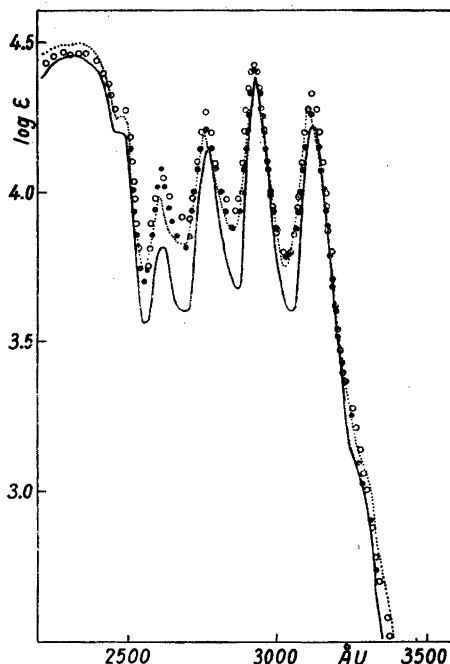
It then became tempting to see whether the matricarianol was a general component of the essential oil of the genus *Aster*. Since no further wild representatives are available in Norway, we cultivated some of the common garden *Asters* from seed samples, most kindly put at our disposal by the Botanical Garden of The University of Copenhagen. The details of this investigation are given in the experimental part. The results may briefly be summarised as follows: Two species: *A. Herveyi*, A. Gray and *A. ptarmicoides* (Nees) T. & G., were lacking acetylenes in all parts of the plants. *A. ptarmicoides* seemed to contain coumarins in the root. Three species: *A. novae angliae* L., *A. lautureanus* Fr. and *A. mongolicus* Fr. were lacking acetylenic compounds in the overground part of the plants, but contained appreciable amounts of the 2-*cis* : 8-*cis* matricaria ester (I) in the root. One species: *A. novi belgii* L. also did not contain acetylenes in the overground part of the plant. The root contained a chromophore with acetylenic spacing between the maxima, which were found at 3 075, 2 900 and (2 710) ÅU, positions close to, but significantly different from the symmetrical diene-diyne grouping of the matricarianols and intermediate between the *cis* and *trans* lachnophyllum esters. Since only traces of oils were available, larger cultivations of this *Aster* are laid out in 1953.

These six *Asters* resemble *Aster tripoleum* in so far as none of them has shown any indication of acetylenic compounds in the flowers or green parts,

Fig. 1. Ultraviolet absorption in hexane of
2-trans : 8-trans-matricarianol



- synthetic
 - - - - - from root of *Aster tripoleum* L.
 ⊙ ⊙ ⊙ from leaves of *Grindelia arenicola* f. *trichophora* Steyermark.
 ● ● ● from root of *Grindelia stricta* D.C.



none of these six, however, has given indications of the presence of matricarianols; four of them contain other acetylenic compounds in the root. It has to be borne in mind that the botanists have put *A. tripoleum* in its own section, *Tripoleum* Nees, *A. ptarmicoides* belongs to the section *Orthomeris* T. & G. *A. novae-angliae* and *A. novi-belgii* belongs to the section *Euaster* Gray. *A. lautureanus* and *A. mongolicus* are by modern botanists mostly transferred into the genus *Asteromoea* Blume⁵.

Aster is a very large genus with at least some twohundred good species, and is subdivided by O. Hoffmann into not less than 15 sections. It is obviously premature to draw any conclusion from their contents of acetylenic compounds, but already it is evident that *Aster* is not at all so constant with regard to the occurrence and number of acetylenic compounds as the botanically closely related genus *Erigeron*, where the occurrence of matricaria and lachnophyllum ester in all parts of the plants is a real chemical characteristic of the genus. If any conclusions should be drawn with regard to *Aster*, the seven species investigated have at least that in common that all of them are lacking acetylenic compounds in the overground parts of the plants, whereas such may occur in the roots.

The chemical similarities between *A. tripoleum* and the two investigated species of the genus *Grindelia* is interesting. The botanists long ago placed *Grindelia* in the tribus *Astereae* sub-tribus *Solidagininae*, whereas Harling⁵ in his recent embryological work points out relations to the tribus *Heliantheae*. In the sub-tribus *Solidagininae* only some three species of the very large genus

Solidago has been investigated as to their contents of acetylenic compounds. As with *Aster* the results are rather conflicting:

Solidago canadensis L. seems to lack acetylenic compounds in all parts of the plant.

Solidago sempervirens L. seems to contain the α,β -dihydro-matricaria ester in the root.

Solidago virga aurea L. lacks acetylenic compounds in the overground part. The roots, however, are the richest source so far known of 2-*cis* : 8-*cis* matricaria ester (8 g of pure (I) from 1 kg of fresh roots).

Only further extensive chemical investigations of the tribus *Astereae* may clear up the rather obscure connections. Since very few representatives of this tribus are available in Europe and seed samples are difficult to obtain, progress will be slow.

EXPERIMENTAL

1. *Grindelia arenicola* f. *trichophora* Steyermark. Cultivated at Trondheim 1952. The young plants did not develop flowers.

a) *Leaves and stems*, 800 g, gave 1.8 % of essential oil. The U.V. spectrum of the crude oil was in good agreement with that of matricarianol. The oil distilled at 70° at 0.001 mm practically without forerun and residue, and, as might then be expected, with very little change in the U.V.-spectrum

$C_{12}H_{12}O_2$	Found	C 76.28, 75.98	H 6.87, 6.96
	Calc.	» 76.60	» 6.38

This formula corresponds to the acetate of matricarianol; in the infrared spectrum there were strong peaks at 1 745 and 1 230 cm^{-1} , characteristic of acetates.

92.4 mg of this ester was hydrogenated with a Pd/BaSO₄-catalyst in alcoholic solution and consumed 80.3 ml H₂, calculated for C₁₂H₁₂O₂, $\delta/\bar{=} 79.7$ ml. The perhydrocompound was distilled and purified through freezing out at -20°. The crystals then melted at -16°, synthetic *n*-decyl-acetate at -14°, mixed m.p. -15°. Of both preparations infrared spectrograms were made with the same cell and on the same recording sheet. From 5-15 μ the two curves coalesced through all 11 maxima.

The acetate from *Grindelia* leaves was saponified under nitrogen with potassium hydroxide. Acetone was added to obtain a homogenous solution. The unsaponifiable part which was isolated in the usual way, crystallised immediately, m.p. after recrystallisation from petroleum ether 80° rose after several recrystallisations to 88-93°, further recrystallisations did not improve the m.p. These 93° crystals were chromatographed from petroleum ether solution on Floridin XXX; elution with benzene-petroleum ether mixtures. The main part of the matricarianol went in the 70 % benzene-petroleum ether eluates; m.p. after recrystallisation from petroleum ether 97°-99°.

3:5-dinitro-benzoate of 2-*trans* : 8-*trans*-matricarianol from *Grindelia arenicola*. 40 mg of the matricarianol fraction above was esterified with 155 mg 3:5-dinitrobenzoyl chloride in anhydrous pyridin at room temperature; and the dinitrobenzoate isolated in the usual way after 24 hours and purified by crystallisation from acetone-petroleum ether. After one recrystallisation from the same solvent mixture the crystals melted at 126.5°-128.2°, given by Bruun *et al.* 126-128°, no depression of m.p. in a 1 : 1 mixture. Debye-Scherrer diagrams (Dr. H. Sörum) were identical.

b) The roots of *Grindelia arenicola* (185 g) were distilled with steam; essential oil 1.9 %. The U.V.-spectrum of the crude oil revealed that this oil besides matricarianol seemed to contain (I) since there occurred a pronounced peak at 3 300 ÅU. The crude essential oil was therefore distilled slowly at 0.001 mm. The matricaria ester became enriched in the fraction b.p. <52°, whereas the matricarianol esters concentrated above 70°; both fractions were still liquid mixtures.

The fraction b.p. <52° was saponified as above, the acid fraction isolated, and in the crude state immediately converted to the methyl ester with diazomethane. The methyl ester was distilled at 50° and 10⁻³ mm. The distillate remained liquid at room temperature, but solidified below zero and then showed m.p. 0°. The spectral curve was identical with

that of 8-*cis* : 2-*trans* matricaria ester m.p. + 2°, which resembles very much the 2-*cis* : 8-*cis* isomer, but differs in a sharper peak at 3 355 and a much narrower inflexion at 3 600 ÅU. *Grindelia arenicola* thus does not seem to contain the more widely distributed 2-*cis* : 8-*cis* ester, but only the low melting 2-*trans* : 8-*cis* isomer.

The fraction b.p. > 70° was saponified as above and the unsaponifiable part purified by chromatography on slightly deactivated alumina. The matricarianol was eluted with ether and showed the correct spectrum of 2-*trans* : 8-*trans*-matricarianol, cf. Fig. 1.

c) *Flowers* of *Grindelia arenicola* (125 g) collected in the summer 1953, were distilled with steam, essential oil 2.4 ‰. The U.V.-spectrum of the crude oil was conformable with that of matricarianol, calculated contents as matricarianol acetate 7.7 ‰. Because of the low concentration no further investigations were carried out; the flowering heads of *G. arenicola* have very herbaceous phyllaries and the origin of the small amount of acetylenic compounds may be these green parts.

2. *Grindelia stricta* D.C., cultivated at Trondheim 1952. Late in the autumn the young plants developed buds, and they were then transferred to a greenhouse, where some of them went into flower. The rest flowered in the spring 1953.

a) The *flowers* gave about 6 ‰ essential oil with only indistinct absorption in U. V. By chromatography on alumina and elution with benzene-petroleum ether mixture followed by pure ether, the oil was divided into six fractions. The two main ones were the petroleum ether washings (47 ‰) and the ether eluate (32 ‰). None of them seemed to contain acetylenic compounds. The first fraction showed only a step out below 2 500 ÅU, the second, which had a strong borneol-like odour exhibited a diene maximum at 2 340 ÅU. The material in 50 ‰ benzene eluate amounted to 10 ‰ and showed a very unsharp matricarianol curve in U. V., from which a maximum contents of 2 ‰ of matricarianol could be estimated. Since *Grindelia stricta* has very great and herbaceous phyllaries these traces of matricarianol might originate from the green part of the flowers, which themselves seem to be devoid of acetylenic compounds.

b) The *leaves and stems* (2 953 g) afforded 1.1 ‰ essential oil. The crude oil has a fair matricarianol spectrum in U.V., but in low concentrations. The oil was chromatographed from petroleum ether solution on slightly deactivated alumina and separated into six fractions as above. Only the material in the 50 ‰ benzene eluate, which amounted to 4 ‰, contained appreciable amounts of matricarianol, about 60 ‰ calculated as the free alcohol. These contents were not changed by distillation, whereby the main part distilled at 60°/0.001 mm. The distillate was saponified as above and the unsaponifiable part showed an U.V.-spectrum identical with that of matricarianol.

c) The *roots* (740 g) furnished 3.6 ‰ essential oil with a typical matricarianol spectrum in U.V., but again the concentration was low. Distillation at 0.001 brought out a fraction b.p. ~70° amounting to 6.5 ‰ of the oil, which showed a good matricarianol spectrum in concentration of about 65 ‰, calculated as free alcohol. This fraction was saponified as above. The unsaponifiable part, however, which showed the correct spectrum of pure matricarianol, remained liquid. In the infrared spectrum there occurred a strong maximum at 716 cm⁻¹, indicating the presence of appreciable amounts of *cis*-bonds. From petroleum ether solution in the cold this matricarianol concentrate deposited crystals, m.p. 87–89°, raised after one recrystallisation to 96–98°, and by further crystallisation finally to 100.5–103.0°. Mixed m.p. with synthetic 2-*trans* : 8-*trans*-matricarianol of m.p. 104° was 102°.

The contents of *cis*-isomers in the *Grindelia stricta* oil, seemed to be appreciably higher than in *G. arenicola*. Trials to isolate one of these liquid *cis*-isomers as a 3:5-dinitrobenzoate were unsuccessful.

3. *Aster tripoleum* L. This plant was collected at different sea-shores in the surroundings of Trondheim. When the available quantities turned out to be insufficient, further quantities of the root were collected on Kadettangen in Sandvika near Oslo, where this *Aster* was abundant.

a) The *flowers* yielded 0.3 ‰ essential oil, which, to judge from the U.V.-absorption, was devoid of acetylenic compounds.

b) The *leaves and stem* gave 0.3 ‰ essential oil, which also seemed to lack acetylenic chromophores.

c. The *roots* afforded only 0.2 ‰ of essential oil, but this oil showed definite absorption maxima in U.V. in accordance with the symmetrical diene-diyne systems. The contents calculated as free matricarianol was about 10 ‰ in the different batches. A portion

of *A. tripoletum* root was extracted with acetone in the cold, and the lipoids isolated in the usual way. The yield of crude lipoids was appreciable, (2.5%), but the yield of matricarianol was the same as when the roots were steam distilled. Some of the crude essential oils were distilled at 0.001 mm; a chromophore with the 3 355 peak of the matricaria esters became enriched in the most volatile fractions (< 55°), but the main fraction, boiling about 70°, was still contaminated with this chromophore and also with another substance with absorption maxima close to those of lachnophyllol (that is at 2 825, 2 665 and 2 520 ÅU). The fractions boiling at 70° were chromatographed on alumina and eluted with petroleum ether-benzene mixtures. The matricarianol chromophore went mainly in the 50% eluates. The best chromatographic fractions from several batches were combined and rechromatographed on alumina and eluted with large quantities of 20, 40 and 60% benzene-petroleum ether mixtures. Each elution mixture was separated into three parts which were investigated separately in U.V. About 20% of the combined fractions was recovered in the first part of the 40% eluate. This fraction showed an almost perfect U.V.-absorption curve for matricarianol with only a weak maximum at 3 355 ÅU.

This fraction was saponified in the usual way; the unsaponifiable part (25 mg) crystallised spontaneously; after recrystallisation from chloroform-petroleum ether the crystals melted at 98.5–102°; the mixed m.p. with authentic 2-*trans*:8-*trans*-matricarianol of m.p. 103–104 was also 98.5–102°. The U.V.-spectrum of this purest fraction was in complete agreement with that of 2-*trans*:8-*trans*-matricarianol.

4. *Aster Herveyi* A. Gray. Seed sample *Hortus Botanicus Hauniensis*. Cultivated Trondheim 1952.

	g	Ess. oil %	U.V.-absorption
Flowers	16.5	1.8	step out below 3 600 ÅU, no selective absorption
Leaves + stems	177	0.5	» » » 3 600 » »
Roots	297	0.5	» » » 3 500 » »

5. *Aster lautureanus* Franchet. Seed samples *Hortus Botanicus Hauniensis*, and *Hortus Bergianus*, cultivated Trondheim 1952–53.

	g	Ess. oil %	
Flowers	55	2.1	step out below 3 100 ÅU
Leaves	693	0.22	» » » 3 400, broad max. at 2 580 ÅU
Roots	470	3.7	close to the standard curve for matricaria ester (I), contents 72%. The crude oil solidified in the cold and pure (I) was obtained after one crystallisation from petroleum ether, m. p. 32.8–33°, undepressed by authentic (I).

6. *Aster mongolicus* Franchet. Seed samples *Hortus Botanicus Hauniensis* and *Hortus Bergianus*.

	g	Ess. oil %	broad max.
Flowers	320	1.5	step out below 2 800 ÅU, at 2 600 ÅU
Leaves	615	0.1	» » » 3 400 » » 2 600 »
Roots	815	2.3	close to the standard curve for matricaria ester (I), contents 72% as with <i>A. lautureanus</i> . Pure (I) was also isolated by one single crystallisation, m.p. 33°.

7. *Aster novae angleae* L. Seed sample *Hortus Botanicus Hauniensis*. Cultivated Trondheim 1952. The plant material was in good agreement with the botanical descriptions, but about one half of it developed curled leaves. Since no infections could be detected, the curled and normal plants were investigated separately, but when no chemical differences were found, the data have been summarised. The plants developed buds only late in the autumn.

	g	Ess. oil %	U.V.-absorption
Buds + leaves + stems	815	0.5	step out below 3 600 ÅU, no selective abs.
Root	540	1.1	close to the standard curve for matricaria ester although with definite indications of presence of <i>cis</i> -lachnophyllum ester, contents

41 %. The crude oil solidified in the cold and furnished crystals, m.p. 19–20° after one crystallisation from petroleum ether.

8. *Aster novi-belgii* L. Cultivated by Mr. R. Persson, Trondheim, season 1952.

	g	Ess. oil %	U.V.-absorption
Flowers	33	0.6	step out below 3 200 ÅU, no selective abs.
Leaves + stem	190	0.2	» » » 3 200 » » » »
Roots	55	0.1	maxima at 3 075, 2 900, (2 710) ÅU

These maxima are some 25 ÅU shorter than those of the symmetrical diene-diyne grouping as present in the matricarianols. They are intermediate between those of *cis*- and *trans*-lachnophyllum ester.

9. *Aster ptarmicoides* (Nees.) T. & G. Seed sample *Hortus Botanicus Hauniensis*, cultivated Trondheim 1952.

	g	Ess. oil %	U.V.-absorption
Flowers	32	2.2	step out below 3 200 ÅU, no selective abs.
Leaves + stem	1 067	0.6	» » » 3 200 » » » »
Roots	270	0.5	maxima at 3 160, 2 670 and 2 565 ÅU

The shape of the curve might indicate the presence of coumarins.

10. *Solidago virga aurea* L. The plants were collected in the hills around Trondheim, July 1951.

	g	Ess. oil %	U.V.-absorption
Flowers	410	1	step out below 3 500 ÅU, no selective abs.
Leaves + stems	2 360	1	» » » 3 500 » » » »
Roots	674	10	the spectrum of the crude oil showed perfect agreement with that of (I). The root oil solidified in the cooler; one single crystallisation from petroleum ether gave pure matricaria ester, m.p. 32.8–33.3°; mixed m.p. with an authentic sample 32.8–33.3°. U.V.-spectrogram identical with the standard curve for (I).

SUMMARY

2-*trans*:8-*trans*-Matricarianol (II) has been isolated from the essential oil of *Aster tripoleum* L., *Grindelia arenicola* f. *trichophora* Steyermark and *G. stricta* D.C. In all three cases (II) occurs as an ester, but only in the case of *G. arenicola* the native ester, which turned out to be the acetate, could be isolated. In the crude esters *cis*-isomers of matricarianol might be present. Some 6 further species of *Aster* investigated did not contain matricarianols, but three of them had 2-*cis*:8-*cis*-matricaria ester in the root. The overground part of members of the genus *Aster* seems to lack acetylenic chromophores.

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