

**Studies Related to Naturally Occurring  
Acetylene Compounds. IX. The Occurrence of Methyl dec-  
8-*cis*-en<sub>4</sub>:6-diynoate (=  $\alpha$ ,  $\beta$ -Dihydro-Matricaria Ester) and  
2-*cis*; 8-*trans*-Matricaria Ester in Nature**

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The methyl-deca-2-*cis*: 8-*cis*-diene-4 : 6-diynoate or matricaria ester discovered in 1941 in the essential oil of scentless mayweed (*Matricaria inodora* L.)<sup>1</sup> has so far turned out to be the most widely distributed acetylenic component of essential oils. The preliminary investigation of some 94 essential oils from plants belonging to the plant family of the *Compositae*, the results of which will be treated in a separate paper in this series, has established the occurrence of the matricaria ester in some 34 different plants. In all these cases the dienediyne ester was crystallized and the pure compound characterized through mixed m.p. and U.V.-absorption.

Some of the essential oils investigated, especially those amongst the fleabane oils, consisted entirely of matricaria ester. The scentless mayweed oil, however, contains an appreciable liquid fraction in the mother liquors after low temperature crystallization of matricaria ester. The essential oil from the flowers contains only small amounts of the hexahydro matricaria ester characteristic of the leaves. When all the *cis* : *cis*-matricaria ester which can be crystallized out from pentane solution at  $-20^{\circ}$  has been removed, the mother liquor still exhibits a U.V.-spectrum above 2900 ÅU similar to matricaria ester with the intensity of absorption depressed only some 20 to 30 %. Below 2900 ÅU there occur new, sharp peaks at 2815, 2650 and 2510 ÅU.

## HYDROCARBONS

We have tried to separate the components in these mother liquors through chromatography on slightly activated alumina. Small amounts of a hydrocarbon passed with the solvent, petroleum ether, through the column. This hydrocarbon showed the composition of a sesquiterpene  $C_{15}H_{24}$ . Density and refraction  $d_4^{20} = 0.8505$  and  $n_D^{20} = 1.4912$ , which gives a molecular refraction of  $M_{D, \text{obs.}} = 69.56$ . This value is very close to the calculated value for an aliphatic sesquiterpene  $M_{D, \text{calc.}} C_{15}H_{24}, 4/\equiv = 69.54$ . However, an aliphatic sesquiterpene should have at least 2 double bonds in conjugation and an exaltation of about 1.5–1.6 to be added. So the molecular refraction is intermediate between an aliphatic and a monocyclic sesquiterpene ( $M_{D, \text{calc.}} = 67.81$ ). Catalytic hydrogenation seemed to confirm this view, since a saturated hydrocarbon was obtained after consumption of 3.1 moles of hydrogen.

As all the known monocyclic sesquiterpenes have density and refraction considerably higher than this hydrocarbon from scentless mayweed and the quantity of material was insufficient for further fractionation, the hydrocarbon and its perhydrocompound was sent to Dr. Josef Plíva, Praha, for examination of their infrared spectra. As will be seen from Fig. 1 the infrared spectra of the sesquiterpene from scentless mayweed and its perhydro compound cannot be distinguished from the spectra of "natural farnesene" and 2 : 6 : 10-trimethyl-dodecane<sup>2</sup>.

"Natural farnesene" was discovered in 1949 by Šorm, Mleziva, Arnold and Plíva<sup>3</sup> in oil of hops, but has since been shown in the laboratory of Professor Šorm to be a component of several essential oils, among others of oil of chamomille (*Matricaria chamomilla* L.), which botanically is closely related to scentless mayweed. Chemically the oil of chamomille is a terpenoid oil; the main constituents, besides »natural farnesene«, being some cyclic sesquiterpenes and sesquiterpene alcohols<sup>4, 5</sup> chamazulene and its precursor chamazulengen<sup>6</sup>.

A spectral investigation of a trade sample of oil of chamomille (Polak and Schwarz) showed 13 % of matricaria ester. This content was so low that a contamination of the chamomille culture with scentless mayweed corresponding to this content seemed rather likely. So in the summer 1950 and 1951 we cultivated genuine *Matricaria chamomilla* L. The spectrographical investigation of this oil gave no indications of matricaria ester. As in contrast to the Polak and Schwarz sample the U.V.-absorption was very strong the oil was partitioned between petroleum ether and 92 % methanol, the hypophasic part distilled at  $10 \div 4$ , and the U.V.-absorption measured for the fraction 50–60°, in which nearly all the matricaria ester would concentrate. This

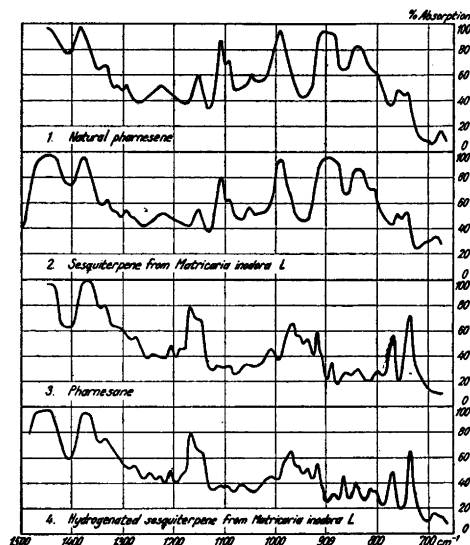


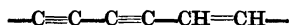
Fig. 1. Infrared spectra Perkin-Elmer infrared spectrometer model 12 B, 60° rock salt prism. All substances in liquid state at room temperature.

fraction had a very strong U.V.-absorption too, but without any resemblance to the known curve of matricaria ester. This fraction was chromatographed on activated alumina according to a procedure found suitable for the isolation of matricaria ester. This chromatography split up the fraction into different compounds, one of them spectroscopically identical with the unknown main component of the essential oil of *Matricaria discoidea* D.C., which may be related to "Composite-cumulen I"<sup>7</sup>, but we were not able to obtain any fraction with a U.V.-spectrum corresponding to that of matricaria ester. So the chemical relations between chamomille and scentless mayweed seem restricted to the common occurrence of "natural farnesene".

"Natural farnesene" has the physical constants  $n_D^{20} = 1.4899$   $d_4^{20} = 0,8363$  which gives  $M_{D, obs.} = 70.58$ ,  $M_{D, calc.} C_{15}H_{24} 4/ = 69.54$ , that is an exaltation of 1.04. The reason for the higher physical constants of the *Matricaria inodora* sesquiterpene might be either impurities or polymerisation. A contamination with cyclic sesquiterpenes would explain that the perhydro compound also has too high a density and refraction. To explain the hydrogenation number (3.12 mols  $H_2$ ) a contamination by 30 % of a tricyclic sesquiterpene would be necessary. Although such a high proportion of cyclic sesquiterpenes is inconsistent with the U.V.- and infrared spectra, the optical activity of the scentless mayweed sesquiterpene  $[\alpha]_D^{20} = -15,5^\circ$  strengthens the suggestion indicated by the molecular refraction of the inhomogeneity of this sesquiterpene fraction.

## ACETYLENIC ESTERS

Elution of the chromatographic column with benzene gave an oil b.p.  $50^{\circ}/10^{\circ}$  with U.V.-absorption close to that of the entire mother liquor, the matricaria ester concentration being about 60 %. The sharp absorption maxima below 2800 ÅU of these mother liquors are very close to the maxima found by Bruun, Haug and Sørensen<sup>8</sup> for lachnophyllol (= dec-2-ene-4:6-diyn-1-ol) viz. 2825, 2665, 2520 and 2395 ÅU. These maxima are characteristic of the unsaturated system



The analytical composition of the distilled oil was C 75.75, H 6.48 Calculated for matricaria ester  $C_{11}H_{10}O_2$  C 75.84, H 5.79; for a dihydro matricaria ester  $C_{11}H_{12}O_2$  C 74.97, H. 6.86.

Thus the most reasonable explanation is that the mother liquor is a mixture of a (liquid?) matricaria ester with its dihydro- compound having interrupted conjugation between the carbomethoxy group and the unsaturated chromophor.

Biosynthetically the most likely dihydromatricaria ester is the  $\alpha,\beta$ -dihydro ester. This compound was therefore synthesized according to the Glaser coupling reaction, compare Christensen and Sørensen<sup>9</sup>. The 8-*trans*- $\alpha,\beta$ -dihydromatricaria ester was a solid with the low m.p.  $15,5^{\circ}$  C, the corresponding free acid showed m.p.  $144^{\circ}$ . The 8-*cis* isomer was a liquid, the 8-*cis* acid melted at  $60-61,5^{\circ}$  C. Both isomers have identical U.V.-absorption curves (within the limits of experimental error), the maxima lie, as would be expected, at

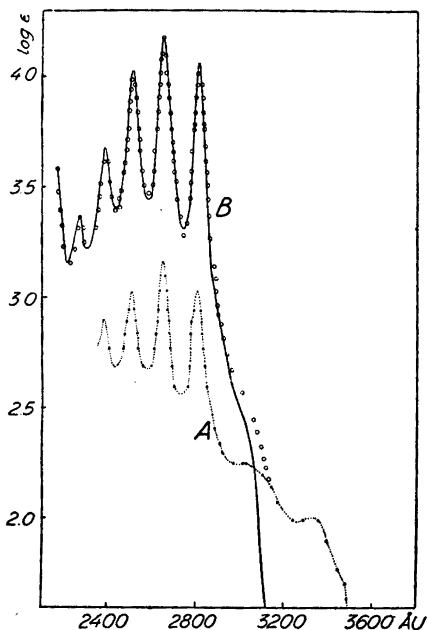
8- <i>cis</i> -	$\alpha,\beta$ -dihydromatricaria ester	2810	2650	2514	2381	2275
8- <i>trans</i>	»	»	»	2814	2653	2510
						2390
						—

The possibility was thus strengthened that the main component of the scentless mayweed mother liquors was the 8-*cis*- $\alpha,\beta$ -dihydro ester. The isolation of this compound from natural essential oils was facilitated since it turned out that some composité oils were enriched in the compound. The spectrum so far has been found present in the oils from: *Amellus strigosus*, (Thunb.) Less., *A. strigosus* var *Wildenowii*, *Cephalophora aromatica* Schrad., *Felicia tenella* (L.) Nees. *Solidago sempervirens* L.

Among these the root oil of *Amellus strigosus* var. *Wildenowii* turned out to be most homogeneous, compare Fig. 2, curve A. Saponification under nitrogen of the root oils gave colourless crystals, m.p.  $61^{\circ}-61,5^{\circ}$ . The U.V.-spectrum substantiated, however, that the crystals were contaminated with

Fig. 2. Ultraviolet absorption of hexane solutions of:

- Curve B. (—). synthetic 8-*cis*- $\alpha,\beta$ -dihydromatricaria ester.  
 › B. (○○○○). 8-*cis*- $\alpha,\beta$ -Dihydromatricaria acid from *Amellus strigosus*.  
 › A. (▲····▲). Essential oil from the root of *Amellus strigosus* var. *Wildenowii*.



some 19 % of a matricaria acid. The amounts of crystals were too small for further purifications. The crude essential oil from the flowers and from the leaves of *Amellus* showed U.V.-spectra very similar to each other and very like the spectra of the mother liquors from scentless mayweed. With this material, which was more abundant than the root oils, the isolation of 8-*cis*- $\alpha,\beta$ -dihydromatricaria acid could be realized. The laborious fractionation of these oils is described briefly in the experimental section. Besides demonstrating the presence of 8-*cis*- $\alpha,\beta$ -dihydromatricaria acid in nature this arduous experimentation was rewarded with the simultaneous isolation of 2-*cis*-8-*trans*-matricaria acid. 2-*cis* : 8-*trans*-Matricaria acid had been prepared earlier both by photoisomerization of 2-*cis* : 8-*cis*-matricaria ester and by total synthesis<sup>10</sup>. The demonstration of the occurrence of this stereoisomer in nature explains why some crude essential oils and some mother liquors which spectroscopically are indicated to have high concentrations of matricaria ester are without any tendency to crystallization. In contrast to the beautifully crystallizing 2-*cis* : 8-*cis*-ester, the 2-*cis* : 8-*trans*-ester m.p. + 2° is very soluble in all solvents and solidifies only when solvent-free and quite pure.

The separation of the *Amellus* oils led further to the discovery of a volatile polyene the U.V.-chromophor of which has an ethylenic fine structure spacing.

In this respect this volatile polyene resembles the »Centaur Y», a compound of unknown constitution found by Löfgren<sup>11</sup> in some extracts of different *Centaurea*-species. We are returning to the investigation of this substance later.

### EXPERIMENTAL

*Matricaria inodora* flower oil mother liquors. The starting materials were two samples of combined mother liquors from the preparation of matricaria ester. In the 1940-experiments of Sörensen and Stene the mother liquors had been sealed under vacuum. The distillation of this material at  $10^{-4}$  mm Hg gave 7.25 g boiling  $< 75^\circ$  (I). The second sample originated from the isolation of matricaria ester in September 1949 and weighed 12 g (II). Both samples were chromatographed on slightly activated alumina from petroleum ether solution. The column was washed with petroleum ether and eluted with petroleum ether with 20 % benzene, ether and ethyl alcohol. Only the petroleum ether washings and the benzene eluate contained appreciable amounts of material.

Sesquiterpene fractions. The petroleum ether washings were evaporated and distilled at  $10^{-3}$  (air bath  $35-40^\circ$  C), I gave 1.2 g  $[\alpha]_D^{20} = -15.5$ , II 3.2 g  $[\alpha]_D^{20} = -14^\circ$ . Analysis showed C 87.42, 87.64 and H 11.57, 11.36 so there must be some oxygen containing impurities present. The combined sesquiterpene fractions were dissolved in equal parts of petroleum ether and methanol and „entmisch” with water to 92 %, the procedure being repeated 3 times and the epiphasic part isolated and distilled.

$C_{15}H_{24}$ (204.3)	Calc.	C 88.16	H 11.84
	Found	» 88.22	» 11.57

Table 1. Dispersion of sesquiterpene.

$$d_4^{20} = 0.8505$$

$\lambda$	$n_\lambda$	$R_\lambda$	$\lambda$	$n_\lambda$	$R_\lambda$
6678.1	1.48841	69.22	5015.6	1.50089	70.72
5895.9	1.49283	69.75	4713.1	1.50491	71.20
5875.7	1.49300	69.77	4471.5	1.50875	71.66
5790.7	1.49359	69.85	4358.3	1.51082	71.90
5460.7	1.49617	70.16			

U.V.-absorption in hexane, compare Fig. 3, where the curve of Šorm *et al.*<sup>3</sup> for "natural farnesene" is given for comparison.

Infrared spectrum, compare Fig. 1.

*Catalytic hydrogenation*: 0.5789 g sesquiterpene in glacial acetic acid (catalyst 2 % Pd on  $BaSO_4$ ) consumed 220 ml  $H_2$ , 742 mm,  $24^\circ$  C, that is 3.12  $\mu$ . The hydrogenation mixture was filtered, ether added and the acetic acid neutralized with sodium hydroxide, the ether solution washed with water, dried and distilled in vacuum at 0.5 mm (air bath  $70^\circ$  C).

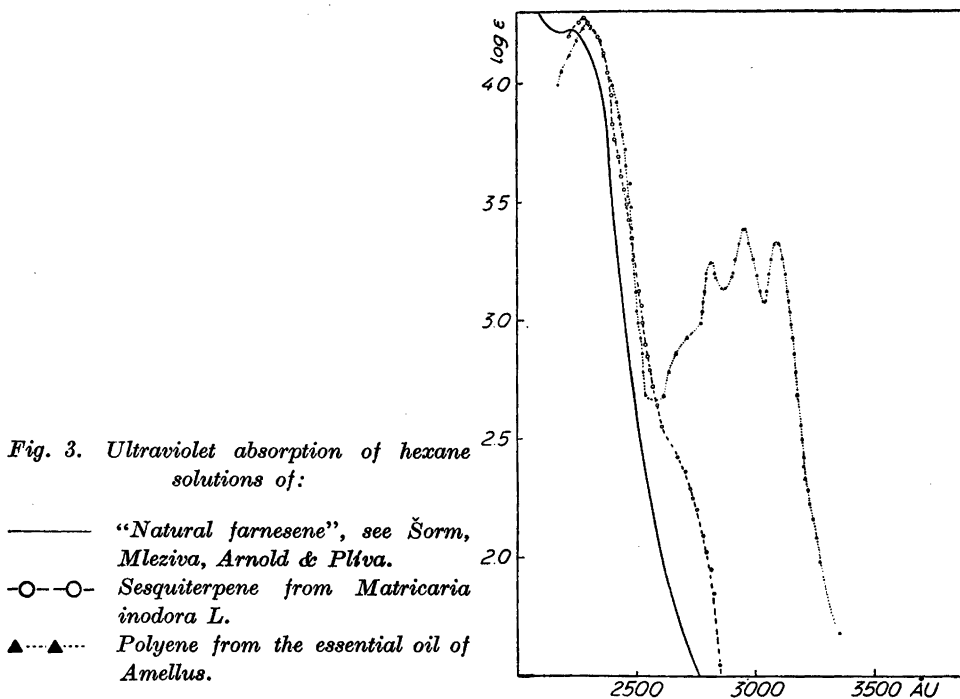


Table 2. Dispersion of perhydrogenated sesquiterpene.

$$d_4^{20} = 0.8029 \quad R_{\lambda, \text{calc}} = \frac{68.179 \cdot \lambda^2}{\lambda^2 + 0.7948 \cdot 10^6}; \lambda_0 = 891.5 \text{ \AA}$$

$\lambda$	$n_{\lambda}$	$R_{\lambda, \text{obs.}}$	$R_{\lambda, \text{calc.}}$	$\lambda$	$n_{\lambda}$	$R_{\lambda, \text{obs.}}$	$R_{\lambda, \text{calc.}}$
6678.1	1.44294	69.41	69.41	4921.9	1.45105	70.51	70.49
5895.9	1.44562	69.77	69.77	4713.1	1.45267	70.73	70.71
5875.7	1.44572	69.79	69.79	4471.5	1.45472	71.01	71.00
5790.7	1.44610	69.84	69.83	4358.3	1.45583	71.16	71.16
5460.7	1.44761	70.05	70.05	4046.6	1.45903	71.59	71.66
5015.6	1.45039	70.42	70.40	—	—	—	—

The dispersion constant is in agreement with the standard value for saturated hydrocarbons,  $\lambda_0 = 886 \text{ \AA}$ , but the density and refraction are too high and the molecular refraction too low compared with 2 : 6 : 10-trimethyl-dodecane<sup>3</sup> :  $d_4^{20} = 0.7767$ ,  $n_D^{20} = 1.4360$ ,  $M_D = 71.51$

Ester fraction: From the benzene eluates the solvent was removed in vacuum and the residue distilled at  $50^\circ/10^{-4} \text{ mm}$ . The distillate was dissolved in petroleum ether and

stored at  $\div 15^\circ$ . Small amounts of matricaria ester crystallized and were removed; the mother liquor was distilled again. The U.V.-spectra then exhibited the following maxima:

I.	$\lambda_{\max}$	3361	3137	2820	2650	2500	ÅU
	$\epsilon_{\max}$	7940	9886	11750	11600	17000	
II.	$\lambda_{\max}$	3350	3125	2820	2654	2500	ÅU
	$\epsilon_{\max}$	6920	8730	10720	12450	14300	

These spectra correspond to mixture of matricaria ester and  $\alpha,\beta$ -dihyromatricaria ester I 59 : 41, II 57 : 43.

	I. C 75.78	H 6.69	II. C 75.70	H 6.27
Matricaria ester $C_{11}H_{10}O_2$	Calc. C 75.84	H 5.79		
Dihyromatricaria ester $C_{11}H_{12}O_2$	» » 74.97	» 6.86		

#### Essential oils of some *Amellus* species

*Amellus strigosus* (Thunb.) Less, and *Amellus strigosus* var. *Wildenowii* were cultivated on open ground at Trondheim in the summer of 1951. The flowers and roots were distilled with steam separately, the leaves and stems were taken together. The following table gives the yields and apparent concentrations of acetylenic compounds in the essential oils.

Table 3.

Species	Part of plant	Essential oil		
		Yield %	Spectroscopically estimated concentrations in % of:	
			Matricaria ester	$\alpha,\beta$ -Dihyromatricaria ester
<i>A. strigosus</i> (Thunb.) Less (Seed: Botanic Garden, Lund)	Root	0.2	20	15
» »	Flowers	5.8	19	15
» »	Rest	1.7	16	18
<i>A. strigosus</i> (Thunb.) Less. (Seed: Botanic Garden, Gent)	Root	0.2	7	84
» »	Flowers	3.8	16	24
» »	Rest	1.6	21	36
<i>A. strigosus</i> var. <i>Wildenowii</i> (Seed: Royal Botanic Gardens, Kew.)	Root	0.1	11	87
» » » » »	Flowers	2.9	24	18
» » » » »	Rest	1.3	20	20



Some of the essential oils of the flowers and of the stem and leaves crystallized at  $-12^{\circ}$ . The semisolid mass was stirred with petroleum ether, filtered and the crystals recrystallized from petroleum ether to give colourless crystals of 2-*cis* : 8-*cis* matricaria ester identical in m.p. and U.V.-spectrum with an authentic sample. The mother liquors were distilled at 0.3 mm Hg, (air bath). A liquid amounting to 10–40 % was collected in the trap at room temperature. This liquid showed a weak but very characteristic U.V.-spectrum, compare Fig. 3. In contrast to all other essential oils from composité plants so far investigated in this laboratory this chromophor has ethylenic spacing:

$E_{1\text{cm}}^{1\%}$	67	78	57	550	
$\lambda$	3091	2959	2822	2300	ÅU
$\nu \cdot 10^{-12}$	970.5	1013.8	1063.1		
$\Delta\nu$	43.3	49.3			

The fractions boiling between 40 and 90°, which contained the acetylenic esters, were then tested in a cooling bath ( $\text{CO}_2$  + acetone). If the fraction solidified readily, it was dissolved in petroleum ether and left for crystallization at first at 0°, the mother liquors then at  $-12^{\circ}$  and  $-30^{\circ}$ . The remaining liquids were then diluted with petroleum ether and chromatographed on Floridin XXX using petroleum ether as solvent and mixtures of benzene and petroleum ether as eluants. The stability of these highly unsaturated compounds is better on Floridin XXX than on alumina; however, although the resolving power is inadequate with both of them, we have not been able to find better adsorbents. Repeated chromatography on Floridin XXX gave concentrates which spectroscopically was estimated to contain 82 % 8-*cis*- $\alpha,\beta$ -dihydromatricaria ester and 18 % matricaria ester. As essential oils or concentrates containing as much as 18 % 2-*cis* - 8-*cis* matricaria ester crystallize readily from hexane solution, whereas these concentrates deposited no crystals, it was obvious that some other stereoisomers of matricaria ester were present. Both the known stereoisomers<sup>6</sup>, viz. 2-*cis*: 8-*trans* and 2-*trans*: 8-*trans* resemble in their U.V.-spectra 2-*cis*: 8-*cis* very much, but the inflexion at 3 600 ÅU is narrower and the first peak at 3 360 ÅU more pronounced in the first named. In actual fact these details were clearly shown by these *Amellus*-concentrates. As 2-*trans*: 8-*trans* esters are still more insoluble than 2-*cis*: 8-*cis*, this modification could be excluded. The 2-*cis*: 8-*trans* matricaria ester m.p.  $+2^{\circ}$  is readily soluble in petroleum ether, a crystallization of this ester from a solvent being so far unknown.

For this reason the chromatographic fractions with the highest matricaria peaks were saponified under nitrogen at 0° C and the free acids recrystallized several times from petroleum ether. The m.p. asymptotically approached the broad m.p. of 2-*cis*: 8-*trans* matricaria acid: 83–91° and Debye-Scherrer diagrammes, most kindly taken by Dr. H. Sörum, proved the identity.

The chromatographic fractions most enriched in the dihydromatricaria ester were saponified as well, and by repeated crystallizations from petroleum ether we succeeded in removing the 2-*cis*: 8-*trans* matricaria acid from the 8-*cis*- $\alpha,\beta$ -dihydroacid. Although the U.V.-spectrum of our purest preparation of the 8-*cis* dihydroacid has a broader "foot" on the long wave length side than the synthetic acid, the 5 sharp maxima and the extinction coefficients were in perfect agreement (compare Fig. 2). As the matricaria peak at 3 360 ÅU stands out markedly at concentrations down to ½ %, this contamination, in our best specimen, must be very low. The m.p. of this best fraction was 64.1–64.5 sharply, that is some 2–3° higher than found for the synthetic acid. The mixed m.p.

was intermediate (62–62.3°) and as a reinvestigation of the synthetic acid showed that this acid in part isomerizes to the corresponding *trans*-acid with depression of the m.p. for low concentrations of the *trans*-acid this difference in m.p. ought to be caused by a small contamination of *trans* acid in the synthetic preparation.

#### SUMMARY

Further investigations of the essential oil of scentless mayweed (*Matricaria inodora* L.) have demonstrated that this oil contains besides the main component 2-*cis*:8-*cis* matricaria ester, the aliphatic sesquiterpene "natural farnesene", 2-*cis*:8-*trans*-matricaria ester and 8-*cis*- $\alpha,\beta$ -dihydromatricaria ester. The isolation of the new acetylenic esters was facilitated through the high concentrations in which they occur in some essential oils of the genus *Amellus*. Spectroscopically the 8-*cis*- $\alpha,\beta$ -dihydromatricaria ester was further demonstrated to be present in *Felicia tenella* (L.) Nees in *Cephalophora aromatica* Schrad. and *Solidago sempervirens* L. Obviously these new acetylenic compounds are widely distributed amongst essential oils of plants belonging to the plant family of the compositae.

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