

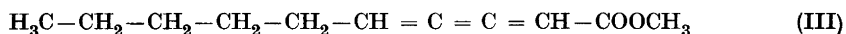
## Studies Related to Naturally-Occuring Acetylene Compounds

### V. \* Dehydro Matricaria Ester (Methyl *n*-decene-triynoate) from the Essential Oil of *Artemisia vulgaris* L.

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The two plants, *Lachnophyllum gossypinum* Bge. and *Matricaria inodora* L., which belong to the family *Compositae*, have as components of their essential oils highly unsaturated derivatives of methyl caprate: viz. the lachnophyllum ester (I)<sup>1</sup>, the matricaria ester (II)<sup>2</sup>, and the cumulene hexahydro



matricaria ester (III)<sup>3</sup>. As mentioned in a previous communication of this series<sup>4</sup>, a crystalline compound m. p. 32.5–33° belonging to this enyne class was isolated in a pure state, as early as 1907, from the essential oil of a plant from Java, which the collector Dr. Carthaus named *Artemisia lavandulaefolia*<sup>5</sup>. Chemical investigations on this crystalline compound were reported in 1910<sup>6</sup>. The composition was given as C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>, and with our knowledge of the properties and reactions of the compounds I–III it became obvious that the compound C<sub>12</sub>H<sub>14</sub>O<sub>2</sub> described by Dr. Carthaus must be closely related. Consequently, we were anxious to re-investigate the constituents of *Artemisia* oil. The paper published in 1910 states, however, that the plant must have been erroneously identified, as *A. lavandulaefolia* does not occur in Java, and in

\* It is considered convenient to classify our papers on natural enynes under a common heading. The first communication of this series is reference 2 of this paper, the second, R. Holman and N. A. Sørensen, *Acta Chem. Scand.* 4 (1950) 416, the third reference 4, and the fourth reference 3 of this paper.

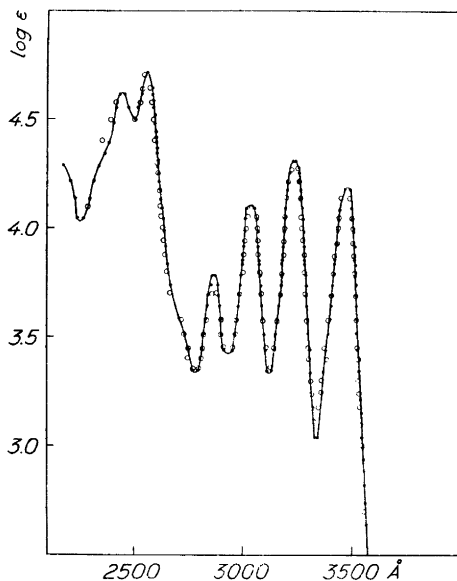


Fig. 1. Ultraviolet absorption of dehydro-matricaria ester in hexane.

— — — — — from the essential oil of *Artemisia vulgaris* L.  
 ○ ○ ○ ○ from cold extracts of *Artemisia vulgaris* L.

$$(\epsilon = \frac{\log I_0/I}{c \cdot d}, c \text{ in mol/l, } d \text{ in cm})$$

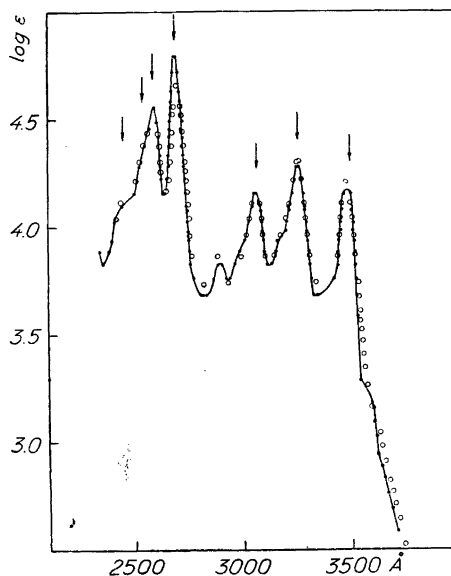
fact Dr. H. M. van Raalte of Treub Laboratorium, Bogor-Djawa (formerly Buitenzorg) states in a private communication that *A. lavandulaefolia* does not exist at all. This name has arisen through a misunderstanding of a Latin term used by N. L. Burman in his *Flora Indica*. According to Dr. van Raalte only *Artemisia vulgaris* L. does occur in Java.

The essential oil of *Artemisia vulgaris* L. and some of its subspecies and variants, which have had a widespread use in medicine, have been investigated a number of times and the older investigations have been summarized by Gildemeister and Hoffmann<sup>7</sup>. The only definitely identified components of the essential oil are cineol and thujyl alcohol.

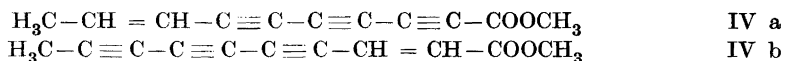
In anticipation of a forthcoming investigation of *A. vulgaris* L. from Java, we have carried out a reinvestigation of the essential oil of European mugwort (*Artemisia vulgaris* L. s. s.). The oil from the leaves and flowering parts of the plant does not show any longwave U. V.-absorption and consequently must be devoid of highly unsaturated compounds such as I—III. The essential oil from the root, however, contains at least three different compounds of this class, two of which crystallize well, but are quite different from the crystalline compound  $C_{12}H_{14}O_2$  described by Dr. Carthaus. Steam distillation of roots yields an oil, which is remarkably dark in colour and which deposits crystals immediately on cooling, a behaviour observed as long ago as 1826<sup>8</sup>.

Fig. 2. Ultraviolet absorption of "Centaur X" fractions.

— · — · — · best chromatographic fraction from mugwort root oil  
 ○ ○ ○ ○ same fraction distilled 65°/10<sup>-4</sup> mm Hg  
 arrows: "Centaur X" maxima after Löfgren<sup>9</sup>



Crystallisation from petroleum ether gave slightly yellow crystalline material of m. p. 112° C which had the composition C<sub>11</sub>H<sub>8</sub>O<sub>2</sub>, thus containing two hydrogen atoms less than the matricaria ester. On hydrogenation it consumed 7 moles of H<sub>2</sub>, the perhydro compound obtained being methyl caprate as is the case with matricaria ester. The only remaining question then is the positions of the ethylenic and the three acetylenic bonds in the carbon chain. It seems probable on account of the high m. p. and the pronounced acetylenic fine structure of the long wave U. V.-absorption band — compare Fig. 1 — that the three acetylenic links lie in conjugation, and so there are the two possible formulae, IV a and IV b.



The choice between these two possibilities will be treated in a following communication.

By extraction with acetone at room temperature and chromatographic analysis of the extract we have established that this dehydro matricaria ester is a genuine component of the mugwort root oil.

Simultaneously, spectrographic investigation of the products from the chromatogram revealed that the mugwort contains at least two more compounds of the same class. Whereas petroleum ether elutes only a sesquiterpene,

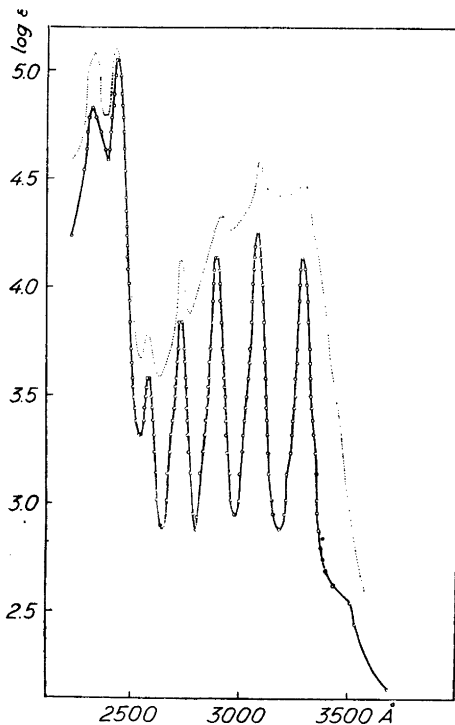


Fig. 3. Ultraviolet absorption of the compound  $C_{12}H_{10}O$  from mugwort root oil in hexane (—○—○—○—) and of its hydrazone with phenylhydrazine *p*-carbonic acid in abs. ethanol (.....)

petroleum ether containing 20 % of benzene takes out a liquid component with a U. V.-spectrum as sharply structured as that of dehydromatricaria ester (compare Fig. 2).

In Fig. 2 the arrows show the positions given by Löfgren<sup>9</sup> for the U. V.-maxima of "Centaur X", a substance of unknown structure discovered by Löfgren in many *Centaurea* species. As will be seen, five of the maxima given by Löfgren coincide with the maxima from this mugwort fraction, and, as far as we can judge from his photographs, the relative intensities of these five bands, which are the main bands, are also in complete agreement. It may be mentioned that a very similar spectrum has been obtained from products prepared by chromatography of extracts of *Matricaria inodora* flowers and from the root of *Erigeron canadense* L., so that we are inclined to suppose that Löfgrens "Centaur X" has a rather widespread occurrence in compositae plants.

Whereas the "Centaur X" extracts from *Matricaria inodora* flowers were very dilute, the mugwort gave more concentrated solutions, with high extinction coefficients. Since "Centaur X" is predominantly epiphasic between petroleum ether b. p. < 40° C and 92 % methanol, whereas matricaria ester and dehydro matricaria ester are predominantly hypophasic, "Centaur X"

should be a highly unsaturated hydrocarbon. A preliminary analysis carried out on an insufficient amount of material supports this assumption. "Centaur X" may be distilled without decomposition at 65° C 10<sup>-4</sup> mm Hg.

The third enyne component of the mugwort oil is eluted along with the dehydro matricaria ester and this mixture is rather difficult to separate because mixed crystals form readily. Only very small amounts of the new compound, which crystallises in colourless needles m. p. 52—52.5° C, have been isolated free from dehydro matricaria ester. The U. V.-spectrum of this third component has the most outstanding fine structure of them all (compare Fig. 3). The fine structure is one of the most beautiful so far observed in solution spectra. The spectrum of benzene, for example, which is well known for the fine structure of its weak long wave U. V.-bands has a half width of only 22 Å, and a ratio (at room temperature) between a maximum and the following minimum of about 4. The corresponding figures for the third component of the mugwort oil are 45 Å and not less than 19.

The elementary composition seems to be C<sub>12</sub>H<sub>10</sub>O and the oxygen atom is present as a carbonyl group as the compound gives a beautifully crystalline hydrazone with phenylhydrazine *p*-carbonic acid. The pronounced acetylenic spacing in the fine structure of the long wave U. V.-spectrum indicates a poly-yne structure. In a carbonyl compound C<sub>12</sub>H<sub>10</sub>O this implies an aliphatic structure containing 14 hydrogen atoms less than the corresponding saturated carbonyl compound. We are inclined to believe that the compound C<sub>12</sub>H<sub>10</sub>O, like dehydro matricaria ester, contains 3 /≡ and 1 /¯. We are returning to the structure of this interesting compound as soon as more starting material is available.

#### EXPERIMENTAL

40 kg of the flowering tops of common mugwort was distilled with steam. The essential oil could be separated directly and amounted to 20 g. This flower oil does not solidify at - 15° C and is devoid of selective absorption above 2 900 Å although the spectrum has a weak inflection, at ca. 3 400 Å.

5.5 kg of the root of mugwort was distilled in the same manner and yielded 1.1 g of yellow-brown oil which was taken up in petroleum ether. The pale yellow needles which separated readily from the petrol solution had m. p. 104—5°, raised by recrystallization to the constant value 113°.

U. V.-spectrum in hexane solution, Fig. 1.

$\lambda_{\max}$	3 486	3 240	3 037	2 867	2 560	2 445
$\nu_{\max} \times 10^{-12}$	860.6	925.9	987.8	1 046.4	1 171.9	1 227.0
$\Delta\nu$ »		65.3	61.9	58.6		

C <sub>11</sub> H <sub>8</sub> O <sub>2</sub> (172.1)	Calc.	C = 76.73	H = 4.68
	Found	» = 76.8	» = 4.9

71.4 mg was hydrogenated at room temperature with 110 mgs of  $\text{PdO}_2\text{-CaCO}_3$  catalyst. The activity of the catalyst was somewhat too great for the analytical measurement of the hydrogen consumption, as the initial rate of absorption (12 ml/min) made the zero reading somewhat uncertain.

$\text{C}_{11}\text{H}_{18}\text{O}_2$ , 3 / $\equiv$ , 1/ $\overline{\equiv}$	Calc.	71.7 ml $\text{H}_2$ (758, 20.5°)
	Found	67.0 ml $\text{H}_2$ (758, 20.5°)

This corresponds to  $6.53/\overline{\equiv}$ .

The perhydro compound which had the characteristic fine strawberry odour of methyl caprate was saponified. The crude acid obtained melted at  $27-28^\circ\text{C}$ , and was at once converted via the acid chloride into the amide, m. p.  $96^\circ$  corr., undepressed by an authentic specimen of capric amide.

1.84 kgs of mugwort root was extracted with acetone at room temperature for 2 days. The acetone extract was diluted with distilled water and extracted with petroleum ether in a atmosphere of carbon dioxide. The combined petroleum ether extracts were cautiously shaken with distilled water until free of acetone, dried over a little anhydrous sodium sulphate, and concentrated below  $25^\circ\text{C}$ .

All long-wave absorbing substances were adsorbed when this solution was passed through a column of slightly deactivated alumina. The petroleum ether filtrate gave a colourless liquid residue, distilling at about  $50^\circ/10^{-3}$  mm Hg.

Dispersion of sesquiterpene from *Artemisia vulgaris* L.

$$d_4^{20} = 0.9270 \quad \lambda_0 = 962.4 \text{ \AA} \quad R_\lambda = \infty = 62.9625$$

$\lambda$	$n_\lambda^{20}$	$R_\lambda$ , obs.	$R_\lambda$ , calc.
6678.1	1.49540	64.29	64.30
5895.9	1.49905	64.69	64.69
5875.7	1.49918	64.70	64.70
5015.6	1.50526	65.37	65.37
4921.9	1.50613	65.46	65.46
4713.1	1.50830	65.70	65.70
4471.5	1.51122	66.02	66.02

$R_D$  tricyclic sesquiterpenes = 64.40

"Centaur X" fraction.

A 20 % benzene/petroleum ether mixture eluted a liquid compound with a remarkable fine structure spectrum, the position of the main bands being in excellent agreement with those recorded for the "Centaur X" of Löfgren<sup>9</sup>. This liquid compound may be distilled unchanged at  $10^{-4}$  mm/ $65^\circ$  (air bath temperature), but the distillation path, must be short, and the time of heating not too prolonged, to avoid serious decomposition. As the extinction coefficient of the distillate is identical with that of the entire 20 % benzene/petroleum ether eluate, "Centaur X" appears to be the only substance eluted by this solvent mixture.

A semi-micro carbon and hydrogen analysis using an inadequate amount of substance gave  $C + H > 100\%$ .

U. V.-spectrum in hexane solution, Fig. 2.

$\lambda_{\max}$	"Centaur X" Löfgren <sup>9</sup> :	3 500, 3 260, 3 070,	2 690, 2 590, 2 540, 2 450	Å
$\lambda_{\max}$	Mugwort hydrocarbon:	3 485, 3 260, 3 064, 2 895,	2 694, 2 592, — —	»
$\nu_{\max} \times 10^{-12}$	»	: 860.8 920.2 979.1 1 036.3	1 113.6 1 157.4	cm <sup>-1</sup>
$\Delta\nu_{\max}$	»	: 59.4 58.9	57.2	

Spectrographical investigation of the epiphase and hypophase of the crude mugwort extract in petrol, revealed that "Centaur X" was predominantly epiphasic (to about 3/4) whereas the rest of the chromophoric substances were predominantly hypophasic (to about 4/5) between petroleum ether and 90 % methanol.

Benzene eluate: Benzene eluted a yellow fraction which crystallized after removal of the solvent *in vacuo*. This material exhibited not less than 8 sharp maxima between 2 320 and 3 490 Å. As different eluates and crude crystals gave identical spectral curves we were at first inclined to suppose that the fraction was homogeneous. However, the m. p. of the first crystals was not sharp (52–103°) and differed appreciably from preparation to preparation.

When a dilute solution of this material in petroleum ether was kept for some days at –15° pale yellow needles of dehydro matricaria ester, m. p. 113°, were deposited (spectrum: Fig. 1). The mother liquor gave crystals whose spectrum again showed 8 maxima with somewhat distorted extinction coefficients. It was found that the mixture could be separated by crystallization from ca. 50 % ethanol at –10° C; the third component then crystallized first in colourless needles, m. p. 52–52.5° C.

U. V.-spectrum of its hexane solution Fig. 3.

$\lambda_{\max}$	3 286,	3 081,	2 890,	2 725,	2 577,	2 425,	2 310	Å
$\nu_{\max} \times 10^{-12}$	913.3	973.7	1 038.1	1 100.9	1 164.1	1 237.1	1 298.7	cm
$\Delta\nu_{\max} \times 10^{-12}$	60.4	64.4	62.8	63.2		61.6		»

19.6 mg gave	60.6 mg CO <sub>2</sub>	11.15 mg H <sub>2</sub> O
C <sub>12</sub> H <sub>10</sub> O	Calc. C 84.66	H 5.92
	Found » 84.3	» 6.32

2.9 mg gave no methoxyl in the semimicro apparatus. (Test with 0.73 mg matricaria ester: Found: OCH<sub>3</sub> 15.6 %, calc. 17.8 %.)

With phenylhydrazine *p*-carbonic acid in diluted ethanol at room temperature the compound C<sub>12</sub>H<sub>10</sub>O slowly yielded beautiful yellow crystals insoluble in petroleum ether. At 180° the hydrazone turns dark and decomposition takes place rapidly, but the substance does not liquify at 230° C.

The U. V.-spectrum in abs. ethanol does not show the beautiful fine structure of the compound C<sub>12</sub>H<sub>10</sub>O (compare Fig. 3) but the maxima do occur at the same wavelengths.

## SUMMARY

Re-investigation of the essential oil from the root of common mugwort (*Artemisia vulgaris* L.) has shown that the readily crystallizing substance in this oil — noticed as early as 1826 — is a methyl *n*-decene-triynoate (IV) or dehydro matricaria ester. Chromatographic analysis of acetone extracts from mugwort root demonstrated that this extremely unsaturated compound occurs as such in the plant.

Together with dehydro matricaria ester, the mugwort root contains a highly unsaturated hydrocarbon with a U. V.-spectrum very similar to that of "Centaur X" of Löfgren and a crystalline acetylenic carbonyl compound,  $C_{12}H_{10}O$ , m. p. 52—52.5° C.

## REFERENCES

1. Wiljams, W. W., Smirnov, V. S., and Goljmov, V. P. *J. Gen. Chem. (U. S. S. R.)* **5** (1935) 1195.
2. Sørensen, N. A., and Stene, J. *Ann.* **549** (1941) 80.
3. Sørensen, N. A., and Stavholt, K. *Acta Chem. Scand.* **4** (1950) 1080.
4. Bruun, T., Haug, C. M., and Sørensen, N. A. *Acta Chem. Scand.* **4** (1950) 850.
5. *Jaarb. Dep. Landb. in Ned. India*, Batavia (1907) 66.
6. *Jaarb. Dep. Landb. in Ned.-Indie*, Batavia (1910) 55.
7. Gildemeister, E., and Hoffmann, Fr. *Die ätherischen Öle III* Miltitz (1931), pp. 1018—1020.
8. Bretz and Elieson *Taschenbuch für Chemiker und Apotheker* (1826) p. 61, compare ref. 7.
9. Löfgren, N. *Acta Chem. Scand.* **3** (1949) 82.

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