

**Studies Related to Naturally Occurring Acetylene
Compounds. XIII. The Occurrence of *trans*-Methyl-*n*-Dec-
2-en-4 : 6 : 8-triyonate in the Genus *Tripleurospermum*
Schultz Bipontinus**

JÖRGINE STENE SÖRENSEN, TORGER BRUUN, DAGNY HOLME
and NILS ANDREAS SÖRENSEN

Institutt for Organisk Kjemi, Norges Tekniske Högskole, Trondheim, Norway

The matricaria ester (I), named so after the discovery of this substance in

$$\text{CH}_3\text{—CH=CH—C}\equiv\text{C—C}\equiv\text{C—CH=CH—COOCH}_3 \text{ (2-}i\text{cis, 8-}i\text{cis) (I)}$$

scentless mayweed¹ (*Matricaria inodora* L) is the acetylenic compound most frequently found in the essential oils of plants belonging to the family of the *Compositae*. It is, however, not in the tribus *Anthemideae* to which *Matricaria* belongs (subtribus *Chrysantheminae*) that (I) has been found to be of general occurrence, but in some genera within the tribus *Astereae*, especially *Amellus*², *Erigeron*^{3,4} and *Felicia*².

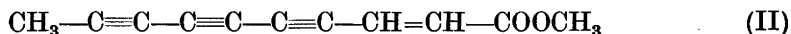
We have, of course, long sought for the matricaria ester in other members of the genus *Matricaria*, but for many years without success. As mentioned in the ninth communication of this series² the oil of chamomile (from *M. chamomilla* L.) is devoid of matricaria ester and other acetylenic compounds. *M. discoidea* DC, which in the last century has invaded large areas of Norway, gives large amounts of essential oil. The dominating chromophores seem to be derivatives of 7-hydroxy-coumarines. Professor Dr. G. Ledyard Stebbins jr. most kindly provided a seed sample of *M. occidentalis* Greene which is endemic to some districts of California. *M. occidentalis* which botanically is closely related to *M. discoidea* DC gave an essential oil, the UV-spectrum of which agreed closely with that of *M. discoidea* in the main chromophores.

Coumarin itself was isolated from *M. glabra* (Lag) Ball from the Mediterranean. In South-Africa there occurs a number of *Matricaria* species, most of them in modern botanical literature transferred to the genus *Pentzia*. Through the most kind assistance of Director R. H. Compton, National Botanic Gardens, Kirstenbosch and chem.eng. F. Hougen, we obtained seed samples of *M. globifera* Fenzl. and *M. multiflora* (Thunb.) Fenzl ex Harv. & Sond. Of these

only *M. multiflora* seemed to contain acetylenic compounds. But the acetylenic compound which is present in the root of *M. multiflora* is different both from (I) and from any other of the acetylenic compounds so far isolated in a pure state. Finally, when in 1952 we cultivated *M. oreades* Boiss. we again obtained a *Matricaria* which contained large amounts of (I) both in the flowers and in the leaves. At that time we became aware, through a note in the newspapers, of a dissertation by the Swedish botanist Gunnar Harling⁵ concerning the embryology of different subtribes of the *Compositae*. It turned out that Dr. Harling had treated very extensively the two tribes *Asteraea* and *Anthemideae* which had been investigated chemically in our institute. It was very interesting to experience that Dr. Harling for embryological reasons had separated *M. inodora* and *M. oreades* from the other *Matricaria* and transferred both to the genus *Tripleurospermum*, erected by C. W. Schultz Bipontinus in 1844 on the basis of the structure of the seed wall and the achenes; a separation partly recommended by other specialists on the *Compositae* in the last century^{6,7}. To this Genus *Tripleurospermum* Harling further transferred for embryological reasons a plant mostly named *Chrysanthemum caucasicum* Pers.

If this transfer was justified, it was to be expected that *Chrysanthemum caucasicum* should behave chemically as *M. inodora* and *M. oreades*. Through the obligingness of the botanical garden of the University of Copenhagen we obtained a small sample of fresh *Chr. caucasicum* plants. The leaves, which constituted most of this late-autumn sample (150 g), furnished appreciable amounts of (I), which according to the U.V.-spectrum is the only acetylene present in this crude essential oil. Only traces of roots (7.4 g) were present in the small sample; the crude essential oil showed a very broad absorption in U.V. from 3 800 ÅU with very little fine structure. This — not very promising spectrum — agreed closely with that of the oil from the root of *M. oreades*. Since both these samples were very small, we turned to the root of *M. inodora* L. The root of scentless mayweed had never been investigated separately in our laboratory. All investigations on scentless mayweed had been carried out before the investigation of European mugwort (*Artemisia vulgaris* L.) had disclosed that the root chemically may differ completely from the rest of the plant.

The root from scentless mayweed afforded a crude oil with the same broad and uncharacteristic spectrum as obtained from *M. oreades* and *Chrysanthemum caucasicum*. It turned out, however, that the component responsible for a small, sharp peak at 2 556 ÅU was very insoluble in petroleum ether. After one recrystallization the m.p. was constant at 105.5° C. The spectrum of this crystalline substance is reproduced in Fig. 1. In this spectrum the maxima 3 440, 3 210, 3 012, 2 832 and 2 556 ÅU coincided with the maxima given by Christensen and Sørensen for the *trans*-isomer of methyl-*n*-dec-2-ene-4:6:8-triynoate (II) m.p. 95.5°



the only one of the four possible dehydromatricaria esters so far prepared synthetically. The spectrum of synthetic (II) differed in the lack of a maximum at 2 445 ÅU and in the occurrence of a small additional maximum on the long-wave side at 3 630 ÅU. As the coincidence in the 5 main maxima and in the

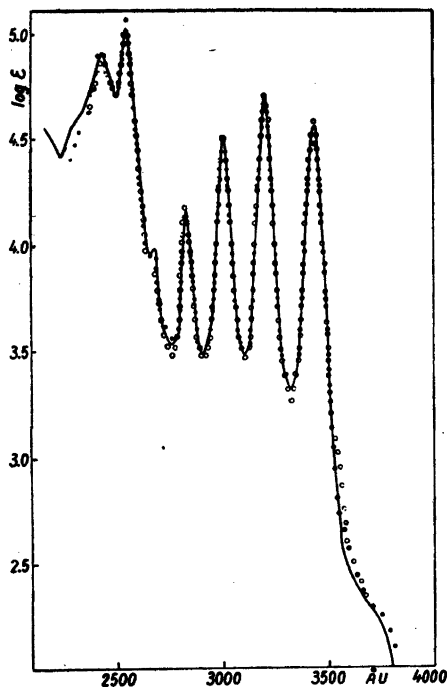


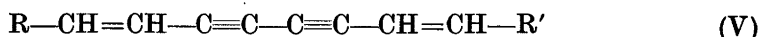
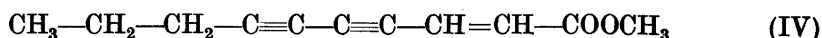
Fig. 1. Ultraviolet absorption in hexane of methyl-n-dec-2-ene-4 : 6 : 8-triynoate.

— synthetic
 ○ ○ ○ ○ from root of *Matricaria inodora* L.
 ● ● ● ● from the root of *Matricaria oreades* Boiss.

general shape of the curve was quite surprising, the original spectrograms taken on synthetic (II) were inspected in the plate archive. It turned out that the maximum at 2 445 ÅU was present on the spectrograms of both synthetic preparations. The position of this band falls in the border region between the Fe-W spectra used for wave-lengths >2 400 ÅU and the Ni spectra used for the region 2 150—2 450 and through this position in the border region this maximum had been completely overlooked. The 3 630 ÅU maximum was definitely present in both preparations and so only the possibility remained that this extra maximum belonged to an unknown impurity which at the same time depressed the m.p. from 105.5° to 95.5°. Primarily, it did not seem very likely that an impurity should be present in exactly the same amount in two parallel syntheses where the isolation of (II) was achieved through chromatography. The resynthesis of (II), carried out by one of us (T. B.) under slightly altered coupling conditions, gave appreciably higher yields and this time (II) was easily purified to m.p. 105° and the U.V.-spectrum of this pure substance was completely identical. (cf. Fig. 1) with that of the substance from the root of scentless mayweed and the identity of the two preparations was further confirmed by a mixed m.p. determination.

The isolation of pure II, m.p. 105.2—105.5° from the root of *M. oreades* was successful too. The amount of oil from *Chrysanthemum caucasicum* was, however, too small to allow the isolation of any pure compound from the complex mixture present. A large scale cultivation of *Chr. caucasicum* in the sum-

The lachnophyllum ester ³ (IV) and symmetrical diene-diyne compounds (V) ^{10,11} very nearly agree in the position of the long-wave band group.



The first maximum is found at about 3 100 ÅU, but the positions of the short-wave band group differ not less than 200 ÅU.

In the same way the *trans*-dehydromatricaria ester (II) and the "Centaur-X"-class hydrocarbons ^{8,12} (VI) agree in the long-wave group, but differ 130 ÅU in the strong, short-wave band group.



It has turned out that the carbomethoxy group is spectroscopically nearly equivalent to one double bond in en-yne as in polyenes ^{13,14,15}. Obviously then (III) should agree in the position of both bond groups with the symmetrical "Centaur-X"-class (VI). So these spectral rules — which in recent months have been strengthened through the outstanding constitutional work of B. Lythgoe ¹⁶ on the diyne-triene toxins of *Cicuta* and *Oenanthe* — make very probable that the constitution of the dehydromatricaria ester from *Artemisia vulgaris* is the 2-*cis*-isomer of (II), that is the *cis*-isomer of the second dehydromatricaria ester found in nature, which so far is known only from the oils from roots of three members of the genus *Tripleurospermum*.

The U.V.-spectrum of (II) has one of the most outstanding fine-structures reported for solution spectra. As the crude oils from the root of the three investigated members of the genus *Tripleurospermum*, as mentioned above, show very broad and undistinctive U.V.-spectra it will be clear that (II) is only a minor component of these oils. The oils from the roots of *M. inodora* and *M. oreades* have been separated into different fractions by chromatography on alumina as described in the experimental part. Two of the components have been obtained in a crystalline state, *viz.* from the 10—25 % benzene in petroleum ether eluates a substance of m.p. 47.5—48.5° with a rather unsharp spectrum (*cf.* curve 3A), and the dehydromatricaria ester (II) which is concentrated in the 50 % benzene petroleum ether eluates. With *M. oreades* root there has been obtained in the 75—90 % benzene-petroleum ether eluates another new compound, m.p. 44—45°, again with a rather undistinctive U.V.-spectrum (curve 3B) with the first maximum at 3 650 ÅU. These two compounds seem to be the main components and it will be obvious that a mixture of these two will give a very broad and very undistinctive spectrum.

Both these substances are very unstable; we hope to obtain sufficient quantities of oil in the summer season of 1953 to get some insight into their constitutions. These preliminary investigations of the oil of the roots of *Matricaria inodora* and its relatives — which in agreement with the proposal of Harling undoubtedly should be transferred to the genus *Tripleurospermum* — demonstrate on the one hand that the composition of the root differs remarkably from that of the overground part of the plants and on the other hand that the roots are good sources for new members of the naturally occurring acetylenic compounds.

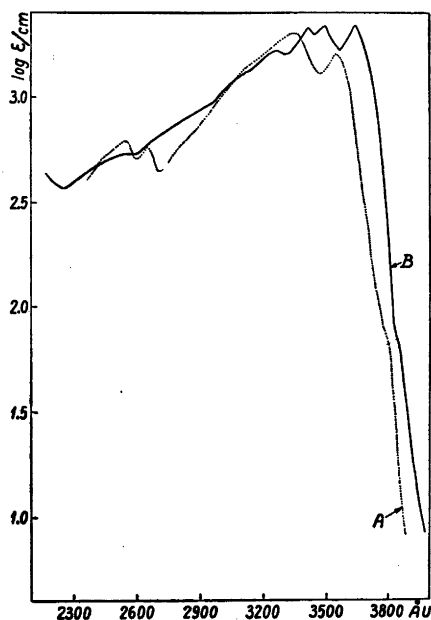


Fig. 3. Ultraviolet absorption in hexane of

- A: Substance m. p. 47.5–48.5 from *Matricaria inodora* L.
 B: » » 44–45 » » *oreades* Boiss.

EXPERIMENTAL

1. *Matricaria inodora* L. Root. Portions of fresh root were collected in the vicinity of Trondheim at the end of October. 2.5 kg were distilled with steam giving 1.1 g of oil, semi-solid in the cold. U.V.-spectrum of the crude oil: very broad absorption from 3 800 with only a small peak at 2 555 Å. When the oil was dissolved in petroleum ether slightly yellow crystals separated, which after recrystallization from ether-petroleum ether melted constantly at 105.5°–106° (corr.). Mixed m.p. with synthetic methyl-*n*-dec-2-en-4 : 6 : 8-triynoate 105.5°.

Another portion of 480 g of roots was extracted with acetone in the cold. The acetone extract was diluted with much water and extracted with ether. The ether solution was washed free from acetone, dried and evaporated in a vacuum at room temperature. Residue, 72.4 mg, yellow oil, which solidified in the cold. Methyl-*n*-dec-2-en-4 : 6 : 8-triynoate was isolated as above, m.p. 105.5°, so there should be no doubt that this dehydromatricaria ester is no artefact.

All mother liquors were combined and the solvents removed. There followed chromatography of the petroleum ether solution on slightly de-activated alumina followed by elution with mixtures of benzene-petroleum ether. In the eluates with 25–40 % benzene-petroleum ether a substance was concentrated with the spectrum given in curve 3A. A very similar chromophore has been observed in the root of *Rudbeckia hirta*, but as this chromophore is eluted with the petroleum ether washings and so far has remained liquid they are scarcely identical. This substance can be distilled at 50–60°/0.0001 mm, but decomposes if the temperature exceeds 70°. The distillate solidified; after recrystallization from petroleum ether, the m.p. was 47.5–48.5°. The substance is rather unstable and the amounts obtained pure were too small for further experiments.

2. *Matricaria oreades* Boiss. Cultivated at Trondheim 1951/52 from a seed sample from *Botanischer Garten München-Nymphenburg*.

a) Flowers (115 g) were distilled with steam; the essential oil, 68.5 mg, crystallized at room temperature. The crystals were recrystallized once from petroleum ether, m.p. 34–34.5°, undepressed on admixture with authentic *matricaria* ester. The U.V.-spectra of these crystals and of the mother-liquor were measured. The spectrum of the former was completely identical with that of *matricaria* ester, that of the latter was conformed with the *matricaria* ester spectrum. Thus no other chromophore seems to be present in this oil.

b) Leaves (1 600 g) were distilled with steam. This essential oil (1.3 g) solidified in the cold; the U.V.-spectrum of the crude oil was not entirely identical with that of *matricaria* ester, but crystallization from petroleum ether at once afforded pure *matricaria* ester.

c) Roots (460 g) were also distilled with steam. The essential oil (1.9 g) was semisolid at room temperature. The U.V.-spectrum of the crude oil: strong absorption from 3 800 ÅU downwards with undistinct maxima at 2 550 and 2 430 ÅU. The oil was dissolved in petroleum ether and then at once there deposited slightly yellow crystals, which were recrystallized from ethanol-water, m.p. 105–105.2°. Spectrum curve 1.

ϵ_{\max}	35 970	45 290	32 810	15 170	8 630	106 200	71 800
λ_{\max}	3 435	3 204	3 008	2 835	2 680	2 550	2 447
$\nu_{\max} \cdot 10^{-12}$	873.4	936.3	997.3	1 058.2	1 119.4	1 176.5	1 226.0
$\Delta\nu \rightarrow$	62.9	61.0	60.9	61.2		49.5	

The mother liquors were chromatographed on alumina of the same quality as above. The chromophore observed with *M. inodora* was concentrated in the 10 % benzene-petroleum ether eluates. Traces of methyl-*n*-dec-2-ene-4 : 6 : 8-triynoate followed in the eluates with about 1 : 1 benzene-petroleum ether. In the 70 % benzene-petroleum ether eluates there was concentrated a new substance with the spectrum given in Fig. 3B. This fraction distilled at 90°/0.0001 mm; the distillate was solid and was recrystallized from petroleum ether, m.p. 44–45°.

3. *Chrysanthemum caucasicum* Pers. The Botanical Garden at the University of Copenhagen most amiably sent us a small sample of the living plant October 1952. Only traces of flowers were present at this late time. The leaves and the stem were separated from the root and distilled with steam, the essential oil (6.3 %) partly solidified in the cooler. One single crystallization from petroleum ether furnished pure *matricaria* ester, m.p. 34.6–34.8°, undepressed on admixture with authentic *matricaria* ester. U.V.-spectra were measured both of the pure crystals and of the mother liquors. That of the former was identical with the prototype spectrum, that of the latter revealed that the *matricaria* ester was the only chromophore present in this essential oil.

4. *trans*-Methyl-*n*-dec-2-ene-4 : 6 : 8-triynoate. Methyl-pent-2-en-4-ynoate (3.75 g) and pentadiyne (2.2 g) in a solution of copper(I)chloride (49.5 g) ammonium chloride (76.4 g) and iron(III)chloride (4.0 g) in water (190 ml) were coupled oxidatively by passing air through the solution for 6.5 hours. Isolation of the methyl-*n*-dec-2-ene-4 : 6 : 8-triynoate as in ⁹ followed by crystallization from petroleum ether, m.p. 105–106°, yielded approximately 0.5 g of crude ester.

SUMMARY

trans-Methyl-*n*-dec-2-ene-4 : 6 : 8-triynoate (II) was resynthesised in better yield which enabled the removal of an impurity present in the preparation described in the first synthesis ⁹. This dehydromatricaria ester was further isolated from the essential oil of the root of *Matricaria inodora* L. and *M. oreades* Boiss. and proved by isolation from acetone extracts in the cold to be no artefact. The corrected spectrum of *trans*-methyl-*n*-dec-2-ene-4 : 6 : 8-triynoate makes very probable that the dehydromatricaria ester m.p. 112.5° found in the root of *Artemisia vulgaris* L. is the 2-*cis*-isomer of (II).

The matricaria ester (I) has been isolated from *M. oreades* and *Chrysanthemum caucasicum* Pers. which, according to recent embryological investigations, together with *M. inodora*, belongs to a special genus *Tripleurospermum* Schultz Bipontinus. Six other species of the genus *Matricaria* belonging to other sections, of this genus have been investigated. They contained neither (I) nor (II) and most of them seemed quite devoid of acetylenic compounds altogether. The power to synthesise acetylenic compounds thus separates *Tripleurospermum* distinctly from *Matricaria*.

These investigations were made possible by grants from *Norges Almenvitenskapelige Forskningsråd*.

REFERENCES

1. Sørensen, N. A., and Stene, J. *J. Ann.* **549** (1941) 80.
2. Stavholt-Baalsrud, Kj., Holme, D., Nestvold, M., Pliva, J., Stene-Sørensen, J., and Sørensen, N. A. *Acta Chem. Scand.* **6** (1952) 883.
3. Sørensen, N. A., and Stavholt, Kj. *Acta Chem. Scand.* **4** (1950) 1575.
4. Tronvold, G. Moen, Nestvold, M., Holme, D., Sørensen, J. Stene, and Sørensen, N. A. *Acta Chem. Scand.* **7** (1953) 1375.
5. Harling, G. *Acta Horti Bergiani* **15** (1950) 185; *16* (1951) 1, 73.
6. Briquet, J., and Cavillier, F., in Burnat, E. *Flora des Alpes Maritimes* Vol. **6**, Part 1, 1916.
7. Hylander, N. *Uppsala Univ. Årsskr.* **1945**, No. 7.
8. Stavholt, Kj., and Sørensen, N. A. *Acta Chem. Scand.* **4** (1950) 1567.
9. Christensen, P. K., and Sørensen, N. A. *Acta Chem. Scand.* **6** (1952) 602.
10. Bruun, T., Christensen, P. K., Haug, C. M., Stene, J., and Sørensen, N. A. *Acta Chem. Scand.* **5** (1951) 1244.
11. Heilbron, I., Jones, E. R. H., and Sondheimer, F. *J. Chem. Soc.* **1947** 1587.
12. Jones, E. R. H., Whiting, M. C., Armitage, J. B., Cook, C. L., and Entwistle, N. *Nature* **168** (1951) 900.
13. Bruun, T., Haug, C. M., and Sørensen, N. A. *Acta Chem. Scand.* **4** (1950) 853.
14. Kuhn, R., and Grundtman, Chr. *Ber.* **70** (1937) 1323.
15. Skattebøl, L., and Sørensen, N. A. *Acta Chem. Scand.* **7** (1953) 1388.
16. Anet, E. F. L. J., Lythgoe, B., Silk, M. H., and Trippett, S. *J. Chem. Soc.* **1953** 309.

Received September 28, 1953.