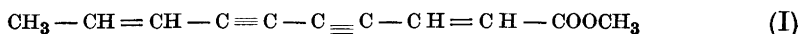


A Hexahydro Matricaria Ester—"Composit-Cumulene I" from Scentless Mayweed (*Matricaria inodora* L.)

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In 1940 Jörgine Stene and N. A. Sörensen¹ investigated the essential oil from the flowers of the very widely distributed weed, scentless mayweed (*Matricaria inodora* L.). To about 4/5 the oil from the flowers consisted of a new very highly unsaturated derivative of methylcaprate the matricaria ester (I) C₁₁H₁₀O₂



In a study of the occurrence of the matricaria ester (I) in the essential oil from Norwegian compositae plants we got indications in the U. V.-spectrograms of its occurrence in oils prepared from the leaves of some plants but absence from the corresponding flower oils. These observations gave rise to an investigation of the essential oil of the non floral parts of scentless mayweed. Whereas the flowers of the fresh plant have only a very faint odour, the tiny leaves of the fresh plant has a rather strong and not very pleasant odour. As is the case when the flowers are steam distilled, the note is strikingly altered; the steam distilled oil possesses a rather mild and sweet smell. The oil from the stems and leaves proved as rich in matricaria ester as the flower oil, the yield of essential oil however amounted only to 1/2 of that from the flowering part of scentless mayweed.

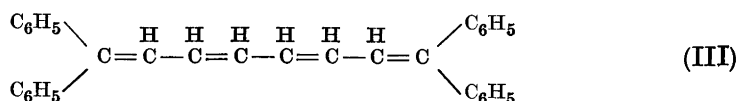
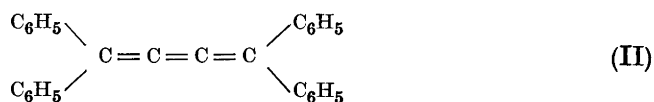
Whereas the mother liquor from the matricaria ester crystallizations of the flower oils has a faint straw-yellow tint remaining approximately constant as the mother liquors are concentrated, the mother liquor from the leave oil got remarkably orange in colour. U. V.-spectrograms indicated dominating amounts of matricaria ester compounds contaminated with small amounts of a compound with rather strong absorption about 3500—3700 ÅU. By chromatography of a petrol solution on Al₂O₃ all unsaturated compounds was

adsorbed, pure benzene eluted the matricaria ester and the contaminant was eluted with alcohol.

The new compound was a yellow oil, distilling at the same temperature — air bath about 50° at 0.0001 mm — as the matricaria ester itself. It analysed $C_{11}H_{16}O_2$, that is a hexahydro matricaria ester. Since the oil was yellow, quite pure matricaria ester, however, colourless, the possibility of a hexahydro matricaria ester of yellow colour was at the first instant rather improbable. On micro-hydrogenation, however, the yellow oil consumed exactly 3 moles hydrogen and gave a colourless oil of the very characteristic “strawberry”-odour of methylcaprate. Unfortunately the amount of hydrogenation product available was insufficient for a more exact identification.

Fig. 1 shows the U. V.-spectra of matricaria ester and of the new compound for which we propose the name “Composit-cumulene I”. Then in our opinion, the scarce facts given above seems to necessitate the assumption of a cumulene structure for the new compound. As stated elsewhere the long-wave U. V.-spectrum of matricaria ester lies in the same region as the spectrum of decatetraenoic acid, and the hydrogenation of one of the double bonds in decatetraenoic acid to get the composition of a hexahydro matricaria ester should displace the U. V.-spectrum at least 200 ÅU towards shorter wavelengths. Only the cumulation of the three remaining double bonds and a conjugation of the cumulene system with the carboxyl group may explain the observed composition and U. V. spectrum.

Aliphatic cumulenes (higher than the allenes) are unknown and so there is some lack of suitable comparison substances. The excellent synthetic work of Kuhn *et. al.*² has, however, presented a series of aromatic cumulenes the simplest member being tetraphenyl-butatriene (II)



The spectra of these aromatic cumulenes are characterized through one broad and intense absorption band at the long wave end of their electronic spectra. Kuhn and Wallenfels² state that the yellow colour of (II) corresponds to that of the 1,1,8-tetraphenyl-octatetraene (III) of Wittig and Klein³. So with identical end substituents the colour of Kuhns cumulene with three double

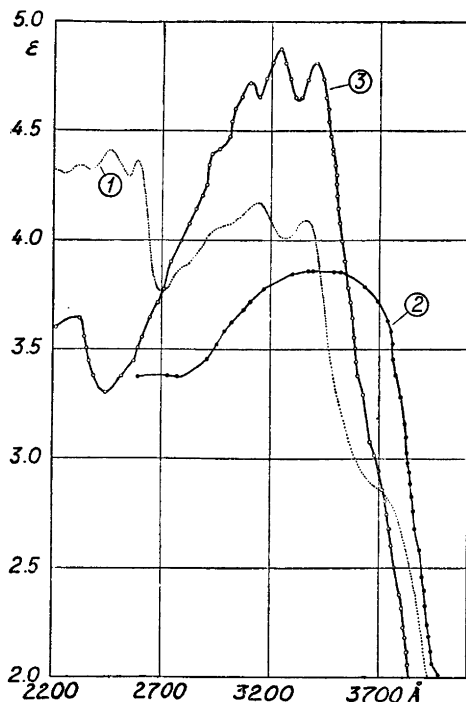


Fig. 1. Ultraviolet absorption of hexane solutions of:

Curve 1 (.....) *Matricaria ester*, see R. Holman and N. A. Sørensen, *Acta Chem. Scand.* 4 (1950) 416.

Curve 2 (—●—●—) *Composit-cumulene I*

Curve 3 (—○—○—) *methyl decatetraenoate*

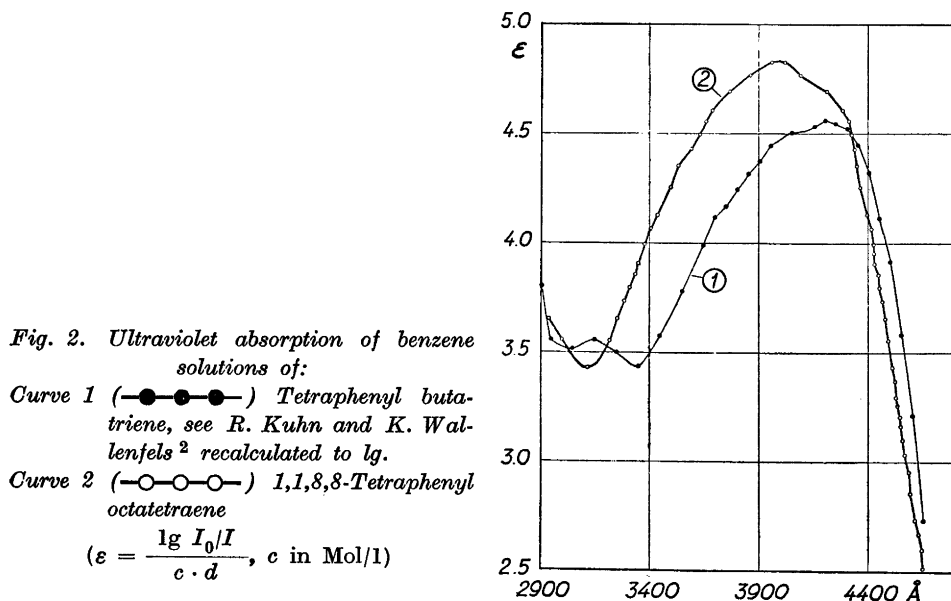
$$\left(\epsilon = \frac{\lg I_0/I}{c \cdot d}, c \text{ in Mol/l}\right)$$

bonds corresponds to Wittig conjugated polyene with four double bonds. Since the comparison of the colour shade of substances with selective absorption in the outskirts of the visible region may introduce considerable uncertainty, we have tried to get all colour comparisons on a spectral curve basis. The U. V.-spectrum of tetraphenyl-butatriene (II) in benzene is given by Kuhn and Wallenfels², presented in Fig. 2, curve I.

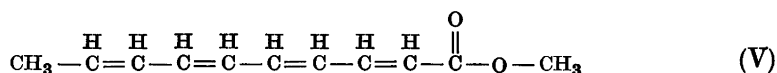
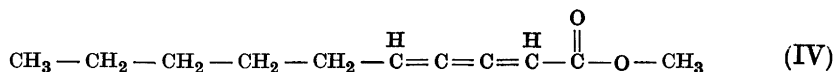
We have been unable to find the spectrum of the 1,1,8,8-tetraphenyl-octatetraene (III) in literature. We are greatly indebted to professor Dr. G. Wittig, Tübingen, who put this polyene at our disposal. The U. V.-spectrum of (III), also in benzene, is presented in Fig. 2, curve II.

The U. V.-spectra are, as will be seen, of a rather similar general character; conclusive for the physiological accordance is the nearly parallel course of the two curves in the blue region.

It is obvious that if the accordance in colour observed by Kuhn and Wallenfels between tetraphenylbutatriene and 1,1,8,8-tetraphenyl-octatetraene is a general one then the U. V.-absorption spectrum of the new compound $C_{11}H_{16}O_2$ (IV) from scentless mayweed as a cumulene with 3 /[≡] ought



to show the same relationship to methyl-decatetraen-oate (V) the polyene with corresponding end groups and 4 /^m.



(V) was synthesized according to Kuhn and Hoffer⁴. The U. V.-spectrum of (V) in hexane is given in Fig. 1, curve III. As will be seen the analogy between the U. V.-spectra of our supposed natural cumulene — “Composit-cumulene I” — and methyl-decatetraen-oate and the two spectra given in Fig. 2 is as close as would be expected. These spectral analogies thus support our assumption that the new compound ought to have the cumulene structure (IV).

EXPERIMENTAL

9 kg scentless mayweed (devoid of all floral parts) was steam-distilled. The essential oil which crystallized when the condensate was cooled, was extracted with petroleum ether, yield 7.4 g oil. Crystallisations from petroleum ether gave 3.9 g matricaria ester followed by further 0.25 + 0.25 g on successive concentrations of the mother liquor. The final, orange coloured mother liquor was separated through chromatography on activated

alumina. With petroleum ether as solvent there was eluted only small amounts of a liquid sesquiterpene. Benzene eluted some further amounts of matricaria ester. Benzene-methanol followed by pure methanol removed a yellow oil total amount 140 mg. This oil distilled at 0.0001 mm at air bath temperature about 50° leaving only a small, brown residue. The distillate, which was somewhat more lemon-yellow gave in hexane the U. V.-spectrum given in Fig. 1, curve II.

$C_{11}H_{16}O_2$ (180.2)	Calc.	C	73.31	H	8.95
	Found	»	73.82	»	8.48

17.4 mg was hydrogenated with $H_2/2\%$ Pd-catalyst in acetic acid. H_2 -consumed 7.5 ml (20°, 728 mm Hg) which corresponds to 3.1 mol H_2 . The perhydrocompound was a neutral compound extractable with ether after neutralisation of the solvent, acetic acid. The colourless liquid distilled at 0.001 mm at air bath temperature 50°, its pleasant "strawberry" odour was the same as that of methyl-caprate.

SUMMARY

From the essential oil of scentless mayweed (*Matricaria inodora* L.) there has been isolated a new compound, $C_{11}H_{16}O_2$, which ought to be a hexahydro matricaria ester with the cumulene structure (IV).

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