

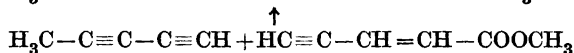
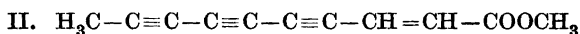
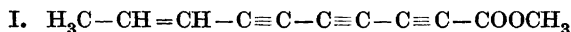
Studies Related to Naturally Occurring Acetylene Compounds

VIII. The synthesis of Methyl *n*-Dec-2-en-4:6:8-triynoate, an Isomer of the Naturally Occurring Dehydromatricaria Ester

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A year ago Kjellrun Stavholt and N. A. Sörensen¹ described in this journal the isolation from European mugwort (*Artemisia vulgaris* L.) of a crystalline methyl ester, C₁₁H₈O₂. Catalytic hydrogenation gave methyl caprate, and for spectral reasons these authors regarded formulae I and II as the most probable for this highly unsaturated compound.



In theory both I and II may occur in *cis* and *trans* modifications. With the object of distinguishing between these 4 possibilities, we have carried out the synthesis of the *trans*-modification of II by Glaser coupling of methyl diacetylene, prepared according to Schlubach and Wolf², and methyl pent-2-en-4-ynoate prepared according to Heilbron, Jones and Sondheimer³. The Glaser coupling gave, as is usual with methyl pent-2-en-4-ynoate, high yields of dimethyl octa-1:7-diene-3:5-diyne-1:8-dicarboxylate, and the asymmetric coupling product, *trans* methyl *n*-dec-2-ene-4:6:8-triynoate, occurred only in traces. The separation of these compounds was achieved by chromatography of the reaction product on alumina. The pure *trans* methyl *n*-dec-2-ene-4:6:8-triynoate was a slightly yellow crystalline substance, m.p. 95.5°, whereas the ester isolated from mugwort root melted at 112–113°. As will be seen from Fig. 1 the U.V. spectra of the synthetic and the naturally occurring methyl *n*-decene-triynoates are very closely related, but with definite and character-

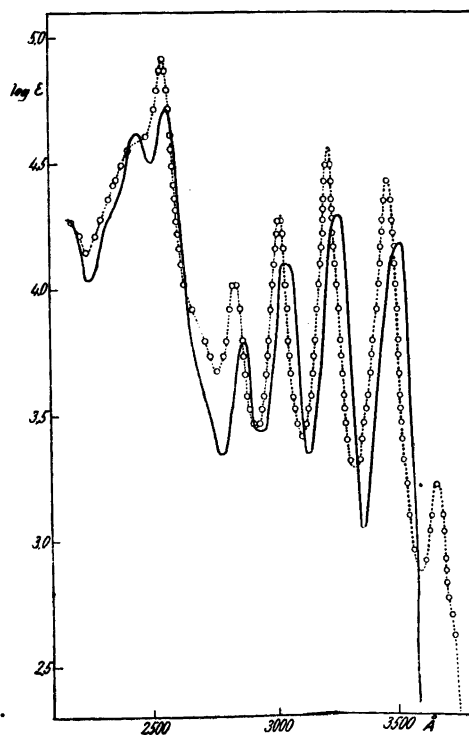


Fig. 1. Ultraviolet absorption of dehydromatricaria ester in hexane.

...○... Ester from European mugwort¹.
 — Methyl n-dec-2-en-4:6:8-triynoate.

ristic small differences. The synthetic isomer has a weak absorption band on the long wave side at 3630 ÅU, which is lacking in the mugwort ester. This band does not follow acetylenic spacing with respect to the following 4 absorption bands and would seem to belong to another band system.

The second difference is that in the synthetic isomer the four very sharp maxima occur at about 35 ÅU towards shorter wavelengths than for the mugwort ester. This difference is of the same magnitude and of the same sign as between *cis* and *trans* Lachnophyllum ester^{4,5}.

In ethylenic chromophors the *trans* isomers absorb at longer wavelengths than the *cis*-isomers, and therefore we hesitate to conclude that the mugwort ester is the *cis*-isomer of II.

Furthermore the very strong band group below 2600 ÅU, which shows fine structure in the mugwort ester, has only a shoulder on the short wave side in the synthetic isomer.

The properties of the synthetic isomer make it very probable that the mugwort ester is one of the 2 possible isomers of formula I or the *cis* isomer of II.

EXPERIMENTAL

trans Methyl *n*-dec-2-ene-4:6:8-triynoate. 3.2 g methyl diacetylene and 5.5 g methyl pent-2-en-4-ynoate was added to a solution of 112 g ammonium chloride and 70 g cuprous chloride in 250 ml water. The suspension was shaken 1 hour in a mechanical shaker, then 1 hour by hand. The reaction mixture showed unusual foaming and gave heavy emulsions when extracted with ether. The ethereal extract, which was solid, was extracted with petroleum ether (b. p. < 40°) the residue went into solution in benzene-petroleum ether (6 : 4). Both solutions were adsorbed on slightly activated alumina and eluted with petroleum ether, benzene-petroleum ether mixture, pure benzene and finally ether. The less soluble fraction, which was dissolved in benzenepetroleum ether (see above), gave only dimethyl octa-1,7-dien-3,5-diyne-1,8-dicarboxylate as crystallizing reaction product. The more soluble part of the reaction product — the petroleum ether solution — afforded in the first ether eluate 50 mg of slightly yellow crystals, which after recrystallization from petroleum ether melted at 95.5° C.

$C_{11}H_{18}O_2$ (172.1)	Calc.	C	76.73	H	4.68
	Found	»	76.4	»	4.53

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

λ_{max}	3630	3440	3210	3012	2832	2556	Å
ν » $\cdot 10^{-12}$	826.4	872.1	934.6	996.0	1059.3		cm^{-1}
$\Delta\nu$ » »		62.5	61.4	63.3			»

Catalytic hydrogenation. 7.2 mg was hydrogenated with PdO_2 -catalyst. The activity of the catalyst which was generated immediately before use, was unexpectedly great and caused some uncertainty in the initial reading. Hydrogen consumption (0°, 760 mm) 6.3 ml; calc. 7.1 ml. The hydrogenation product had the characteristic strawberry odour of methyl caprate.

SUMMARY

Glaser coupling of methyl diacetylene with methyl pent-2-en-4-ynoate, gave the *trans* isomer of methyl *n*-dec-2-en-4:6:8-triynoate (II), m.p. 95.5° C. This synthetic dehydromatricaria ester is different from the dehydroester found in European mugwort. The U.V.-absorption of the two isomers is closely related and strengthens the supposition that the naturally occurring dehydromatricaria ester is either the *cis*-isomer of II or one of the isomers of I.

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