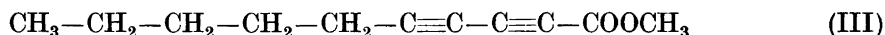
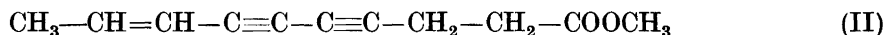
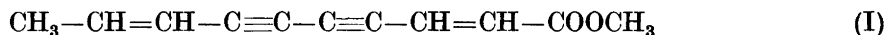


Studies Related to Naturally Occuring Acetylene Compounds. XII. The Synthesis of Methyl *n*-Deca-2 : 4-diynoate

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In the tenth communication¹ of this series some di- and tetrahydro derivatives of the matricaria ester (I) were synthesised with the object of obtaining comparison material for the identification and isolation of such compounds from essential oils. This work was so far immediately successful as the *cis*-isomer of the α,β -dihydromatricariaester (II) turned out to be rather widely distributed — mostly as a minor constituent — in oils of the *Compositae*².



As mentioned in the tenth communication we had also tried to synthesise the ester (III) = methyl *n*-deca-2 : 4-diynoate. The Glaser coupling from hept-1-yne and propiolic acid methyl ester, however, failed completely, because propiolic acid methyl ester was removed very rapidly by self-coupling.

The reason for our particular interest in (III) was the presence of an unknown compound in the oils from roots of some *Helipterum* species. The crude oils show sharp peaks of low intensity in positions close to but significantly different from the maxima of (II), *viz.*

λ_{max} , II	2 810	2 650	2 514	2 381	2 275	ÅU
» Crude <i>Helipterum</i> oils	2 862	2 650	—	—	—	»

Since a carbomethoxy-group has turned out to be about equivalent to one double bond³, the possibility existed that the chromophore present in (III) was responsible for the maxima in the *Helipterum* oils. The synthesis of (III) was finally accomplished by introduction of the carboxyl group in amyldiacetylene by a Grignard reaction. Amyldiacetylene was synthesised analogously to the procedures given by Armitage *et al.*⁴ for the synthesis of monoalkylacetylenes, *cf.* Experimental part.

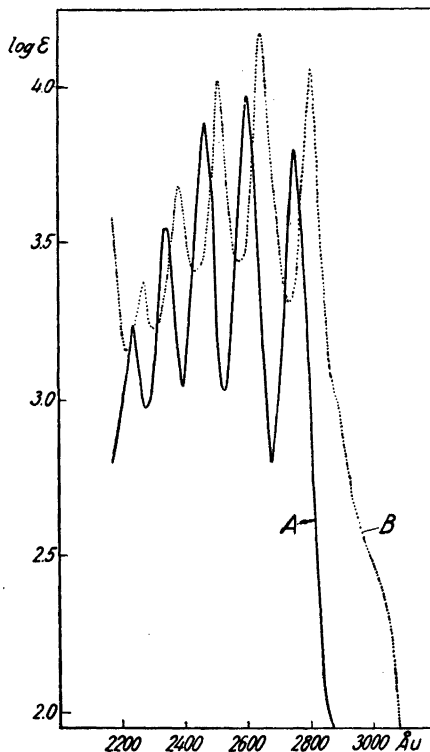


Fig. 1. Ultraviolet absorption in hexane of A: methyl *n*-deca-2:4-diyn-1-oate, B: methyl *n*-deca-8-ene-4:6-diyn-1-oate (α,β -dihydro *matricaria* ester).

Methyl *n*-deca-2:4-diyn-oate was a colourless liquid with freezing point below zero. The free acid and the methyl ester (III) showed a beautiful fine-structure spectrum in U.V., cf. Fig. 1, curve A. The maxima of III, however, are displaced some 50 ÅU towards shorter wave-lengths relative to II, whilst the unknown chromophore from *Helipterum* was displaced about 50 ÅU towards longer wave-lengths. The carbomethoxy group thus seems to be a little less active than one double bond. With the broad and undistinct spectra such as those given by the shorter polyenes — cf. the ethylenic analogue of III-sorbic acid — with only one broad maximum at 2 610 ÅU — such small differences cannot easily be verified. With the remarkable fine-structure of acetylenic compounds this difference is easily established and may be useful by the identification of unknown chromophores. So far the maxima shown by (III) have not been observed in any of the essential oils studied in this laboratory.

It is hoped to obtain enough *Helipterum* oils in the season 1953 to get insight into the structure of the substance with the unknown chromophore.

For comparison with very long-waved chromophores found in some *Coreopsis*-oils amyldiacetylene was coupled to diamyl-tetraacetylenes according to ⁵. This tetra-acetylene is rather stable; the spectral properties was found in excellent agreement with the data given for dialkyltetra-acetylenes by Armitage *et al* ⁵.

EXPERIMENTAL

1. *Amyl-diacetylene*. In 1 l. liq. ammonia sodamide was prepared in the usual way* from 35 g of sodium metal and 0.4 g ferric nitrate. To the solution was added slowly 62 g of freshly distilled 1 : 4-dichloro-2-butyne during 1.5 hours, then followed by 75 g of *n*-amylbromide, also freshly distilled, during 1 hour. After 3.5 hours 200 ml ether was added and the ammonia slowly evaporated. To the semi-solid residue some ammonium-chloride was added and then 500 ml ether. The ether solution was dried, evaporated carefully and the residue distilled at 3 mm. Amyldiacetylene was a colourless liquid which soon discoloured in air. B.p. 46–48° at 3 mm, $n_D^{19} = 1.4808$, yield 19 g (31 %).

2. *Methyl n-deca-2 : 4-diynoate*. From 16 g of ethylbromide the Grignard compound was prepared in the usual way. The solution was cooled to -25° and freshly distilled amyldiacetylene added drop by drop during 40 min. with vigorous stirring. The reaction mixture was left until it had reached room temperature and was then refluxed for 2 hours. The solution of amyldiacetylene magnesium bromide was then cooled to -50° and a stream of dry carbon dioxide passed through for 3 hours. A thick dark liquid separated and the temperature rose to -30° . A few lumps of solid carbon dioxide were added and the reaction mixture left for 10 hours. After addition of a solution of 50 g sodiumbisulphate in 100 g of water and cooled to -15° the mixture was extracted with ether. The ether solution was evaporated finally at the oil pump at 25° . The residue solidified and the acid parts were taken up in soda solution and the acids set free with cold sulphuric acid and extracted with petroleum ether. Some volatile acids were evaporated at $20^\circ/0.001$ mm and the residue crystallised from petroleum ether. The deca-2 : 4-diyne-1-carboxylate crystallised in colourless needles which very rapidly turned yellow even at 0° C, and because of this marked unstability the acid was immediately converted to the methyl ester. 1 g of the acid in 50 ml of methanol and 1.5 ml of conc. sulphuric acid was left for 5 days in the cold and the ester worked up in the usual way. Yield 0.65 g.

Methyl *n*-deca-2 : 4-diynoate distilled as a colourless liquid, b.p. $40^\circ/0.001$ mm.

$C_{11}H_{14}O_2$ (178.1)	Calc.	C 74.1	H 7.92
	Found	» 73.8, 73.8	» 7.89, 8.14

U.V.-spectrum (Fig. 1, curve A):

in hexane	ϵ_{max}	6 240	9 340	7 770	3 550	1 740
	λ_{max}	2 755	2 602	2 463	2 342	2 234
	$\nu_{max} \times 10^{12}$	1 088.9	1 153.0	1 218.0	1 281.0	1 342.9
	$\Delta\nu_{max} \times 10^{12}$		64.1	65.0	63.0	61.9
in alcohol	ϵ_{max}	5 630	7 080	6 320	3 240	1 700
	λ_{max}	2 772	2 610	2 474	2 360	2 258
The free acid in alcohol:	λ_{max}	2 750	2 600	2 465	2 345	—

3. *Octadeca-6 : 8 : 10 : 12-tetrayne*. From 4 g of ethyl bromide the Grignard compound was prepared in the usual way. To this solution amyldiacetylene (4.5 g) was added slowly at -25° , the reaction mixture was left until it had attained room temperature and then refluxed for 2 hours. To the cooled solution 8.4 g of anhydrous cupric bromide was added in small portions; finally the solution was refluxed for half an hour. Decomposed with ice and the hydrocarbon extracted with ether and distilled at $80^\circ/0.0001$ mm. Bright yellow oil, which crystallised at about -30° .

Spectrum in hexane:

	ϵ_{max}	369	572	1 140	2 170	1 870	396 000	300 000
	λ_{max}	3 557	3 330	(3 075)	2 885	2 718	2 386	2 272
	$\nu_{max} \times 10^{12}$	843.4	900.9	975.6	1 039.9	1 103.8	1 257.3	1 320.4
	$\nu\Delta_{max} \times 10^{12}$	57.5	74.7	64.3		63.9		63.1
	Given by Armitage <i>et al.</i> for dialkyl-tetra-acetylenes*:							
	λ_{max}	3 550	3 295	3 070	2 875	2 380	2 270	2 170

SUMMARY

Methyl *n*-deca-2 : 4-diyne-oate (III) has been synthesised by carboxylation of amyldiacetylene. The U.V.-spectrum of this ester demonstrates that the carbomethoxy group is a little less active than one double bond when conjugated with acetylenic bonds.

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