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Studies Related to Naturally Occurring Acetylene Compounds. VII. The Synthesis of two Stereoisomers of Methyl *n*-Decadiene-2,8-diyn-4,6-oates; the Configuration of Matricaria Ester

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A year ago Bruun, Haug and Sörensen described in this journal[1] the synthesis of methyl *n*-decene-2-diyn-4,6-oate, the *trans* form of the lachnophyllum ester, isolated in 1935 from the composité plant *Lachnophyllum gossypinum* Bge [2]. The synthesis was accomplished through oxidative coupling according to Glaser [3] of pentyne-1 with penten-3-yn-1-ol-5 [4] to the alcohol decene-2-diyn-4,6-ol-1 which was oxidized with chromium trioxide to the corresponding acid. This synthesis was carried through as a model experiment for the synthesis of matricaria ester, methyl *n*-decadiene-2,8-diyn-4,6-oate (I), which two of us [5] isolated in 1941 from scentless mayweed (*Matricaria inodora* L.)

For a comparable synthesis of matricaria ester the starting materials must be the same penten-3-yn-1-ol-5 (IV) and penten-3-yne-1 (V). When our synthetic work was initiated some years ago there was no reliable method of preparation for this simple hydrocarbon. A short note by Henne and Greenlee [6] indicated that, in the reaction of dibromo-1,3-propane with acetylene to prepare heptadiyne-1,6, a small forerun was obtained (about 15 %) which was tentatively regarded as penten-3-yne-1.

In agreement with Henne and Greenlee we obtained a fore-run in this reaction, but the amounts were quite insufficient for determination of structure and for preparative purposes.

Since ethylidenacetone is a readily available substanc, we tried to convert this ketone into 2,2-dichloropentene-3 and then to split off 2 moles of hydrogen

chloride. The reaction of ethylidenacetone with PCl_5 was vigorous; the reaction product distilled over a broad temperature range and was obviously not homogeneous. Chlorine analysis revealed that it mainly consisted of 2-chloropentadiene with varying amounts of 2,2-dichloro-pentene-3. As the loss of one mole hydrogen chloride at this stage was inconsequential, we used the crude chlorination product as such. We tried several different methods for the removal of the second mole of hydrogen chloride, but invariably met with bad yields. However, since the crude pentenyne (boiling range 50—60° C) in test experiments gave a readily crystallizing decadienediynol on oxidative coupling with penten-3-yn-1-ol-5, large quantities of the starting materials were prepared for a synthesis along these lines.

At that time Dr. B. C. L. Weedon of Imperial College (London) who, through one of us (T. B.), was aware of our experiments, made available to us an (at that time) unpublished method for the preparation of penten-3-yne-1 (V), worked out by Eglinton and Whiting in the laboratories of Professor E. R. H. Jones at Manchester and subsequently published. Pentyn-4-ol-2 is esterified with p-toluene-sulphonyl chloride and the ester decomposed with hot concentrated potassium hydroxide. This elegant synthesis gives very good yields (>90 % of theory based on pentyn-4-ol-2).

The b.p. of penten-3-yne-1 prepared according to Eglinton and Whiting, is however 46—48° C. This discrepancy gave rise to a more detailed investigation of the pentenynes obtained by these two different methods. Both are conjugated enynes since both exhibit a maximum in the U.V. at 2 240 Å ($\varepsilon = 16\,000$), the two absorption curves being practically identical. The spectrum of the pentenyne prepared according to Henne and Greenlee is also identical (*cf.* Fig. 1).

The physical properties of the preparations of pentenyne differ remarkably (Table 1).

Table 1.

Pentenyne according to	d_4^{20}	n_D^{20}	M_D	B. p. °C
Henne & Greenlee [6]	0.7415 [6]	1.4491 [6]	23.9	59.2
	0.738 *	1.4501 *	24.1 *	58.5—59 *
From ethylidenacetone		1.4480 *		57—60 *
Eglinton & Whiting [7]	—	1.4356 at 19°		46—48
	0.7288 *	1.43532 *	23.7 *	47.5—48 *

* This paper.

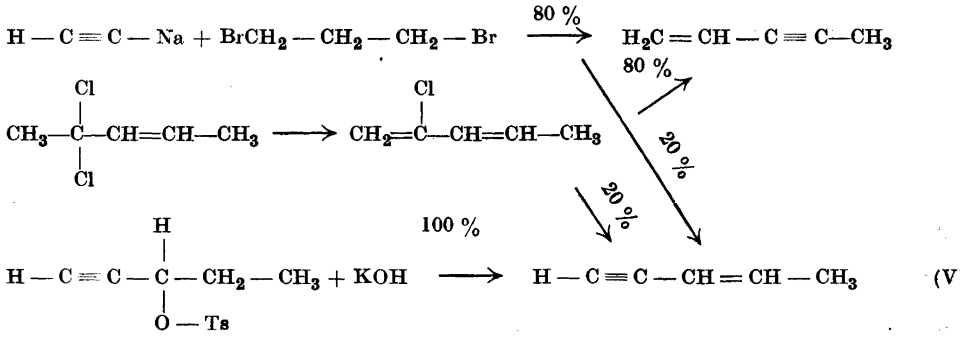
The refraction, and dispersion too (cfr. experimental part), reveal the conjugation of the double and triple bond. The exaltation for sodium light being 1.2 for the pentenyne prepared according to Henne and Greenlee, 0.9 for the pentenyne according to Eglinton and Whiting.

All three preparations of the crude pentenynes gave precipitates with silver nitrate, and all three reacted in the oxidative coupling according to Glaser.

Refractionation and determination of acetylenic hydrogen with methyl magnesium iodide showed that only the preparation according to Eglinton and Whiting is pure penten-3-yne-1 (V). The purest fraction, b.p. 58.5° of the pentenyne from ethylidenacetone gave no active hydrogen. The crude preparations contained about 20 % of monosubstituted acetylene, which gave rise to the silver reaction and the Glaser coupling. The preparations b.p. 58—59° then must be penten-1-yne-3; the physical properties are in excellent agreement with data given by

Carothers and Jacobson[8]: b.p. 59.2° $d_4^{20} = 0.7401$, $n_D^{20} = 1.4496$, $M_D = 23.94$ and by Schlubach and Wolf [9]: b.p. 59.2—60.1 $n_D^{20} = 1.4492$ for this compound.

As will be seen from the reaction scheme, unexpected rearrangements occur in the two first reactions. These rearrangements follow the same lines as do some of the reactions studied by Schlubach and Wolf [9].



Penten-3-yne-1 may occur in a *cis*- and a *trans* modification. Eglinton and Whiting supposed their preparation to be homogeneous (*trans*), since reaction with *cyclo*hexanone gave a good yield of a crystalline reaction product. Our experiences with their penten-3-yne-1 indicate strongly that it must be a mixture of both stereisomeric modifications. In accordance with our synthesis of lachnophyllum ester, penten-3-yne-1 (V) was first condensed with pent-2-en-4-yn-1-ol (IV). This oxydative coupling gave rise to two isomeric decadienediynols (III). Since pent-2-en-4-yn-1-ol (IV) has been used frequently in synthetic work without reports of resulting stereoisomers, the origin of our

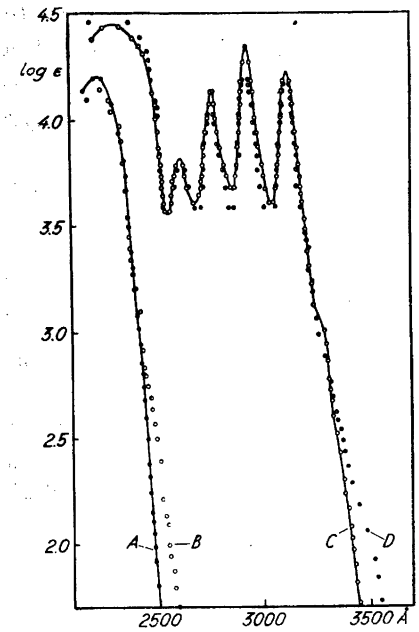


Fig. 1. Ultraviolet absorption in hexane of:
A: —●—●— $CH_3-CH=CH-C\equiv CH$[7]
B: ○○○○○ $CH_3-C\equiv C-CH=CH_2$
C: —○—○— *Matricarianol m. p. 104°*
D: ◑◑◑◑◑ *Matricarianol, liquid*
($\varepsilon = \frac{\log I_0/I}{c \cdot d}$, *c in mol/l, d in cm)*

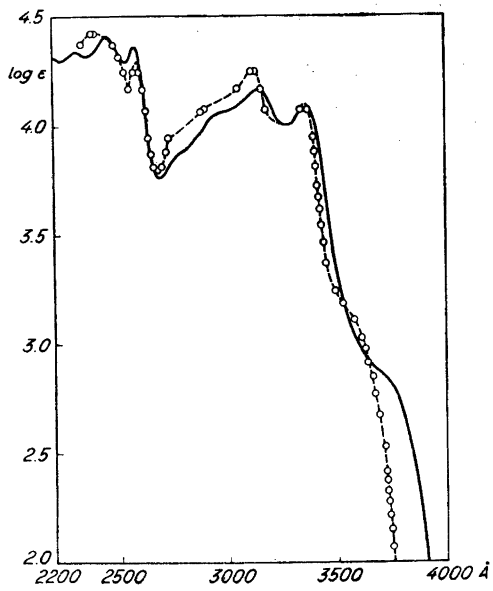


Fig. 2. Ultraviolet absorption in hexane of:
cis, cis-Matricaria ester
——— *R. T. Holman and N. A. Sørensen*
--○---○-- *trans, trans-Matricariaester synthetic, this paper*

isomeric decadienediynols must be sought in the pentenyne moiety of the reaction components. In accordance with this view the other products of the oxidative coupling were the decadiene-2,8-diyne-4,6-diol-1,10 m.p. 153—155° of Heilbron, Jones and Sondheimer[4] and at least two decadiene-2,8-diynes-4,6, one of them being a readily crystallizing compound, m.p. 96.5—97.5°. Of these two decadiene-2,8-diyn-4,6-ols-1 (= "matricarianols") (III) one was a solid, m.p. 104—105°, the other a liquid; their U.V.-spectra, *cf.* Fig. 1, were almost identical. They were characterized through their 3,5-dinitrobenzoates. The solid matricarianol gave a 3,5-dinitrobenzoate of m.p. 126—128°, the corresponding ester from the liquid form one of m.p. 82—84°. Both matricarianols were hydrogenated to *n*-decanol, characterized again as the 3,5-dinitrobenzoate, m.p. and mixed m.p. 54—55°. The difference between the two synthetic matricarianols must therefore be configurational.

Oxydation of the two matricarianols with chromic acid according to Bowden *et.al.*[10] gave, only in the case of the matricarianol of m.p. 104—105°, a decadiene-2,8-diyn-4,6-oic acid or "matricaria acid" (II). The liquid matricarianol suffered oxidative destruction. The acid was isolated as the methyl ester $C_{11}H_{10}O_2$, m.p. 60—61°, that is some 26° higher than the matricaria ester isolated from the essential oil of scentless mayweed. That this synthetic ester, m.p. 60—61°, had the constitution of methyl *n*-decadiene-2,8-diyn-4,6-oate (I) was proved by its U.V.-spectrum *cf.* Fig. 2 which was very similar to that of the natural stereoisomer and further through catalytic hydrogenation to methyl caprate which was saponified to capric acid, converted to the acid chloride and thence to the amide, m.p. 96°, alone and in 1:1 mixture with an authentic specimen.

From the pure methyl ester, m.p. 60—61°, the corresponding acid (II) was prepared by saponification under nitrogen. The free acid crystallized in yellow needles which show no definite m.p. but decomposed at about 173°. Re-esterification with diazo-methane gave back the 61°-matricaria ester.

The stereoisomeric difference between the synthetic 61° and the naturally occurring matricaria ester made it very desirable to realize the synthesis of some of the remaining three stereoisomers of methyl *n*-decadiene-2,8-diyn-4,6-oate. Our failure in the oxidation of the liquid isomer of matricarianol was overcome through the analogous Glaser coupling of penten-3-yne-1 (V) with methyl pent-2-en-4-yn-oate (VI). This ester was synthesized in 1947 by Heilbron *et. al.*[4] from pent-2-en-4-yn-ol-1.

Oxidative coupling of penten-3-yne-1 (prepared according to Eglinton and Whiting) with methyl pent-2-en-4-yn-oate gave rise to a mixture of the 61° matricaria ester mentioned above with a liquid isomer. To obtain a satisfactory enrichment in both stereoisomers the penten-3-yne-1 was fractionated in a spinning band column according to Björkman-Olavi. This column is not constructed for b.ps. below 55—60° and we did not succeed in a complete separation into *cis* and *trans* penten-3-yne-1. Between 46—46.8° we obtained, however, fractions with $n_D^{20} = 1.4230—1.4340$; the higher boiling part 47°—48.9° C had n_D^{20} about 1.4400.

The lowest boiling fractions of penten-3-yne-1 on coupling with methyl pent-2-en-4-yn-oate gave a liquid matricaria ester mixture from which only about 4 % could be separated as the 61°-ester. The residual liquid after distillation in a high vacuum showed $n_D^{20} = 1.6236$ and m.p., 2° C.

The high boiling pentenyne fractions when submitted to the same coupling reaction gave a solid product in good yield, m.p. 60.5° after one crystallisation, no depression with the above mentioned 61°-matricaria ester.

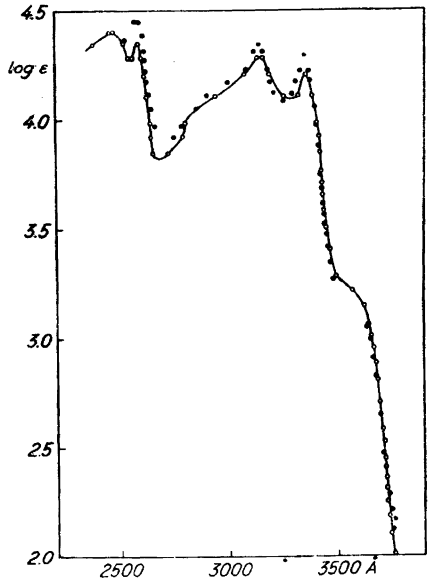


Fig. 3. Ultraviolet absorption in hexane of 2trans, 8cis-matricaria ester
—○—○— *synthetic*
● ● ● ● ● *photoisomer of the naturally occurring cis, cis-isomer (= "trans"-matricaria ester)*

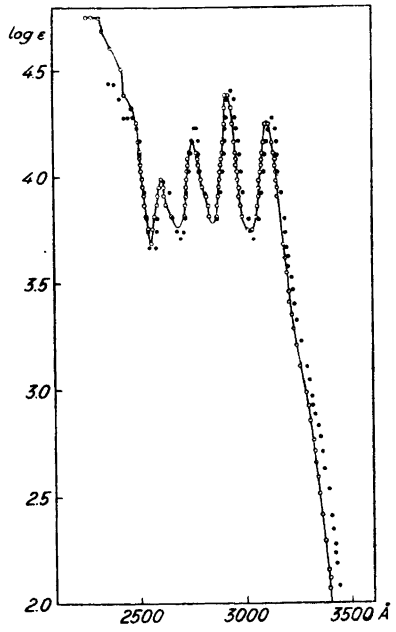


Fig. 4. Ultraviolet absorption in hexane of:
—○—○— *Deca-2,8-dien-4,6-diyn m.p. 97.5*
● ● ● ● ● *Deca-2,8-dien-4,6-diyn-1,10-diol*

Both these synthetic matricaria esters were saponified to furnish the free acids. The 60.5°-ester gave slightly yellow needles which decomposed at about 172°. The 2°-ester afforded colourless leaflets which melted unsharply at 82.5—91°. Obviously, none of the synthetic matricaria acids or esters is identical with the stereoisomer found in nature. From Table 2 it will be seen that the low melting synthetic stereoisomer has physical properties very close to the socalled "*trans*-matricaria ester" prepared by two of us [5] in 1941 through isomerisation of the naturally occurring matricaria ester with U.V.-light. This photoisomer was provisionally given the prefix "*trans*" because its molecular refraction and refractive dispersion were somewhat higher than those for the naturally occurring matricaria ester.

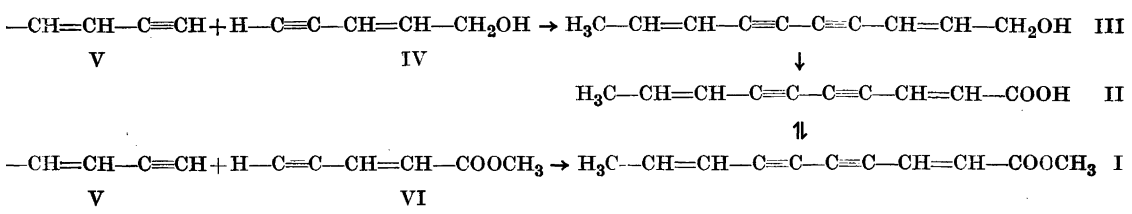
Table 2. Physical constants of the stereoisomeric methyl decadiene-2,8-diyn-4,6-oates ("matricaria esters").

	Synthetic I	Synthetic II	Photoisomer "*trans*"	Naturally occurring
M. p. of methyl ester	61°	+ 2°	− 2 − + 1°	+ 37°
n_D^{20} » » »	—	1.6236	1.6247	—
M. p. » free acid	Decomp. 173°	82.5 − 91°	83 − 91°	98 − 99°

The U.V. spectrum of the synthetic isomer II (methyl ester) is, within the limits of experimental error, identical with that of the "*trans*"-matricaria ester, *cf.* Fig. 3. The U.V. spectra of the stereoisomers differ very little, as will be seen from a comparison of Fig. 2 and Fig. 3. The reason for this similarity may be the rod-shaped diacetylene grouping which separates the end groups sufficiently to allow a planar conformation to be adopted by all stereoisomers.

To strenghten the identity of the liquid synthetic isomer (II) with the "*trans*" matricaria ester, this photoisomer was prepared once more and saponified to give the free acid, the m.p. of which was found to be 84.5 − 91.5° in agreement with the original statement. The mixed m.p. with the synthetic acid was 83.5 − 91° C. Chem.eng. H. Sörum took Debye-Scherrer diagrams of both acids and thus definitely established their identity. We are greatly indebted to Mr. Sörum for his valuable assistance.

The synthetic work described above-summarized in the reaction scheme — confirms beyond doubt the constitution I given to matricaria ester in 1941 on the basis of degradation with alkali.



At the same time these syntheses render valuable hints as to the stereochemistry of the matricaria esters. With the starting materials used here in the oxydative coupling the synthetic isomers must be the 2-*trans*-8-*trans* and the 2-*trans*, 8-*cis* isomers. In all probability the high melting decadienediynol and the corresponding high melting matricaria acid and its methyl ester are the 2-*trans*, 8-*trans* modifications. The low melting synthetic series where the

methyl ester is identical with the photoisomer "*trans*" matricaria ester thus must be the 2-*trans*-8-*cis* isomers. The crystalline isomer found in the essential oil of scentless mayweed then must be the 2-*cis*-8-*cis* isomer. Only with this configuration is the photoisomerisation a simple process, involving a change from *cis* to *trans* at the 2.3-double bond. Were the matricaria ester the fourth isomer, 2-*cis*, 8-*trans*, the photoisomerisation would have to invert the 2.3-double bond to *trans* and the 8.9-double bond to *cis*, which is rather unlikely.

The 2-*cis*, 8-*cis* configuration for the naturally occurring solid matricaria ester implies interesting stereochemical relations for some of the other highly unsaturated derivatives of methyl caprate. The main component of the essential oil from the root of European mugwort (*Artemisia vulgaris* L.) is a dehydro-matricaria ester [11]. The position of the third acetylenic bond and the configuration at the double bond are so far unknown, but in all probability the matricaria ester m.p. 37°, which is widely distributed amongst some subgroups of the plant family of the Compositae is its dihydro-derivative.

Formally the hydrogenation of the 8.9-double bond in the 2-*cis*-8-*cis* matricaria ester gives the lachnophyllum ester [2] for which the Russian discoverers established the *cis*-configuration of the 2.3-double bond. The lachnophyllum ester has recently [12] been shown to occur in some fleabane oils (*Erigeron acre* L. and *E. uniflorum* L.) Its occurrence in some further composite oils will be described in a forthcoming paper. Some other, botanically closely related, fleabanes contain exclusively the *cis*, *cis*-matricaria ester.

It is worthy of note that three isobutylamides of different unsaturated capric acids have so far been found in nature, *viz.* affinin = N-isobutyl-deca-trien-2,6,8-amide [13], spilanthol = N-isobutyl-decadien-4,6-amide [14] and pellitorine = N-isobutyl-decadien-2,6-amide [15]. The configuration at the double bonds in these interesting isobutyl-amides are not exactly known. In all of them there must occur at least one *cis*-bond, since the synthetic all *trans* isomers are different from the naturally occurring compounds. These three isobutylamides of unsaturated normal C_{10}-acids have been isolated from species belonging to the plant family of the Compositae, which so far has furnished all the known acetylenic C_{10}-acids (as methyl esters).

EXPERIMENTAL

Penten-1-yne-3 according to Henne and Greenlee [6]

In a series of experiments carried out with only small variations of the instructions given in the original paper [6], only a very few experiments gave a small fore-run of pentenyne. In the best experiment (on a four mole scale) the crude product gave 28 g boiling below 100° at ordinary pressure. This fraction was dried and distilled again,

affording 8 g boiling below 90°. Slow refractionation under nitrogen gave 4 g b. p. 57—61°, n_D^{20} = 1.4530. Fractions corresponding to this one from two experiments were combined and refractionated slowly, giving I 2.2 g, b. p. 57.5—58.5 and II, 3 g b. p. 58.5—60°. U. V. absorption in hexane, *cf.* Fig. 1 curve B, I, λ_{max} = 2 245, ε = 14 100 II, λ_{max} = 2 230, ε = 12 500.

Table 3. Dispersion of penten-1-yne-3 prepared according to Henne and Greenlee.

I	d_4^{20} = 0.7378	λ_0 = 1 228 Å	$R_{\lambda=\infty}$ = 23.02	$R_{D\ theory}$ = 22.82
II	» = 0.7388	» = 1 225 »	» = 23.00	» = 22.82

	I			II		
λ	n_λ^{20}	$R_{\lambda,\ obs.}$	$R_{\lambda,\ calc.}$	n_λ^{20}	$R_{\lambda,\ obs.}$	$R_{\lambda,\ calc.}$
6678.1	1.44502	23.83	23.83	1.44526	23.81	23.80
5895.9	1.45001	24.06	24.06	1.45024	24.04	24.04
5875.7	1.45022	24.07	24.07	1.45046	24.05	24.05
5790.7	1.45090	24.10	24.10	1.45109	24.08	24.08
5460.7	1.45386	24.24	24.25	1.45404	24.21	24.22
5015.6	1.45924	24.48	24.49	1.45945	24.46	24.46
4471.5	1.46835	24.90	24.89	1.46848	24.87	24.87
4358.3	1.47082	25.01	25.01	1.47085	24.98	24.97

Penten-1-yne-3 from ethylidenacetone. The ethylidenacetone was prepared according to [16].

2,2-Dichloropentene-3. To 250 g PCl_5 suspended in 150 ml carbon disulfide and cooled with ice, 90.7 g ethylidenacetone was added slowly. After half an hour the temperature was raised slowly to 55—58° C and maintained there for 40 minutes. The reaction mixture was then cooled to 5° C and poured on 100 g ice. The carbon disulphide phase was washed successively with water, twice with dilute sodium bicarbonate solution, once again with water and then dried over $CaCl_2$. The carbon disulphide was distilled off at ordinary pressure, and then the reaction mixture was distilled at reduced pressure (110 mm). Between 65—80° there passed fractions with a chlorine content of 38—44 %; between 80—90° fractions with the correct composition $Cl_{calc.}$ = 51.0 %, Cl_{found} = 51.3 %, n_D^{20} = 1.4667. The dichloride readily looses hydrogen chloride. For conversion into *2-chloro-pentadiene-1,3* it was found to be sufficient to distill the crude reaction solution with steam. The pale yellow carbondisulphide phase was removed from this distillate, dried over $CaCl_2$ and distilled. The main fraction passed over at 130° 760 mm, n_D^{20} = 1.4558, $Cl_{calc.}$ = 34.57 %, $Cl_{found.}$ = 35.2 %.

Many attempts were made to remove all the chlorine from 2,2-dichloro-pentene-3 and 2-chloropentadiene-1,3. Sodium or sodium amide in liquid ammonia or in liquid paraffin, with temperatures from ÷ 40—160°, gave only traces of hydrocarbon. Similar results were obtained with most of the experiments with potassium hydroxide. The following procedure was more successful. 35 g potassium hydroxide were dissolved in

180 g diethyleneglycol monomethyl ether ("Carbitol") and the solution heated to 150—155° in a stream of pure nitrogen. 51.5 g 2-chloropentadiene1.3 was then added through a capillary terminating below the "carbitol" surface. The condensate (17 g) was distilled in a stream of nitrogen, crude fraction was collected below 86° (8.4 g). Refractionation gave 4.1 g (12 % of theory) b-range 57—60°, $n_D^{20} = 1.4480$.

Penten-3-yne-1 (V) prepared according to Eglinton and Whiting

The procedure kindly placed at our disposal by professor E. R. H. Jones was practically identical with that given in [7]. The yields of pentyn-4-ol-2-tosylate and pent-3-en-1-yne were excellent with very good reproducibility. U. V. absorption, *cf.* Fig. 1, curve A, $\lambda_{max} = 2\,240$, $\varepsilon_{max} = 16\,200$.

Table 4. Dispersion of penten-3-yne-1.

$d_4^{20} = 0.7288$ $\lambda_0 = 1\,208$ Å $R_{\lambda=\infty} = 22.67$

λ	n_λ^{20}	$R_{\lambda,\,obs.}$	$R_{\lambda,\,calc.}$
6678.1	1.43056	23.44	23.44
5895.9	1.43532	23.66	23.66
5875.7	1.43544	23.67	23.67
5790.7	1.43610	23.70	23.70
5460.7	1.43883	23.83	23.84
5015.6	1.44381	24.06	24.07
4471.5	1.45217	24.46	24.46
4358.3	1.45451	24.57	24.56

Decadiene-2,8-diyn-4,6-ol-1 (III)

Penten-3-yn-1-ol-5 was prepared according to [17] and coupled with penten-3-yne-1 according to [1] *. The mixture of condensation products was taken up in ether and further treated thus: After evaporation of the ether the residue was partially distilled at 0.001 mm and 40° in the air bath. The hydrocarbons produced (the decadienediynes) then distilled into a trap cooled to −80°. To the solid left was added 5 ml chloroform; the suspension was heated in a water bath to 60—70°, and then filtered rapidly with suction. The decadiene-2,8-diyne-4,6-diol-1,10 [4], which invariably was a by-product, was left mainly undissolved. The filtrate was evaporated to dryness in a vacuum. The residue was heated with portions of petroleum (b.r. 60—80°) and filtered. On cooling mainly the solid form of the matricarianol was precipitated, whilst the liquid one mainly remained in solution. After evaporation of the petroleum the carbinol was distilled at 70° (bath)/0.001 mm. The best yields, obtained from 5.0 g penten-3-yne-1 (V) and 6.2 g penten-3-yn-1-ol-5 (IV), were: 1.2 g hydrocarbons, 1.5 g crude, solid matricarianol, 0.7 g of distilled liquid matricarianol and 4.2 g decadiene-2,8-diyne-4,6-diol-1,10.

* Owing to a clerical error the amount of cuprous chloride was not given. It should be 72.5 g.

Matricarianol m.p. 104—105° (= *trans, trans* decadiene-2,8-diyn-4,6-ol-1.)

Crystallisation of the crude, solid carbinol (above) from petroleum (b.r. 60—80°) gave a slightly yellow substance, crystallizing in plates, m.p. 104—105° U.V.-absorption in petroleum ether, *cf.* Fig. 1.

ε_{max}	16 000	21 000	14 000	6 500	27 500	
λ_{max}	3 122	2 930	2 765	2 615	2 300	Å
$\nu_{max.10^{-12}}$	960.9	1 023.9	1 085.0	1 147.2	1 304.4	cm^{-1}
$\Delta\nu$ »	63.0	61.1	62.2			cm^{-1}

3,5-Dinitrobenzoate of matricarianol, m.p. 104—105°

To a solution of 96 mg of the matricarianol m.p. 104—105° in dry pyridine was added a pyridine solution of the calculated amount (150 mg) of 3,5-dinitrobenzoyl chloride. The reaction mixture was left under nitrogen for 24 hours and worked up in the usual way. Crystallisation from petroleum afforded faintly yellow plates, m.p. 126—128°. U.V.-absorption in ethanol:

ε_{max}	17 500	20 500	16 500
λ_{max}	3 146	2 945	2 755

$C_{17}H_{12}N_2O_6$ (340.3) Calc. C 60.0 H 3.55
Found » 59.7 » 3.80

n-Decanol from matricarianol m.p. 104—105°

73.3 mg matricarianol was hydrogenated with 150 mg palladium on $BaSO_4$ catalyst (2 % Pd). Hydrogen consumption (760 mm, 0°) calc. 67.5 ml, found 63.4 ml, which corresponds to $5.64\sqrt{=}$. The liquid hydrogenation product was esterified with 3,5-dinitrobenzoyl chloride in pyridine. Crystallization from petroleum (b.r. 60—80°) gave *n*-decanol 3,5-dinitrobenzoate, m.p. 54—55°, undepressed in m.p. on admixture with an authentic specimen (m.p. 56—57°)[18].

Matricarianol, liquid isomer (2-trans, 8-cis-Decadiene-2,8-diyn-4,6-ol-1)

The fraction which distilled at 70° (bath)/0.001 mm (above) showed U.V.-absorption in petroleum ether very similar to that of the matricarianol of m.p. 104—105°.

ε_{max}	16 000	22 000	13 000	6 500	28 000	
λ_{max}	3 132	2 938	2 755	2 612	2 320	Å
$\nu_{max\ 10^{-12}}$	957.9	1 021.1	1 098.9	1 148.5	1 293.1	cm^{-1}
$\Delta\nu$ »	63.2	67.8	59.6			cm^{-1}

3,5-Dinitrobenzoate of the liquid matricarianol

202 mg of the liquid matricarianol was esterified as above with 320 mg 3,5-dinitrobenzoyl chloride. The crude ester was an oil, but a petroleum solution deposited yellow plates, m.p. about 80°, which after one more crystallization from petroleum (b.r. 60—80°) melted constantly at 83—84.5°.

U.V.-absorption in alcohol:

ε_{max}	17 500	20 000	17 000
λ_{max}	3 140	2 945	2 766

$C_{17}H_{12}N_2O_6$ (340.3)	Calc.	C 60.0	H 3.55
	Found	» 59.8	» 3.40

n-Decanol from the liquid matricarianol

70.2 mg was hydrogenated with $Pd/BaSO_4$ as above. Hydrogen consumption: calc. 64.7 ml (0°, 760 mm), found 61.2 ml corresponding to $5.67/\overline{=}$. The liquid hydrogenation product was esterified with 3,5-dinitrobenzoyl chloride as above. M. p. of the 3,5-dinitrobenzoate 54—55°, mixed m. p. with authentic ester 54—57°.

Decadiene-2,8-diynes-4,6. In the trap two different substances were distinctly visible. The one precipitated on the upper parts of the wall was solid at room temperature, whilst the other, precipitated on the lower parts liquified at room temperature.

Decadiene-2,8-diyne-4,6, solid form. The precipitated solid was dissolved in ether in which it was relatively sparingly soluble. Recrystallization from this solvent produced colourless, flexible blades, m. p. 97.5°.

$C_{10}H_{10}$ (130.2)	Calc.	C 92.3	H 7.75
	Found	» 92.4	» 7.85

U. V.-absorption in petroleum ether, *cf.* Fig. 4.

ε_{max}	18 200	25 100	15 000	9 700	
λ_{max}	3 100	2 915	2 755	2 605	Å
$\nu_{max}\ 10^{-12}$	967.7	1029.2	1088.9	1151.6	cm^{-1}
$\Delta\nu_{max}$ »	59.5	59.7	62.7		»

Hydrogenation. 30.2 mg decadienediyne was hydrogenated with $Pd/BaSO_4 \cdot C_{10}H_{10}$ $2/\overline{=}$, $2/\equiv$ calc. 31.2 ml (0°, 760 mm), found 30.4 ml corresponding to $5.85/\overline{=}$.

Decadiene-2,8-diyne-4,6 (liquid form)

The liquid in the trap was redistilled slowly at 0.1 mm and 40° C.

U. V.-absorption in petroleum ether:

ε_{max}	20 500	23 500	16 000	7 000	31 500	
λ_{max}	3 120	2 930	2 758	2 618	2 320	Å
$\nu_{max}\ 10^{-12}$	961.5	1023.9	1087.7	1145.9	1293.1	cm^{-1}
$\Delta\nu_{max}$ »	62.4	63.8	58.2			»

Table 5. Dispersion of liquid decadiene-2,8-diyne-4,6.

$d_4^{20} = 0.8696$	$\lambda_0 = 1565$ Å		$R_{\lambda=\infty} = 47.95$
λ	n_λ^{20}	R_λ obs.	R_λ calc.
6678.1	1.59392	50.76	50.74
5895.9	1.60585	51.59	51.59
5875.7	1.60631	51.62	51.62
5790.7	1.60763	51.71	51.73
5460.7	1.61564	52.26	52.25
5015.6	1.62926	53.18	53.13
4046.6	1.67675	56.33	56.39

The U. V.-absorption, the refraction and the dispersion of decadienediyne are in good agreement with those for its 3,7-dimethyl homologue [19]. Exaltation for the sodium line for $C_{10}H_{10}$ = 8.2, for $C_{12}H_{14}$ = 7.5.

Matricaria ester, m. p. 61°. (= Methyl decadiene-2 *trans*-8 *trans*-diyn-4,6-oate) from the matricarianol of m. p. 104—105°.

The oxidation of matricarianol with CrO_3 to the corresponding acid and conversion to the methyl ester was carried out in the same way as the conversion of lachnophyllol to lachnophyllum acid methyl ester [1]. The matricarianol m. p. 104—105° was recrystallized immediately before the oxidation was carried out. From 3.2 g of crystallized carbinol there was obtained from the acid fraction 420 mg of methyl ester b. p. up to 66° (bath)/ 0.001 mm, which, after crystallisation from petroleum ether, gave 350 mg of faintly yellow crystalls, m. p. 60—61°.

U. V.-absorption in petroleum ether (cf. Fig. 2).

ε_{max}	18 000	19 000	14 000	21 000	25 000	
λ_{max}	3 345	3 145	2 950 *	2 570	2 450	Å

Methyl caprate from synthetic matricaria ester, m. p. 61°

83.2 mg of the synthetic matricaria ester m. p. 61° was hydrogenated with $Pd/BaSO_4$ catalyst. $C_{11}H_{10}O_2$ $2/\overline{=}$, $2/\overline{=}$ calc. 64.4, found 61.5 ml hydrogen. The liquid perhydro compound had the characteristic strawberry odour of methyl caprate. It was saponified to capric acid, which was converted to its acid chloride and then to capric amide, m. p. 96°, m. p. on admixture with an authentic specimen m. p. 96°.

Matricaria acid, m. p. 173° = decadiene-2 *trans*, 8 *trans*-diyn-4,6-oic-1 acid

To 51 mg of the synthetic matricaria ester m. p. 61° dissolved in 4 ml methanol was added 96 mg of potassium hydroxide in 4.5 ml water. The solution, which was prepared under pure nitrogen, was shaken under pure nitrogen in a bath of ice-water for 5 hours

* Inflexion.

until all the ester had dissolved. The soap solution was diluted with water and extracted with ether. The alkaline solution was then acidified with very dilute, cold sulphuric acid and the liberated acid extracted with ether. The ether solution was dried and the ether evaporated. The matricaria acid was crystallized from a mixture of very little acetone with much petroleum ether as yellow needles decomposing at 169—173°.

U. V.-absorption: (the acid was dissolved in a few drops of chloroform and quickly diluted with petroleum ether).

ε_{max}	13 000	16 500	21 000	29 500	
λ_{max}	3 310	3 090	2 585	2 435	Å

Re-esterification of the acid with diazomethane produced the original ester, m. p. 59°, no depression on admixture with the starting material.

Methyl decadiene-2,8-diyn-4,6-oate-1 from methyl penten-2-yn-4-oate-1

Methyl penten-2-yn-4-oate-1 was prepared according to [4], m. p. 18—19° C.

U. V.-absorption in hexane

λ_{max} = 2 400 Å with inflexion at 2 510 Å
ε_{max} = 30 000 ε = 24 000

Heilbron *et. al.*[4] give for alcoholic solutions

λ_{max} = 2 440 Å with inflexion at 2 510 Å
ε_{max} = 18 000 ε = 15 500

Penten-3-yne-1 prepared according to [7] was refractionated with a spinning band column (Björkman-Olavi). The oxidative coupling was carried out as in [1] with omission of free ammonia to avoid saponification.

I. 7.3 g methyl penten-2-yn-4-oate-1 was coupled with 6 ml penten-3-yne-1 b. p. 46.1—46.8°. The reaction mixture was worked up as above; distillation at 0.001 mm gave 522 mg condensate boiling at < 75°. Of this crude distillate 20 mg could be separated as crystalls, solid at room temperature. The rest after redistillation showed m. p. + 2° n_D^{20} = 1.6236.

$C_{11}H_{10}O_2$ (174.2)	Calc.	C	75.84	H	5.79
	Found	»	75.16	»	5.62

U. V.-absorption in hexane; *cf.* Fig. 3.

ε_{max}	1 600	15 800	19 500	11 200	22 400	25 100	
λ_{max}	3 580 *	3 355	3 140	2 850 *	2 582	2 460	Å

* Inflexion.

Hydrogenation: 36.0 mg matricaria ester, m. p. + 2°, was hydrogenated with 2 % $Pd/BaSO_4$. Calc. H_2 = 27.9 ml, found 27.0 ml (0°, 760 mm) corresponding to 5.81/=. The methyl caprate generated was isolated and the saponification value determined:

$$M_{calc.} = 186.0 \qquad M_{found} = 188.5$$

Free matricaria acid from methyl decadiene-2,8-diyn-4,6-oate-1 m. p. + 2° C

The saponification was carried out under pure nitrogen. The only difference to the procedure given above was the application of acetone-water as a solvent. The free acid was recrystallized from ether-petroleum ether, as leaflets with unsharp m. p. The melting starts at about 82.5° and is completed at 91°. This melting interval, previously described for "*trans*"-matricaria acid by Sörensen and Stene [5], has in the meantime been confirmed by J. Stene in connection with unpublished work (rearrangement at 47—48° when the acid is heated, then the substance remains quite solid until melting starts at 83°, completed at 89.5°) and was confirmed again with "*trans*"-matricaria acid prepared once according to the original procedure: melting starts at 84.5, completed at 91.5°. A 1 : 1 mixture of this synthetic matricaria acid with "*trans*"-matricaria acid starts melting at 83.5, completed at 91°.

Since it is obvious that some phase transformation takes place when this stereoisomer of matricaria acid is heated, Debye-Scherrer diagrams were taken. These definitely established the identity of the synthetic acid with the photoisomer of the naturally occurring acid.

II. Methyl penten-2-yn-4-oate-1 was coupled as above with 2 ml penten-3-yne-1, b. p. 47—48.9°. Yield of crude distillate boiling at < 75° at 0.001 mm was 840 mg ester. After one crystallization from petroleum ether slightly yellowish needles were obtained m. p. 60.5°.

$C_{11}H_{10}O_2$ (174.2)	Calc.	C	75.84	H	5.79
	Found	»	75.56	»	5.67

U. V.-absorption in hexane, *cf.* Fig. 2.

ε_{max}	1 260*	12 600	17 800	12 600*	19 500	26 900	
λ_{max}	3 600*	3 355	3 125	2 900*	2 585	2 390	Å

Hydrogenation: 10.1 mg ester, m. p. 60.5°, was hydrogenated with 2 % $Pd/BaSO_4$. Calc. 7.8 ml H_2, Found 8.1 ml (0°, 760 mm), corresponding to 6.2/=.

Free matricaria acid from methyl decadiene-2,8-diyn-4,6-oate-1 m. p. 60.5°

The saponification was carried out as above for the liquid ester. The crude acid showed decomposition from 167° C, after recrystallization from ether-petroleum-ether the decomposition starts at 172°. The acid does not melt, but decomposition takes place giving dark solids before melting is completed.

* Inflexion.

SUMMARY

Two stereoisomers of decadiene-2,8-diyn-4,6-ol-1 and the corresponding acids and their methyl esters have been synthesized through oxydative coupling of acetylenic precursors according to the method of Glaser. Depending on the route of synthesis the two series must represent the 2-*trans*, 8-*trans* and the 2-*trans*, 8-*cis* isomers. The methyl decadiene-2*trans*, 8-*cis*-diyn-4,6-oate-1 was shown to be identical with the photoisomeric „*trans*"-matricaria ester, prepared in 1941 through the action of U.V.-light on the naturally occurring matricaria ester. The configuration of the latter must be 2-*cis*, 8-*cis*.

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