Studies Related to Naturally Occurring Acetylene Compounds. X. The Synthesis of some Hydrogenated Relatives of Matricaria Ester

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From the essential oil of various plants belonging to the family of the Compositae the following closely related highly unsaturated derivatives of methyl caprate\(^1\) amongst others have been isolated:

I. \(\text{H}_3\text{C} \equiv \text{CH} = \text{CH} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH} = \text{CH} \equiv \text{COOCH}_3\) Lachnophyllum ester

II. \(\text{H}_3\text{C} \equiv \text{CH} = \text{CH} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH} = \text{CH} \equiv \text{COOCH}_3\) Matricaria ester

III. \(\text{H}_3\text{C} \equiv \text{CH} = \text{CH} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{COOCH}_3\) Dehydro matricaria ester

Further investigation in this plant family made it probable that this series might be extended in the hydrogenated direction (compare the preceeding paper of Stavholt-Baalsrud et.al.\(^4\)).

For purpose of comparison the following new members of the hydrogenated series have been synthesized through oxidative coupling according to Glaser.

<table>
<thead>
<tr>
<th>Methyl ester</th>
<th>Free acid</th>
<th>m.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV. (\text{CH}_3 \equiv \text{CH} = \text{CH} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}_2 \equiv \text{CH}_2 \equiv \text{COOCH}_3)</td>
<td>(\text{cis}) liq.</td>
<td>60.5°</td>
</tr>
<tr>
<td></td>
<td>(\text{trans}) 15.5°</td>
<td>144°</td>
</tr>
<tr>
<td>V. (\text{CH}_3 \equiv \text{CH}_2 \equiv \text{CH}_2 \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}_2 \equiv \text{CH}_2 \equiv \text{COOCH}_3)</td>
<td>liq.</td>
<td>92°</td>
</tr>
<tr>
<td>VI. (\text{CH}_3 \equiv \text{CH}_2 \equiv \text{CH}_2 \equiv \text{CH}_2 \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}_2 \equiv \text{COOCH}_3)</td>
<td></td>
<td>53°</td>
</tr>
</tbody>
</table>

The preparations of IV to VI, and the unavoidable by-products, are given in the experimental part.

It turned out that the 8-\textit{cis}-\textit{a,\beta}-dihydromatricaria ester IV is identical with an ester rather widely distributed in nature (compare\(^4\)).
The 2 : 8-tetrahydro matricaria ester (V) and methyl deca-3 : 5-diyn-1-oate (VI) only show very weak selective absorption in U.V. below 2700 ÅU corresponding to dialkyl diacetylenes. The esters themselves will be very difficult to detect through the U.V. spectroscopy of natural essential oils, even when present in high concentrations as, at least most, composite oils contain small amounts of strong chromophors which will hide the spectrum of these esters completely. So far no indications have been found of the occurrence of V and VI in nature.

In the synthesis of VI by Glaser coupling dimethyl octa-3 : 5-diyn-1 : 8-dioate (VII)

\[ \text{H}_3\text{COOC}-\text{CH}_2-\text{C}≡\text{C}-\text{C}≡\text{C}-\text{CH}_2-\text{COOCH}_3 \]

results as a by-product in fair yield. This substance shows the interesting property of turning beautifully violet-red on standing. The coloration accelerates in light, but some crystals remain colourless, so obviously some catalysing impurities are co-responsible for the colour development. The red material is insoluble in organic solvents, unchanged VII is extracted by attempts of recrystallization. These secondary crystalline fractions repeat the curious colouration. A similar colouration was discovered by Castille\textsuperscript{5} in 1939 with the acetylenic fatty acids from *Ongokea Klaineana* Pierre. The true nature of the component of the *Ongokea* acids responsible for their colouration is not known. Castille's formula for the main acid, which he on account of this colour development named erythrogenic acid, is — as was emphasized first by professor E. R. H. Jones\textsuperscript{6} — obviously not in accordance with its spectral properties. None of our synthetic or natural acetylenic compounds with an isolated diyne or enediynie grouping have shown this colouration phenomenon.

The red material has the unchanged composition (C\textsubscript{5}H\textsubscript{3}O\textsubscript{2})\textsubscript{2}. This fact in connection with its extreme insolubility points to a polymeric nature. The beautiful colour necessitates conjugation in the polymer material. In analogy with the deeply coloured polyenes, which Eisler *et al.*\textsuperscript{7} recently have synthesized from cyclopentadiene, formula VIII, is put forward as a working hypothesis.

\[ \text{VIII.} \]

Finally it should be mentioned that we have tried to synthesize methyl deca-2 : 4-diyn-1-oate through the coupling of n-hept-1-yne with propiolic acid
methyl ester. We were not able to isolate any amount of the desired asymmetric coupling product; besides tetradeca-6 : 8-diyne a colourless compound, m.p. 54.5°, was isolated in the same yield as when n-heptyne is omitted from the reaction. The elementary composition corresponds to C₈H₈O₆. Since dimethyl adipate is generated by catalytic hydrogenation with consumption of about 4 Mol H₂ this compound must originate by a Glaser coupling of the ester of propiolic acid with, formally, addition of water and one atom of oxygen.

Shortening the reaction time in the Glaser coupling gave a mixture of C₈H₈O₆ with a new compound C₈H₈O₅.

We are returning later to the investigation of the constitution of these compounds. The tendency of diacetylene dicarboxylic acid to add water might be one of the reasons for the difficulty which different investigators have met when trying to repeat the classical condensations of A. v. Bayer.

**EXPERIMENTAL**

*α,β-Dihydromatricaria ester (IV).* Pent-3-en-1-yne was prepared according to Eglinton and Whiting and fractionated as described in. Methyl pent-4-yn-1-oate was prepared from tribromopropane and ethyl acetacetate according to T. E. Gardner and W. H. Perkin jr.

*cis Isomer:* 4 ml pent-3-en-1-yne b.r. 46—48° and 4 ml methyl pent-4-yn-1-oate were coupled under the experimental conditions worked out for the analogous synthesis of the matricaria esters. By the distillation at 10⁻⁴ mm Hg the hydrocarbon fraction passed into the trap, the desired dihydromatricaria ester was distilled over until the temperature reached 65° air bath and redistilled slowly, b.p. 50—53° Yield 1.1 g. The *cis* isomer is an oil m.p. < −17°.

<table>
<thead>
<tr>
<th>C₁₁H₁₂O₂ (176.2)</th>
<th>Calc. C 74.97</th>
<th>H 6.86</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td>75.09, 74.82</td>
<td>6.80, 6.75</td>
</tr>
<tr>
<td>ρ₂₀ = 1.0017</td>
<td>ρ₀ = 1.5450</td>
<td>M⁻ = 55.6</td>
</tr>
<tr>
<td>M⁻ calc. C₁₁H₁₂O₂</td>
<td>2 /², 1 /² = 50.14</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Dispersion of cis α,β-dihydro-matricaria ester.

\[ R_\lambda \text{ calc.} = \frac{52.817 \cdot \lambda^2}{\lambda^2 - 1.7393 \cdot 10^6} \]  \( (\lambda_0 = 1319 \text{ ÅU}) \)

<table>
<thead>
<tr>
<th>( \lambda )</th>
<th>( n^2_\lambda )</th>
<th>( R_\lambda, \text{ obs.} )</th>
<th>( R_\lambda, \text{ calc.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5895.9</td>
<td>1.54500</td>
<td>55.61</td>
<td>55.60</td>
</tr>
<tr>
<td>5790.7</td>
<td>1.54618</td>
<td>55.71</td>
<td>55.71</td>
</tr>
<tr>
<td>5460.7</td>
<td>1.55092</td>
<td>56.11</td>
<td>56.09</td>
</tr>
<tr>
<td>4358.3</td>
<td>1.57458</td>
<td>58.09</td>
<td>58.14</td>
</tr>
</tbody>
</table>
U.V.-absorption, in hexane, Fig. 1 curve 1.

\[ \begin{array}{cccccc}
\varepsilon_{\text{max}} & 11350 & 15140 & 11100 & 4900 & 2400 \\
\lambda_{\text{max}} & 2810 & 2650 & 2514 & 2381 & 2275 \\
\nu_{\text{max}} \cdot 10^{-12} & 1067.6 & 1132.1 & 1193.3 & 1260.0 & 1318.7 \\
\Delta \nu & 64.5 & 61.2 & 66.7 & 58.7 \\
\end{array} \]

Catalytic hydrogenation: 59 mg cis-ester was hydrogenated with Pt in alcoholic solution. Calc. 2/3, 1/3 20°, 740 mm 41.3 ml. Found 41.2 ml H₂. The perhydroester = methyl caprate was distilled \( n_D^{20} = 1.4288 \), methyl caprate 1.4265. The hydrogenation product, which had the characteristic strawberry odour of methyl caprate, was saponified and the free capric acid isolated in the usual way; m.p. and mixed m.p. with authentic capric acid 31° C.

cis-\( \alpha, \beta \)-Dihydromatricaria acid. The cis methyl ester was saponified under nitrogen as in (9) and recrystallized from petroleum ether, m.p. = 60.5°. Re-esterification with diazo-methane gave the liquid methyl ester with unchanged U.V.-spectrum.

trans-Isomer. 2 ml Pent-3-en-1-yne b.r. 52–53° and 3 ml methyl pent-4-yn-1-oate were coupled as above. The crude distillate, b.r. < 61° at 10⁻⁴ mm Hg (0.86 g), was recrystallized from petroleum ether as colourless leaflets, m.p. 15.5° C.

\[ \begin{array}{cccc}
C_{11}H_{12}O_2 & (176.2) & \text{Calc.} & C 74.97 \\
& & & H 6.86 \\
\text{Found} & 74.76, 75.09, 75.11 & \times 6.87, 6.87, 6.88 \\
d_4^{20} = 0.9940 & n_D^{20} = 1.5496 & M_D, \text{obs.} = 56.14 & M_D, \text{calc.} C_{11}H_{12}O_2 2/3, 1/3 = 50.14 \\
\end{array} \]

Table 2. Dispersion of trans-\( \alpha, \beta \)-dihydromatricaria ester.

\[ R_{\lambda}, \text{calc.} = \frac{53.545 \cdot \lambda^2}{\lambda^2 - 1.78 \cdot 10^8}, (\lambda_0 = 1334 \text{ AU}) \]

\| \lambda \& n_D^{20} \& R_{\lambda, \text{obs.}} \& R_{\lambda, \text{calc.}} \\
| 5895.9 & 1.54963 & 56.44 & 56.44 \\
| 5790.7 & 1.55112 & 56.56 & 56.55 \\
| 5460.7 & 1.55577 & 56.96 & 56.94 \\
| 4358.3 & 1.58063 & 59.04 & 59.08 \\

U.V.-absorption in hexane. Fig. 1 curve 2.

\[ \begin{array}{cccccc}
\varepsilon_{\text{max}} & 17780 & 22650 & 16600 & 10720 \\
\lambda_{\text{max}} & 2814 & 2653 & 2510 & 2390 \\
\nu_{\text{max}} \cdot 10^{-12} & 1066.1 & 1130.8 & 1195.2 & 1255.2 \\
\Delta \nu_{\text{max}} \cdot 10^{-12} & 64.7 & 64.4 & 60.0 \\
\end{array} \]

Catalytic hydrogenation: 81.45 mg trans-ester was hydrogenated with a Pt-catalyst in alcoholic solution. Calc. 18.5°, 738 mm 57.0 ml. Found 58.6 ml H₂, that is 5.14/3. The perhydroester had the characteristic strawberry odour and showed \( n_D^{20} = 1.4284 \) (methyl caprate \( n_D^{20} = 1.4265 \)). Saponification gave the free acid m.p. and mixed m.p. with authentic capric acid 31° C.
trans-a,β-Dihydromatricaria acid. The trans ester was saponified cautiously under nitrogen according to the usual procedure. Crystallization from petroleum ether gave colourless prisms m.p. 144° (corr.).

Re-esterification with diazomethane gave the trans ester m.p. 15.5°. The U.V.-absorption spectrum of this regenerated ester has the data given above. In the U.V.-spectrum of the trans ester isolated primarily from the Glaser coupling a weak band occurred, maximum 3112 Å (log ε = 2.92). This impurity could not be eliminated through recrystallization. The four main maxima were in identical positions, the extinction coefficients of the regenerated ester lying some 10% higher.

**Dimethyl deca-4 : 6-diyne-1 : 10dioate** [(H₂COOC-CH₂-CH₂-C≡C-C≡C-CH₂-CH₂-COOCH₂)] The residues from the distillation of the cis- and trans dihydroesters above solidified on cooling and were recrystallized from petroleum ether, m.p. 37.5°.

\[
\text{C}_{12}\text{H}_{14}\text{O}_4 \quad (222.2) \quad \text{Calc.} \quad \text{C} \quad 64.84 \quad \text{H} \quad 6.35 \\
\text{Found} \quad \text{64.79, 64.62} \quad \text{6.21, 6.22}
\]

U.V.-absorption in hexane:

<table>
<thead>
<tr>
<th>ε max</th>
<th>380</th>
<th>560</th>
<th>660</th>
<th>840</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ max</td>
<td>2814</td>
<td>2662</td>
<td>2515</td>
<td>2392</td>
</tr>
<tr>
<td>ν max \times 10^{-12}</td>
<td>1066.1</td>
<td>1127.0</td>
<td>1192.8</td>
<td>1254.2</td>
</tr>
<tr>
<td>Δν max \times 10^{-12}</td>
<td>60.9</td>
<td>65.8</td>
<td>61.4</td>
<td></td>
</tr>
</tbody>
</table>
Catalytic hydrogenation: 69.6 mg in alcoholic solution with a Pt-catalyst. C\textsubscript{12}H\textsubscript{14}O\textsubscript{4}, 2 \textdegree = \text{calc.} 19\degree, 740 mm 30.8 ml. Found 30.4 ml H\textsubscript{2}. The hydrogenation product was saponified, and the crystalline acid recrystallized from alcohol. M.p. and mixed m.p. with authentic sebacic acid, 134\degree.

Methyl deca-4 : 6-diyln-1-oate ( = 2 : 8-tetrahydromatricaria ester (V)). 3.4 g Pent-\(\text{yne prepared according to (11), and 3.6 g methyl pent-4-yn-1-oate prepared according to (12) were added to 112 g ammonium chloride, 70 g cuprous chloride and 2 ml 2 N ammonia in 250 ml water. The suspension was shaken mechanically for 2 hours without additional introduction of air. The reaction mixture was distilled at 10^{-4}, the hydrocarbon fraction passing into the trap. 1.73 g Tetrahydromatricaria ester distilled between 55-58\degree in the air-bath. Colourless liquid m.p. \textless-12\degree.

\[
\begin{align*}
C\textsubscript{11}H\textsubscript{14}O\textsubscript{2} & \quad \text{(178.2)} \quad \text{Calc.} \quad C \ 74.11 \quad H \ 7.92 \\
\text{Found} & \quad 73.7 \quad 7.8 \\
\eta^\text{20}_D & = 1.5000, \quad \delta^\text{20}_D = 0.9792, \quad M_D, \text{obs.} = 53.87, \quad M_D, \text{calc.} C\textsubscript{11}H\textsubscript{14}O\textsubscript{2}, \text{2 \textdegree} = 50.65
\end{align*}
\]

U.V.-spectrum in hexane:

\[
\begin{align*}
\epsilon_{\text{max}} & = 235 \quad 425 \quad 495 \\
\lambda_{\text{max}} & = 2530 \quad 2386 \quad 2256 \\
\nu_{\text{max}} \cdot 10^{-12} & = 1185.8 \quad 1257.3 \quad 1329.8 \\
\Delta\nu_{\text{max}} \cdot 10^{-12} & = 71.5 \quad 72.5
\end{align*}
\]

Catalytic hydrogenation: 41.5 mg in alcoholic solution with PdO-catalyst, 19\degree, 760 mm. Calc. 2 \textdegree = 23.2 ml, found 21.7 ml H\textsubscript{2}.

2 : 8-Tetrahydromatricaria acid. The methyl ester was saponified at 0\degree under nitrogen and worked up as above. The free acid was recrystallized from petroleum ether as colourless leaflets m.p. 92\degree.

Methyl deca-3 : 5-diyln-1-oate VI. n-Hex-1-yne was prepared according to (13). For the synthesis of methyl but-3-yn-1-oate ethylene oxide was reacted with sodium acetylide according to Henne and Greenlee\textsuperscript{14} to give but-3-yn-1-ol, which was oxidized with chromic acid to but-3-yn-1-oic acid according to the procedure given by Heilbron, Jones and Sondheimer\textsuperscript{16}. This acid was esterified with the calculated amount of diazomethane in anhydrous ether and the liquid ester distilled, b.p. 28\degree at 8 mm Hg. 4.1 g n-Hexyne and 4.9 g methyl-but-3-yn-1-oate were added to a solution of 112 g ammonium chloride, 70 g cuprous chloride and 2 ml 2 N ammonia in 286 ml water and the suspension shaken in a flask for 1 hour mechanically, then one hour more by hand with connection to the air. The reaction mixture was distilled at 10^{-4} mm Hg and the fractions 50-70\degree and 90-100\degree C redistilled slowly. Methyl deca-3 : 5-diyln-1-oate distilled at 55\degree/10^{-4} mmHg as a liquid m.p. \textless-18\degree C.

\[
\begin{align*}
C\textsubscript{11}H\textsubscript{14}O\textsubscript{2} & \quad \text{(178.2)} \quad \text{Calc.} \quad C \ 74.11 \quad H \ 7.92 \\
\text{Found} & \quad 73.9 \quad 7.83 \\
\eta^\text{20}_D & = 1.4978, \quad \delta^\text{20}_D = 0.9478, \quad M_D, \text{obs.} = 55.09, \quad M_D, \text{calc.} C\textsubscript{11}H\textsubscript{14}O\textsubscript{2}, \text{2 \textdegree} = 50.65
\end{align*}
\]

Catalytic hydrogenation: PdO\textsubscript{2} catalyst, alcoholic solution, 60.7 mg 740 mm, 17.5\degree C. Calc. 33.4 ml, Found 33.8 ml H\textsubscript{2}, that is 2.02 \textdegree = -264.4 mg, 745 mm, 21.5\degree C. Calc. 146.0, Found 144 ml, that is 1.96 \textdegree. The hydrogenated ester was isolated in the usual way and distilled, \(n^\text{20}_D = 1.4291\); methyl caprate 1.4265. The hydrogenated ester was saponified and the free acid isolated m.p. and mixed m.p. with authentic caprylic acid 31\degree C.

Deca-3 : 5-diyln-1-oic acid. The methyl ester was saponified under pure nitrogen at 0\degree C. The free acid formed colourless leaflets m.p. 53\degree.
Dimethyl octa-3 : 5-diyn-1 : 8-oate $\text{H}_2\text{COOC-CH}_2\text{C}=\text{C} \cdots \text{C}=\text{C} \cdots \text{CH}_2\cdots \text{COOCH}_3$. The fraction boiling range 90 — 100°/10^{-4} solidified and was recrystallized from petroleum ether. In the light about one half of the crystals turned a beautiful violet-red. The m.p. of both the colourless and the red crystals was 54° C.

$$\text{C}_{10}\text{H}_{18}\text{O}_4 \ (194.2) \ \text{Calc.} \ C \ 61.84 \ H \ 5.19$$

$$\text{Found} \ 61.55, \ 62.05 \ 5.06, \ 5.21$$

Catalytic hydrogenation: PdO$_2$, in alcoholic solution.

$$\text{229.3 mg, } 745 \text{ mm, } t = 19.5° C \ \text{Calc.} \ 2 / f = 116 \text{ ml, Found 114 ml}$$

$$37.6 \ 740 \ t = 20° C \ 2 \ 19.15 \ 19.6$$

The hydrogenation product was a colourless liquid m.p. = —6 — — 5.5° C. Synthetic dimethyl suberate melted at — 6.5 — 6° C, mixed m.p. — 6 — 5.5° C.

$$\text{C}_{10}\text{H}_{18}\text{O}_4 \ (202.2) \ \text{Calc.} \ C \ 59.49 \ H \ 8.97$$

$$\text{Found} \ 59.5 \ 8.93$$

**Glaser coupling of propiolic acid methyl ester.** 4.2 g Propiolic acid methyl ester prepared according to 13, 14 was added to a solution of 112 g ammonium chloride, 70 g cuprous chloride and 1 ml 2 N ammonia in 250 ml H$_2$O. The suspension was shaken mechanically for 1 hour and then stirred by a stream of air for 2 hours. The reaction mixture was worked up as usual and distilled at 10^{-3} mm Hg. The main fraction, boiling about 62° (air bath temperature), solidified and was recrystallized from 100 ml petroleum ether. Yield 0.8 g colourless needles m.p. 54.5° C.

$$\text{C}_8\text{H}_8\text{O}_6 \ (200.1) \ \text{Calc.} \ C \ 48.0 \ H \ 4.03$$

$$\text{Found} \ 47.5, \ 47.7 \ 3.47, \ 3.58$$

Ultra violet absorption, Fig. 1 curve 3.

Catalytic hydrogenation: PdO$_2$, in alcoholic solution.

$$39.4 \text{ mg, } 745 \text{ mm, } t = 21° C \ \text{Consumed} \ 18.5 \text{ ml H}_2, \text{ Calc.} \ 4 \text{ MolH}_2 \ 19.4$$

$$40.4 \ 745 \ 18.9 \ 4 \ 19.9$$

The hydrogenation product was not homogeneous. On distillation at 10^{-3} mm there passed over a main fraction at about 45° C as a colourless liquid,

$$\text{C}_8\text{H}_{14}\text{O}_4 \ (174.2) \ \text{Calc.} \ C \ 55.15 \ H \ 8.10$$

$$\text{Found} \ 54.9, \ 55.6 \ 8.06, \ 8.17$$

The hydrogenation product was saponified and the free acid isolated, m.p. 149°, authentic adipic acid 150.5°, mixed m.p. 150°.

Second fraction, b.r. 70 — 80/10^{-3}, colourless liquid.

$$\text{C}_8\text{H}_{14}\text{O}_5 \ (190.2) \ \text{Calc.} \ C \ 50.52 \ H \ 7.42$$

$$\text{Found} \ 50.3 \ 7.13$$

Shortening of coupling time: Experimental conditions as above, but the aeration time cut down to 1 ½ hour. The reaction mixture was isolated as usual and distilled at 10^{-3} mm. The fraction of b.p. about 45° (air bath temperature) (450 mg) solidified at room temperature. It crystallized from petroleum ether, as colourless needles, m.p. 37 — 41° C.

$$\text{C}_8\text{H}_{8}\text{O}_5 \ (184.1) \ \text{Calc.} \ C \ 52.19 \ H \ 4.38$$

$$\text{Found} \ 52.7, \ 52.7 \ 4.04, \ 4.01$$

No selective absorption in U.V., but stepping out below 2700 Å.

**SUMMARY**

The following unsaturated derivatives of methyl caprate has been synthesized by means of Glaser coupling of their acetylenic moieties:
α,β-Dihydromatricaria ester (IV) 8-cis and 8-trans
Methyl deca-4 : 6-diyn-1-oate (V)
Methyl deca-3 : 5-diyn-1-oate (VI)
So far only the 8-cis α,β-dihydromatricaria ester has been found in nature.

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