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SYNTHESIS AND PROPERTIES OF SOME NEW C_{15}-ω-ALICYCLIC AND ACYCLIC ACIDS

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The methyl esters of the following C_{15}-acids were synthesised: ω-cyclobutylundecanoic acid, ω-cyclopentyldecanoic acid, ω-cyclohexylnonanoic acid, 9-pentadecenoic acid, and 6,12-pentadecadienoic acid. The melting points, refractive indices, surface tensions, gas chromatographic behaviour and IR-, NMR- and mass-spectral properties of these compounds were studied.

Introduction

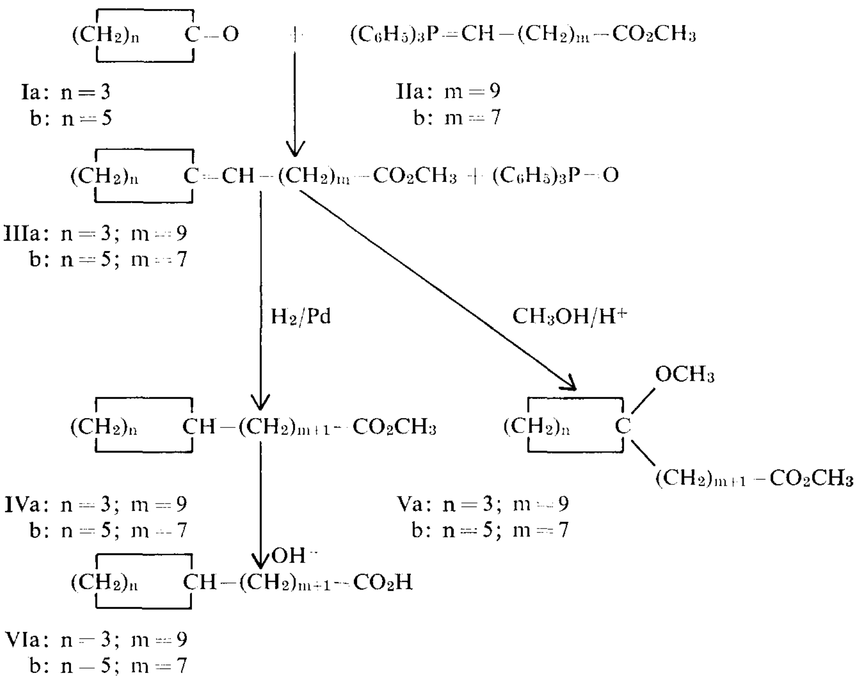
Fats of natural origin often contain cyclic fatty acids[1]). These can be subdivided into two principal classes, namely those which contain a cyclopentene ring at the terminal carbon atom of a saturated or unsaturated aliphatic chain and those which contain a cyclopropene ring approximately at the middle of the chain. The former constitutes a close group of compounds prevalent in oils generally designated as chaulmoogra oils while the latter are constituents of a variety of seed oils of tropical origin and also of some bacterial lipids[1]). The recent isolation and identification of ω-cyclohexylundecanoic acid in fats of entirely different origin[2]) has led us to begin to examine the possibility of ω-alicyclic substituted acids with different ring sizes being present in trace amounts in common fats. We know that the characterisation of the ring system in the alicyclic and aromatic fatty acid mixtures formed on subjecting unsaturated fatty acids to catalytic hydrogenation[3]), heating with alkali[4]) and thermal maltreatment[5]) often presents great difficulties. Therefore, we decided to synthesise a few selected C_{15}-acids with different alicyclic substituents on the terminal carbon of the aliphatic chains, as well as two C_{15} unsaturated acyclic acids, and to investigate their physical properties, including spectral and gas chromatographic behaviour, as a function of their structure.

Synthesis of the acids

PENTADECANOIC ACID

A commercial sample of pentadecanoic acid was esterified with methanol in the presence of catalytic amounts of sulphuric acid and purified by distillation. Saponification of the pure ester gave pentadecanoic acid.

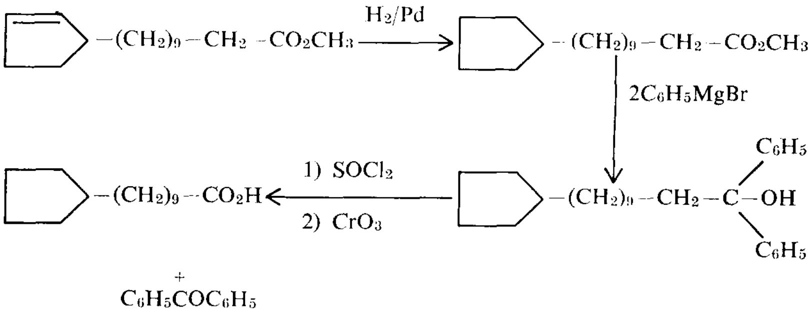
ω-CYCLOBUTYLUNDECANOIC ACID



Cyclobutanone (Ia) was subjected to a Wittig-Reaction[6]) with ω-carbomethoxydecylidene triphenyl phosphorane (IIa)[7]) to give methyl ω-cyclobutylidene undecanoate (IIIa) which was hydrogenated with Pd/C to give methyl ω-cyclobutyl undecanoate (IVa). Its saponification gave the corresponding acid (VIa). (IIIa) reacts with methanol in the presence of catalytic amounts of H_2SO_4, producing methyl ω-(1-methoxy-cyclobutyl)-undecanoate (Va). Acid-catalysed addition of alcohols to semicyclic double bonds is known and has already been investigated systematically by Treibs[8]).

SYNTHESIS OF ω-CYCLOPENTYLDECANOIC ACID

ω-Cyclopentyldecanoic acid was prepared by Barbier-Wieland degradation[9]) of methyl dihydrohydnocarpate, which could easily be obtained by hydrogenation of the methyl ester of the naturally occurring hydnocarpic acid[10]).


VII

SYNTHESIS OF ω-CYCLOHEXYLNONANOIC ACID

Reaction of cyclohexanone (Ib) with ω-carbomethoxyoctylidene triphenyl phosphorane (IIb) and subsequent catalytic hydrogenation of IIIb led to the product IVb in good yield. The needed phosphonium iodide, which has been described in the literature[7]) as a non crystallisable oil, could be obtained by us as a crystalline compound[11]). Saponification of purified IVb gave the corresponding acid VIb. Analogous to methyl cyclobutylidene undecanoate (IIIa), methyl ω-cyclohexylidene nonanoate (IIIb) reacted with methanol under acid-catalysis to add methanol across the semi-cyclic double bond, producing methyl ω-(1-methoxy-cyclohexyl)-nonanoate (Vb).

SYNTHESIS OF METHYL 9-PENTADECENOATE

Methyl 9-pentadecenoate, which is also produced as a result of the thermal decomposition of methyl 9,12-linoleate at 280 °C in an inert atmosphere[12]), was synthesised by the Wittig-Reaction of hexanal and ω-carbomethoxyoctylidene triphenyl phosphorane.

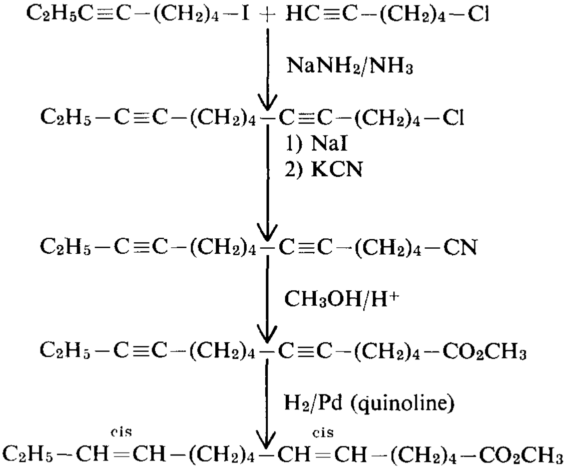
$$C_5H_{11}CHO + (C_6H_5)_3P{=}CH{-}(CH_2)_7{-}CO_2CH_3$$

$$\overset{\text{cis}}{C_5H_{11}CH{=}CH}{-}(CH_2)_7{-}CO_2CH_3 + (C_6H_5)_3P{=}O$$

The resulting olefinic double bond was nearly entirely of cis-configuration; a very weak IR-band at 10.33 μ indicated some trans-contamination.

SYNTHESIS OF METHYL 6,12-PENTADECADIENOATE

8-Iodo-oct-3-yne[13]) was condensed with 6-chloro-hex-1-yne[13]) in the presence of equimolar amount of sodamide in liquid ammonia to 14-chlorotetradeca-3,9-diyne which was converted via iodide and nitrile to methyl



$$\begin{gathered}
C_2H_5C{\equiv}C-(CH_2)_4-I + HC{\equiv}C-(CH_2)_4-Cl \\
\Big\downarrow \; NaNH_2/NH_3 \\
C_2H_5-C{\equiv}C-(CH_2)_4-C{\equiv}C-(CH_2)_4-Cl \\
\Big\downarrow \; \begin{matrix} \text{1) NaI} \\ \text{2) KCN} \end{matrix} \\
C_2H_5-C{\equiv}C-(CH_2)_4-C{\equiv}C-(CH_2)_4-CN \\
\Big\downarrow \; CH_3OH/H^+ \\
C_2H_5-C{\equiv}C-(CH_2)_4-C{\equiv}C-(CH_2)_4-CO_2CH_3 \\
\Big\downarrow \; H_2/Pd\ (\text{quinoline}) \\
C_2H_5-\overset{\text{cis}}{CH{=}CH}-(CH_2)_4-\overset{\text{cis}}{CH{=}CH}-(CH_2)_4-CO_2CH_3
\end{gathered}$$

6,12-pentadecadiynoate. Catalytic hydrogenation with $Pd/CaCO_3$ in ethyl acetate in the presence of quinoline gave methyl 6,12-pentadecadienoate. The olefinic double bonds had mainly the cis-configuration. A weak IR-band at 10.33 μ was indicative of slight trans-contamination.

Properties of the acids and their methyl esters

MELTING POINTS

The methyl esters were all liquid at room temperature. Table 1 shows the melting points of the free fatty acids.

It is interesting to note that the melting points of the three ω-alicyclic C_{15}-acids decrease with increasing ring size. If one should also consider the reported melting points of ω-cyclopentyl-undecanoic acid^{10}) (m.p. 63.5 °C) and ω-cyclohexylundecanoic acid^{2}) (m.p. 53.5 °C), it appears that for one type of ring, i.e. cyclopentyl or cyclohexyl, the melting point increases with increasing aliphatic chain length. It is also noteworthy that in the case of the three substituted undecanoic acids there is no correlation between ring size and melting point.

REFRACTIVE INDEX

The refractive index of the C_{15}-methyl esters are given in table 1.

Methyl pentadecanoate has the lowest refractive index as is to be expected. The refractive index of the ω-alicyclic C_{15}-methyl esters increase with increasing ring size of the alicyclic substituent and there seems to be some regularity as far as the increments are concerned. It is interesting to note that the cyclobutyl isomer has the lowest refractive index among the

TABLE 1

Physical properties of the acids and their methyl esters

Acids	M.p. of the acids (°C)	Refractive index of methyl esters n_D^{20}	Surface tension in 0,1 N NaOH σ = dyn/cm	Equiv. chain length of methyl esters at 179 °C	
				on 20% Reoplex	on 3% Apiezon L
Pentadecanoic	52.0	1.4387	54.2	15.0	15.0
9-Pentadecenoic	below 20	1.4505	not measured	15.4	14.8
6,12-Pentadecadienoic	below 20	1.4587	not measured	16.1	14.6
ω-Cyclobutylundecanoic	59.5	1.4501	40.8	16.1	15.6
ω-Cyclopentyldecanoic	55.5	1.4537	43.3	16.5	15.8
ω-Cyclohexylnonanoic	46.0	1.4567	45.5	16.7	15.9

cyclic compounds although the cyclobutane ring has the highest strain compared to cyclopentane and cyclohexane. Methyl 9-pentadecenoate has practically the same refractive index as methyl ω-cyclobutyl undecanoate whereas the value for methyl 6,12-pentadecadienoate lies much higher than those for the cyclic compounds.

SURFACE TENSION

The surface tension of 0.01% solutions of the ω-alicyclic acids in 0.1N caustic soda was measured. The values are shown in table 1. The soaps of the cyclic fatty acids show lower surface tension than sodium pentadecanoate.

GAS CHROMATOGRAPHY

Table 1 shows the equivalent chain length (ECL) of the methyl esters determined for polar (20% Reoplex 400 on Celite 545) and apolar (3% Apiezon L on Aeropak 30) phases at 179 °C on 1200-cm columns.

The ECL of the unsaturated esters are higher than 15 on the polar phase. Methyl 6,12-pentadecadienoate and ω-cyclobutyl undecanoate both have an ECL of 16.1. Methyl ω-cyclopentyldecanoate and ω-cyclohexylnonanoate have substantially higher ECL values than the cyclobutyl isomer but differ little between each other. On the apolar phase the unsaturated esters are eluted before the methyl ester of the saturated C_{15}-acid. The cyclic esters all have higher retention times than the corresponding acyclic ones. Thus methyl 6,12-pentadecadienoate and ω-cyclobutyl undecanoate which could not be separated by chromatography on the polar phase, are separated on the apolar phase. On the other hand, methyl ω-cyclopentyldecanoate and ω-cyclohexylnonanoate have very similar retention times on apolar phase and the former appears as a weak shoulder on the peak of the latter.

SPECTRAL BEHAVIOUR

IR-Spectra

The IR-spectra of the C_{15}-cyclic methyl esters in the liquid state closely resemble the spectra of other saturated straight chain fatty acid esters. Only in the spectrum of methyl ω-cyclobutylundecanoate a characteristic band appears at 915 cm^{-1} which is to be ascribed to the cyclobutyl ring system [14–16]). The rocking vibration of the polymethylene side chain gave a single band at 720 cm^{-1} for all the liquid methyl esters examined. Apparently the methylene groups of the ring systems do not influence the polymethylene rocking of the side chain.

In the solid state, however, polymethylene compounds show a regular band progression in the 1350–1180 cm^{-1} region[17]). It has been claimed[17]) that the chain length of fatty acids can be determined and even positional isomers identified by a study of this band progression[18]). We were therefore interested to see if and in which way the methylene groups of the ring systems influence the band progression and whether the ring size can be directly correlated to the IR-spectra.

In order to eliminate the strong carboxyl band near 1300 cm^{-1} which would interfere with the polymethylene rocking and/or twisting bands in the region 1350–1180 cm^{-1} [18]), we prepared the silver salts of our acids and recorded the spectra in a KBr-matrix[19]). The unsaturated C_{15}-acids were not measured since it is known that for cis-unsaturation the progression becomes irregular[20]).

In the spectrum of silver pentadecanoate (fig. 1a) we observed, in agreement with the empirical relationship suggested by Meiklejohn[19]), 8 bands in the region 1350–1180 cm^{-1}. ω-Cyclobutylundecanoic acid has a straight chain consisting of 11 carbon atoms and according to Meiklejohn *et al.*[19]) 6 bands in the progression region were to be expected, provided the cyclobutyl ring does not affect the spectrum in this region. Fig. 1b shows that 9 well defined bands appeared. Similar anomalies were also encountered with ω-cyclopentyldecanoic (fig. 1c) and ω-cyclohexylnonanoic (fig. 1d) acids, each of which showed 7 bands in the said region whereas only 5 bands were to be expected[19]). The cyclic substituents apparently influence the structure of the band progression. In order to gain more insight into the nature of the influence of the alicyclic substituent on the band progression we also recorded the spectra of ω-cyclopentylundecanoic acid[10]), (fig. 1e) and dihydrochaulmoogric (ω-cyclopentyltridecanoic) acid[10]) (fig. 1f) and compared these with that of ω-cyclopentyldecanoic acid (fig. 1c). Fig. 1e and 1f show that the bands in the progression region are unevenly spaced with the indication of many shoulders which makes the counting of the peaks rather

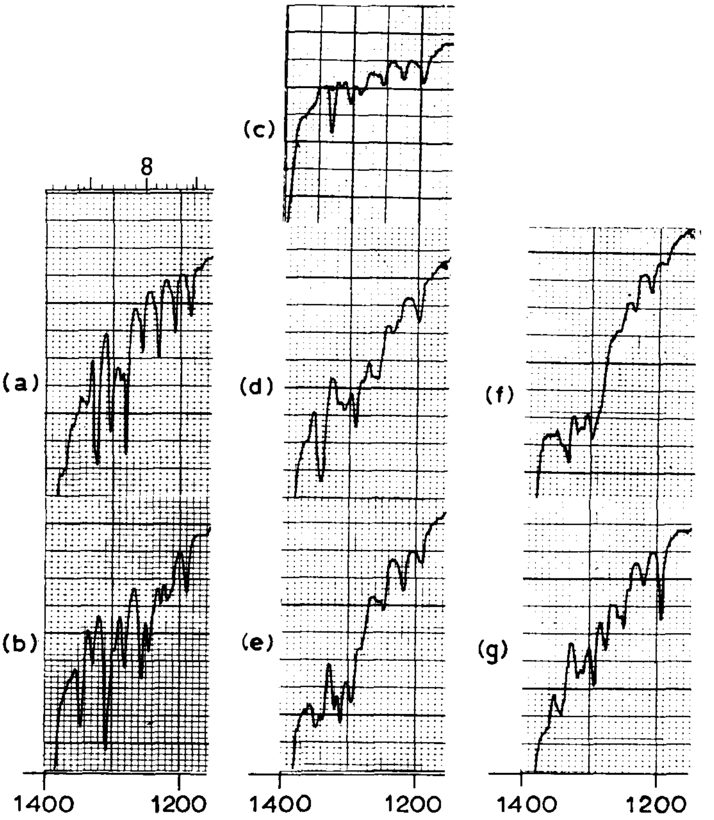


Fig. 1a-g.

uncertain. Thus even the comparison of the spectra within a homologous series did not allow a conclusive deduction to be made regarding the effect of the cyclopentyl substitution on the polymethylene twisting and/or rocking bands. Analogous results were obtained by comparing the spectra of ω-cyclohexylnonanoic acid (fig. 1d) and ω-cyclohexylundecanoic acid[2]) (fig. 1g). On the basis of these observations we conclude that it is neither possible to deduce the length of the aliphatic chain of cyclic fatty acids nor to determine the structure of the ring system by studying the IR-spectra in the region 1350–1180 cm^{-1}.

NMR-Spectra

The NMR-spectra of the methyl esters of the C_{15}-ω-alicyclic substituted acids showed a complex series of multiplets between $\delta = 1.4$ and 1.9 ppm*).

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* The NMR-spectra were measured in $CDCl_3$ with a Varian A 60 instrument. Tetramethylsilane was used as internal standard ($\delta = 0$). Our thanks are due to Dr. Trautwein of the Chemisches Staatsinstitut, Hamburg, for recording these spectra.

Although the protons of unsubstituted cyclopentane and cyclohexane show very discrete and characteristic bands in NMR-spectra[21]), the introduction of one alkyl substitution makes the spectra very complex and unsuitable for identification of the ring system**).

Mass-Spectra

The spectrum of methyl ω-cyclohexylnonanoate showed the usual ester peaks at $m/e=74$, 87 and $87+n\times 14$. The molecular ion M^+ was found at $m/e=254$ and a strong peak at $m/e=223$ indicated the fragmentation $[M-\dot{O}CH_3]$. Very characteristic were the strong peaks at $m/e=171$ and 83 corresponding to $[(CH_2)_8CO_2CH_3]^+$ and the unsubstituted cyclohexyl ion $C_6H_{11}^+$ respectively.

In the spectrum of methyl ω-cyclopentyldecanoate the peak of the molecular ion M^+ appeared at $m/e=254$ and the corresponding peak after the splitting of the methoxyl radical $[M-\dot{O}CH_3]^+$ at $m/e=223$. The other usual ester fragmentation gave a series of peaks at $m/e=74$, 87 and $87+n\times 14$. Characteristic and important for the ring structure were the strong peaks $m/e=185$ and 69 corresponding to the side chain $[(CH_2)_9-CO_2CH_3]^+$ and the unsubstituted cyclopentyl ring $C_5H_9^+$ respectively.

In the spectrum of methyl ω-cyclobutylundecanoate the peaks of the molecular ion and the other usual ester peaks appeared as mentioned above. In addition a strong peak was observed at $m/e=222$ corresponding to $[M-CH_3OH]^+$.

No peak, however, could be observed which would characterise the side chain $[(CH_2)_{10}-CO_2CH_3]^+$ or the ring system $C_4H_9^+$. This is due to the fact that the cyclobutane ring system collapses[22,23]) under electron impact with the loss of ethylene so that no fragmentation of the intact ring system can be observed. The fragmentation of ethylene led to the appearance of a very strong peak at $m/e=194$ corresponding to $M-CH_3OH-C_2H_4$.

The mass spectrometry thus turned out to be the most important tool for the structure elucidation of cyclic fatty acids. Applied to pure compounds it can be used for the identification of the ring systems. Even multiple substituents present no big hindrance for elucidation of the ring structure[24]).

Experimental

METHYL ω-CYCLOBUTYLIDENE UNDECANOATE (IIIa)

17.65 g ω-carbomethoxydecyl triphenyl phosphonium iodide was converted into the corresponding phosphorane by the action of sodium ethoxide

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** Comp. the NMR-Spectra of methyl cyclopentane and hexyl cyclohexane, Sadtler Standard Spectra No. 3436M and 3964, resp.

(derived from 0.69 g Na) in 75 ml dimethylformamide (DMF) at 20 °C. 2.1 g cyclobutanone in 10 ml DMF were added to the phosphorane solution under stirring at room temperature. Stirring was continued for 2 h and the reaction mixture allowed to stay over night under purified argon. Cold diluted HCl was then added and the mixture extracted thrice with petrol ether (b.p. 35–50 °C). The petrol ether extract gave on evaporation 7.3 g crude product which was chromatographed on a silica gel column. Elution with a mixture of petrol ether and ether (19:1 v/v) gave 3.2 g of ester which was saponified with alcoholic caustic potash. The free acid so obtained was reesterified with diazomethane to give IIIa. It was purified by molecular distillation. $\mathrm{B.p._{0.7}} = 115\,°\mathrm{C}$ (bath); $n_D^{20} = 1.4617$.

$C_{16}H_{28}O_2$ (252.4) cal. C = 76.14% H = 11.18%;
found C = 75.87% H = 11.43%.

METHYL ω-CYCLOBUTYLUNDECANOATE (IVa)

2.11 g of IIIa were hydrogenated in 30 ml methanol with 200 mg 5% Pd on charcoal. 1.05 mol. equiv. H_2 was consumed. The product had a purity of about 95%. It was further purified by preparative gas chromatography, whereafter no impurities could be detected gas chromatographically. $n_D^{20} = 1.4505$.

$C_{16}H_{30}O_2$ (254.4) cal. C = 75.53% H = 11.89%
found C = 75.35% H = 12.16%.

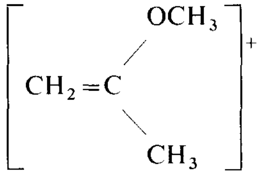
METHYL ω-(1-METHOXYCYCLOBUTYL)-UNDECANOATE (Va)

0.3 ml conc. H_2SO_4 was added to a solution of 3.2 g of IIIa in 30 ml methanol and the mixture refluxed for 2 h, then diluted with water and extracted thrice with ether. The ethereal solution was dried over Na_2SO_4 and evaporated to dryness. 3.7 g of crude product was obtained which was chromatographed on silica gel. Elution with a mixture of petrol ether and ether (98:2 v/v) gave 2.05 g IIIa. Further elution with petrol ether/ether mixture (95:5 v/v) gave 1.45 g of Va which was purified by molecular distillation. $\mathrm{B.p._{0.0002}} = 75\,°\mathrm{C}$ (bath); $n_D^{20} = 1.4539$.

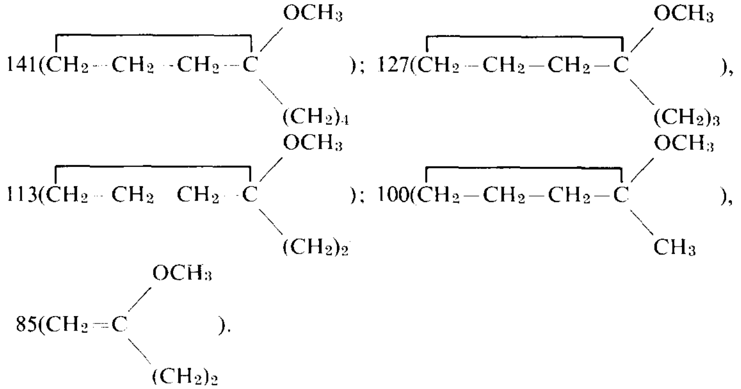
$C_{17}H_{32}O_3$ (268.4) cal. C = 71.78% H = 11.34% OCH_3 = 21.84%
found C = 71.52% H = 11.40% OCH_3 = 22.29% (Zeisel)

IR: 1740 $\mathrm{cm^{-1}}$ (C=O ester); 1080 $\mathrm{cm^{-1}}$ ($C-O-CH_3$);
925 $\mathrm{cm^{-1}}$ (cyclobutyl ring)

NMR: multiplet = 1.00–2.05 (cyclobutyl ring protons);
singlet = 3.61 (ester CH_3O);
singlet = 3.02 (CH_3O on tert. C);
no signal due to $-CC-OCH_3$ which excludes a secondary OCH_3-group.

Mass spectrum:
The molecular ion appeared at *m/e* 284. The base peak at *m/e* 72 is to be ascribed to  $[CH_2{=}C(OCH_3)(CH_3)]^+$. The most characteristic ions are given below together with their assignments:

256($M-C_2H_4$); 241($M-C_3H_7$); 224($M-CH_3OH-C_2H_4$), 221($M-CH_3OH-OCH_3$); 213($M-C_5H_{11}$), 209($M-C_3H_7-CH_3OH$), 203($M-CH_3OH-OCH_3-H_2O$), 192($M-2CH_3OH-C_2H_4$),


141($CH_2-CH_2-CH_2-C(OCH_3)(CH_2)_4$); 127($CH_2-CH_2-CH_2-C(OCH_3)(CH_2)_3$), 113($CH_2-CH_2-CH_2-C(OCH_3)(CH_2)_2$); 100($CH_2-CH_2-CH_2-C(OCH_3)CH_3$), 85($CH_2{=}C(OCH_3)(CH_2)_2$).

ω-CYCLOBUTYLUNDECANOIC ACID (VIa)

To a solution of 0.53 g of IVa in 5 ml ethanol 0.8 ml of 8 N KOH was added and the mixture boiled under reflux for 30 min. Water and diluted HCl were added and the precipitated free acid filtered off. After two recrystallisations from aqueous acetone it melted at 59.5 °C.

$C_{15}H_{28}O_2$ (240.4) cal. C = 74.95% H = 11.74%;
found C = 75.05% H = 11.74%.

METHYL ω-CYCLOPENTYLDECANOATE

Methyl dihydrohydnocarpate was prepared by catalytic hydrogenation of the methyl esters of hydnocarpus oil and carefully fractioned on a 60-cm column packed with 2 × 2 mm wire netting. The pure methyl dihydrohydnocarpate showed the following constants:

b.p.$_{0.05}$ = 81–83 °C; $n_D^{30} = 1.4512$;
Lit. 10): b.p.$_{10}$ = 187–188 °C; $n_D^{30} = 1.4523$

and was gas chromatographically pure. The free acid obtained by hydrolysis melted at 63.5 °C; (Lit. 10: m.p. 64–65 °C, Lit. 25: m.p. 63 °C).

8.04 g methyl dihydrohydnocarpate was reacted in 60 ml absolute ether with phenyl magnesium bromide obtained from 1.70 g magnesium turnings and 10.72 g bromobenzene. After working up 13.5 g crude reaction product was obtained which was chromatographed on 100 g silica gel. Elution with a mixture of petrol ether and ether (98:2 v/v) yielded 10.0 g of a product which contained according to IR-analysis mostly the required 1,1-diphenyl-11-cyclopentyl-undecanol-1 but was contaminated with a small amount of unchanged methyl dihydrohydnocarpate. The whole was therefore dissolved in 50 ml pyridine and treated under ice cooling with 10 ml thionyl chloride. The ice bath was removed after 2 h and the reaction mixture allowed to stand over night at room temperature, thereafter diluted with 350 ml ether and repeatedly washed with dilute HCl until it was free from pyridine. On evaporation of the ethereal solution 8.6 g of a viscous oil was obtained which was taken up in 50 ml petrol ether and filtered through a silica gel column which was finally eluted with further 300 ml of petrol ether. The petrol ether eluates gave on evaporation 7.0 g 1,1-diphenyl-11-cyclopentyl-undecene-1.

$n_D^{20} = 1.5444$.

UV: $\lambda_{max} = 250.5$ mμ; $\varepsilon = 1.29 \times 10^4$

IR: no OH-bands; 1618 cm^{-1} (strong): olefinic double bonds; 1760–1970 cm^{-1}: characteristic band progression of monosubstituted benzene

$C_{28}H_{38}$ (374.6) cal. C=89.77% H=10.23%;
found C=89.88% H=10.31%.

6.8 g of 1,1-diphenyl-11-cyclopentyl-undecene-1 were dissolved in a mixture of 30 ml glacial acetic acid and 100 ml acetone and treated with a solution of 3.5 g CrO_3 in 3 ml H_2O. The reaction mixture was held for 2 h at 50 °C, then diluted with cold 10% H_2SO_4, the whole saturated with common salt and extracted repeatedly with petrol ether. The combined petrol ether extracts were washed with water, dried over Na_2SO_4 and evaporated in vacuo to yield 6.6 g of crude product which was subsequently chromatographed on 120 g silica gel. Elution with benzene gave 3.1 g benzophenone which was identified by direct comparison with an authentic sample. Further elution of the column with ether gave 2.8 g of an acid (VII) which was esterified with diazomethane. The methyl ester of ω-cyclopentyldecanoic acid was purified by preparative gas chromatography.

$n_D^{20} = 1.4537$.

$C_{16}H_{30}O_2$ (254.4) cal. C=75.53% H=11.89%;
found C=75.52% H=11.95%.

ω-CYCLOPENTYLDECANOIC ACID

Methyl ω-cyclopentyldecanoate was saponified as already described. After

two recrystallisations from aqueous acetone it melted at 55.5 °C.
$C_{15}H_{28}O_2$ (240.4) cal. C = 74.95% H = 11.74%;
found C = 74.73% H = 11.61%.

ω-CYCLOHEXYLIDENE NONANOATE (IIIb)

44.6 g of ω-carbomethoxyoctyl triphenyl phosphonium iodide[11]) in 100 ml DMF were converted to the corresponding phosphorane by the action of $NaOC_2H_5$ derived from 1.72 g Na and then treated under argon at room temperature with 7.5 g cyclohexanone in 20 ml DMF. After the reaction mixture was allowed to stay over night it was diluted with about 200 ml icecold 2 N HCl and extracted repeatedly with petrol ether. The combined petrol ether extracts yielded on evaporation 18.6 g of a crude product which was chromatographed on 180 g silica gel. Elution of the column with a mixture of petrol and ether (97:3 v/v) yielded 6.1 g of IIIb which was saponified by refluxing with alcoholic caustic potash. The free acid so obtained was reesterified with diazomethane and purified by molecular distillation. Yield: 5.1 g. $B.p._{0.0008} = 75$ °C (bath); $n_D^{20} = 1.4665$.
The structure was confirmed by mass spectrometry. Molecular weight = 252.

METHYL ω-CYCLOHEXYLNONANOATE (IVb)

2.3 of IIIb was hydrogenated in methanol with 5% Pd on charcoal. The product, which was free of impurities, was molecularly distilled. $B.p._{0.0004} =$ 74 °C (bath);
$n_D^{20} = 1.4567$.
$C_{16}H_{30}O_2$ (254.4) cal. C = 75.53% H = 11.89%;
found C = 75.42% H = 11.90%.

METHYL ω-(1-METHOXYCYCLOHEXYL)-NONANOATE(Vb)

193 mg of IIIb, 3 ml methanol and 0.04 ml conc. H_2SO_4 were refluxed for 6 h, then diluted with water and extracted exhaustively with ether. The ether extracts yielded on evaporation was 198 mg of an oil which was chromatographed on 5 g silica gel. Elution with petrol ether/ether (19:1 v/v) gave 134 mg unchanged IIIb, while further elution with petrol ether/ether (17:3 v/v) yielded 50 mg of Vb, the structure of which was confirmed by mass spectrometry. The molecular ion showed at *m/e* 284 and the base peak at 113 due to the ion $(C_6H_{10}{\cdot}OCH_3)^+$. The most characteristic peaks are interpreted as follows*):

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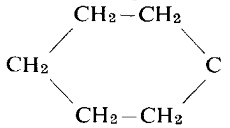
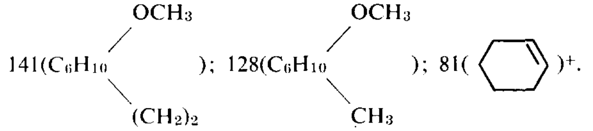
* The fragment C_6H_{10} stands for the following structure



253(M$-OCH_3$); 252(M$-CH_3OH$); 241(M$-C_3H_7$); 228(M$-C_4H_8$); 221(M$-OCH_3-CH_3OH$); 213(M$-C_5H_{11}$); 209(M$-C_3H_7-CH_3OH$); 203(M$-OCH_3-CH_3OH-H_2O$); 181(M$-C_5H_{11}-CH_3OH$); 157[$(CH_2)_7-CO_2CH_3$];



$141\left(C_6H_{10}\overset{OCH_3}{\underset{(CH_2)_2}{}}\right)$; $128\left(C_6H_{10}\overset{OCH_3}{\underset{CH_3}{}}\right)$; 81( )$^+$.

ω-CYCLOHEXYLNONANOIC ACID

The alkaline saponification of IVb gave VIb which was recrystallised twice from aqueous acetone. M.p. 46 °C.

$C_{15}H_{28}O_2$ (240.4) cal. C = 74.95% H = 11.74%;
found C = 75.06% H = 11.94%.

METHYL 9-PENTADECENOATE

2.8 g of ω-carbomethoxyoctyl triphenyl phosphonium iodide was converted to the corresponding phosphorane in 10 ml DMF and treated with 0.5 g hexanal in 2 ml DMF. Usual working up and purification by chromatography on silica gel gave 0.85 g methyl Δ^9-pentadecenoate which was further purified by molecular distillation.

B.p.$_{0.0003}$ = 70 °C (bath); $n_D^{20} = 1.4505$.
$C_{16}H_{30}O_2$ (254.4) cal. C = 75.53% H = 11.89%;
found C = 75.39% H = 12.01%.
IR: weak band at 965 cm^{-1} indicated slight trans contamination.

METHYL 6,12-PENTADECADIYNOATE

To a solution of 4 g sodium in 250 ml liquid ammonia 60 mg hydrated ferric nitrate were added in small portions until all of the sodium had been converted into sodamide. 22 g of 6-chlorohex-1-yne[13]) were now added dropwise under stirring and allowed to react 90 min. 41 g 8-iodo-oct-3-yne[13]) in 50 ml dry ether were added to the reaction mixture and the whole stirred for 3 h. Water was then carefully added and the whole extracted with petrol ether. The petrol ether extract yielded on evaporation 41 g of crude product which was distilled in vacuo. During the vacuum distillation interhalogenation took place so that a part of the unchanged 5-iodo-oct-1-yne reacted with the product 14-chloro-tetradeca-3,9-diyne to give chlorooctyne and 14-iodo-tetradeca-3,9-diyne. The lower boiling fraction (18 g, b.p.$_{11}$ 35–81 °C) containing chlorohexyne, chlorooctyne and iodooctyne was rejected. The higher boiling fraction (23 g, b.p.$_{0,5}$ 140–210 °C) contained 14-chloro- and 14-iodo-tetradeca-3,9-diyne. 10.3 g of the latter mixture were iodinated by refluxing 32 h in 350 ml dry acetone with 25 g sodium iodide. On working up 12.3 g crude 14-iodo-3,9-tetradecadiyne were obtained which, without further purification was directly converted into the corresponding nitrile by refluxing with 8.37 g KCN in 140 ml aqueous ethanol. After 12 h the reaction mixture was diluted with water and extracted with ether. Evaporation of the ethereal extracts gave 7.8 g of crude nitrile which was methanolysed at 0 °C in 150 ml methanol which contained 25% by weight of gaseous HCl and 622 mg H_2O. After 18 h much water was added and the methyl 6,12-penta-decadiynoate was exhaustively extracted with petrol ether. Yield: 7.8 g crude ester.

The crude ester was chromatographed on 160 g silica gel. After initial elution of the column with 2000 ml petrol ether, 7.5 g of methyl 6,12-pentadecadiynoate was eluted with 2500 ml petrol ether/ether (98:2 v/v) and subsequently purified by molecular distillation.

B.p.$_{0.0006}$ = 64 °C (bath); $n_D^{20} = 1.4711$.

$C_{16}H_{24}O_2$ (248.3) cal. C = 77.37% H = 9.74%;
found C = 76.55%*) H = 9.72%.

METHYL 6,12-PENTADECADIENOATE

3.4 g methyl 6,12-pentadecadiynoate were hydrogenated in 100 ml ethyl acetate in presence of 0.6 g 5% $Pd/CaCO_3$ and 0.6 g quinoline at 20 °C. In course of 5 h 2 mol. equiv. H_2 were taken up when the hydrogenation was stopped. The product was purified by distillation in a 25-cm spinning band column. The final product had a purity of over 99%. B.p.$_1$ = 164 °C; n_D^{20} = 1.4586.

$C_{16}H_{28}O_2$ (252.4) cal. C = 76.14% H = 11.18%
found C = 75.72% H = 11.55%

Mol. wt. = 252 (mass spectrometrically)

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* The value for C-analysis is somewhat low, probably due to incomplete combustion caused by multiple acetylenic bonds. The same observation was also made during the combustion of a number of authentic acetylenic compounds used as tests.

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