Studies of the Pyrolysis of Triglycerides

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The pyrolysis of triglycerides (trilaurin and tripalmitin) in an atmosphere of nitrogen at 300—700°C has been attempted. Fatty acids, acrolein, ketones, and olefins have been identified as pyrolysis products. As intermediates of the pyrolysis, unsaturated glycol difatty acid esters and acid anhydrides were also detected. These results suggest a reaction mechanism of the pyrolysis involving the above compounds.

Numerous studies of the thermal oxidation ofglycerides have been reported, but only a few papers have dealt with the pyrolysis of glycerides in the absence of air. The pyrolysis of glycerides may be expected to be different in the absence of and in the presence of air.

Crossley[1] has reported studies of the pyrolysis of glycerides with and without air, but he has not described in detail the mechanism of pyrolysis in the absence of air.

The present author has prepared pure trilaurin and tripalmitin and then pyrolyzed them in an atmosphere of nitrogen at 300—700°C. The pyrolysis products have been analyzed and indentified, and the mechanism of a series of pyrolysis reactions has elucidated.

Experimental

Pyrolysis Apparatus and Procedure. The pyrolysis apparatus used was the same as that illustrated in a previous paper.[2] When the temperature in the quartz tube reached a fixed temperature, a throughly-dried sample (about 0.5 g) in a porcelain boat was introduced to the center of the tube by means of a steel rod driven by a magnet. A slow stream of purified nitrogen (20 m*l*/min) was passed through the quartz tube during the pyrolysis. The products of the pyrolysis were collected in the N_1 trap (cooled by ice and salt) and in the N_2 and N_3 traps (cooled by dry ice and acetone), and were then submitted to analysis.

Preparation of Samples. Purified fatty acids were converted to acid chlorides,[3] and these were then treated with glycerol in chloroform and pyridine to give the triglycerides.[4] After repeated recrystallization from acetone, thin-layer chromatography (tlc) (coating material : silica gel G; developing solvents : petroleum ether : diethyl ether : acetic acid, 70 : 30 : 2) showed no impurities. The melting points and saponification values (S.V.) of the samples are shown in Table 1.

Table 1. Melting points and saponification values of the samples

Sample	Mp (°C)	S.V.
Trilaurin	45.0—45.8	263.0
Tripalmitin	65.5—65.7	207.7

Analysis of Pyrolysis Products. The pyrolysis products were dissolved in carbon tetrachloride, and were then separated into acidic and neutral fractions with 10% K_2CO_3. After the methylation of the acidic fractions, the methyl esters were analyzed by gas-liquid chromatography (glc).[5] The neutral fractions were analyzed by column chromatography, by tlc, by a study of the infrared spectrum (IR),[6] and by chemical analysis.

Results and Discussion

Acidic and Neutral Fractions. Using a 0.5-g sample each time, a series of ten pyrolyses was performed. The total weights of the acidic and neutral fractions are shown in Table 2.

Table 2. Acidic fractions and neutral fractions

Sample	Pyrolysis temperature (°C)	Acidic fraction (g)	Acidic fraction (%)	Neutral fraction (g)	Neutral fraction (%)
Trilaurin	550	1.50	30.0	1.90	38.0
Tripalmitin	450	2.22	44.3	1.63	32.5

Fatty Acids. A part of the carbon tetrachloride solutions of the pyrolysis products were titrated with with standard alkali; the acid values (A.V.) thus obtained are shown in Fig. 1. The A.V. were most in the pyrolysis products at 550°C(trilaurin) and at 450°C (tripalmitin). At these temperature, the fatty acid yields were 46.9% (trilaurin) and 54.8% (tripalmitin).

The pyrolysis temperatures, 450°C and 550°C, are considered to be favorable for the most effective performance of the pyrolysis. Tlc showed also that no pyrolysis took place at 300°C, that at 450—550°C the spots of the pyrolysis products appeared most clearly, and that at 700°C the spots were not clear and that carbonization probably took place. Accordingly, pyrolysis can best be performed at 450—550°C.

Glc analysis of the acidic fractions in pyrolysis products showed that the main parts are the component fatty acids of the samples. In addition to these, many saturated and unsaturated lower acids were found to be present in very small amounts.

Unsaturated Glycol Difatty Acid Esters. In previous reports on the pyrolysis of ethylene glycol fatty acid esters,[2] monoglycerides[7] and diglycerides[8] in an atmosphere of nitrogen, the main decomposition

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[1] A. Crossley, T. D. Heyes, and B. J. F. Hudson, *J. Amer. Oil Chemists' Soc.*, **39**, 9 (1962).

[2] K. Kitamura and N. Tachikawa, *J. Japan Oil Chemists' Soc.*, **14**, 250 (1965).

[3] I. Imai and T. Wakabayashi, *ibid.*, **10**, 435 (1961).

[4] B. F. Daubert and A. R. Baldwin, *J. Amer. Chem. Soc.*, **66**, 997 (1944).

[5] A Yanagimoto GCG-2 Gas Chromatograph with a thermal-conductivity detector was used.

[6] A Hitachi EPI-S_2 Infrared Spectrophotometer was used.

[7] K. Kitamura, S. Kajita, A. Sasaki, and Y. Inoue, *Memoirs of the Res. Inst. of Sci. and Eng., Ritsumeikan Univ.*, **15**, 53 (1966).

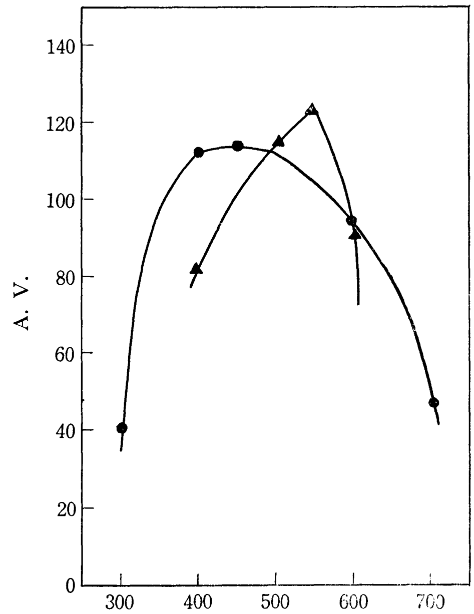


Fig. 1. Effect of the pyrolysis temperature on A.V. of the pyrolysis products.
▲: Trilaurin; ●: Tripalmitin

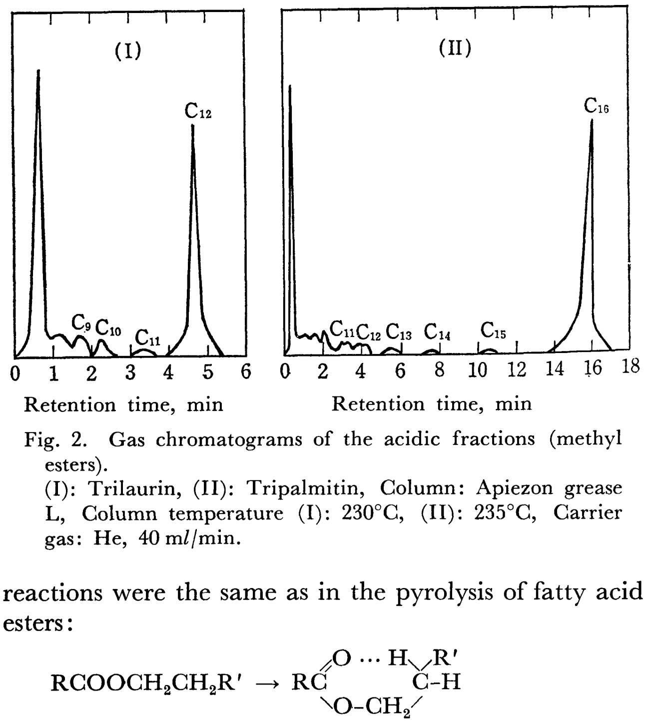
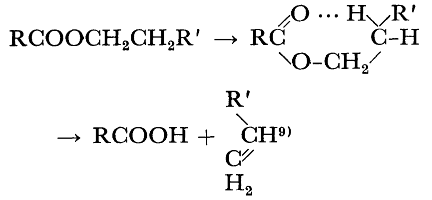


Fig. 2. Gas chromatograms of the acidic fractions (methyl esters).
(I): Trilaurin, (II): Tripalmitin, Column: Apiezon grease L, Column temperature (I): 230°C, (II): 235°C, Carrier gas: He, 40 m*l*/min.

reactions were the same as in the pyrolysis of fatty acid esters:

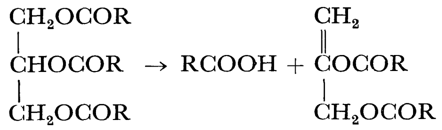


$$\mathrm{RCOOCH_2CH_2R'} \rightarrow \mathrm{RC}\begin{matrix}/\!\!/\mathrm{O}\cdots\mathrm{H}\diagdown\diagup\mathrm{R'}\\ \qquad\qquad\qquad \mathrm{C{-}H}\\ \diagdown\mathrm{O{-}CH_2}\diagup\end{matrix} \rightarrow \mathrm{RCOOH} + \begin{matrix}\mathrm{R'}\\ \diagdown\\ \mathrm{CH}^{9)}\\ \mathrm{C}/\!\!/\\ \mathrm{H_2}\end{matrix} \tag{1}$$

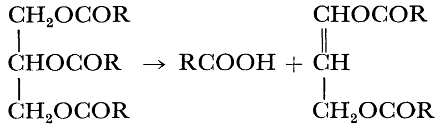
In the pyrolysis of ethylene glycol fatty acid esters, the pyrolysis products were obtained purely and were identified:[2)]

$$\begin{matrix}\mathrm{CH_2OCOR}\\ |\\ \mathrm{CH_2OCOR}\end{matrix} \rightarrow \mathrm{RCOOH} + \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CHOCOR}\end{matrix} \tag{2}$$

Therefore, in the pyrolysis of triglycerides (trilaurin and tripalmitin), the first decomposition process should proceed by means of the formation of fatty acids and unsaturated glycol difatty acid esters (UGDE), as is shown in the following equations:



$$\begin{matrix}\mathrm{CH_2OCOR}\\ |\\ \mathrm{CHOCOR}\\ |\\ \mathrm{CH_2OCOR}\end{matrix} \rightarrow \mathrm{RCOOH} + \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{COCOR}\\ |\\ \mathrm{CH_2OCOR}\end{matrix} \tag{3}$$



$$\begin{matrix}\mathrm{CH_2OCOR}\\ |\\ \mathrm{CHOCOR}\\ |\\ \mathrm{CH_2OCOR}\end{matrix} \rightarrow \mathrm{RCOOH} + \begin{matrix}\mathrm{CHOCOR}\\ \|\\ \mathrm{CH}\\ |\\ \mathrm{CH_2OCOR}\end{matrix} \tag{3'}$$

$R = C_{11}H_{23}$ or $C_{15}H_{31}$

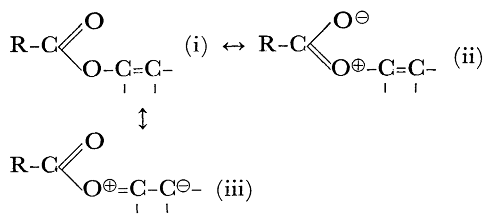
About 1 g of the neutral fraction of the pyrolysis product (tripalmitin) was separated by column chromatography with silica gel (50 g) as the adsorbent and with petroleum ether and ether (7:3) as developers. A substance (0.06—0.1 g), the I.V. of which was about 20.0 (halogen addition hindrance by carbonyl), was obtained from the middle part of the column. The S.V. of this substance was 170.4 (84% of the theoretical).

This substance shows IR adsorption peaks at 1780 and 1680 cm^{-1} ($-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\mathrm{C}{=}\mathrm{C}-$); 1740 cm^{-1} ($-\mathrm{C}{=}\mathrm{O}$); 1180 and 1110 cm^{-1} ($=\mathrm{C}-\mathrm{O}-\mathrm{C}-$);[10)] 1160 and 1110 cm^{-1} ($=\mathrm{C}-\mathrm{O}-\mathrm{C}=$);[11)] 870 cm^{-1} ($\mathrm{CH_2}{=}\mathrm{C}\langle$).[12)]

From these results, it can be deduced that this substance has the structure of UGDE shown in Eq. (3).

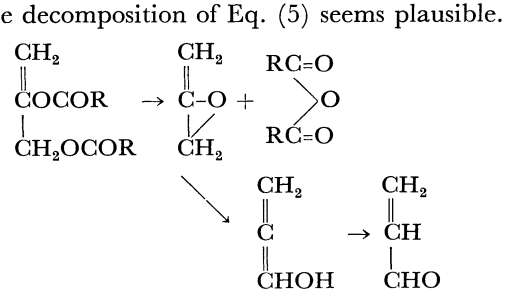
In the case of trilaurin, the results obtained were almost the same.

Acid Anhydrides. In Eq. (4), because of the resonance of (iii), the pushing-out of the electron to



$$\mathrm{R{-}C}\begin{matrix}/\!\!/\mathrm{O}\\ \diagdown\mathrm{O{-}\underset{|}{C}{=}\underset{|}{C}{-}}\end{matrix}\ \text{(i)} \leftrightarrow \mathrm{R{-}C}\begin{matrix}\diagup\mathrm{O}^{\ominus}\\ \backslash\!\!\backslash\mathrm{O}^{\oplus}\mathrm{{-}\underset{|}{C}{=}\underset{|}{C}{-}}\end{matrix}\ \text{(ii)} \updownarrow \mathrm{R{-}C}\begin{matrix}/\!\!/\mathrm{O}\\ \diagdown\mathrm{O}^{\oplus}\mathrm{{=}\underset{|}{C}{-}\underset{|}{C}^{\ominus}{-}}\end{matrix}\ \text{(iii)} \tag{4}$$

the carbonyl oxygen of (ii) is considered to decrease. For this reason, the (1)-type decomposition of UGDE in Eq. (3) cannot be considered to proceed. Accordingly, the decomposition of Eq. (5) seems plausible.



$$\begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{COCOR}\\ |\\ \mathrm{CH_2OCOR}\end{matrix} \rightarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{C{-}O}\\ |\diagup\\ \mathrm{CH_2}\end{matrix} + \begin{matrix}\mathrm{RC{=}O}\\ \rangle\mathrm{O}\\ \mathrm{RC{=}O}\end{matrix} \searrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{C}\\ \|\\ \mathrm{CHOH}\end{matrix} \rightarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH}\\ |\\ \mathrm{CHO}\end{matrix} \tag{5}$$

$R = C_{11}H_{23}$ or $C_{15}H_{31}$

[8)] K. Kitamura, *ibid.*, **17**, 85 (1968).

[9)] F. Krafft, *Ber.*, **16**, 1719, 3018 (1883); C. D. Hurd and F. H. Blunk, *J. Amer. Chem. Soc.*, **60**, 2419 (1938).

[10)] K. Nakanishi, "IR Absorption Spectroscopy—Practical" (in Japanese), Nankodo, Tokyo (1960), p. 100 (D.M.S. 2200).

[11)] K. Nakanishi *et al.*, "Jikken Kagaku Koza," Vol. 1, Maruzen, Tokyo (1957), pp. 366, 370.

[12)] *Ibid.*, p. 370.

On the contrary, UGDE in Eq. (3)′seems clearly not to decompose to acid anhydride and acrolein; this is supported by the fact that the yield of acrolein does not exceed about 50% of the theory.

The detection of the acid anhydrides in the neutral fractions was attempted in three ways. First, the IR spectra of the neutral fractions (pyrolysis temperature: 550°C) showed strong bands at 1810 cm^{-1} and 1740 cm^{-1}; these bands are characteristic of acid anhydrides. Secondly, the neutral fractions were analyzed quantitatively by the morpholine method;[13] the results are shown in Table 3.

Table 3. Acid anhydrides formation

Sample	Pyrolysis temperature (°C)	Acid anhydride (%)	From free acid
Trilaurin	450	4.3	
	550	6.0	2.2
Tripalmitin	450	2.7	0.8
	550	6.4	4.1

Acid anhydrides are also formed on the pyrolysis of free acids—on, for instance, the pyrolysis of lauric and palmitic acid at 550°C and 450°C respectively; the acid anhydrides from each acid are also listed in Table 3

Finally, tlc was carried out and the acid anhydrides were identified by comparing them with authentic samples.

Acrolein. In a series of ten experiments, about 0.3 m*l* of liquid was collected in the N_2 and N_3 traps; the major part of the liquid was acrolein, which was detected by glc in comparison with an authentic sample. In these cases, however, the pyrolysis products were passed directly into the 2,4-dinitrophenylhydrazine hydrochloride solution to form hydrazones (2,4-DNPH). Ketones (see below) were condensed in the N_1 trap; a small amount of acrolein was also obtained from the N_1 trap by the distillation of the carbon tetrachloride solution. This was converted to 2,4-DNPH and then added to the 2,4-DNPH obtained from the N_2 and N_3 traps. One example of these results is shown in Table 4.

Table 4. Acrolein formation

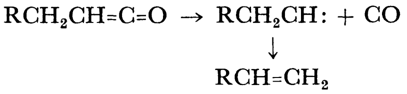
Sample (g)	2,4-DNPH (g)	Acrolein (g)	Yield (%)	
			Found	Theoretical
Trilaurin 0.490	0.073	0.017	3.5	8.8
Tripalmitin 0.500	0.076	0.018	3.6	6.9

α-Olefins. Authentic samples of lauric and palmitic anhydride were pyrolyzed; they gave the corresponding acids in almost quantitative yields, which can be accounted for by the following reaction equation:

$$(RCH_2CO)_2O \rightarrow RCH_2COOH + RCH{=}C{=}O \quad (6)$$

$$R = C_{10}H_{21} \text{ or } C_{14}H_{29}$$

Thus, it was confirmed that acid anhydrides decomposed to acids and aldoketenes. However, as the ketenes formed seemed to be less volatile because of the long alkyl radical, and also not to be so stable because of the ketene group, they are thought to decompose during the pyrolysis as follows:[14]



$$RCH_2CH{=}C{=}O \rightarrow RCH_2CH\!: + CO \quad (7)$$
$$RCH_2CH\!: \rightarrow RCH{=}CH_2$$

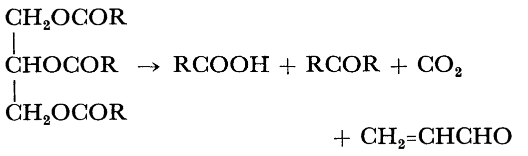
Using alumina as an adsorbent, the column chromatography of the pyrolysis products of triglycerides was carried out; the fractions eluted by petroleum ether showed IR spectra identical with α-olefins (1810,1645, 1420, 990, and 910 cm^{-1}).

The tlc of the pyrolysis products of triglycerides, using the pyrolysis products of alkyl ketene dimers (next paragraph) as the standard, also indicated the existence of α-olefins ($Rf \fallingdotseq 1$).

Because of the unstability of ketene, these ketene monomers have not yet been isolated.[15] Therefore, the decyl ketene dimer and the tetradecyl ketene dimer were prepared from acid chlorides and triethylamine[16] respectively: they were pyrolyzed, and the IR of the expected ketenes were measured. In these cases, however, the IR spectra were the same as those of α-olefins.

Ketones. Laurone and palmitone were detected in the pyrolysis products by tlc, and were identified by using authentic samples as the standard. Oximes of laurone (mp 36—37°C) and palmitone (mp 59—60 °C) were also obtained. In addition to these ketones, various other ketones seemed to be formed.[2]

In this experiment, laurone (from trilaurin) and palmitone (from tripalmitin) have been identified, although they were present in small amounts. Accordingly, it seems that these ketones were not formed directly from triglycerides, but that they were formed secondarily from fatty acids which were themselves originated by the decomposition of triglycerides.[2] Supposing that the ketones are formed from the triglycerides directly, Eq. (8) (Crossley[1]) has to hold:



$$CH_2OCOR\text{–}CHOCOR\text{–}CH_2OCOR \rightarrow RCOOH + RCOR + CO_2 + CH_2{=}CHCHO \quad (8)$$

$$R = C_{11}H_{23} \text{ or } C_{15}H_{31}$$

The fatty acids obtained in this experiment account for about 50%, but their the oretical yields, as calculated from Eq. (8), are about 30%. This difference is fairly

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[13] J. B. Johnson and G. L. Funk, *Anal. Chem.*, **27**, 1464 (1955).

[14] L. Knentzel, *NASA Tech. Publ. Announcements*, **2**, 1063 (1962).

[15] E. S. Rothman, *J. Amer. Oil Chemists' Soc.*, **45**, 189 (1968).

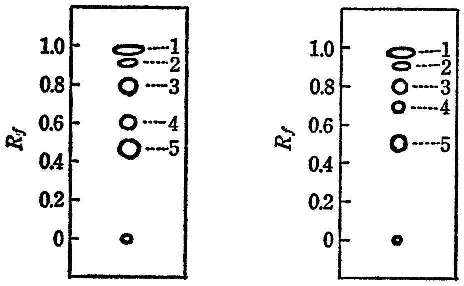
[16] J. C. Sauer, *J. Amer. Chem. Soc.*, **69**, 244 (1947); I. Imai, T. Wakabayashi, M. Yoshino, and S. Komiya, *J. Japan Oil Chemists' Soc.*, **10**, 208 (1961).

Table 5. The results of pyrolysis

Pyrolysis product	Pyrolysis intermediate product	Unchanged sample	Yield (%)
Fatty acids			45.0—55.0
Acrolein			3.5—4.0
α-Olefin			small amount
Ketones			small amount
	Unsaturated glycol difatty acid esters		small amount
	Acid anhydrides		2.5—6.5
		Triglycerides	10.0

large. This fact is one of the reasons why the present author cannot accept Eq. (8).

The tlc of the neutral fractions of the pyrolysis products discussed above are shown in Fig. 3.

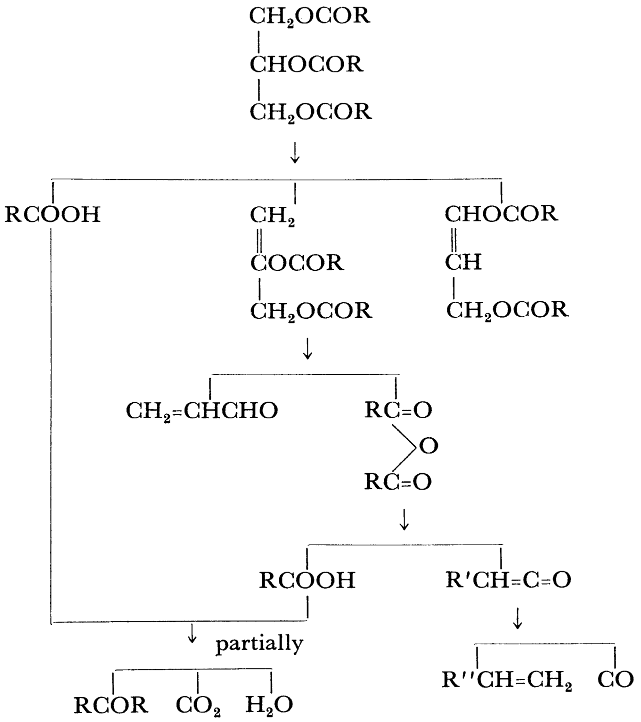


(I) (II)

Fig. 3. Thin-layer chromatograms of the neutral fractions.
(I): Trilaurin (II): Tripalmitin
1: α-Olefins (from ketenes)
2: Ketones 3: Triglycerides
4: UGDE 5: Acid anhydrides
Coating material: Silica gel G
Developing solvents: Petroleum ether, ether and acetic acid (70 : 30 : 2)
Indicator: Sulfuric acid and charring

Conclusion

The main pyrolysis products and pyrolysis intermediate products, *etc.* discussed above, are summarized in Table 5. According to these experimental results and the discussion, the reaction mechanism of the pyrolysis of triglycerides in an atmoshere of nitrogen may be postulated to be as follows:



$R=C_{11}H_{23}$ or $C_{15}H_{31}$

$R'=C_{10}H_{21}$ or $C_{14}H_{29}$

$R''=C_9H_{19}$ or $C_{13}H_{27}$