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γ-INDUCED ADDITION REACTION OF METHANOL TO METHYL OLEATE

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Methyl 9- and 10-methoxystearates were obtained by the γ-induced addition reaction of methanol to methyl oleate in the absence or presence of methanol. Yield of the adducts increased with the increase of methanol added in the reaction systems.

During the course of a radiation chemical investigation of methyl oleate (I), we found methanol addition compounds of (I) together with methyl stearate in the radiolysis products. There have been a few studies on the radiolysis of oleic acid[1] and (I),[2] which undergo cis-trans isomerization, decarboxylation, polymerization, hydrogenation, etc. However no methanol addition reaction has been known in the case of (I). Pieces of work on the photo- or radiation-induced addition reaction of alcohol to the double bond of olefins have been reported. The reactions can be classified into two groups according to the addition behavior of alcohol; the one is addition of hydroxyalkyl group and the other is that of alkoxyl group. The former has mainly been observed in the case of radiation-induced addition,[3] while the latter has taken place in that of the photo-induced reaction.[4] This report deals with the structure of the adducts and the effect of the concentration of methanol added in the reaction systems on the yield of the adducts.

Samples, which were sealed in a glass tube after deoxygenation with nitrogen, were irradiated with ^{60}Co γ-rays at room temperature. The products were analyzed mainly by means of gas chromatography (column: 25%DEGS, 4mm x 3m) and combined gas chromatography-mass spectrometry.

The crude adducts, which were isolated by a preparative thin-layer chromatography, were characterized by the presence of methoxyl proton signal at τ 6.75(singlet) in addition of esteric methyl proton signal at τ 6.45(singlet). Moreover, IR spectrum of adducts showed no absorption of hydroxy group at region of 3200 — 3600cm.$^{-1}$ Mass spectrum of the adducts of methanol is shown in Fig.1. The molecular ion of m/e 328 is present. In the high mass range, peaks are found at m/e 313, 297, and 264, corresponding to M-CH_3, M-OCH_3, and M-2(CH_3OH), respectively. In addition, characteristic peaks which indicate the scission at the bonds shown in Fig.1 are seen at m/e 157, 171, 201, and 215. From the fact that the ratio of peak intensity of m/e 157 to 171 is nearly equal to that of m/e 201 to 215, we consider that the amount of C-9-adduct to C-10-adduct is equal. Consequently, the structure of the adducts were determined to be methyl 9- and 10-methoxystearates (II). The spectral data presented here were identical with those of a synthetic sample which was prepared by the reaction of methyl 9- and 10-bromostearates and sodium methoxide.

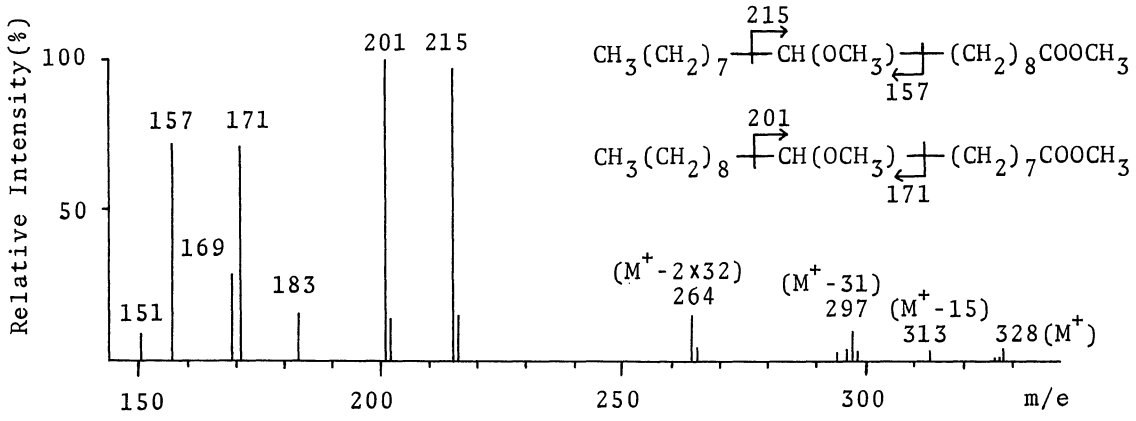


Fig. 1. Illustrative Mass Spectrum of Methanol Adducts of Methyl Oleate

Table 1 shows the dose-dependence of radiolysis of (I) in the presence and absence of methanol. Regardless of presence or absence of methanol, the % yield of (II) increases with dose. However, the effect of dose on the G value of (II) in the presence of methanol is different from that in the absence of methanol, i.e., the latter case showed a constant value. While, the decrease of (I) in the presence of methanol is larger than that of in the absence of methanol. This may be due to the secondary effect of radiolysis product of methanol.

Table 1. Effect of Dose on the Yield of Methyl 9- and 10-Methoxystearates (II) in the Presence and Absence of Methanol

Dose	Yield of (II)[a]				Recovery of (I)[b]	
x 10^8 rad	Addition of 5% methanol		Without methanol		Addition of 5% methanol	Without methanol
	%	(G value)	%	(G value)	%	%
0.3	0.9	(0.91)	0.1	(0.10)	87.7	91.5
0.5	1.3	(0.78)	0.2	(0.12)	80.0	86.4
1.0	2.6	(0.78)	0.4	(0.12)	62.3	73.6
2.0	3.6	(0.54)	0.9	(0.14)	40.5	54.2
3.0	3.8	(0.38)	1.2	(0.12)	27.5	38.3

a) based on the starting (I)

b) containing trans-form of (I)

Table 2. Effect of Concentration of Methanol on the Yield of Methyl 9- and 10-Methoxystearates

	Concentration of methanol (%)					
	0	1	3	5	10	20
Yield (%)	0.6	1.8	2.7	3.2	3.7	3.7
G value	0.14	0.42	0.63	0.74	0.86	0.86

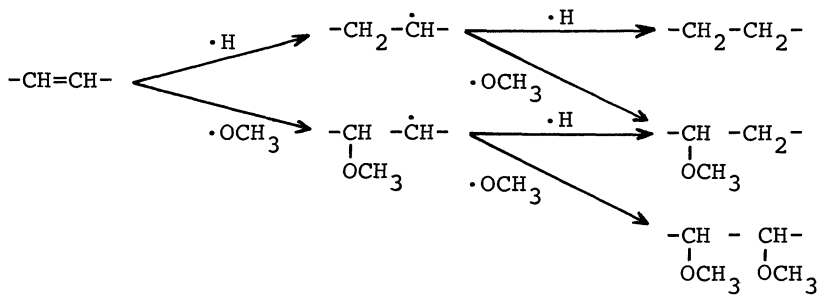
(Dose : 1.3×10^8 rad)

As shown in Table 2, the yield of (II) increases with the concentration of methanol, but when its concentrations are over 10% no increase is observed. Methanol added in the reaction system may contribute to generation of both hydrogen and methoxyl radical.

In the course of radiolysis of methanol, hydroxymethyl radical has been well known, whereas methoxyl radical is also reported as primary radical by M. Imamura et al.[6] Recently, the latter radical has been confirmed in the γ-irradiated methanol by means of spin trapping technique.[7] The mechanism of γ-induced hydrogenation of oleic acid[1b] has been explained by the addition of hydrogen radical, which is produced by C-H bond homolysis and also by charge neutralization of carboxonium and carbonium ions. Moreover, the fact that (II) is given even in the absence of methanol indicates the possibility of the presence of methoxyl radical which is produced by the cleavage of esteric group.

$$RCOOCH_3 \xrightarrow{\sim\sim} RCO\cdot + \cdot OCH_3$$

We postulated the following pathways of competitive addition reactions of methoxyl and hydrogen radicals.



A trace amount of methyl 9,10-dimethoxystearate[5] (III) has also been identified on the gas chromatogram of a fraction separated by a thin-layer chromatography. However, further quantitative investigation of (III) was not carried out because of

its minute yield. Moreover, the addition of hydroxymethyl radical to the (I) should be considered, this is now under investigation.

In conclusion, although this reaction may be of little value as a synthetic method of (II), it is noted that the addition of methoxyl group, which occurs generally in the case of photo-induced addition, is observed in the radiolysis of (I).

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