TABLE I

YIELDS BASED ON CO_2 CONSUMED

	CO_2 Excess, 25°									Metal Excess, 25°									CO_2 Excess, 180°								
	Na	K	Li	Mg	Ca	Rb	Cs	Sr	Ba	Na	K	Li	Mg	Ca	Rb	Cs	Sr	Ba	Na	K	Li	Mg	Ca	Rb	Cs	Sr	B
Carbon monoxide	0	27	0	7	3	29	30	3	2	0	20	0	10	2	29	30	1	1	0	4	0	25	7	20	34	4	4
Carbonate	5	38	28	24	27	63	66	30	26	1	20	20	27	26	35	37	32	19	8	6	20	20	29	24	35	31	32
Formate	1	2	1	2	1	1	1	0	0	3	49	6	2	3	25	32	2	0	2	2	1	1	1	0	0	0	0
Acetate	0	1	0	10	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	2	0	17	2	0	0	0	0
Glycolate	6	0	0	2	4	0	0	0	0	68	1	3	4	6	3	0	4	0	0	0	4	0	5	0	0	0	0
Oxalate	83	20	19	27	16	3	0	46	63	7	4	1	6	12	2	0	2	33	87	84	18	4	31	55	30	32	45
Malonate	0	3	2	6	3	0	0	2	1	0	2	6	4	7	0	0	8	0	1	1	1	3	4	0	0	3	2
Tartronic	2	8	43	7	40	3	1	19	8	1	3	59	23	5	5	1	39	22	2	1	50	10	19	1	1	30	17
Total CO_2	97	99	93	85	94	99	100	100	100	80	99	95	76	61	99	100	88	75	100	100	94	80	98	100	100	100	100

In other experiments it has been found that carbon monoxide does not react under the conditions used to obtain the data of Table I; hence, carbon monoxide is not an intermediate step in the formation of other products. The reduction of carbon dioxide occurred only in the presence of an alkali or alkaline earth metal, no reduction was obtained with amalgams of manganese, zinc, cadmium, gallium, or with mercury alone.

Certain other reducing systems were investigated in cursory fashion. A 50:50 solution of sodium in mercury has formic acid as the chief product at 100°; at 280° the products were formate (10%), malonate (25%), oxalate (45%), and tartronate (20%). A 50:50 mixture of sodium and potassium at 80° gave oxalate and glycolate. A mixture of sodium in Woods metal at 170° produced formate.

Labeling Fatty Acids by Exposure to Tritium Gas. III. Methyl Stearolate and Methyl Linolenate

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Saturated fatty acid methyl esters, to C_{18} as previously shown,[1] are labeled in high specific activity by the Wilzbach method[2] of exposure to tritium gas; tritium substitutes for hydrogen in the aliphatic chain as was predicted.[2] It was discovered, however, that on exposure of methyl oleate, tritium exclusively added to the double bond, yielding radioactive methyl stearate.[3] Further, the 12,13- and the 9,10-double bonds of methyl linoleate were shown to add tritium in a ratio of 1.4 to 1, respectively.

The acetylenic fatty acid ester—methyl stearolate—on exposure to tritium and on subsequent analysis is shown herein to yield *cis*- and *trans*-9,10-tritioöctadecenoate as the major radiochemical product and to give minor amounts of radioactive methyl stearate (saturation) and stearolate (substitution) as shown in Table I. Radioactivity observed in the C_9 dibasic and C_9 monobasic acids results from substitution by tritium for the carbon-bonded hydrogen at carbon atoms other than numbers 9 and 10. Radioactivity in the C_9 mono- and dibasic acids corresponds to the 3–4% tritiated methyl stearolate isolated by liquid-liquid chromatograph and gas-liquid chromatography be-

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[1] R. F. Nystrom, L. H. Mason, E. P. Jones, and H. J. Dutton, *J. Am. Oil Chemists' Soc.*, **36**, 212 (1959).

[2] K. E. Wilzbach, *J. Am. Chem. Soc.*, **79**, 1013 (1957).

[3] E. P. Jones, L. H. Mason, H. J. Dutton, and R. F. Nystrom, *J. Org. Chem.*, **25**, 1413 (1960).

TABLE I

TRITIUM INCORPORATION AND DISTRIBUTION

Tritiated esters or acids	Stearolate	Linolenate
Tritium source (c.)	2.6	2.6
Exposure (days)	20	14
Tritium incorporated (mc.)	210	239
Recovery as acid (%)	79.6	91.6

Chromatographic analysis

	Active		Inactive		Active		Inactive	
	GLC	LLC	GLC	LLC	GLC	LLC	GLC	LLC
Stearate	8.7	10.9				2.0		
Oleate (monoene)	88.6	85.0				3.7		
Linoleate (diene)					79.7	92.5		
Linolenate (triene)					20.3	1.8	100	100
Stearolate (acetylenic)	2.7	4.1	100	100				

Mole % of acids after cleavage

Monobasic								
C_6						24.8		1.0
C_8		8.1		0.3		3.8		4.3
C_9		25.7		49.0				44.7
C_{18}		52.5		0.7		2.4		
Dibasic								
C_6						14.0		
C_7								
C_8				1.0				4.3
C_9		13.7		48.8				45.0
C_{10}				0.7		18.1		0.7
C_{12}						24.9		
C_{14}						12.0		

fore oxidation; radioactive stearic acid corresponds to the 9% tritiated stearic acid similarly isolated by chromatography of the uncleaved fatty acid esters. The 9,10-octadecenoate-H^3 would be expected to give inactive scission acids.

The octadecatrienoate ester—methyl linolenate—on tritium exposure and oxidative cleavage yields some radioactive mono- and dibasic acids, corresponding to the addition of tritium to its double bonds and some acids unaccounted for by a simple addition mechanism.

The major radioactive product on gas chromatography comes at the position of octadecadienoate as expected from the earlier work on tritiation of methyl linoleate and from the hypothesis that tritium adds to either the 9,10-, 12,13-, or 15,16-double bond in a "single-hit" process. Quite unexpected was the comparatively large amount of activity (20.3%) associated with the linolenate peak, indicative of considerable reaction by substitution.

According to a simple concept of tritium addition, cleavage acids possessing activity should consist of C_6 monobasic, C_6 dibasic, and C_{12} dibasic acids. These are, in fact, the major radioactive scission acids. The relatively large amount of C_{10} dibasic acid shown in Table I is not explained. Besides addition or substitution of tritium, migration of unsaturation to the 10,11-position is required. The rationalization of the C_6 radioactive monobasic acid also requires tritium incorporation in the alkyl end of the molecule and with migration of unsaturation to the 10,11-position.

Experimental

The techniques involved in exposure of the compounds to tritium gas and subsequent purification, degradation, and assay were as described previously.[1,3]

Gram samples of methyl stearolate and methyl linolenate were irradiated with 2.6 curies (1 ml. STP) of tritium gas.

By means of the "mixed chromatograph" technique in which inactive known esters are added to unknown mixtures, the position of the major radiochemical component of methyl stearolate is shown to coincide in elution with that of inactive methyl oleate and the radiochemical shoulder with inactive methyl stearate. Only a trace of radioactivity coincided with the position of inactive methyl stearolate. Gas chromatographic and oxidative cleavage results are given in Table I.

The configuration of double bond in the 9,10-octadecenoate-H^3 was studied in the following manner: A portion (1 mg. and 21 μc.) of the irradiated product was added to 7 g. of a methyl oleate–methyl elaidate mixture. This solution was countercurrently distributed in a 200-tube automatic instrument between pentane–hexane and 0.1 *M* silver nitrate in 90% methanol.[4] Recycling was continued until, as shown by the monitoring curve of the recording refractometer, the head of the elaidate band nearly caught up to the tail of the oleate band. Upper layers were then withdrawn into the collector according to the single withdrawal principle. Radioactivity peaks were coincident in position with those for methyl oleate and elaidate, and the integrated counts under the respective peaks indicated that the ratio of *cis*- to *trans*-9,10-octadecenoate-H^3 was 2:1. This ratio is approximately the equilibrium attained by selenium or nitrous oxide isomerization of methyl oleate.

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(4) C. R. Scholfield, E. P. Jones, and H. J. Dutton, *Chem. Ind.* (London), 1874 (1961).