118. *A Quantitative Study of the Autoxidation Products of Oleic Acid.*

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Oleic acid has been oxidised with gaseous oxygen at room temperature, at 49° and at 78°, with and without a cobalt catalyst. Oxidation of the pure acid at room temperature is very slow, the principal products being oxo-acids, but in the presence of cobalt relatively high yields of 8- and 11-oxo-oleic acids,* epoxide, and cleavage products are obtained.

At 49° and 78° the oxidations follow the same general patterns as those already observed with elaidic acid but, in the absence of a catalyst, derivatives of both forms of 9 : 10-dihydroxystearic acid are produced, whereas elaidic acid appears to give only the higher-melting, *erythro*-form.

A detailed quantitative study of the autoxidation of elaidic acid has already been made,[1] and the present communication records similar work on oleic acid, prepared from the commercial redistilled acid by low-temperature crystallisation from acetone.[2]

When dispersed on filter paper and exposed to air at room temperature oleic acid was oxidised extremely slowly, giving about 4% of conjugated unsaturated keto-acids (8- and 11-oxo-oleic),* 8% of other oxo-acids, 2—3% of peroxides, and little or no epoxide or ketol after 2 years (Tables 1 and 7). When oxygen was bubbled through oleic acid containing 0·5% of cobalt for 28 days, however, a relatively high content (15%) of conjugated unsaturated ketonic acids was found, together with appreciable amounts of other oxo-acids, epoxide, ketol, and cleavage products, but very little dihydroxystearic acid was obtained on saponification (Tables 2 and 8). As in other cobalt-catalysed autoxidations of oleic and elaidic acids the peroxide concentration remained quite low.

In experiments at 49° the course of oxidation closely resembled that observed with elaidic acid [1] under similar conditions, but the formation of dihydroxystearic esters and of oxo-acids other than 8- and 11-oxo-acids was greater during the earlier stages than in the case of elaidic acid. The concentration of these other oxo-acids (whose identity has not been established) fell sharply, however, during the later stages of non-catalytic oxidations, suggesting that they are less stable than the corresponding elaidic acid derivatives. Prolonged oxidation in the presence of cobalt gave much higher yields of fission products (volatile acids such as nonanoic, and water-soluble acids such as azelaic) than uncatalysed oxidations or comparable oxidations of elaidic acid (Tables 9 and 10) (cf. Ellis [3]).

The similarities between the oxidations of oleic acid and elaidic acid at 78° were equally striking, and in both cases, in the absence of a catalyst, peroxides reached a peak value before the other products. A notable difference was observed, however, in non-catalytic experiments, the concentration of combined dihydroxystearic acid remaining below 7% after 8 days in the case of oleic acid, whereas with elaidic acid it exceeded 27%. On the other hand, in the presence of cobalt the concentrations of dihydroxystearic acid were about equal, but the amounts of fission products were much higher in the case of oleic acid (Table 12). The dihydroxystearic acid isolated after hydrolysis of the products resulting from the non-catalytic autoxidation of oleic acid consisted of a mixture of the two stereoisomeric forms, m. p.s 95° and 132° (cf. Skellon; [4] Feuell and Skellon [5]). This may explain the low values of dihydroxystearic acid isolated in some cases (see, *e.g.*, Table 7), since the greater solubility of the lower-melting (*threo*) form renders its quantitative isolation much more difficult. In the presence of cobalt only the *erythro*-form has so far been observed.

Although no free ketol-acid has actually been isolated from autoxidised oleic or elaidic acid, Feuell and Skellon [5] have recently separated a small quantity of the 9 : 10-hydroxy-oxostearic acids from the products of the autoxidation of propyl oleate in the presence of 0·05% of uranium at 120°.

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* CO_2H = 1. In *J.*, 1954, 2114, these acids were named as, *e.g.*, η- and κ-oxo-oleic acid.

[1] King, *J.*, **1954**, 2114.

[2] Brown and Shinowara, *J. Amer. Chem. Soc.*, 1937, **59**, 6.

[3] Ellis, *Biochem. J.*, 1936, **30**, 753.

[4] Skellon, *J. Soc. Chem. Ind.*, 1931, **50**, 382T.

[5] Feuell and Skellon, *J.*, 1954, 3414.

TABLE 1. *Autoxidation at room temperature without a catalyst.*

Time (months)	3	6	12	24
Physical condition	Pale yellow oil	Pale yellow oil	Yellow oil	Rather viscous oil
Reduction of Fehling's soln.	None	None	Trace	Weak
Equiv. wt.	286	284	295	304
Iodine value	79	78	63	59
$E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	8·7	11·3	19·1	30·0
Neutral, steam-volatile oil (mainly nonanal and nonan-2-one) (%)	0·31	0·37	0·55	0·48
Volatile oil (nonanal and nonanone) resulting from hydrolysis on distilln. with 0·5N-NaOH (%)	Trace	0·02	1·20	1·15
Nonanal on distilln. of the residual solution from the above hydrolysis with KIO_4 at pH 8·0 (%)	0·40	0·51	1·50	1·64
Saponification value	9	10	41	46
Nonanal resulting from oxidn. with KIO_4 at pH 8·0 (%)	0·18	0·18	0·0	0·0
Carbonyl (%)	0·49	0·68	0·87	1·24
Oxiran-O (%)	0·0	0·0	0·0	0·0
Active O (%)	0·04	0·06	0·13	0·13
Steam-volatile acids, mequiv. (%)	10	23	54	28
Non-volatile, water-soluble acids, mequiv. (%)	6	7	25	25

TABLE 2. *Autoxidation at room temperature in the presence of* 0·5% *of cobalt.*

Time (days)	1	2	4	7	14	28
Physical condition	Oil	Oil	Oil	Oil	Rather viscous oil	Viscous oil
Reduction of Fehling's soln.	None	None	Trace	Slight	Slight	Weak
Equiv. wt.	285	284	277	270	254	232
Iodine value	78	74	66	61	50	32
$E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	25·0	46·4	75·9	82·1	94·1	88·8
Neutral, steam-volatile oil (mainly nonanal and nonan-2-one) (%)	Trace	Trace	0·20	0·35	0·35	0·35
Volatile oil (nonanal and nonanone) resulting from hydrolysis on distilln. with 0·5N-NaOH (%)	1·32	2·65	4·61	5·31	6·22	5·50
Nonanal on distilln. of the residual solution from the above hydrolysis with KIO_4 at pH 8·0 (%)	Trace	0·34	0·50	1·13	1·96	2·78
Saponification value	7	10	17	22	33	45
Nonanal resulting from oxidn. with KIO_4 at pH 8·0 (%)	0·0	0·22	0·36	0·51	0·61	1·07
Carbonyl (%)	0·69	1·22	2·02	2·26	2·63	3·05
Oxiran-O (%)	0·10	0·18	0·24	0·40	0·38	0·59
Active O (%)	0·05	0·06	0·08	0·09	0·08	0·11
Steam-volatile acids, mequiv.	4	—	—	18	23	64
Non-volatile, water-soluble acids, mequiv. (%)	9	—	—	41	67	110

TABLE 3. *Autoxidation at* 49° *without a catalyst.*

Time (days)	7	14	21	28
Physical condition	Oil	Oil	Oil	Slightly viscous
Reduction of Fehling's soln.	None	Trace	Weak	Weak
Equiv. wt.	289	308	310	310
Iodine value	81	70	57	42
$E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	10·1	27·3	41·3	52·1
Neutral, steam-volatile oil (mainly nonanal and nonan-2-one) (%)	0·36	0·95	1·53	1·62
Volatile oil (nonanal and nonanone) resulting from hydrolysis on distilln. with 0·5N-NaOH (%)	0·53	1·90	3·16	3·88
Nonanal on distilln. of the residual solution from the above hydrolysis with KIO_4 at pH 8·0 (%)	0·84	3·22	4·41	4·72
Saponification value	19	34	54	70
Nonanal resulting from oxidn. with KIO_4 at pH 8·0 (%)	0·08	0·46	0·53	0·98
Carbonyl (%)	0·56	1·41	1·78	1·79
Oxiran-O (%)	0·24	0·28	0·51	0·51
Active O (%)	0·24	0·44	0·55	0·47
Steam-volatile acids, mequiv. (%)	15	25	27	31
Non-volatile, water-soluble acids, mequiv. (%)	5	20	35	44

Considerable amounts of carbon dioxide were evolved in catalysed oxidations at 49° and at 78° (cf. Ellis;[6] Skellon and Thruston[7]) and its formation was increased both absolutely and relatively to that of formic acid by the catalyst (Table **13**). Probably formic acid is itself oxidised under these conditions. The formation of formic acid from pure oleic acid (which may well involve preliminary α-oxidation) has been reported previously,[4] but it is known to result also from the catalysed autoxidation of saturated compounds such as stearic acid and hexadecane.[8]

TABLE 4. *Autoxidation at* 49° *in the presence of* 0·5% *of cobalt.*

Time (hr.)	8	16	24	48	72	96	168
Physical condition	Oil	Oil	Oil	Rather viscous Few crystals	Some crystals	Pasty	Pasty
Reduction of Fehling's soln.	None	None	Slight	Moderate	Moderate	Moderate	Rather strong
Equiv. wt.	287	282	274	263	253	220	194
Iodine value	84	73	62	51	39	16	9
$E^{1\%}_{1\,\mathrm{cm.}}$ at 224 mμ	17·3	44·8	68·1	75·2	71·4	46·6	20·2
Neutral, steam-volatile oil (mainly nonanal and nonan-2-one) (%)	0·20	0·43	0·74	0·80	0·86	1·13	0·87
Volatile oil (nonanal and nonanone) resulting from hydrolysis on distilln. with 0·5N-NaOH (%)	0·75	3·03	4·44	4·74	4·73	2·46	0·91
Nonanal on distilln. of the residual solution from the above hydrolysis with KIO_4 at pH 8·0 (%)	0·22	0·85	1·56	2·47	3·04	3·62	4·78
Saponification value	3	14	21	32	44	80	99
Nonanal resulting from oxidn. with KIO_4 at pH 8·0 (%)	0·14	0·21	0·15	0·40	0·56	1·10	1·49
Carbonyl (%)	0·49	1·08	1·67	2·04	2·32	2·09	2·01
Oxiran-O (%)	0·19	0·33	0·45	0·75	0·91	0·87	0·45
Active O (%)	0·02	0·06	0·04	0·04	0·04	0·11	0·10
Steam-volatile acids, mequiv. (%)	9	21	36	48	55	100	121
Non-volatile, water-soluble acids, mequiv. (%)	12	15	33	52	68	135	193

TABLE 5. *Autoxidation at* 78° *without a catalyst.*

Time (days)	1	2	4	6	8
Physical condition	Oil	Oil	Rather viscous	Rather viscous	Viscous some crystals
Reduction of Fehling's soln.	None	Trace	Weak	Fairly strong	Strong
Equiv. wt.	283	296	307	310	297
Iodine value	81	67	38	25	15
$E^{1\%}_{1\,\mathrm{cm.}}$ at 224 mμ	7·6	21·3	45·5	44·3	32·2
Neutral, steam-volatile oil (mainly nonanal and nonan-2-one) (%)	0·13	0·24	0·76	0·69	0·68
Volatile oil (nonanal and nonanone) resulting from hydrolysis on distilln. with 0·5N-NaOH (%)	0·24	1·18	2·61	2·05	1·56
Nonanal on distilln. of the residual solution from the above hydrolysis with KIO_4 at pH 8·0 (%)	0·24	0·56	4·18	4·48	4·98
Saponification value	5	23	70	102	134
Nonanal resulting from oxidn. with KIO_4 at pH 8·0 (%)	0·12	0·88	0·84	1·18	1·92
Carbonyl (%)	0·44	0·94	1·84	2·14	1·99
Oxiran-O (%)	0·15	0·44	0·68	0·51	0·12
Active O (%)	0·19	0·44	0·33	0·15	0·14
Steam-volatile acids, mequiv. (%)	14	24	41	52	66
Non-volatile, water-soluble acids, mequiv. (%)	4	16	48	70	83

The iodine and saponification values were similar to those obtained with elaidic acid under comparable conditions. It is significant that the high saponification value found after oleic acid had been oxidised at 78° for 8 days without a catalyst was not associated with a particularly high content of dihydroxystearic acid (Tables 5 and **11**; cf. elaidic acid)

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[6] Ellis, *Biochem. J.*, 1950, **46**, 129; 1932, **26**, 791.

[7] Skellon and Thruston, *J.*, 1949, 1630.

[8] Salway and Williams, *J.*, 1922, 1343.

TABLE 6. *Autoxidation at 78° in the presence of* 0·5% *of cobalt.*

Time (hr.)	4	8	12	16	32
Physical condition	Oil	Oil	Few crystals	Viscous; some crystals	Semi-crystalline
Reduction of Fehling's soln.	Trace	Slight	Moderate	Moderate	Fairly strong
Equiv. wt.	292	284	273	259	204
Iodine value	78	60	45	35	14
$E^{1\%}_{1\,\mathrm{cm.}}$ at 224 mμ	25·9	48·5	59·5	49·7	19·7
Neutral, steam-volatile oil (mainly nonanal and nonan-2-one) (%)	0·33	0·74	0·85	0·84	0·88
Volatile oil (nonanal and nonanone) resulting from hydrolysis on distilln. with 0·5N-NaOH (%)	1·45	2·87	2·89	2·69	0·81
Nonanal on distilln. of the residual solution from the above hydrolysis with KIO_4 at pH 8·0 (%)	0·71	1·81	2·87	3·49	3·99
Saponification value	18	35	55	66	102
Nonanal resulting from oxidn. with KIO_4 at pH 8·0 (%)	0·09	0·27	0·48	0·59	1·04
Carbonyl (%)	0·58	1·42	1·86	2·06	2·12
Oxiran-O (%)	0·11	0·47	0·54	0·72	0·24
Active O (%)	0·04	0·04	0·03	0·03	0·03
Steam-volatile acids, mequiv. (%)	17	35	46	57	99
Non-volatile, water-soluble acids mequiv. (%)	10	31	53	78	155

TABLE 7. *Composition* (%) *of non-gaseous products obtained by autoxidation at room temperature without a catalyst.*

Time (months)		3	6	12	24
8- and 11-Oxo-oleic acids, $C_{18}H_{32}O_3$, deduced from	(*a*) $E^{1\%}_{1\,\mathrm{cm.}}$ val.	0·3	0·7	2·2	4·2
	(*b*) hydrolysis products	Trace	0·9	3·3	3·2
9 : 10-Ketol-acids, as $C_{18}H_{34}O_4$		1·0	1·0	0·0	0·0
Other oxo-acids, as $C_{18}H_{32}O_3$		3·3	4·7	5·8	7·9
9 : 10-Epoxystearic acid		0·0	0·0	0·0	0·0
Hydroperoxyoleic acid		0·8	1·2	2·5	2·6
Dihydroxystearic acid (combined)	(*a*) KIO_4 method	Trace	0·7	4·0	4·4
	(*b*) isolated	0·0	0·0	0·2	0·7
Steam-volatile acids, as nonanoic		1·6	3·6	8·5	4·4
Non-volatile, water-soluble acids, as azelaic		0·6	0·7	2·4	2·3
Neutral, steam-volatile oil (mainly nonanal and nonanone)		0·3	0·4	0·5	0·5
Unchanged oleic acid (calc.)		84	81	60	52

TABLE 8. *Autoxidation at room temperature in the presence of* 0·5% *of cobalt.*

Time (days)		1	2	4	7	14	28
8- and 11-Oxo-oleic acids, $C_{18}H_{32}O_3$, deduced from	(*a*) $E^{1\%}_{1\,\mathrm{cm.}}$ val.	2·8	6·7	12·2	13·4	15·6	14·6
	(*b*) hydrolysis products	3·7	6·9	11·4	12·9	14·7	13·1
9 : 10-Ketol-acids, as $C_{18}H_{34}O_4$		0·0	1·2	2·0	2·8	3·4	6·0
Other oxo-acids, as $C_{18}H_{32}O_3$		4·5	5·0	6·8	7·2	8·3	11·3
9 : 10-Epoxystearic acid		1·9	3·4	4·5	7·4	7·0	11·0
Hydroperoxyoleic acid		0·9	1·2	1·6	1·8	1·6	2·1
Dihydroxystearic acid (combined)	(*a*) KIO_4 method	0·0	0·0	0·0	0·0	0·8	1·6
	(*b*) isolated	0·0	0·0	0·0	0·0	0·15	0·6
Steam-volatile acids, as nonanoic		0·7	—	—	2·9	3·6	10·1
Non-volatile, water-soluble acids, as azelaic		0·9	—	—	3·8	6·3	10·4
Neutral, steam-volatile oil (mainly nonanal and nonanone)		Trace	Trace	0·2	0·3	0·3	0·3
Unchanged oleic acid (calc.)		79	70	53	46	31	8

TABLE 9. *Autoxidation at 49° without a catalyst.*

Time (days)		7	14	21	28
8- and 11-Oxo-oleic acids, $C_{18}H_{32}O_3$, deduced from	(*a*) $E^{1\%}_{1\,\mathrm{cm.}}$ val.	0·6	3·8	6·4	8·4
	(*b*) hydrolysis products	1·5	4·8	7·5	8·9
9 : 10-Ketol-acids, as $C_{18}H_{34}O_4$		0·4	2·6	2·9	5·5
Other oxo-acids, as $C_{18}H_{32}O_3$		4·2	6·7	6·6	2·1
9 : 10-Epoxystearic acid		4·5	5·2	9·4	9·5
Hydroperoxyoleic acid		4·7	8·7	10·8	9·2
Dihydroxystearic acid (combined)	(*a*) KIO_4 method	0·6	5·7	8·1	8·5
	(*b*) isolated	0·0	0·0	0·5	3·6
Steam-volatile acids, as nonanoic		2·4	4·0	4·3	4·9
Non-volatile, water-soluble acids, as azelaic		0·5	1·9	3·3	4·1
Neutral, steam-volatile oil (mainly nonanal and nonanone)		0·4	0·9	1·5	1·6
Unchanged oleic acid (calc.)		82	60	42	28

TABLE 10. *Autoxidation at 49° in the presence of 0·5% of cobalt.*

Time (hr.)		8	16	24	48	72	96	168
8- and 11-Oxo-oleic acids, $C_{18}H_{32}O_3$, deduced from ...	(*a*) $E^{1\%}_{1\,cm.}$ val.	1·4	6·5	10·8	12·2	11·5	6·9	2·0
	(*b*) hydrolysis products...	2·1	7·2	10·1	10·8	10·7	6·1	2·5
9 : 10-Ketol-acids, as $C_{18}H_{34}O_4$		0·8	1·2	0·8	2·2	3·1	6·1	8·3
Other oxo-acids, as $C_{18}H_{32}O_3$		2·6	2·9	4·5	5·7	8·3	7·2	9·7
9 : 10-Epoxystearic acid		3·5	6·2	8·3	14·0	17·0	16·2	8·4
Hydroperoxyoleic acid		0·5	1·1	0·8	0·8	0·8	2·1	2·0
Dihydroxystearic acid (combined)	(*a*) KIO_4 method	0·0	Trace	2·1	3·5	4·4	4·5	6·8
	(*b*) isolated	0·0	0·0	Trace	0·8	1·3	3·9	4·6
Steam-volatile acids, as nonanoic		1·5	3·4	5·7	7·7	8·7	15·8	19·2
Non-volatile, water-soluble acids, as azelaic ...		1·1	1·4	3·1	4·9	6·4	12·7	18·1
Neutral, steam-volatile oil (mainly nonanal and nonanone)		0·2	0·4	0·7	0·8	0·9	1·1	0·9
Unchanged oleic acid (calc.)		89	71	54	39	24	3	1

TABLE 11. *Autoxidation at 78° without a catalyst.*

Time (days)		1	2	4	6	8
8- and 11-Oxo-oleic acids, $C_{18}H_{32}O_3$, deduced from	(*a*) $E^{1\%}_{1\,cm}$ val.	0·2	2·7	7·2	6·9	4·7
	(*b*) hydrolysis products...	0·7	3·1	6·4	5·2	4·1
9 : 10-Ketol-acids, as $C_{18}H_{34}O_4$		0·7	4·9	4·7	6·5	10·6
Other oxo-acids, as $C_{18}H_{32}O_3$		3·6	2·2	6·3	7·0	4·9
9 : 10-Epoxystearic acid		2·8	8·1	12·7	9·6	2·2
Hydroperoxyoleic acid		3·7	8·3	6·4	3·0	2·7
Dihydroxystearic acid (combined)	(*a*) KIO_4 method	0·0	0·0	6·7	6·7	6·5
	(*b*) isolated	0·0	0·3	4·0	5·4	7·0
Steam-volatile acids, as nonanoic		2·3	3·8	6·5	8·2	10·4
Non-volatile, water-soluble acids, as azelaic		0·4	1·5	4·6	6·6	7·8
Neutral, steam-volatile oil (mainly nonanal and nonanone) ...		0·1	0·2	0·8	0·7	0·7
Unchanged oleic acid (calc.)		83	62	24	11	5

TABLE 12. *Autoxidation at 78° in the presence of 0·5% of cobalt.*

Time (hr.)		4	8	12	16	32
8- and 11-Oxo-oleic acids, $C_{18}H_{32}O_3$, deduced from	(*a*) $E^{1\%}_{1\,cm.}$ val.	3·0	7·2	9·3	7·4	1·9
	(*b*) hydrolysis products ...	3·8	6·9	7·0	6·5	2·2
9 : 10-Ketol-acids, as $C_{18}H_{34}O_4$		0·5	1·5	2·7	3·3	5·8
Other oxo-acids, as $C_{18}H_{32}O_3$		2·0	4·9	6·2	9·5	13·3
9 : 10-Epoxystearic acid		2·1	8·7	10·0	13·4	4·4
Hydroperoxyoleic acid		0·8	0·7	0·6	0·6	0·6
Dihydroxystearic acid (combined)	(*a*) KIO_4 method	0·4	2·5	4·5	5·6	6·2
	(*b*) isolated	Trace	0·3	1·2	2·2	7·9
Steam-volatile acids, as nonanoic		2·6	5·6	7·3	9·0	15·7
Non-volatile, water-soluble acids, as azelaic		1·0	2·9	5·0	7·3	14·6
Neutral, steam-volatile oil (mainly nonanal and nonanone)		0·3	0·7	0·8	0·8	0·9
Unchanged oleic acid (calc.)		81	54	34	22	0

TABLE 13. *Gaseous (or vaporised) products per* 100 *g. of oleic acid* (a) *alone,* (b) *with* 0·5% *of cobalt.*

	Room		49°		78°	
	a	*b*	*a*	*b*	*a*	*b*
Temp.	28 days	28 days	28 days	7 days	8 days	32 hr.
CO_2 (g.)	Trace	0·72	2·23	10·5	4·71	10·3
Formic acid (g.)	Trace	0·52	0·53	0·86	1·11	0·13

TABLE 14. *Maximum observed yields (% of total non-gaseous products) of some autoxidation products of oleic acid.*

Product	Yield (%)	Co catalyst (%)	Time	Temp.
8- and 11-Oxo-oleic acids	15·6	0·5	14 days	Room
Ketol-acids (as $C_{18}H_{34}O_4$)	10·6	0	8 days	78°
Other oxo-acids (as $C_{18}H_{32}O_3$)	13·3	0·5	32 hr.	78
Epoxystearic acid	17·0	0·5	3 days	49
Dihydroxystearic acid	8·5	0	28 days	49
Hydroperoxyoleic acid	10·8	0	21 days	49
Cleavage products (such as nonanoic and azelaic acids)	37·3	0·5	7 days	49

FIG. 1. *At room temperature, with* 0·5% *of cobalt.*

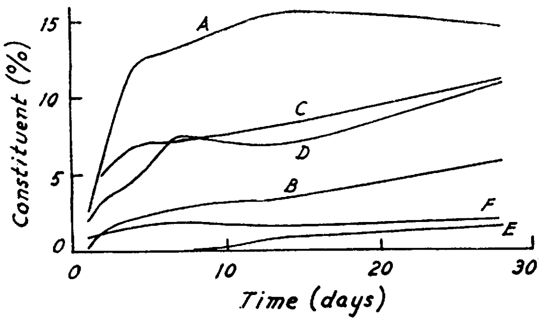
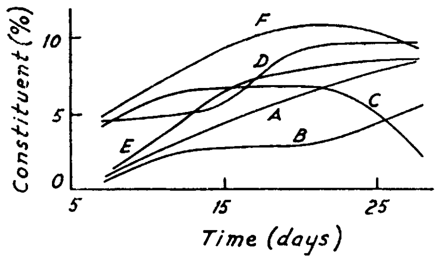


FIG. 2. *At* 49°, *without catalyst.*



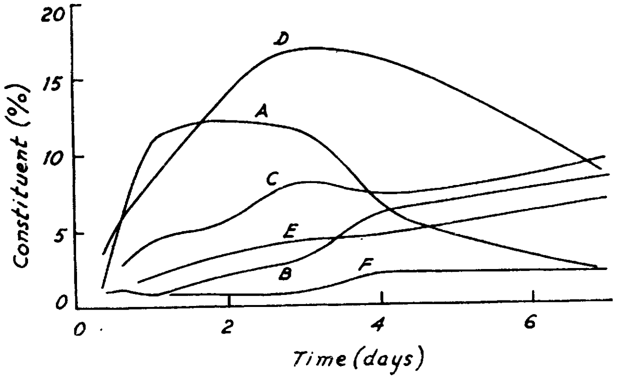


FIG. 3. A*t* 49°, *with* 0·5% *of cobalt.*

FIG. 4. *At* 78°, *without catalyst.*

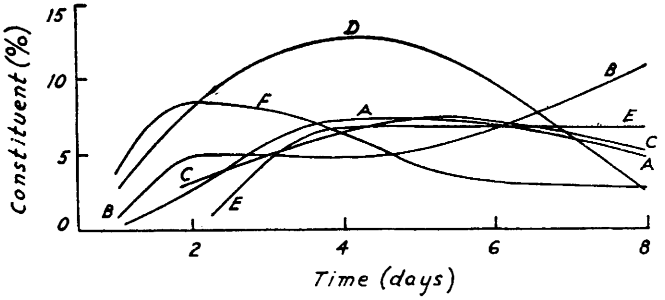
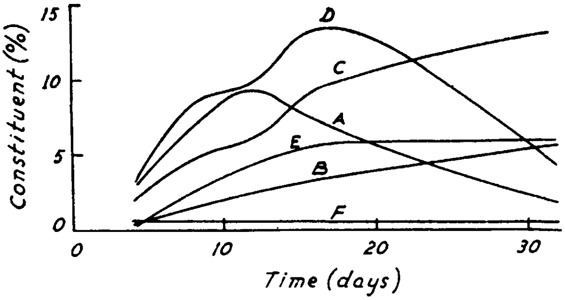


FIG. 5. *At* 78°, *with* 0·5% *of cobalt.*



Percentages refer to the total non-gaseous oxidation products (as 100%).

A, 8- *and* 11-*Oxo-oleic acids.*
B, 9 : 10-*Ketol-acids, as* $C_{18}H_{34}O_4$.
C, *Other oxo-acids, as* $C_{18}H_{32}O_3$.
D, 9 : 10-*Epoxystearic acid.*
E, *Dihydroxystearic acid (combined).*
F, *Peroxides, as hydroperoxyoleic acid.*

and could not therefore have been due solely to the hydrolysis of acyl derivatives of the latter.

The percentage compositions of the total non-gaseous products (Tables 7—12) were calculated from the analytical data as in the previous communication, but further work remains to be done on the qualitative resolution and characterisation of the unidentified oxo- and other acids, including polymeric material, before a complete analysis is possible. The quantitative methods were substantially the same as those used for autoxidised elaidic acid, but a more accurate allowance has been made for the effect of peroxides on the carbonyl determination. In calculating the percentages of cleavage products (as nonanoic and azelaic acids) the very slight steam-volatility and water-solubility of pure oleic acid have been neglected.

EXPERIMENTAL

Methods.—The method of oxidation and the methods of estimation were similar to those described for elaidic acid and its autoxidation products,[1] with certain modifications mentioned below. The oleic acid used in these experiments, purified by low-temperature crystallisation from acetone, had m. p. 6—7°; equiv., 282; I val., 86—87; $E^{1\%}_{1\,\text{cm.}}$ (at 224 mμ), 6·5—8; active O, negligible.

Neutral, Steam-volatile Oil (*mainly Nonanal and Nonan-*2-*one*) *and Ketol.*—The product (*ca.* 4 g.) was dissolved in sufficient cold N-sodium hydroxide (20—25 ml.) and water (100 ml.), and the solution was brought to pH 8·0 (pH meter) by addition of dilute sulphuric acid and diluted to 210 ml. Of the uniform solution (or suspension), portions (100 ml.) were used for the estimation of neutral, volatile oil and of ketol as described in the previous communication.

8- *and* 11-*Oxo-oleic Acids.*—These were determined spectrophotometrically and by hydrolysis as for the corresponding elaidic acid derivatives, *trans*-11-oxoheptadec-9-ene-1-carboxylic acid, m. p. 50·5°, being used as reference compound.

Carbonyl.—The hydroxylamine hydrochloride method was used as before, but titrations of liberated acid were carried out after 5 min., 30 min., 1 hr., and subsequently every hr. for several hours. The titrations were corrected for blanks done similarly (only the carbonyl compound being omitted), and a plot made of the resulting titration values from 30 min. onwards against time. Since the carbonyl compounds react quantitatively with hydroxylamine in less than 30 min., the subsequent liberation of acid is due to the relatively slow oxidation of the reagent by the peroxides in the sample. By extrapolating the curve to zero time, therefore, the true amount of acid liberated by the carbonyl may be deduced. If this amount is T ml. of 0·1N-sodium hydroxide, then the percentage of carbonyl in the substance is $0{\cdot}28T/m$, where m is the mass taken.

It was found that the action of peroxides, present in the autoxidation products, on the hydroxylamine reagent required 24 hr. or more for completion and that 16 g. of active oxygen liberated a total of 6—7 g.-equiv. of acid. The apparent percentage of carbonyl calculated on the 30-min. titration values, needed to be corrected by about 1·5 times the percentage of active oxygen (rather than 0·875 times, as previously suggested [1]), but the figure varied considerably with different samples in keeping with the view that the peroxides are heterogeneous in type. Hence the values for carbonyl and " other oxo-acids " in autoxidised elaidic acid given in the previous paper may be a little too high, more especially in non-catalytic experiments where the peroxide content is appreciable.

9 : 10-*Dihydroxystearic Acids.*—Oxygen was bubbled through pure oleic acid at 78° for 8 days. The product (25 g.) was saponified by refluxing it with N-alcoholic potassium hydroxide (250 ml.) for 1·25 hr. The recovered acids, filtered from oil and washed with light petroleum, were crystallised from chloroform and fractionally crystallised from ethanol, giving *erythro*-dihydroxystearic acid (1·04 g.), m. p. and mixed m. p. 130—131°, and the *threo*-acid (1·03 g.), m. p. and mixed m. p. 93—94°.

The dihydroxy-acid from oleic acid autoxidised at 49° was also a mixture of the two isomers, but appeared to contain rather more of the *threo*-form. That from catalysed oxidations, however, consisted almost entirely of the *erythro*-form, none of the lower-melting isomer being isolated.

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