Hydrogenation and Deuteration of Conjugated Isomers of Linoleate and Linolenate with Palladium, Platinum, Nickel and Lindlar Catalysts[1]

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ABSTRACT

Conjugated isomers of methyl linoleate and linolenate were reduced with palladium, platinum, nickel and Lindlar catalysts at atmospheric hydrogen or deuterium pressure. After the products were separated, positions of their double bonds were determined by ozonolysis. Palladium and platinum catalysts reduced β-eleostearate directly to monoene. Nickel reduced β-eleostearate to dienes chiefly by 1,2-addition and to a lesser extent by 1,4- and 1,6-addition, whereas Lindlar catalyst reduced by 1,2- and 1,6-addition only. All catalysts reduced conjugated linoleate isomers by both 1,2- and 1,4-addition, with nickel being somewhat preferential for 1,2-addition. Selectivity for the catalytic reduction of dienes to monoenes decreased in the order: nickel, palladium and platinum. Lindlar catalyst did not isomerize or reduce monoenes that formed during reduction. Palladium and platinum did not isomerize conjugated dienes and trienes during their reduction, whereas nickel and Lindlar catalysts isomerized them slightly. Some deuterium was found in unreacted conjugated diene and triene with nickel and Lindlar catalysts, but none with palladium or platinum. Deuterated products contained a wide range of isotopic isomers with some products having up to 31 deuterium atoms. This wide deuterium distribution resulted from (a) exchange followed by addition, (b) addition followed by exchange and (c) exchange-addition-exchange reactions.

INTRODUCTION

It is generally believed that the preferential hydrogenation of polyunsaturated over monounsaturated esters is due to the formation of highly reactive conjugated intermediates (1-4). There is only scant information concerning the mode of hydrogen addition to conjugated double bonds in fatty acids. Allen (5) found that *cis,cis*-conjugated double bonds are reduced with nickel catalyst by both 1,2- and 1,4-addition of hydrogen, the latter producing a new bond in *trans* configuration. Scholfield et al. (6) obtained similar results when they hydrogenated *cis,trans*- and *trans,trans*-conjugated dienes as soaps. Recent developments in kinetics and mechanism of hydrogenation of unsaturated fatty acids resulting from improved methodology have been reviewed (7,8). This latest study concerns addition, exchange and isomerization reactions of conjugated dienes and triene with hydrogen or deuterium in the presence of palladium, platinum, nickel and Lindlar catalysts.

EXPERIMENTAL PROCEDURES

β-Eleostearic acid was prepared from tung oil by low temperature crystallization (9). *trans*-9,*trans*-11-Octadecadienoic acid was synthesized from castor oil (10). The acids were converted to methyl esters with methanolic hydrochloric acid and 2,2-dimethoxypropane (11). *trans*-10,*cis*-12-Octadecadienoate was obtained from methyl esters of alkali-isomerized linoleic acid (12). *trans*-10,*trans*-12-Octadecadienoate was prepared from the *trans*-10,*cis*-12-isomer by iodine isomerization (13) and isolated by argentation chromatography (14). Methyl *cis*-9,*cis*-11-octadecadienoate was obtained from dehydrated ricinoleate by argentation chromatography and low temperature crystallization from acetone. This preparation contained ca. 13% of *cis*-8,*cis*-10-isomer as an impurity. Conjugated esters were stored under nitrogen at -20 C, and before hydrogenation and deuteration were freshly distilled under vacuum.

Deuterations were performed at atmospheric pressure in a glass manometric apparatus described previously (15). Catalysts were successively evacuated and exposed to deuterium several times before introducing the ester. After

TABLE I

Fatty Acid Composition of Products Formed During Partial Deuteration of Conjugated Esters with Palladium, Platinum, Nickel and Lindlar Catalysts

Substrate and catalyst	Composition,[a] wt %					K_{CD}/K_M
	CT	*t,t*-CD	*c,t*-CD	M	St	
β-Eleostearate + Pd	73.9	0.7	0.0	24.1(80)[b]	1.3	
β-Eleostearate + Pt	75.9	0.2	0.0	16.0(70)	7.9	
β-Eleostearate + Ni	54.7	23.1	4.7[c]	14.9	0.5	
β-Eleostearate + Lindlar	68.1	15.7	1.8	14.4	0.0	
t-9,*t*-11-CD + Pd		53.0	0.0	44.9(88)	2.1	8
t-9,*t*-11-CD + Pt		60.6	0.0	29.6(82)	9.7	1
t-9,*t*-11-CD + Ni		48.2	1.3	49.9(95)	0.6	33
t-9,*t*-11-CD + Lindlar		62.1	1.1	36.8(98)	0.0	
t-10,*c*-12-CD + Pd		1.0	51.4	45.0(73)	2.6	6
t-10,*c*-12-CD + Pt		0.8	58.3	31.3(63)	9.6	1
t-10,*c*-12-CD + Ni		2.6	44.6	52.7(70)	0.1	>200
t-10,*c*-12-CD + Lindlar		1.7	51.6	46.7(85)	0.0	

[a] CT, conjugated triene; CD, conjugated diene; M, monoene, St, stearate; *t, trans; c, cis;* K, reaction rate.
[b] Number in parentheses indicates per cent *trans* in monoene.
[c] Also, 2.1% nonconjugated diene.

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[2] ARS, USDA.

TABLE II

Composition of Conjugated Diene Isomers Formed During Deuteration of β-Eleostearate with Nickel and Lindlar Catalysts

Diene isomer	Mol %	
	Ni	Lindlar
$\Delta^{8,10}$	2	
$\Delta^{9,11}$	44	31
$\Delta^{10,12}$	16	36
$\Delta^{11,13}$	37	33
$\Delta^{12,14}$	1	

ca. 0.5 mole of gas per mole of ester was consumed, the product was separated from the catalyst by filtration.

Catalysts came from the following commercial sources: 65% nickel on Kiesulghur (G-49A, Girdler catalysts, Chemetron Corp.), 5% palladium on carbon (Baker & Co.) and 5% platinum on carbon (Engelhard Industries). These were employed at 100 C, 25 C and 60 C, respectively. The concentration (w/v) of nickel, palladium and platinum was 0.6%, 0.05% and 0.25%, respectively. Lindlar catalyst (16) was used at 15 C at a palladium concentration of 0.5%. Reductions with Lindlar catalyst were carried out in petroleum ether with quinoline serving as a poison.

Fatty acid compositions of partially deuterated products were determined with a Varian Aerograph GC instrument equipped with dual 6 ft x 1/8 in. stainless steel columns, packed with 15% EGSS-X on Gas-Chrom P, and with flame ionization detectors. The columns were held at 190 C with a nitrogen gas flow of 20 ml/min. Peak areas were determined with a disc integrator. Selectivity ratios (K_{CD}/K_M) were determined with a digital computer based on a program, written by Butterfield and Dutton (17), where CD = conjugated diene; M = monoene; and K = reaction rate. Deuterated products were separated into stearate, monoene, diene and triene fractions by reverse-phase chromatography on a rubber column (18). Monoene fractions were further separated into *cis*- and *trans*-monoenes on a silver-exchanged resin column (14). Percentage *trans* in the monoene was calculated on the basis of weight recovery of *cis*- and *trans*-monoenes. Conjugated dienes were separated from nonconjugated dienes by preparative gas liquid chomatography (GLC).

Positional isomers of various monoene, conjugated diene and triene fractions were determined by reductive ozonolysis (19) followed by temperature-programed (50-190 C at 6 C/min) GC of aldehydes and aldehyde esters. The mole per cent of each isomer was calculated by triangulation of the aldehyde ester peaks.

Isotopic analyses of various fractions were determined with a Nuclide mass spectrometer. Deuterium distributions were calculated from parent peak heights after correcting for the natural abundance of carbon, hydrogen and oxygen isotopes.

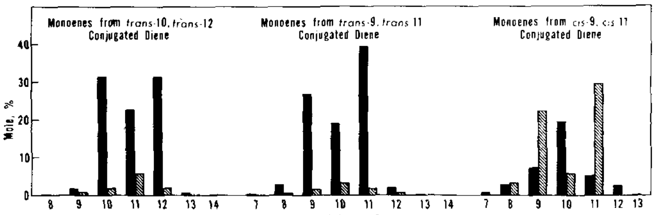

FIG. 1. Double bond distribution in monoenes formed during hydrogenation of *trans,trans*- and *cis,cis*-conjugated dienes with nickel catalysts. Final product composition with *trans*-10,*trans*-12-conjugated diene: stearate (St), 0.7%; *trans*-monoene, 59.0%; *cis*-monoene, 7.3%; conjugated diene, 33.0%; with *trans*-9,*trans*-11-conjugated diene: St, 3.2%; *trans*-monoene, 85.1%; *cis*-monoene, 8.4%; conjugated diene, 3.3%; with *cis*-9,*cis*-11-conjugated diene: St, 6.2%; *trans*-monoene, 36.3%; *cis*-monoene, 56.9%; conjugated diene, 0.6% ■ *trans*, ▨ *cis*.

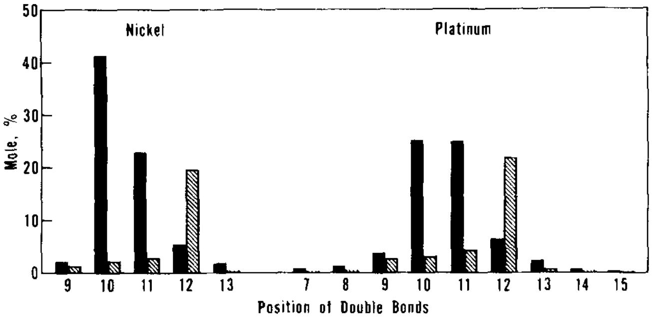

FIG. 2. Double bond distribution in monoenes formed during hydrogenation of *trans*-10,*cis*-12-conjugated diene. Final composition with nickel: St, 2.4%; *trans*-monoene, 64.8%; *cis*-monoene, 23.3%; conjugated diene, 9.5%; with platinum: St, 20.6%; *trans*-monoene, 41.9%; *cis*-monoene, 21.6%; conjugated diene, 15.9% ■ *trans*, ▨ *cis*.

Reductions with hydrogen gas were carried out with nickel (G-70 or G-15 Girdler catalyst) at 140 C or 5% platinum on carbon at 50 C in a modification of the apparatus described by Rohwedder (20). Approximately 1 mole of hydrogen per mole of ester was added, and the product was separated as described earlier for deuteration. Double bond positions in the *cis*- and *trans*-monoene fractions were determined by reductive ozonolysis in an integrated microreactor apparatus described by Johnston and Dutton (21).

RESULTS AND DISCUSSION

Fatty Acid Composition

Composition of the products formed during partial deuteration of conjugated esters is shown in Table I. Both palladium and platinum catalysts reduced β-eleostearate directly to monoene, a phenomenon commonly referred to as a shunt. Apparently both conjugated triene and the intermediate conjugated diene are adsorbed so strongly on these catalyst surfaces that they do not desorb until 2 moles of hydrogen have been taken up and monoene is formed. Deuterium tracer studies (see below) reinforce this hypothesis. Computer simulation of this reaction (17) with nickel and Lindlar catalysts according to the scheme triene → diene → monoene → stearate gave selectivity ratios (K_{CT}/K_{CD}) of 0.8 and 0.3, respectively. These anomalously low selectivity values indicate that part of the triene is reduced directly to monoene. Bailey (22), and later Scholfield et al. (23) observed a similar shunt (linolenate → monoene) during hydrogenation of linseed oil and methyl linolenate. However the extent of the shunt was small compared to what is observed here for conjugated triene. In addition to conjugated dienes, nickel catalyst also formed minor amounts (2.1%) of nonconjugated diene.

All catalysts, except Lindlar, formed stearate during reduction of conjugated esters. Nickel catalyst exhibited selectivity for the deuteration of conjugated dienes over monoenes. Palladium showed lower selectivity; platinum showed none. Reduction of conjugated dienes with nickel and Lindlar catalysts was accompanied by minor amounts (up to 2%) of geometric isomerization of unreacted dienes, whereas palladium and platinum exhibited no such isomerization. The small amounts of *trans,trans*-conjugated diene in the products of *trans*-10,*cis*-12-conjugated diene reduction with palladium and platinum were present in the starting material. This behavior is in contrast to copper catalyst which isomerized conjugated dienes and triene extensively (24).

Reduction of the all-*trans* conjugated triene and diene with palladium and platinum resulted in considerable amounts of *cis*-monoenes, i.e., up to 30% of the total monoene. Since these catalysts did not isomerize the starting triene, *cis,trans* isomerization of monoenes is indicated.

Isomer Distribution

The composition of conjugated diene isomers formed from β-eleostearate is given in Table II. With nickel catalyst, 81% of the conjugated diene isomers was formed by 1,2-addition (44% of $\Delta^{9,11}$ + 37% of $\Delta^{11,13}$). 1,6-Addition occurred to a lesser degree to give 16% of $\Delta^{10,12}$-conjugated diene. The minor amounts of $\Delta^{8,10}$- and $\Delta^{12,14}$-isomers can be attributed to the isomerization of conjugated dienes, since isomerization in unreacted triene was virtually absent with all catalysts. 1,4-Addition also occurred to a limited extent, since the small amount of nonconjugated diene (ca. 7% of the total diene) consisted of $\Delta^{9,12}$- and $\Delta^{10,13}$-isomers.

While the nickel catalyst showed preference for 1,2-addition, Lindlar catalyst formed equal amounts of the three 1,2- and 1,6-addition products. 1,2-Addition to the middle double bond would produce nonconjugatable diene. However none of the catalysts formed this diene. Apparently this reaction is inhibited owing to steric hindrance, because 1,2-addition to the middle double bond in methyl linolenate is facile (25,26).

The distribution of isomers in various monoenes formed during deuteration and hydrogenation of conjugated esters is shown in Table III and Figures 1 and 2. Despite differences in reaction conditions, almost similar monoene distributions resulted with nickel and platinum catalysts after 1 mole of hydrogen or 0.5 mole of deuterium per mole of conjugated diene was added. Therefore the isotope effect for addition or isomerization reactions must be small.

Palladium and platinum catalysts reduced *trans*-9,*trans*-11-conjugated diene to form equal amounts of Δ^{9}-, Δ^{10}- and Δ^{11}-*trans*-monoenes; thus both 1,2- and 1,4-addition reactions seem to occur with equal ease. Lindlar catalyst was somewhat selective for 1,4-addition since more Δ^{10}-monoene than Δ^{9} or Δ^{11} was formed. The presence of 32 and 47% of Δ^{9}- and Δ^{11}-*trans*-monoenes, respectively, vs. only 12% of Δ^{10}-*trans*-monoene in the products of nickel reduction indicates that this catalyst is highly selective for 1,2-addition. Also hydrogenation of *trans*-10,*trans*-12-; *trans*-9,*trans*-11-; and *cis*-9,*cis*-11-conjugated dienes with nickel catalyst formed more 1,2-addition products than 1,4-addition products.

With *trans*-10,*cis*-12-conjugated diene, 1,2-addition will form *trans*-10- and *cis*-12-monoenes, whereas 1,4-addition will form *trans*-11-monoene. Platinum catalyst formed equal amounts of the three isomers. Nickel catalyst showed preference for 1,2-addition over 1,4-addition, while palladium and Lindlar catalysts showed slight preference for 1,4-addition. Since nickel, palladium and platinum catalysts formed more *trans*-10- than *cis*-12-monoene, preferential 1,2-addition to the *cis* double bond over *trans* double bond is indicated.

With all catalysts, 1,4-addition to *trans,trans*- and *trans,cis*-conjugated dienes resulted predominantly, if not exclusively, in the formation of a *trans* double bond. Apparently these catalysts chemisorb conjugated dienes in transoid (anti) conformation (27). Generally the *cis*-monoenes show a maximum at the double bond, which corresponds to 1,4-addition. Because this maximum could not occur solely by isomerization of formed monoenes, apparently a small amount of *cis*-monoene is formed by 1,4-addition to conjugated dienes in a *cisoid* (syn) conformation. With *cis*-9,*cis*-11-isomer, it could not be ascertained whether 1,4-addition resulted in *cis*-10-monoene because of the large amount of *cis*-8,*cis*-10-isomer present as an impurity. It may very well be that the *cis,cis*-isomer cannot exist in a *cisoid* form due to steric hindrance as suggested

TABLE III

Double Bond Distribution in Monoenes Formed During Deuteration of Conjugated Esters with Palladium, Platinum, Nickel and Lindlar Catalysts

Double bond position	Mol %																					
	Monoenes from β-eleostearate with						Monoenes from *t*-9,*t*-11-CD with								Monoenes from *t*-10,*c*-12-CD with							
	Pd		Pt				Pd		Pt		Ni		Lindlar		Pd		Pt		Ni		Lindlar	
	trans	*cis*	*trans*	*cis*	Ni	Lindlar	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*
6	Tr[a]	Tr	Tr	Tr				Tr		Tr												
7	1	Tr	1	Tr			Tr	Tr	1	Tr		Tr			Tr	Tr	Tr	Tr				
8	3	1	3	2	2		3	2	4	1	2	Tr		Tr	1	Tr	1	Tr				
9	15	3	9	4	23	13	26	2	25	3	32	1	28	Tr	4	2	4	2	3	1	1	Tr
10	14	4	13	6	17	23	27	4	23	8	12	2	40	1	27	3	23	3	42	2	39	Tr
11	16	4	15	5	19	29	26	2	23	3	47	1	30	Tr	32	2	25	5	19	2	45	Tr
12	14	5	14	6	15	23	3	2	3	2	2	Tr		Tr	5	18	6	24	3	24	Tr	14
13	13	2	10	3	24	12	1	Tr	2	Tr		Tr			3	Tr	3	1	4			
14	3	1	3	2	1			Tr		Tr					Tr	Tr	Tr	Tr				
15	Tr	Tr	1	Tr																		
16	Tr	Tr		Tr																		

[a] Trace.

TABLE IV

Distribution of Deuterium in Products Formed During Reaction of Conjugated Esters with Deuterium

No. of deuterium atoms	Wt %										
	t, Monoene from β-eleostearate + Pd	CD from β-eleostearate +		*t*, Monoene from *t*-9,*t*-11-CD +			*t*, Monoene from *t*-10,*c*-12-CD +			Unreacted *t*,*t*-CD +	
		Ni	Lindlar	Pd	Ni	Lindlar	Pt	Ni	Lindlar	Pt	Ni
0	7.1	2.7	4.1	22.0	13.4	4.6	17.4	13.3	4.2	99.8	92.1
1	12.9	15.8	24.6	29.2	30.5	23.6	29.1	30.9	26.3	0.2	5.7
2	17.8	75.2	57.7	20.0	39.1	62.1	24.3	35.5	64.0		1.2
3	17.3	4.7	11.0	10.7	9.5	7.6	12.0	10.2	4.3		0.6
4	13.8		1.8	6.0	3.2	1.4	6.2	4.1			0.3
5	8.7			3.7	1.5		3.6	2.3			0.1
6	6.0			2.6			2.4	1.2			
7	4.0			1.6			1.5				
8	2.9			1.3			1.0				
9	2.3										
10	1.5										
11	1.1										
Other	4.6	1.5	0.8	2.9	2.8	0.7	2.5	2.5	1.2		
D_{av}[a]	4.10	1.87	1.84	2.19	1.82	1.80	2.15	1.90	1.72		0.11

[a] Average number of deuterium atoms per molecule.

by Allen (5), but this restriction does not hold for the other geometric conjugated isomers.

Only traces of positional isomerization (2%) were found in the unreacted conjugated dienes with nickel and Lindlar catalysts, whereas palladium and platinum showed none. In this respect these catalysts behaved quite differently from copper catalysts (24), which isomerized conjugated dienes extensively.

Several monoene isomers, other than 1,2- and 1,4-addition products, were formed during reduction of conjugated dienes with palladium, platinum and nickel catalysts. Since isomerization of conjugated dienes is either absent or negligible, these isomers must arise by isomerization of monoenes. Palladium and platinum isomerized monoenes more extensively than nickel. Lindlar catalyst neither isomerized nor reduced the formed monoenes.

The composition of monoene isomers formed during deuteration of β-eleostearate with all catalysts can be explained by assuming stepwise addition of hydrogen to form first conjugated dienes and then monoenes. Positional isomerization of monoenes was greater with palladium and platinum catalysts than with nickel, as evidenced from the monoene isomers whose double bonds are situated beyond the 9 to 13 positions. Again Lindlar catalyst did not isomerize monoenes.

Deuterium Distributions

Typical deuterium distributions in some fractions from the deuterated products are listed in Table IV. Isotopic isomers amounting to less than 1% were combined and reported as "other." Simple addition of two deuterium atoms across a double bond would give a d_2-product. Reduction of β-eleostearate with nickel and Lindlar catalysts chiefly occurred by this process, giving 75 and 58%, respectively, of d_2-product. Addition reaction is usually accompanied by isomerization and consequent exchange of hydrogen atoms of the reactant and product for deuterium atoms by half hydrogenation mechanism (28). Isomerization of conjugated triene and diene was absent with palladium and platinum catalysts, and deuterium was not incorporated into these esters. These esters apparently are strongly adsorbed on these catalyst surfaces, and desorption does not take place until reduction to monoene occurred. A similar conclusion was reached from the analytical data in Table I. On the other hand nickel and Lindlar catalysts showed slight isomerization, and deuterium was incorporated into unreacted conjugated esters (D_{av} 0.05 to 0.11). As seen in Table IV, up to five deuterium atoms have been incorporated into *trans,trans*-conjugated diene during deuteration with nickel catalyst. These catalysts are distinguished from copper catalysts (29), which show considerable exchange during deuteration of conjugated esters.

One consequence of exchange is to increase the concentration of hydrogen on the catalyst surface, which contained only deuterium at the beginning of the reaction. This hydrogen participates in other addition, isomerization and exchange reactions, since hydrogen-deuterium exchange (formation of HD an; H_2 in the gas phase) is suppressed during olefin reduction and virtually inhibited during diolefin reduction (27,30). If no hydrogen escaped into the gas phase, the average deuterium content of the product would be two atoms per double bond reduced. A value of essentially 2.0 (1.97 to 1.98) was calculated for nickel catalyst during deuteration of conjugated dienes and triene. Palladium and platinum, however, gave higher values (2.09 to 2.29). These high values mean that some hydrogen escaped into the gas phase by hydrogen-deuterium exchange. This type of exchange reaction occurs during deuteration of monoenes (28), and some monoene was reduced to stearate with these catalysts. Less than the theoretical amount of deuterium (1.79 to 1.89) was found in the products with Lindlar catalyst. The remainder was possibly exchanged (31) with quinoline, employed to poison the catalyst.

Deuteration of conjugated esters is further complicated, because the product monoene is capable of undergoing further addition, isomerization and exchange reactions. Since isomerization and exchange of conjugated esters is absent with palladium and platinum catalysts, the wide distribution of deuterium in the monoene products must be due to isomerization and exchange of monoenes. The monoene from β-eleostearate reduction contained traces of isotopic isomers having up to 31 deuterium atoms. The monoenes therefore adsorb and desorb (exchange) freely from palladium and platinum catalyst surfaces during reduction of β-eleostearate.

Further reaction of monoenes was absent with Lindlar catalyst, and isotopic distribution of monoenes was due to exchange of conjugated esters followed by addition. During reduction with nickel catalyst, both conjugated esters and monoenes isomerized and exchanged. The extent of these two isomerization reactions must be slight, since deuterium is not so widely distributed in monoene products with nickel catalyst as those from palladium and platinum catalysts.

Because of increased hydrogen concentration on the catalyst surface due to exchange, addition occurs with both hydrogen and deuterium. Hence monoene products from conjugated diene having zero, one and two deuterium atoms represent chiefly mere addition-reaction products.

Some d_1- and d_2-products undoubtedly form either through exchange followed by addition or addition followed by exchange, e.g., addition of hydrogen and deuterium to d_1-diene or addition of hydrogen and deuterium followed by exchange. All other monoene products from conjugated diene having three or more deuterium atoms and those from conjugated triene having five or more must have resulted by (a) exchange followed by addition, (b) addition followed by exchange and (c) exchange-addition-exchange reactions.

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REFERENCES

1. Hilditch, T.P., Nature 157:586 (1946).
2. Feuge, R.O., E.R. Cousins, S.P. Fore, E.F. Dupré and R.T. O'Connor, JAOCS 30:454 (1953).
3. Allen, R.R., and A.A. Kiess, Ibid. 33:355 (1956).
4. Coenen, J.W.E., and H. Boerma, Fette Siefen Anstrichm. 70:8 (1968).
5. Allen, R.R., JAOCS 33:301 (1956).
6. Scholfield, C.R., E.P. Jones, J.A. Stolp and J.C. Cowan, Ibid. 35:405 (1958).
7. Dutton, H.J., Progr. Chem. Fats Other Lipids 9:349 (1971).
8. Frankel, E.N., and H.J. Dutton, Top. Lipid Chem. 1:161 (1970).
9. Hoffman, J.S., R.T. O'Connor, D.C. Heinzelman and W.R. Bickford, JAOCS 34:338 (1957).
10. Schneider, W.J., L.E. Gast and H.M. Teeter, Ibid. 41:605 (1964).
11. Radin, N.S., A.K. Hajra and Y. Akari, J. Lipid Res. 1:250 (1960).
12. Scholfield, C.R., and S. Koritala, JAOCS 47:303 (1970).
13. Tolberg, W.E., and D.H. Wheeler, Ibid. 35:385 (1958).
14. Emken, E.A., C.R. Scholfield and H.J. Dutton, Ibid. 41:388 (1964).
15. Johnston, A.E., D. Macmillan, H.J. Dutton and J.C. Cowan, Ibid. 39:273 (1962).
16. Lindlar, H., Helv. Chim. Acta 35:446 (1952).
17. Butterfield, R.O., and H.J. Dutton, JAOCS 44:549 (1967).
18. Hirsch, J., Colloq. Int. Centre Nat. Rech. Sci. (Paris) 99:11 (1961).
19. Stein, R.A., and N. Nicolaides, J. Lipid Res. 3:476 (1962).
20. Rohwedder, W.K., J. Catal. 10:47 (1968).
21. Johnston, A.E., and H.J. Dutton, JAOCS 49:98 (1972).
22. Bailey, A.E., Ibid. 26:644 (1949).
23. Scholfield, C.R., J. Nowakowska and H.J. Dutton, Ibid. 39:90 (1962).
24. Koritala, S., Ibid. 47:269 (1970).
25. Scholfield, C.R., R.O. Butterfield, V.L. Davison and E.P. Jones, Ibid. 41:615 (1964).
26. Scholfield, C.R., E.P. Jones, R.O. Butterfield and H.J. Dutton, Anal. Chem. 35:386 (1963).
27. Bond, G.C., and P.B. Wells, Advan. Catal. 15:91 (1959).
28. Dutton, H.J., C.R. Scholfield, E. Selke and W.K. Rohwedder, J. Catal. 10:316 (1968).
29. Koritala, S., and E. Selke, JAOCS 48:222 (1971).
30. Burwell, R.L., Jr., Accounts Chem. Res. 2:289 (1969).
31. Calf, G.E., J.L. Garnett and V.A. Pickels, Aust. J. Chem. 21:961 (1968).

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