Methyl Oct-*cis*-2-enoate. Its Synthesis, GLC Behaviour and Infrared Spectra

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Abstract

Methyl oct-*cis*-2-enoate was synthesized by selective hydrogenation of methyl oct-2-ynoate at atmospheric pressure with quinoline poisoned palladium as catalyst. The resulting product contained only 7% of the *trans* form, as determined by GLC. The structure was confirmed by infrared spectra. Analysis of the infrared spectra is given. The *cis* and *trans* forms of methyl oct-2-enoate were separable by GLC in polar or non-polar columns. GLC runs in polar and non-polar phases showed that the *a* position of the double bond of methyl oct-2-enoate so affects its properties, that practically no interaction was observed between the double bond and the polar phase. Consequently volatility was the main factor determining the retention times of *cis* and *trans* methyl oct-2-enoate in the polar and non-polar phases studied.

Introduction

DURING the course of our experiments on biological precursors of linoleic acid in animals, it was necessary to synthesize methyl oct-*cis*-2-enoate, controlling its purity. The typical malonic synthesis (1) can be used to obtain 2-octenoic acid, but the resulting product is a mixture of *cis* and *trans*-isomers, the latter predominating markedly. The use of isomerization methods to obtain a *cis* structure (2) leads to unsatisfactory results. It was decided to use the safer method of partial hydrogenation of the triple bond of 2-octynoic acid, which had been used by Knight and Diamond (3). This method produces only an acid with *cis* structure. In order to obtain 2-octynoic acid the bromination and debromination of commercially available *trans* 2-octenoic acid was tested. These experiments showed that transforming the acid into the corresponding acetylenic acid is incomplete, because of interaction of the carboxyl group with the double bond in the *a* position. This had already been shown by Owen (4) and Schjanberg (5). Nevertheless, the 2-octynoic acid could be synthesized from heptiliden chloride (6) by the reaction with monosodic acetylide (7), although later a commercial product was used. In the hydrogenation of 2-octynoate, instead of Knight and Diamond's catalyst, quinoline palladium was used. The purity of the synthesized product was tested by GLC, and it was observed that the *cis* and *trans* forms had different retention times. IR spectrophotometry was used to confirm these observations. Identification of unsaturated compounds by IR spectra is almost exclusively restricted to the analysis of the most characteristic frequencies, arising from C-H group stretching, from C-H out of plane deformations, and from the C-H group attached to the double bond. Methyl-oct-*cis*-2-enoate (I), and methyl-oct-*trans*-2-enoate (II), are of a favourable type because they are non-symmetrical molecules and *a*, *β* conjugated. Therefore the number of vibrations is enhanced.

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Experimental

2-Methyl octynoate was from the Givaudan Laboratories, Switzerland. Purity of the product was controlled by GLC in a 10% Apiezon N column in a Pye apparatus. It was 99% pure. Methyl-oct-*trans*-2-enoate (II) was from Theodor Schuchardt's Laboratories, Germany. Selective catalyst was obtained by Lindlar's method (8). It consists of palladium chloride reduced on a calcium carbonate support and poisoned with quinoline (Merck).

Synthesis of methyl-oct-*cis*-2-enoate. 10 g of 2-methyl octynoate dissolved in 20 ml of normal hexane was mechanically shaken with 1 g of the selective catalyst at room temp in hydrogen at atmospheric pressure. During the process the speed of hydrogen consumption was approximately 10 ml per min and diminished greatly when it neared the theoretical value of semi-saturation of the triple bond. At that time, samples of the hydrogenated material were taken periodically and their composition checked by GLC (Pye apparatus) in a 10% Apiezon N (in Celite BDH, 80–120 mesh) and 15% polyethylene glycol adipate (in Celite BDH, 80–120 mesh) columns, 4 ft long and 4 mm thick, at 100C and 10 psi. Hydrogenation was stopped when the methyl octynoate peaks disappeared. The ester was purified by vacuum distillation. The yield was 99% of theoretical. The product was a transparent liquid with 192.2C bp (Seliwanoff's method corrected for emergent stem) whereas the bp of the methyl-oct-*trans*-2-enoate and methyl octanoate were respectively 200.6C and 193–194C (9). The unsaturation of the product was determined by means of hydrogenation as the iodine index gives erroneous results. The special structure of methyl-oct-2-enoate with a double bond in the *a* position from the carboxyl group prevents normal iodine addition. The iodine index by hydrogenation, Tiong and Waterman's method (10), gave 164.2 (theoretical 162.6). The position of the double bond was proved by oxidative ozonization,

TABLE I

Relative Retention Times [a]

	15% Polyethylene glycol adipate column [b]	10% Apiezon N column [c]
Methyl-oct-*cis*-2-enoate[d]	1.09	0.97
Methyl oct-*trans*-2-enoate	2.04	1.51
Methyl oct-2-yonate	3.90	1.57
Methyl octanoate	1.00	1.00

[a] Time corrected for the gas hold up.
[b] Experimental conditions: temp 100C; Pressure 10.0 psi; sample size 0.25 *μl*; attenuation 10; detector voltage 1000 v; chart speed 1 in./10 min; flow rate 32.3 ml/min; air peak elution 0.14 cm; methyl octanoate peak elution 2.70 cm.
[c] Experimental conditions: temp 100C; pressure 10.0 psi; sample size 0.25 *μl*; attenuation 10; detector voltage 750 v; chart speed 1 in./10 min; flow rate 61.2 ml/min; air peak elution 0.15 cm; methyl octanoate peak elution 3.06 cm.
[d] Synthesized product.

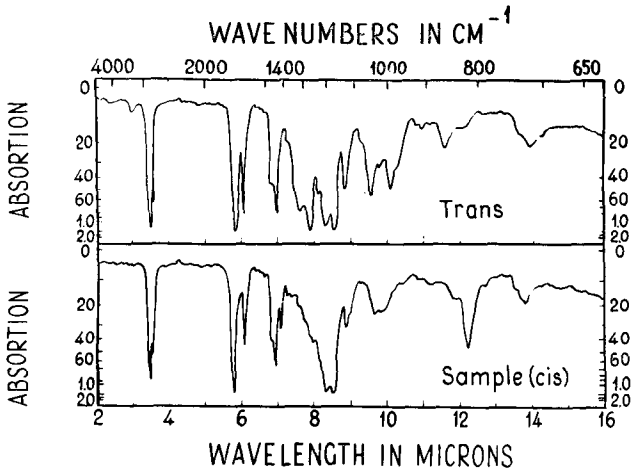


FIG. 1. IR spectra of *trans* and *cis* forms of methyl oct-2-enoate.

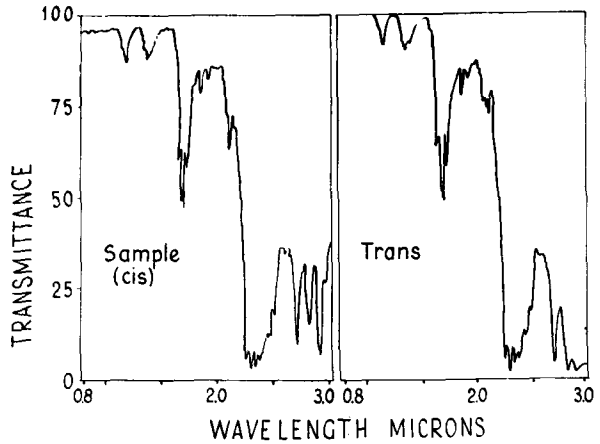


FIG. 2. Near-IR spectra of *trans* and *cis* forms of methyl oct-2-enoate.

Klenk and Faillar's method (11), which produced oxalic and hexanoic acids.

The purity of the resulting product was also checked by GLC in the Pye apparatus, which employs an ionization detector and argon as carrier gas. Columns of 10% Apiezon N and 15% polyethylene glycol adipate were used at 100C.

Resulting retention times were compared to those of the *trans* isomer methyl octanoate and 2-methyl-octynoate (Table I). The synthesized product was 93% of the *cis* form and 7% of the *trans* form as determined by measuring the areas of the peaks.

IR spectra of the prepared product (I) and commercial *trans* isomer (II) set between salts, were recorded with a Beckman IR-5 double beam spectrophotometer, with a sodium chloride prism. The spectra were recorded in the 650–5000 cm^{-1} region (Fig. 1).

A Beckman DK-2 spectrophotometer was used for recording near-IR spectra. All measurements were made on solutions in carbon tetrachloride which is transparent in the range studied. Solutions were usually 10% w/v, the cell was 1.0 cm, and tracings were begun at about 0.8 μ and run to 3.0 μ (Fig. 2). For recording complete near-IR spectra as in Figure 2, the instrument was set up as follows: scanning time 2, scale expansion 2X, time constant 0.2, sensitivity 30, scale 0 to 100% transmittance. CCl_4 was used in the reference beam. The spectra were always determined at room temp.

Table II and III show results of the IR and near-IR data. Figures 1 and 2 reproduce the spectra obtained.

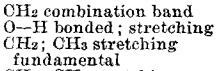
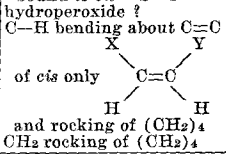
Discussion

2-Methyl-octenoate was obtained with good efficiency reducing 2-methyl-octynoate with hydrogen at atmospheric pressure in presence of Lindlar's catalyst. The iodine index by hydrogenation proved the existence of only one double bond, which by means of oxidative ozonization was recognized to be in the α position. Nevertheless, the peak corresponding to the synthesized ester emerged practically superposed with methyl octanoate, when GLC was attempted with a polar column of 15% polyethylene glycol adipate. This result does not agree with the behaviour of unsaturated acid esters, which are retained in polar columns for a longer time than the saturated ones, due to interaction between the double bond and the polar phase. On the contrary, the retention time of the methyl-oct-*trans*-2-enoate, in the polar column was longer than the corresponding saturated ester. In the non-polar chromatographic column (10% Apiezon N) the principal factor determining the position of the peaks was the volatility of the substance. In this column the peak of the synthesized product was again superposed on the methyl octanoate, whereas the *trans* form had a longer retention time. When the boiling points of the three substances were compared it was deduced that the volatility was the principal factor determining the retention times of the three substances in both columns. The saturated ester (bp 192.2C) and the synthesized product (bp 193–194C) had very close boiling points, whereas the *trans* form was higher (200.6C). As it was proved that the synthesized product is a monoethylenic ester, with only one double bond in the α position and, having different boiling points and chromatographic behaviours compared with those of the methyl oct-*trans*-2-enoate, it necessarily had to be methyl-oct-*cis*-2-enoate. The *cis* structure of the synthesized product was also proved by IR spectra.

As the three different peaks appeared in both phases in the same order, it can be deduced that the ester group affects a double bond in the α position in such a way that the latter loses almost completely its action on the polar phase. The influence of the proximity of the double bond to the carboxyl group has been observed by Landowne and Lipsky (14) with different positional isomers of methyl linoleate. They deduced that the double bonds are much more polarizable by the polar phases the farther they are from the carboxyl group.

The data from IR spectra show in Tables II and III. It can be predicted from theoretical considerations that no C=C stretching vibration will appear in the IR from compounds with a *trans* double bond at a center of symmetry. This is because IR absorption takes place only where there is a change of dipole moment, and there is no appreciable change involved in the C=C stretching vibration of a *trans* symmetrical molecule. On the other hand, some changes will occur in the dipole moment in the case of compounds with *cis* double bonds (15). The presence of the C=C stretching vibration in both our compounds (Table II), confirmed the non-symmetrical structure and the position of the double bond C=C. Both intensities were strong enough to prove that the intensity of the C=C double bond in the IR diminishes when the double bond moves from the end of a chain towards the center and the molecule becomes more

TABLE II
Positions and Intensities of Infrared Absorption Bands of the Synthesized Product and Methyl oct-*trans*-2-enoate

Synthesized product			Methyl oct-*trans*-2-enoate			Assignment
λ	ν	Intensity [a]	λ	ν	Intensity	
(μ)	(cm⁻¹)		(μ)	(cm⁻¹)		
2.34	4274	vw	2.34	4274	vw	CH_2 combination band
			2.94	3401	w	O—H bonded; stretching
3.43	2915	vw	3.43	2915	vw	CH_2; CH_3 stretching fundamental
3.49	2865	s	3.50	2857	s	CH_2; CH_3 stretching fundamental
5.79	1727	vs	5.79	1727	vs	C=O stret. of esters  R—C=C — C=O α β unsaturated
6.07	1647	s	6.03	1658	vs	C=C stret. of esters
6.65	1504	w				CH
6.83	1464	s	6.83	1464	s	CH_2 group; C—H deformation saturated group
6.95	1439	vs	6.96	1437	vs	—C—CH_3 group; asymmetrical deformation
7.10	1408	m				In plane bending of H attached to a *cis*—C=C— group
7.26	1377	w	7.26	1377	w	—C—CH_3 group; symmetrical deformation
7.42	1348	w	7.48	1337	s	—C—H— group; C—H deformation sat. group
7.56	1323	w	7.56	1323	vs	deformation O—H of hydroperoxide
			7.62	1312	vs	
7.88	1269	m	7.88	1269	vs	C—O stret. of esters
8.02	1247	m	8.14	1229	s	C—O stret. of esters
8.34	1199	vs	8.31	1203	vs	C—O stret. of esters
8.53	1172	vs	8.54	1171	vs	C—O stret. of esters
8.91	1122	m	8.87	1127	s	C—O stret. of esters
9.59	1043	m	9.58	1044	s	
9.95	1005	m	9.82	1018	m	
10.08	992	m				C—H deformation about a C=C of *cis, trans* conjug.
10.53	950	w				C—H deformation about a C=C of *cis, trans* conjug.
			10.12	988	s	C—H deformation about a C—C of *trans,trans* conjug.
			10.21	979	m	C—H deformation about a C—C of *trans,trans* conjug.
10.89	918	w	10.96	912	w	
11.24	890	w				O—O of hydroperoxide ?
			11.65	858	m	
11.85	844	m				O—O of hydroperoxide ?
12.28	814	s	12.23	817	w	O—O of hydroperoxide ?
12.74	785	w				out of plane rocking of H bound to *cis* —C=C— hydroperoxide ?
			13.78	725	m	
13.86	721	m				C—H bending about C=C  of *cis* only and rocking of $(CH_2)_4$
			13.99	715	m	CH_2 rocking of $(CH_2)_4$

[a] vw very weak; w weak; m medium; s strong; vs very strong.

TABLE III
Positions and Intensities of near-Infrared Absorption Bands of the Synthesized Product and Methyl oct-*trans*-2-enoate

Synthesized product		Methyl oct-*trans*-2-enoate		Assignment
λ	Intensity [a]	λ	Intensity	
(μ)		(μ)		
0.85	vw			Third overtone of C—H stretching vibration (12)
1.03	vw			*cis* —C=C— (13)
1.19	w	1.19	w	Second overtone of C—H stretching vibration
1.38	w	1.38	w	$-CH_3$; $>CH_2$
1.41	w	1.41	w	$-CH_3$; $>CH_2$
1.42	vw	1.42	vw	$-CH_3$; $>CH_2$
1.45	vw	1.45	w	O—H of hydroperoxide —O—O—H
1.67	m	1.67	m	First overtone of C—H stretching vibration
1.69	s	1.69	s	First overtone of C—H stretching vibration (CH_3; CH_2; fundamental at 3.50 μ)
1.71	s	1.71	s	First overtone of C—H stretching vibration (CH_3; CH_2; fundamental at 3.50 μ)
1.76	m	1.76	s	First overtone of C—H stretching vibration
1.89	w	1.89	w	Second overtone of C=O stretching vibration
1.96	vw	1.96	w	Second overtone of C=O stretching vibration
2.10	vw	2.10	w	O—H of hydroperoxide
2.11	w	2.11	w	
2.14	m	2.14	w	*cis* unsaturation —CH=CH and also present in methyl esters
2.19	w			*cis* unsaturation —CH=CH—
2.27	vs	2.27	vs	$-CH_3$
2.29	vs			$-CH_3$; $>CH_2$
2.32	vs	2.32	vs	$-CH_3$; $>CH_2$
2.36	vs	2.36	vs	$-CH_3$; $>CH_2$
2.39	vs	2.39	vs	$>CH_2$
2.42	vs	2.41	vs	$>CH_2$
2.44	vs	2.46	vs	$>CH_2$
2.47	vs	2.47	vs	Combination band of C—H stretching and other vibrat.
2.49	vs			Combination band of C—H stretching and other vibrat.
2.53	vs	2.51	vs	
2.63	s	2.60	s	
2.67	s			
2.73	vs	2.72	vs	Overtone of C=O and C=C
2.77	s			
2.83	vs	2.83	vs	Overtone of C=O and C=C
2.93	vs	2.90	vs	Overtone of C=O and C=C
2.98	s	2.98	vs	Overtone of C=O and C=C

[a] vw very weak; w weak; m medium; s strong; vs very strong.

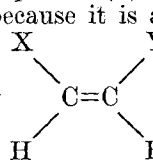
symmetrical in agreement with Bellamy's observations (15).

It is also a general, but not invariable, rule that the C=C absorption of *cis* isomers is a little lower than that of the corresponding *trans* compounds (16). In this case the *cis* form (I) has C=C stretching vibration band at 1647 cm^{-1} and the *trans* form (II) at 1658 cm^{-1}, i.e., the former was 11 cm^{-1} lower than the latter.

Conjugation of the double bond with the carboxyl grouping resulted in a low frequency shift of the C=C absorption which is similar to that arising from a normal pair of conjugated double bonds. These bands were very strong, as was expected because in all cases of conjugation a considerable enhancement of intensity is observed in the IR (15).

One of the most widely studied methods of detecting carbon-carbon double bonds, and of differentiating the various types, is through a study of the out-of-plane deformation of the attached hydrogen atoms. These gave rise to highly characteristic absorptions in the region 1000–800 cm^{-1}, which are almost completely independent of the nature of the surrounding structure, and they have been employed for qualitative and quantitative work in a wide variety of fields (15). It should be observed that, in such measurements as these, high resolution is required to determine accurately the exact positions of maxima, which have been studied by several investigators (17–19). With the limitation of Beckman Model IR-5, the values listed in Table II were found. They confirm the *cis-trans* conjugated structure for compound I and the *trans-trans* conjugated structure for compound II.

Compound I had also a medium band at 7.10 μ (1408 cm^{-1}). All *cis*-compounds have a medium to a weak band at 7.00–7.09 μ, which is in-plane bending of hydrogen attached to a *cis* C=C group (20) of disubstituted ethylenes (15).

A broad absorption band at 13.86 μ was observed in the spectra of compound (I) and indicated *cis* unsaturation (21), because it is a C—H bending about a C=C of *cis* only  (8). This band also corresponds to the $-CH_2-$ rocking of $-(CH_2)_4-$.

One of the most valuable tools of detection of *cis*-double bonds, is near-IR spectroscopy. With few expections, all of the absorption bands observed in the near-IR region (13,22,23) arise from overtones and combinations involving hydrogenic stretching vibrations. The most characteristic of these bands are identified in Table III. They proved again the *cis* structure of the synthesized product.

The two kinds of spectra exhibited several unexpected bands that warrant mention. For example, both esters have some absorption at 800–850 cm^{-1}, which might indicate O—O of hydroperoxide (Table II). The *trans* compound exhibited another band that

indicated O—H of hydroperoxide (Table II). In the near-IR region several bands were attributed to the —O—O—H group, (Table III). These bands indicated that there was some autoxidation of the product during the time elapsed (over 3 months) between synthesis and the IR spectra determination. It also explained the higher iodine index of the product compared to the theoretical value, which was estimated nearly 5 months after the synthesis.

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Stearyl Monoglyceridyl Citrate as an Emulsifier Enhancer[1]

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Abstract

Stearyl monoglyceridyl citrate, a fatty acid ester, is a semisolid compound with a slightly acidic flavor. In its liquid state it is completely miscible with vegetable and animal fats and oils. Although the compound exhibits surfactant activity and reduces interfacial tensions, its major function is emulsifier enhancement and emulsion stabilization when used in shortening systems along with accepted emulsifiers.

Very acceptable liquid and plastic shortenings can be prepared through the addition of stearyl monoglyceridyl citrate and primary emulsifiers. Effective levels of stearyl monoglyceridyl citrate in shortenings enhance performance and permit use of lower levels of primary emulsifiers. Shelf-life stabilities, smoke points, plasticity, and compatibility with primary emulsifiers in finished shortenings are good.

Additions to margarines and whip toppings and performance in baked goods, as well as food additives status, are discussed.

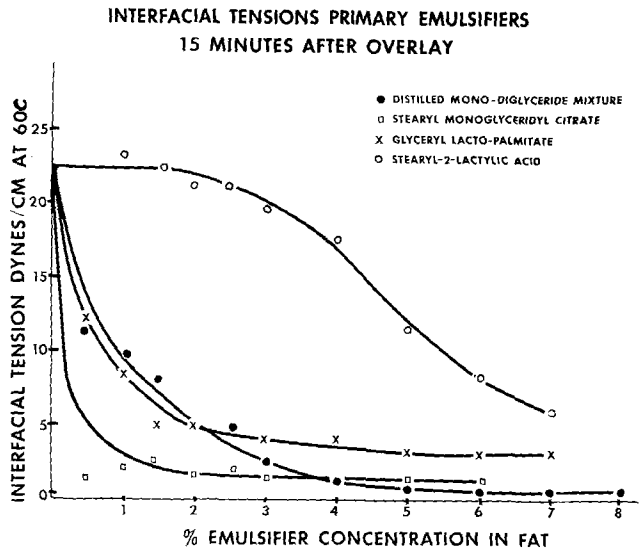

FIG. 1.

Introduction

STEARYL monoglyceridyl citrate is the reaction product of stearyl alcohol, monoglycerides (glyceryl esters of fatty acids derived from cottonseed oil), and citric acid. This fatty acid ester is a somewhat sticky, waxy semi-solid and has a slightly acidic, astringent taste. The compound has acid value 40–52, saponification number 215–255, and a citric acid content of 15–18%. The compound melts at ca. 130F, and in the liquid state is miscible at all levels with vegetable and animal fats and oils; it is insoluble and does not disperse in water.

The physical characteristics and the general configuration of stearyl monoglyceridyl citrate indicate hydrophilic and lipophilic tendencies. Interfacial tension determinations, using cottonseed oil as the emulsifier carrier, confirmed the expected surface or interfacial tension-depressant effects. Figure 1 shows that stearyl monoglyceridyl citrate had a greater interfacial tension-depressant effect at levels under 2% in the fat phase than did the distilled mono-diglyceride mixture (monoglycerides and diglycerides of fatty acids derived from cottonseed oil), glyceryl lacto-palmitate (glycerol ester of palmitic and lactic acids)

TABLE I

Interfacial Tensions of Emulsifier Combinations in Cottonseed Oil (15 min after overlay)

System	Interfacial tension
	dynes/cm, 60C
Cottonseed oil control	21.4
0.10% Stearyl monoglyceridyl citrate	8.5
0.10% Glyceryl lacto-palmitate	21.2
0.10% Stearyl monoglyceridyl citrate + 0.10% Glyceryl lacto-palmitate	8.1
0.10% Distilled mono-diglyceride mixture	20.4
0.10% Stearyl monoglyceridyl citrate + 0.10% Distilled mono-diglyceride mixture	4.8
0.10% Stearyl-2 lactylic acid	23.4
0.10% Stearyl monoglyceridyl citrate+ 0.10% Stearyl-2 lactylic acid	5.8
0.10% Sorbitan monostearate	4.5
0.05% Stearyl monoglyceridyl citrate+ 0.05% Sorbitan monostearate	4.1
0.10% Polyoxyethylene (20) sorbitan monostearate	3.7
0.05% Stearyl monoglyceridyl citrate+ 0.05% Polyoxyethylene (20) sorbitan monostearate	4.5

[1] Presented at the AOCS meeting in New Orleans, 1962.