portion is then extracted in a Waring Blendor and oil determined by the procedure previously described or a modification herein described. To approximate closely the values that would be obtained by the strictly accurate but more laborious method of separating kernels from hull and shell and extracting the kernels only (component method), a correction is required for non-oil substances extracted from the hull and for factors such as adsorption of the kernel oil on particles of hull and decreased efficiency of extraction of the kernel oil in the presence of ground hull and shell. This correction factor is not constant throughout the whole range in oil content found in whole tung fruits, and the best estimate of true tung oil content is obtained by the formula:

Estimated component value = 0.8958 (value by whole fruit method) + 1.37.

The use of a regression equation such as that above in relating results of two empirical chemical methods is believed to be of very general application. The specific formula here arrived at was determined from 97 samples of air dry fruit ranging in oil content from 16.0 to 25.0%. It is not recommended for use with commercial samples of tung fruit, which vary widely in moisture content and usually range from 10.0 to 20.0% in oil content until adequate tests with such samples have been made.

REFERENCES

1. Hamilton, J., and Gilbert, S. G., Anal. Chem., *19*, 453 (1947).
2. Holmes, R. L., and Pack, F. C., Proc. Amer. Tung Oil Asso., 1946, 40-46.
3. Lagasse, F. S., Sell, H. M., Johnston, F. A., and Potter, G. F., U. S. Dept. Agric. Circular No. 806 (1949).
4. McKinney, R. S., Halbrook, N. J., and Agee, G. W., Proc. Amer. Tung Oil Asso., *1948*, 66-71.
5. McKinney, R. S., Halbrook, N. J., and Agee, G. W., Jour, Am. Oil Chem. Soc., *25*, 265-267 (1948).
6. Pack, F. C., Holmes, R. L., and Agee, G. W., Proc. Amer. Tung Oil Asso., *1949*, Part II, 31-39.
7. Snedecor, G. W., "Statistical Methods," 4th edition, ch. 6, Ames, Iowa, Iowa State College Press, 1946.

[Received July 14, 1950]

Syntheses of Cis- and Trans-7- and 8-Octadecenoic Acids: Comparison of the Properties of Cis- and Trans-6-, 7-, 8-, 9-, and 11-Octadecenoic Acids

SALVATORE A. FUSARI,[1,2] K. W. GREENLEE, and J. B. BROWN, Laboratory of Physiological Chemistry, Ohio State University, Columbus, Ohio

As a result of extensive investigations on both animal and seed fats Millican and Brown (1) postulated the natural occurrence of appreciable quantities of isomeric octadecenoic acids occurring along with oleic acid. However they did not isolate these isomeric acids for lack of methods for effecting the necessary separations. In keeping with one of the principal research objectives of this laboratory, that of developing methods for the isolation and purification of naturally occurring fatty acids, it was desired to prepare pure octadecenoic acids with the double bond in various positions near that found in oleic acid so that solubilities of these acids could be determined and methods for separation worked out.

In order to initiate this program it became necessary to prepare pure samples of iso-oleic acids by methods which would lead unequivocally to pure products. Since it seemed more likely that the most probable naturally occurring iso-oleic acids would be those with the double bond close to the 9-position, we decided to synthesize the cis-7-, 8-, and 11-octadecenoic acids. In addition, pure cis-6-(petroselenic) and cis-9-(oleic) octadecenoic acids were prepared by a combination of fractional distillation and low temperature crystallization. Isomerization of all of these cis acids with selenium, followed by low temperature crystallization, gave us the pure trans acids. Thus five cis-trans pairs of octadecenoic acids were available for various types of study, including solubility and infra-red examination. The infra-red studies were particularly significant in view of the recent reports by Swern, Heether, *et al.* (14).

Our syntheses were patterned after the work of Ahmad and Strong (2) on cis- and trans-11-octadecenoic acids. Our results with these acids checked theirs very closely and hence will not be described here. Our synthesis of the 7- and 8- acids followed their basic pattern with important modifications. Their method (2) involved the condensation of an alkynyl sodium derivative with a chloro-iodoalkane to give a 1-chloroalkyne which could then be converted to an alkynoic acid and thence to an alkenoic acid.

$$R{-}(CH_2)_n{-}C{\equiv}C{-}Na + I(CH_2)_nCl \xrightarrow[\text{Liq. } NH_3]{}$$

$$R{-}(CH_2)_n{-}C{\equiv}C{-}(CH_2)_nCl$$

$$\xrightarrow[\text{KOH; HCL}]{\text{KCN}}$$

$$R{-}(CH_2)_n{-}C{\equiv}C{-}(CH_2)_nCOOH \xrightarrow[H_2]{\text{W—6 Raney Ni}}$$

$$R(CH_2)_n{-}CH{=}CH{-}(CH_2)_n{-}COOH$$

We found that bromo-chloroalkanes are superior to the iodo-chloroalkanes when the alkyl carbon chain is C_6 or less. If $I(CH_2)_4Cl$ or $I(CH_2)_5Cl$ or the respective bromo-chloroalkanes are desired, then tetrahydrofuran and tetrahydropyran are much better starting materials for these syntheses than are either $HO(CH_2)_4OH$ or $HO(CH_2)_5OH$, the compounds which would be called for if the original method (2) of preparation is followed.

Experimental

Cis- and Trans-7-Octadecenoic Acids

ω-Chloro-amyl Acetate. ω-Chloro-amyl acetate was prepared according to Synerholm (3), by treating 734 g. of tetrahydropyran with 735 g. of acetyl chlo-

---

[1] Submitted to the Graduate School, Ohio State University, in partial fulfillment of the requirements for the Ph.D. degree.

[2] Present address: Parke Davis and Company, Detroit, Mich.

ride and 68 g. of freshly fused $ZnCl_2$ in a 5-liter flask. Fractional distillation of the product gave 965 g. (69%) of ω-chloro-amyl acetate: n^{20}, 1.4376; Cl, 21.1% (theory, 21.5%); and 250 g. (23.4%) of 1,5-dichloropentane.

1-Chloro-5-iodopentane. 965 g. of ω-chloro-amyl acetate, 940 g. of methanol, and 13 g. of p-toluenesulfonic acid were rectified until 526 g. of the methanol-methyl acetate azeotrope were collected. Remaining solvent was removed in vacuo at room temperature to avoid cyclization of the resulting 1-chloro-5-pentanol. To this product (715 g., 97.4%), without further purification, was added 58 g. of red phosphorus and 774 g. of iodine in small portions with constant stirring. After heating at 140° for 12 hours, the reaction mixture was filtered to remove unreacted phosphorus; and an ether solution of the product was washed repeatedly with dilute sodium thiosulfate solution and finally with water. Fractionation of the product gave 791 g. (60%) of $I(CH_2)_5Cl$: b.p. 7_{mm} 107-111°; n^{20}, 1.5300; and a residue of 400 g. of 1,5-diiodopentane. Since the alkyl iodochlorides decompose during heating, liberating iodine, no further purification was attempted.

Analysis:

Calcd. for $C_5H_{10}ClI$:	Cl 15.21%	Total Halogen—2 eq./mole
Found	Cl 15.67%	Total Halogen—2.01 eq./mole

1-Dodecyne. An attempt to produce 1-dodecyne by condensing sodium acetylide with decyl iodide for 54 hours at the boiling point of liquid ammonia resulted in only a 12% yield; most of the decyl iodide was recovered unchanged. However condensation of either decyl iodide or decyl bromide with sodium acetylide in a steel bomb under its own pressure at room temperature gave excellent yields of 1-dodecyne.

Sodium acetylide was prepared from 92 g. of sodium in 1.5 liters of liquid ammonia, according to Henne and Greenlee (4). The resulting ammonia solution of $Na{-}C{\equiv}CH$ was transferred to a previously cooled (dry ice and acetone) 3.5-liter, high-pressure steel hydrogenation bomb, and 663 g. of cold decyl iodide was added. After securing the bomb, its contents were allowed to react at room temperature for 24 hours. The product was recovered, washed three times with water, extracted with ether, dried, and fractionally distilled to give 258 g. (69.5%) of 1-dodecyne: b.p. 4_{mm} 91°; n^{20}, 1.4343.

1-Chloro-6-Heptadecyne. 791 g. of $I(CH_2)_5Cl$ was added rapidly to an ammonia solution of dodecynyl Na, prepared from 104 g. of Na, 750 g. of 1-dodecyne, and 2 g. of $FeCl_3$ in 3 liters of liquid NH_3; the reaction mixture was refluxed until it gave a negative test for organic iodine (56 hrs.). Water was added cautiously to destroy excess dodecynyl Na. The organic layer was taken up in ether, washed with water to remove inorganic salts and NH_3, and dried. Low boiling products of the reaction included 630 g. of unreacted dodecyne, but no $I(CH_2)_5Cl$ could be recovered. The high boiling residue was distilled in vacuo to give 177 g. (19.3%) of 1-chloro-6-heptadecyne: n^{20}, 1.4645.

Analysis:

Calcd. for $C_{17}H_{31}Cl$:	Cl 13.08%	I.N. 93.7
Found	Cl 12.70%	I.N 92.0 (Wijs, 1 hr.)

7-Octadecynoic Acid. 175 g. of 1-chloro-6-heptadecyne, 1500 cc. of 95% ethanol, 85.0 g. of KCN, and 4.3 g. of KI were refluxed with continuous stirring for 96 hrs. The resulting alcoholic solution of the nitrile was treated with 73 g. of KOH in 275 cc. of H_2O; after the alcohol was removed, 3 liters of H_2O were added, the product was acidified and the free acid separated by extraction with ether and dried; yield, 169 g. (60%). Crystallization of a 10% solution of the crude acid in acetone at −20° gave 131 g. (48%) of 7-octadecynoic acid: N.E., 283.8 (about 1% inert impurity). After removal of this impurity from 70 g. of the acid by saponification, extraction of the soaps with ether, and acidification, recrystallization from petroleum ether gave 66 g. of 7-octadecynoic acid: m.p. 48.8-49°; N.E., 280.3 (theory 280.4); H_2 uptake, 1.98 moles (theory 2 moles).

7,8-Diketostearic Acid. This compound was made by the method of Khan, *et al.* (17) to serve as a derivative of 7-octadecynoic acid. The product from 1 g. of the acid was twice crystallized from 80% alcohol to give 0.8 g. of 7,8-diketostearic acid, m.p. 87°.

Cis-7-Octadecenoic Acid. Two 16-g. batches of 7-octadecynoic acid, dissolved in 200 cc. of absolute ethanol, were selectively reduced each with 2 g. of freshly prepared W-6 Raney Ni as catalyst (5). The mixture was shaken under an initial hydrogen pressure of 35 psi at room temperature until H_2 uptake was 110% of theory. The crude product from the two runs was recovered and cooled to −20° in 70 cc. acetone to remove stearic acid. The filtrate fraction, after removal of solvent, was distilled to give 23.91 g. (74%) of pure cis-7-octadecenoic acid; m.p., 12.5-13.1°.

Analysis:	Calcd. for $C_{18}H_{34}O_2$:	N.E. 282.5	I.N. 89.90
	Found :	N.E. 282.5	I.N. 89.79

Trans-7-Octadecenoic Acid. 10 g. of cis-7-octadecenoic acid was isomerized by heating under nitrogen gas for 10 minutes at 200° with 100 mg. of Se. The product was cooled, decolorized with Darco, filtered through a fine sintered glass filter to remove Se, and then recrystallized 3 times from 10 parts of acetone at −20° to give 3.51 g. of trans-7-octadecenoic acid, m.p. 44.2-44.5°.

Analysis:	Calcd. for $C_{18}H_{34}O_2$:	N.E. 282.5	I.N. 89.90
	Found :	N.E. 281.6	I.N. 88.72

Reisomerization of the filtrate fractions of the above gave an additional quantity of the trans-acid.

7,8-Dihydroxystearic Acids. a) From cis-7-octadecenoic acid: oxidation of 1 g. of cis-7-octadecenoic acid with performic acid according to the method of Swern (16) gave after 2 crystallizations from alcohol, 0.80 g. of 7,8-dihydroxystearic acid, m.p. 94-94.5°; b) from trans-7-octadecenoic acid: similarly 0.5 g. of trans-7-octadecenoic acid gave 0.48 g. of 7,8-dihydroxystearic acid, m.p. 130.5-131°.

Oxidative Degradation of 7,8-Dihydroxystearic Acid. 250 mg. of 7,8-dihydroxystearic acid (m.p. 94-94.5°) was oxidatively cleaved with periodic acid according to King (7) to give an aldehyde and aldehyde-acid. The aldehyde was converted to its 2,4-dinitrophenylhydrazone, m.p. 103.5-104°. Undecanal 2,4-dinitrophenylhydrazone melts at 104°. The aldehydo acid fraction was oxidized with dilute alkaline $KMnO_4$ (8) to a dibasic acid which was then isolated as its p-toluidide, m.p. 205-206°. The p-toluidide of pimelic acid melts at 205-206° and a mixed melting point showed no depression. The double bond is therefore in the expected position.

Cis- and Trans-8-Octadecenoic Acids. The synthesis of cis- and trans-8-octadecenoic acids was accomplished by the procedure used for the 7- and 11- acids, except for 2 important modifications. These include the preparation of $HO(CH_2)_6Cl$ as the precursor of both $I(CH_2)_6Cl$ and $Br(CH_2)_6Cl$, and the use of $Br(CH_2)_6Cl$ in the condensation with undecynyl Na. $Br(CH_2)_6Cl$ was found superior to $I(CH_2)_6Cl$ for several reasons including:

a) Thermal stability which allows for easy purification of the bromochlorides by precise fractional distillation. This is almost impossible with the iodochlorides.

b) Better yields of $Br(CH_2)_6Cl$ (79.3%) are possible from $HO(CH_2)_6Cl$ than are the corresponding yields of somewhat impure $I(CH_2)_6Cl$ (47%) from $Cl(CH_2)_6Cl$.

c) Better yields of 1-chloro-7-heptadecyne (73%) are possible when $Br(CH_2)_6Cl$ is condensed with undecynyl Na than when $I(CH_2)_6Cl$ is used (9%) (see Discussion).

Hexamethylene Chlorohydrin. Commercial adipic acid (duPont) was converted to the diethyl ester and hydrogenated over copper chromium oxide catalyst at 250° at pressures ranging from 3,000-4,500 psi. Isolation of the product, followed by fractional distillation, gave a 78.6% yield of 1,6-hexanediol. The diol (570 g.) was converted to 1-chloro-6-hydroxyhexane (hexamethylene chlorohydrin) by the method of Bywater and Coleman (9). Careful fractional distillation of the product at 2_{mm} gave 276 g. (42%) of $HO(CH_2)_6Cl$: b.p. 2_{mm} 94°; n^{20}, 1.4555; and 211 g. (28.1%) of 1,6-dichlorohexane; b.p. 2_{mm} 74°; n^{20}, 1.4563.

Hexamethylene Bromochloride. The hexamethylene chlorohydrin was converted to $Br(CH_2)_6Cl$ (10) by reaction of 370 g. of $HO(CH_2)_6Cl$ with 366 g. of PBr_3 to give, after careful fractional distillation, 429 g. (79.3%) of $Br(CH_2)_6Cl$: b.p. 2_{mm} 109-110°; n^{20}, 1.4806. Total halogen, 101% of theoretical.

Hexamethylene Iodochloride. By the procedure of Huffman (11) 330 g. of 1,6-dichlorohexane were treated with 320 g. of NaI in 3500 cc. acetone; yield, 241 g. (47%) of $I(CH_2)_6Cl$: n^{20}, 1.5252; b.p. 4_{mm}, 84-88°. The product was used without further purification.

1-Undecyne. By the procedure described previously for the synthesis of 1-dodecyne, 1-undecyne was prepared from 800 g. of nonyl iodide and $Na—C\equiv CH$, made from 116 g. Na, in 6 l. of liquid NH_3. The product was recovered, dried, and fractionally distilled to give 293 g. (61.3%) of 1-undecyne: n^{20}, 1.4328.

1-Cl-7-heptadecyne. A preliminary attempt to condense 1.05 moles of undecynyl Na with 1 mole of $I(CH_2)_6Cl$ gave only a 9% yield; almost all of the undecyne was recovered unchanged. No $I(CH_2)_6Cl$ was recovered, indicating extensive ammonolysis. Since alkyl bromides are known to be less susceptible to ammonolysis than alkyl iodides (12), $Br(CH_2)_6Cl$ was used in the next run. To sodamide, prepared from 22.5 g. of Na and 1 g. of $FeCl_3$ in 2 liters of liquid NH_3, 146 g. of undecyne was added in a slow, fine stream during continuous and vigorous stirring. The mixture was refluxed for 6 hours in order to insure complete conversion of undecyne to undecynyl sodium. 178 g. of $Br(CH_2)_6Cl$ was added, and the whole was refluxed with vigorous stirring for 48 hrs. The product was worked up to give 174 g. (73%) of 1-chloro-7-heptadecyne: n^{20}, 1.4637; Cl, 13.78% (theory 13.08%).

8-Octadecynoic Acid. 174 g. of 1-Cl-7-heptadecyne was converted to 8-octadecynoic acid, as described previously for 1-Cl-6-heptadecyne, to give 152 g. (83.5%) of crude 8-octadecynoic acid. Crystallization of this acid from a 5% solution petroleum ether at —20° gave 134 g. (74%) yield of 8-octadecynoic acid. Further purification, after extraction of the Na soap solution in 20% ethanol with ether, gave 8-octadecynoic acid: m.p. 46-46.5°; N.E., 280.6 (theory, 280.4). The diketo-acid melted at 92.5-93°.

Cis-8-Octadecenoic Acid. 16.5 g. of 8-octadecynoic acid was reduced with W-6 Raney Ni as described for 7-octadecynoic acid. Stearic acid was removed by cooling a 5% solution in acetone to —20°. Further crystallization of the filtrate fraction at —50°, followed by vacuum distillation, gave 8.3 g. (50%) of cis-8-octadecenoic acid: n^{30}, 1.4557; N.E., 282.9 (theory, 282.5); I.N., 89.9 (theory, 89.9).

Trans-8-Octadecenoic Acid. 12 g. of cis-8-octadecenoic acid was isomerized by heating with Se to give, after three crystallizations from acetone, 4.56 g. (38%) of trans-8-octadecenoic acid, m.p. 50.5-50.7°.

Analysis:			
	Calcd. for $C_{18}H_{34}O_2$:	N.E. 282.5	I.N. 89.9
	Found :	N.E. 282.1	I.N. 90.0

8,9-Dihydroxystearic Acids. a) Performic acid oxidation of 1.5 g. of cis-8-octadecenoic acid gave, after 2 crystallizations from ethanol, 1.1 g. (73%) of 8,9-dihydroxystearic acid, m.p. 94-94.3°.

b) Similar treatment of 0.5 g. of trans-8-octadecenoic acid gave, after 2 crystallizations from ethanol, 0.38 g. (76%) of 8,9-dihydroxystearic acid, m.p. 118-119°.

Degradation of 8,9-Dihydroxystearic Acid. Oxidative degradation of 250 mg. of the 8,9-dihydroxy-acid, as described previously, gave decanoic and suberic acids, as identified by their p-toluidides, thus showing the double bond to be in the desired 8-position.

Preparation and Constants of Cis- and Trans-6-, 9-, and 11-Octadecenoic Acids. Cis-6-octadecenoic (petroselenic acid) was prepared by low temperature crystallization of the C_{18} fraction of the methyl esters of parsley seed oil: m.p., 30-30.2°; N.E., 281.7; I.N., 88.73. Petroselaidic acid was prepared by isomerization of petroselenic acid: m.p., 52.8-53.0°; N.E., 281.9; I.N., 89.22.

Oleic acid was prepared by low temperature crystallization of the C_{18} Me esters of olive oil (13); m.p., 13.3-13.5°; I.N., 89.98; N.E., 282.5. Elaidic acid (m.p. 44°) was prepared by Se isomerization of oleic acid followed by three crystallizations of a 10% solution in acetone, once at —20° and then twice at —5°. Cis- and trans-11-octadecenoic acids were prepared according to Ahmad and Strong (2). Analytical data on these acids follow: cis-11-octadecenoic acid: m.p., 14.5-15.5°; N.E., 282.7; I.N., 88.5; trans-11-octadecenoic acid: m.p., 43.6-44°; N.E., 282.5; I.N., 88.33.

Infra-red Examination of Cis- and Trans-Octadecenoic Acids. The 5 pairs of octadecenoic acids, described previously, were checked for purity by infra-red analysis according to the method of Swern, *et al.* (14). These workers showed that trans monounsaturated compounds have a strong characteristic absorption in the infra-red region at 10.36 microns whereas the cis and saturated compounds do not.

Based on this difference in absorption at 10.36 microns, they developed a method for the determination of trans-octadecenoic acids and esters in the presence of cis-octadecenoic and saturated acids and esters. A Beckman IR-2 spectrophotometer was used in our work, and all measurements were made in a liquid cell which consisted of two rock salt windows separated by an amalgamated lead spacer. The cell thickness was 0.1 mm. Approximately 50-mg. samples were weighed into 5-ml. volumetric flasks and diluted to the mark with pure CS_2. The flasks were allowed to stand at 21° for at least 1 hour in an air conditioned room. All measurements were made under these conditions. A portion of the solution was introduced into the absorption cell by a hypodermic syringe, and the optical density of the solution plus cell at exactly 10.36 microns was measured by the null method. The optical density of the cell filled with CS_2 was then measured under identical conditions, and the difference was taken as absorption due to solute. This optical density difference was then used to calculate the extinction coefficient, E, by the formula $E = \frac{d}{c\ l}$ where *d* is the optical density, *c* is the concentration in grams per liter, and *l* is the cell thickness in centimeters. The results of the analysis are presented in Table I.

TABLE I

Infrared Absorption Data[a]

Octadecenoic Acid	Concn. Mg./5 cc.	Optical Density		Optical Density Difference	E Calcd.
		Sample + CS_2	CS_2		
Trans-Octadecenoic Acids					
Trans 9-	50	0.090	0.043	0.047	0.47
Trans 6-	50	0.089	0.042	0.047	0.47
Trans 6-	50	0.090	0.042	0.048	0.48
Trans 7-	50	0.089	0.041	0.048	0.48
Trans 8-	50	0.085	0.042	0.043	0.43
Trans 11-	50	0.090	0.041	0.049	0.49
Cis-Octadecenoic Acids					
Cis 9-	60	0.060	0.043	0.017	0.14
Cis 6-	50	0.055	0.041	0.014	0.14
Cis 7-	57	0.060	0.043	0.017	0.15
Cis 8-	60	0.063	0.043	0.020	0.17
Cis-11-	55	0.060	0.042	0.018	0.16

[a] Grateful acknowledgment is made to C. L. Wilson and Mrs. Arlene Brooks for the infra-red determinations.

The calculated E for the trans-acids is almost identical for the 6-, 7-, 9-, and 11-octadecenoic acids; the trans-8-isomer shows a slightly lower extinction coefficient. This finding may be due to an actual lower absorption for trans-8-octadecenoic acid at 10.36 microns since three different specimens showed the same value.

Specimens of these, as well as of the cis-acids, have been sent to Dr. Swern at the Eastern Regional Research Laboratory for further examination and final evaluation. The cis-octadecenoic acids show extinction coefficients of almost equal magnitude. The two naturally occurring cis-octadecenoic acids, petroselenic and oleic, both show a calculated E of 0.14. The synthetic cis-acids show slightly greater extinction coefficients, which may indicate either that these compounds absorb more strongly or that the extra absorption at 10.36 microns is due to the presence of very small quantities of the corresponding trans-isomers, due to failure to achieve complete stereochemical specificity in Raney Ni reductions.

Discussion

Several questions have arisen as a result of the synthetic program. For example, it may be asked which type of mixed alkyl halide is best suited for their condensation with alkynl sodium derivatives. From our experience, coupled with the work of Ahmad and Strong (15), a qualitative answer to this question may be given. The alkyl bromochlorides appear to be superior to the alkyl iodochlorides for condensations involving mixed halides up to the C_6 or C_7 series; the alkyl iodochlorides are probably superior in condensations involving longer chain mixed halides. This contention is supported by several facts. Ahmad and Strong (15) found that the condensation reaction between 1-chloro-4-iodobutane and hexynyl Na to 1-chloro-5-decyne gave only a 36% yield whereas reaction between 1-chloro-9-iodononane and octynyl Na gave 95.3% yield. Our own experience has been that the condensation of dodecynyl Na with $I(CH_2)_5Cl$ gave a yield of 19% whereas with $Br(CH_2)_6Cl$ the yield was 73%. We can also compare the 73% yield obtained with $Br(CH_2)_6Cl$ against only a 9% yield obtained with $I(CH_2)_6Cl$. It is believed that the bromides are better because they are more resistant to ammonolysis than are the iodides (12). However when the carbon chain length increases, ammonolysis to form amines does not take place so readily at atmospheric pressure and at the boiling point of liquid NH_3 so that the more reactive iodides can be used more effectively than the bromides. This view is supported by a comparison of the yields obtained from the condensation of nonyl halides with sodium acetylide. Vaughn (16) condensed nonyl bromide with sodium acetylide in an autoclave (100-250 psi) at room temperature to obtain a 51% yield of 1-undecyne whereas we obtained a 61% yield of 1-undecyne by condensing nonyl iodide with sodium acetylide under much less forcing conditions, that is, at atmospheric pressure at —34°. This fact when viewed in the light of the excellent yield (95.3%) obtained by Ahmad and Strong (2) when they condensed 1-iodo-9-chlorononane with octynyl Na leads one to believe that the iodides are much to be preferred with the longer chain alkyl halides.

With respect to the selective hydrogenation of octadecynoic acids to cis-octadecenoic acids (5), our results show that this operation can be successfully carried out with W-6 Raney Ni catalyst. Since it is much easier to separate the resulting octadecenoic acid from stearic acid than from unreacted octadecynoic acid, the best procedure in these reductions is to overhydrogenate the mixture, to the extent of about 10% (17). The reduction product will then consist of a binary mixture of the desired octadecenoic acid and stearic acid, which can be separated easily by low temperature crystallization.

We have observed alternating melting point patterns with the cis- and trans-octadecenoic acids and the dihydroxy derivatives of the latter, as shown in Table II.

Summary

1. The cis- and trans-modifications of 7-, 8-, and 11-octadecenoic acids were synthesized by methods which leave no doubt as to their structure.

2. Many new compounds have been reported including 7-octadecynoic acid, 8-octadecynoic acid, 7,8-diketostearic acid, 8,9-diketostearic acid, cis- and

TABLE II

Melting Points of Cis- and Trans-Octadecenoic Acids and the Dihydroxy Derivatives of the Latter

Octadecenoic Acid	m.p. °C.	Octadecenoic Acid	m.p. °C.	Dihydroxy Acid	m.p. °C.
Cis 6-	30 -30.2	Trans 6-	52.8-53.0	Trans 6-	121-121.5
Cis 7-	12.5-13.1	Trans 7-	44.2-44.5	Trans 7-	130.5-131
Cis 8-	22.8-24.2	Trans 8-	50.5-50.7	Trans 8-	117.5-118
Cis 9-	13.3-13	Trans 9-	44.0	Trans 9-	130-130.5
Cis 11-	10.5-12[a] 14.5-15.5	Trans 11-	43.6-44.0	Trans 11-	127.5-128

[a] Ahmad and Strong (2).

trans-7-octadecenoic acids and their 7,8-dihydroxystearic acid derivatives, and cis- and trans-8-octadecenoic acid derivatives and their 8,9-dihydroxystearic acid derivatives.

3. A new series of intermediate reaction products has been reported although these compounds were not fully characterized. These compounds include hexamethylene bromochloride, hexamethylene iodochloride, 1-chloro-6-heptadecyne, and 1-chloro-7-heptadecyne.
4. The extinction coefficients at 10.36 microns of the cis and trans-6-, 7-, 8-, 9-, and 11-octadecenoic acids have been calculated and compared.
5. The melting points of the cis- and trans-octadecenoic acids and their dihydroxy derivatives were shown to exhibit alternating patterns.

Addendum

After the present work was completed, we received a communication from W. F. Huber of the Procter and Gamble Company with a copy of a paper they were submitting to another journal, describing synthesis of a more extended series of octadecenoic acids, including 7- through 12- and 17-octadecenoic acids. Except for the 17-acid, the pattern of synthesis was essentially that of Ahmad and Strong. After examining Dr. Huber's paper, we feel that publication of our results is warranted because of certain novel and improved details of our synthesis of the 7- and 8-acids and our infra-red data. In view of his results it does not seem necessary to continue our work, as planned, which included synthesis of 10-octadecenoic acid.

REFERENCES

1. Millican, R. C., and Brown, J. B., J. Biol. Chem., *154*, 437 (1944).
2. Ahmad, K., and Strong, F. M., J. Am. Chem. Soc., *70*, 3391 (1948).
3. Synerholm, M., J. Am. Chem. Soc., *69*, 2581 (1947).
4. Henne, A. L., and Greenlee, K. W., J. Am. Chem. Soc., *67*, 484 (1945). Henne and Greenlee, "Inorganic Syntheses," Vol. II, McGraw-Hill, 1944.
5. Adkins, H., and Billica, H. R., J. Am. Chem. Soc., *70*, 695 (1948).
6. Swern, D., Findley, T. W., Billen, G. N., and Scanlan, J. T., J. Am. Chem. Soc., *67*, 1786 (1945).
7. Shriner, R. L., and Fuson, R. C., "Qualitative Organic Analysis," John Wiley and Sons, 1948.
8. King, G., J. Chem. Soc., 1826 (1938).
9. Bywater, W. G., and Coleman, W. R., J. Am. Chem. Soc., *66*, 1821 (1944).
10. Starr, D., and Hixon, R. M., J. Am. Chem. Soc., *56*, 1595 (1934).
11. Huffman, H. C., and Hass, H. B., J. Am. Chem. Soc., *63*, 1233 (1941).
12. Jacobs, T. L., "Organic Reactions," Vol. V., ch. 1, John Wiley and Sons, 1949.
13. Foreman, H. D., and Brown, J. B., Oil and Soap, *21*, 183 (1944).
14. Swern, D., Knight, H. B., Shreve, O. D., Heether, M. R., J. Am. Oil Chem. Soc., *27*, 17 (1950); Anal. Chem., *22*, 836 (1950).
15. Ahmad, K., and Strong, F. M., J. Am. Chem. Soc., *70*, 1699 (1948).
16. Vaugn, T. H., Hennion, G. F., Vogt, R. R., and Nieuwland, J. A., J. Org. Chem., *2*, 1 (1937).
17. Khan, N. A., Deatherage, F. E., and Brown, J. B., J. Am. Oil Chem. Soc., *28*, 27 (1951).

[Received January 26, 1951]

Modification of Vegetable Oils. XI. The Formation of Trans Isomers During the Hydrogenation of Methyl Oleate and Triolein[1,2]

R. O. FEUGE, M. B. PEPPER JR., R. T. O'CONNOR, and ELSIE T. FIELD, Southern Regional Research Laboratory,[3] New Orleans, Louisiana

THE formation of isomeric oleic acids during the hydrogenation of vegetable oils has been the subject of considerable speculation and experimental work, but the phenomena involved are not well understood. It is recognized that the extent to which isomeric oleic acids are present in a plastic fat is of considerable practical importance. In margarine oils, for example, a high content of solid iso-oleic acid glycerides is highly desirable while in shortenings the reverse is true.

During hydrogenation of oils containing oleic and/or polyethenoid acids, both positional and geometric isomers of oleic acid are produced, and several investigators have concluded that both types are present in partially hydrogenated monoesters of oleic acid. Moore (7) examined ethyl oleates which had been partially hydrogenated in the presence of palladium and nickel catalysts and concluded that the solid iso-oleic acids were composed of $\Delta^{9,10}$-, $\Delta^{11,12}$-, and possibly $\Delta^{10,11}$-iso-oleic acids. The $\Delta^{9,10}$ isomer was considered to be elaidic acid, and the two positional isomers probably also possessed trans configurations. Hilditch and Vidyarthi (5) reported that hydrogenation of methyl oleate gave in addition to some elaidic acid, both $\Delta^{8,9}$- and $\Delta^{10,11}$-oleic acids. Moore (7) found that hydrogenation of ethyl oleate resulted in a definite ratio (*ca.* 10:15) of liquid oleic to solid iso-oleic acids. Somewhat later Hilditch and Jones (4) reported the results of an investigation similar to that of Moore but using partially hydrogenated cottonseed and olive oils instead of ethyl oleate. They found no constant proportion of solid to liquid oleic acids but instead a gradual accumulation of iso-oleic acids up to a point corresponding to the maximum observed by Moore, followed by a decline.

Mazume (6) investigated the hydrogenation of methyl oleate and concluded that large amounts of iso-oleic acids were formed during the initial stages of hydrogen addition, followed by a gradual transformation into oleic acid on further hydrogenation.

Recently Swern and co-workers (10, 12) described an infra-red spectrophotometric method for the determination of *trans*-octadecenoic acids and esters in the

---

[1] Report of study made under the Research and Marketing Act of 1946.

[2] Presented at the 24th Fall Meeting of the American Oil Chemists' Society, San Francisco, Calif., Sept. 26-28, 1950.

[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.