Anodic Syntheses. Part XII. Synthesis of* cis- *and* trans-*Octadec-11-enoic Acid, with a Note on the Nature of "Vaccenic Acid."*

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The *cis*- and *trans*-forms of octadec-11-enoic acid have been prepared from palmitoleic acid by stereospecific routes. The literature on natural and synthetic specimens of these two isomeric acids is reviewed. The present results support the contention that natural "vaccenic acid" is a mixture in which *trans*-octadec-11-enoic acid is the main constituent.

BOTH the *cis*- and the *trans*-form of octadec-11-enoic acid have been reported to occur naturally. The *cis*-isomer was identified by Morton and Todd (*Biochem. J.*, 1950, **47**, 327) with the hæmolytic factor of horse brain, and was later shown by Hofmann *et al.* (Hofmann, Lucas, and Sax, *J. Biol. Chem.*, 1952, **195**, 473; Hofmann and Sax, *ibid.*, 1953, **205**, 55) to be the principal unsaturated fatty acid in *Lactobacillus arabinosus* and *L. casei.* Many years earlier Bertram (*Biochem. Z.*, 1928, **197**, 433) isolated "vaccenic acid" from ox and sheep body fats and from butter fat, and assigned to it the *trans*-octadec-11-enoic acid structure, from degradative and elaidinisation studies.

Vaccenic acid, although only a minor constituent of fats, has attracted considerable attention for two reasons. First, it was until recently the only natural monoethenoid acid known with a *trans*-configuration. Secondly, it was at one time reported to be a growth-promoting factor for rats. This claim has not, however, been confirmed by subsequent investigations (for references see Gupta, Hilditch, Paul, and Shrivastava, *J.*, 1950, 3484; also *Ann. Rev. Biochem.*, 1952, **21**, 349). It is possible that vaccenic acid is merely the product of some secondary changes in the natural *cis*-glycerides, and that no special biological significance attaches to it (cf. *idem, loc. cit.*; Swern, Knight, and Eddy, *J. Amer. Oil Chem. Soc.*, 1952, **29**, 44).

The difficulties encountered in isolating "vaccenic acid" have lead to a search for alternative methods of preparation. Partial reduction of elaeostearic (octadeca-9 : 11 : 13-trienoic) acid, or its esters, is reported to be a convenient route (Böeseken, van Krimpen, and Blanken, *Rec. Trav. chim.*, 1930, **49**, 247; Groot, Kentie, and Knol, *ibid.*, 1947, **66**, 633; Woltemate and Daubert, *J. Amer. Chem. Soc.*, 1950, **72**, 1233), but it is doubtful whether any of the products obtained in this way has been homogeneous (cf. Gupta *et al.*, *loc. cit.*; Begemann, Keppler, and Boekenoogen, *Rec. Trav. chim.*, 1950, **69**, 439).

A total synthesis was first devised by Strong and his collaborators (Ahmad, Bumpus, and Strong, *J. Amer. Chem. Soc.*, 1948, **70**, 3391), who used acetylenic intermediates to prepare octadec-11-ynoic acid, and partially reduced the latter over Raney nickel to *cis*-octadec-11-enoic acid. Elaidinisation then furnished a mixture from which *trans*-octadec-11-enoic acid was isolated. It had a melting point and infra-red absorption spectrum very similar to those of a highly purified specimen of natural vaccenic acid, but differed from the latter in its *X*-ray diffraction properties (Benedict and Daubert, *ibid.*, 1949, **71**, 4113). Having carefully confirmed the structure of the synthetic acid by degradation, and thus excluded the possibility of any appreciable double-bond migration during the elaidinisation step, Strong *et al.* suggested that the differences were due to the presence of isomeric acids in the natural material (Bumpus, Taylor, and Strong, *ibid.*, 1950, **72**, 2116). The conclusion that "vaccenic acid" is heterogeneous has also been drawn by Hilditch and his co-workers (*loc. cit.*). They state that all the samples examined by them yielded mixtures of mono- and of di-carboxylic acids on oxidation, and that "vaccenic acid" is therefore "a mixture of more than one *trans*-ethenoid acid, and certainly contains *trans*-octadec-10-enoic as well as *trans*-octadec-11-enoic acid." This view is not, however, shared by Begemann, Keppler, and Boekenoogen (*loc. cit.*) who examined chromatographically the diacid fraction produced by oxidation of a sample of vaccenic acid from

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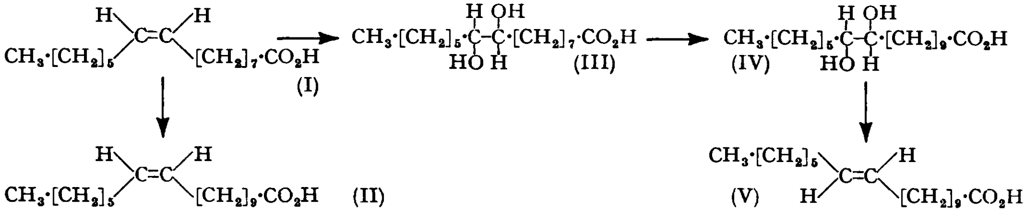
* Part XI, *J.*, 1954, 1804.

butter fat, and concluded that " hendecanedioic acid is obtained exclusively " as required by Bertram's structure.

The synthesis of octadec-11-enoic acid by Strong's acetylenic route has been repeated, with minor modifications and improvements, by several other workers (Fusari, Greenlee, and Brown, *J. Amer. Oil Chem. Soc.*, 1951, **28**, 416; Huber, *J. Amer. Chem. Soc.*, 1951, **73**, 2730; Hofmann and Sax, *J. Biol. Chem.*, 1953, **205**, 55; cf. Morton and Todd, *loc. cit.*). Syntheses by two other routes have also been reported. Reaction of *n*-pentylmagnesium bromide with methyl 13-bromotridec-11-enoate gave, after hydrolysis, a mixture of products from which *trans*-octadec-11-enoic acid was separated (Gensler, Behrmann, and Thomas, *J. Amer. Chem Soc.*, 1951, **73**, 1071; cf. Gensler and Thomas, *ibid.*, 1952, **74**, 3942). Malonate chain extension of palmitoleic (*cis*-hexadec-9-enoic) acid furnished a mixture of *cis*- and *trans*-octadec-11-enoic acid from which the *trans*-isomer was isolated by fractional crystallisation of the lead salts (van Loon and van der Linden, *Rec. Trav. chim.*, 1952, **71**, 292).

From the foregoing summary it will be apparent that although *cis*-octadec-11-enoic acid may be formed from the corresponding acetylenic acid by a partial reduction which is nearly, if not entirely, stereospecific (cf. Crombie, *Quart. Reviews*, 1952, **6**, 128), no similarly selective synthesis of the *trans*-isomer has yet been achieved. Both to furnish a convenient route of this type and to provide independent information on the properties of *cis*- and *trans*-octadec-11-enoic acid, it seemed worth while to undertake the synthesis of these two isomeric acids by the anodic methods described in Part IX of this series (*J.*, 1953, 2393). Palmitoleic acid was chosen as the starting material; it is potentially readily available being one of the main fatty acids in many marine animal oils (Hilditch, " The Chemical Constitution of Natural Fats," Chapman and Hall, London, 1947).



(Each of the dihydroxy-acids is represented by only one of its enantiomorphs.)

Electrolysis of palmitoleic acid (I) in the presence of a large excess of methyl hydrogen succinate gave methyl adipate (34%) and triaconta-7 : 23-diene (8%), by symmetrical coupling of the two components, and, after hydrolysis, *cis*-octadec-11-enoic acid (II) by crossed coupling. The low yield (12%) of the acid was due mainly to losses incurred in purification (*via* the lithium salt), which proved unexpectedly difficult. It seems probable that during the electrolysis some of the palmitoleic acid was esterified with the methanol used as a solvent (cf. formation of methyl oleate from oleic acid; Part IX), and that subsequent hydrolysis of the crude methyl octadecenoate gave a product contaminated with the starting material. Methods of avoiding such disadvantages in small-scale reactions involving the chain extension of fatty acids by only a few carbon atoms are now being developed and will be reported separately. When the product of cross coupling differs appreciably in chain length from the starting materials, no difficulty arises and ease of purification of the product is normally one of the chief merits of the anodic route to fatty acids.

Hydroxylation of palmitoleic acid by means of performic acid furnished, by *trans*-addition to the (*cis*) double bond (cf. Swern, " Organic Reactions," Vol. VII, p. 378), *threo*-9 : 10-dihydroxypalmitic acid (III). The structure of the latter was confirmed by oxidation to heptaldehyde and azelaic acid. Electrolysis of the dihydroxy-acid in the presence of excess of methyl hydrogen succinate gave methyl adipate (45%), triacontane-7 : 8 : 23 : 24-tetraol (18%), and, after hydrolysis, *threo*-11 : 12-dihydroxystearic acid (IV) (23%). The dihydroxy-acid, unlike the unsaturated acid, was readily purified by crystallisation. By standard procedures of bromination and debromination (cf. Part IX;

Ames and Bowman, *J.*, 1951, 1079), it was then converted into *trans*-octadec-11-enoic acid in 42% overall yield. The *trans*-acid was characterised by hydroxylation with performic acid to give *erythro*-11 : 12-dihydroxystearic acid.

The methods used in the present work were shown in the erucic–brassidic series (Part IX) to give pure products without any stereomutation. We therefore feel justified in regarding the samples of *cis*- and *trans*-octadec-11-enoic acid now obtained as homogeneous. Their melting-points, and those of their dihydroxy-derivatives, are compared in the accompanying table with the values reported previously for other samples of these acids.

Melting points of octadec-11-*enoic acids and derivatives.*

	Octadec-11-enoic acid		11 : 12-Dihydroxy-stearic acid			
Authors	*cis*	*trans*	*erythro*	*threo*		
Hofmann and Sax[1] ...	13·4—14·4°	—	—	91·4—93·2°	Natural materials and their derivatives	
Bertram[2]	—	39·0°	—	—		
Boer *et al.*[3]	—	36	—	—		
Geyer *et al.*[4]	—	34·5—36	—	—		
Begemann *et al.*[5]	—	37·0	—	—		
Rao and Daubert[6] ...	—	42·5	—	—		
Hilditch *et al.*[7]	—	—	126°	94·5		
Böeseken *et al.*[8]	—	37—38	—	—	elaeostearic route	Synthetic materials and their derivatives
Groot *et al.*[9]	—	38·4	—	—		
Begemann *et al.*[5]	—	36—37 *	—	—		
Woltemate and Daubert[10]	—	40·0	—	—		
Hilditch *et al.*[7]	—	38·5—40·5 *	—	—		
Strong *et al.*[11]	10·5—12	43—44	127—128	93—94	acetylenic route	
Morton and Todd[12]...	10—11	—	125·5—126	—		
Fusari *et al.*[13]	14·5—15·5	43·6—44	—	—		
Huber[14]	13·0—14·0	43·5—44·5	129—130	94·5—96		
Hofmann and Sax[1] ...	12·4—13·0	—	—	92·2—94·0		
Gensler *et al.*[15]	—	45—45·5 †	—	—		
van Loon and van der Linden[16]	—	(38)				
Present	13·5—14·5	43·4—43·7	129	93·7—94·0	anodic route	

* Sample shown to contain other acids.
† Sinters at 44·5°. A sample prepared by a modified procedure had m. p. 44·5—45°.

Comparison of octadec-11-*enoic acid samples.*

cis-Acid			*trans*-Acid.		
Sample	M. p.	Mixed m. p.	Sample	M. p.	Mixed m. p.
Strong's	10·5—12°	11·3—12·0°	Gensler's	45—45·5°	42·5—44°[15]
Anodic	13·5—14·5	13·2—14·2	Strong's	43—44 *	42·2—43·2
Huber's	13·0—14·0		Anodic	43·4—43·7	
			Huber's	43·5—44·5 †	43·3—43·6
L. arabinosus[17] ...	13·2—14·0	no depression[1]	Strong's	43—44	42·0—42·5[11]
L. casei	13·4—14·4		Rao and Daubert	42·5	
Hofmann's synthetic	12·4—13·0	12·4—13·2[1]	Woltemate and Daubert	40·0	no depression[10]

* The sample kindly supplied by Professor Strong used in mixed m. p. with anodic specimen had m. p. 42·2—42·8°. † The sample kindly supplied by Dr. Huber used in mixed m. p. with anodic specimen had m. p. 43·2—43·6°.

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[1] Hofmann and Sax, *J. Biol. Chem.*, 1953, **205**, 55. [2] Bertram, *Biochem. Z.*, 1928, **197**, 433. [3] Boer, Jansen, and Kentie, *J. Nutrition*, 1947, **33**, 339. [4] Geyer, Nath, Barki, Elvehjem, and Hart, *J. Biol. Chem.*, 1947, **169**, 227. [5] Begemann, Keppler, and Boekenoogen, *Rec. Trav. chim.*, 1950, **69**, 439. [6] Rao and Daubert, *J. Amer. Chem. Soc.*, 1948, **70**, 1102. [7] Gupta, Hilditch, Paul, and Shrivastava, *J.*, 1950, 3484. [8] Böeseken, van Krimpen, and Blanken, *Rec. Trav. chim.*, 1930, **49**, 247. [9] Groot, Kentie, and Knol, *ibid.*, 1947, **66**, 633. [10] Woltemate and Daubert, *J. Amer. Chem. Soc.*, 1950, **72**, 1233. [11] Ahmad, Bumpus, and Strong, *ibid.*, 1948, **70**, 3391. [12] Morton and Todd, *Biochem. J.*, 1950, **47**, 327. [13] Fusari, Greenlee, and Brown, *J. Amer. Oil Chem. Soc.*, 1951, **28**, 416. [14] Huber, *J. Amer. Chem. Soc.*, 1951, **73**, 2730. [15] Gensler, Behrmann, and Thomas, *ibid.*, 1951, **73**, 1071; cf. Gensler and Thomas, *ibid.*, 1952, **74**, 3942. [16] van Loon and van der Linden, *Rec. Trav. chim.*, 1952, **71**, 292. [17] Hofmann, Lucas, and Sax, *J. Biol. Chem.*, 1952, **195**, 473.

The melting points of some mixtures of the unsaturated acids from different sources are also given. From these data we draw the following conclusions:

(1) The acid isolated by Hofmann *et al.* is *cis*-octadec-11-enoic acid and identical with the sample prepared anodically, and with three of those synthesised by the acetylenic route; the remaining two have low melting points, and presumably contain traces of impurities (possibly stearic acid formed during the reduction stage; cf. Hofmann and Sax, *loc. cit.*).

(2) Both the anodic and the acetylenic route yield pure *trans*-octadec-11-enoic acid.

(3) The product obtained by Gensler *et al.* is probably also the pure *trans*-acid, but the reason for the slightly higher melting point is not clear.

(4) van Loon and van der Linden's *trans*-acid is impure. The authors themselves emphasise that no special precautions were taken over purity. It is of interest that malonate chain extension of palmitoleic acid, unlike the anodic method, resulted in stereomutation (cf. synthesis of nervonic acid; Part X, *J.*, 1954, **448**).

(5) The materials obtained by partial reduction of elaeostearic acid, or its esters, are also impure. By carefully controlled oxidations, Begemann *et al.* (*loc. cit.*) have shown that some samples contain only 25—30% of octadec-11-enoic acid.

(6) Whilst the published degradative evidence indicates that the various samples of natural "vaccenic acid" consist mainly of *trans*-octadec-11-enoic acid, the low melting points show that some other acid(s) must be present, as suggested by Hilditch and by Strong and their co-workers. This conclusion conflicts with the view of Begemann *et al.* mentioned earlier, but we do not think it is inconsistent with their experimental results. These indicate that oxidation of their vaccenic acid may have given small amounts of dodecanedioic acid in addition to hendecanedioic acid. The Dutch authors presumably attributed this by-product to a secondary reaction, but if that be the explanation, then the absence of at least a comparable amount of sebacic acid is surprising. Furthermore, and this is no doubt the more important consideration, the iodine value of their vaccenic acid indicates that it may have contained some saturated acid (8—9%), which would not, of course, have been revealed in their degradation experiments.

(7) The evidence available from the dihydroxy-acids is consistent with the above conclusions.

EXPERIMENTAL

M. p.s are corrected. Iodine values were determined by using Rosenmund and Kuhnhenn's reagent (cf. Benham and Klee, *J. Amer. Oil Chem. Soc.*, 1950, **27**, 127). Electrolyses were carried out by using the cell "B" and the general procedure described in Part IX (*J.*, 1953, 2393).

Palmitoleic (cis-*Hexadec*-9-*enoic*) *Acid*.—This was isolated from a mixture of sperm-oil fatty acids for which the authors thank Messrs. Price's (Bromborough) Limited. The acids were converted into their methyl esters which were fractionally distilled through a Stedman column (60 × 2 cm.). The fractions, b. p. 127—130°/0·75 mm., n_D^{19} 1·4507—1·4465, I.V. 89·5—76·0, were hydrolysed and a portion of the resulting mixture of C_{16}-acids was fractionally crystallised from acetone at low temperature, giving palmitoleic acid, m. p. 0·5—1·5°, n_D^{20} 1·4583 (Found: equiv., 255·0; I.V., 99·5. Calc. for $C_{16}H_{30}O_2$: equiv., 254·5; I.V., 99·7) (Baudart, *Bull. Mat. grasses Inst. colonial Marseille*, 1945, **29**, 75; *Chem. Abs.*, 1946, **40**, 5398, gives m. p. *ca.* 1° for the natural acid; Boughton, Ames, and Bowman, *J.*, 1952, 671, give m. p. 0—0·5°, n_D^{20} 1·4585, for a synthetic specimen).

threo-9 : 10-*Dihydroxypalmitic Acid*.—(*a*) Oxidation of pure palmitoleic acid (m. p. 0·5—1·5°; 220 mg.) with performic acid (cf. Swern, Billen, Findlay, and Scanlan, *J. Amer. Chem. Soc.*, 1945, **67**, 1786), and hydrolysis of the initial product, gave a solid (211 mg., 85%), m. p. 86·5—87°. Crystallisation from methanol gave *threo*-9 : 10-dihydroxypalmitic acid as rectangular plates (56%), m. p. 88—88·5° (Found: C, 66·65; H, 11·0. Calc. for $C_{16}H_{32}O_4$: C, 66·65; H, 11·2%) (Baudart, *loc. cit.*, gives m. p. 86—87°; Boughton, Ames, and Bowman, *loc. cit.*, give m. p. 85—86°).

(*b*) Similar hydroxylation of a mixture of the C_{16}-acids (84·5 g.; m. p. 15—33°; equiv., 256; I.V., 87·3), obtained as described from sperm-oil fatty acids, and extraction of the crude product with light petroleum (b. p. 60—80°; 300 c.c.) gave a solid (62 g.), m. p. 78—81°. Two crystallisations from alcohol–ether (1 : 1) and several from benzene–methanol (20 : 1) gave *threo*-9 : 10-dihydroxypalmitic acid (19·5 g.), m. p. and mixed m. p. with the specimen from (*a*), 87·5—88° (Found : equiv., 288·0. Calc. for $C_{16}H_{32}O_4$: equiv., 288·5).

Oxidation of threo-9 : 10-*Dihydroxypalmitic Acid*.—Oxidation of the preceding dihydroxy-acid (0·58 g.) with periodic acid (cf. Huber, *J. Amer. Chem. Soc.*, 1951, **73**, 2730), and steam distillation of the product, gave heptanal. The 2 : 4-dinitrophenylhydrazone, after chromatographic adsorption on alumina from benzene solution, and crystallisation from alcohol, formed needles (32% overall yield), m. p. and mixed m. p. 105—106° (Malkin and Tranter, *J.*, 1951, 1178, give m. p. 106·5°).

Permanganate oxidation of the residue from the steam-distillation gave a solid (0·096 g., 28%), m. p. 102—105°. Crystallisation from benzene–ethyl acetate (charcoal), and then from water, gave azelaic acid, m. p. and mixed m. p. 106·5—107·5° (Huber, *loc. cit.*, gives m. p. 105—106°).

cis-*Octadec*-11-*enoic Acid*.—A mixture of palmitoleic acid (8·46 g., 0·033 mole; m. p. 0·5—1·5°) and methyl hydrogen succinate (20 g.) (*Org. Synth.*, 1945, **25**, 19) in methanol (50 c.c.) was electrolysed in the usual way (current 1·3 A; faradays passed, *ca.* 1·2 times theoretical). Towards the end of the reaction the current tended to drop, but was restored to its former value by the addition of more half-ester (a total of 30 g., 0·23 mole was used). After completion of the electrolysis the alkaline contents of the cell were neutralised with glacial acetic acid and evaporated. The residue, in ether, was washed thoroughly with 2% sodium hydroxide and then with water, and dried (Na_2SO_4). Distillation gave methyl adipate (8·6 g.), b. p. 66—68°/2 mm., n_D^{21} 1·4291, and a fraction (1·5 g.), b. p. 77—132°/2 mm., from which no pure product could be isolated. The high-boiling residue (*ca.* 5·0 g.) was hydrolysed with aqueous methanolic potassium hydroxide (10% w/v), and the crude product thus obtained was dissolved in hot methanol and neutralised with aqueous lithium hydroxide. The solution was evaporated and the residue was extracted first with light petroleum (b. p. 60—80°) (centrifuge), then with methanol–light petroleum (b. p. 60—80°) (3 : 1; 6 c.c.), and finally, in a Soxhlet extractor, with light petroleum (b. p. 60—80°). Crystallisation of the residue, m. p. 201—209°, from 80% aqueous alcohol (charcoal) gave lithium octadecenoate as plates (1·32 g.), m. p. 216—221° (uncorr.; sealed capillary), unchanged by further recrystallisation. Regeneration from the salt gave *cis*-octadec-11-enoic acid (1·1 g.), b. p. 158—163°/0·4 mm., m. p. 13·5—14·5°, n_D^{20} 1·4598 (Found : C, 76·7; H, 12·1%; equiv., 283·0; I.V., 89·5. Calc. for $C_{18}H_{34}O_2$: C, 76·55; H, 12·15%; equiv., 282·5; I.V., 89·8).

Evaporation of the light petroleum extracts from the crude lithium salt, and distillation of the residue, gave an oil (0·5 g.), b. p. 150—160° (bath temp.)/10^{-4} mm., m. p. 6—7°. Crystallisation from light petroleum (b. p. 40—60°) at −20° yielded *triaconta*-cis-7 : cis-23-*diene* as needles, m. p. 8·5—9·5° (Found : C, 85·6; H, 14·0. $C_{30}H_{58}$ requires C, 86·0; H, 14·0%).

threo-11 : 12-*Dihydroxystearic Acid*.—A solution of *threo*-9 : 10-dihydroxypalmitic acid (18·8 g., 0·065 mole; m. p. 87·5—88°) and methyl hydrogen succinate (34 g.) in methanol (90 c.c.) was electrolysed (current 1·5 A; faradays passed *ca.* 1·5 times theoretical). At intervals towards the end of the reaction more half-ester was added (total used 52 g., 0·391 mole). After the electrolysis the cell contents were cooled to 0°. The solid (2·9 g.), m. p. 122—123°, which separated was collected and crystallised from methanol giving *triaconta*-threo-7 : 8-threo-23 : 24-*tetraol*, m. p. 123·5—124·5° (Found : C, 73·8; H, 13·0. $C_{30}H_{62}O_4$ requires C, 74·0; H, 12·85%). The filtrate was neutralised with glacial acetic acid and then evaporated. The filtrate was extracted with ether. On acidification of the insoluble portion *threo*-9 : 10-dihydroxypalmitic acid (1·6 g.) was recovered. The ethereal extract was washed with 2% sodium hydroxide and then with water, dried (Na_2SO_4), and evaporated. Distillation gave methyl adipate (15·4 g.), b. p. 74—78°/2 mm., n_D^{21} 1·4283. The high-boiling residue was hydrolysed with aqueous methanolic sodium hydroxide (8% w/v). The excess of alkali was then neutralised with 2N-hydrochloric acid and the mixture evaporated. The residual crude sodium salt was extracted (Soxhlet) overnight with benzene and then acidified. The product was washed with boiling water, dried, and extracted with benzene (15 c.c.) giving a solid (4·7 g.), m. p. 89·5—91°. Crystallisation from 65% aqueous alcohol gave *threo*-11 : 12-dihydroxystearic acid as rectangular plates (2·9 g.), m. p. 93·7—94·0° (Found : C, 68·3; H, 11·6%; equiv., 319. Calc. for $C_{18}H_{36}O_4$: C, 68·3; 11·45%; equiv., 316·5). A mixture with a specimen, m. p. 91·5—92·5°, supplied by Prof. Strong had m. p. 92·8—93·8°.

trans-*Octadec*-11-*enoic Acid*.—The procedure used to convert the preceding dihydroxy-acid into *trans*-octadec-11-enoic acid was identical with that previously described for the conversion of *threo*-13 : 14-dihydroxybehenic acid into brassidic acid (Part IX, *J.*, 1953, 2393; cf. Ames and Bowman, *J.*, 1951, 1079).

threo-11 : 12-Dihydroxystearic acid (2·68 g.) was converted into *ethyl* erythro-11 : 12-*dibromostearate* (2·73 g., 69%), b. p. 122—128° (bath temp.)/10^{-4} mm., n_D^{20} 1·4860 (Found : C, 51·2; H, 8·3. $C_{20}H_{38}O_2Br_2$ requires C, 51·05; H, 8·1%), which was debrominated in alcohol with zinc giving ethyl *trans*-octadec-11-enoate (1·28 g., 71%), b. p. 119—121°/0·04 mm., n_D^{21} 1·4500. Hydrolysis, and isolation of the acidic product, gave a solid (0·95 g., 84%), m. p. 41—42·5°. Two crystallisations from 75% aqueous alcohol at 0° gave *trans*-octadec-11-enoic acid as plates (0·64 g.), m. p. 43·4—43·7° unchanged by further recrystallisation, n_D^{50} 1·4472 (Found : C, 76·4; H, 12·3%; equiv., 284; I.V., 89·5. Calc. for $C_{18}H_{34}O_2$: C, 76·55; H, 12·15%; equiv., 282·5; I.V., 89·8).

erythro-11 : 12-*Dihydroxystearic Acid* (cf. Huber, *J. Amer. Chem. Soc.*, 1951, **73**, 2730).—Oxidation of *trans*-octadec-11-enoic acid (100 mg.) with performic acid, and hydrolysis of the initial product, gave a solid (90 mg., 80%), m. p. 127·5—128°. Crystallisation from methanol gave *erythro*-11 : 12-dihydroxystearic acid (57 mg., 50%) as rhombs, m. p. 129° undepressed on admixture with a specimen, m. p. 129°, supplied by Prof. Strong.

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