1043. *Essential Fatty Acids. Part II.*[1] *Synthesis of (±)-Vernolic, Linoleic, and γ-Linolenic Acid.*

By J. M. Osbond.

The first synthesis of a naturally occurring unsaturated epoxy-acid, vernolic acid (X), is described. 1-Bromo-oct-*cis*-2-ene (II), and the di-Grignard complex of dec-9-ynoic acid gave octadeca-*cis*-12-en-9-ynoic acid (V). Partial reduction then gave linoleic acid (XII); epoxidation of the acid (V) followed by stereoselective reduction of the acetylenic bond gave (±)-vernolic acid (X). Similarly 1-bromoundeca-2,5-diene (IV) and hept-6-ynoic acid gave the C_{18}-dienynoic acid (VII) which on partial reduction furnished γ-linolenic acid (XIII).

THE principal seed-oil acid from *Vernonia anthelmintica*,[2] vernolic acid, is an epoxy-acid that until recently was unique. The structure of vernolic acid was determined by Gunstone and his co-workers [2,3] as *cis*-12,13-epoxyoctadec-*cis*-9-enoic acid (X) and the acid was later obtained crystalline by Smith, Koch, and Wolff [4] and by Chisholm and Hopkins.[5]. *V. anthelmintica* is an Indian plant with alleged medicinal value (cf. Gunstone [1] for leading references; in particular, Majumdar [6] found the seed oil effective against round-worms). Other members of this group have now been isolated from various seed oils, namely, *cis*-15,16-epoxylinoleic acid,[7] *cis*-9,10-epoxyoctadec-*cis*-12-enoic acid [8] and *cis*-9,10-epoxystearic acid.[9] None of these unsaturated epoxy-acids has so far been synthesised. In Part I,[1] 1,4-diacetylenic and *cis*-1,4-dienoic acids (" skipped unsaturation ") were synthesised by addition of a propargyl halide to the di-Grignard complex of an ω-acetylenic acid followed by partial reduction. This route allowed a synthesis of vernolic acid to be made.[10] The synthesis depends on the greater rate of epoxidation of ethylenic than of acetylenic bonds,[11] and the selective stereospecific partial reduction of an acetylenic bond without the opening of a neighbouring epoxide ring.

Oct-*cis*-2-en-1-ol (I), containing only traces of the *trans*-isomer, was prepared from

[1] Part I, Osbond, Philpott, and Wickens, *J.*, 1961, 2779.
[2] Gunstone, *J.*, 1954, 1611.
[3] Bharucha and Gunstone, *J.*, 1956, 1611.
[4] Smith, Koch, and Wolff, *J. Amer. Oil Chemists' Soc.*, 1959, **36**, 219.
[5] Chisholm and Hopkins, *Chem. and Ind.*, 1960, 1134.
[6] Majumdar, *Indian J. Pharmacol.*, 1943, **5**, 61.
[7] Gunstone and Morris, *J.*, 1959, 2127.
[8] Smith, Bagby, Lohmar, Glass, and Wolff, *J. Org. Chem.*, 1960, **25**, 218.
[9] Chisholm and Hopkins, *Chem. and Ind.*, 1959, 1154.
[10] Osbond, *Proc. Chem. Soc.*, 1960, 221.
[11] Cf. Raphael, " Acetylenic Compounds in Organic Chemistry," Butterworths Scientific Publ., London, 1955, p. 33.

$$CH_3 \cdot [CH_2]_4 \cdot [CH \overset{c}{=\!=} CH \cdot CH_2]_x \cdot X$$

(I) $x = 1$; X = OH
(II) $x = 1$; X = Br
(III) $x = 2$; X = OH
(IV) $x = 2$; X = Br

$$CH_3 \cdot [CH_2]_4 \cdot [CH \overset{c}{=\!=} CH \cdot CH_2]_x \cdot C \equiv C \cdot [CH_2]_y \cdot CO_2H$$

(V) $x = 1$; $y = 7$; m. p. 14—16°
(VI) $x = 1$; $y = 8$; m. p. 8—9°
(VII) $x = 2$; $y = 4$; b. p. 162°/0·02 mm.

$$CH_3 \cdot [CH_2]_4 \cdot \overset{\displaystyle O}{\overset{\displaystyle \diagup \diagdown}{CH\!-\!-\!CH}} \cdot CH_2 \cdot C \equiv C \cdot [CH_2]_y \cdot CO_2H$$

(VIII) $y = 7$; m. p. 55—57°
(IX) $y = 8$; m. p. 52·5—54·5°

$$CH_3 \cdot [CH_2]_4 \cdot \overset{\displaystyle O}{\overset{\displaystyle \diagup \diagdown}{CH\!-\!-\!CH}} \cdot CH_2 \cdot CH \overset{c}{=\!=} CH \cdot [CH_2]_y \cdot CO_2H$$

(X) $y = 7$; m. p. 35—36°
(XI) $y = 8$; m. p. 40—41°

$$CH_3 \cdot [CH_2]_4 \cdot [CH \overset{c}{=\!=} CH \cdot CH_2]_x \cdot [CH_2]_y \cdot CO_2H$$

(XII) $x = 2$; $y = 6$
(XIII) $x = 3$; $y = 3$

$$CH_3 \cdot [CH_2]_4 \cdot [\overset{\displaystyle O}{\overset{\displaystyle \diagup \diagdown}{CH\!-\!-\!CH}} \cdot CH_2]_2 \cdot [CH_2]_6 \cdot CO_2H$$

(XIV) m. p. 76·5—77·5°
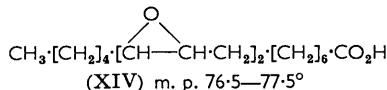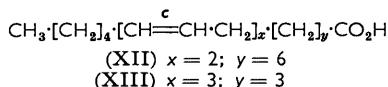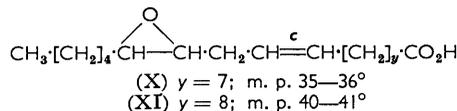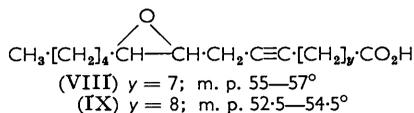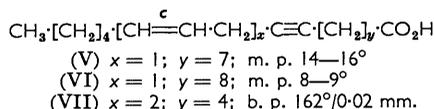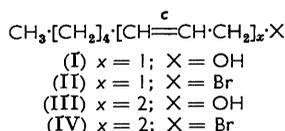
oct-2-yn-1-ol by partial reduction with Lindlar's catalyst.[12]   Its reaction with phosphorus tribromide and pyridine was carried out under a variety of conditions; in nearly all cases the proportion of the *trans*-bromide (cf. II) formed was high as shown by the infrared band at $\nu_{max.}$ 965 cm.$^{-1}$; the bands at 1657 (*trans*-C=C) and 1645 cm.$^{-1}$ (*cis*-C=C) were also found to be useful (see Experimental section).   Conditions for avoiding this not unexpected easy stereomutation were found and essentially pure *cis*-bromide (II) was then obtained in high yield.   The avoidance of pyridine and light was important.   Similarly partial reduction of undeca-2,5-diyne-1-ol[1] gave undeca-*cis*-2,5-diene-1-ol (III) with only a trace of *trans*-isomer;   reaction with phosphorus tribromide under similar conditions gave 1-bromoundeca-*cis*-2,5-diene (IV) although in this case some *trans*-isomer was invariably formed.

The di-Grignard reagent from dec-9-ynoic acid in tetrahydrofuran and the bromide (II) were condensed in the presence of cuprous cyanide,[1] to give crystalline octadec-*cis*-12-en-9-ynoic acid (V) in 64% yield; the infrared spectrum showed only a trace of *trans*-isomer.   The linearity of the acid was confirmed by reduction over Adams catalyst to pure stearic acid in 90% yield after an uptake of 6·35 equiv. of hydrogen.   Similarly the di-Grignard derivative of undec-10-ynoic acid with the bromide (II), and hept-6-ynoic acid with 1-bromoundeca-*cis*-2,5-diene (IV), gave nonadeca-*cis*-13-en-10-ynoic acid (VI) and octadeca-*cis*-9,10-dien-6-ynoic acid (VII), respectively; in the spectrum of the latter acid a distinct *trans*-band was noted at 965 cm.$^{-1}$.

Partial reduction of the C_{18}-enynoic (V) and the C_{18}-dienynoic acids (VII) with Lindlar catalyst in light petroleum furnished a new route to linoleic (XII) and γ-linolenic acid (XIII), both previously synthesised from polyacetylenic acids.[1,13]   The crude acids were characterised by formation of the known crystalline 9,10,12,13-tetrabromo- and 6,7,9,10,12,13-hexabromo-stearic acid, respectively.

Treatment of the C_{18}-*cis*-enynoic acid (V) with peracetic acid in glacial acetic acid gave, after 75% of the peracetic acid had been consumed (4 hr.), a crystalline epoxide (VIII) in 52% yield; similarly the C_{19}-enynoic acid (VI) gave the crystalline epoxide (IX).   In both cases the presence and nature of the oxygen atom was shown by analysis (the oxiran oxygen was determined by the direct titration method of Durbetaki[14]) and by the infrared spectra (*cis*-epoxide bands[15] at 775 and 810 cm.$^{-1}$; no *cis*-ethylenic bands at 3040 and 1650 cm.$^{-1}$).   The final step was effected with Lindlar's catalyst, which was found to be

[12] Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.
[13] Raphael and Sondheimer, *J.*, 1950, 2100; Gensler and Thomas, *J. Amer. Chem. Soc.*, 1951, **73**, 4601; Walborsky, Davis, and Howton, *ibid.*, p. 2590.
[14] Durbetaki, *Analyt. Chem.*, 1956, **28**, 2000.
[15] Cf. Shreve, Heether, Knight, and Swern, *Analyt. Chem.*, 1951, **23**, 277;   Patterson, *ibid.*, 1954, **26**, 823.

very suitable for the partial stereospecific reduction of the acetylenic bond to the *cis*-ethylenic bond. Thus the C_{18}-epoxide (VIII) gave the crystalline *cis*-12,13-epoxyoctadeca-*cis*-9-enoic acid [(±)-vernolic acid] (X) in 70% yield and the C_{19}-epoxide (IX) gave the crystalline C_{19}-*cis*-epoxy-*cis*-enoic acid (XI). Analysis of both acids indicated one double bond (iodine value) and one oxiran oxygen; [14] the infrared spectra showed a *cis*-double bond (no *trans*-band and a *cis*-epoxide). The melting point of our synthetic (±)-vernolic acid (m. p. 35—36° was higher than that recorded for the natural isomer (m. p. 25—28°; [3] 30—31° [4]) or the partially synthetic material obtained from linoleic acid [16] (m. p. 18—19°). To prove the structure (X) for our product two transformations were carried out. Following Bharucha and Gunstone [3] we converted the epoxide (X) by acetic acid into (±)-*threo*-12,13-dihydroxyocta-9-enoic acid, which on reduction gave (±)-*threo*-12,13-dihydroxystearic acid, both having correct m. p.s. Secondly, the epoxide (X) with one equivalent of peracetic acid gave *cis*-9,10,12,13-diepoxystearic acid (XIV), m. p. 76·5—77·5°; the diepoxide derived from linoleic acid was then prepared [17] (m. p. 78°) and found to be identical with the totally synthetic material (XIV) by mixed melting point and infrared spectral comparison.

EXPERIMENTAL

The infrared spectra were determined by Dr. A. Wagland for liquid films or, for solids, Nujol suspensions, unless otherwise stated.

Oct-cis-2-*en*-1-*ol* (I).—Oct-2-yn-1-ol (100·9 g., 0·8 mole) in purified light petroleum (b. p. 69—77°; 2 l.) containing quinoline (1 c.c.) was hydrogenated with Lindlar catalyst [12] (12·0 g.) at 20°/1 atm. with stirring. The uptake of hydrogen (19·7 l.; theor., 19·24 l.) was complete in 4·5 hr. and then stopped completely. The solution was filtered, washed with 2N-hydrochloric acid and water, and dried (Na_2SO_4). The distilled product had b. p. 98—102°/10—15 mm., n_D^{21} 1·4472 (97·0 g., 98%). The infrared spectrum showed only a trace of *trans*-double bond at 965 cm.$^{-1}$. (Colonge and Poilane [18] give b. p. 88°/11 mm., n_D^{20} 1·4470.)

1-*Bromo-oct*-cis-2-*ene* (II).—Oct-*cis*-2-en-1-ol (38·5 g.; 0·3 mole) in dry ether (400 c.c.) was treated with phosphorus tribromide (29·8 g., 10·2 c.c.) during 0·5 hr.; the solution was stirred and protected from light. The solution was refluxed for 2·5 hr., cooled, poured on ice-water, shaken, and extracted 3 times with ether. The extracts were combined, washed with saturated sodium hydrogen carbonate solution and water (twice), and dried (Na_2SO_4). The ether was removed and the bromide (55 g., 96%) was used directly; this material contained very little *trans*-isomer (band at 965 cm.$^{-1}$) but each batch should be checked for this impurity. The amount of *cis*-isomer is difficult to estimate; however, two peaks occur at 1657 and 1645 cm.$^{-1}$, the former is associated with *trans*-, the latter with *cis*-double bonds (C=C stretching bonds [19]). In good samples (mostly *cis*) only one peak at 1645 cm.$^{-1}$ was observed and *vice versa*. The *bromide* (45·9 g.) has b. p. 104—106°/35 mm., n_D^{20} 1·4762, but distillation slightly increases the amount of *trans*-isomer (Found: C, 50·4; H, 7·9; Br, 41·45%; I val., 133. $C_8H_{15}Br$ requires C, 50·3; H, 7·9; Br, 41·8%; I val., 132).

Undeca-cis-2,5-*dien*-1-*ol* (III).—Undeca-2,5-diyne-1-ol [1] (17·9 g.) in purified light petroleum (b. p. 60—80°; 300 c.c.) was reduced with Lindlar catalyst (4 g.) in the presence of 5% quinoline–light petroleum solution (5 c.c.). The uptake of hydrogen stopped at 4850 c.c. (theor., 5150 c.c.). The solution was filtered, washed with 2N-sulphuric acid and water, dried (Na_2SO_4), and evaporated. The *alcohol* was distilled (b. p. 100—101°/0·005 mm.) and had $n_D^{20·5}$ 1·4709 (86% yield) (Found: C, 77·9; H, 12·0%; I val., 301·2. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%; I val., 301·7). The infrared spectrum showed only a small amount of *trans*-double bond; the ultraviolet absorption maximum (in EtOH) was at 229 mμ ($E_{1\,cm.}^{1\%}$ 23·4).

1-*Bromoundeca*-cis-2,5-*diene* (IV).—The alcohol (III) (15·3 g.) in dry ether (200 c.c.) was treated dropwise at 20° with phosphorus tribromide (9·02 g.) during ½ hr. in the dark. The

[16] Pigulevskii and Naidenova, *J. Gen. Chem. (U.S.S.R.)*, 1958, **28**, 234.
[17] Swern and Dickel, *J. Amer. Chem. Soc.*, 1954, **76**, 1957; Pigulevskii and Kuranova, *Zhur. priklad. Khim.*, 1955, **28**, 1353.
[18] Colonge and Poilane, *Compt. rend.*, 1954, **238**, 1821.
[19] Cf. Cross, "Introduction to Practical Infra-Red Spectroscopy," Butterworths Scientific Publ. London, 1960, p. 58.

solution was refluxed for $2\frac{1}{2}$ hr., cooled, poured on ice-water, and extracted 3 times with ether; the extracts were washed, etc., as above. The *bromide* had b. p. 88—91°/0·005 mm. (18·05 g., 86%), n_D^{18} 1·4929 (Found: C, 57·1; H, 8·3; Br, 34·3. $C_{11}H_{19}Br$ requires C, 57·15; H, 8·25; Br, 34·6%). The infrared spectrum showed some *trans*-isomer to be present.

Octadeca-cis-12-*en*-9-*ynoic Acid* (V).—To magnesium (14·6 g., 0·6 g.-atom) under tetrahydrofuran (120 c.c.) was added ethyl bromide (71·9 g., 0·66 mole) in tetrahydrofuran (200 c.c.) dropwise with stirring at 0°. The solution was then stirred at room temperature for 2 hr., cooled to 0°, and treated dropwise with dec-9-ynoic acid [20] (50·4 g., 0·3 mole) in tetrahydrofuran (200 c.c.) in $1\frac{1}{2}$ hr. The whole was then stirred at 20° for 2 hr. Cuprous cyanide (2·0 g.) was added followed by 1-bromo-oct-*cis*-2-ene (57·4 g., 0·3 mole) in tetrahydrofuran (50 c.c.) in 10 min. The mixture became warm and refluxed slightly. After being stirred at 20° overnight under nitrogen the solution was poured on ice and 2N-sulphuric acid and extracted thrice with ether. The ether extracts were shaken with 2N-ammonia; this alkaline extract was acidified with concentrated hydrochloric acid, and extracted with ether, which was then washed with water, dried (Na_2SO_4), and distilled, giving unchanged dec-9-ynoic acid (17·1 g.), b. p. 78—160°/0·01—0·005 mm., n_D^{20} 1·4592, and the *enynoic acid* (35·3 g., 64% based on unrecovered decynoic acid), b. p. 166—172°/0·005 mm., n_D^{20} 1·4730. This material was sufficiently pure for the next stage. Crystallisation from light petroleum (b. p. 40—60°) at −20° gave the pure acid as plates, m. p. 14—16°, n_D^{20} 1·4734, transparent to ultraviolet light (the infrared spectrum showed only a trace of *trans*-double bond) (Found: C, 77·4; H, 10·8. $C_{18}H_{30}O_2$ requires C, 77·65; H, 10·9%).

Nonadeca-cis-13-*en*-10-*ynoic Acid* (VI).—Similarly the di-Grignard complex of undec-10-ynoic acid (54·7 g., 0·3 mole) was prepared as described above from magnesium (14·6 g.) and ethyl bromide (71·9 g.) in tetrahydrofuran (520 c.c.) at 0°. To this solution was added cuprous cyanide (2·0 g.) and 1-bromo-oct-*cis*-2-ene (57·0 g.) in tetrahydrofuran (50 c.c.) at 20°. The resulting *acid*, b. p. 156—172°/0·06—0·1 mm., n_D^{21} 1·4719 (21·47 g.), was acccompanied by recovered undec-10-ynoic acid (18·2 g.). Crystallisation from light petroleum at −30° gave the pure acid, m. p. 8—9° (trace of *trans*-double bond) (Found: C, 77·6; H, 11·1. $C_{19}H_{32}O_2$ requires C, 78·0; H, 11·0%), having no ultraviolet absorption above 220 mµ.

Octadeca-cis-9,12-*dien*-6-*ynoic Acid* (VII).—Similarly ethyl bromide (25·1 g.) in tetrahydrofuran (25 c.c.) was added to magnesium (4·9 g.) under tetrahydrofuran (25 c.c.) at 0° during $\frac{1}{2}$ hr. After a further $\frac{1}{2}$ hr. at 20° hept-6-ynoic acid (12·6 g.) in tetrahydrofuran (25 c.c.) was added dropwise at 0° (ice–salt cooling) in $\frac{1}{2}$ hr. A further 50 c.c. of tetrahydrofuran was then added and the mixture stirred at 20° for 2 hr., then cuprous cyanide (0·5 g.) was added. 1-Bromo-undeca-*cis*-2,5-diene (11·6 g.) in tetrahydrofuran (25 c.c.) was added at 20° in $\frac{1}{2}$ hr. under nitrogen and the mixture stirred for 16 hr. The *acid*, isolated in the usual way, had b. p. 162—164°/0·0025 mm., $n_D^{18·5}$ 1·4830 (9·8 g., 70%) (Found: C, 78·45; H, 10·0. $C_{18}H_{26}O_2$ requires C, 78·2; H, 10·2%). A band at 965 cm.⁻¹ showed some *trans*-isomer to be present.

Stearic Acid.—Octadeca-*cis*-12-en-9-ynoic acid (2·62 g.) in methanol (25 c.c.) containing prereduced Adams catalyst (0·1 g.) was reduced at 20°/1 atm. Absorption (750 c.c.; theor., 709 c.c.) was rapid (20 min.) and the resulting acid crystallised. The solution was warmed, filtered, and cooled to 0°. Stearic acid separated as plates (2·40 g., 90%), m. p. 69·5—70°. A mixed m. p. with an authentic sample was 68—70°.

Octadeca-cis-9,12-*dienoic Acid* (*Linoleic Acid*) (XII).—Octadeca-*cis*-12-en-9-ynoic acid (V) (5·27 g.) in light petroleum (b. p. 67—70°; 130 c.c.) and a 5% solution of quinoline in light petroleum (3 c.c.) was hydrogenated at 20°/1 atm. with Lindlar's catalyst (1·0 g.). After absorption of one mol. of hydrogen (458 c.c.; theor., 483 c.c.) there was a sharp break in the hydrogenation curve and the reaction was stopped. The filtered solution was treated with bromine dropwise at 0° with stirring until a red colour persisted. The solid was filtered off, washed with light petroleum, and dried. The 9,10,12,13-tetrabromostearic acid (3·8 g.), crystallised from methylene chloride, had m. p. 114—115·5° (Found: C, 36·0; H, 5·3; Br, 53·4. Calc. for $C_{18}H_{32}Br_4O_2$: C, 36·2; H, 5·4; Br, 53·3%). A mixed m. p. with a specimen (m. p. 115—116°) prepared from poppy-seed oil [21] gave no depression. A comparison of their infrared spectra showed no differences.

Octadeca-cis-6,9,12-*trienoic Acid* (γ-*Linolenic Acid*) (XIII).—Similarly the dienynoic acid (VII) (4·06 g.) in light petroleum (b. p. 60—80°; 60 c.c.) with 5% quinoline–light petroleum

[20] Black and Weedon, *J.*, 1953, 1785; Crombie and Jacklin, *J.*, 1957, 1622.
[21] McCutcheon, *Org. Synth.*, 1942, **22**, 75.

(2 c.c.) and Lindlar catalyst (1·2 g.) (uptake, 355 c.c.; theor., 355 c.c.) gave γ-linolenic acid that was treated in ether with bromine at 0°. The insoluble 6,7,9,10,12,13-hexabromostearic acid (1·10 g.), when crystallised from ethyl methyl ketone, had m. p. 201·5—202° alone or mixed with a previous specimen [1,22] (Found: C, 28·8; H, 3·9; Br, 62·7. Calc. for $C_{18}H_{30}Br_6O_2$: C, 28·5; H, 4·0; Br, 63·3%).

Octadeca-cis-12,13-*epoxy*-9-*ynoic Acid* (XIII).—Octadeca-*cis*-12-en-9-ynoic acid (V) (30·0 g.) was treated at 5° with an 8·36% solution of peracetic acid in glacial acetic acid (107·8 c.c., 1·1 moles). The solution was kept at 5° for 1 hr. and at 20° for 3 hr., then poured on ice-water. In a preliminary experiment portions were withdrawn at intervals and the peracetic acid content determined by titration: after 4 hr. *ca.* 75% had been consumed and little more reacted after this time. The sticky white solid (31·2 g.) was filtered off, washed with water, dried, and crystallised from light petroleum (b. p. 40—60°; 150 c.c.) at 0°, giving the *epoxide* (16·4 g., 52%), m. p. 52·5—55°. Recrystallisation from light petroleum gave a sample, m. p. 55—57° (Found: C, 73·1; H, 10·2; O, 16·8; oxiran-O, 5·2. $C_{18}H_{30}O_3$ requires C, 73·4; H, 10·3; O, 16·3; oxiran-O, 5·4%), $v_{max.}$ (in CS_2) 810 (*cis*-epoxide), 775 and 1000 cm.⁻¹.

Nonadeca-cis-13,14-*epoxy*-10-*ynoic Acid* (IX).—Similarly, nonadeca-*cis*-13-en-10-ynoic acid (VI) (21·5 g.) gave a crude product (25·8 g.) that, crystallised from light petroleum (b. p. 40—60°; 100 c.c.), afforded the crude epoxide (12·23 g.), m. p. 46—48°. Several crystallisations from light petroleum or methanol gave the *epoxide* (3·9 g.) as needles, m. p. 52·5—54·5° (Found: C, 73·7; H, 10·4. $C_{19}H_{32}O_3$ requires C, 74·0; H, 10·5%). This had no infrared band at 3040 or 1650 cm.⁻¹ (*cis*-double bond), but an epoxide band at 810 cm.⁻¹ and an additional band at 775 cm.⁻¹.

Octadeca-cis-12,13-*epoxy*-cis-9-*enoic Acid* (X) [(±)-*Vernolic Acid*].—The epoxy-acetylenic acid (VIII) (5·88 g.) in purified light petroleum (b. p. 67—77°; 200 c.c.) and a 5% quinoline–light petroleum solution (8 c.c.) was hydrogenated with Lindlar catalyst (2·0 g.) at 20°/1 atm. (uptake, 496 c.c.; 1 mol., 491 c.c.). The solution was filtered, concentrated to *ca.* 50 c.c., and cooled in ice–salt. The colourless prisms (4·17 g., 70%), m. p. 32·5—35°, were collected and recrystallised from light petroleum (b. p. 40—60°) at −10°. The pure epoxy-acid had m. p. 35—36°. Natural vernolic acid is recorded as being liquid at room temperature with $[α]_D$ −8°,[2] and as having m. p. 25—28°[4] and 30—31°.[5] The partially synthetic (±)-form had m. p. 18—19°[16] (Found: C, 72·6; H, 10·8; O, 15·9; oxiran-O, 5·4%; I val., 93, 94. Calc. for $C_{18}H_{32}O_3$: C, 72·9; H, 10·9; O, 16·2; oxiran-O, 5·4%; I val., 85·6). The infrared spectrum (in CS_2) showed bands at 820 (*cis*-epoxide), 775, and 1105 cm.⁻¹. A double bond was shown at 720, 1650, and 3040 cm.⁻¹; there was no *trans*-isomer band at 965 cm.⁻¹.

cis-13,14-*Epoxynonadeca*-cis-10-*enoic Acid* (XI).—Similarly the epoxy-acetylenic acid (IX) (3·08 g.) gave an epoxy-enoic *acid* (XI) that crystallised from light petroleum (b. p. 40—60°) as prisms, m. p. 40—41° (also m. p. 35·5—36·5°; the infrared spectra of the two samples were identical) (Found: C, 74·1; H, 11·3; O, 15·1%; I val., 82. $C_{19}H_{34}O_3$ requires C, 73·5; H, 11·0; O, 15·5%; I val., 81·75), $v_{max.}$ 815 (epoxide), 715 (cis C≡C), and 2980 cm.⁻¹ (no *trans*-double bond).

(±)-threo-12,13-*Dihydroxyoctadec*-9-*enoic Acid*.—cis-12,13-Epoxyoctadeca-*cis*-9-enoic acid (1·84 g.) in glacial acetic acid (50 c.c.) was heated at 95° for 9 hr. The acetic acid was removed under reduced pressure and the resulting syrup boiled with potassium hydroxide (5 g.) in water (20 c.c.) and methanol (80 c.c.) for 2 hr. The methanol was removed and the solution made acid with 2N-hydrochloric acid and extracted twice with ether. The extracts were washed with water and dried (Na_2SO_4). The acid separated from ethyl acetate–light petroleum (b. p. 40—60°) at −40° as prisms (0·9 g.), m. p. 45—48°, and recrystallisation gave the pure acid, m. p. 52—53° [lit.,[2,3] m. p. for the (−)-form, 53—54°, 52—55°; (±)-form [5] 52·5—53°) (Found: C, 69·1; H, 10·9%; I val., 82, 83. Calc. for $C_{18}H_{34}O_4$: C, 68·7; H, 10·9%; I val., 80·7).

(±)-threo-12,13-*Dihydroxystearic Acid*.—The above dihydroxy-acid (0·26 g.) in ethyl acetate (20 c.c.) was hydrogenated with prereduced Adams catalyst (0·05 g.) at 20°/1 atm. (uptake, 21 c.c.; theor., 20·5 c.c.). The filtered, concentrated solution deposited crystals (0·13 g.), m. p. 96—97° [lit.,[23] for (±)-form, m. p. 98·5(?)—97°; the (+)-form [3,5] m. p. 95—96°, 96·5—97°] (Found: C, 68·6; H, 11·5. Calc. for $C_{18}H_{36}O_4$: C, 68·3; H, 11·5%).

cis-9,10,12,13-*Diepoxystearic Acid* (XIV).—(*a*) (±)-Vernolic acid (X) (0·89 g.) was treated with a 9·45% solution of peracetic acid in glacial acetic acid (2·6 c.c.) at 20° for 4 hr., then poured on ice-water. The product (0·88 g.; m. p. 58—68°) was filtered off, washed with water, dried,

[22] Nevenzel and Howton, *J. Org. Chem.*, 1958, **23**, 933.
[23] Huber, *J. Amer. Chem. Soc.*, 1951, **73**, 2730.

and recrystallised thrice from ethanol, to give the diepoxystearic acid, m. p. and mixed m. p. 76·5—77·5° (Found: C, 68·75; H, 10·2; O, 20·6. Calc. for $C_{18}H_{32}O_4$: C, 69·2; H, 10·3; O, 20·5%), $\nu_{max.}$ (in CS_2) 815 cm.$^{-1}$ (shoulder at 830) (*cis*-epoxide), identical with that of the specimen recorded below.

(*b*) Linoleic acid (5·35 g.), treated as above, gave the diepoxy-acid, m. p. 78° (lit.,[17] m. p. 77·8—78·2°, 78°) (Found: C, 69·4; H, 10·1; oxiran-O, 9·5. Calc. for $C_{18}H_{32}O_4$: C, 69·2; H, 10·3; oxiran-O, 10·2%).