469. *Lipids. Part VIII.* Syntheses of* cis-13- *and* trans-*Octadec*-13-*ene*-9,11-*diynoic Acids, and Octadeca*-cis-13,trans-15- *and* -trans-13,trans-15-*diene*-9,11-*diynoic Acids: Their Status in Nature.*

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Syntheses of *cis*- and *trans*-octadec-13-ene-9,11-diynoic acids are described. The latter acid is identical with that isolated by Australian authors from *Exocarpus cupressiformis* root-fats. A conjugated dienediynoic acid from *Leptomeria aphylla* had been suspected of being octadeca-*trans*-13,*trans*-15-diene-9,11-diynoic acid; this has been synthesised, together with its *cis*-13,*trans*-15-stereoismer, but their properties do not correspond with those of the natural acid.

The number of known natural acetylenic compounds has increased greatly over the past decade but few new acetylenic glyceride-acids have come to light. A recent investigation of fats from the Olacaceae and Santalaceae has, however, resulted in the discovery of at least three members of the group.[1,2] Octadeca-*trans*-11,*trans*-13-dien-9-ynoic acid (III) was found in *Ximenia americana* Linn. (Olacaceae), and an acid with a conjugated dienediyne chromophore in *Leptomeria aphylla* R.Br. (Santalaceae).[2] The main acid from the root-fat of *Exocarpus cupressiformis* Labill (Santalaceae) was identified as *trans*-octadec-13-ene-9,11-diynoic acid (II) although in the seed oil ximenynic acid [*trans*-octadec-11-en-9-ynoic acid (I)] predominates.[1] This paper deals with synthetic work on these acetylenic acids.

$$CH_3\cdot[CH_2]_5\cdot\overset{t}{CH{=}CH}\cdot C{\equiv}C\cdot[CH_2]_7\cdot CO_2H \quad (I)$$

$$CH_3\cdot[CH_2]_3\cdot\overset{t}{CH{=}CH}\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_7\cdot CO_2H \quad (II)$$

$$CH_3\cdot[CH_2]_3\cdot\overset{t}{CH{=}CH}\cdot\overset{t}{CH{=}CH}\cdot C{\equiv}C\cdot[CH_2]_7\cdot CO_2H \quad (III)$$

Syntheses of both *cis*- and *trans*-ximenynic acid have been described [3,4] and octadeca-*trans*-11-*trans*-13-dien-9-ynoic acid was made as a synthetic precursor for punicic acid [5] before its discovery in Nature. The synthetic and the natural acids are identical. Octadec-13-ene-9,11-diynoic acid has also been made in another connexion,[5] but it is now certain that the liquid acid isolated was a *cis–trans*-mixture. The pure stereoisomers have therefore been made as follows.

The toluene-*p*-sulphonate of 4-hydroxyoct-1-yne was treated with sodamide in liquid ammonia to give, in 60% yield, a mixture of *cis*- 79% and *trans*-oct-3-en-1-yne 21% (estimated by gas–liquid chromatography). Efficient fractional distillation gave the *cis*-hydrocarbon containing less than 2% of *trans*-isomer, and the *trans*-hydrocarbon containing less than 0·5% of *cis*-isomer. Oxidative crossed coupling of oct-*trans*-3-en-1-yne with dec-9-ynoic acid (or, in much better yield, Chodkiewicz coupling [6] with 10-bromodec-9-ynoic acid) gave *trans*-octadec-13-ene-9,11-diynoic acid (II), identical with the natural acid from *Exocarpus cupressiformis* (mixed m. p. and infrared spectrum). The unnatural *cis*-acid was prepared similarly. Partial hydrogenation of the *trans*-enediyne acid over Lindlar catalyst gave octadeca-*cis*-9,*cis*-11,*trans*-13-trienoic acid, m. p. 61·5—62·5°, a fourth pure stereoisomer of the elæostearic acid series (the all-*trans*, *cis*-9,*trans*-11,*trans*-13,

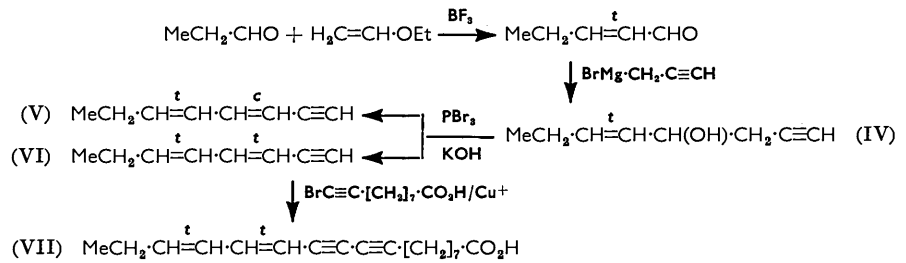
* Part VII, *J.*, 1958, 4435.

[1] Hatt, Triffett, and Wailes, *Austral. J. Chem.*, 1959, **12**, 190.
[2] Hatt, Triffett, and Wailes, *Austral. J. Chem.*, 1960, **13**, 488.
[3] Crombie and Jacklin, *J.*, 1957, 1622.
[4] Crombie and Griffin, *J.*, 1958, 4435.
[5] Crombie and Jacklin, *J.*, 1957, 1632.
[6] Chodkiewicz, *Ann. Chim.* (*France*), 1957, **2**, 819.

and *cis*-9,*trans*-11,*cis*-13-acid are already known).* Two of the stereoisomers occur naturally, and all can be obtained synthetically.[5]

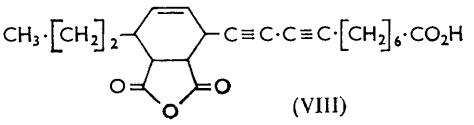
Attention was next turned to the interesting conjugated dienediyne acid from *Leptomeria aphylla*. The natural acid is extremely difficult to isolate and handle, but preliminary studies by the Australian authors [2] indicated the conjugated chromophore and a C_{18} chain. Considering its biogenetic relationships and postulating that the unsaturation begins at C-9, it was felt that a 13,15-diene-9,11-diyne was a reasonable working structure.[2,7] The acid formed a maleic anhydride adduct, indicating a *trans*-13,*trans*-15-diene arrangement. In view of experimental difficulties with the natural acid, synthetic work aimed at octadeca-*trans*-13,*trans*-15-diene-9,11-diynoic acid was therefore carried out. This followed the pattern given earlier and, since the appropriate *cis-trans*-dienyne became available as a by-product, the *cis*-13,*trans*-15-acid was also made.

trans-Pent-2-enal, made from propionaldehyde and ethyl vinyl ether by the cyclic acetal technique,[8] was treated with propargylmagnesium bromide, to give *trans*-oct-5-en-1-yn-4-ol (IV). The elimination procedure *via* the toluene-*p*-sulphonate gave poor results and was replaced by conversion into the bromide and dehydrohalogenation. As the octa-3,5-dien-1-ynes thus formed are thermally unstable and moderately large batches were required for efficient fractionation, separation of the geometrical isomers was effected by preparative gas–liquid chromatography over dinonyl phthalate on Celite at 78·5°. This gave pure *cis*-3,*trans*-5- and *trans*-3,*trans*-5-hydrocarbons (V and VI). The latter was coupled [6] with 10-bromodec-9-ynoic acid to give octadeca-*trans*-13,*trans*-15-diene-



9,11-diynoic acid (VII), crystalline but unstable and rapidly becoming blue in light. The acid formed a maleic anhydride adduct and was hydrogenated to stearic acid with absorption of six mols. of hydrogen. The corresponding *cis*-13,*trans*-15-stereoisomer was made by the same route.

Ultraviolet data for the *Leptomeria* dienediyne acid were almost identical with those for the synthetic *trans*-13,-*trans*-15-acid, but the melting points indicated non-identity. Revision of the tentative structure of the natural acid, provided that the evidence for the



(VIII)

$CH_3·[CH_2]_2·CH=CH·CH=CH·C{\equiv}C·C{\equiv}C·[CH_2]_6·CO_2H$ (IX)

chain-length and maleic anhydride addition is sound, requires re-orientation of the diene-diyne system and/or, its movement along the chain. Recently, as a result of these findings, Dr. Wailes has informed us [7] that by using glycerides containing 5% of the dienediyne, but almost no other diene, a maleic anhydride adduct has been made and oxidised under very mild conditions. Suberic acid was the main dicarboxylic acid formed,

* Recently Hopkins and Chisholm (*J.*, 1962, 573) discovered the *trans*-9,*trans*-11,*cis*-13-stereoisomer in Nature.

[7] Wailes, personal communication.

[8] Hoaglin and Hirsh, U.S.P. 2,628,257; *Chem. Abs.*, 1954, **48**, 1423.

together with shorter-chain dicarboxylic acids. This suggests that the maleic anhydride adduct is (VIII) and the parent acid (IX).

Experimental

Oct-1-yn-4-ol.—After initiation of the reaction with a few drops of propargyl bromide and a little mercuric chloride, propargyl bromide (240 g.) in dry ether (1 l.) was added slowly to magnesium turnings covered with ether; the temperature was kept below 20°. The Grignard reagent was then treated with valeraldehyde (172 g.) in ether (150 ml.) at <0°. After refluxing for 45 min., the mixture was poured into cold saturated ammonium chloride solution and extracted with ether, and the extract was worked up in the usual way, to give oct-1-yn-4-ol (117 g., 48%), b. p. 71·5—75·5°/15 mm., n_D^{21} 1·4440—1·4450 (lit.,[5] b. p. 77—85°/10 mm., n_D^{20} 1·4462—1·4485), $\nu_{max.}$ 3401 (OH) and 3311, 2132 cm.$^{-1}$ (C≡CH). There was no allenic infrared absorption. The *α-naphthyurethane* had m. p. 94—94·5° [from light petroleum (b. p. 60—80°)] (Found: C, 77·6; H, 6·9. $C_{19}H_{21}NO_2$ requires C, 77·3; H, 7·2%).

cis- *and* trans-*Oct-3-en-1-yne.*—Oct-1-yn-4-ol (173·5 g.) was treated with toluene-*p*-sulphonyl chloride (261 g.) in pyridine (111 ml.). The oily 4-toluene-*p*-sulphonyloxyoct-1-yne (360 g.) which was isolated was dissolved in ether (300 ml.) and added to sodamide [from sodium (63·5 g.) and ferric nitrate catalyst (1·5 g.)] in liquid ammonia (3·5 l.), and the whole was stirred overnight. Ammonium chloride (500 g.) was added and the ammonia allowed to evaporate. Water and ether were added and the ethereal extracts were washed with 2N-hydrochloric acid, saturated sodium hydrogen carbonate solution, and then water. After drying, the product from two such batches was distilled, to give octenyne (195 g., 60%) as a mixture of *cis-* and *trans*-isomers (*cis-* 79%, *trans-* 21%), b. p. 61—85°/10 mm.

This mixture was fractionated under 100 mm. of nitrogen, through an electrically heated gauze-packed Stedman column with manostatic control. A reflux ratio of 40 : 1 was used. The first five fractions, b. p. mainly 60—61·8°/100 mm., n_D^{19} 1·4472 (72·1 g.), were cis-*oct-3-en-1-yne* (Found: C, 88·7; H, 11·3. C_8H_{12} requires C, 88·8; H, 11·2%), containing less than 2% of *trans*-isomer; it had $\lambda_{max.}$ 222·8 mμ (ε 12,800) and $\nu_{max.}$ (film) 3322, 2114 (C≡CH), 1618 (conj. CH=CH), 748 (*cis*-CH=CH def.), and 961vw cm.$^{-1}$. After three mixed fractions, pure trans-*oct-3-en-1-yne*, b. p. 71·8°/100 mm., n_D^{19} 1·4553 (17·5) g.), was obtained containing less than 0·5% of *cis*-isomer (Found: C, 88·7; H, 11·4%), $\lambda_{max.}$ 223·6 (ε 13,800), $\nu_{max.}$ (film) 3344, 2123 (C≡CH), 1637 (CH=CH) and 961 cm.$^{-1}$ (*trans*-CH=CH def.).

The *trans-* was more stable than the *cis*-hydrocarbon and differed in odour. It gave *di*-(trans-*oct-3-en-1-ynyl*)*mercury*, m. p. 74·5—75° (Found: C, 46·4; H, 5·4. $C_{16}H_{22}Hg$ requires C, 46·2; H, 5·4%), when treated in methanol with potassium mercuric iodide solution, but the *cis*-derivative was an oil below room temperature.

trans-*Octadec-13-ene-9,11-diynoic Acid.*—Dec-9-enoic acid was made in 39% yield by Barbier–Wieland degradation [9] of undec-10-enoic acid and converted into dec-9-ynoic acid by bromination and dehydrobromination with sodamide in liquid ammonia. The acid formed in 69% yield and had b. p. 100—108°/0·17—0·23 mm., n_D^{20} 1·4558—1·4565 (lit.,[9] b. p. 88°/0·1 mm., n_D^{27} 1·4565).

(*a*) *By Glaser oxidative crossed coupling.* *trans*-Oct-3-en-1-yne (6·4 g.) and dec-9-ynoic acid (10 g.) in methanol (240 ml.) were added to a solution of cuprous chloride (30 g.) and ammonium chloride (100 g.) in 0·08N-hydrochloric acid (240 ml.). The mixture was shaken in oxygen until gas absorption ceased and the green suspension was digested with hydrochloric acid and extracted with ether. The extract was washed thoroughly with sodium carbonate solution. Acidification of the carbonate extract gave, with the aid of ether, crude acids (13·5 g.) which, when extracted with cold light petroleum, left eicosa-9,11-diyndioic acid (7·0 g.), m. p. 120° (from ethanol) (lit.,[9] m. p. 120°). The petroleum extract was evaporated, to give trans-*octadec-13-ene-9,11-diynoic acid* (5·5 g., 33%), m. p. 42·5—43·5° after crystallisation from pentane, plates which became blue on exposure to light (Found: C, 78·5; H, 9·5. $C_{18}H_{26}O_2$ requires C, 78·8; H, 9·55%), $\lambda_{max.}$ (in hexane) 229, 240, 253, 267·5, and 283·5 mμ (ε 3790, 6950, 15,100, 22,500, and 18,200), $\nu_{max.}$ (mull) 2247, 2155 (C≡C·C≡C), 1692 (CO_2H), 1631 (CH=CH) and 956 (*trans*-CH=CH def.). On microhydrogenation the acid absorbed 4·94 mols. of hydrogen to give stearic acid, m. p. and mixed m. p. 68·5—69·5°. The *4-bromophenacyl ester* of the *trans*-enediyne acid, had m. p. 57—58° (from ethanol) (Found: C, 66·2; H, 6·6; Br, 16·9. $C_{26}H_{31}BrO_3$ requires C, 66·2; H, 6·6; Br, 16·95%).

[9] Black and Weedon, *J.*, 1953, 1785.

(*b*) *By Chodkiewicz coupling.* Dec-9-ynoic acid (9 g.) in 10% potassium hydroxide (25 ml.) was added slowly to a solution of bromine (2·75 ml.) and potassium hydroxide (18 g.) in water (100 ml.) at $<0°$. The product was acidified and extracted with ether, to give 10-*bromodec*-9-*ynoic acid* (12·2 g., 92%), m. p. 42—42·5° (from pentane) (Found: C, 48·6; H, 6·2; Br, 32·1. $C_{10}H_{15}BrO_2$ requires C, 48·6; H, 6·2; Br, 32·3%). *trans*-Oct-3-en-1-yne (2·15 g.), hydroxylamine hydrochloride (2 g.), and cuprous chloride (0·04 g.) were dissolved in methanol (20 ml.) and ethylamine (15 ml.). 10-Bromodec-9-ynoic acid (4·20 g.) in methanol (20 ml.) was added slowly, in 30 min., to the solution, which was stirred under nitrogen at 10°. The mixture was stirred for a further 15 min., poured into ice–water, acidified, and extracted with ether, to give *trans*-octadec-13-ene-9,11-diynoic acid (4·35 g., 93%). One crystallisation from pentane raised the m. p. to 42·5—43·5°, identical (mixed m. p.) with the product from the Glaser coupling.

The two synthetic specimens were identical with the enediyne acid from *Exocarpus cupressiformis* which has [1] m. p. 42·2—43°, $\lambda_{max.}$ 229, 240, 252·5, 266·5, and 282 mμ (ε 3500, 7000, 14,900, 23,300, and 17,000), and gave a 4-bromophenacyl ester, m. p. 57—58°.

cis-*Octadec*-13-*ene*-9,11-*diynoic Acid.*—*cis*-Oct-3-en-1-yne (15 g.) and dec-9-ynoic acid (15 g.) were oxidatively cross-coupled by the Glaser technique, as described above, to give crude acids (18 g.). Extraction with light petroleum left eicosa-9,11-diynedioic acid. The petroleum extract was washed with dilute ammonia solution, and magnesium sulphate and ammonium chloride solution were added to the ammonia washings. The precipitated magnesium salt was washed and decomposed, to give cis-*octadec*-13-*ene*-9,11-*diynoic acid* (7 g., 27%), which after low-temperature crystallisation from pentane had m. p. 19—19·5°, rapidly decomposing in air and becoming pink in light (Found: C, 79·4; H, 9·6; O, 11·2. $C_{18}H_{26}O_2$ requires C, 78·8; H, 9·55; O, 11·7%), $\lambda_{max.}$ (in hexane) 229, 240, 253, 267, and 283 mμ (ε 3880, 6960, 14,400, 21,800, and 17,600), $\nu_{max.}$ (film) 2247, 2151 (C≡C·C≡C), 1704 (CO_2H), 1610 (CH=CH str.), and 746 cm.$^{-1}$ (*cis*-CH=CH def.). An earlier report [10] that the ε value for a *cis*-enediyne was appreciably lower than for a *trans*-isomer over-estimates any difference that exists. The 4-*bromophenacyl ester* of the *cis*-enediyne acid, crystallised from ethanol, had m. p. 33—34° (Found: C, 66·0; H, 6·6; Br, 16·9%). On microhydrogenation the acid absorbed 5·05 mols. of hydrogen, to give stearic acid, m. p. and mixed m. p. 68—69°.

Octadeca-cis-9,cis-11,trans-13-*trienoic Acid.*—*trans*-Octadec-13-ene-9,11-diynoic acid (1·005 g.) was hydrogenated over Lindlar's catalyst (0·3 g.) in light petroleum (50 ml.; b. p. 80—100°; stored over Raney nickel) containing quinoline (0·3 g.), until 221·5 ml. of hydrogen (20°/767·6 mm.) had been absorbed. The semi-hydrogenation of two acetylenic linkages was calculated to require 215·4 ml. The usual isolation procedure gave octadeca-*cis*-9,*cis*-11,*trans*-13-trienoic acid (1·0 g.), m. p. 61·5—62·5° (from pentane), $\nu_{max.}$ (crystalline film) 1692 (CO_2H), 1639 (CH=CH str.), 989, 973, 943 (*trans*-olefinic def.), and 746 cm.$^{-1}$ (*cis*-olefinic def.), $\lambda_{max.}$ 261, 270, 280 mμ (ε 30,600, 37,600, and 28,100). This compares with $\lambda_{max.}$ 263, 271, 280 (ε 27,200, 32,300, 24,800) for an earlier specimen known [5] to be impure: the infrared spectrum of this acid was similar to that of the pure acid. When treated with iodine in pentane in the presence of light β(all *trans*)-elæostearic acid was formed (m. p. and mixed m. p. 66—67·5°). On hydrogenation 2·95 mols. of hydrogen were absorbed and stearic acid, m. p. and mixed m. p. 67·5—68° was obtained. The *cis*-9,*cis*-11,*trans*-13-triene gave a 4-phenylphenacyl ester, m. p. 55—56°.

trans-*Pent*-2-*enal.*—Propionaldehyde (522 g.) and ethyl vinyl ether (216 g.) were mixed and added slowly to boron trifluoride–ether complex (2·5 ml.) in ether (40 ml.) at 53°. The mixture was stirred for 1 hr. at 53°, 10% aqueous sodium acetate (150 ml.) was added, and the mixture was stirred for 2½ hr. The organic layer was separated and dried, and ether and propionaldehyde (87 g.) were removed by distillation. After refluxing of the residue with 5% sulphuric acid for 10 min. propionaldehyde (177 g.) was distilled off. The residue was steam-distilled and the distillate was extracted with ether. On washing, drying, evaporation, and distillation, the ethereal extract gave *trans*-pent-2-enal (70 g., 28%), b. p. 123—133°, n_D^{18} 1·4408.

Authenticity of the product was checked by comparing it (infrared spectrum, 2,4-dinitrophenylhydrazone) with a sample made from valeraldehyde.[11,12] The latter was α-brominated and treated with ethanol to give α-bromovaleraldehyde diethyl acetal (51%), b. p. 87—94°/9 mm., n_D^{20} 1·4440, which was dehydrobrominated to 1,1-diethoxypent-2-ene (80%), b. p.

[10] Crombie and Manzoor-i-Khuda, *J.*, 1957, 2767.
[11] Kuhn and Grundmann, *Ber.*, 1937, **70**, 1894.
[12] Prévost, *Bull. Soc. chim. France*, 1944, **11**, 218; Schinz and Rossi, *Helv. Chim. Acta*, 1948, **31**, 1953.

56—60°/9 mm., n_D^{22} 1·4170—1·4189; this was hydrolysed to *trans*-pent-2-enal (72%), b. p. 44°/41 mm., $\nu_{max.}$ (film) 2718 (CHO), 1685 (α-unsaturated CHO), 1640 (CH=CH), and 968 cm.$^{-1}$ (*trans*-CH=CH def.). The 2,4-dinitrophenylhydrazone had m. p. 158° and the semicarbazone, m. p. 180° (lit.,[12] m. p. 160° and 179°, respectively).

trans-*Oct*-5-*en*-1-*yn*-4-*ol*.—Propargylmagnesium bromide was prepared under nitrogen at 20° from magnesium turnings (13·2 g.) and propargyl bromide (70 g.) in dry ether (150 ml.). The solution was cooled to 0° and *trans*-pent-2-enal (42 g.) in ether (100 ml.) was added slowly. After 1 hour's refluxing the product was kept overnight, poured into iced ammonium chloride solution, and extracted with ether. Drying, evaporation, and distillation gave *trans*-oct-5-en-1-yn-4-ol (30·5 g., 49%), b. p. 77—80°/9 mm., n_D^{18} 1·4665, $\nu_{max.}$ (liquid) 3400 (OH), 3315, 2132 (C≡CH), 1671 (CH=CH str.), and 969 cm.$^{-1}$ (*trans*-CH=CH def.). The *α-naphthylurethane* had m. p. 99·5—100° (Found: C, 77·4; H, 6·3. $C_{19}H_{19}NO_2$ requires C, 77·8; H, 6·5%).

Octa-3,5-*dien*-1-*yne*.—Phosphorus tribromide (5·8 ml.) was added slowly to stirred *trans*-oct-5-en-1-yn-4-ol (20 g.) and pyridine (1 ml.) in dry ether (50 ml.) at 0°. The mixture was stirred for a further hour at 0° and cold 2N-hydrochloric acid was added. The organic matter was separated and combined with two extracts of the aqueous layer and washed with sodium hydrogen carbonate solution and water. After drying and evaporation, the crude bromide was dissolved in ethanol (20 ml.) and refluxed for 15 min. under nitrogen with potassium hydroxide (20 g.) in ethanol (100 ml.). Working up, with pentane for extractions, and distillation gave crude octa-3,5-dien-1-yne (9·5 g., 56%), b. p. 39—63°/13 mm., n_D^{22} 1·5145—1·5218. Infrared and gas–liquid chromatographic analysis showed this to contain two stereoisomers. The stereoisomeric hydrocarbons were also made by conversion of *trans*-oct-5-en-1-yn-4-ol into its toluene-*p*-sulphonate (51%) and deacylation with sodium butoxide in butan-1-ol (21% yield).

The octa-3,5-dien-1-ynes (from the dehydrobromination route) were separated by gas–liquid chromatography at 78·5° on a column (6 ft. × 1·3 cm.) of 25% dinonyl phthalate on 80—100 mesh Celite. A nitrogen flow of 400 ml./min. was used, with charges of 0·52 g. of mixed hydrocarbons. Octa-*cis*-3,*trans*-5-dien-1-yne was eluted after 62 min. and the *trans*-3,*trans*-5-compound after 87 min. The two isomers were not completely separated but collection of suitable cuts in U-tubes at −78° gave each isomer in 99·5% purity (gas–liquid chromatography) with an average recovery of 50%. *Octa*-cis-3-,trans-5-*dien*-1-*yne* had n_D^{18} 1·5140 (Found: C, 89·8; H, 9·7. C_8H_{10} requires C, 90·5; H, 9·5%), $\lambda_{max.}$ 259 mμ (ε 23,500), $\nu_{max.}$ (liquid) 3340, 2105 (C≡CH), 1641 (CH=CH conj.), 983 (*trans*-CH=CH), 944 (*cis-trans* conj. diene), and 747 cm.$^{-1}$ (*cis*-CH=CH). *Octa*-trans-3,trans-5-*dien*-1-*yne* had n_D^{18} 1·5252 (Found: C, 89·8; H, 9·7%), $\lambda_{max.}$ 259 mμ (ε 29,800), $\nu_{max.}$ (liquid) 3333, 2105 (C≡CH), 1641 (CH=CH conj.), and 986 cm.$^{-1}$ (*trans*-CH=CH). Both stereoisomers decomposed rapidly at 0° under nitrogen.

Octadeca-trans-13,trans-15-*diene*-9,11-*diynoic Acid*.—Octa-*trans*-3,*trans*-5-dien-1-yne (1·13 g.), cuprous chloride (0·02 g.), and hydroxylamine hydrochloride (1 g.) in methanol (50 ml.) and ethylamine (10 ml.) were stirred under nitrogen at 10° and 10-bromodec-9-ynoic acid (2·60 g.) in methanol (20 ml.) was added slowly. After being stirred for 15 min. the mixture was poured into iced 2N-hydrochloric acid and extracted with ether. Working up gave *octadeca*-trans-13,-trans-15-*diene*-9,11-*diynoic acid* (2·60 g., 95·5%), which, when crystallised twice from pentane and thrice from acetonitrile, gave plates, m. p. 62·5—63°, rapidly becoming blue in light (Found: C, 78·5; H, 8·85. $C_{18}H_{24}O_2$ requires C, 79·4; H, 8·9%), $\nu_{max.}$ (mull) 2219, 2141 (C≡C·C≡C), 1686 (CO_2H), 1635 (CH=CH conj.), and 983 cm.$^{-1}$ (*trans*-CH=CH), $\lambda_{max.}$ 226·5, 235·5, 293·5, and 310 infl. mμ (ε 23,600, 40,400, 34,400, and 27,900). On microhydrogenation 5·80 mols. of hydrogen were absorbed, to form stearic acid, m. p. and mixed m. p. 68—69°. The maleic anhydride adduct, crystallised from benzene–light petroleum, had m. p. 81—82°, $\lambda_{max.}$ 226 infl., 242, 255, 269, and 285 mμ (ε 1060, 825, 558, 272, and 206), $\nu_{max.}$ (mull) 2276, 2163 (C≡C·C≡C·), 1851, 1777 (5-membered anhydride), and 1710 cm.$^{-1}$ (CO_2H). The ultraviolet figures indicate that about 1% of the adduct consists of isomerised material in which the cyclohexene double bond has shifted into conjugation with the diyne. The dienediyne acid formed a 4-phenylphenacyl ester, m. p. 66—67°, and a 4-bromophenacyl ester, m. p. 55—56°. Both derivatives were unstable and rapidly became gummy. The acid from *Leptomeria aphylla*[2,7] had m. p. 76·5—78·5°, $\lambda_{max.}$ 226, 236, 293, and 310 mμ (ε 25,000, 40,900, 34,800, and 28,600) with infrared bands at 2240, 2150, 1633, 1617, and 983 cm.$^{-1}$.

Octadeca-cis-13,trans-15-*diene*-9,11-*diynoic Acid*.—By the above technique, octa-*cis*-3,*trans*-5-dien-1-yne (0·53 g.) and 10-bromodec-9-ynoic acid (1·10 g.) gave octadeca-*cis*-13,*trans*-15-diene-9,11-diynoic acid (1·07 g., 83%) as a yellow oil. This was chromatographed on silica

and eluted with light petroleum containing 20% of ether, and then had m. p. 8—9°, $\lambda_{max.}$ 228·5, 239, 291, and 305 mμ (ε 14,300, 22,100, 18,350, and 16,500), $\nu_{max.}$ (liquid) 2258, 2151 (C≡C·C≡C), 1708 (CO_2H), 1639 (CH=CH conj.), 983 (*trans*-CH=CH), 942 (*cis-trans*-conj. diene), and 744 $cm.^{-1}$ (*cis*-CH=CH). The low ε values for this acid indicates that it is not pure. However, on microhydrogenation 6·09 mols. of hydrogen were absorbed, to give stearic acid, m. p. and mixed m. p. 68—69°. The 4-bromophenacyl ester had m. p. 43·5—44°, and the 4-phenylphenacyl ester had m. p. 49—50°: both were unstable.

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