

### 311. *Lipids. Part VI.\* Total Synthesis of $\alpha$ - and $\beta$ -Elæostearic and Punicic (Trichosanic) Acid.*

By L. CROMBIE and A. G. JACKLIN.

Trichosanic is shown to be identical with punicic acid. As a preliminary to synthetic work, the stereochemistry of the natural octadeca-9 : 11 : 13-trienoic acids is discussed. Octadeca-*cis*-9 : *trans*-11 : *trans*-13-trienoic acid is synthesised and is identical with natural  $\alpha$ -elæostearic acid. The synthesis involves propargylic Reformatski reaction with hept-2-enal, followed by formal dehydration to deca-3 : 5-dien-1-yne. Chain extension with 1-chloro-7-iodoheptane and nitrile synthesis gives octadeca-*trans*-11 : *trans*-13-dien-9-ynoic acid which is stereospecifically hydrogenated. The synthetic *cis*-9 : *trans*-11 : *trans*-13-acid is stereomutated, and the all-*trans*-product is identical with  $\beta$ -elæostearic acid.

Similarly, hept-2-ynal is converted into dec-3-ene-1 : 5-diyne, and octadec-11-ene-9 : 13-diyneic acid built up. Stereospecific partial hydrogenation gives octadeca-*cis*-9 : *trans*-11 : *cis*-13-trienoic acid which is identical with natural punicic (trichosanic) acid (previously thought to be a *trans* : *cis* : *cis*-stereoisomer). Oxidative coupling of oct-3-en-1-yne with dec-9-ynoic acid, followed by esterification, gives octadec-13-ene-9 : 11-diyneate. Partial hydrogenation and hydrolysis gives octadeca-*cis*-9 : *cis*-11 : *trans*-13-trienoic acid which was not fully purified but differs from the natural acids. Octadeca-*trans*-9 : *trans*-11-dienoic acid is synthesised by a new variant of the Wittig reaction : this indicates an alternative route to octadeca-9 : 11 : 13-trienoic acids.

$\alpha$ -ELÆOSTEARIC ACID, m. p. 48°, is the principal fatty acid of tung oil<sup>1,2</sup> which is expressed from the seeds of *Aleurites fordii* and *A. montana* (family Euphorbiaceae). Other natural sources of  $\alpha$ -elæostearic acid are known,<sup>2</sup> and the acid was first investigated by Cloez<sup>3</sup> in 1875. For some time it was thought to be octadeca-9 : 13-dienoic acid, as valeraldehyde and 8-formyloctanoic acid were produced by ozonolysis, whilst on treatment with bromine a tetrabromide was obtained.<sup>4</sup> The correct structure, octadeca-9 : 11 : 13-trienoic acid (X) was not appreciated until 1925 when Böeseken and Ravenswaay<sup>5</sup> found that the acid absorbed three mols. of hydrogen over a catalyst and had a high exaltation of molecular refractivity. Eibner and Rossmann then showed that ozonolysis also gave glyoxal.<sup>6</sup> Formation of a hexabromide,<sup>7</sup> and ultraviolet absorption data,<sup>8</sup> support the conjugated triene structure. There are eight geometrical isomers possible for structure (X), and on treatment with iodine in the presence of ultraviolet light a second stereoisomer,  $\beta$ -elæostearic acid, m. p. 71°, is produced. From time to time other possible stereoisomers have been alleged to exist in Nature but some have been shown to be mixtures, and others are now known to have entirely different structures. Nevertheless, two other natural triene acids are usually accepted as stereoisomers of (X) : they are punicic and trichosanic acids.

Punicic acid, m. p. 43.5—44°, was isolated by Toyama and Tsuchiya<sup>9</sup> from seed oil

\* Part V, preceding paper.

<sup>1</sup> *Inter al.*, O'Connor, Heinzelman, Freeman, and Pack, *Ind. Eng. Chem. Analyt.*, 1945, **17**, 467; Hilditch and Riley, *J. Soc. Chem. Ind.*, 1946, **65**, 74.

<sup>2</sup> For general information consult Eckey, "Vegetable Fats and Oils," Reinhold, New York, 1954; Hilditch, "The Chemical Constitution of Natural Fats," Chapman and Hall, London, 1956; Ralston, "Fatty Acids and their Derivatives," Wiley, New York, 1948; Markley, "Fatty Acids," Interscience Publ. Inc., New York, 1947.

<sup>3</sup> Cloez, *Compt. rend.*, 1875, **81**, 469; 1876, **82**, 501; 1876, **83**, 943.

<sup>4</sup> Maquenne, *ibid.*, 1902, **135**, 696; Kametaka, *J.*, 1903, 1042; Majima, *Ber.*, 1909, **42**, 674.

<sup>5</sup> Böeseken and Ravenswaay, *Rec. Trav. chim.*, 1925, **44**, 241.

<sup>6</sup> Eibner and Rossmann, *Chem. Umschau*, 1928, **35**, 197.

<sup>7</sup> Bauer and Rohrbach, *ibid.*, p. 53; van Loon, *Rec. Trav. chim.*, 1931, **50**, 32.

<sup>8</sup> Manecke and Volbert, *Farben Ztg.*, 1927, 2829, 2887.

<sup>9</sup> Toyama and Tsuchiya, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1935, **38**, 182b.

of the pomegranate, *Punica granatum* (family Punicaceae), and gives azelaic and *n*-valeric acid on ozonolysis; oxalic acid and glyoxal are also probably formed. The methyl ester gives methyl hydrogen azelate and a corresponding semialdehyde when ozonised. Punicic acid is readily isomerised to  $\beta$ -elæostearic acid. Trichosanic acid, m. p. 35—35.5°, was originally isolated by the same authors<sup>10</sup> from the seed oil of the Japanese snake-gourd or karasu-uri, *Trichosanthes cucumeroides* (family Cucurbitaceae), and shown to be isomerised to  $\beta$ -elæostearic acid by iodine. Lately<sup>11</sup> the same acid, m. p. 34—35°, has been reported in Indian snake-gourd oil (*T. anguina*). We deal first with the individuality of these acids.

$\alpha$ - and  $\beta$ -Elæostearic acid are thoroughly characterised. Punicic acid was carefully re-examined by Farmer and van den Heuvel<sup>12</sup> who were convinced that it was a third stereoisomer of (X): the present work is in full agreement. Punicic acid depresses the m. p. of  $\alpha$ - and  $\beta$ -elæostearic acids and has different spectral characteristics. Toyama and Tsuchiya's grounds<sup>10</sup> for considering trichosanic acid as a fourth stereoisomer were

TABLE 1. Ultraviolet light absorption data for octadeca-9 : 11 : 13-trienoic acids.

Acid	Natural			Synthetic				
	M. p.	$\lambda_{\max}$ (m $\mu$ )	$10^{-2}\epsilon$	M. p.	$\lambda_{\max}$ (m $\mu$ )	$10^{-2}\epsilon$		
$\beta$ -Elæostearic * [ <i>trans</i> -9 : <i>trans</i> -11 : <i>trans</i> -13]	72°	259	47.0	71°	258	42.0		
		268	61.0		268	58.0		
		279	49.0		279	45.5		
$\alpha$ -Elæostearic * [ <i>cis</i> -9 : <i>trans</i> -11 : <i>trans</i> -13]	48	261	36.0	47	261	35.0		
		271	47.0		270	47.0		
		281	38.0		281	36.5		
Punicic [ <i>cis</i> -9 : <i>trans</i> -11 : <i>cis</i> -13]	43.5—44	264	35.0	43—43.5	264	34.0		
		274	46.0					
		285	36.5					
Japanese trichosanic [ <i>cis</i> -9 : <i>trans</i> -11 : <i>cis</i> -13]	43—43.5	264	33.5				274	45.5
		274	44.5				285	34.0
		285	35.5					
Indian trichosanic [ <i>cis</i> -9 : <i>trans</i> -11 : <i>cis</i> -13 + 20% of satd. acids] .....	43	264	26.5					
		274	37.0					
		285	29.0					

\* Data for these two natural acids from Crombie and Tayler.<sup>41</sup>

TABLE 2. Infrared extinction data (CS<sub>2</sub>) for octadeca-9 : 11 : 13-trienoic acids and related compounds.\*

Acid	$\lambda_{\max}$ (cm. <sup>-1</sup> )	$\epsilon^a$	$\epsilon_2/\epsilon_1^a$	$\epsilon^b$	$\epsilon_2/\epsilon_1^b$	$\lambda_{\max}^c$ (cm. <sup>-1</sup> )	$\epsilon^c$	$\epsilon_2/\epsilon_1^c$
$\beta$ -Elæostearic .....	994	760	5.65	795	4.3	995	545	3.2
$\alpha$ -Elæostearic .....	992	365	2.7	400	2.15	992	395	2.3
	963	40	—	100	—	964	115	—
Punicic .....	987	160	1.2	190	1.05	988	175	1.05
	937	105	—	195	—	937	195	—
Trichosanic (Jap.) ...	987	155	—	190	—	—	—	—
	937	100	—	195	—	—	—	—
Trichosanic (Indian)	986	125	—	150	—	—	—	—
	936	80	—	170	—	—	—	—
Elaidic .....	965	135	1	185	1	967	170	1
Ximenynic .....	951	172	—	230	—	—	—	—

\* Slit width 0.21 mm. : the absolute value for  $\epsilon$  must be expected to vary according to the spectrometer used.  $\epsilon_2/\epsilon_1$  is the ratio of  $\epsilon$  for the sample to that of elaidic acid. All acids are of natural origin : data for synthetic acids are in the Experimental section.

<sup>a</sup> Background absorption eliminated by extrapolation. <sup>b</sup> Background absorption not eliminated. <sup>c</sup> Values by Ahlers *et al.*<sup>21, 24</sup> (calc. from their values for specific extinction coefficient).

its m. p., and the depression of m. p. observed when it was mixed with punicic or  $\alpha$ -elæostearic acid. Recently, Ahlers and Dennison,<sup>13</sup> who examined the infrared spectra of Japanese and Indian snake-gourd oils, suggested that it might be identical with punicic

<sup>10</sup> Toyama and Tsuchiya, *ibid.*, 1935, **38**, 185B; contrast Toyama and Uozaki, *ibid.*, 1937, **40**, 249.

<sup>11</sup> Soni and Aggarwal, *J. Sci. Ind. Res., India*, 1949, **8**, B, 150.

<sup>12</sup> Farmer and van den Heuvel, *J.*, 1936, 1809.

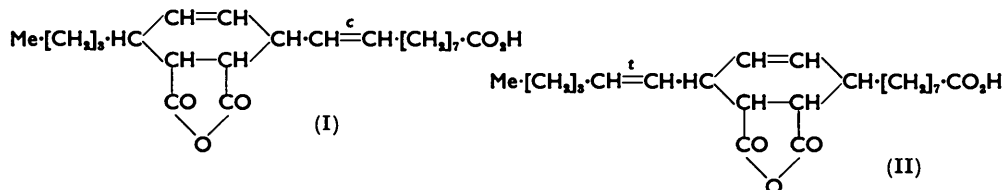
<sup>13</sup> Ahlers and Dennison, *Chem. and Ind.*, 1954, 603.

acid, or else be a stereoisomer with the orientation of the triene unit reversed relatively to punicic acid.

In our hands, Japanese snake-gourd oil yielded an acid, m. p. 43—43.5°, which absorbed three mols. of hydrogen to give stearic acid, and was readily stereomutated to  $\beta$ -elaeostearic acid. It depressed the m. p. of  $\alpha$ -elaeostearic but not punicic acid. Spectroscopic comparison (ultraviolet and infrared solid film) left no doubt that it was identical with the latter. Indian snake-gourd oil, when worked up by a procedure omitting purification by magnesium acetate, also gave an acid of m. p. 43° which showed similar mixed m. p. behaviour. The infrared and ultraviolet data (Table 1) supported the identity with punicic acid but it was observed that ultraviolet intensities were lower than expected, and so were intensities of characteristic infrared bands at 986 and 936  $\text{cm}^{-1}$  (Table 2). These results suggested that there might be a saturated acid as impurity in this sample of trichosanic acid, and this view was strengthened by the low hydrogen uptake and poor analyses. Reversed-phase chromatography<sup>14</sup> then revealed 4% of palmitic and 16% of stearic acid. This Japanese trichosanic acid is thus pure, and Indian trichosanic acid impure, punicic acid. Earlier specimens must have been very impure.

Trichosanic acid being eliminated, we need to know the stereochemistry of  $\alpha$ - and  $\beta$ -elaeostearic acid and punicic acid before opening synthetic work. Unfortunately, methods for the diagnosis of configuration in trienes are not well established, largely because negligible synthetic work has been carried out and model substances of known configuration are not available. Despite this handicap considerable progress has been made on the octadeca-9:11:13-trienoic acid system, and this has enabled us to concentrate our synthetic efforts on the correct stereoisomers.

Morrell and Samuels<sup>15</sup> demonstrated that  $\alpha$ - and  $\beta$ -elaeostearic acid gave different maleic adducts, and showed, by oxidative degradation, that these were (I) and (II) respectively. Morrell and Davis<sup>16</sup> proposed a *cis*-9 : *trans*-11 : *trans*-13-structure for the  $\alpha$ -acid and a *trans*-9 : *cis*-11 : *cis*-13-structure for the  $\beta$ -acid, but the reasoning is not fully



acceptable as it assumes that *cis*-containing dienes add maleic anhydride with ease.<sup>17</sup> More convincing is the work of Paschke *et al.*<sup>18</sup> which extends that of Chin<sup>19</sup> who used the maleic adducts to support his view that the  $\alpha$ -acid is the *cis*-9 : *trans*-11 : *trans*-13- and the  $\beta$ -acid the *trans*-9 : *trans*-11 : *cis*-13-form. They find, by infrared analysis, that the adduct (I) contains an extracyclic *cis*-linkage whilst the isomer (II) has a *trans*-linkage. Since only *trans* : *trans*-dienes add maleic anhydride with ease,  $\alpha$ -elaeostearic acid is the *cis*-9 : *trans*-11 : *trans*-13- and the  $\beta$ -acid is the *trans*-9 : *trans*-11 : *trans*-13-form. Bickford *et al.*<sup>20</sup> reach similar conclusions and, from a study of the epoxides of the maleic adducts, have found that maleic anhydride adds to  $\beta$ -elaeostearic acid at the 11 : 14- as well as the 9 : 12-positions. This, too, supports the all-*trans*-assignment.

<sup>14</sup> Howard and Martin, *Biochem. J.*, 1950, **46**, 532; Crombie, Comber, and Boatman, *ibid.*, 1955, **59**, 309.

<sup>15</sup> Morrell and Samuels, *J.*, 1932, 2251; Rinkes, *Rec. Trav. chim.*, 1943, **62**, 557.

<sup>16</sup> Morrell and Davis, *Trans. Faraday Soc.*, 1936, **32**, 209; *J.*, 1936, 1481.

<sup>17</sup> Contrast, *inter al.*, Robey, Morrell, and Wiese, *J. Amer. Chem. Soc.*, 1941, **63**, 627; Robey, *Science*, 1942, **96**, 47; Craig, *J. Amer. Chem. Soc.*, 1943, **65**, 1006; Snyder, Stewart, and Meyers, *ibid.*, 1949, **71**, 1055; Snyder and Poos, *ibid.*, 1950, **72**, 4104; von Mikusch, *Angew. Chem.*, 1950, **62**, 475; Alder and Vogt, *Annalen*, 1951, **571**, 137; and ref. 22c.

<sup>18</sup> Paschke, Tolberg, and Wheeler, *J. Amer. Oil Chemists' Soc.*, 1953, **30**, 97.

<sup>19</sup> Chin, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1950, **53**, 333; *Chem. Abs.*, 1953, **47**, 7435.

<sup>20</sup> Bickford, Du Pré, Mack, and O'Connor, *J. Amer. Oil Chemists' Soc.*, 1953, **30**, 376.

Ahlers *et al.*<sup>21</sup> find that the extinction coefficient of the band at 995 cm.<sup>-1</sup> in  $\beta$ -elæostearic acid is about three times that of the band at 968 cm.<sup>-1</sup> in elaidic acid (Table 2), and since the bands are probably similar in origin, commend the all-*trans*-structure.  $\alpha$ -Elæostearic acid has two bands in this region (see Table 2). As the band at 992 cm.<sup>-1</sup> is about twice as strong as that of elaidic acid at 968 cm.<sup>-1</sup> Ahlers *et al.* suggest that one *cis*-linkage is present and that the configuration is *trans*-9 : *cis*-11 : *trans*-13, *trans*-9 : *trans*-11 : *cis*-13, or *cis*-9 : *trans*-11 : *trans*-13. They discount the first structure on grounds which seem questionable—"... if the two absorption bands noted were presumed to correspond to the two sets of adjacent conjugated pairs of double bonds present, the central *cis*-system might be excluded on symmetry considerations since *cis-trans* and *trans-cis* would not be expected to yield two absorption bands." It is known that a *cis-trans*-diene itself gives two absorption bands in the 1010—930 cm.<sup>-1</sup> region.<sup>22</sup> Examining pomegranate seed oil,<sup>23</sup> and later puniic acid,<sup>24</sup> Ahlers *et al.* deduced from the ultraviolet data and the extinction coefficient at 988 cm.<sup>-1</sup> that two *cis*-double bonds were present. This leads to three possible structures—*cis*-9 : *cis*-11 : *trans*-13, *trans*-9 : *cis*-11 : *cis*-13, and *cis*-9-*trans*-11 : *cis*-13. Because the ratio of intensities at 988 cm.<sup>-1</sup> and 937 cm.<sup>-1</sup> resembled those of *cis-trans*-conjugated "linoleates," Ahlers *et al.*<sup>23,24</sup> preferred one of the first two structures, but could not distinguish between them.

In the light of this information we felt it reasonable to accept the *cis*-9 : *trans*-11 : *trans*-13-structure for  $\alpha$ -elæostearic acid, and the all-*trans*-structure for the  $\beta$ -acid, but rejection by Ahlers and his co-workers of the *cis*-9 : *trans*-11 : *cis*-13-structure for puniic acid seemed unconvincing and we were faced with three possible structures. Our choice for synthesis, *cis*-9 : *trans*-11 : *cis*-13, was based largely on expediency and by good fortune proved to be correct.

The general techniques used for synthesis were developed from Parts II and V and a preliminary note relating to  $\alpha$ -elæostearic acid has been published.<sup>25</sup> Hexynylmagnesium bromide with ethyl orthoformate gave 1 : 1-diethoxyhept-2-yne (III),<sup>26</sup> which was semi-hydrogenated and hydrolysed to give hept-*trans*-2-enal (IV) (the *cis*-aldehyde is stereomutated by acid).<sup>27</sup> A Reformatski reaction with propargyl bromide gave dec-1-yn-*trans*-5-en-4-ol (V) containing some allenic material.<sup>28</sup> Unsuccessful attempts to dehydrate an homologous alcohol with toluene-*p*-sulphonic acid or by treating the toluene-*p*-sulphonate with aqueous potassium hydroxide were reported by Hill *et al.*<sup>29</sup> We have found three successful methods for the formal dehydration. Heating the alcohol (V) with phosphorus oxychloride in pyridine gave a 23% yield of deca-3 : 5-dien-1-yne (VI), whilst preparation of the toluene-*p*-sulphonate followed by treatment with sodium *n*-butoxide in butanol gave 30—36% yields. When the alcohol was treated with phosphorus trichloride followed by 15—20% alcoholic potassium hydroxide, the hydrocarbon (VI) was formed in 30% yield. Deca-3 : 5-dien-1-yne was extremely unstable, absorbed 3.85 mols. of hydrogen over a catalyst, and had the expected ultraviolet absorption (Table 3). It is known<sup>30</sup> that treatment of 1-methylbut-3-ynyl toluene-*p*-sulphonate gives a mixture of *cis*- and *trans*-pent-2-en-4-yne when treated with alkali, so comment must be made on the stereochemistry of our material. In the main synthetic work deca-3 : 5-dien-1-yne

<sup>21</sup> Ahlers, Brett, and McTaggart, *J. Appl. Chem.*, 1953, **3**, 433.

<sup>22</sup> (a) Jackson, Paschke, Boyd, Tolberg, and Wheeler, *J. Amer. Oil Chemists' Soc.*, 1952, **29**, 229; (b) Celmer and Solomons, *J. Amer. Chem. Soc.*, 1953, **75**, 3430; (c) Crombie, *J.*, 1955, 1007; (d) Allan, Meakins, and Whiting, *J.*, 1955, 1874.

<sup>23</sup> Ahlers and McTaggart, *J. Sci. Food Agric.*, 1954, **2**, 75.

<sup>24</sup> Ahlers, Dennison, and O'Neill, *Nature*, 1954, **173**, 1045.

<sup>25</sup> Crombie and Jacklin, *Chem. and Ind.*, 1955, 1186.

<sup>26</sup> Kranzfelder and Vogt, *J. Amer. Chem. Soc.*, 1938, **60**, 1714; Moureu and Delange, *Bull. Soc. chim. France*, 1904, **31**, 1333.

<sup>27</sup> Raphael and Sondheimer, *J.*, 1951, 2693; Crombie, Harper, and Thompson, *J.*, 1951, 2906.

<sup>28</sup> See Parts II and V for references.

<sup>29</sup> Hill, Lythgoe, Mirvish, and Trippett, *J.*, 1955, 1770.

<sup>30</sup> Bruun, Christensen, Haug, Stene, and Sørensen, *Acta Chem. Scand.*, 1951, **5**, 1244; Allan and Whiting, *J.*, 1953, 3314.

prepared by the phosphorus trichloride route was used and its infrared spectrum was the same as that of the sample from the phosphorus oxychloride procedure. Dehydrochlorinations of this type are known to give *trans*-isomers in other cases<sup>31</sup> and we have no reason to suspect considerable contamination with *cis*-material (cf. dec-3-en-1-yne, Part IV): nevertheless, this stage is not claimed to be stereospecific. Chain extension of

TABLE 3. Ultraviolet data for acetylenic intermediates.\*†

Me·[CH <sub>2</sub> ] <sub>5</sub> ·CH=CH·C≡CH	223 (11,000)
Me·[CH <sub>2</sub> ] <sub>5</sub> ·CH=CH·C≡CH <sup>•</sup>	222 (10,200)
Me·[CH <sub>2</sub> ] <sub>5</sub> ·CH=CH·CH=CH·C≡CH	260·5 (29,000)
Me·[CH <sub>2</sub> ] <sub>5</sub> ·CH=CH·CH=CH·C≡CH <sup>•</sup>	260 (30,000)
Me·[CH <sub>2</sub> ] <sub>5</sub> ·C≡C·CH=CH·C≡CH	257 (22,500); 271 (20,500)
Me·[CH <sub>2</sub> ] <sub>5</sub> ·CH=CH·CH=CH·C≡C·[CH <sub>2</sub> ] <sub>7</sub> ·Cl	266·5 (32,000)
Me·[CH <sub>2</sub> ] <sub>5</sub> ·C≡C·CH=CH·C≡C·[CH <sub>2</sub> ] <sub>7</sub> ·Cl	261 (31,000); 276 (30,000)
Me·[CH <sub>2</sub> ] <sub>5</sub> ·CH=CH·CH=CH·C≡C·[CH <sub>2</sub> ] <sub>7</sub> ·CO <sub>2</sub> H	267 (36,500) [infl. 277 (28,400)]
Me·[CH <sub>2</sub> ] <sub>5</sub> ·C≡C·CH=CH·C≡C·[CH <sub>2</sub> ] <sub>7</sub> ·CO <sub>2</sub> H	261 (32,000); 276 (30,500)
Me·[CH <sub>2</sub> ] <sub>5</sub> ·CH=CH·C≡C·C≡C·[CH <sub>2</sub> ] <sub>7</sub> ·CO <sub>2</sub> Me	229 (3000); 240 (6000); 253 (12,500); 267 (20,000); 283 (15,500)
Me·CH=CH·C≡C·C≡CH <sup>•</sup>	230 (2250); 238 (5000); 251 (10,000); 264 (14,000); 280 (11,000)
Me·[CH <sub>2</sub> ] <sub>2</sub> ·C≡C·C≡C·CH=CH·CH <sub>2</sub> ·OH <sup>•</sup>	239·5 (7300); 252 (14,600); 266·5 (21,850); 282·5 (19,440)

• Wavelength m $\mu$ ;  $\epsilon$  in parentheses.

† Infrared data for most of these compounds are given in the Experimental section.

• Part V. • Bohlmann and Viehe.<sup>28</sup> • Armitage *et al.*<sup>25</sup> • Bruun *et al.*<sup>26</sup>

sodiodeca-3 : 5-dien-1-yne in liquid ammonia, with 1-chloro-7-iodoheptane,<sup>32</sup> gave 17-chloroheptadeca-5 : 7-dien-9-yne (VII) in 53% yield. The ultraviolet maximum was shifted to 266·5 m $\mu$  compared with 260·5 m $\mu$  for the monosubstituted dienyne.

The chloroheptadecadienyne failed to give a Grignard reagent under a variety of conditions, but, by using experience from the ximenynic acid synthesis (Part V), it was possible to convert it into the iodide and then the nitrile (VIII). In subsequent experiments the latter was not isolated but hydrolysed directly to octadeca-11 : 13-dien-9-ynoic acid (IX). The product was a red oil and light-absorption data suggested that it was about 60% pure : it was unchanged by irradiation in light petroleum solution containing iodine. Purification was effected through the urea inclusion compound, and the acid obtained pure and crystalline. On catalytic hydrogenation it absorbed 4 mols. of hydrogen and gave stearic acid. In view of the method of synthesis, its purification by crystallisation and clathrate formation, and its resistance to stereomutation, there is little doubt that octadeca-11 : 13-dien-9-ynoic acid is the *trans-trans*-form. Subsequent synthetic work supports this.

When octadeca-*trans*-11 : *trans*-13-dien-9-ynoic acid was hydrogenated over Lindlar's catalyst<sup>33</sup> in the presence of quinoline until one mol. of hydrogen was absorbed, octadeca-*cis*-9 : *trans*-11 : *trans*-13-trienoic acid (X) was obtained, which, after crystallisation, was identical with  $\alpha$ -elæostearic acid (mixed m. p., ultraviolet spectrum, infrared spectrum in CS<sub>2</sub> and as a solid film). When this was treated with iodine,  $\beta$ -elæostearic acid was formed and shown to be identical with a specimen obtained by isomerising the natural acid. We have not carried out a separate synthesis of  $\beta$ -elæostearic acid as the fact that it has a higher m. p. and is a less soluble substance obtained by stereomutating a precursor containing only one *cis*-double bond, adequately confirms its structure and stereochemistry.

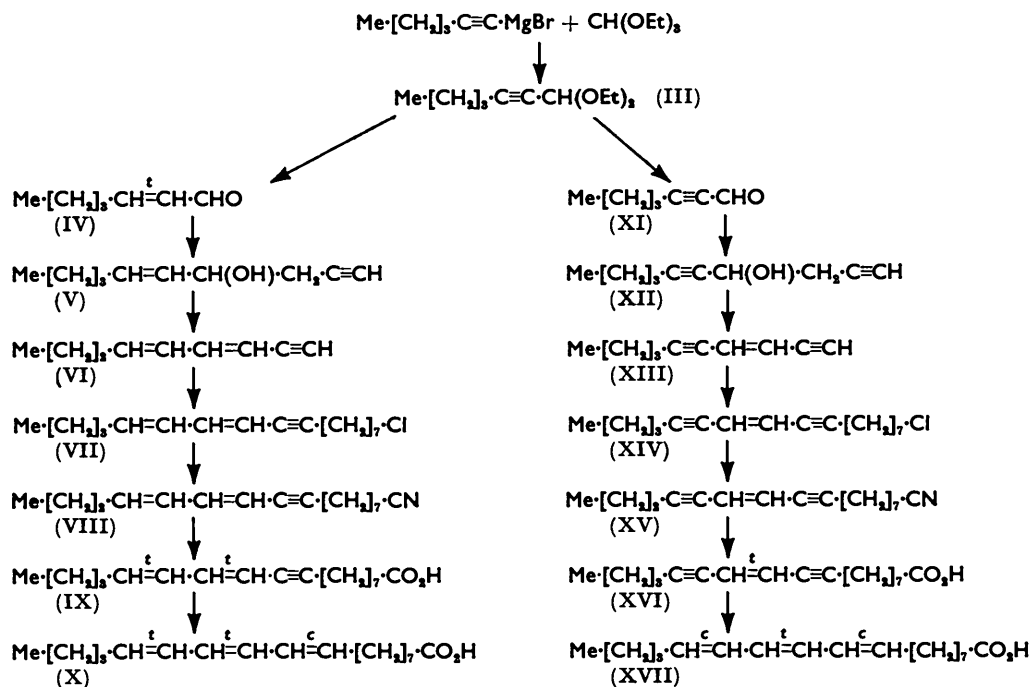
For synthesis of punicic acid, hept-2-ynal (XI) was prepared by acid hydrolysis of the acetal (III) and converted by propargylic Reformatski reaction into deca-1 : 5-diyn-4-ol (XII) (containing allene). Treatment with phosphorus tribromide, followed by dehydrohalogenation with 20% alcoholic potassium hydroxide, gave dec-3-ene-1 : 5-diyne (XIII), an extremely unstable substance : after 16 hr. at 0° *in vacuo*, approximately half was lost

<sup>31</sup> *E.g.*, (a) Grigor, MacInnes, McLean, and Hogg, *J.*, 1955, 1069; (b) ref. 22c.

<sup>32</sup> Part V; also Huber, *J. Amer. Chem. Soc.*, 1951, **73**, 2730.

<sup>33</sup> Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

as tar on redistillation. From its method of preparation, we consider that it is largely or entirely in the *trans*-form. The ynenyne system is a new type of chromophore (see Table 3 for data). Chain extension with 1-chloro-7-iodoheptane in liquid ammonia gave 17-chloroheptadec-7-ene-5 : 9-diyne (XIV) (54%). When left in air in the presence of light the substance became dark green, but, when pure, it showed no change *in vacuo* at 0° in subdued light. Conversion of this product (XIV) into the iodide, and then the nitrile, and hydrolysis with 20% aqueous-ethanolic potassium hydroxide, gave a dark

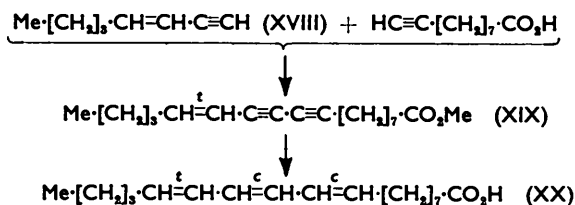


green solid from which octadec-*trans*-11-ene-9 : 13-diyne acid (XVI) was obtained in colourless plates. It did not form a clathrate compound with urea. The fairly high m. p. (76°) and low solubility in cold light petroleum seem to be consequences of the rigid ynenyne system. The acid was considerably more stable than its relative (IX) and survived exposure to air for 12 hr. at 20° : an explanation may lie in the absence of hydrogen atoms  $\alpha$ - to the ethylenic linkage. The structure (XVI) was confirmed by the ultraviolet and infrared data ; and on hydrogenation five mols. of hydrogen were absorbed, giving stearic acid. Hydrogenation in ethyl propionate, with Lindlar's catalyst and quinoline, until two mols. of hydrogen had been absorbed, gave octadeca-*cis*-9 : *trans*-11 : *cis*-13-trienoic acid (XVII) which after purification had m. p. 43—43.5° and was identical with puniceic (trichosanic) acid (mixed m. p. and infrared criteria). It was stereomutated to  $\beta$ -elæostearic acid.

In view of the opinions of Ahlers *et al.*<sup>23,24</sup> we have made an approach to the synthesis of octadeca-*cis*-9 : *trans*-11 : *trans*-13-trienoic acid (XX). A Reformatski reaction between *n*-valeraldehyde and propargyl bromide gave oct-1-yn-4-ol (infrared examination showed allenic impurity). This was converted into the chloride with thionyl chloride and pyridine, but dehydrohalogenation with boiling 15% ethanolic potassium hydroxide was slow. Preparation of the toluene-*p*-sulphonate and treatment with sodamide in liquid ammonia gave oct-3-en-1-yne (XVIII) (55%). Oxidative coupling with dec-9-ynoic acid, followed by distillation, gave only an oil and much tar, in agreement with a report by Black.<sup>24</sup>

<sup>24</sup> Black, Ph.D. Thesis, London, 1955.

The reaction was therefore repeated and the crude acid esterified with diazo-methane. Distillation now gave pure methyl octadec-13-ene-9 : 11-diynoate (XIX)



showing the characteristic five-banded spectrum of an enediyne (Table 3).<sup>35,36</sup> In unpublished work with M. Manzoor-i-Khuda we have found that the *cis*- and *trans*-Me·CH=CH·C≡C·C≡C·[CH<sub>2</sub>]<sub>8</sub>·R chromophores have the following light absorptions (mμ) :

<i>cis</i> : λ <sub>max.</sub> ...	240	253	267	282	<i>trans</i> : λ <sub>max.</sub> ...	239	252	266	282
ε .....	4250	8500	12,950	10,700	ε .....	5500	13,200	19,400	15,000

Comparison indicates that (XIX) must be *trans*-ester containing little, if any, *cis*-isomer. Hydrolysis gave an acid, partially solid at 0°, which was not amenable to purification by low-temperature crystallisation or distillation at 10<sup>-6</sup> mm. and did not form a urea clathrate compound.

Methyl octadec-*trans*-13-ene-9 : 11-diynoate itself was therefore hydrogenated over Lindlar's catalyst in the presence of quinoline until two mols. of hydrogen had been absorbed. On hydrolysis octadeca-*cis*-9 : *cis*-11 : *trans*-13-trienoic acid (XX) was isolated and further purified by crystallisation at -70°. The acid was a highly unstable crystalline substance, m. p. 35—38°, which decomposed in 14 days at 0° *in vacuo*, and proved very difficult to handle. In the ultraviolet region, octadeca-*cis*-9 : *cis*-11 : *trans*-13-trienoic acid showed only one peak at 271 mμ (ε 32,300) with inflexions at 263 mμ (ε 27,200) and 280 mμ (ε 24,800). When a trace of iodine was added a well-defined triplet immediately developed with maxima at 257 (ε 42,900), 268 (ε 44,400), and 278 mμ (ε 33,000). The latter spectrum is characteristic of β-elæostearic acid, though the intensities are below those for the pure material. This would be explained if the solution contained an equilibrium mixture of stereoisomers, but in view of the m. p. range of 3°, we consider that our specimen was not pure. Nevertheless its infrared spectrum has yielded the data we require, for this stereoisomer could not be confused with punicic acid. α- and β-Elæostearic acid and punicic acid have characteristic bands below 950 cm.<sup>-1</sup> (compared as solid films or paraffin mulls) which are absent from the spectrum of the *cis*-9 : *cis*-11 : *trans*-13-acid.

In connection with synthetic work on octadeca-9 : 11 : 13-trienoic acids we briefly indicate another type of route which eliminates the chloro-iodide chain extension. Its disadvantage is lack of stereochemical specificity. Ethyl undecenoate was treated with *N*-bromosuccinimide, to give a mixture of two allylic bromides (XXI) and (XXII).<sup>37</sup> Bohlmann and Viehe<sup>38</sup> have demonstrated that mixtures of other allylic bromides can be



used to give straight-chain isomers in the Wittig reaction,<sup>39</sup> only the primary bromide reacting; so the mixture was treated with triphenylphosphine. The salt was treated with sodium ethoxide in ethanol to form the ester (XXIV), and then with heptaldehyde.

<sup>35</sup> Armitage, Cook, Entwistle, Jones, and Whiting, *J.*, 1952, 1998.

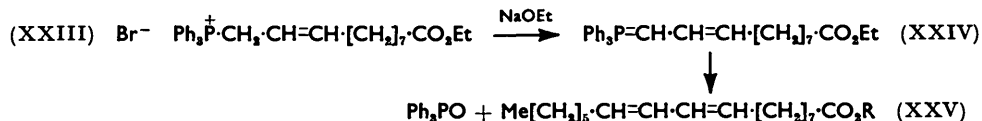
<sup>36</sup> Bruun, Haug, and Sørensen, *Acta Chem. Scand.*, 1950, 4, 850.

<sup>37</sup> Gensler, Behrmann, and Thomas, *J. Amer. Chem. Soc.*, 1951, 73, 1071.

<sup>38</sup> Bohlmann and Viehe, *Chem. Ber.*, 1955, 88, 1245.

<sup>39</sup> Wittig and Schollkopf, *Chem. Ber.*, 1954, 87, 1318; Wittig and Haag, *ibid.*, 1955, 88, 1654.

Distillation of the product gave a diene ester in 23% yield with the expected light absorption max. for the ester (XXV; R = Et). There was no infrared band near 905—915  $\text{cm}^{-1}$ , so the product is probably free from vinylic isomer, but bands at 986 and 948  $\text{cm}^{-1}$  show



it to contain *cis-trans*-material. Some of the *cis*-material might originate from the bromo-ester (XXII) as some oleic acid is formed when this reacts with heptylmagnesium bromide.<sup>37</sup> Much probably arises from the Wittig reaction which is known in other cases to give *cis-trans*-mixtures about the newly formed olefinic linkage.<sup>39</sup> Hydrolysis of the mixture of diene esters gave a small yield of octadeca-*trans*-9 : *trans*-11-dienoic acid (XXV; R = H), m. p. 53° (in agreement with recorded data<sup>21, 31a</sup>). Improvements to this preliminary experiment are possible and the use of hept-2-enal or hept-2-ynal could lead to other syntheses of octadeca-9 : 11 : 13-trienoic acids.

Although the syntheses of  $\alpha$ - and  $\beta$ -elæostearic and punicic acid may not be fully stereospecific because of the formal dehydration stage, there can now be little doubt about the stereochemistry of these acids. The spectral data given can be safely used for comparison with conjugated trienes of unknown geometrical configuration. It remains to point out a few features of interest. In the ultraviolet spectra, there is a general shift of maximal absorption ( $\sim 3 \text{ m}\mu$ ) to long wavelengths, accompanied by a decline in extinction coefficient, through the series *trans*-9 : *trans*-11 : *trans*-13, *cis*-9 : *trans*-11 : *trans*-13, to *cis*-9 : *trans*-11 : *cis*-13. (The main maximum for the *cis*-9 : *cis*-11 : *trans*-13- is at the same position as for the *cis*-9 : *trans*-11 : *trans*-13-stereoisomer, but as we have reservations about the purity of the former, it is unprofitable to consider  $\epsilon$ .) This general behaviour parallels that of conjugated dienes which show similar variations through the series *trans-trans*, *cis-trans* or *trans-cis*, to *cis-cis*.<sup>40</sup>

As expected, in solution or a mull, all-*trans*-octadeca-9 : 11 : 13-trienoic acid shows only one strong band in the CH=CH out-of-plane deformation region: *trans-trans*-dienes show similar behaviour, and in both cases the frequency is higher than that of an isolated *trans*-CH=CH bond which absorbs at  $\sim 968 \text{ cm}^{-1}$ . The band is split in the solid film spectrum (Figure). In the spectra of *cis*-9 : *trans*-11 : *trans*-13- and *cis*-9 : *trans*-11 : *cis*-13-compounds, two bands are present in this out-of-plane deformation region (Table 2, Figure): again *cis-trans*-dienes show a comparable doublet.<sup>22</sup> The *cis*-9 : *cis*-11 : *trans*-13-stereoisomer shows three bands at 987, 965, and 942  $\text{cm}^{-1}$  (solid film; mull spectrum similar).

Our infrared extinction data (except for  $\beta$ -elæostearic acid) agree moderately with those of Ahlers *et al.* only if background absorption is added in. It is clear from the  $\epsilon_2/\epsilon_1$  columns that there is not an additive contribution to  $\epsilon$  for a single isolated *trans*-double bond each time another *trans*-linkage is introduced into a *cis*-triene. The position is worse when correction is made for background absorption (as it should be) than when it is retained. Nevertheless, there is an increasing increment to  $\epsilon_2/\epsilon_1$  of  $>1$  each time a new *trans*-linkage is introduced, and this fact alone may be of qualitative value.

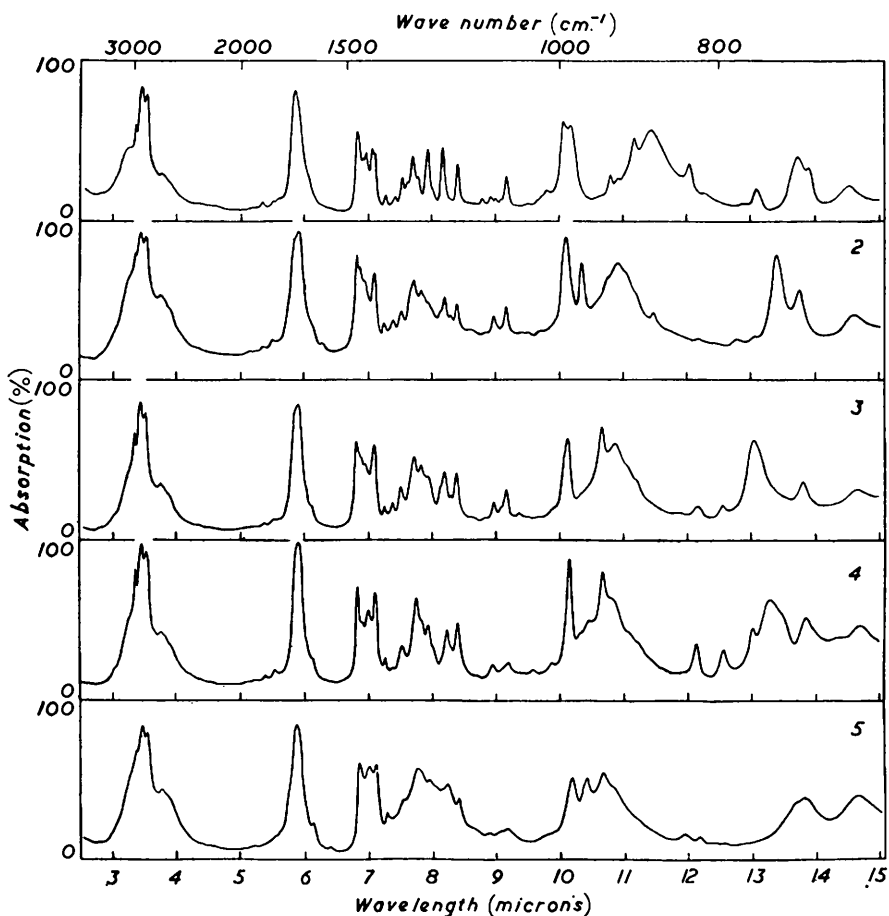
Crystalline-film spectra for some octadeca-9 : 11 : 13-trienoic acids are shown in the Figure. Specimens were prepared by allowing the compound to melt on warmed rock-salt plates, and then cool to room temperature or 0°. In the case of punicic acid two types of solid-film spectrum (due to differing arrangements of the molecules in the crystal lattice) could be obtained, depending on room temperature. One of the forms (A) could

<sup>40</sup> (a) Nichols, Herb, and Riemenschneider, *J. Amer. Chem. Soc.*, 1951, **73**, 247; (b) Allan, Jones, and Whiting, *J.*, 1955, 1862; refs. 22b and c.

<sup>41</sup> Crombie and Taylor, *J.*, 1954, 2816.



Crystalline-film spectra of some octadeca-9 : 11 : 13-trienoic acids.



- (1) *trans*-9 : *trans*-11 : *trans*-13 ( $\beta$ -Elaostearic acid). (Peaks at 3095, 2985, 2905, 2835, 2665, 1864, 1806, 1784, 1704, 1464, 1446, 1435, 1414, 1406, 1375, 1346, 1327, 1312, 1299, 1284, 1261, 1225, 1192, 1139, 1123, 1113, 1103, 1092, 1056, 1025, 998, 986, 928, 918, 897, 876, 832, 816, 777, 765, 730, 720, 690  $\text{cm}^{-1}$ .)
- (2) *cis*-9 : *trans*-11 : *trans*-13 ( $\alpha$ -Elaostearic acid). (Peaks at 2995, 2920, 2850, 2660, 1866, 1813, 1698, 1686, 1587, 1465, 1456, 1439, 1408, 1377, 1353, 1328, 1297, 1278, 1271, 1261, 1232, 1222, 1208, 1193, 1166, 1134, 1117, 1093, 1066, 1054, 1036, 993, 969, 931, 918, 908, 874, 822, 784, 767, 746, 728, 685  $\text{cm}^{-1}$ .)
- (3) *cis*-9 : *trans*-11 : *cis*-13 (A) (Punicic acid). (Peaks at 2985, 2905, 2835, 2655, 1850, 1799, 1685, 1630, 1462, 1455, 1448, 1435, 1406, 1376, 1352, 1329, 1293, 1276, 1258, 1229, 1220, 1204, 1192, 1114, 1101, 1092, 1070, 1009, 989, 938, 920, 894, 823, 797, 768, 725, 683  $\text{cm}^{-1}$ .)
- (4) *cis*-9 : *trans*-11 : *cis*-13 (B) (Punicic acid). (Peaks at 2990, 2900, 2835, 2655, 1848, 1799, 1692, 1629, 1463, 1446, 1426, 1404, 1376, 1351, 1327, 1291, 1279, 1261, 1250, 1215, 1192, 1120, 1088, 1046, 1014, 987, 971, 958, 938, 925, 904, 891, 825, 797, 769, 754, 723, 696, 678  $\text{cm}^{-1}$ .)
- (5) *cis*-9 : *cis*-11 : *trans*-13. (Peaks at 2995, 2905, 2835, 2655, 1921, 1704, 1634, 1565, 1462, 1427, 1406, 1376, 1329, 1291, 1261, 1219, 1192, 1128, 1104, 1093, 1026, 987, 965, 942, 839, 822, 733, 726, 684  $\text{cm}^{-1}$ .)

be reproduced if cooling was allowed to take place at  $0^\circ$ . Comparison of such spectra is a much more stringent test of identity than solution spectra because the bands are sharper and more numerous. Paraffin mulls are generally satisfactory, though they may be unreproducible if the acid is partially soluble in paraffin.

## EXPERIMENTAL

Analyses were carried out in the microanalytical laboratory of Imperial College (Miss J. Cuckney). Infrared measurements were made by Mr. R. L. Erskine, B.Sc., A.R.C.S., using a Grubb-Parsons double-beam instrument; extinction data were determined in CS<sub>2</sub> solutions. Ultraviolet measurements (in pure EtOH) were made with a Unicam S.P. 500 instrument. For many physical data see Tables.

*α- and β-Elæostearic Acids.*<sup>42</sup>—Tung oil (515 g.) was heated in nitrogen, under reflux, with potassium hydroxide (200 g.) in ethanol (2 l.). The solution was acidified with 2N-sulphuric acid (about 5 l.), then the upper brown layer was washed with hot distilled water (2 × 750 ml.). After 1 hr. at 0° the solid was filtered off and recrystallised four times from ethanol (500 ml. portions) (charcoal) and twice from pentane, to give *α*-elæostearic acid (186 g.), white plates, m. p. 47–48°. Another crystallisation raised the m. p. to 48°.

*β*-Elæostearic acid was prepared by adding a crystal of iodine to a solution of the *α*-form in pentane and setting aside for a few hr. After cooling at 0°, the *β*-acid was filtered off and when crystallised from ethanol had m. p. 72°.

*Punicic Acid.*—Pomegranate seeds were washed and dried *in vacuo*. Crushed seeds (18.5 g.) were continuously extracted (3 hr.) with light petroleum (b. p. 40–60°) and then reground and extracted for 5 hr. more. Evaporation of the solvent left a viscous yellow oil (1.45 g.) with maxima at 264 (ε 26,000), 274 (ε 33,000), and 285 mμ (ε 26,000), corresponding to a content of 71% punicic acid. The oil (1.45 g.) was hydrolysed by potassium hydroxide (1.7 g.) in boiling 85% ethanol (25 ml.) for 1 hr. Isolation of the acid with ether, and evaporation *in vacuo*, gave yellow crystals: crystallisation from 80% ethanol (15 ml.) at 0° gave punicic acid (0.87 g.), m. p. 40–42°, raised by two more crystallisations from pentane to m. p. 43.5–44° (white plates) (Found: C, 77.6; H, 11.1. Calc. for C<sub>18</sub>H<sub>30</sub>O<sub>2</sub>: C, 77.65; H, 10.85%). Microhydrogenation 2.95H<sub>2</sub>. On hydrogenation stearic acid, m. p. 70°, was obtained, which did not depress the m. p. of an authentic specimen of m. p. 69°. When isomerised with iodine in pentane, punicic acid gave *β*-elæostearic acid, m. p. and mixed m. p. 71.5°.

*Trichosanic acid.*—(A) *From Japanese snake-gourd seeds.* Kernels (10.7 g.) were extracted from the cracked gourd seeds (25.1 g.), crushed, and extracted under nitrogen with light petroleum (b. p. 40–60°) for 9 hr. Evaporation of the solvent *in vacuo* gave an oil (5.59 g.). Continued extraction gave no further oil. Japanese snake-gourd oil had maxima at 264 (ε 13,700), 274 (ε 18,500), and 285 mμ (ε 14,300), corresponding to about 44% of the triene. There were infrared bands (liquid film) at 1740s, 989m, and 939m cm.<sup>-1</sup>. Saponification of the oil (5.59 g.) with potassium hydroxide (2.0 g.) in water (2 ml.) and ethanol (18 ml.), by refluxing in nitrogen (2 hr.), gave a crude acid (5.10 g.) which melted below 20°. In accordance with published directions,<sup>10, 11</sup> it was dissolved in 90% ethanol (15 ml.), neutralised to phenolphthalein with 5% potassium hydroxide in 90% ethanol, heated to boiling with a solution of magnesium acetate (1.5 g.) in 90% ethanol (15 ml.), and then set aside at 0° (3 hr.). The precipitated magnesium salts (0.35 g.) were filtered off and rejected. The filtrate was acidified and extracted with ether. The extracts were dried and evaporated, to give an oil which crystallised from 80% ethanol at 0°, giving impure trichosanic acid (1.37 g.), m. p. 35–38°. Two crystallisations from pentane (10 ml.) raised the m. p. to 43–43.5° (long narrow plates) (Found: C, 77.4; H, 11.2%). Microhydrogenation 2.8H<sub>2</sub>. Hydrogenation gave stearic acid, m. p. 70° (and mixed m. p.). Iodine-catalysed stereomutation gave *β*-elæostearic acid, m. p. 71.5° (mixed m. p. and infrared mull comparison).

(B) *From Indian snake-gourd oil.* The gourd seeds (29.7 g.) gave kernels (14.5 g.) which were crushed and extracted with light petroleum (b. p. 40–60°) for 8 hr. under nitrogen, to give the oil (8.59 g.). Ultraviolet maxima were at 264 (ε 16,000), 274 (ε 21,500), and 285 mμ (ε 16,500), corresponding to about 48% of the triene. The oil was hydrolysed (1½ hr.) by boiling 80% ethanol (50 ml.) containing potassium hydroxide (5.0 g.). The acids were isolated with ether in the usual way and obtained semi-solid (8.0 g.). Crystallisation from 80% ethanol at 0° gave trichosanic acid, m. p. 36.5–38.5°, raised by another crystallisation from pentane to 39–41° (2.03 g.). Two similar recrystallisations raised the m. p. to 43° (constant) (Found: C, 77.2; H, 11.4%). Microhydrogenation 2.1H<sub>2</sub>. The m. p. was undepressed by admixture with Japanese trichosanic acid or punicic acid. Ultraviolet maxima at 264 (ε 26,400), 274

<sup>42</sup> Thomas and Thompson, *J. Amer. Chem. Soc.*, 1934, **56**, 898.

( $\epsilon$  36,800), and 285  $\mu$  ( $\epsilon$  28,900). These intensities are 80% of those for punicic acid. Infra-red max. (in  $\text{CS}_2$ ): 986 ( $\epsilon$  124) and 936  $\text{cm}^{-1}$  ( $\epsilon$  82). These intensities are 77% of those for punicic acid and were not increased by recrystallising the trichosanic acid.

A specimen of Indian trichosanic acid (5.9 mg.) was chromatographed on a kieselguhr-paraffin column, elution being with aqueous acetone.<sup>14</sup> Elution was begun at 50% acetone and the concentration increased in 5% steps. Trichosanic acid (4.56 mg.) was eluted in 60%, palmitic acid (0.23 mg.) in 65%, and stearic acid (0.93 mg.) in 70% acetone. The recovery was 5.72 mg. (97%). The composition is thus trichosanic acid 79.7%, palmitic acid 4.1%, and stearic acid 16.2%. These figures are in good agreement with the spectroscopic estimation of punicic acid content and with the analytical data.

1 : 1-Diethoxyhept-2-yne (III).—Hexyne, prepared<sup>43</sup> in 64% yield, had b. p. 71–73°,  $n_D^{19}$  1.3995. Hexyne (164 g.) was added to a Grignard reagent prepared by passing methyl bromide vapour into stirred ether (1 l.) containing magnesium (54 g.). The mixture was set aside for 16 hr. and heated under reflux for 1 hr. After cooling, the solution was treated with ethyl orthoformate (320 g.) and then stirred and heated under reflux for 24 hr. The ether was poured off and reserved, the white residue dissolved in iced acetic acid, and the solution extracted with ether. All the ethereal solutions were united and washed with sodium hydrogen carbonate solution and then dried ( $\text{Na}_2\text{SO}_4$ ), evaporated, and distilled, to give 1 : 1-diethoxyhept-2-yne (318 g., 86%), b. p. 97–98°/12 mm.,  $n_D^{20}$  1.4337. Kranzfelder and Vogt<sup>26</sup> give b. p. 97–98°/10 mm.,  $n_D^{27}$  1.4320 (69%).

1 : 1-Diethoxyhept-cis-2-ene.—1 : 1-Diethoxyhept-2-yne (184.3 g.) was hydrogenated over 3% palladium–barium sulphate in ethyl acetate (200 ml.). When 21.66 l. (N.T.P.) had been absorbed (96.5% of calc. volume for semi-hydrogenation), the reaction was interrupted and the catalyst filtered off. Evaporation and distillation through a 10" Fenske column gave 1 : 1-diethoxyhept-cis-2-ene (139 g., 75%), b. p. 86°/10 mm.,  $n_D^{19}$  1.4261 (Found : C, 71.35; H, 11.95.  $\text{C}_{11}\text{H}_{22}\text{O}_2$  requires C, 70.9; H, 11.9%).

Hept-trans-2-enal (IV).—1 : 1-Diethoxyhept-cis-2-ene (135 g.) was heated under reflux (45 min.) with water (500 ml.) containing concentrated sulphuric acid (12 ml.) and then steam-distilled (3 hr.). The upper layer was separated and the lower layer twice extracted with ether, and the extracts were united with the upper phase. Drying ( $\text{Na}_2\text{SO}_4$ ), evaporation, and distillation through a 12" Dufton column gave hept-trans-2-enal (70 g., 86%), b. p. 70–73°/19 mm.,  $n_D^{20.5}$  1.4480. Ultraviolet max. : 219  $\mu$  ( $\epsilon$  13,200) in hexane. Lit.,<sup>44</sup> b. p. 165–167°,  $n_D^{17}$  1.4468.

Dec-5-en-1-yn-4-ol (V).—Zinc (43.5 g.) in dry tetrahydrofuran (120 ml.) was treated with part of a mixture of hept-2-enal (66.6 g.) and propargyl bromide (71.4 g.) in tetrahydrofuran (250 ml.). Mercuric chloride (50 mg.) was added to start the reaction, and then the remainder of the reactants added dropwise. Finally, the product was heated under reflux (15 min.), and set aside overnight. Iced dilute acetic acid was added, and the upper layer separated. The aqueous phase was extracted with ether, and the extracts were added to the upper layer. The ethereal solution was washed with saturated sodium hydrogen carbonate solution and dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation and distillation gave dec-5-en-1-yn-4-ol (38.0 g., 42%), b. p. 72–75°/0.02 mm.,  $n_D^{23}$  1.4642–1.4666 (Found : C, 78.65; H, 10.6.  $\text{C}_{10}\text{H}_{16}\text{O}$  requires C, 78.9; H, 10.6%). Microhydrogenation  $3\text{O}_2$ . There were infrared bands at 3248s (OH), 2123m ( $\text{C}\equiv\text{CH}$ ), 1955m ( $\text{C}=\text{C}=\text{C}$ ), 1668ms ( $\text{C}=\text{C}$ ), and 970s  $\text{cm}^{-1}$  (*trans*- $\text{CH}=\text{CH}$ ). The tetrahydropyranyl ether, prepared in the usual way, had b. p. 92–96°/0.04 mm.,  $n_D^{22}$  1.4682 (Found : C, 76.05; H, 10.3.  $\text{C}_{15}\text{H}_{24}\text{O}_2$  requires C, 76.2; H, 10.25%).

Deca-3 : 5-dien-1-yne (VI).—(A) Toluene-*p*-sulphonyl chloride (10.0 g.) was dissolved in warm pyridine (5 ml.) and ice-cooled whilst dec-5-en-1-yn-4-ol (7.6 g.) was added with stirring. The product was set aside at 20° overnight and then treated with ice-cold 2*N*-hydrochloric acid and ether. The ether extracts were washed with dilute acid, and then aqueous sodium hydrogen carbonate, and dried ( $\text{MgSO}_4$ ). Evaporation gave an oil (8.8 g.). Sodium (1.37 g.) was dissolved in butan-1-ol (100 ml.), heated to 65°, and mixed with the crude toluene-*p*-sulphonate dissolved in a little butanol. Immediate precipitation and warming occurred. The solution was warmed on a steam-bath (15 min.), then cooled, and pentane (250 ml.) was added. After being washed six times with water, the pentane solution was dried ( $\text{MgSO}_4$ ), and the solvent distilled off through a column. Distillation of the residue gave deca-3 : 5-dien-1-yne (2.01 g.,

<sup>43</sup> "Organic Reactions," Vol. V, p. 48.

<sup>44</sup> Delaby and Guillot-Allègre, *Bull. Soc. chim. France*, 1933, 53, 301.

30%), b. p. 72—74°/12 mm.,  $n_D^{21.5}$  1.5022 (Found: C, 88.6; H, 10.75.  $C_{10}H_{14}$  requires C, 89.5; H, 10.5%). Ultraviolet max.: 260.5  $m\mu$  ( $\epsilon$  25,900).

(B) Dec-5-en-1-yn-4-ol (15.2 g.), dissolved in dry pyridine (8 ml.), was stirred at 0° whilst phosphorus trichloride (6.2 g.) in ether (10 ml.) was added dropwise. Stirring was continued for 2½ hr. at 20°, water and ether were then added, and the ethereal extracts washed with 2N-hydrochloric acid, followed by sodium hydrogen carbonate solution. The ethereal solution was dried and evaporated, and the crude chloride (12.8 g.) added to a solution of potassium hydroxide (10 g.) in ethanol (60 ml.). Immediate reaction occurred and the mixture was heated in nitrogen under reflux for 35 min. Working up as usual gave deca-3:5-dien-1-yne (4.02 g., 31%), b. p. 56—58°/4 mm.,  $n_D^{27}$  1.5040—1.5058. Ultraviolet max.: 260  $m\mu$  ( $\epsilon$  29,100). Infrared bands at 3257s, 2101mw ( $C\equiv CH$ ), 1932vw ( $C=C=C$ ), 1638ms ( $C=C$ ), 1595vw, 1575w, 983s (*trans*-CH=CH), and 943m  $cm^{-1}$  (*trans*-CH=CH conjugated with  $C\equiv C$ ). The allene band was very weak.

(C) Dec-5-en-1-yn-4-ol (5.45 g.) was dissolved in dry pyridine (10 ml.) and cooled in ice. Phosphorus oxychloride (8 ml.) in dry pyridine (20 ml.) was added dropwise with shaking. After 30 min. the mixture was heated in nitrogen at 100° for 30 min. and then cooled and poured into 2N-hydrochloric acid at 0°. Isolation with ether in the usual way gave, after removal of solvent through a Dufton column and then distillation, deca-3:5-dien-1-yne (1.09 g., 23%), b. p. 74—79°/10 mm.,  $n_D^{29}$  1.4940—1.4967. Microhydrogenation 3.85H<sub>2</sub>. Ultraviolet max.: 260—261  $m\mu$  ( $\epsilon$  20,800). The  $\epsilon$  value is probably low because the spectrum was not determined immediately. Infrared bands were at 3258s, 2122w, 2098mw, 1637s, 1594vw, 1573w, 984s, and 943m  $cm^{-1}$ . There was no allenic absorption.

17-Chloroheptadeca-5:7-dien-9-yne (VII).—Deca-3:5-dien-1-yne (4.02 g.) in ether (10 ml.) was stirred (5 hr.) with sodamide [from sodium (0.75 g.)] in liquid ammonia (150 ml.). 1-Chloro-7-iodoheptane (8.2 g.) was added, and stirring continued overnight. The ammonia was allowed to evaporate, water and ether were added, and the ethereal extracts washed with water, 2N-hydrochloric acid, and sodium hydrogen carbonate solution. Drying, evaporation, and distillation gave the chloroheptadecadienyne (4.06 g., 51%), b. p. 132—135°/0.05 mm.,  $n_D^{21}$  1.5112 (Found: C, 76.8; H, 10.5; Cl, 13.9.  $C_{17}H_{27}Cl$  requires C, 76.5; H, 10.2; Cl, 13.3%).

Magnesium was activated as follows.<sup>45</sup> Magnesium (4 g.) was covered with dry ether, and iodine (1 g.) added. Reaction occurred with disappearance of the iodine colour. The ether was decanted and the residue heated gently with a Bunsen flame. Iodine was evolved, leaving dull, greyish magnesium which was found to be highly active for preparing octadecylmagnesium chloride. 17-Chloroheptadeca-5:7-dien-9-yne (1.08 g.) was dissolved in dry ether (10 ml.), and treated with magnesium. Reaction was not induced, on refluxing, by addition of iodine: after 3 hours' refluxing no Grignard reagent had been formed (Michler's ketone test<sup>46</sup>). In an attempt to facilitate reaction a little methyl iodide was added (immediate reaction) and refluxing continued overnight on a steam-bath. After treatment with carbon dioxide gas (2 hr.) and working up there was no long-chain acidic product, and only recovered chloride (0.68 g.) was isolated. Two further runs gave similar results. The chloroheptadecadienyne was then converted into the bromide with sodium bromide in boiling methanol (nitrogen)<sup>47</sup> and the iodide by similar treatment with sodium iodide in acetone. Both failed to react with magnesium even in the presence of mercuric chloride or methyl iodide.

17-Cyanoheptadeca-5:7-dien-9-yne (VIII).—17-Chloroheptadeca-5:7-dien-9-yne (217 mg.), sodium iodide (135 mg.), and sodium cyanide (95 mg.) in ethanol (3.0 ml.) and water (0.5 ml.) were heated under reflux (nitrogen) for 41 hr. Isolation of the product gave the nitrile (107 mg.), b. p. 148—152°/0.02 mm.,  $n_D^{20}$  1.5058 (Found: C, 84.55; H, 10.65; N, 5.2.  $C_{18}H_{27}N$  requires C, 84.0; H, 10.6; N, 5.45%). Ultraviolet max.: 266  $m\mu$  ( $\epsilon$  26,500). Infrared max.: 2260m ( $C\equiv N$ ), 2225w ( $C\equiv C$ ), 1639m ( $C=C$ ), 986s (*trans*-CH=CH), and 941  $cm^{-1}$  (*trans*-CH=CH conjugated with  $C\equiv C$ ).

Octadeca-trans-11:trans-13-dien-9-ynoic Acid (IX).—17-Chloroheptadeca-5:7-dien-9-yne (4.06 g.), sodium iodide (2.0 g.), and sodium cyanide (2.0 g.) in ethanol (20 ml.) and water (5 ml.) were heated under reflux in nitrogen for 48 hr. Potassium hydroxide (10 g.) in water (25 ml.) was added and refluxing continued for a further 48 hr. The yellow solution was extracted with ether and the extract rejected. Acidification of the aqueous phase, extraction

<sup>45</sup> Underwood and Gale, *J. Amer. Chem. Soc.*, 1934, **56**, 2118.

<sup>46</sup> Gilman and Schulze, *ibid.*, 1925, **47**, 2002.

<sup>47</sup> Bailey and Fujiwara, *ibid.*, 1955, **77**, 165.

with ether, drying, and evaporation gave an oil (3.68 g., 87%), ultraviolet max. 266  $\mu$  ( $\epsilon$  21,000) (Found: equiv., 283.6.  $C_{18}H_{30}O_2$  requires equiv., 276.4). It failed to give a crystalline *S*-benzylthiuronium or benzylamine salt or a *p*-bromophenacyl ester: attempts to distil it caused decomposition. The crude acid (3.68 g.) was dissolved in methanol (40 ml.) containing urea (15 g.) and crystallised at 0°. The clathrate compound was filtered off: when the filtrate was treated with more urea, no further solid was obtained. The clathrate compound was added to dilute acid and extracted with ether. When washed with water, dried, and evaporated, the extracts gave a solid which was twice crystallised from pentane, to give *octadeca-trans-11:trans-13-dien-9-ynoic acid* (0.73 g., 20%), m. p. 43–44°, raised by further crystallisation to m. p. 45–46° (Found: C, 78.05; H, 10.2.  $C_{18}H_{30}O_2$  requires C, 78.2; H, 10.2%). Microhydrogenation 3.95 $H_2$ . The hydrogenation product had m. p. 70°, undepressed when admixed with stearic acid. Infrared bands (solid film) at 2222 ( $C\equiv C$ ), 1702 ( $CO_2H$ ), 1639, 1602 ( $C=C$ ), 984 (*trans-CH=CH*), and 941  $cm^{-1}$  (weak: *trans-CH=CH* conjugated with  $C\equiv C$ ). The *p-bromophenacyl ester* crystallised from ethanol in plates, m. p. 62–63° (Found: C, 65.35; H, 7.1.  $C_{26}H_{33}O_3Br$  requires C, 65.95; H, 7.05%). Treating the dienyne acid (67.2 mg.) with maleic anhydride (25 mg.) in benzene under nitrogen for 20 hr. at 20° and for 7 hr. at 100° gave an oil which failed to crystallise. It was not unchanged acid, being insoluble in light petroleum (b. p. 40–60°).

*Octadeca-cis-9:trans-11:trans-13-trienoic ( $\alpha$ -Elaeostearic) Acid* (X).—*Octadeca-trans-11:trans-13-dien-9-ynoic acid* (106 mg.), Lindlar's catalyst (115 mg.), and quinoline (33.6 mg.) in ethyl propionate (5 ml.) were treated with hydrogen until 9.40 ml. of hydrogen were absorbed at 24°/719 mm. (95% of that required for semihydrogenation of one acetylenic linkage). The catalyst was removed and the filtrate diluted with ether, washed with 2*N*-hydrochloric acid, and water, dried, and evaporated. The residue was twice crystallised from pentane, to give *octadeca-cis-9:trans-11:trans-13-trienoic acid* (21 mg.), m. p. 47°, undepressed by admixture with natural  $\alpha$ -elaeostearic acid, m. p. 48° (Found: C, 77.4; H, 11.0.  $C_{18}H_{30}O_2$  requires C, 77.65; H, 10.85%). Infrared spectrum (solid film): 1686 ( $CO_2H$ ), 993, and 969  $cm^{-1}$  (*trans-CH=CH* in *trans-trans-cis*-conjugated system). The spectrum was identical with that of the natural acid. Isomerisation with iodine gave *octadeca-trans-9:trans-11:trans-13-trienoic acid*, m. p. 71°, undepressed by authentic  $\beta$ -elaeostearic acid derived from natural  $\alpha$ -acid. The infrared spectrum (paraffin mull) showed bands at 1709s ( $CO_2H$ ) and 986s  $cm^{-1}$  (*trans-CH=CH* in all-*trans*-conjugated triene system) and was indistinguishable from that of  $\beta$ -elaeostearic acid.

*Hept-2-ynal* (XI).—1:1-Diethoxyhept-2-yne (100 g.) was heated under reflux in nitrogen with water (350 ml.) containing sulphuric acid (14 g.) for 4 hr. Extraction with ether and purification as usual gave *hept-2-ynal* (42.5 g., 70%), b. p. 64–67°/15 mm.,  $n_D^{20}$  1.4560. Lunt and Sondheimer<sup>48</sup> give b. p. 52–54°/13 mm.,  $n_D^{20}$  1.4521 (Found: C, 75.85; H, 9.25. Calc. for  $C_7H_{10}O$ : C, 76.3; H, 9.15%).

*Deca-1:5-diyn-4-ol* (XII).—*Hept-2-ynal* (40 g.) and propargyl bromide (44 g.) in tetrahydrofuran (150 ml.) were added dropwise to zinc wool (32 g.; treated with a little mercuric chloride) in tetrahydrofuran (75 ml.). The product was worked up as described above (see *dec-5-en-1-yn-4-ol*). Distillation gave *deca-1:5-diyn-4-ol* (24.5 g., 45%), b. p. 79–82°/1 mm.,  $n_D^{20}$  1.4729–1.4749 (Found: C, 79.75; H, 9.6.  $C_{10}H_{14}O$  requires C, 79.95; H, 9.4%). Microhydrogenation 3.9 $H_2$ . The *tetrahydropyranyl ether*, prepared in 89% yield by the usual method, had b. p. 90°/0.05 mm.,  $n_D^{21}$  1.4756 (Found: C, 76.7; H, 9.55.  $C_{15}H_{22}O_2$  requires C, 76.9; H, 9.45%).

*Dec-3-ene-1:5-diyne* (XIII).—*Deca-1:5-diyn-4-ol* (8.06 g.) was dissolved in ether (15 ml.) and pyridine (1 ml.), cooled in ice, and stirred whilst phosphorus tribromide (4.2 ml.) was added dropwise. After 1 hour's stirring at 0° iced 2*N*-sulphuric acid was added and the bromide isolated as usual but not distilled. Potassium hydroxide (10 g.) in ethanol (50 ml.) was added and the mixture heated under reflux in nitrogen (15 min.). Working up as usual, the solvent being removed through a Dufton column, gave *dec-3-ene-1:5-diyne* (2.5 g., 35%), b. p. 64–65°/5 mm.,  $n_D^{20}$  1.5080–1.5097 (Found: C, 90.4; H, 9.5.  $C_{10}H_{12}$  requires C, 90.85; H, 9.15%). Microhydrogenation 4.7 $H_2$ . Infrared max. (liquid film): 3247s ( $C\equiv CH$ ), 2336w, 2217ms ( $C\equiv C$ ), 2105mw ( $C\equiv CH$ ), 1589m, 1575w ( $C=C$ ), 939s  $cm^{-1}$  (*trans-CH=CH* conjugated with  $C\equiv C$ ). Weak absorption at 1940  $cm^{-1}$  suggests a little allenic contaminant.

17-*Chloroheptadec-7-ene-5:9-diyne* (XIV).—Sodamide was prepared from sodium (0.82 g.)

<sup>48</sup> Lunt and Sondheimer, *J.*, 1950, 3361.

in liquid ammonia (200 ml.; dried over sodium and redistilled), and dec-3-ene-1 : 5-diyne (3.83 g., in ether 20 ml.) was added : the mixture was stirred for 3 hr. 1-Chloro-7-iodoheptane (8.4 g.) was added and the mixture stirred overnight. Ammonium chloride (3 g.) was added, the ammonia allowed to evaporate, and the product isolated with ether. Distillation gave 17-chloroheptadec-7-ene-5 : 9-diyne (4.16 g., 54%), b. p. 134—138°/10<sup>-4</sup> mm.,  $n_D^{25}$  1.5140—1.5159 (Found : Cl, 13.0. C<sub>17</sub>H<sub>25</sub>Cl requires Cl, 13.35%). Infrared max. (liquid film) at 2229m (C≡C) and 937s cm.<sup>-1</sup> (*trans*-CH=CH conjugated with C≡C). The low frequency of the *trans* out-of-plane deformation mode is noteworthy (see other instances in this paper). The shift caused by conjugation with one acetylenic linkage is still further enhanced.

*Octadec-trans-11-ene-9 : 13-diynoic Acid* (XVI).—The preceding chloride (4.16 g.), sodium iodide (2.0 g.), and sodium cyanide (2.0 g.) were heated under reflux in ethanol (20 ml.) and water (4 ml.) in nitrogen for 42 hr. Potassium hydroxide (8.0 g.) in water (20 ml.) was added, and heating continued (24 hr.) until evolution of ammonia ceased. Water and ether were added and the ethereal layer rejected. The aqueous phase was acidified and the crude acid isolated as usual : it was dark green. Recrystallisation from light petroleum (b. p. 60—80°) gave an almost colourless acid (1.743 g., 40%), m. p. 75—76° which became green on the surface whilst being filtered. *Octadec-trans-11-ene-9 : 13-diynoic acid* was again crystallised and formed white plates, m. p. 76° (Found : C, 78.55; H, 9.6. C<sub>18</sub>H<sub>26</sub>O<sub>2</sub> requires C, 78.8; H, 9.55%). Microhydrogenation 5.0H<sub>2</sub>. Infrared max. (paraffin mull) at 2224mw (C≡C), 1688s (CO<sub>2</sub>H), 946ms cm.<sup>-1</sup> (*trans*-CH=CH conjugated with C≡C). Hydrogenation gave stearic acid, m. p. 70° (and mixed m. p.). The enediyne did not form a urea complex.

*Octadeca-cis-9 : trans : 11-cis-13-trienoic Acid* (XVII).—Octadec-*trans*-11-en-9 : 13-diynoic acid (446 mg.) was hydrogenated in ethyl propionate (25 ml.) over Lindlar's catalyst (434 mg.) in the presence of quinoline (145 mg.) until hydrogen (81.5 ml. at 24°/736 mm.) had been absorbed (semihydrogenation of the two acetylenic linkages needs 81.6 ml.). The catalyst was removed and the filtrate diluted with ether, washed with 2*N*-hydrochloric acid and water, dried (MgSO<sub>4</sub>), and evaporated. One crystallisation from pentane gave *octadeca-cis-9 : trans-11 : cis-13-trienoic acid* (0.313 g., 70%), m. p. 35—38° raised by one recrystallisation to 41° (0.175 g.), and by two further crystallisations to m. p. 43—43.5° (Found : C, 77.4; H, 10.8%). The acid crystallised in needles or plates. Infrared bands (CS<sub>2</sub>) at 987 cm.<sup>-1</sup> (ε 154) and 937 cm.<sup>-1</sup> (ε 104) (cf. Table 2). The m. p. was undepressed on admixture with natural punicic (m. p. 43.5—44°) or trichosanic (m. p. 43—43.5°) acid. The infrared spectra of all three acids, compared as solid films or in CS<sub>2</sub> solution, were identical. The synthetic acid was isomerised in pentane solution with iodine to β-elæostearic acid, m. p. 71° (from ethanol) undepressed by the naturally derived acid.

*Oct-1-yn-4-ol*.—A Reformatski reaction between valeraldehyde (32 g.) and propargyl bromide (45 g.) in dry tetrahydrofuran (200 ml.), by use of zinc (29.5 g.) covered with tetrahydrofuran (150 ml.), gave *oct-1-yn-4-ol* (19.8 g., 42%), b. p. 77—85°/10 mm.,  $n_D^{25}$  1.4462—1.4485 (Found : C, 75.7; H, 11.35. C<sub>8</sub>H<sub>14</sub>O requires C, 76.15; H, 11.2%). Infrared bands were at 3384s (OH), 3300s, 2128m (C≡CH), and 1963m cm.<sup>-1</sup> (C=C=C).

*Oct-3-en-1-yne* (XVIII).—The toluene-*p*-sulphonate was prepared from *oct-1-yn-4-ol* (19.8 g.), by means of toluene-*p*-sulphonic acid (30.8 g.) and pyridine (12.4 ml.). The crude red oil (39.4 g., 89%) was added in ether (50 ml.) to sodamide [from sodium (7.6 g.)] in liquid ammonia (250 ml.), and the mixture stirred for 5 hr. Ammonium chloride (20 g.) and water (250 ml.) were added and the mixture worked up in the usual way, to give *oct-3-en-1-yne* (8.4 g., 55%), b. p. 126—128°,  $n_D^{25}$  1.4431 (Found : C, 88.5; H, 11.35. C<sub>8</sub>H<sub>12</sub> requires C, 88.8; H, 11.2%). Infrared bands at 3268s, 2112w (C≡CH), 1616w (CH=CH), and 960m cm.<sup>-1</sup> (*trans*-CH=CH conjugated with C≡CH). There was no allenic absorption. Black<sup>34</sup> gives b. p. 72—73°/110 mm.,  $n_D^{25}$  1.4430—1.4440, but prepared the compound by a different procedure.

*Oct-1-yn-4-ol* (21 g.) and pyridine (13 ml.) were cooled to -10° and thionyl chloride (24.7 g.) added dropwise, with stirring. After 12 hr., the mixture was worked up in the usual way, to give 4-chloro-*oct-1-yne* (13.7 g., 58%), b. p. 90—105°/40 mm.,  $n_D^{25}$  1.4500—1.4510. Attempts to dehydrochlorinate this chloride with 15% ethanolic potassium hydroxide gave only small yields of impure *oct-3-en-1-yne*.

*Methyl Octadec-trans-13-ene-9 : 11-diynoate* (XIX).—*Oct-3-en-1-yne* (8.4 g.) and dec-9-ynoic acid (13 g.) in methanol (250 ml.) were mixed with a solution of cuprous chloride (33 g.) and ammonium chloride (100 g.) in 0.08*N*-hydrochloric acid (250 ml.). After 80 minutes' shaking in oxygen, gas absorption ceased (approx. 3 l. used). The solution was acidified and

extracted with ether. The ether solutions were extracted with alkali, and the acidic product isolated in the usual way and esterified with diazomethane. Distillation gave *methyl octadec-trans-13-ene-9:11-diyanoate* (5.47 g., 24%), b. p. 137—141°/0.001 mm.,  $n_D^{19}$  1.5129 (Found: C, 78.65; H, 9.85.  $C_{19}H_{38}O_2$  requires C, 79.1; H, 9.8%). Infrared bands at 2242mw ( $C\equiv C$ ), 2146w, 1737s ( $CO_2Me$ ), 956m  $cm^{-1}$  (*trans-CH=CH* conjugated with  $C\equiv C$ ).

The ester (5.45 g.) was hydrolysed with potassium hydroxide (5.0 g.) in ethanol (45 ml.) and water (5 ml.), but the acid produced was an uncrystallisable yellow oil which failed to form a urea complex. Re-esterification gave methyl octadec-13-ene-9:11-diyanoate, b. p. 132—134°/0.001 mm.,  $n_D^{20}$  1.5112.

*Partial Hydrogenation of Methyl Octadec-trans-13-ene-9:11-diyanoic Acid.*—The enediyne ester (1.145 g.) was hydrogenated in ethyl propionate (50 ml.) over Lindlar's catalyst (1.128 g.) in the presence of quinoline (0.35 ml.) until hydrogen (190 ml. at 25.5°/730 mm.) had been absorbed (202 ml. required for semihydrogenation of the two acetylenic linkages). The catalyst was filtered off, leaving an oil. Ultraviolet max.: 271  $m\mu$  ( $\epsilon$  22,500), with inflexions at 264—265 ( $\epsilon$  19,600) and 279—280  $m\mu$  ( $\epsilon$  17,400). Saponification of the crude ester, by potassium hydroxide (1.5 g.) in 90% ethanol (15 ml.) under reflux in nitrogen, gave the crude acid which was dissolved in 80% ethanol (10 ml.) and cooled to 0°. A small quantity of solid was removed. The filtrate was evaporated *in vacuo* and the residual oil dissolved in pentane (10 ml.) and crystallised at -70°. A solid (0.32 g.) was obtained which after further low-temperature crystallisation from pentane had m. p. 35—38°. Attempts to form a urea complex from the filtrate from the first pentane crystallisation gave a solid product which on decomposition yielded only an oil (0.26 g.) at 20° (solid at 0°). Repetition of this experiment gave a similar triene acid, m. p. 35—39°, with ultraviolet max. 271  $m\mu$  ( $\epsilon$  30,000). The acid was extremely unstable.

*Octadeca-9:11-dienoic Acid* (XXV; R = H).—A mixture of ethyl 11-bromoundec-9-enoate (XXII) and ethyl 9-bromoundec-10-enoate (XXI) was prepared according to directions in the literature.<sup>37</sup> The mixed bromo-esters (4.2 g.) and triphenylphosphine (4.2 g.) were dissolved in benzene (20 ml.) and set aside for 48 hr. On dilution with ether (50 ml.) a colourless oil was precipitated which solidified at 0°. It was dissolved in benzene, then reprecipitated with ether, and the solvent was decanted. The residual oil (6.4 g.) was dissolved in dry ethanol (30 ml.) and treated with sodium ethoxide [from sodium (0.27 g.)] in ethanol (15 ml.). After 16 hr. *n*-heptaldehyde (1.6 ml.) was added and the mixture again set aside (16 hr.). Most of the solvent was removed *in vacuo*, 2*N*-hydrochloric acid added, and the solution extracted with ether. After evaporation of the ether extract, pentane was added and triphenylphosphine oxide filtered off. Evaporation and distillation gave a fraction, b. p. 80—83°/5 × 10<sup>-3</sup> mm.,  $n_D^{21}$  1.4528 (0.8 g.), and ethyl octadeca-9:11-dienoate (0.846 g., 19%), b. p. 118—120°/5 × 10<sup>-4</sup> mm.,  $n_D^{21}$  1.4772. A little triphenylphosphine oxide was slowly deposited from the latter fraction and the ester was decanted. Ultraviolet max. 230—232  $m\mu$  ( $\epsilon$  24,500). It had infrared bands at 1733s ( $CO_2Et$ ), 985m, and 948mw  $cm^{-1}$  (*trans-cis*-diene). There was no vinyl absorption at 905—915  $cm^{-1}$ . On hydrolysis in 90% ethanol (5 ml.) containing potassium hydroxide (0.59 g.), under reflux (1 hr.), the ester (0.54 g.) gave an oily acid. Crystallisation from light petroleum (b. p. 40—60°) (charcoal) gave octadeca-*trans*-9:*trans*-11-dienoic acid, m. p. 53.5° (Found: C, 76.9; H, 11.8. Calc. for  $C_{18}H_{32}O_2$ : C, 77.1; H, 11.5%). Ultraviolet max. 231  $m\mu$  ( $\epsilon$  36,000). Infrared bands (mull): 1709s ( $CO_2H$ ), 982s  $cm^{-1}$  (*trans-trans*-diene). Lit.,<sup>21, 21a</sup> m. p. 53—54°, ultraviolet max. 232  $m\mu$  ( $\epsilon$  32,000). The filtrate from the crystallisation contained a mixture of acids (presumably stereoisomers) which was solid at 0°; they were not further investigated.

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