Anodic Syntheses. Part XI. Synthesis of Tariric and Petroselinic Acid.*

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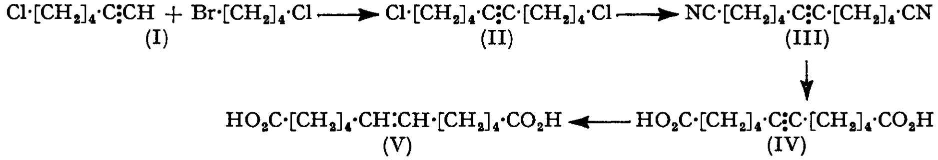
Dodec-6-ynedioic acid and the corresponding ethylene, intermediates for the synthesis of unsaturated fatty acids, have been prepared from 6-chlorohex-1-yne.

Tariric acid has been synthesised by anodic "crossed" coupling of methyl hydrogen dodec-6-ynedioate with octanoic acid, and partially reduced to petroselinic acid.

The two preceding papers in this series described the chain extension of unsaturated acids by electrolysis with half esters of dicarboxylic acids. In continuation of this study of anodic routes to long-chain unsaturated fatty acids, the use of components of the type $HO_2C{\cdot}[CH_2]_n{\cdot}X{\cdot}[CH_2]_n{\cdot}CO_2H$ where X is either an ethylenic or an acetylenic group, is now being examined for the introduction of the unsaturated centre. By "crossed" coupling first at one end of the molecule with a monocarboxylic acid, and then, if desired, at the other with a half ester, a very flexible route to unsaturated acids is available. One minor limitation, which may be inferred from the results of previous workers on the electrolysis of olefinic acids (see a summary by Weedon, *Quart. Reviews*, 1952, **6**, 380), is that *n* must be >1. In this paper we report the preparation of the previously unknown dodecynedioic (IV) and dodecenedioic † acids (V), and the use of the former for the synthesis of tariric (VII) and petroselinic acid (*cis*-VIII); the last two fatty acids occur in the seed fats of the genus *Picramnia* (Simarubaceae) and of the Umbelliferæ respectively. The synthesis of tariric acid by a different route, and its reduction to petroselinic acid, were recently achieved by Lumb and Smith (*J.*, 1952, 5032).



$$\begin{tikzcd}
\underset{\text{(I)}}{\mathrm{Cl{\cdot}[CH_2]_4{\cdot}C{\vdots}CH}} + \mathrm{Br{\cdot}[CH_2]_4{\cdot}Cl} \arrow[r] & \underset{\text{(II)}}{\mathrm{Cl{\cdot}[CH_2]_4{\cdot}C{\vdots}C{\cdot}[CH_2]_4{\cdot}Cl}} \arrow[r] & \underset{\text{(III)}}{\mathrm{NC{\cdot}[CH_2]_4{\cdot}C{\vdots}C{\cdot}[CH_2]_4{\cdot}CN}} \arrow[d] \\
& \underset{\text{(V)}}{\mathrm{HO_2C{\cdot}[CH_2]_4{\cdot}CH{:}CH{\cdot}[CH_2]_4{\cdot}CO_2H}} & \underset{\text{(IV)}}{\mathrm{HO_2C{\cdot}[CH_2]_4{\cdot}C{\vdots}C{\cdot}[CH_2]_4{\cdot}CO_2H}} \arrow[l]
\end{tikzcd}$$

Condensation in liquid ammonia of the sodio-derivative of 6-chlorohex-1-yne (I) (Newman and Wotiz, *J. Amer. Chem. Soc.*, 1949, **71**, 1294) with tetramethylene bromide chloride gave (45%) the dichlorodecyne (II). This was converted, *via* the corresponding di-iodide, into the dinitrile (III) in 85% overall yield. Hydrolysis then furnished the dodecynedioic acid (IV) in 89% yield. Malonate chain extension of the di-iodide, followed by hydrogenation of the resulting tetra-ester, hydrolysis, and decarboxylation, led to tetradecanedioic acid, which was compared directly with an authentic specimen.

Partial reduction of the dodecynedioic acid over palladium on barium sulphate gave the corresponding ethylenic compound (V) almost quantitatively. From the known stereochemical course of reduction of acetylenes over supported palladium catalysts (cf. Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 148; Crombie, *Quart. Reviews*, 1952, **6**, 128) this product undoubtedly consists very largely, or exclusively, of the *cis*-isomer. Its structure was confirmed by catalytic hydrogenation to dodecanedioic acid, and by oxidative degradation of its dihydroxy-derivative (see below) to adipic acid.

An attempt to prepare *trans*-dodecenedioic acid by reduction of the acetylenic acid with sodium in liquid ammonia (cf. Howton and Davis, *J. Org. Chem.*, 1951, **16**, 1405) was unsuccessful, probably owing to insolubility of the sodium salt of the acid. The inversion of the *cis*-isomer was therefore attempted. Although stereomutation occurred readily on

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* Part X, *J.*, 1954, 448.

† The formation of small amounts of dodec-6-enedioic acid, as a by-product in the thermal decomposition of *N*-nitrosohexanolactam, was recently postulated by Heyns and Woyrsch (*Chem. Ber.*, 1953, **86**, 76); it was not isolated, but converted by oxidative degradation into adipic acid.

treatment of *cis*-dodecenedioic acid with nitrous acid, the product melted over a range of 5°, even after repeated crystallisation, and was considered to be contaminated with the *cis*-isomer and/or positional isomers. Inversion of the *cis*-acid by a method very similar to that used by Hunsdiecker (*Ber.*, 1944, **77**, 185) in the eicos-9-enedioic acid series, was somewhat more successful. Oxidation of the *cis*-dodecenedioic acid with performic acid led to 6 : 7-dihydroxydodecanedioic acid, which with a mixture of hydrogen bromide, acetic acid, and sulphuric acid (cf. Ames and Bowman, *J.*, 1951, 1079) gave 6 : 7-dibromododecanedioic acid. By analogy with the products from similar reactions of numerous related compounds, the dihydroxy- and the dibromo-dodecanedioic acid may be assigned the *threo-* and the *erythro*-configuration respectively. Esterification of the dibromo-compound, debromination of the ester with zinc dust, and hydrolysis then furnished the required *trans*-dodecenedioic acid in 23% overall yield from the *cis*-isomer. However this product also melted over a slight range (3°), suggesting some contamination with the *cis*-acid. This is more likely to be due to the presence in the starting material of traces of *trans*-dodecenedioic acid, formed during the partial reduction of the acetylenic acid (cf. Crombie, *loc. cit.*), than by lack of stereospecificity in the various reactions employed in the inversion (cf. Ames and Bowman, *loc. cit.*). The latter possibility cannot, however, be entirely excluded.

$$\mathrm{CH_3{\cdot}[CH_2]_6{\cdot}CO_2H + HO_2C{\cdot}[CH_2]_4{\cdot}C{\vdots}C{\cdot}[CH_2]_4{\cdot}CO_2Me} \quad \text{(VI)}$$

$$\downarrow$$

$$\text{(VII)} \quad \mathrm{CH_3{\cdot}[CH_2]_{10}{\cdot}C{\vdots}C{\cdot}[CH_2]_4{\cdot}CO_2H} \longrightarrow \mathrm{CH_3{\cdot}[CH_2]_{10}{\cdot}CH{:}CH{\cdot}[CH_2]_4{\cdot}CO_2H} \quad \text{(VIII)}$$

To illustrate the route to unsaturated fatty acids, dodecynedioic acid (IV) was converted (47%) into the half ester (VI), and the latter was electrolysed with an excess of octanoic acid. By distillation of the mixture of products, formed by both symmetrical and "crossed" coupling of the two components, and subsequent hydrolysis, octadec-6-ynoic acid (VII) was readily isolated in 23% yield. Its m. p. was in excellent agreement with that reported for natural tariric acid (Arnaud, *Compt. rend.*, 1892, **114**, 79; Steger and van Loon, *Rec. Trav. chim.*, 1933, **52**, 593). Partial hydrogenation of the synthetic acid over lead-poisoned palladium * (Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446) gave octadec-*cis*-6-enoic acid (VIII), which was identified with natural petroselinic acid by direct comparison. The yield (47%) was very similar to that obtained by Lumb and Smith (*loc. cit.*) who used a Raney nickel catalyst.

EXPERIMENTAL

1 : 10-*Dichlorodec*-5-*yne*.—A solution of sodamide (from 38 g. of sodium) in liquid ammonia (1 l.) (cf. Vaughn, Vogt, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120) was added during 2 hr. to a stirred solution of 1-chlorohex-5-yne (200 g.) (Newman and Wotiz, *ibid.*, 1949, **71**, 1294) in liquid ammonia (2 l.). After ½ hr., 1-bromo-4-chlorobutane (300 g.) (Starr and Hixon, *ibid.*, 1934, **56**, 1595) was added during 3½ hr. and the mixture was stirred overnight. Ammonium chloride (100 g.) was added and the ammonia was then evaporated. The residue was extracted thoroughly with ether, and the extract was washed with 2N-hydrochloric acid, then with water, and dried (Na_2SO_4). Distillation yielded: (i) 1 : 10-Dichlorodec-5-yne (153 g.), b. p. 105—113°/1 mm., n_D^{19} 1·4841—1·4858. Analyses of the product from several preparations gave results which were consistently high in carbon and low in chlorine, suggesting that the dichlorodecyne contained small amounts ($\ngtr$10%) of a chlorodecenyne formed by partial dehydrochlorination. (ii) A liquid (35 g.), b. p. 173—176°/0·5 mm., n_D^{19} 1·4970—1·4978.

Dec-5-*yno*-1 : 10-*dinitrile*.—A solution of 1 : 10-dichlorodec-5-yne (110 g.) and sodium iodide (235 g.) in dry acetone (1600 c.c.) was stirred under reflux for 24 hr. After the solid had been filtered off, the solvent was evaporated under reduced pressure. The residue was extracted with ether, and the ethereal solution was washed with aqueous sodium thiosulphate and dried (Na_2SO_4). Evaporation of the ether gave crude 1 : 10-di-iododec-5-yne (192·5 g.). A mixture of the latter, potassium cyanide (98 g.), water (165 c.c.), and acetone (410 c.c.) was vigorously stirred under reflux for 45 hr. About 300 c.c. of the solvent were evaporated, and the residue was extracted with ether. The extract was washed successively with 2N-sodium hydroxide,

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* This catalyst was not available when the partial reduction of the dodecynedioic acid was studied. Its use for the reduction of stearolic to oleic acid will be reported in a separate communication.

aqueous sodium thiosulphate, and water, and then dried (Na_2SO_4) and evaporated. Distillation of the residue gave *dec*-5-*yno*-1 : 10-*dinitrile* (85 g., 85%), b. p. 150—156°/0·6 mm., n_D^{20} 1·4740—1·4755 (Found : C, 76·85; H, 8·4%), which solidified at 0°. Crystallisation from ether-pentane gave a solid, m. p. 19·5—20° (Found : C, 76·6; H, 8·7. $C_{12}H_{16}N_2$ requires C, 76·55; H, 8·55%).

Dodec-6-*ynedioic acid.*—A mixture of the preceding dinitrile (86 g.), and a solution of potassium hydroxide (110 g.) in water (1 l.) and alcohol (500 c.c.), was stirred vigorously and boiled under reflux until the evolution of ammonia ceased (5 days). The resulting solution was acidified with 6N-hydrochloric acid, and the precipitate thus formed was collected and dried. One crystallisation from benzene gave a micro-crystalline powder (92 g., 89%), m. p. 116—118°. Two further crystallisations from the same solvent gave the *diacid*, m. p. 118·5° (Found : C, 63·95; H, 8·05%; equiv., 114. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%; equiv., 113).

A solution of the preceding diacid (45 g.) and concentrated sulphuric acid (12 g.) in methanol (40 c.c.) and benzene (100 c.c.) was boiled under reflux for 21 hr. Dilution with water and isolation of the product with ether in the usual way gave the *dimethyl ester* (43 g., 86%), b. p. 120°/0·3 mm., n_D^{19} 1·4605 (Found : C, 66·1; H, 8·6. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·7%).

Methyl Hydrogen Dodec-6-*ynedioate.*—(a) *Half-esterification method* (cf. Swann, Oehler, and Buswell, *Org. Synth.*, Coll. Vol. II, p. 276). A mixture of dodec-6-ynedioic acid (20 g.), the corresponding methyl ester (13·0 g.), *n*-butyl ether (6 c.c.), concentrated hydrochloric acid (2·5 c.c.), and anhydrous methanol (5·3 c.c.) was heated rapidly to 160°, then boiled gently under reflux at 130° for 2 hr. Methanol (1·7 c.c.) was added, and heating was continued for a further 2 hr. Distillation of the product gave methyl dodec-6-ynedioate (18—20 g.) and the *half-ester* (10·0 g., 47%), b. p. 183—186°/0·6 mm., 157°/0·3 mm., n_D^{20} 1·4689 (Found : C, 65·05; H, 8·55. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·4%). In a smaller-scale experiment, the yield was 54%.

(b) *Half-hydrolysis method* (cf. Signer and Sprecher, *Helv. Chim. Acta*, 1947, **30**, 1001). A solution of methyl dodec-6-ynedioate (35 g.) in methanol (160 c.c) was shaken vigorously for 48 hr. with methanolic N-barium hydroxide (136 c.c., 1 equiv.). The precipitated barium salts were collected, dried, and converted into the sodium salts by shaking them with sodium sulphate (11·5 g.) in water (440 c.c.). The mixture was filtered, and the solution of sodium salts was acidified with dilute hydrochloric acid. The resulting flocculent precipitate (19·7 g.) was collected, and crystallised from benzene, giving dodec-6-ynedioic acid (5·6 g.). Evaporation of the benzene mother-liquors yielded the half-ester (10·5 g., 32%), b. p. 110° (bath-temp.)/10^{-5} mm., m. p. 22·3—22·9° (Found : equiv., 235. Calc. for $C_{13}H_{20}O_4$: equiv., 240). The benzylamine salt melted below 20°, and neither the piperazine nor the morpholine salt could be purified.

Dodec-cis-6-*enedioic Acid.*—A solution of dodec-6-ynedioic acid (21·9 g.) in dioxan (250 c.c.) was shaken in hydrogen in the presence of palladium on barium sulphate (2·5 g.; 0·3% of Pd). When 1 mol. of hydrogen had been taken up, the rate of absorption dropped markedly, and the reaction was interrupted. Removal of catalyst and solvent, and crystallisation of the residue from 50% aqueous methanol, gave the *diacid* (20 g.), m. p. 60·5—61·5° (Found : C, 63·1; H, 8·85. $C_{12}H_{20}O_4$ requires C, 63·15; H, 8·85%). The *benzylamine* salt crystallised from dioxan and from ethyl acetate and had m. p. 124·5—125·5° (Found : C, 70·3; H, 8·75. $C_{26}H_{38}O_4N_2$ requires C, 70·55; H, 8·65%). After generation from this salt, and one crystallisation from aqueous methanol, the diacid had m. p. 62—63·5°.

Reduction of methyl dodec-6-ynedioate in ethyl acetate over palladium on calcium carbonate (0·3% of Pd), and interruption of the reaction after 1 mol. of hydrogen had been absorbed, gave a mixture.

Dodecanedioic Acid.—A solution of the preceding diacid (0·15 g.) in dioxan (15 c.c.) was shaken in hydrogen in the presence of Adams catalyst until absorption was complete. Removal of catalyst and solvent, and crystallisation of the residue first from ethyl acetate and then from water, gave dodecanedioic acid (0·07 g.) as plates, m. p. 127·5—128·5° (Walker and Lumsden, *J.*, 1901, **79**, 1200, give m. p. 126·5—127°).

threo-6 : 7-*Dihydroxydodecanedioic Acid* (cf. Swern, Billen, Findley, and Scanlan, *J. Amer. Chem. Soc.*, 1945, **67**, 1786).—Hydrogen peroxide (5·85 g.; 90—100-vol.) was added in one portion to a stirred solution of dodec-*cis*-6-enedioic acid (10·0 g.) in formic acid (36 c.c.; 98—100%) at 40°. The mixture was stirred at 40° for 4½ hr. and the formic acid was then removed by steam-distillation (1½ hr.). Evaporation of the residue under reduced pressure, and crystallisation from ethyl acetate, gave threo-6 : 7-*dihydroxydodecanedioic acid* (5·3 g., 46%), m. p. 125·5—127·5° (Found : C, 55·35; H, 8·65. $C_{12}H_{22}O_6$ requires C, 54·95; H, 8·45%).

Oxidation of threo-6 : 7-*Dihydroxydodecanedioic Acid.*—A solution of periodic acid (1·2 g.) in water (60 c.c.) was added to one of *threo*-6 : 7-dihydroxydodecanedioic acid (1·0 g.) in water (70 c.c.) at 40°. The mixture was kept at 20° for 3 hr., then diluted with water (to 250 c.c.) and thoroughly extracted with ether. The extract was evaporated and the liquid residue was treated, in 2N-sulphuric acid at 50°, with excess of solid potassium permanganate. The suspension was kept at 50° for 2 hr. and then treated with excess of sulphur dioxide. Concentration of the resulting solution yielded a solid (0·7 g., 64%), which was crystallised from ethyl acetate, giving adipic acid, m. p. and mixed m. p. 149—151°.

Dodec-trans-6-*enedioic Acid.*—(*a*) Concentrated sulphuric acid (6 c.c.) was added in small portions to a cooled solution of *threo*-6 : 7-dihydroxydodecanedioic acid (5·0 g.) in hydrogen bromide–acetic acid (61 c.c.; 20% w/v). The mixture was kept at 20° for 42 hr., and then heated at 100° for 7½ hr. (after 4 hr. a further 6·5 c.c. of hydrogen bromide–acetic acid was added) and again cooled. Water was added, and the resulting precipitate was collected. Crystallisation from benzene gave erythro-6 : 7-*dibromododecanedioic acid* (6·0 g., 81%), m. p. 133—136° (Found : C, 37·15; H, 5·35; Br, 41·25. $C_{12}H_{20}O_4Br_2$ requires C, 37·15; H, 5·2; Br, 41·2%).

Azeotropic esterification of the dibromo-diacid (4·7 g.) gave the corresponding diethyl ester (4·95 g., 93%). A solution of this ester in alcohol (60·5 c.c.) was boiled under reflux and stirred vigorously for 1 hr. with activated zinc dust (12·1 g.) in an atmosphere of nitrogen. Filtration and isolation of the product with light petroleum (b. p. 60—80°) in the usual way gave *ethyl dodec*-trans-6-*enedioate* (2·5 g., 79%), b. p. 95—110°/0·1 mm., $n_D^{21·5}$ 1·4491 (Found : C, 67·45; H, 9·95. $C_{16}H_{28}O_4$ requires C, 67·55; H, 9·9%). Hydrolysis of the diester (2·4 g.) with aqueous-methanolic potassium hydroxide (*ca.* 10% w/v) in an atmosphere of nitrogen gave *dodec*-trans-6-*enedioic acid* (1·6 g., 83%), which crystallised from aqueous methanol as plates, m. p. 134—137° (Found : C, 63·05; H, 8·9. $C_{12}H_{20}O_4$ requires C, 63·15; H, 8·85%).

(*b*) By elaidinisation. Dodec-*cis*-6-enedioic acid (1·0 g.) was mixed with a solution of sodium nitrite (65 mg.) in water (0·25 c.c.), and the mixture was heated to 80°, whereupon it became homogeneous. Nitric acid (0·6 c.c.; 35% w/w) was added and the solution was stirred rapidly. After 1 min. the solution solidified and heating was discontinued. Crystallisation of the solid from benzene gave plates (318 mg.), m. p. 122—135°. Subsequent crystallisation from benzene, then from aqueous methanol, and finally from ethyl acetate, gave the diacid, m. p. 130—135°, not raised by further crystallisation (Found : C, 63·0; H, 9·0%).

Ethyl Dodec-6-*ynetetracarboxylate.*—1 : 10-Di-iododec-5-yne, prepared as described above from the dichloro-compound (25 g.), in absolute alcohol (80 c.c.) was added to a boiling and vigorously stirred solution of ethyl sodiomalonate (from 5·0 g. of sodium and 34·5 g. of ethyl malonate) in alcohol (85 c.c.). The mixture was stirred and heated under reflux for 15 hr. and then cooled and filtered. The filtrate was concentrated under reduced pressure and then poured into water. Isolation of the product with ether and distillation gave a liquid (5·0 g.), b. p. 170—205°/0·2 mm., n_D^{21} 1·4640, which contained iodine, and the *tetra-ester* (25 g., 50%), b. p. 155—165° (bath-temp.)/10^{-5} mm., n_D^{22} 1·4590 (Found : C, 63·05; H, 8·4. $C_{24}H_{38}O_8$ requires C, 63·4; H, 8·45%).

Tetradecanedioic Acid.—A solution of the tetra-ester (295 mg.) in ethyl acetate (16 c.c.) was shaken with Adams catalyst (26 mg.) in an atmosphere of hydrogen until absorption ceased (34·2 c.c. at 23°/772 mm., equiv. to 2·2 double bonds). After removal of the catalyst and solvent, the residue was hydrolysed with aqueous-methanolic potassium hydroxide, giving the tetra-acid. This was heated to 165° until the evolution of carbon dioxide was complete. Crystallisation of the residue (120 mg., 71%) from aqueous ethanol gave tetradecanedioic acid, m. p. and mixed m. p. 124—125·5° (Chuit, Boelsing, Hausser, and Malet, *Helv. Chim. Acta*, 1927, **10**, 113, give m. p. 124·8—125·4°).

Octadec-6-*ynoic Acid* (*Tariric Acid*).—Octanoic acid (7·2 g., 3 mols.; equiv., 144) and methyl hydrogen dodec-6-ynedioate (4·0 g., 1 mol.) were added to a solution of sodium methoxide (from *ca.* 30 mg. sodium) in methanol (25 c.c.). The solution was electrolysed in cell " A " (cf. Part X) (current 1·3—1·5 amp.; faradays passed *ca.* 1·25 times theoretical), the temperature of the electrolyte being kept below 50°. Towards the end of the reaction, when the current began to drop, a further quantity of octanoic acid (2·4 g., 1 mol.) was added and the electrolysis was continued until the electrolyte became slightly akaline. The cell contents were then acidified with 2N-hydrochloric acid, and the solvent was removed under reduced pressure. The residue, in ether, was washed with 0·5N-sodium hydroxide, and water, and then dried ($MgSO_4$). Distillation gave tetradecane (3·4 g., 51%), b. p. 60—64°/3 × 10^{-3} mm., n_D^{24} 1·4310, and a mixture of esters (2·4 g.), b. p. 132—156°/3 × 10^{-3} mm., n_D^{25} 1·4462—1·4558. Hydrolysis of the latter with aqueous-alcoholic potassium hydroxide (10%) gave the crude acid, which after crystallisation from light petroleum (b. p. 40—60°) and from aqueous alcohol yielded octadec-6-ynoic acid as needles (1·1 g.), m. p. 50·0—50·5° (corr.) (for tariric acid, Arnaud, *Compt. rend.*, 1892, **114**, 79, and Steger and van Loon, *Rec. Trav. chim.*, 1933, **52**, 593, give m. p. 50·5°) (Found: C, 76·8; H, 11·55%; equiv., 279. Calc. for $C_{18}H_{32}O_2$: C, 77·1; H, 11·5%; equiv., 280). The hydrogen no. was 143, equiv. to 1·95 double bonds. The di-iodide, prepared by the method of Arnaud and Posternak (*Compt. rend.*, 1909, **149**, 220), crystallised from glacial acetic acid in clusters of needles (37%), m. p. 37—38°, containing solvent of crystallisation (Lumb and Smith, *J.*, 1952, 5032, give m. p. 37—38°). By keeping the product under reduced pressure over potassium hydroxide the solvent-free di-iodide was obtained and had m. p. 47—48° (Arnaud and Posternak, *loc. cit.*, give m. p. 48·5°).

Electrolysis of the half-ester (8·5 g.) in methanol (30 c.c.) was accompanied by the deposition on the electrodes of large amounts of polymeric material. Isolation of the product in the usual way gave *docosa*-6 : 16-*diynedioic acid* which crystallised from aqueous methanol in plates (54 mg.), m. p. 102—104° (Found: C, 73·2; H, 9·6. $C_{22}H_{34}O_4$ requires C, 72·9; H, 9·45%). The diacid (8·821 mg.) in acetic acid was shaken in hydrogen with Adams catalyst until absorption was complete (2·038 c.c. at N.T.P., equiv. to 3·75 double bonds). Removal of catalyst and solvent, and crystallisation of the residue from alcohol, gave docosanedioic acid, m. p. 124·5—125·5°, undepressed on admixture with an authentic specimen.

*Octadec-*cis*-6-enoic Acid* (*Petroselinic Acid*).—A solution of octadec-6-ynoic acid (253 mg.) in ethyl acetate (25 c.c.) and quinoline (103 mg.) was shaken in hydrogen in the presence of a lead-poisoned palladium-on-calcium carbonate catalyst (255 mg.; Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446) until absorption ceased (20 c.c. at 18°/758 mm.; 0·93 mol.). The catalyst was removed by filtration through kieselguhr, and the filtrate was washed with 2N-hydrochloric acid (to remove quinoline), and then dried ($MgSO_4$). Removal of the solvent under reduced pressure and crystallisation of the residue from light petroleum (b. p. 60—80°) and from aqueous alcohol, gave octadec-*cis*-6-enoic (121 mg.), m. p. 28·7—29·4° (corr.), raised by further crystallisation to 29·0—29·5°. A mixture with a specimen of natural petroselinic acid, m. p. 28·4—28·8° (kindly supplied by Dr. J. H. Skellon), from parsley oil had m. p. 28·6—29·0° (van Loon, *Rec. Trav. chim.*, 1927, **46**, 492, gives m. p. 29·4°).

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