982. *Higher Aliphatic Compounds. Part X.* A Synthesis of Tariric and Petroselinic Acids.*

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The naturally occurring acetylenic acid, tariric acid, has been synthesised. Partial reduction of the synthetic acid yields *cis*-octadec-6-enoic acid,† identical with the petroselinic acid of parsley seed oil.

Tariric acid, the glyceride of which forms up to 90% of the fat of seeds from *Picramnia Sow* (Steger and Van Loon, *Rec. Trav. chim.*, 1933, **52**, 593), was shown by Arnaud (*Compt. rend.*, 1892, **114**, 79; 1896, **122**, 100; 1902, **134**, 473) to be an acetylenic compound, octadec-6-ynoic acid. This acid has now been synthesised by using the reaction between tridecynyllithium and 1-chloro-3-iodopropane to yield 1-chlorohexadec-4-yne which, after conversion into 1-iodohexadec-4-yne gives, by the malonic ester synthesis, solid hexadec-4-ynylmalonic acid. The octadec-6-ynoic acid † which is formed on decarboxylation agrees in properties with, and gives derivatives identical with those recorded for, natural tariric acid.

Partial reduction of the sodium salt with hydrogen and Raney nickel gave *cis*-octadec-6-enoic acid, identical with petroselinic acid, the glyceride of which forms up to 75% of the fat of parsley seed oil (and the oils of other *Umbelliferae*).

It is interesting that after Ahmad, Bumpus, and Strong (*J. Amer. Chem. Soc.*, 1948, **70**, 3391) had synthesised vaccenic (*trans*-octadec-11-enoic) acid from 1-chloro-9-iodononane and octynylsodium (followed by the cyanide synthesis and partial reduction of the octadec-11-ynoic acid), Taylor and Strong (*ibid.*, 1950, **72**, 4263) failed to obtain petroselinic acid by

* A Synthesis of Hydnocarpic Acid (Diaper and Smith, *Biochem. J.*, 1948, **42**, 581) is to be regarded as Part IX of this series; Part VIII, *J.*, 1939, 974.

† Geneva nomenclature ($CO_2H = 1$).

the route through tridec-1-yne and chloroiodobutane. They concluded that the condensation would proceed satisfactorily to give $CH_3{\cdot}[CH_2]_m{\cdot}C{:}C{\cdot}[CH_2]_n{\cdot}Cl$ where $m<10$ and n may vary from 3 to at least 9. Huber (*ibid.*, 1951, **73**, 2730) prepared octadecynoic and octadecenoic acids within these limits, which exclude petroselinic acid, where $m = 10$ and $n = 4$.

It seemed that the use of the lithium instead of the sodium salt of the acetylene (tridec-1-yne) might lead to the desired reaction with 1-chloro-3-iodopropane, and the product would then react with ethyl sodiomalonate. Although we failed to prepare tridecynyl-lithium satisfactorily in liquid ammonia solution and to condense it with 1-chloro-3-iodopropane in the same solvent, the lithium salt was obtained in dioxan from the reaction between lithium metal and di(tridecynyl)mercury (cf. Elsner and Paul, *J.*, 1951, 893). When this solution of the lithium salt was condensed with 1-chloro-3-iodopropane a 67% yield of crude 1-chlorohexadec-4-yne resulted.

As a derivative of tariric acid Arnaud and Posternak (*Compt. rend.*, 1909, **149**, 220) prepared the di-iodide, m. p. 48·5°. In the present investigation this derivative was found to be very soluble in ethanol. When crystallised from acetic acid it formed clusters of needles which, however, melted at 37° and were found to contain 1 mol. of acetic acid of crystallisation. After elimination of the acetic acid the remaining halide had m. p. 47—48°.

The synthetic tariric acid on ozonolysis gave adipic and lauric acids, showing the 6-position of the triple bond.

Experimental

1-Chloro-3-iodopropane.—1 : 3-Dichloropropane (49 g., 1 mol.; b. p. 122—123°/753 mm.; n_D^{25} 1·4660) was mixed with acetone (170 c.c.) in a 2-l. flask with a mercury-seal stirrer, dropping funnel, and reflux condenser. During 3 hours sodium iodide (65 g., 1 mol.) in acetone (520 c.c.) was added with heating and stirring; the mixture was refluxed for a further 5 hours, with stirring to prevent bumping. The crude, olive-green product (95 g.), on distillation through a 15-cm. Fenske column, gave fractions (i), b. p. 121—122°/750 mm. (12 g.), 1 : 3-dichloropropane, (ii), b. p. 74°/35 mm., n_D^{20} 1·5472 (39 g.), 1-chloro-3-iodopropane, and (iii), b. p. 111—113°/31 mm. (28 g.), 1 : 3-di-iodopropane. B.P. 581,899 (29/10/1946) (I.C.I. Ltd.) records n_D^{20} 1·5472 for 1-chloro-3-iodopropane.

1-Bromoundecane.—Ethyl undecanoate (from ethyl undecenoate, hydrogen, and Raney nickel) gave, by reduction with sodium and ethanol, 82—87% yields of undecanol, b. p. 140—141°/21 mm., n_D^{20} 1·4403. The bromide, b. p. 137—138°/18 mm., n_D^{20} 1·4576, was obtained in 90% yields (*Org. Synth.*, Coll. Vol. I, 1944, p. 29).

Tridec-1-yne.—Following Elsner and Paul (*loc. cit.*), 1-bromoundecane (46·7 g., 1 mol.) was introduced into a steel autoclave which had been cooled with liquid air, and the solution of sodium acetylide added (from sodium, 6·93 g., 1 g.-atom, in ammonia and excess of dry acetylene). After 20 hours' shaking at room temperature the mixture yielded tridec-1-yne (30·0 g., 84%), b. p. 118·5°/18·5 mm., f. p. 1°, n_D^{20} 1·4374. Elsner and Paul (*loc. cit.*) give m. p. 2·5°, n_D^{20} 1·4374.

1-Chloro- and 1-Iodo-hexadec-4-yne.—Attempts to condense tridec-1-yne with 1-chloro-3-iodopropane under the following conditions failed: (*a*) A suspension of lithamide in liquid ammonia was shaken in an autoclave with tridec-1-yne and the halide: 92% of the tridecyne was recovered. (*b*) A suspension of lithamide in liquid ammonia was stirred with tridecyne and ether; to the resulting solution of tridecynyl-lithium the halide was added and the mixture stirred for 4 hours: this gave a 61% recovery of the acetylene and a 26% yield of crude 1-chlorohexadec-4-yne. (*c*) Tridecyne was refluxed with lithamide in dioxan (m. p. 12°), and the resulting tridecynyl-lithium allowed to react for 3 hours with 1-chloro-3-iodopropane: 84% of the halide and of the acetylene were recovered.

The following procedure was successful: By the method of Johnson and McEwen (*J. Amer. Chem. Soc.*, 1926, **48**, 469) the acetylene was converted in 87% yield into di(tridecynyl)-mercury of m. p. 87° [Elsner and Paul (*loc. cit.*) give m. p. 87—88°]. Lithium (1·0 g., 1·5 g.-atom, as thin foil) was stirred with a refluxing solution of di(tridecynyl)mercury (27 g., 1·0 mol.) in pure dioxan (400 g., m. p. 12°) under nitrogen. After 4 hours' refluxing the liquid was sucked through a glass-wool plug into a second flask. (From the residual lithium amalgam dilute hydrochloric acid liberated 9·23 g. of mercury, equiv. to 96% of the dialkynyl-mercury used.) To the clear solution of tridecynyl-lithium 1-chloro-3-iodopropane (21·1 g., 1·07 mol.) was added and the mixture stirred and refluxed continuously. After 24 hours the dioxan was distilled off (Dufton column), while the mixture was stirred vigorously to prevent bumping.

From the residual oily slurry there were obtained (by use of ether and water followed by distillation) a high-boiling, unsaturated oil containing both chlorine and iodine (b. p. 122—150°/0·1 mm., m. p. −7° to −5°, 22·1 g.) and a solid residue (2 g.). By the action of sodium iodide in acetone this oil was converted into 1-*iodohexadec*-4-*yne*, b. p. 142—150°/0·1 mm., m. p. −3° to −2° (22·6 g.). A specimen, crystallised twice from acetone at −20°, gave colourless plates, f. p. 0·8°, n_D^{25} 1·4929 (Found : I, 35·8. $C_{16}H_{29}I$ requires I, 36·5%). From the solid by-product mentioned above, extraction with acetone and recrystallisation from acetone (charcoal) gave feathery crystals, f. p. 34·8°, m. p. 35—36° (capillary tube), of *nonacosa*-12 : 17-*diyne* (Found : 86·9; H, 13·1. $C_{29}H_{52}$ requires C, 87·0; H, 13·0%).

Octadec-6-*ynoic* (*Tariric*) *Acid*.—A suspension of ethyl sodiomalonate (from malonic ester, 6·4 g., 1·6 mol., and sodium, 0·92 g., 1·6 atom) in a solution of 1-iodohexadec-4-yne (13·7 g., 1·0 mol.; m. p. −2°) in benzene (120 c.c.) was boiled for 5 hours. The ester, hydrolysed with alcoholic potassium hydroxide, gave 9·4 g. (74%) of the malonic acid, m. p. 82—84°, which was decarboxylated, without further purification, at 140—150°/20 mm. for 2·5 hours, and then for 15 minutes at 180° : the product solidified at 48°. After two crystallisations at 0° from light petroleum (b. p. 40—60°) the acid had m. p. 50—51° (yield 6·05 g., 77%) (Found : C, 77·0; H, 11·4. Calc. for $C_{18}H_{32}O_2$: C, 77·15; H, 11·4%). Steger and Van Loon (*Rec. Trav. chim.*, 1933, **52**, 593) found m. p. 50·5° for tariric acid extracted from seeds of the *Picramnia* species of Central America.

The di-iodide was prepared by the action of iodine (1·2 mol.) on an acetic acid solution of the acetylenic acid (1·0 mol.) for 4 hours at 55° (Arnaud and Posternak, *Compt. rend.*, 1909, **144**, 220). On cooling, this solution deposited clusters of needles, m. p. 37—37·5°, which were very soluble in ethanol and, after crystallisation from acetic acid, melted at 37—38°, unchanged by further crystallisation (Found : C, 40·7; H, 5·9; I, 42·6. $C_{18}H_{32}O_2I_2,CH_3{\cdot}CO_2H$ requires C, 40·4; H, 6·1; I, 42·75%). Above 40° the *solvate* lost acetic acid and, after a specimen had been heated to 50° and allowed to cool in a vacuum-desiccator (4 times), it assumed the m. p. 47—48·5° in agreement with Arnaud and Posternak's value (Found : C, 40·3; H, 5·9; I, 47·6. Calc. for $C_{18}H_{32}O_2I_2$: C, 40·4; H, 6·0; I, 47·6%).

Ozonolysis of Octadec-6-*ynoic Acid to Adipic and Lauric Acids*.—The synthetic acid (0·75 g.; m. p. 50—51°) in pure chloroform (15 c.c.) was ozonised at 0° for 2 hours. After most of the chloroform had been evaporated, water was added and the mixture left overnight. Light petroleum (b. p. 40—60°; 10 c.c.) and water (25 c.c.) were added and the products separated into water-soluble and light petroleum-soluble portions. The aqueous extracts gave 0·23 g. (59%) of crude adipic acid, m. p. 146·5—149·5° (*lit.*, 153°). The *p*-bromophenacyl ester (obtained in 62% yield) melted at 153—154·5°, alone or when mixed with an authentic specimen. From the light-petroleum extract of the ozonolysis product there was obtained a pale yellow solid containing peroxides (starch–iodide test). Oxidation of this with potassium permanganate (0·1 g.), sodium carbonate (0·25 g.), and warm water (15 c.c.) for 0·5 hour and then acidification gave an acid (0·5 g.), m. p. 36—38·5° (lauric acid melts at 44°) (*p*-bromophenacyl ester, m. p. 73—74°; mixed with a specimen of ester, m. p. 75°, from lauric acid of m. p. 44·2°, this melted at 73—74·5°.

Reduction of Octadec-6-*ynoic Acid. Octadecoic Acid* (cf. Collaud, *Helv. Chim. Acta*, 1943, **26**, 1065).—A solution of the acetylenic acid (1·00 g.) in ethanol was exactly neutralised with N-sodium hydroxide. On shaking with hydrogen at 1 atm. in presence of Raney nickel, 1 equiv. (82 c.c.) of hydrogen was absorbed at the rate of 2 c.c./min. The rate than fell to 0·5 c.c./min. and reduction was allowed to continue overnight. The product, twice crystallised from acetone, was obtained in 72% yield and melted at 69·8° alone, or at 69·8—70° when mixed with an authentic specimen of stearic acid, m. p. 70·3°.

cis-*Octadec*-6-*enoic* (*Petroselinic*) *Acid*.—A solution of the acetylenic acid (2·0 g.) in ethanol (5 c.c.) was made just alkaline to phenolphthalein with N-sodium hydroxide, and water (60 c.c.) was then added. The solution was shaken with hydrogen at approx. 1 atm. in presence of Raney nickel until 1 mol. of hydrogen (171 c.c., moist, at 16·5°/753 mm.) had been absorbed. On acidification and extraction with ether a solid (1·96 g.), mainly of m. p. 22—24°, was obtained. High-melting impurities were eliminated by dissolving the crude product (1·96 g.) in light petroleum (10 c.c.; b. p. 40—60°) and cooling the solution slowly to 0°. The colourless plates (0·23 g.; m. p. 23—48°; crop I) which formed probably contained acetylenic and stearic acids. At −15° the mother-liquor deposited crop II (1·24 g.; m. p. 25—27·5°); on evaporation of the mother-liquor a residue of m. p. 22—23° remained and, after crystallisation from acetone, melted at 25—26·5° (crop III; 0·2 g.). Systematic crystallisation of crops II and III from acetone gave 1·04 g. (50%) of *cis*-octadec-6-enoic acid, m. p. 28·5—29·2°. Hilditch and Jones

(*J. Soc. Chem. Ind.*, 1927, **46**, 174T) found m. p. 30° for petroselinic acid (from *Umbelliferae* species), and Van Loon (*Rec. Trav. chim.*, 1927, **46**, 492) recorded m. p. 29·4°. Two derivatives, petroselaidic acid and *erythro*-6 : 7-dihydroxystearic acid, were prepared.

trans-*Octadec*-6-*enoic* (*Petroselaidic*) *Acid.*—The *cis*-acid (0·6 g.; m. p. 29·2°), shaken at 30—40° for 5 minutes with nitric acid (30%) and a crystal of sodium nitrite, gave a solid product, but the mixture was set aside overnight. The product (0·6 g.) on crystallisation from acetone gave 0·3 g. (50%) of needles, m. p. 52—53° (Found : C, 76·7; H, 11·9. Calc. for $C_{18}H_{34}O_2$: C, 76·6; H, 12·1%). Steger and Van Loon (*ibid.*, 1927, **46**, 703) record petroselaidic acid as melting at 52·7°.

erythro-6 : 7-*Dihydroxyoctadecoic Acid.*—A solution of *cis*-octadec-6-enoic acid (0·5 g.; m. p. 28°) in aqueous potassium hydroxide (1%), cooled to 0°, was added to 1% potassium permanganate solution (50 c.c.) at 0°. After occasional shaking during 20 minutes the solution was decolorised by sulphur dioxide, and the precipitated acid collected. From the dried product, non-hydroxy-acids were eliminated by shaking with light petroleum; the portion insoluble in light petroleum, on recrystallisation from ether (30 c.c.), gave a white powder, m. p. 121·5° (0·36 g., 64%) (Found : C, 67·9; H, 11·3. Calc. for $C_{18}H_{36}O_4$: C, 68·3; H, 11·4%). Steger and Van Loon (*loc. cit.*, p. 703) give m. p. 122·2°.

threo-6 : 7-*Dihydroxyoctadecoic Acid.*—Hydroxylation of *trans*-octadec-6-enoic acid (0·15 g.; m. p. 52—53°) in sodium hydroxide solution at 10° with 1% potassium permanganate solution (12 c.c.) gave, after 20 minutes, a white solid on passage of sulphur dioxide. Warm light petroleum (b. p. 40—60°; 20 c.c.) extracted 0·09 g. of unchanged olefinic acid, m. p. 49—51°; the residue, crystallised from ether, gave fine needles, m. p. 116·5° (0·05 g.) (Found : C, 68·5; H, 11·7. Calc. for $C_{18}H_{36}O_4$: C, 68·3; H, 11·4%). Steger and Van Loon (*loc. cit.*, p. 703) give m. p. 117·2°.

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