590. *Higher Aliphatic Compounds. Part XI.* A Synthesis of* DL-*Ricinoleic Acid.*

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Methyl 12-hydroxyoctadec-*cis*-9-enoate has been synthesised from 8-chloro-oct-1-yne and shown to be identical with methyl DL-ricinoleate prepared from racemised " natural " D-ricinoleic acid. Hydrolysis of the ester completes the synthesis of DL-ricinoleic acid.

10-Hydroxyhexadec-8-ynoic acid was synthesised in the course of the investigation.

Ricinoleic acid, the chief acid of castor oil, was shown by Goldsobel [1] to be 12-hydroxyoctadec-9-enoic acid, and not 12-hydroxyoctadec-10-enoic acid as proposed by Krafft.[2] Oxidation at the double bond by modern methods [3] has confirmed the Goldsobel formula.

Total syntheses of DL-ricinoleic acid were briefly announced (Crombie and Jacklin; [4a] Kendall, Lumb, and Smith [5]) in August 1954 and by Gensler and Abrahams [6] in 1957. The present memoir gives details of the second of these syntheses.

The main obstacle to the synthesis has been the difficulty of building the $\cdot CH(OH)\cdot CH_2\cdot CH{:}CH\cdot$ system into the C_{18} chain. *n*-Heptaldehyde, one of the products of pyrolysis of ricinoleic acid, is an obvious starting material, but a Reformatsky reaction with 1-bromo-9-chloronon-2-yne (II) led mainly to a branched-chain product, an allene, (III) (cf. Wotiz [7]). The successful route involved a Grignard reaction between *n*-hexylmagnesium bromide and a βγ-olefinic aldehyde (VI).

From 1-chloro-6-iodohexane, by the acetylene synthesis,[8] the lithium derivative of 8-chloro-oct-1-yne (I) was prepared and, in a slow reaction with bromoacetaldehyde dimethyl acetal, gave 10-chloro-1 : 1-dimethoxydec-3-yne (IV). All methods of hydrolysing this acetal caused simultaneous hydration of the triple bond, but the corresponding *cis*-olefinic acetal (V) could be hydrolysed normally with aqueous tartaric acid. Reaction of the aldehyde (VI) with *n*-hexylmagnesium bromide gave the olefinic alcohol (VII) in which the chlorine could be exchanged for iodine. A malonic ester synthesis from the iodo-compound, followed by hydrolysis and decarboxylation, gave a gum which, esterified and fractionally distilled, gave a small yield of methyl DL-12-hydroxyoctadec-9-enoate, m. p. −17° to −15°, n_D^{20} 1·4631. Methyl DL-ricinoleate, prepared from the " natural " D-acid by racemisation at the CH(OH) group, melted at −13·5° and had n_D^{20} 1·4631; methyl

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* Part X, *J.*, 1952, 5032.

[1] Goldsobel, *Ber.*, 1894, **27**, 3121.

[2] Krafft, *Ber.*, 1888, **21**, 2730.

[3] Haller and Brochet, *Compt. rend.*, 1910, **150**, 496; Brady, *J. Amer. Chem. Soc.*, 1939, **61**, 3464; Scanlan and Swern, *ibid.*, 1940, **62**, 2309.

[4] Crombie and Jacklin, (*a*) *Chem. and Ind.*, 1954, 1197; (*b*) *J.*, 1955, 1740.

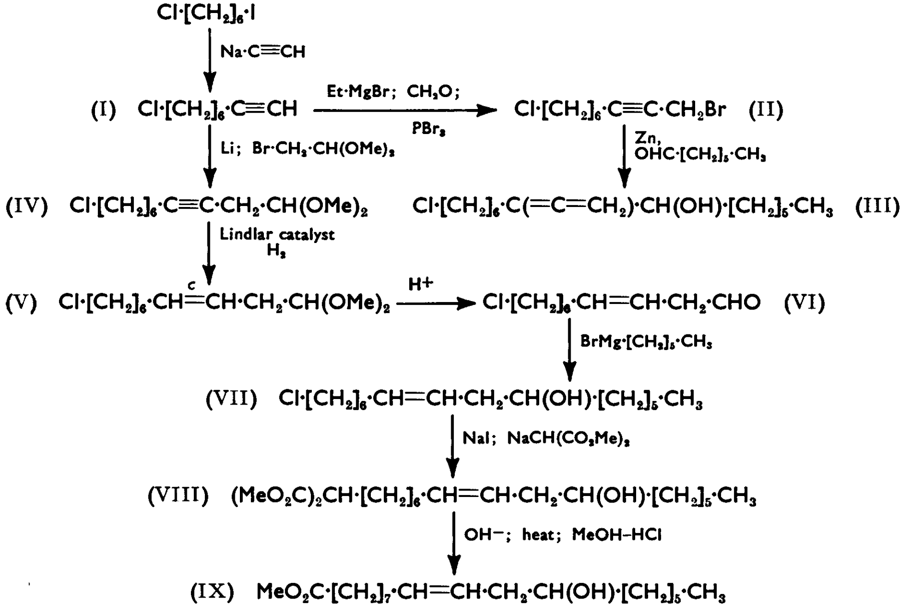
[5] Kendall, Lumb, and Smith, *Chem. and Ind.*, 1954, 1228.

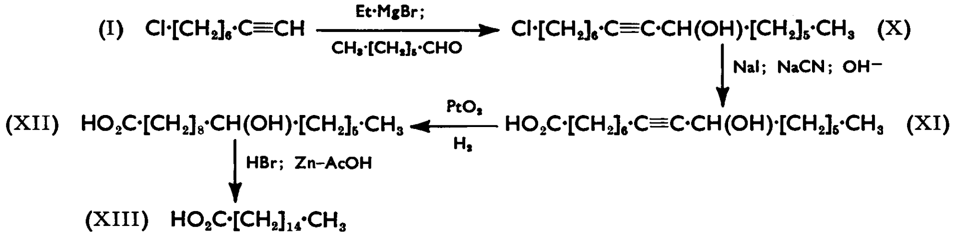
[6] Gensler and Abrahams, *ibid.*, 1957, 47.

[7] Wotiz, *J. Amer. Chem. Soc.*, 1951, **73**, 693.

[8] Ahmad, Bumpus, and Strong, *ibid.*, 1948, **70**, 3391.

D-ricinoleate melts [9] at −4°, with n_D^{20} 1·4629. In the infrared spectrum of the synthetic ester there was a weak band at 10·15 μ, due to some conjugated dienoic ester not completely removed by the fractional distillation. Otherwise there was identity of the spectra of synthetic and "natural" methyl ricinoleate. Hydrolysis of the synthetic DL-ester (refluxing for 2·5 hr. with methanolic potassium hydroxide) and distillation of the brownish product gave an acid of the expected carbon and hydrogen content. The infrared spectrum was identical with that of natural D-ricinoleic acid except for weak absorption at 10·1 μ, as with the synthetic methyl ester. The melting point was 3°, whereas the D-acid melts at 5°, with polymorphous forms (more difficult to obtain) of m. p.s 7° and 16—17°. Addition of the synthetic acid to twice its bulk of D-acid (m. p. 16—17°) gave a mixture of m. p. 16—17°, but there was insufficient material for further experiments. DL-Ricinoleic acid, m. p. 23—24·5°, was later obtained by racemisation of the D-acid *via* 12-oxo-octadec-9-enoic acid (Crombie and Jacklin [4b] give m. p. 23—24°; Gensler and Abrahams [6] give m. p. 22—24°). From this racemised acid the methyl ester was prepared: it melted, after low-temperature crystallisation, at −13·5°. On rapid hydrolysis with methanolic potassium hydroxide it gave back the DL-acid, melting (crude) at 15—17° and, after recrystallisation from ether–light petroleum, at 22·5—24·5°, thus completing the synthesis of DL-ricinoleic acid.





During the early stages of this work the reaction between the acetylenic Grignard reagent from 8-chloro-oct-1-yne (I) and *n*-heptaldehyde was investigated. The product,

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[9] Brown and Green, *J. Amer. Chem. Soc.*, 1940, **62**, 738.

1-chloropentadec-7-yn-9-ol (X), was converted by the cyanide synthesis into 10-hydroxyhexadec-8-ynoic acid (XI), which was shown [by reduction through 10-hydroxyhexadecanoic acid (XII) to palmitic acid (XIII)] to have a normal chain.

EXPERIMENTAL

1-*Chloro*-6-*iodohexane*.—Hexane-1 : 6-diol (m. p. 41°) was converted by thionyl chloride and pyridine into the dichloride (95%; b. p. 92°/18 mm., n_D^{20} 1·4570—1·4574) which with sodium iodide in acetone gave the chloroiodide (34%), b. p. 85°/2 mm., 61°/0·32 mm., n_D^{20} 1·5232—1·5238. Recovered dichloride was used again, so that finally a 50% conversion of diol into chloroiodide was achieved. Raphael and Sondheimer [10] give b. p. 73—74°/0·7 mm. and n_D^{24} 1·5248. Crombie and Jacklin [4b] give n_D^{21} 1·5234—1·5245.

8-Chloro-oct-1-yne, prepared by the interaction of 1-chloro-6-iodohexane and sodium acetylide in liquid ammonia, had b. p. 69—70°/10 mm., 87—88°/21 mm., n_D^{20} 1·4534—1·4542. Raphael and Sondheimer [10] give b. p. 73—76°/10 mm., n_D^{12} 1·4590. With alkaline potassium mercuri-iodide solution it gave spear-shaped crystals of the mercuric salt, m. p. 39—40°.

10-*Chloro*-1 : 1-*dimethoxydec*-3-*yne*.—To a suspension of lithamide (from 2·5 g. of lithium, 1·03 atom-equiv.) in liquid ammonia (800 ml.), a solution of 8-chloro-oct-1-yne (50 g., 1 mol.) in dry ether (125 ml.) was added during 1 hr., and stirring continued 4 hr. After most of the ammonia had evaporated (overnight) pure dioxan (350 ml.) was added and the mixture refluxed for 1 hr. while a slow current of nitrogen swept out the ammonia. Bromoacetaldehyde dimethyl acetal (72 g., 1·22 mol.) in dioxan (85 ml.) was added slowly with stirring; refluxing was continued for 30 hr. under nitrogen. After removal of most of the dioxan the solution was poured into water and the mixture extracted with ether (3 × 200 ml.). The extract, after filtration, was washed with water, dried ($MgSO_4$), and evaporated and the residue distilled rapidly (oil-pump). Redistillation through a Vigreux column gave 10-*chloro*-1 : 1-*dimethoxydec*-3-*yne* (24·5 g., 30%), b. p. 113°/0·5 mm., n_D^{20} 1·4677—1·4687 (Found : C, 61·6; H, 9·2; Cl, 14·8. $C_{12}H_{21}O_2Cl$ requires C, 61·9; H, 9·0; Cl, 15·2%). The corresponding *diethyl acetal*, made from di-(8-chloro-oct-1-ynyl) mercury *via* the lithium salt (cf. Lumb and Smith [11]) and reaction with bromoacetaldehyde diethylacetal in 33% yield, boiled at 106—110°/0·02 mm. and had n_D^{20} 1·4638 (Found : C, 64·3; H, 9·4; Cl, 13·4. $C_{14}H_{25}O_2Cl$ requires C, 64·4; H, 9·6; Cl, 13·6%). Hydrolysis of these acetals under a wide variety of conditions resulted in hydration of the triple bond : the products reacted with approx. 1½ mol. of 2 : 4-dinitrophenylhydrazine.

10-*Chloro*-1 : 1-*dimethoxydec*-3-*ene*.—A solution of the acetylenic chloride (3·75 g.) in purified light petroleum (b. p. 80—100°; 12 ml.) was shaken with Lindlar's [12] palladium–lead catalyst (0·5 g.) and hydrogen at 2 atm. After 2 hr. no more hydrogen was absorbed and, by distillation at 92—94°/0·3 mm., a viscous oily *ethylene* was obtained (average n_D^{20} 1·4631; yield 95%) (Found : C, 61·5; H, 9·75. $C_{12}H_{23}O_2Cl$ requires C, 61·4; H, 9·85%).

10-*Chlorodec*-3-*enal*.—10-Chloro-1 : 1-dimethoxydec-3-ene (2·0 g.), refluxed for 1 hr. with saturated aqueous tartaric acid (30 ml.),[13] gave an orange oil which, isolated with ether, boiled at 98°/0·7 mm. and had n_D^{20} 1·4764. The oil rapidly gave Schiff's test and yielded a 2 : 4-*dinitrophenylhydrazone*, orange-red needles (from methanol), m. p. 108·5° (Found : N, 14·9. $C_{16}H_{21}O_4N_4Cl$ requires N, 15·2%). The semicarbazone, recrystallised from aqueous ethanol, but not analysed, melted at 148°.

16-*Chlorohexadec*-9-*en*-7-*ol*.—A suspension of 10-chloro-1 : 1-dimethoxydec-3-ene in saturated aqueous tartaric acid was maintained for 30 min. near reflux temperature and stirred with a current of nitrogen. The mixture was then steam-distilled for 3 hr. under nitrogen and, when the distillate (at 600 ml.) no longer gave a positive Schiff's test within 30 sec., the oily aldehyde was extracted with ether, and the extract washed with water and dried ($MgSO_4$). After evaporation, finally by heating *in vacuo* (oil-pump), the residue (10 ml.) was added in dry ether (under nitrogen) to a solution of *n*-hexylmagnesium bromide (from 8·7 g. of *n*-hexyl bromide of n_D^{20} 1·4480, and 1·3 g. of magnesium in 50 ml. of dry ether). This mixture boiled during the addition and was heated under reflux for 1 hr. longer, then left for 12 hr., always under nitrogen. Worked up in the usual way it gave a sweet-smelling, yellow oil from which a main fraction (4·1 g.) of n_D^{20} 1·4709 and b. p. 124—152°/0·6 mm., was obtained. (The b. p. varied greatly with

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[10] Raphael and Sondheimer, *J.*, 1950, 2100.
[11] Lumb and Smith, *J.*, 1952, 5032.
[12] Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.
[13] Fischer and Löwenberg, *Annalen*, 1932, **494**, 272.

the rate of distillation.) A viscous residue (2·9 g.) remained. Redistillation gave 3·3 g. of b. p. 126—148°, with constant n_D^{20} 1·4710. The yield was 30%, calculated on the acetal (Found : C, 70·0; H, 11·1; Cl, 12·75. $C_{16}H_{31}OCl$ requires C, 70·0; H, 11·3; Cl, 12·9%). Refluxing two batches of this *chlorohexadecenol* with sodium iodide in acetone and working up in the usual way gave the crude iodo-analogue.

Dimethyl 10-*Hydroxyhexadec*-7-*enylmalonate*.—A solution of dimethyl malonate (3·9 g., 1·6 mol.; n_D^{20} 1·4138) in pure benzene (40 ml.) was added to a suspension of powdered sodium (0·53 g., 1·3 g.-atom) in benzene (10 ml.) and the mixture refluxed for 4 hr. under nitrogen. 16-Iodohexadec-9-en-7-ol (6·4 g., 1·0 mol.; n_D^{20} 1·5052) in pure benzene (20 ml.) was added and boiling continued for 20 hr. under nitrogen. The resulting dimethyl ester was an oil (6·3 g.), b. p. 160—170°/0·1 mm., n_D^{20} 1·4739, containing a trace of halogen.

Methyl DL-*Ricinoleate*.—The dimethyl hydroxyhexadecenylmalonate, without purification, was hydrolysed by being kept for 24 hr. in 3% methanolic potassium hydroxide (40 ml.). Decarboxylation of the product at 120—160° in a vacuum left a gum (4 g.) which was esterified (to allow distillation) by refluxing for 24 hr. in methanol (50 ml. containing 1 g. of hydrogen chloride). The ester (4 g.) was distilled rapidly in small batches at 0·005 mm., and then redistilled through a micro-Vigreux column. The main fraction, b. p. 157—160°/0·005 mm., had n_D^{20} 1·4632 (Found : C, 73·0; H, 11·2. Calc. for methyl ricinoleate, $C_{19}H_{36}O_3$: C, 73·1; H, 11·5%). This oil froze at −20° and melted at −17° to −15° (wrongly given as −7° to −5° in ref. 5). As methyl DL-ricinoleate, from racemised D-ricinoleic acid, was not at the time available, the synthetic DL-ester was compared with the "natural" D-ester. Addition of a small amount of the D-ester (m. p. −4°) to the synthetic ester changed the m. p. to −16° to −14°. The refractive indices of the esters were n_D^{20} 1·4631 (synthetic) and 1·4629 (natural); the infrared spectra were superposable, except for slight absorption at 10·15 μ in the synthetic ester. Methyl DL-ricinoleate, prepared from racemised ricinoleic acid, had m. p. −13·5° and n_D^{20} 1·4631. Hydrolysis of the synthetic methyl DL-ricinoleate (0·26 g.) by refluxing 6% methanolic potassium hydroxide (2 ml.) for 2½ hr. caused some darkening. The resulting acid distilled at approx. 180°/0·005 mm. (Found: C, 72·6; H, 11·1. Calc. for $C_{18}H_{34}O_3$: C, 72·5; H, 11·4%). Apart from a weak band at 10·1 μ (probably due to dienoic acid, as indicated also by the slightly high refractive index, 1·4728, instead of 1·4717) the infrared spectrum was identical with that of the D-acid. The m. p. was 3° and, in the expectation that the substance could exist in a high-melting polymorphous form, one drop of the synthetic acid was mixed with a partly molten specimen of the β-form (m. p. 16—17°) of D-ricinoleic acid. After the mixture had been stirred and cooled it melted at 16—17°. Unfortunately there was insufficient material left for recrystallisation : it should have been possible to raise the m. p. of the synthetic acid to 23°. As the following experiments show, a "relay" was provided by converting natural D-ricinoleic acid into the DL-acid and this into methyl DL-ricinoleate. The ester was then successfully hydrolysed.

D-*Ricinoleic Acid*.—The commercial ricinoleic acid, from castor oil, was converted into methyl acetylricinoleate by Rider's procedure,[14] and the fraction of b. p. 180—185°/0·3 mm., n_D^{20} 1·4549, accepted.

This ester (87 g.) in a mixture of potassium hydroxide (56 g.), water (25 ml.), and methanol (250 ml.) gave, after 10 minutes' refluxing, orange-coloured ricinoleic acid (72 g., 96%), m. p. 5—7°, n_D^{20} 1·4720. Recrystallised from acetone at −50° it yielded colourless D-ricinoleic acid, n_D^{20} 1·4717, m. p. 5° (γ-form), 7—8° (α-) and, after prolonged stirring at 7°, m. p. 16—17° (β-). Hawke [15] gives m. p.s 5·0°, 7·7°, and 16·0° respectively. The acid, in small batches, could be distilled, b. p. 180°/0·005 mm. (approx.), and the distillate had n_D^{20} 1·4718. Refluxing the pure acid for 10 hr. with methanol and hydrogen chloride gave the methyl ester which, recrystallised from acetone at −50°, melted at −4° and had n_D^{20} 1·4629. Brown and Green [9] give m. p. −4°.

DL-*Ricinoleic Acid and Methyl* DL-*Ricinoleate from* D-*Ricinoleic Acid*, via *the Keto-acid*.—Purified D-ricinoleic acid (60 g., n_D^{20} 1·4720; 1 mol.) in acetic acid (150 ml.) was oxidised at 14—15° with chromium trioxide (14·5 g., 0·7 mol.) in water (10 ml.) and acetic acid (100 ml.), following Ellis's procedure.[16] The product, recrystallised from 80% ethanol and then from light petroleum (b. p. 40—60°), formed prisms (7 g.; m. p. 38—39°; rapidly oxidising in the air). Crombie and Jacklin [4b] give m. p. 38—39·5°; Ellis [16] gives m. p. 39°. To a solution of

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[14] Rider, *J. Amer. Chem. Soc.*, 1931, **53**, 4130.

[15] Hawke, *J. S. African Chem. Inst.*, 1949, **2**, 1 and 125.

[16] Ellis, *J.*, 1950, 9.

potassium borohydride (2·0 g.) in methanol (200 ml.) at 5° the keto-acid (7 g.) in methanol (70 ml.) was added gradually. After 2 hr. a further 2·0 g. of potassium borohydride were added and the temperature was kept for 2 hr. at 16°. Acidification with cold hydrochloric acid yielded an oil which slowly crystallised. Recrystallisation from a mixture of ether–light petroleum at –30° gave DL-ricinoleic acid, m. p. 23—24·5°, n_D^{20} (supercooled) 1·4716, n_D^{25} 1·4702. Crombie and Jacklin[4b] give m. p. 23—24°, n_D^{19} 1·4723; Gensler and Abrahams[6] give m. p. 22—24°, n_D^{25} 1·4702.

The pure DL-acid (6·3 g.), refluxed with 3% methanolic hydrogen chloride for 24 hr., gave 5·85 g. of ester, b. p. 166°/0·1 mm., m. p. –15° to –14°. Two recrystallisations at –50° from acetone gave a product, m. p. –13·5°, n_D^{20} 1·4631 (Found: C, 73·55, 72·8; H, 11·5, 11·3. Calc. for $C_{19}H_{36}O_3$: C, 73·1; H, 11·5%).

Hydrolysis. To a solution of potassium hydroxide (1·5 g.) in water (1 ml.) and methanol (4 ml.), methyl DL-ricinoleate (2 g.) in methanol (3 ml.) was added and the mixture refluxed for 6 min. The cooled mixture was added to water and the pale yellow acid (m. p. 16—19°) isolated by ether-extraction. Recrystallisation from ether–light petroleum at –30° gave colourless plates of the DL-acid, m. p. 22·5—24·5°.

Reformatsky Reaction with 1-*Bromo*-9-*chloronon*-2-*yne*.—9-*Chloronon*-2-*yn*-1-*ol*. A filtered solution of ethylmagnesium bromide (from 5·2 g. of magnesium and 27 g. of ethyl bromide) was added gradually to a stirred solution of 8-chloro-oct-1-yne (29 g.) in ether (100 ml.). Ethane was evolved and the mixture was refluxed for 2 hr.; it was then cooled to 0° and a slow stream of dry formaldehyde (16 g.) and nitrogen was passed in. After 3 hr. at 0° the mixture was left overnight; it gave, as main product, the *alcohol* (19·9 g., 66%), b. p. 113°/1 mm., n_D^{20} 1·4760 (Found: C, 61·4; H, 8·8; Cl, 20·1. $C_9H_{15}OCl$ requires C, 61·8; H, 8·7; Cl, 20·3%) (cf. Lai[17]). Oxidation in light petroleum with fresh, dry manganese dioxide gave the corresponding aldehyde, which yielded a *semicarbazone* crystallising from aqueous alcohol in plates, m. p. 88° (Found: C, 51·9; H, 6·7; Cl, 15·4. $C_{10}H_{16}ON_3Cl$ requires C, 52·2; H, 7·0; Cl, 15·4%).

1-*Bromo*-9-*chloronon*-2-*yne*. 9-Chloronon-2-yn-1-ol (15·0 g.), dry pyridine (1 ml.) and dry ether (15 ml.) were stirred and cooled in ice-salt while phosphorus tribromide (11·7 g.) in dry ether (7 ml.) was run in during 1 hr.; the mixture was then heated for 2 hr. on a steam-bath. The *product*, a yellow oil, gave a main fraction (15·4 g., 75%), b. p. 99—102·5°/0·5 mm., n_D^{20} 1·5089 (Found: C, 45·7; H, 5·86; Cl + Br, 47·6. $C_9H_{14}BrCl$ requires C, 45·6; H, 5·9; Cl + Br, 48·7%).

Reformatsky Reaction with n-*Heptaldehyde* (cf. Zeile and Meyer[18]).—The exothermic reaction between 1-bromo-9-chloronon-2-yne, zinc wool, and *n*-heptaldehyde in benzene at the b. p., yielded, as main fraction, an *alcohol*, b. p. 130—134°/0·02 mm., n_D^{20} 1·4807, which did not solidify even at –70° (Found: C, 69·4; H, 10·8; Cl, 12·9. $C_{16}H_{29}OCl$ requires C, 70·3; H, 10·7; Cl, 13·0%). Exchange of chlorine for iodine followed by a malonic ester synthesis, hydrolysis, and decarboxylation yielded an acid which did not solidify. (DL-Ricinstearolic acid, the expected product, melts at 51—52°.[4b]) This acid was reduced only slowly with Raney W7 nickel[19] and hydrogen. (12-Hydroxystearic acid, m. p. 79°,[20] was not detected.) As the infrared spectrum showed strong absorption at 5·1 μ and medium absorption at 11·8 μ it was obvious that an allene was present.

Synthesis of 10-*Hydroxyhexadec*-8-*ynoic Acid*.—15-*Chloropentadec*-8-*yn*-7-*ol*. The solution of ethylmagnesium bromide obtained from ethyl bromide (15·3 g., 1·4 mol.) and magnesium (3·25 g., 1·35 g.-atom) in pure ether (75 ml.) was filtered into a dropping funnel and transferred to a flask fitted with stirrer, reflux condenser, and a nitrogen inlet. 8-Chloro-oct-1-yne (14·5 g., 1 mol.) in ether (25 ml.) was added and the stirred mixture refluxed for 2 hr. Freshly distilled *n*-heptaldehyde (16 g., 1·4 mol.; b. p. 53·5—54·5°/20 mm.) in ether (50 ml.) was run in during 40 min., the mixture being stirred for 5 hr. at 0°. After 12 hr. at room temperature the mixture was decomposed with ammonium chloride solution, yielding an oil (31·7 g.). Distillation through a 10-cm. Vigreux column gave a main fraction (19·9 g.) of b. p. 132—134°/0·02 mm., n_D^{20} 1·4735. By redistillation an *alcohol* of b. p. 128—129°/0·01 mm., n_D^{20} 1·4737, m. p. –3° to –1·5°, was obtained (Found: C, 69·5; H, 10·4; Cl, 13·8. $C_{15}H_{27}OCl$ requires C, 69·6; H, 10·5; Cl, 13·7%).

[17] Lai, *Bull. Soc. chim. France*, 1933, **53**, 682.

[18] Zeile and Meyer, *Ber*, 1942, **75**, 356.

[19] Billica and Adkins, *Org. Synth.*, 1942, **29**, 24.

[20] Tomecko and Adams, *J. Amer. Chem. Soc.*, 1927, **49**, 527.

10-*Hydroxyhexadec*-8-*ynoic acid.* The foregoing chloride and sodium iodide in acetone gave the iodo-compound (13 g.) which was refluxed in ethanol (30 ml.) with sodium cyanide (5 g.) in water (7 ml.) for 48 hr. under nitrogen. The crude nitrile (9·3 g.) was refluxed with potassium hydroxide (10 g.), water (15 ml.), and ethanol (100 ml.) for 48 hr. under nitrogen. From the waxy, acidic product low-temperature crystallisation from acetone gave slow-growing crystals of acetylenic *acid*, m. p. 35° (Found: C, 71·4; H, 10·15. $C_{16}H_{28}O_3$ requires C, 71·6; H, 10·45%), and the p-*bromophenacyl ester*, recrystallised from aqueous ethanol, melted at 66° (Found: C, 62·0; H, 7·1; Br, 17·35. $C_{24}H_{33}O_4Br$ requires C, 61·9; H, 7·1; Br, 17·2%).

10-*Hydroxyhexadecanoic acid.* 10-Hydroxyhexadec-8-ynoic acid (1·12 g.) in ethanol (100 ml.), shaken with Adams catalyst (0·1 g.) and hydrogen (5 atm.) for 3 hr., gave the saturated *acid* (1·10 g.) which, recrystallised from benzene, melted at 71—72° (Found: C, 71·0; H, 11·8. $C_{16}H_{32}O_3$ requires C, 70·6; H, 11·8%). The p-*bromophenacyl ester*, glistening plates from aqueous alcohol, melted at 98—99° (Found: C, 61·1; H, 7·95; Br, 17·4. $C_{24}H_{37}O_4Br$ requires C, 61·3; H, 7·9; Br, 17·1%).

This acid (0·5 g.) was heated for 3 hr. under reflux with hydrobromic acid (5 ml.; *d* 1·5) and sulphuric acid. The oily bromo-acid, isolated by dilution and then extraction with ether, was dissolved in acetic acid (15 ml.), and zinc dust was added in small portions during 8 hr. After dilution with water and extraction with ether the mixture yielded a waxy solid which, recrystallised at 0° from light petroleum (b. p. 60—80°), formed plates (0·1 g.) of m. p. 61·5—61·8°. Addition of pure palmitic acid, m. p. 63·0°, gave a mixture of m. p. 62—63°.

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