

to moderate the exothermic reaction and then warmed at 40° for 20 hr., more formic acid (10 c.c.) and hydrogen peroxide (2.5 c.c.) being added after 2 hr. The gum obtained by evaporation *in vacuo* was refluxed for 4 hr. with ethanol (100 c.c.) and 5*N*-sodium hydroxide (100 c.c.). Acidification, followed by isolation with ethyl acetate, gave the *dihydroxy-acid*, plates, m. p. 99—100° (from ethyl acetate) (Found: C, 69.6; H, 10.0. C₁₆H₃₄O₄ requires C, 69.9; H, 10.5%).

8-Bromo-octanoic Acid.—6-Bromohexan-1-ol⁶ (181 g., 1 mol.) was added to sodiomalonic ester (1.2 mol.) in ethanol (500 c.c.) and the mixture was refluxed for 6 hr. After removal of most of the solvent by distillation, dilute sulphuric acid was added and the product isolated in benzene. The solvent-free oil was slowly distilled with acetic acid (200 c.c.) and 48% hydrobromic acid (200 c.c.) for 4 hr.; 20*N*-sulphuric acid (20 c.c.) was added and the mixture was refluxed until decarboxylation was complete. 48% Hydrobromic acid (250 c.c.) and concentrated sulphuric acid (75 c.c.) were added and the mixture was heated at 110° (internal) for a further 7 hr. After addition of water (1250 c.c.) and repeated extraction with carbon tetrachloride, the combined organic layers were washed with 2*N*-sodium acetate and water, dried (Na₂SO₄) and distilled. The bromo-acid (151 g., 68%), b. p. 149—153°/1.5 mm., had m. p. 34—36°. Chuit and Hausser⁷ gave m. p. 38.5—39°.

8-Bromo-*NN*-dimethyloctanamide.—The bromo-acid (151 g.) was warmed with thionyl chloride (180 c.c.) at 30° for 1 hr. and then at 100° for 2 hr. After removal of excess of thionyl chloride, dimethylamine was passed into an ice-cooled, stirred solution of the acid chloride in ether (200 c.c.) until the exothermic reaction ceased. The mixture was washed with water, 2*N*-sulphuric acid, 2*N*-sodium carbonate, and water, dried (Na₂SO₄), and evaporated. The *amide* was a yellow oil (142 g.), b. p. 133—136°/0.8 mm., *n*_D²⁰ 1.4920 (Found: C, 48.0; H, 8.1; N, 5.2. C₁₀H₂₀BrNO requires C, 48.0; H, 8.0; N, 5.6%).

***NN*-Dimethyldec-9-ynamide.**—Acetylene was passed into a stirred suspension of sodamide (25 g.) in liquid ammonia (700 c.c.) and tetrahydrofuran (700 c.c.) for 1.5 hr. The bromo-amide (122 g.) in tetrahydrofuran (250 c.c.) was added and the mixture was refluxed for 5 hr. and then allowed to evaporate. Addition of water and isolation with ether yielded the acetylenic *amide* which was distilled through a short Fenske column. This product (79 g.) had b. p. 103—105°/0.15 mm. and solidified as large prisms, f. p. 25° (thermometer in liquid) (Found: C, 74.1; H, 11.2; N, 7.0. C₁₂H₂₁NO requires C, 73.8; H, 10.8; N, 7.2%).

trans-*NN*-Dimethyloctadec-12-en-9-ynamide.—*NN*-Dimethyldec-9-ynamide (25.4 g.) in dry tetrahydrofuran (150 c.c.) was added to a stirred suspension of sodamide (5.1 g.) in liquid ammonia (250 c.c.). After 1 hr., oct-2-enyl bromide (32.9 g.) in tetrahydrofuran (50 c.c.) was added and the mixture was stirred under reflux for 5 hr. When the ammonia had evaporated, the product was isolated in the usual manner. The *enynamide* (20 g.) distilled as a pale yellow oil, b. p. 175—177°/0.15 mm., *n*_D²⁰ 1.4812 (Found: C, 78.2; H, 11.6; N, 4.3. C₂₀H₃₅NO requires C, 78.6; H, 11.5; N, 4.6%).

erythro-12,13-Dihydroxyoctadec-9-ynoic Acid.—The enynamide (50.5 g.) in chloroform (190 c.c.) was treated with 380 c.c. of 0.52*M*-perbenzoic acid in chloroform at 0°. After 18 hr., 1 mol. of per-acid had been consumed; the solution was washed with 2*N*-sodium carbonate and water and evaporated. After the addition of 98% formic acid (100 c.c.) the solution was refluxed for 1 hr. and then evaporated *in vacuo*. The residual oil was refluxed with potassium hydroxide (60 g.) in water (60 c.c.) and 2-methoxyethanol (600 c.c.) under nitrogen for 14 hr. Water (100 c.c.) was added and solvent (350 c.c.) was removed by distillation. The hot solution was acidified with acetic acid and then poured into ice-dilute sulphuric acid. erythro-12,13-Dihydroxyoctadec-9-ynoic acid (20 g.), prisms, m. p. 93.5—94.5°, was obtained by filtration and recrystallisation from methanol (Found: C, 69.0; H, 10.7. C₁₈H₃₂O₄ requires C, 69.2; H, 10.3%).

erythro-12,13-Dihydroxyoctadecanoic Acid.—The acetylenic acid (250 mg.) in ethanol (50 c.c.) was hydrogenated over 5% palladised charcoal (100 mg.). Filtration and evaporation gave the dihydroxy-acid, prisms (from methanol), m. p. 117—118° (Found: C, 68.5; H, 11.3. Calc. for C₁₈H₃₆O₄: C, 68.3; H, 11.5%). Huber² gives m. p. 119—120°

erythro-cis-12,13-Dihydroxyoctadec-9-enoic Acid.—erythro-12,13-Dihydroxyoctadec-9-ynoic acid (4.0 g.) in methanol (80 c.c.) was hydrogenated over 5% palladised barium sulphate (0.2 g.) in the presence of quinoline (0.2 g.).³ The rate of absorption fell sharply when about 0.98 mol. of hydrogen had been taken up; hydrogenation was then interrupted and the filtered

⁶ Degering and Boatright, *J. Amer. Chem. Soc.*, 1950, **72**, 5137.

⁷ Chuit and Hausser, *Helv. Chim. Acta*, 1929, **12**, 466.

solution was evaporated. Recrystallisation from methanol gave erythro-cis-12,13-dihydroxy-octadec-9-enoic acid (3.1 g.), prisms, m. p. 76—77.5° (Found: C, 69.1; H, 11.0. $C_{18}H_{34}O_4$ requires C, 68.8; H, 10.9%). This compound was mentioned by Reinger⁸ who did not report the m. p. Barucha and Gunstone⁹ described an optically active form, m. p. 87—88°.

threo-threo-9,10,12,13-Tetrabromooctadecanoic Acid.—Bromine in chloroform (358 c.c. of 0.406N-solution) was added dropwise to the olefinic acid (22.8 g.) in chloroform (700 c.c.) at 20°. The solution was washed with water, dried (Na_2SO_4), and evaporated but the dibromodihydroxy-acid did not crystallise. It was dissolved in hydrogen bromide in acetic acid (344 c.c.; *d* 1.3) and concentrated sulphuric acid (86 c.c.). Next day the solution was warmed to 100° during 1 hr. and kept at 100° for 7 hr., more hydrogen bromide-acetic acid (86 c.c.) being added after 3 hr. The cooled solution was poured into water (2 l.) and extracted with 1:1 ether-light petroleum (b. p. 40—60°). Evaporation of the washed and dried extracts gave oil containing some solid, which was recrystallised from ethylene dichloride. The tetrabromo-acid (8.5 g.) had m. p. 114—115°, undepressed on admixture with a sample prepared from natural linoleic acid.¹⁰

Ethyl Linoleate.—The tetrabromo-acid (10 g.) was esterified azeotropically with benzene (400 c.c.), ethanol (200 c.c.), and concentrated sulphuric acid (1 c.c.). The ester (9 g.), isolated in the usual manner, had m. p. 58—59°. Palmer and Wright¹¹ give m. p. 58—58.5°.

Zinc dust (15 g.) was heated with ethanol (150 c.c.) to the b. p. and 48% hydrobromic acid (0.1 c.c.) was added. After the mixture had been refluxed under nitrogen for 5 min., the bromo-ester (9.0 g.) in ethanol (50 c.c.) was added slowly and the mixture was refluxed for 1 hr. The zinc was collected and washed with light petroleum; after the combined filtrates had been poured into dilute sulphuric acid, the separated organic layer was washed with water, dried (Na_2SO_4), and distilled under nitrogen. Ethyl linoleate (3.6 g.) thus obtained had b. p. 156°/0.5 mm., n_D^{22} 1.4581 [Found: C, 78.2; H, 11.7%; I val. (Wijs 30 min.), 162.2. Calc. for $C_{20}H_{36}O_2$: C, 77.9; H, 11.8%]. It showed λ_{max} 235 (ϵ 48) and 278 $m\mu$ (ϵ 11) and a weak band at 969 cm^{-1} corresponding to 2—3% of *trans*-isomers.

Linoleic Acid.—The ester (3.6 g.) was dissolved in 5% ethanolic sodium hydroxide (50 c.c.) under argon and left overnight at room temperature. After addition of warm water (100 c.c.), the solution was washed with ether, and the aqueous layer was acidified with dilute sulphuric acid. Isolated with ether, the linoleic acid was distilled under argon; it (2.3 g.) had b. p. 177°/0.5 mm., n_D^{23} 1.4672, m. p. -6° to -6.5° (capillary) [Found: C, 77.4; H, 11.5%; I val. (Wijs, 30 min.), 179.4. Calc. for $C_{18}H_{32}O_2$: C, 77.1; H, 11.5%]. It showed λ_{max} 238 (ϵ 15.0) and 270 $m\mu$ (ϵ 18.2). The infrared spectra of both acid and ester were superimposable on those of specimens obtained from natural sources.

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⁸ Reinger, *Ber. Pharm. Ges.*, 1922, **32**, 124.

⁹ Bharucha and Gunstone, *J.*, 1956, 1611.

¹⁰ McCutcheon, *Org. Synth.*, Coll. Vol. III, p. 526.

¹¹ Palmer and Wright, *J. Ind. Eng. Chem.*, 1914, **6**, 822.