Conjugated Acids from Castor Oil. Octadeca-9 : 11-*dienoic Acid and Octadec*-11-*en*-9-*ynoic Acid* (*Ximenynic or Santalbic Acid*).

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Ximenynic acid has been prepared from castor oil. The acid thus prepared is identical with the natural acid and also with santalbic acid.

Castor oil has been dehydrated by use of a variety of catalysts (Forbes and Neville, *Ind. Eng. Chem.*, 1940, **32**, 535), the extent of conjugated dienic esters formed being around 30% (Grummit and Gleming, *ibid.*, 1945, **37**, 485). The acids present have been investigated by Priest and von Mikusch (*ibid.*, 1940, **32**, 1314), who have shown that octadeca-9 : 12-dienoic acid is present in greater quantity than the isomeric 9 : 11-dienoic acid. Mangold (*Monatsh.*, 1894, **15**, 307) prepared *trans-trans*-octadeca-9 : 11-dienoic acid, m. p. 54°, by the distillation of ricinelaidic acid, and Schmidt and Lehmann (*Helv. Chim. Acta*, 1939, **33**, 1494) prepared a geometrical isomer, m. p. 32—33°, of this acid by allylic bromination of methyl oleate followed by dehydrobromination and hydrolysis of the bromo-ester.

While investigating the dehydrating action of thionyl chloride on ricinoleic and ricinelaidic esters, we find that chlorination occurs to give the unstable 12-chloro-esters, which undergo partial loss of hydrogen chloride when subjected to vacuum distillation. Subsequent dehydrohalogenation and hydrolysis of the chloro-esters with alkali gives Mangold's acid, m. p. 54°. If in place of the pure methyl esters, castor oil is treated with thionyl chloride, and the resulting chloroglycerides are refluxed or autoclaved with potassium hydroxide, the unsaturated acids produced may be distilled as methyl esters, and from the distillate Mangold's acid is again obtained on hydrolysis.

A parallel series of reactions with methyl ricinstearolate (methyl 12-hydroxyoctadec-9-ynoate) again yielded an unstable chloro-ester, which on hydrolysis and dehydrohalogenation gave *trans*-octadec-11-en-9-ynoic acid. The infrared spectrum (in carbon disulphide) showed a maximum at 955 cm.$^{-1}$ indicative of a *trans*-olefinic bond, while ultraviolet absorption data [maximum 2290 Å ($\varepsilon = 16{,}610$), inflection at 2400 Å ($\varepsilon = 12{,}200$)] agree with those published for ximenynic acid, which has been obtained from three species of *Ximenia* genus (Ligthelm and Schwartz, *J. Amer. Chem. Soc.*, 1950, **72**, 1868; Ligthelm and von Holdt, *J.*, 1952, 1088). Moreover, the melting points of our material, its amide, and *p*-bromophenacyl ester agree with the values for the natural acid and the corresponding derivatives.

Ximenynic acid is the major component of the seed fats of two Australian members of the *Santalaceae* (Hatt and Szumer, *Chem. and Ind.*, 1954, 962), and these authors have suggested that "santalbic acid," $C_{18}H_{30}O_2$, obtained by Madhuraneth and Manjunath (*J. Indian Chem. Soc.*, 1938, **15**, 389) from the seed fat of the sandalwood tree, *Santalum album*, Linn., will probably prove to be identical with ximenynic acid. In a preliminary note (*Chem. and Ind.*, 1954, 1112), we have shown that our ximenynic acid is in fact identical with "santalbic acid" obtained by Gunstone and McGee (*ibid.*, p. 1112). Oxidation of synthetic *trans*-octadec-11-en-9-ynoic acid according to the method of Swern *et al.* (*J. Amer. Chem. Soc.*, 1951, **73**, 2730) gave 11 : 12-dihydroxyoctadec-9-ynoic acid), identical with the product obtained by Gunstone and McGee (*loc. cit.*) from "santalbic acid." Hydrogenation of the dihydroxyacetylenic acid gave 11 : 12-dihydroxystearic acid, m. p. 128—129°. Huber (*J. Amer. Chem. Soc.*, 1951, **73**, 2730) has prepared 11 : 12-dihydroxystearic acids, m. p.s 95—96° and 129—130°, from the corresponding *cis*- and *trans*-ethylenic acids, hence the *trans*-configuration of the olefinic bond in ximenynic acid is confirmed. The infrared spectrum of the synthetic acid is identical with that of "santalbic acid" (Gunstone and McGee, *loc. cit.*), moreover both acids give identical *p*-bromophenacyl esters, and both have been hydroxylated to identical dihydroxystearolic acids.

EXPERIMENTAL

Ultraviolet spectra were determined in ethanol on a Unicam SP. 500 spectrophotometer, and infrared spectra were obtained in carbon disulphide on a Perkin-Elmer double-beam instrument.

Methyl 12-*Chloro-oleate.*—Thionyl chloride (40 g.) was added slowly to methyl ricinoleate (40 g.) at 0° with occasional shaking, and the mixture left at room temperature overnight. Excess of thionyl chloride was removed, the residue dissolved in ether, and the solution washed with sodium carbonate solution and water, and dried (Na_2SO_4). Removal of ether gave ***methyl*** *12-chloro-oleate* (23 g.), b. p. 158—163°/0·18 mm. (Found: C, 69·5; H, 10·9; Cl, 8·7. $C_{19}H_{35}O_2Cl$ requires C, 69·0; H, 10·7; Cl, 10·7%). Redistillation of the ester is accompanied by loss of hydrogen chloride.

Methyl 12-*Chloroelaidate.*—Prepared as above from methyl ricinelaidate, the 12-chloro-compound had b. p. 155—157°/10^{-3} mm. (Found: C, 68·9; H, 10·7; Cl, 10·1%).

Octadeca-9 : 11-*dienoic Acid.*—(*A*) Methyl 12-chloroelaidate (10 g.) in ethanol (200 ml.) was refluxed with potassium hydroxide (10 g.) in water (10 c.c.) for 10 hr. On acidification, a clear oil (7·5 g.) separated, which was extracted, washed, and stored at 0°, and then deposited octadeca-9 : 11-dienoic acid, m. p. 53—54° alone or mixed with a specimen prepared according to Mangold (*loc. cit.*). Light absorption: Max. 2320 Å; $\varepsilon = 32,000$.

(*B*) *From castor oil.* Thionyl chloride (52·5 g.) was added slowly to castor oil (100 g.) with occasional shaking, and the mixture left overnight. Removal of excess of thionyl chloride left a dark red oil which was washed in ethereal solution with sodium carbonate (5%) and water. Removal of ether left a red oil (94·5 g.) which was refluxed with potassium hydroxide (50 g.) in ethanol (400 ml.) for 24 hr. The mixture was poured into water and acidified. Isolation gave a mixture of acids containing 47·5% of conjugated diene. [A second run in which the mixed glycerides were hydrolysed at 180° for 6 hr. gave crude acids containing 54% of conjugated diene (light absorption: Max. 2300 Å; $\varepsilon = 17,150$).] The mixed acids were esterified to give methyl esters, b. p. 128—132°/2 × 10^{-3} mm. Hydrolysis of the esters (35 g.) with sodium hydroxide (2N; 90 ml.) in methanol (160 ml.) followed by extraction with ether gave an oil (24·5 g.) which slowly deposited crude acid, m. p. 37—46°. Recrystallization from methanol gave octadeca-9 : 11-dienoic acid, m. p. 53—54° undepressed when mixed with an authentic sample. Light absorption: Max. 2320 Å ($\varepsilon = 32,500$).

(*C*) Similar treatment of methyl 12-chloro-oleate also produced Mangold's acid, m. p. 53—54°.

Octadeca-9 : 11-*dienoamide.*—Prepared from methyl octadeca-9 : 11-dienoate and liquid ammonia in an autoclave at 150° for 15 hr., the *amide* had m. p. 98—99° (Found: C, 77·2; H, 11·6; N, 4·9. $C_{18}H_{33}ON$ requires C, 77·4; H, 11·8; N, 5·0%). Light absorption: Max. 2300 Å ($\varepsilon = 32,000$). The amide was also obtained from methyl 12-chloro-oleate and liquid ammonia at 160° for 15 hr. The S-*benzylthiuronium salt* formed needles, m. p. 127—129°. from alcohol (Found: C, 70·3; H, 9·6. $C_{26}H_{42}O_2N_2S$ requires C, 70·0; H, 9·4%).

Ricinstearolic Acid.—The following modification of Mühle's method (*Ber.*, 1913, **46**, 2096) was employed. To castor oil (200 g.) in ethyl alcohol (100 g.) at −30°, bromine was added in a thin stream with stirring. When addition was complete, the product was refluxed for 10 hr. with potassium hydroxide (240 g.) in water (160 g.). The mixture was poured into water (1·2 l.), acidified with sulphuric acid (5N), and set aside overnight. The hard cake of crude acid was removed and dissolved in ether, and the solution dried (Na_2SO_4). Removal of ether gave ricinstearolic acid (142 g.) as plates from light petroleum (b. p. 40—60°), m. p. 49—50°.

Methyl Ricinstearolate.—Prepared from the acid (36·5 g.) and isolated in the uusal way, the ester (24 g.) had m. p. 19—20°, b. p. 148—150°/2 × 10^{-3} mm. Mühle (*loc. cit.*) describes the ester as a liquid, b. p. 225°/12 mm.

Octadec-11-*en*-9-*ynoic Acid.*—Freshly purified thionyl chloride (40 g.) was added dropwise with stirring to methyl ricinstearolate (85 g.) at −10°. After addition was complete, stirring was continued for 2 hr., and the mixture left overnight at room temperature. Excess of thionyl chloride was removed under reduced pressure, and an ethereal solution of the residue was washed with water, sodium carbonate solution, and water, and dried (Na_2SO_4). The residue (86 g.) of crude methyl 12-chlorostearolate was refluxed with ethanolic potash (15%; 280 c.c.) for 24 hr., and the mixture poured into water, acidified, and extracted with ether. Removal of ether gave a fraction (41 g.), b. p. 198/7·5 × 10^{-2} mm. Several crystallizations from acetone (10 c.c./g.) at −25°, followed by crystallization from light petroleum (b. p. 40—60°) at −10° gave *octadec*-11-*en*-9-*ynoic acid* (34 g.), m. p. 38—39° alone and when mixed with a specimen of "santalbic acid" (Found: C, 77·3; H, 10·7. $C_{18}H_{30}O_2$ requires C, 77·7; H, 10·9%). Light absorption : Max. 2290 Å (ε = 16,610) ; inflection at 2400 Å (ε = 12,200). Infrared absorption peak at 955 cm.$^{-1}$ (*trans*-olefinic bond). The infrared absorption curve was identical with that obtained from " santalbic acid." The p-*bromophenacyl ester* formed needles, m. p. 54°, from alcohol and did not depress the m. p. of the *p*-bromophenacyl ester of santalbic acid (Found : C, 65·4; H, 7·6. $C_{26}H_{35}O_3Br$ requires C, 65·7 ; H, 7·4%).

Octadec-11-*en*-9-*ynoamide*.—The methyl ester (980 mg.) in ethanol (20 ml.) was heated with liquid ammonia (70 ml.) in a sealed tube at 75° for 24 hr. Isolation in the usual way gave *octadec*-11-*en*-9-*ynoamide* (690 mg.), m. p. 105°, as needles (from aqueous methanol) (Found : C, 78·0; H, 11·0. $C_{18}H_{31}ON$ requires C, 77·8; H, 11·3%).

11 : 12-*Dihydroxystearolic Acid*.—Octadec-11-en-9-ynoic acid (2·8 g.) in formic acid (98% ; 30 ml.) and hydrogen peroxide (30% ; 1·6 ml.) was stirred at 50° for 1½ hr. Isolation in the usual manner and crystallization from ether–petroleum, initially at −20° and then at room temperature, gave 11 : 12-dihydroxystearolic acid (1·9 g.) as plates, m. p. 89—90° alone and when mixed with a specimen prepared by Dr. Gunstone (*loc. cit.*) from "santalbic acid" (Found : C, 69·0; H, 10·2. Calc. for $C_{18}H_{32}O_4$: C, 69·2; H, 10·3%).

11 : 12-*Dihydroxystearic Acid*.—11 : 12-Dihydroxystearolic acid (95 mg.) in ethyl acetate–acetic acid (5 : 1; 30 ml.) was shaken in hydrogen with platinum (20 mg.) for 2 hr. Isolation in the usual manner gave 11 : 12-dihydroxystearic acid (70 mg.), m. p. 128—129°, as plates from ethanol. Huber (*loc. cit.*) records m. p. 129—130°.

Stearic Acid.—Complete hydrogenation of octadec-11-en-9-ynoic acid gave stearic acid, m. p. and mixed m. p. 69—70°.

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