was gradually raised to 140° during 30 min. At this temperature a vigorous reaction occurred. The bath temperature was then raised to 160° during 15 min. The mixture was allowed to cool with continued stirring until stirring became difficult; the stirrer was then raised clear of the thick mixture. After the mixture had cooled to room temperature, 175 ml. of ether and 175 ml. of 3 *N* hydrochloric acid solution were added. After 30–40 min. of vigorous stirring, the reaction mixture was completely dissolved and distributed between the two layers. The ether layer, to which was added a 100-ml. ether extract of the aqueous layer, was washed with water (2 × 100 ml.), 5% ammonium hydroxide solution (3 × 100 ml.), and again with water (2 × 100 ml.). The ether solution was dried over sodium sulfate, and removal of the ether left 19.7 g. of dark viscous oil. This material was distilled *in vacuo* and yielded 15.8 g. (55%) of viscous orange oil, b.p. 152–158° at 0.03–0.04 mm.

A 5.0-g. sample of the distilled ester material was saponified during 1 hr. in a boiling solution consisting of 60 ml. of water, 15 ml. of ethanol, and 5.0 g. of sodium hydroxide. The resulting clear orange solution was treated with Norit and filtered. The yellow filtrate was chilled and 3 *N* hydrochloric acid solution was added dropwise until precipitation ceased. The resulting yellow precipitate amounted to 3.8 g. (85%). This material was dissolved in 30 ml. of boiling acetone, and the solution was treated with Norit. The faintly yellow filtrate was carefully concentrated by boiling at atmospheric pressure until crystallization barely commenced; 50 ml. of boiling chloroform was then added all at once. The cooled mixture deposited 3.0 g. of white crystals, m.p. 180–182° (decomp.). Further recrystallizations from acetone–chloroform, aqueous ethanol, methanol, and benzene–heptane did not change the melting point. The infrared spectrum of this material is qualitatively identical with the spectra of deliberate mixtures of the two pure isomers with indication that the 6-chloro isomer is present in about 5–6% dominance.

Isolation and Structure of a New Conjugated Triene Fatty Acid[1]

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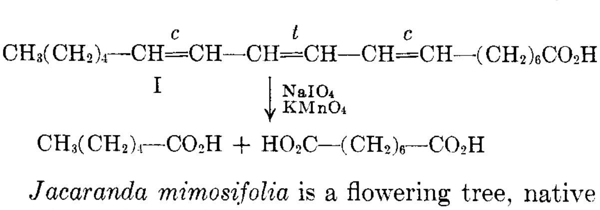
A fatty acid, found as a major component in the seed oil of *Jacaranda mimosifolia* D. Don,[2] is shown to be the hitherto unknown *cis*-8-*trans*-10-*cis*-12-octadecatrienoic acid.

The first 8,10,12-octadecatrienoic acid was discovered as a component of the seed oil of *Calendula officinalis* (family Compositae) by McLean and Clark[3] in 1956. It was converted by them to the all-*trans* form before isolation. Chisholm and Hopkins[4] isolated the original acid in 1960 and proved its configuration to be *trans*-8-*trans*-10-*cis*-12. A new geometric isomer of this acid has been found in the present work in the seed oil of *Jacaranda mimosifolia* (family Bignoniaceae). It is shown to be *cis*-8-*trans*-10-*cis*-12-octadecatrienoic acid (I) and is therefore an analog of punicic acid (*cis*-9-*trans*-11-*cis*-13-octadecatrienoic acid).



$$CH_3(CH_2)_4{-}\overset{c}{CH{=}CH}{-}\overset{t}{CH{=}CH}{-}\overset{c}{CH{=}CH}{-}(CH_2)_6CO_2H$$

I

$$\Big\downarrow{\scriptstyle NaIO_4,\ KMnO_4}$$

$$CH_3(CH_2)_4{-}CO_2H + HO_2C{-}(CH_2)_6{-}CO_2H$$

Jacaranda mimosifolia is a flowering tree, native to Argentina, which is grown for ornament in tropical and subtropical areas. The thin, winged seeds weigh about 0.01 g. and are rich in oil. The oil was found to have a high refractive index and its ultraviolet absorption spectrum indicated a large content of conjugated triene acid. Repeated crystallization of the mixed fatty acids at low temperature gave the pure triene acid. Its melting point, 43.5–44°, and ultraviolet spectrum, λ_{max} 265, 275, 287 mμ, were almost identical with those of punicic acid, m.p. 44°, λ_{max} 265, 275, 287 mμ. However, the melting point was depressed about 10° by mixing with punicic acid.

Elemental analysis, the ultraviolet data, and hydrogenation to stearic acid established that the jacaranda acid is a straight-chain, conjugated, octadecatrienoic acid. Oxidative splitting by von Rudloff's method[5] gave suberic and hexanoic acids, showing that the triene grouping is 8,10,12. This was confirmed by stereomutation of the original acid to the all-*trans* form, which was identified as *trans*-8-*trans*-10-*trans*-12-octadecatrienoic acid by mixed melting point with an authentic sample of this acid prepared from calendula seed oil.

The geometric configuration of the triene grouping was investigated. The acid did not form an adduct with maleic anhydride under the appropriate conditions for this reaction, hence the grouping does not include a *trans,trans*-diene linkage. This observation eliminates three of the eight possible isomers, *viz.*, *ctt*, *ttc*, and *ttt*.[6] Further, the *ttc* and *ttt* forms are known and the jacaranda acid depressed the melting point of both.

Examination of the ultraviolet and infrared spectra and comparison with the spectra of the analogous 9,11,13-octadecatrienoic acids ruled out

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[1] To be presented before the Division of Agricultural and Food Chemistry, 142nd Meeting of the American Chemical Society, Atlantic City, New Jersey, September 9–14, 1962. Issued as N.R.C. No. 6938.

[2] Synonym, *J. ovalifolia* R. Br.

[3] John McLean and A. H. Clark, *J. Chem. Soc.*, 777 (1956).

[4] M. J. Chisholm and C. Y. Hopkins, *Can. J. Chem.*, **38**, 2500 (1960).

[5] R. U. Lemieux and E. von Rudloff, *ibid.*, **33**, 1701 (1955).

[6] *c* = *cis*; *t* = *trans*.

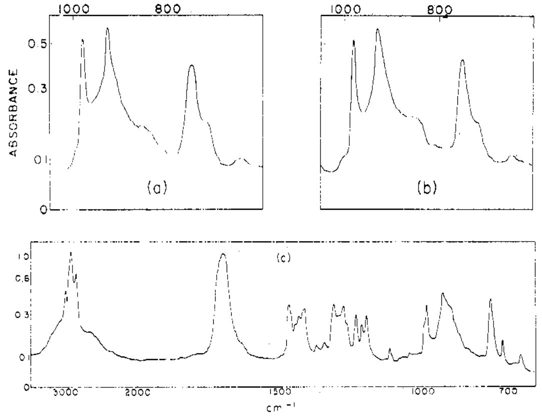

Fig. 1.—Infrared spectra: (a) jacaranda acid (in CS_2); (b) punicic acid (in CS_2); (c) jacaranda acid, solid film.

certain other configurations. Thus the strong infrared peak given by the jacaranda acid at 982 cm.$^{-1}$, characteristic of a conjugated *trans* double bond, could not arise from the *ccc* isomer. The *cct*-9,11,13-octadecatrienoic acid was synthesized by Crombie and Jacklin.[7] Its ultraviolet and infrared spectra were markedly different from those of the jacaranda acid. Its ultraviolet spectrum had only one peak at 271 mμ with inflections at 263 and 280 mμ, in contrast to the three peaks at 265, 275, and 287 mμ in the jacaranda acid spectrum. These data are considered sufficient to eliminate both the *cct* and the *tcc* configurations since the spectra of these two may be expected to be practically identical (*cf.* spectra of *ctt*- and *ttc*-9,11,13-octadecatrienoic acids,[8] Table I). The same conclusion is reached from consideration of the infrared spectra (Table II).

There remain only two possible configurations, *ctc* and *tct*. The *tct* acid is not known in either the 8,10,12 or 9,11,13 series but its infrared spectrum would almost certainly reflect the presence of the two *trans* bonds by a very strong peak in the region 900–1000 cm.$^{-1}$. O'Connor[9] has pointed out that the intensity of the *trans* peak in such compounds is roughly proportional to the number of *trans* double bonds. The intensity of the peak at 982 cm.$^{-1}$ for the jacaranda acid corresponds to one *trans* bond (Fig. 1). Hence the new acid is considered to be *cis*-8-*trans*-10-*cis*-12-octadecatrienoic acid, *i.e.*, the analog of punicic acid.

The close similarity of its light absorption properties to those of punicic acid provides confirmation of this structure (Tables I and II). The ultraviolet maxima are at the same position and the absorptivities are of the same order (jacaranda acid, $E^{1\%}_{1\,\mathrm{cm}}$ 1722 at 275 mμ; punicic acid, $E^{1\%}_{1\,\mathrm{cm}}$ 1694 at 275 mμ). The infrared spectrum almost coincides with that of punicic acid (Fig. 1). The nonidentity of the jacaranda acid and punicic acid is apparent from the mixed melting point of the acids and of their *p*-phenylphenacyl esters, as well as from the chain length of the fragments obtained by oxidative splitting. Conjugated triene acids give few derivatives suitable for identification purposes but it was found that the *p*-phenylphenacyl esters could be prepared in essentially pure condition. They are unstable like the acids.

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA FOR C-18 CONJUGATED TRIENE ACIDS (IN CYCLOHEXANE), mμ

Configuration	Δ 8,10,12	Δ 9,11,13
cis-trans-cis	265, 275, 287 (Jacaranda)[a]	265, 275, 287 (Punicic)[a]
cis-cis-trans	Not known	271[b]
cis-trans-trans	Not known	261, 272, 282 (α-Eleostearic)[c]
trans-trans-cis	262, 272, 283 (Calendula)[d]	262, 272, 283 (Catalpa)[e]
trans-trans-trans	259, 269, 280 (Calendula)[d]	260, 269, 281 (β-Eleostearic)[c]

[a] Present work. [b] See ref. 7. [c] F. D. Gunstone, "An Introduction to the Chemistry of Fats and Fatty Acids," Chapman and Hall, Ltd., London, 1958, p. 25. [d] See ref. 4. [e] See ref. 8.

TABLE II

INFRARED ABSORPTION MAXIMA FOR C-18 CONJUGATED TRIENE ACIDS (IN CS_2 SOLUTION), CM.$^{-1}$

Configuration	Δ8,10,12	Δ9,11,13
cis-trans-cis	982, 929[a] (Jacaranda)	981, 931[a]
cis-cis-trans	. . .	987, 965, 942[b] (Solid film)
cis-trans-trans	. . .	987, 958[a]
trans-trans-cis	987, 955[c]	986, 957[d]
trans-trans-trans	990[c]	988[a]

[a] Present work. [b] See ref. 7. [c] See ref. 4. [d] See ref. 8.

Although only a dozen of the 600 species of Bignoniaceae have been studied to date, it is apparent that there is great diversity in the fatty acid composition of their seed oils. Thus *Catalpa ovata* yielded a new acid, *trans*-9-*trans*-11-*cis*-13-octadecatrienoic[8]; *Chilopsis linearis* is reported by Earle and co-workers[10] to contain both a conjugated diene and a conjugated triene acid, neither of which has been characterized; *Jacaranda mimosifolia* contains *cis*-8-*trans*-10-*cis*-12-octadecatrienoic acid (present work); *Crescentia* sp.[11,12] and *Oroxylum indicum*[13] appear to contain no conjugated acids; and examples of four other genera[14] contained no conjugated acids. It is interesting that both the 8,10,12- and the 9,11,13-trienoic acids should occur in the same plant family. It is also notable that the *ctt* isomer of 9,11,13-octadecatrienoic acid (α-eleostearic) appears to be the most common isomer of this acid in nature, while the

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(7) L. Crombie and A. G. Jacklin, *J. Chem. Soc.*, 1632 (1957).

(8) C. Y. Hopkins and M. J. Chisholm, *ibid.*, 573 (1962).

(9) R. T. O'Connor in K. S. Markley, "Fatty Acids," Part 1, Interscience, Inc., New York, 1960, p. 436.

(10) F. R. Earle, C. A. Glass, G. C. Geisinger, and I. A. Wolff, *J. Am. Oil Chemists' Soc.*, **37**, 440 (1960).

(11) B. A. Smith and F. G. Dollear, *ibid.*, **24**, 52 (1947).

(12) M. L. Van Séveren, *ibid.*, **37**, 402 (1960).

(13) C. R. Mehta, *Proc. Indian Acad. Sci.*, **9A**, 390 (1939).

(14) M. J. Chisholm and C. Y. Hopkins, to be published.

ctt isomer of 8,10,12-octadecatrienoic acid has not yet been discovered.

Experimental[15]

Jacaranda Seed Oil.—Seed of *Jacaranda mimosifolia* was obtained from a reliable commercial source. The oil content was 32%, air-dry basis. The main portion of the seed was ground and extracted at room temperature by stirring with petroleum ether (b.p. 30–60°). The solvent was removed at 25–30° under nitrogen. The oil had iodine value (Wijs, 30 min.) 146.6; $n^{25°}_{D}$ 1.4935; ultraviolet spectrum, λ_{max} 265, 275, 287 mμ; absorptivity $E^{1\%}_{1\,cm}$ 508 at 275 mμ, equivalent to about 30% of conjugated triene acid.

Isolation of *cis*-8-*trans*-10-*cis*-12-Octadecatrienoic Acid.—The oil was hydrolyzed by refluxing it for 30 min. with 10% ethanolic potassium hydroxide under nitrogen. The unsaponifiable matter was removed by extracting the alkaline solution with petroleum ether. The soap solution was acidified with 2 *N* hydrochloric acid in the presence of a layer of petroleum ether which dissolved the fatty acids as formed and ensured the complete conversion of soaps. The solvent was evaporated under nitrogen at room temperature and reduced pressure. The fatty acids (17.0 g.) were dissolved in acetone (140 ml.) and the solution was cooled to −20°. The precipitate (3.0 g.), mostly saturated acids, was filtered off and the filtrate was cooled to −45°. The crystals formed at this temperature were recovered and recrystallized from acetone (50 ml.) at −45°, yielding 3.7 g. of acid, m.p. 36–39°. This material was crystallized four times from pentane at −10°, giving 0.96 g. of pure acid, m.p. 43.5–44°; λ_{max} 265, 275, 287 mμ; $E^{1\%}_{1\,cm}$ 1722 at 275 mμ; ν_{max} 982s, 929s cm.$^{-1}$ (conjugated *cis, trans* linkage). The melting point was depressed to 32–37° in admixture with punicic acid.

Anal. Calcd. for $C_{18}H_{30}O_2$: C, 77.65; H, 10.85. Found: C, 77.52; H, 10.78.

The acid was moderately soluble in pentane and very soluble in acetone and in ethanol. It was unstable in air, becoming sticky if exposed for a few minutes at room temperature. It was stored under nitrogen at −80°.

The acid (0.1 g.) was added to maleic anhydride (0.1 g.) in benzene (10 ml.) and refluxed under nitrogen for 5 hr. On evaporating the solvent and washing the residue with water, the triene acid was recovered substantially unchanged, m.p. 41–42°.

Hydrogenation, Stereomutation, and Oxidative Splitting.—The acid (0.2 g.) was hydrogenated in methanol with Adams catalyst and crystallized from ethanol, giving stearic acid, m.p. and mixed m.p. 69–69.5°.

The triene acid (0.1 g.) was dissolved in pentane containing a trace of iodine and allowed to stand in daylight for 1 hr. The resulting precipitate was washed with cold pentane and crystallized from ethanol, giving all-*trans*-8,10,12-octadecatrienoic acid, m.p. and mixed m.p. 76–77°.

Oxidative splitting of the acid (0.14 g.) by permanganate-periodate[5] was carried out. The resulting acids were recovered as methyl esters in pentane solution by the method previously described[8] and submitted to gas chromatography. Large peaks corresponding to hexanoate and suberate were observed.

Punicic Acid.—Punicic acid was prepared from seeds of *Punica granatum* L. and *Momordica balsamina* L.[14] by the same procedure as described above. The light absorption data are given in Tables I and II. Melting points of the isomeric acids are shown in Table III.

TABLE III

MELTING POINTS OF THE KNOWN C-18 CONJUGATED TRIENE ACIDS, °C.

Configuration	Δ8,10,12	Δ9,11,13	Δ10,12,14
cis-trans-cis	43.5–44[a]	43.5–44[b]	...
cis-cis-trans	...	35–38[b]	...
cis-trans-trans	...	48[b]	...
trans-trans-cis	40–40.5[c]	31.5–32[d]	...
trans-trans-trans	77–78[e]	72[b]	79[f]

[a] Present work. [b] See ref. 7. [c] See ref. 4. [d] See ref. 8. [e] See ref. 3. [f] J. P. Kass and J. O. Burr, *J. Am. Chem. Soc.*, **61,** 3292 (1939).

***p*-Phenylphenacyl Esters of the Jacaranda Acid and Punicic Acid.**—2-Bromo-4′-phenylacetophenone (0.2 g.) and the jacaranda acid (0.2 g.) were dissolved in 20 ml. of ethanol, treated with 10 ml. of 0.1 *N* aqueous sodium hydroxide and made acid to phenol red with 0.1 *N* hydrochloric acid. The mixture was refluxed under nitrogen for 30 min. and then cooled in ice. The product was filtered off and crystallized three times from ethanol at 0°, giving *p*-phenylphenacyl *cis*-8-*trans*-10-*cis*-12-octadecatrienoate, m.p. 70–72°. It was unstable in air to the same degree as the free acid.

Anal. Calcd. for $C_{32}H_{40}O_3$: C, 81.31; H, 8.53. Found: C, 81.24; H, 8.39.

Punicic acid, when treated in the same way, gave *p*-phenylphenacyl *cis*-9-trans-11-*cis*-13-octadecatrienoate, m.p. 61.5–63.5°. It was also unstable in air.

Anal. Calcd. for $C_{32}H_{40}O_3$: C, 81.31; H, 8.53. Found· C, 81.10; H, 8.34.

Acknowledgment.—The authors are indebted to Mr. R. Lauzon for determination of infrared spectra and to Mr. H. Seguin for C and H analyses.

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[15] Melting points were determined in capillary tubes and are corrected. Ultraviolet spectra were determined in cyclohexane solution with a Beckman DU spectrophotometer. Infrared spectra were determined in carbon disulfide, except where noted, in a Perkin-Elmer Model 21 spectrophotometer with sodium chloride prism.