was identical with that of N-benzyloxy-N′-phenylurea, and a mixed melting point of the two samples did not depress.

Pyrolysis of Phenylcarbamoyl Benzyl Acetohydroxamate.—Phenylcarbamoyl benzyl acetohydroxamate, 0.73 g., was refluxed at 1 mm., for 1 hr. The effluent gas was trapped in a Dry Ice–cooled trap containing cyclohexanol. The material in the trap was recrystallized from ethanol–water mixture and was obtained in a 0.1-g. yield, m.p. 81–83°. A mixed melting point with cyclohexyl phenylurethan did not depress. The material remaining in the boiling flask had an infrared spectrum identical to that of benzyl acetohydroxamate.

Pyrolysis of Phenylcarbamoyl Benzyl Benzohydroxamate.—When 0.1 g. of phenylcarbamoyl benzyl benzohydroxamate was heated at 87° at atmospheric pressure as long as the odor of phenylisocyanate could be detected, an oil remained which gradually solidified. The solid was recrystallized from an ether–petroleum ether (b.p. 30–60°) mixture, m.p. 103–105°. Infrared spectrum in Nujol was identical to that of benzyl benzohydroxamate.

Substituted Indole-3-acetic Acids by the Reformatsky Reaction

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4-Chloro-2-methyl-, 5-chloro-2-methyl-, and 6-chloro-2-methylindole-3-acetic acids have been synthesized *via* the Reformatsky reaction applied to the appropriate chloro-substituted derivatives of 1-acetyl-2-methylindoxyl. The Fischer indole synthesis applied to ethyl levulinate *m*-chlorophenylhydrazone gave, after hydrolysis, a eutectic mixture of 4-chloro-2-methyl- and 6-chloro-2-methylindole-3-acetic acids.

The auxinlike activity of substituted derivatives of the natural plant growth hormone indole-3-acetic acid (*heteroauxin*) varies with the nature and positions of substituent groups.[2] 4-Chloro-2-methyl- and 6-chloro-2-methylindole-3-acetic acids would be of interest for phytological studies in this connection. Apparently a eutectic mixture of these acids was obtained following application of the Fischer indole synthesis to ethyl levulinate *m*-chlorophenylhydrazone. Analogous results were obtained by Fox and Bullock[3] with succinaldehydic acid *m*-chlorophenylhydrazone. An unambiguous method of synthesis was required to obtain the separate isomers and to show that the product of the Fischer synthesis was indeed a mixture of the two.

A synthesis based on the work of Pretka and Lindwall[4] appeared more promising than alternative possible routes such as those involving reduction of 2,β-dinitrostyrenes[5] or reduction of *o*-nitrobenzyl carbonyl compounds[6]; syntheses of the Madelung type apparently fail when substituents other than alkyl groups are desired in the benzene moiety.[7] The key step in the method of Pretka and Lindwall is a Reformatsky reaction applied to a 1-acetylindoxyl. We extended this approach to the synthesis of 4-chloro-2-methyl-, 5-chloro-2-methyl-, and 6-chloro-2-methylindole-3-acetic acids.

Two of the chloroanthranilic acids required for preparing the appropriately substituted indoxyls were prepared from the corresponding chloro-substituted *o*-toluidines. The *N*-acetyl derivatives of 5-chloro-2-methylaniline and 3-chloro-2-methylaniline were oxidized by hot aqueous potassium permanganate solution buffered by magnesium sulfate. Subsequent acid hydrolysis of the resulting *N*-acetyl derivatives of the chloroanthranilic acids gave 4-chloro- and 6-chloroanthranilic acids. 5-Chloroanthranilic acid was obtained from a commercial source.

1-Acetyl-4-chloro-2-methylindoxyl and the 5-chloro and 6-chloro isomers were prepared by methods similar to those employed by Pretka and Lindwall in their preparation of 1-acetyl-2-methylindoxyl. Condensation of the chloroanthranilic acids with α-chloropropionic acid in aqueous sodium carbonate solution afforded *N*-(1-carboxyethyl)-4-chloroanthranilic acid and the 5-chloro- and 6-chloro isomers (group I). Heating solutions of the chloro-substituted *N*-(1-carboxyethyl)anthranilic acids with sodium acetate in acetic anhydride provided 1-acetyl-4-chloro-2-methylindoxyl acetate and the 5-chloro and 6-chloro isomers (group II). Selective hydrolysis of the *O*-acetyl function of the indoxyl acetates with sodium sulfite in aqueous dioxane gave 1-acetyl-4-chloro-2-methyl-

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(2) F. J. Stevens and H. C. Su, *J. Org. Chem.*, **27**, 500 (1962), and references cited therein; R. M. Muir and C. Hansch, *Plant Physiol.*, **28**, 218 (1953).

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(4) J. E. Pretka and H. G. Lindwall, *J. Org. Chem.*, **19**, 1080 (1954).

(5) C. Nenitzescu, *Ber.*, **58**, 1063 (1925); J. van der Lee, *Rec. trav. chim.*, **44**, 1089 (1925); H. N. Rydon and C. A. Long, *Nature*, **164**, 575 (1949); *cf.* H. N. Rydon and J. C. Tweddle, *J. Chem. Soc.*, 3499 (1955).

(6) A. Baeyer and O. R. Jackson, *Ber.*, **13**, 187 (1880); **14**, 879 (1881); A. B. Sen and P. M. Bhargava, *J. Indian Chem. Soc.*, **25**, 282, 403 (1948); R. Giuliano and M. L. Stein, *Ann. Chim.* (Rome), **48**, 1284 (1958); W. Borsche, *Ber.*, **42**, 601 (1909); A. Reissert and H. Heller, *ibid.*, **37**, 4364 (1904).

(7) L. Marion and W. R. Ashford, *Can. J. Research*, **23B**, 26 (1945); E. Hardegger and H. Corrodi, *Helv. Chim. Acta*, **39**, 514 (1956); J. A. Barltrop and D. A. H. Taylor, *J. Chem. Soc.*, 3399 (1954); H. Burton, J. A. Duffield, and P. F. G. Praill, *ibid.*, 1062 (1950).

TABLE I

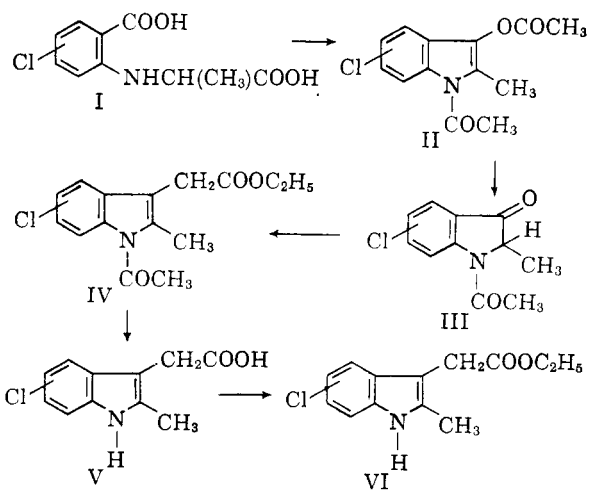
SYNTHESIS OF 4(5- AND 6)-CHLORO-2-METHYLINDOLE-3-ACETIC ACIDS *via* THE REFORMATSKY REACTION

Group	Chlorine position	M.p., °C.[a]	Yield, %	Molecular formula	Nitrogen, % Calcd.	Nitrogen, % Found
I	4	251–252 (dec.)	62	$C_{10}H_{10}ClNO_4$	5.75	5.71
	5	247–248 (dec.)	75			5.73
	6	175–176 (dec.)	34			5.50
II	4	99–99.5	59	$C_{13}H_{12}ClNO_3$	5.27	5.07
	5	117–118	37			5.28
	6	131–132	31			5.31
III	4	144–145	53	$C_{11}H_{10}ClNO_2$	6.26	6.07
	5	134–135	88			6.23
	6	111–112	86			6.21
IV	4	102–103	36	$C_{15}H_{16}ClNO_3$[b]	4.77	4.69
	5	100–100.5	43			4.78
	6	85.5–86.5	39			4.68
V	4	210–214 (dec.)[c]	79	$C_{11}H_{10}ClNO_4$[d]	6.26	6.08
	5	189–190 (dec.)	79			...
	6	205–208 (dec.)	74			6.33
VI	4	101.5–102	89	$C_{13}H_{14}ClNO_2$	5.57	5.56
	6	87.5–88	90			5.58

[a] Melting points were taken on a Fisher-Johns block and are uncorrected. [b] C and H analysis of Group IV: Calcd.: C, 61.34; H, 5.49. Found: 4-Cl isomer-C, 61.36; H, 5.66. 5-Cl isomer-C, 61.08; H, 5.43. 6-Cl isomer-C, 61.36; H, 5.41. [c] Varies with rate of heating; the powdered sample was placed on the block approximately 20° below the estimated decomposition point, and the temperature was raised 1–2° per minute. [d] Neutralization equivalent: Calcd.: 223.7. Found: 4-Cl isomer, 223; 6-Cl isomer, 225.

indoxyl and the 5-chloro and 6-chloro isomers (group III).

The 1-acetyl-chloro-2-methylindoxyls gave the expected Reformatsky reaction products with zinc and ethyl bromoacetate in ether–benzene solution. The tertiary alcohol products were obtained as non-crystallizable orange oils; but, after dehydration with phosphoric anhydride in benzene, ethyl 1-acetyl-4-chloro-2-methylindole-3-acetate and the 5-chloro and 6-chloro isomers (group IV) were readily obtained in pure form. Hydrolysis of these compounds gave 4-chloro-2-methylindole-3-acetic acid and the 5-chloro and 6-chloro isomers (group V). The melting point and infrared spectrum of the expected 5-chloro isomer are identical with those of 5-chloro-2-methylindole-3-acetic acid prepared from levulinic acid *p*-chlorophenylhydrazone by the Fischer synthesis.[8]



(8) F. J. Stevens and S. W. Fox, *J. Am. Chem. Soc.*, **70**, 2263 (1948).

The infrared spectrum of the mixture of acids obtained following application of the Fischer synthesis to ethyl levulinate *m*-chlorophenylhydrazone is identical with spectra of deliberate mixtures of the two unambiguously prepared isomers.[9] Further, the spectrum of the 6-chloro isomer reveals a strong absorption band at 800 cm.$^{-1}$, while the 4-chloro isomer does not absorb at this frequency; the 4-chloro isomer has two strong bands at 773 cm.$^{-1}$ and 740 cm.$^{-1}$, while the 6-chloro isomer does not absorb at either of these frequencies. Comparisons of the absorption intensities of these three prominent bands in the spectra of deliberate mixtures of the two isomers with the spectrum of the eutectic mixture indicate the 6-chloro isomer to be in dominance by approximately five to six per cent.

Experimental

4(5- and 6)-Chloroanthranilic Acids.—Commercially available technical grade 5-chloroanthranilic acid was purified by repeated recrystallizations from aqueous ethanol. The 4-chloro and 6-chloro isomers were prepared by the following operations.

A solution of 70.8 g. (0.500 mole) of the appropriate chloro-substituted *o*-toluidine (5-chloro-2-methylaniline or 3-chloro-2-methylaniline) in 70 ml. of glacial acetic acid was gradually treated with stirring with 52.0 g. (0.510 mole) of acetic anhydride. The resulting solution was refluxed 30 min. and was then poured into 500 ml. of water. The precipitated acetyl derivative was collected and pressed as dry as possible. The damp acetyl derivative was suspended with vigorous stirring (Hershberg stirrer) in 2 l. of 0.25 *M* magnesium sulfate solution heated to 85°. A total of 240 g. of solid potassium permanganate was gradually added to the vigorously stirred mixture during 1.5 hr. with intermittent heating so that the temperature was maintained at 85–90°.

(9) The infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer using the pressed potassium bromide disk technique.

The mixture was stirred 1.5 hr. longer at 85–90°. The excess potassium permanganate was then destroyed by the dropwise addition of saturated sodium bisulfite solution. The mixture was filtered, and the thick cake of manganese dioxide was thoroughly stirred in 1 l. of warm water. This mixture was filtered, and the extraction process was repeated. Acidification of the combined filtrates with 20% sulfuric acid solution precipitated the *N*-acetyl derivative of the chloroanthranilic acid. The white precipitate was collected, pressed on the funnel, and used as such in the deacetylation step.

The means of hydrolysis of the acetyl derivatives and the isolations of the products necessarily differ; a separate description for each follows.

The damp *N*-acetyl-4-chloroanthranilic acid was mixed with 400 ml. of concentrated hydrochloric acid, and the mixture was stirred and heated at 70–80° for about 8 hr. The mixture was cooled, and the white crystalline hydrochloride was collected. The product was then suspended in 300 ml. of water, and solid sodium acetate trihydrate was added in portions with good stirring until the pH of the mixture was about 5. The insoluble 4-chloroanthranilic acid was collected and recrystallized from ethanol; yield, 53.2 g. of slightly yellow thick needles (62% based on 5-chloro-2-methylaniline), m.p. 239–240°; lit.[10] m.p. 240°.

The damp *N*-acetyl-6-chloroanthranilic acid was suspended in 400 ml. of concentrated hydrochloric acid, and the mixture was stirred and heated at 55–60° for 24 hr. (The desired compound decarboxylates readily in concentrated hydrochloric acid at higher temperatures.) The mixture was cooled, and the white crystalline hydrochloride was collected and washed with ether. The dried hydrochloride (weight: 76 g.) was suspended in about 400 ml. of glacial acetic acid, and 30 g. of anhydrous sodium acetate was gradually added with good mixing. The mixture was then heated to boiling and filtered. The cooled filtrate deposited 6-chloroanthranilic acid as short white needles. This material was recrystallized again from glacial acetic acid; yield, 45.0 g. (52% based on 3-chloro-2-methylaniline), m.p. 149–150°; lit.[11] m.p. 146–147° (from benzene).

***N*-(1-Carboxyethyl)-4(5- and 6)-chloroanthranilic Acids (Group I).**—A mixture of 40.0 g. (0.243 mole) of the appropriate chloroanthranilic acid, 30.0 g. (0.276 mole) of α-chloropropionic acid, and 120 g. (1.13 moles) of sodium carbonate in 170 ml. of water was refluxed with stirring for 12 hr. An additional 30 g. of α-chloropropionic acid and 50 ml. of water were then added, and refluxing with stirring was continued 12 hr. longer. The mixture was then cooled and carefully treated with 140 ml. of concentrated hydrochloric acid. The precipitated crude product was recrystallized from 5 *N* acetic acid solution (Norit). The 4-chloro isomer was obtained as short white needles, the 5-chloro as an off-white crystalline powder, and the 6-chloro as slightly yellow tiny needles.

1-Acetyl-4(5- and 6)-chloro-2-methylindoxyl Acetates (Group II).—A stirred mixture of 19.0 g. (0.078 mole) of the appropriate group I compound and 20 g. (0.244 mole) of anhydrous sodium acetate in 100 ml. of acetic anhydride was refluxed for 1 hr. The resulting dark solution was allowed to cool somewhat, and 20 ml. of water was slowly added dropwise with vigorous stirring. Most of the resulting acetic acid was removed under reduced pressure, and the residue was poured into 200 ml. of water. The oily precipitate soon solidified. Recrystallization from ethanol (Norit) gave the 5-chloro and 6-chloro isomers as white needles and the 4-chloro isomer as white granular crystals.

1-Acetyl-4(5- and 6)-chloro-2-methylindoxyls (Group III).—A mixture of 15.0 g. (0.0565 mole) of the group II compound, 20.0 g. (0.159 mole) of sodium sulfite, 125 ml. of dioxane, and 200 ml. of water was refluxed with stirring for 4–6 hr. (The 4-chloro isomer required a 24-hr. reflux period.) The water and dioxane were removed under reduced pressure, and the residue was washed with several portions of water. Recrystallization of the remaining yellow solid from ethanol (Norit) provided the 4-chloro isomer as white granular crystals, the 5-chloro as white hexagonal plates, and the 6-chloro as white needles.

Ethyl 1-Acetyl-4(5- and 6)-chloro-2-methylindole-3-acetates (Group IV).—A mixture consisting of 50 ml. of ether, 50 ml. of benzene, 6.0 g. of the appropriate group III compound, 10 g. of 20-mesh granular zinc, 4 ml. of ethyl bromoacetate, and a tiny crystal of iodine was refluxed with stirring. After 45 min. a second addition of 10 g. of zinc and a crystal of iodine was made. Four more additions of these quantities of zinc and iodine were made at 45-min. intervals. Two more additions of 4-ml. portions of ethyl bromoacetate were made at 1.5-hr. intervals. The total reflux time was 5 hr. Decomposition of the insoluble addition compound by the dropwise addition of a solution consisting of 5 ml. of methanol and 5 ml. of glacial acetic acid produced a clear yellow solution above the excess zinc. The solution was decanted from the zinc, and the zinc was rinsed with several 10-ml. portions of ether containing a few drops of glacial acetic acid. The decantates were combined and added to 75 ml. of water in a separatory funnel. Acetic acid was added dropwise to the intermittently shaken mixture until the aqueous layer became clear. The organic layer, to which was added a 50-ml. ether extract of the aqueous layer, was washed with 5% ammonium hydroxide solution (3 × 50 ml.) and finally with 50 ml. of water. The solution was dried over sodium sulfate, and removal of the solvents under reduced pressure left a thick orange oil. The oil was dissolved in 50 ml. of benzene, 10 g. of phosphoric anhydride was added, and the mixture was refluxed 1 hr. The clear benzene solution was decanted from the dark residue, and the residue was rinsed twice with 20-ml. portions of boiling benzene. The combined decantate was washed with water (3 × 50 ml.) and dried over sodium sulfate. Removal of the benzene under reduced pressure left an orange oil that crystallized on cooling. Recrystallization from aqueous ethanol (Norit) provided the pure product as white needles.

4(5- and 6)-Chloro-2-methylindole-3-acetic Acids (Group V).—A 500-mg. sample of the group IV compound was hydrolyzed during 1 hr. in a boiling solution composed of 4 ml. of methanol, 6 ml. of water, and five sodium hydroxide pellets. The resulting yellow solution was treated with Norit and filtered. The filtrate was chilled, and 3 *N* hydrochloric acid solution was added dropwise until precipitation ceased. The white crystalline precipitate was collected, washed with water, and dried *in vacuo*. The dried sample was dissolved in the minimum volume of boiling acetone, and 10 ml. of boiling chloroform was added. Slow cooling afforded white crystals.

Ethyl 4(and 6)-Chloro-2-methylindole-3-acetates (Group VI).—A solution composed of 1.50 g. of the group V compound, 40 ml. of ethanol, 8 ml. of benzene, and 4 drops of concentrated sulfuric acid was refluxed under a 50-cm. Vigreux column for 2 hr. The solution was then slowly distilled until the boiling point of ethanol was attained. The cooled residual solution was poured in 100 ml. of 1% sodium bicarbonate solution. Stirring and cooling soon induced crystallization. Recrystallization from aqueous ethanol afforded the 4-chloro isomer as white granular crystals and the 6-chloro as tiny white plates.

Eutectic Mixture of 4(and 6)-Chloro-2-methylindole-3-acetic Acids by the Fischer Indole Synthesis.—A stirred (Teflon paddle) mixture of about 40 g. of anhydrous zinc chloride[12] and 30.0 g. of ethyl levulinate *m*-chlorophenylhydrazone[13] in a 500-ml. three-necked flask was heated under nitrogen by means of an oil bath. The bath temperature

(10) E. B. Hunn, *J. Am. Chem. Soc.*, **45**, 1024 (1923).
(11) P. Cohn, *Monatsh.*, **22**, 487 (1901).
(12) A. R. Pray, *Inorg. Syn.*, **5**, 153 (1957).
(13) M. W. Bullock and J. J. Hand, *J. Am. Chem. Soc.*, **78**, 585 1956); F. J. Stevens and D. H. Higginbotham, *ibid.*, **76**, 2206 (19544.)

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).

$$\underset{\text{I}}{\overset{c \quad t \quad c}{CH_3(CH_2)_4{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_6CO_2H}} \xrightarrow[KMnO_4]{NaIO_4} CH_3(CH_2)_4{-}CO_2H + HO_2C{-}(CH_2)_6{-}CO_2H$$

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

(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*.