No big difference was found between the Arrhenius parameters of jojoba wax and those of lower esters such as dimethyl maleate (15).

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Methanesulfonic Acid Catalyzed Addition of Aromatic Compounds to Oleic Acid

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ABSTRACT

The addition of aromatic compounds to the double bond of oleic acid has been studied using methanesulfonic acid as the acid catalyst. When alkylbenzenes were reacted with oleic acid, the yield of addition product was dependent on the electron density of the benzene ring. For example, a 76% yield of addition product was obtained with toluene, whereas for benzene and monochlorobenzene, the yields of addition products were 60% and 2%. The addition of phenol to oleic acid gave 2 types of addition products, an ether-type (phenylether) product and a ring-substituted product (hydroxyphenylstearic acid). The ratio of the 2 products varied with the reaction temperature and the amount of methanesulfonic acid. The ring-substituted product predominated at a high molar ratio of methanesulfonic acid to oleic acid (6:1) and elevated reaction temperature (50 C). Thiophenol was found to add to oleic acid to form a thioether derivative exclusively.

INTRODUCTION

The addition of aromatic compounds to oleic acid has been studied using various types of Lewis and Bronsted acids as catalysts. Stirton (1) reported the synthesis of arylstearic acid from oleic acid by the Friedel Crafts alkylation reaction. Both sulfuric acid and a strong acid cation exchange resin were used for the addition of phenol to oleic acid by Roe (2). Later, Ault and Eisner reported that methanesulfonic acid was the preferred acid catalyst for the addition of aromatic compounds to unsaturated compounds because this acid gave not only high yields of addition products, but less colored products (3-5).

A structural study of the addition products obtained from the $AlCl_3$ catalyzed reaction of benzene with oleic acid has been made by Smith et al. (6-10). By means of a CrO_3 oxidation procedure, these workers demonstrated that the phenylstearic acid obtained was a mixture of positional isomers with the phenyl substituent located at C_3 to C_{17} of the hydrocarbon chain. Although yields of the addition products have been reported, none of the by-products have been identified, so that overall, the reaction pathway has not been fully studied.

This study was undertaken to elucidate the pathway by which oleic acid reacts with aromatic compounds by identifying all of the reaction products formed when aromatic compounds are reacted with oleic acid in the presence of methanesulfonic acid.

EXPERIMENTAL

Materials

Oleic acid (98%) was obtained from Applied Science Laboratories (State College, PA). Methanesulfonic acid was purchased from Fisher Chemical Company (King of Prussia, PA) and was distilled before it was used. All other reagents were used as received from commercial suppliers. Methyl esters were prepared by the boron trifluoride method (12).

Gas liquid chromatography (GLC) was conducted with a Hewlett Packard Model 7620 chromatograph equipped with dual flame ionization detectors. Separations were obtained on 8-ft × 1/8-in. silanized stainless-steel columns packed with 7.5% EGA + 2% H_3PO_4 on 90/100 mesh Anakron ABS or 3% SP-2100 DOH on 100/120 Supelcoport. Thin layer chromatography (TLC) was performed on Silica gel G plates (250 micron) obtained from Analtech (Newark, DE). Plates were developed with toluene:ether (90:10) and visulalization was accomplished by spraying the plates with 50% H_2SO_4 and charring. A Perkin-Elmer model 720 B infrared spectrophotometer was used for IR analyses. Mass spectra were obtained on a Hewlett Packard Model 5995 GC-MS mass spectrometer. Column chromatography was carried out on Silica gel 60 A (75-150 micron) using hexane:methylene chloride gradients as the eluant. Fractions (100 mL) from the column were monitored by TLC.

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[1] Agricultural Research Service, US Department of Agriculture. Reference to a brand or firm name does not constitute endorsement by the USDA over others of a similar nature that are not mentioned.

Reaction Procedure

A typical procedure is given. Oleic acid, 5 g (17.73 mmol), and benzene, 6.91 g (88.65 mmol), were placed in a 100-mL round-bottom flask equipped with thermometer, condenser, magnetic stirring bar, and addition funnel. Methanesulfonic acid, 10.21 g (106.38 mmol), was added drop by drop into the flask, stirring, at 25 C for a 10-min period, then the reaction was continued for 48 hr. Cold H_2O (50 mL) was added to the flask, and the reaction products were extracted with ether (2 × 100 mL). After washing with water until the pH was ca. 7, the combined organic solution was dried over $MgSO_4$, and the ether and benzene were removed in vacuo. The reaction products were esterified by BF_3-CH_3OH reagent, then separated by column chromatography. The isolated products were identified by GC, MS, TLC, and IR.

Similar reactions were carried out varying the reaction temperature, time, or molar ratio of reactants.

RESULTS AND DISCUSSION

When benzene or an alkylbenzene, such as toluene, was reacted with oleic acid in the presence of methanesulfonic acid (Scheme 1), ring-substituted products ([3][2]), and γ and δ stearolactones, ([4] and [5]), were isolated as the major products. At a temperature of 25 C and a 48-hr reaction time, toluene gives 71% addition products, whereas benzene gives 46% (Table I). Higher temperature (50 C) increases the yield of addition products for both toluene and benzene, and the reactions are complete in 6 hr. Also, with benzene, an increase in alkylbenzene products is observed, as well as decrease in total lactone formation (Table I). When toluene was added to the double bond of oleic acid, the IR spectrum of product [3] shows the orientation of methyl group position ordering: para > ortho > meta. When monochlorobenzene, a deactivated

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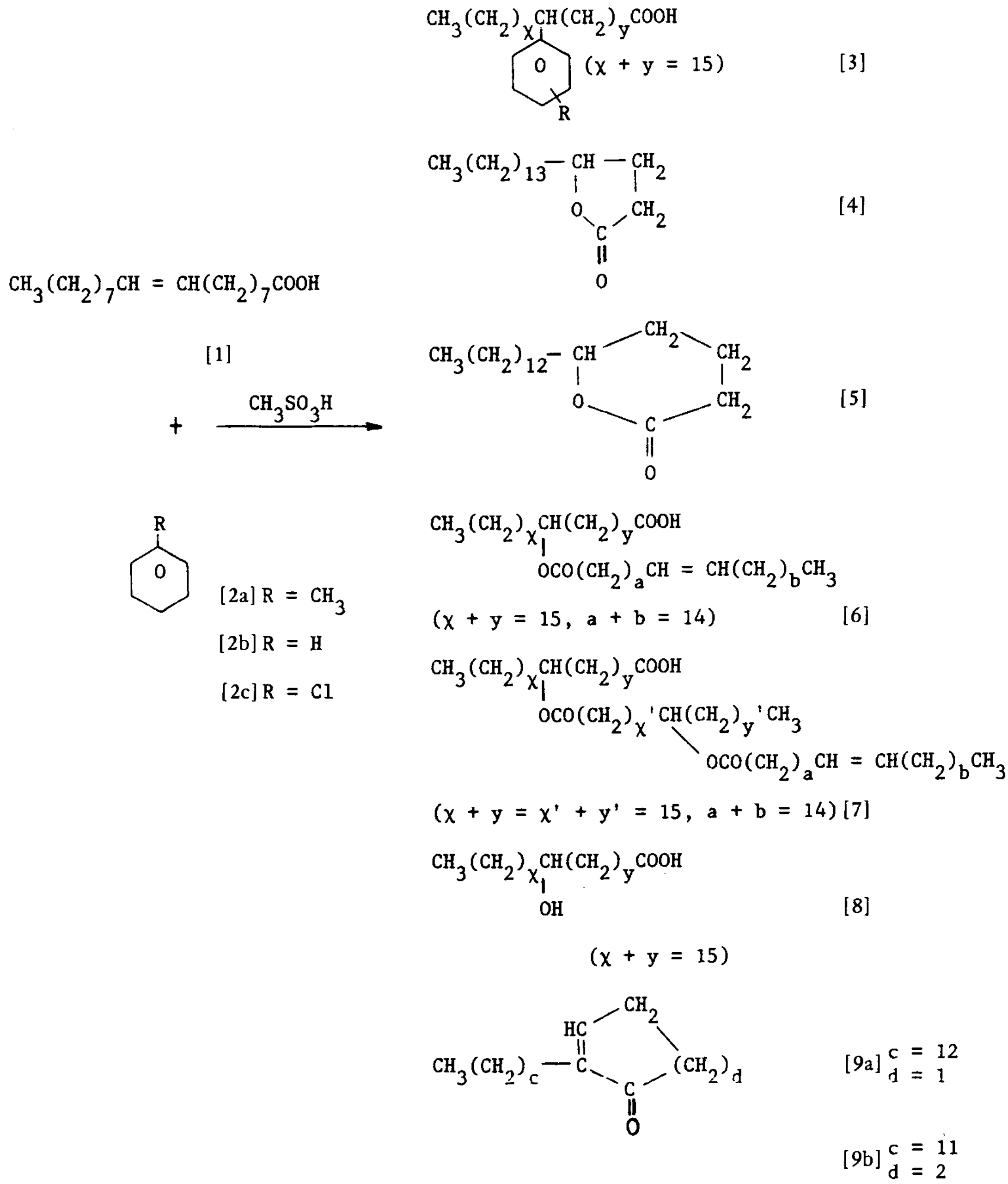
[2] Bracketed numbers refer to numbers in tables.



Scheme 1

TABLE I

Reaction of Oleic Acid with Alkylbenzene $C_6H_5R^a$

R	Temperature (C)	Time (hr)	Phenylstearate 3 (%)	γ-Stearolactone 4 (%)	γ-Stearolactone 5 (%)	6+7 (%)	8 (%)	9a + 9b (%)
CH_3	25	48^b	71	4	14	5	1	4
CH_3	50	6^b	76	6	9	2	1	5
H	25	48^c	46	7	25	11	3	5
H	50	6^c	59	9	17	4	2	6
Cl	50	6^d	2	15	35	10	9	9

[a] Oleic acid:C_6H_5R:CH_3SO_3H = 1:5:6 (molar ratio).
[b] Conversion 99%.
[c] Conversion 97%.
[d] Conversion 80%.
[e] Yields recovered from column chromatography were based on oleic acid.

aromatic compound toward electrophilic substitution, was used in this reaction, only 2% ring-addition product was obtained and 50% lactone was formed. This result confirms that the addition reaction is strongly dependent on the electron density of the aromatic ring.

The initial step of the reaction is protonation of the double bond of oleic acid by methanesulfonic acid to give an alkyl carbonium ion. The latter may attack the aromatic ring to give the alkylbenzene derivative or undergo internal cyclization to give lactone derivatives after the migration of the carbonium ion along the hydrocarbon chain.

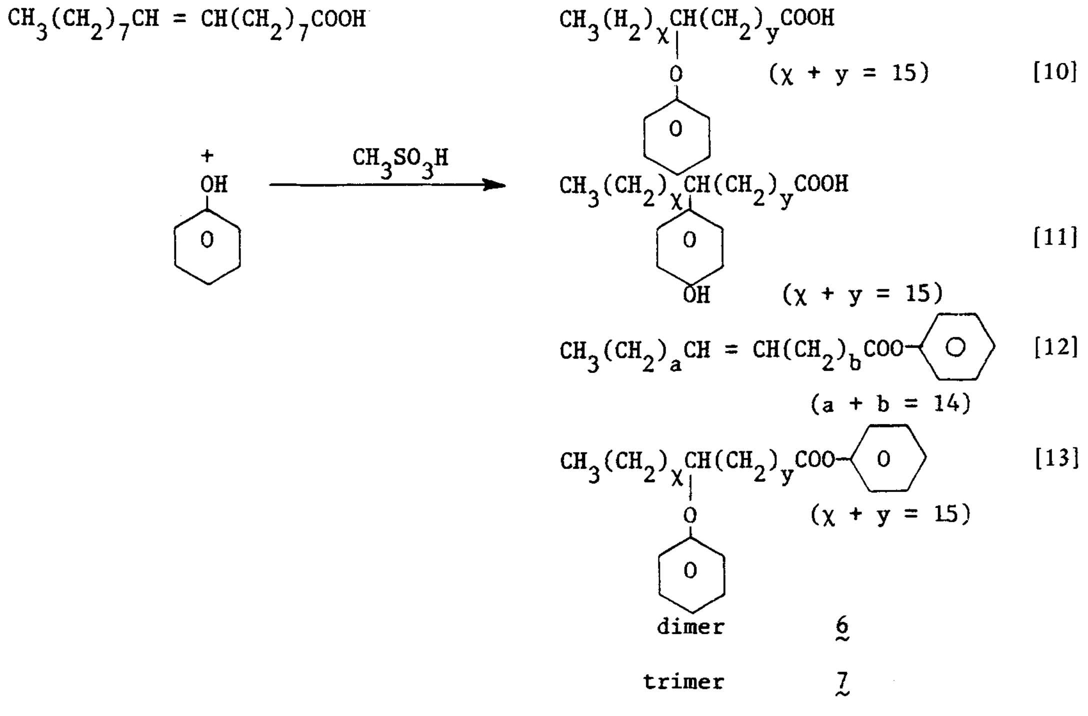
As Showell reported (11), dimer [6] and trimer [7] seemed to form by the reaction of oleic acid with carbonium ion. Similarly, cyclic ketones ([9a] and [9b]) could be formed through the protonation of the carboxyl group of oleic acid to give an acylium ion, followed by an intramolecular cyclization.

When phenol was reacted with oleic acid in the presence of methanesulfonic acid (Scheme 2), 2 types of addition products, phenylether [10] and hydroxyphenylstearic acid [11], were obtained was the major products. The yields of these 2 types of products varied with the reaction temperature and the amount of methanesulfonic acid employed (Table II). Phenol esters [12] or [13] and dimer [6] and trimer [7] of oleic acid were formed as the minor products. Unlike with the toluene or benzene reactions, no lactones were detected.

As shown in Table II, phenylether [10] formed favorably over hydroxyphenylstearic acid [11] when low molar amounts of methanesulfonic acid were used. For example, 46% of [10] and 7% of [11] were obtained at a 1:1 molar ratio of methanesulfonic acid to oleic acid at 25 C, whereas, at a 6:1 molar ratio, an 88% yield of [11] was obtained.

The yield variation between [10] and [11] with the reaction temperature was observed particularly when methanesulfonic acid was employed with oleic acid at a molar ratio of 2:1. The phenylether [10] was formed favorably over hydroxyphenylstearic acid [11] (54% [10], 17% [11]) at 25 C, whereas yields were reversed (1% [10], 82% [11]) at 50 C (Table II).

Hydroxyphenylstearic acids [11] were the predominant form (88% [11], 2% [10]) even at 25 C, when large amounts of methanesulfonic acid were employed, such as 6:1. The formation of dimer and trimer of oleic acid ([6] and [7]) was increased by the temperature or the amount of methanesulfonic acid. Unlike the toluene reaction, orthosubstituted addition products were formed in preference to parasubstituted products, with a ratio of



Scheme 2

TABLE II

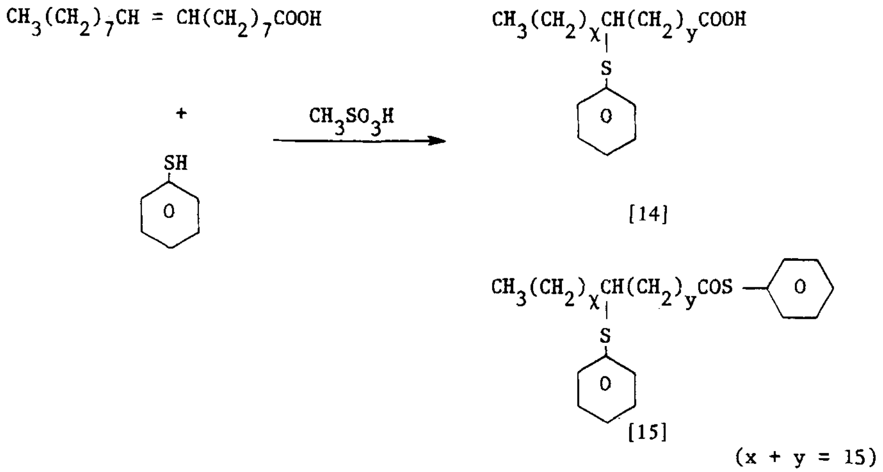
Reaction of Oleic Acid with Phenol[a]

Oleic acid/CH_3SO_3H (molar ratio)	Temperature (C)	Conversion (%)	Phenylether 10 (%)	Hydroxyphenylstearate[bc] 11 (%)	12 (%)	13 (%)	6 + 7 (%)
1/0.5	25	32	28	2	2	–	–
1/0.5	50	80	41	13	6	16	4
1/0.0	25	65	46	7	2	5	5
1/1.0	50	87	25	39	4	9	10
1/2.0	25	82	54	17	2	5	4
1/2.0	50	97	1	82	2	–	12
1/6.0	25	98	2	88	1	–	7

[a]Time 6 hr, oleic acid:C_6H_5OH = 1:5 (molar ratio).

[b]Ortho:para ∿ 4:1.

[c]Yields were based on oleic acid.



Scheme 3

4:1, as determined by GLC and IR spectroscopy.

When phenol was reacted with oleic acid in the presence of methanesulfonic acid at a molar ratio of 2:1:6, the reaction mixture was analyzed periodically by GLC and TLC. We found that phenylether [10] formed faster than hydroxyphenylstearic acid [11] in the initial reaction stage (30 min), then [10] decreased gradually. Hydroxyphenylstearic acid forms slowly in the early stages; then the yield increases to over 80% after a 4-hr reaction time. These results suggest as reported by others (4), that hydroxyphenylstearic acid might be formed by the rearrangement of the phenyl ether.

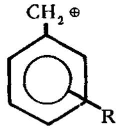
To clarify this point, the methyl ester of phenylether [10] was isolated by column chromatography and resubjected to the reaction conditions.

At a 1 to 5 molar ratio of phenylether [10] to methanesulfonic acid, 90% of the phenylether rapidly decomposed to phenol and methyl octadecenoate in less than 30 min, and hydroxyphenyloctadecenoate [11] formed gradually.

From these experiments, we concluded that phenylether [10] did not rearrange to form hydroxyphenyloctadecenoate, but instead decomposes to phenol and octadecenoate in the presence of large amounts of methanesulfonic acid, and that hydroxyphenyloctadecenoate is formed by the direct reaction of phenol with oleic acid (octadecenoic acid).

As shown in Scheme 3, unlike phenol, thioether [14] was the only addition product obtained when thiophenol was reacted with oleic acid in the presence of methanesulfonic acid. In this instance, the addition reaction was so fast that 77% of the addition product was formed in 30 min at 25 C when 1 mol of oleic acid was reacted with 5 mol thiophenol in the presence of 6 mol methanesulfonic acid. The thioester of the thioether [15] was also formed as the by-product, however, no trace of thiophenylstearic acid (ring-addition product) could be detected. Thioether [14] apparently is very stable under the strong acid condition employed.

Mass spectra of these aromatic addition products to oleic acid clearly showed the structural difference between benzene ring-addition type products and phenylether-type products. Phenol and thiophenol were the most intense ion fragment peaks from phenylether [10] or thioether [14], whereas substituted benzyl cation



was the most intense peak from benzene ring-addition products [3] or [11].

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♣The Fatty Acid Composition of Gymnospermae Seed and Leaf Oils

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ABSTRACT

Of 12 Gymnospermae seed and leaf oils, only 2 contained cyclopropene fatty acids. All-*cis* 5, 11, 14, 17-eicosatetraenoic acid occurred in concentrations up to 11.9% in 6 seed oils, and up to 61% in 2 leaf oils. The structure of this acid, as its methyl ester, was established by the combination of physical (UV, IR, ^{1}H- and ^{13}C-NMR and mass spectra) and chemical techniques. Arachidonic acid also occurred in 2 seed oils.

INTRODUCTION

Berry (1) first reported the occurrence of cyclopropene fatty acids (CPFA) in Gymnospermae species, finding 40-50% in the seed and leaf oils of *Gnetum gnemon;* a tree widely cultivated in Southeast Asia. Takagi and Itabashi (2) reported significant amounts of non-methylene-interrupted polyenoic acids in various species in the Cupressaceae, Pinaceae, Podocarpaceae and Taxodiaceae families, including up to 8.5% of all-*cis* 5, 11, 14, 17-eicosatetraenoic acid in the seed oils of 3 species in each of the Cupressaceae and Taxodiaceae families.

All-*cis* 5, 8, 11, 14- and all-*cis* 5, 11, 14, 17-eicosatetraenoic acids were found by Schlenk and Gellerman (3) in mosses and in the leaves and seeds of *Ginkgo biloba.* Kleiman et al. (4) identified the all-*cis* 5, 11, 14, 17-acid in the seed oil of *Ephedra campylopoda,* while Jamieson and Reid (5) found up to 7.7% of this acid in the leaf acids of 33 conifer species.

The fatty acids of the seed oils of 9 Australian Gymnospermae species and 3 leaf oils have been assayed for the presence of CPFA and eicosatetraenoic acids.

EXPERIMENTAL PROCEDURES

Material

Seeds and leaves were collected in New South Wales, Queensland and Tasmania.

General Procedures

The methods used for the extraction of the oils, the preparation of methyl esters, the Halphen color test, the determination of CPFA and the gas chromatography procedures were similar to those described in two previous papers (6, 7).

Separation and Identification of Methyl Eicosatetraenoate

The methyl ester was separated in 80-90% purity by fractionation of the ester mixtures on a column (30 cm X 1.5 cm) of Adsorbosil CABN containing 25% silver nitrate (Applied Science Laboratories, State College, PA) using a series of eluting solvents—toluene-hexane (50:50, v/v), toluene-hexane (75:25, v/v), toluene (100%) and ether-hexane (25:75, v/v). Most of the ester appeared in the 2 later eluents. The purity of these fractions was raised to 95-98% by fractionation on TLC plates, 0.5 mm thick, prepared from Silica gel PF$_{254}$ (E. Merck AG, Darmstadt, W. Germany) containing 16% silver nitrate, using ether-hexane (12:88, v/v) at 20 C as the developing solvent. Alternately, toluene-hexane (90:10, v/v) at –20 C was used. The tetraenoate occurred in the narrow band remaining at the origin. Samples of the ester for spectroscopic examination were further purified by gas liquid chromatography (GLC) using a stainless steel capillary column (150 m long and 0.75 mm i.d.), the walls coated with Silicone OV-101. The ultraviolet (UV) spectrum of the ester (in hexane) was recorded on a Gilford 2600 spectrophotometer, the infrared (IR) spectrum (as a thin film) on a Perkin Elmer 521 spectrometer, and the ^{1}H- and ^{13}C-nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra (as C_6D_6 solutions) on a Bruker CXP100 spectrometer. The low-resolution and high-resolution mass spectra were recorded using a Varian MAT-311A mass spectrometer. The products obtained from the hydrazine reduction (8) of the tetraenoate were isolated by argentation TLC at –20 C (9) and were identified by GLC and mass spectrometry. Products obtained from the oxidative cleavage (10) of the monoenoates derived from the partial reduction of the tetraenoate were identified by GLC using a glass column (4 m long, 2 mm i.d.) packed with 10% Silar 10C on Gas-Chrom Q. The dimethyl dicarboxylates were identified by comparison of their GLC retention times with those of a standard ester mixture.

RESULTS AND DISCUSSION

The results of the assay of the methyl esters and the average mass and oil contents of the air-dried seeds without testa are given in Table I.

Oil Contents

The oil contents of the seeds ranged from high (13.5%) in *Athrotaxis selaginoides* to low values (0.6-1%) in *Macrozamia communis* and *Podocarpus elatus.*

Cyclopropene Fatty Acids

Malvalic and sterculic acids occurred in moderate amounts in only 2 species – *Macrozamia communis* and *Callitris rhomboidea.* These results, together with those previously reported by Vickery (6), indicate that the occurrence of CPFA is erratic in most plant families except Malvaceae, Sterculiaceae and Bombacaceae.