# Fatty Acid Composition of Seed Oils of the Meliaceae, Including One Genus Rich in *cis*-Vaccenic Acid

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## ABSTRACT

The seed lipids of three species of *Entandraphragma* (Meliaceae) contain the largest proportion (31-50%) of *cis*-vaccenic acid ever found in nature. The acid is not indicative of the family as a whole and is found as a major fatty acid in the seed of only one additional species, besides *Entandraphragma*, out of the 30 analyzed from this family. With the total oil comprising between 45 and 62% of *Entandraphragma* seed, these species should be considered as a source of undecadioic acid for the production of nylon 11.

## INTRODUCTION

*Cis*-vaccenic (*cis*-11-octadecenoic) acid is most likely as ubiquitous in seed oil lipids as oleic acid, but in almost all cases is not as abundant. This acid often is not reported as a constituent of such lipids because it is not readily separable from the generally more abundant oleic acid. With capillary column technology becoming more available in gas chromatographic systems, *cis*-vaccenic (11-18:1) is becoming easier to identify and quantitate. When found, 11-18:1 is generally 0.1-3% of the total acyl groups. Some reports, however, show 15% of the seed oil acyl groups to be 11-18:1 (1,2). We found that seed oils from three species of the genus *Entandraphragma* (Meliaceae family) contain up to 50% of their acids as 11-18:1, the greatest concentration of this acid ever found in nature. These species also are relatively abundant in 16:1 and 16:2 as well as in total oil content (45-62%). Although the composition of several species of the Meliaceae have been reported previously (3), none have been analyzed for 11-18:1. To learn if 11-18:1 was chemotaxonomically indicative of the family, we analyzed 30 species of the Meliaceae by capillary column GC. Only a few species were richer than usual in this fatty acid.

Although this plant family is known for its quality timber, especially mahoganies (4), its seed oils have not been utilized except for a few species used locally for medicinal purposes or for soap (5). These oils generally are not useful for food, but the 11-18:1 from *Entandraphragma* seed oils could be important industrially. Undecadionic acid produced from the cleavage of 11-18:1 at the double bond could be used for the production of nylon 11. Besides the undecadioic acid, this reaction also would produce heptanoic acid, which is potentially useful in lubricants.

## EXPERIMENTAL

Seeds were collected in the wild or obtained from commercial seed houses. Protein was determined by standard Kjeldahl procedures or by autoanalyzer following sulfuric acid digestion (6). Oil content was determined by Butt extraction of ground seed with petroleum ether as in AOCS Method Ad 6-52. Methyl esters were prepared from acyl constituents using $BF_3$-methanol (7) and subsequently were analyzed by packed column gas chromatography (GC) as previously described (8). Capillary column GC was accomplished using a Packard Model 428 gas chromatograph equipped with a 25 M × 0.2 mm glass column coated with SP-1000 and held at 190 C. Separations were similar to those made by Slover and Lanza (9).

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Thin-layer plates coated with a 2-mm layer of Silica Gel G impregnated with 20% $AgNO_3$ were used to separate esters of *E. angolense* seed oil according to the number of double bonds. Benzene was used as the developing solvent. The resulting fractions were then separated into individual fatty ester species by HPLC using a Partisil M-9 10/50 ODS-2 column (Whatman) with methanol as the eluting solvent (5 ml/min) and a refractometer as detector.

Double bonds of unsaturated methyl esters were converted to monomethoxy derivatives (10) and subsequently analyzed by mass spectrometry to locate the position of the olefinic bond. Infrared spectra were obtained with a Perkin-Elmer 137 spectrophotometer using liquid films on sodium chloride discs.

## RESULTS AND DISCUSSION

Thin-layer separation of the esters from *E. angolense* seed

**TABLE I**

**Ions Defining Double Bond Locations from Methoxylated Isolated Esters of *Entrandrophragma angolense***

| Ester | Fragment[a] type | m/z | Relative abundance | Location |
|---|---|---|---|---|
| 16:1 | b | 129 | 100 | |
| | | | | n-7 |
| | b | 143 | 77 | |
| | a | 201 | 77 | |
| | | | | Δ 9 |
| | a | 215 | 77 | |
| | b | 101 | 8 | |
| | | | | n-5 |
| | b | 115 | 7 | |
| | a | 229 | 3 | |
| | | | | Δ 11 |
| | a | 243 | 2 | |
| 16:2 | a | 87 | 27 | |
| | | | | n-4 |
| | a | 101 | 19 | |
| | b | 201 | 14 | |
| | | | | Δ 9 |
| | b | 215 | 10 | |
| 18:1 | b | 129 | 100 | |
| | | | | n-7 |
| | b | 143 | 89 | |
| | a | 229 | 82 | |
| | | | | Δ 11 |
| | a | 243 | 68 | |
| | b | 157 | 4 | |
| | | | | n-9 |
| | b | 171 | 4 | |
| | a | 201 | 7 | |
| | | | | Δ 9 |
| | a | 215 | 6 | |
| 18:2 | b | 115 | 45 | |
| | | | | n-6 |
| | b | 129 | 25 | |
| | a | 201 | 54 | |
| | | | | Δ 9 |
| | a | 215 | 18 | |

[a] a = $CH_3-\overset{O}{\overset{\|}{C}}-(CH_2)_x-\overset{OCH_3}{\overset{\backslash}{CH}}{}^{\oplus}$. b = $\overset{OCH_3}{\overset{|}{CH}}-(CH_2)_y-CH_3$

**TABLE II**

**Seed Composition of the Meliaceae**

| Species | Identification no. | Source | % Oil, D.B. | % Protein, D.B. | Fatty acids, area % by GC | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 14:0 | 16:0 | 16:1[a] | 18:0 | 18:1[9] | 18:1[11] | 18:2 | 18:3 | 20:0 | 20:1 | 22:0 | 22:1 | Others |
| *Aglaia cordata* Hiern. | 62550 | Thailand | 0.6 | 8.4 | 8.7 | 23.5 | TR | 7.7 | 30.2 | 0.8 | 20.0 | 1.0 | – | TR | – | 1.4 | 6.4[b] |
| *Aglaia odoratissma* Blume | 62610 | Thailand | 3.2 | 21.8 | 0.2 | 22.3 | 0.4 | 7.4 | 10.4 | 1.0 | 46.0 | 6.7 | 1.5 | 2.4 | 0.4 | | 1.2 |
| *Azadirachta indica* A. Juss. | 62154 | India | 42.9 | | 0.1 | 18.1 | 0.2 | 14.2 | 50.4 | 0.8 | 13.3 | 0.5 | 1.4 | 0.1 | 0.2 | | 0.7 |
| *Carapa procera* DC. | 61505 | Ghana | 68.9 | 8.1 | 0.2 | 25.6 | 0.6 | 9.1 | 45.3 | 0.4 | 16.4 | 0.2 | 1.6 | 0.2 | 0.5 | | |
| *Cedrela odorata* | 16572 | Florida | 21.4 | 25.4 | 0.1 | 9.3 | 0.3 | 4.8 | 5.6 | 0.7 | 42.5 | 29.1 | TR | 0.2 | | | 7.4[c] |
| *Cedrela toona* Roxb. ex. Rottl. & Willd. | 61740 | India | 1.0 | | 0.3 | 11.7 | 0.5 | 4.3 | 10.1 | 0.9 | 38.5 | 24.6 | 0.9 | 0.1 | 1.1 | | 7.0[c] |
| *Chickrassia tabualris* A. Juss. | 46603 | India | 45.9 | 27.1 | – | 9.6 | TR | 4.9 | 10.0 | 1.0 | 45.9 | 28.2 | | | | | 0.3 |
| *Dysoxylum malbaricum* Bedd. ex. C.DC. | 62060 | India | 7.4 | 26.2 | | 20.3 | 4.8 | 8.0 | 14.1 | 11.4 | 27.5 | 9.0 | 0.8 | | | | 4.0 |
| *Dysoxylum reticulatum* King | 62096 | India | 5.2 | 12.8 | 1.4 | 50.3 | 0.5 | 6.8 | 13.5 | 0.9 | 17.2 | 2.0 | 0.5 | 0.2 | | | 6.5[c] |
| *Dysoxylum spectabile* (Forst. F.) Hook. F. | 61922 | New Zealand | 34.1 | 13.7 | 0.4 | 51.5 | 0.4 | 4.8 | 3.3 | 0.5 | 35.6 | 3.1 | 0.2 | | | | 0.1 |
| *Entandrophragma angolense* (Welw.) C. DC. | 61528 | Ghana | 62.4 | | TR | 6.4 | 16.5 | 15.4 | 2.6 | 39.4 | 12.1 | 0.1 | 1.5 | | | | 6.0[d] |
| *Entandrophragma clindricum* (Sprague) Sprague | 61412 | Ghana | 45.2 | 26.4 | 0.2 | 4.0 | 7.2 | 16.0 | 7.1 | 49.7 | 5.3 | 6.0 | 1.1 | | | | 3.4[e] |
| *Entandrophragma utile* (Dawe and Sprague) Sprague | 61512 | Ghana | 53.7 | 20.4 | – | 3.0 | 2.4 | 3.3 | 4.4 | 30.8 | 9.1 | 46.2 | TR | TR | | | 0.8 |
| *Khaya anthotheca* (Welw.) C. DC. | 61497 | Ghana | 37.9 | 9.3 | 0.1 | 18.5 | 0.3 | 6.2 | 48.8 | 1.0 | 23.9 | 0.2 | 0.5 | 0.2 | 0.2 | | 0 |
| *Khaya grandifolia* C. DC. | 61769 | Ghana | 43.0 | | TR | 10.5 | 0.2 | 11.0 | 67.9 | 1.3 | 6.5 | 0.5 | 0.7 | 0.1 | 0.5 | | 0.7 |
| *Lansium domesticum* Corr. | 62581 | Thailand | 2.5 | 11.7 | 1.1 | 42.1 | 0.9 | 7.6 | 18.2 | 5.5 | 17.5 | 7.1 | – | – | – | | |
| *Melia azedarach* L. | 60598 | Pakistan | 42.3 | | TR | 7.4 | 0.1 | 3.1 | 13.5 | 0.8 | 74.1 | 0.2 | 0.2 | 0.4 | | | 0.1 |
| *Melia burmanica* Kerz. | 63731 | India | 45.5 | | TR | 8.6 | 0.1 | 4.5 | 19.9 | 0.6 | 64.9 | 0.4 | 0.3 | 0.3 | | | 0.4 |
| *Melia dubia* Cav. | 49442 | India | 41.3 | 29.7 | TR | 7.5 | 0.1 | 4.2 | 19.2 | 0.6 | 67.1 | 0.3 | 0.3 | 0.3 | TR | TR | 0.4 |
| *Pseudobersama mossambicensis* (Sim) Verdc. | 62535 | Kenya | 22.0[f] | | 0.3 | 29.9 | 1.2 | 5.0 | 21.6 | 1.0 | 38.9 | 1.5 | 0.3 | | | | 0.3 |
| *Sandoricum koetjape* (Burm. F.) Merr. | 62560 | Thailand | 1.7 | 8.1 | 2.1 | 29.0 | – | 6.4 | 17.3 | 3.3 | 30.3 | 9.3 | | | 0.4 | 0.8 | 1.1 |
| *Swietenia macrophylla* King. | 46641 | India | 65.7 | 12.9 | TR | 11.6 | 0.3 | 14.4 | 29.4 | 1.0 | 29.3 | 11.9 | 1.5 | 0.1 | 0.1 | | 0.3 |
| *Swietenia mahogani* (L.) Jacq. | 46642 | India | 64.9 | 13.5 | TR | 12.0 | 0.3 | 14.4 | 27.4 | 0.9 | 30.5 | 12.5 | 1.5 | 0.1 | 0.2 | | 0.2 |
| *Toona sinensis* A. Juss. | 46627 | India | 35.8 | 37.9 | 0.1 | 9.9 | 0.4 | 3.6 | 9.1 | 1.5 | 43.3 | 27.1 | 1.6 | 0.5 | | | 1.8 |
| *Trichilia connaroides* (Wight & Am.) Bentvelzen | 62854 | India | 48.9 | 12.2 | TR | 6.7 | 0.2 | 7.3 | 77.4 | 1.8 | 4.5 | 1.0 | 0.5 | 0.3 | | | 0.3 |
| *Trichilia hendelotti* Planch. ex. Oliver | 61424 | Ghana | 50.7 | 11.9 | 1.5 | 39.3 | 1.0 | 1.8 | 32.9 | 1.7 | 19.2 | – | 1.2 | | | | 1.4 |
| *Trichilia prieureana* A. Juss. | 62024 | Ghana | 11.5 | 11.2 | 0.6 | 25.2 | 0.2 | 7.6 | 21.5 | 1.3 | 28.7 | 7.9 | 0.7 | 0.3 | TR | | |
| *Trichilia roka* (Forsk.) Chiov. | 61457 | Ghana | 49.8 | 19.9 | 0.2 | 60.9 | 2.1 | 1.3 | 20.4 | 2.7 | 11.4 | 0.7 | TR | TR | | | TR |
| *Trichilia rubescens* Oliver | 61824 | Ghana | 57.8 | 10.5 | 0.1 | 49.0 | 1.6 | 2.5 | 26.0 | 2.0 | 18.6 | TR | 0.2 | | | | |
| *Trichilia triphyllaria* C. DC. | 45441 | Uruguay | 24.7 | 10.1 | TR | 35.5 | 3.9 | 38.6 | 2.3 | 16.9 | 0.2 | 0.1 | | | | | 1.6 |

[a]9-16:1 + 11-16:1.
[b]6.4%-12:0.
[c]Many small unidentified components.
[d]Includes 5.3%-16:2.
[e]Includes 1.4%-16:2.
[f]Oil on as-is basis.

oil resulted in two fractions, saturates + monoenes and dienes. HPLC of these fractions resulted in isolates of nearly pure (>95%) 16:1, 16:2, 18:1 and 18:2. Mass spectral analysis of the saturated methoxy derivatives of these esters gave rise to ions that define the location of their double bonds (Table I). The absence of IR absorption bands, indicative of *trans* unsaturation and these ions, defines the unsaturated esters as 9c-16:1, 11c-16:1, 11c-18:1, 9c-18:1, 9c,12c-16:2 and 9c,12c-18:2. Concentrations of these acyl groups are shown in Table II. These same results were obtained from the esters of *E. clindricum* seed oil.

Quantification and identification of esters derived from other esters in this study were made by capillary GC analysis. Identification was made primarily through the use of equivalent chainlengths (ECL). The ECL of the monoenoic esters are: 9-16:1—16.24, 11-18:1—18.26, 11-16:1—16.36, 9-18:1—18.20.

Although *cis*-vaccenic acid might be a chemotaxonomic marker for the genus *Entandraphragma* (31-50%), it certainly is not for the entire family. We found only one other species, *Dysoxylum malbaricum,* with 11-18:1 as a major component (11%). Other species in the genus *Dysoxylum* had less than one per cent 11-18:1 (Table II). As previously observed (3), the family can be more generally characterized by the large amounts of saturated acyl groups. We found 16:0 values as high as 61% and 18:0 reaching 16%.

It has been generally accepted (11-17) that *cis*-vaccenic acid results from the elongation of 9-16:1 in the biosynthetic process. Kuemmel and Chapman (12) present data from a number of diverse biological systems and show a good relationship between the log of the 9-16:1 concentration and the concentration of 11-18:1. The most obvious anomaly was that from *Asclepias syriaca,* the richest source of 11-18:1 in their study. Our data, from the Meliaceae with more than 5% 11-18:1, when fitted to this line, also deviate greatly. The values from *Ephedra intermedia* (Ephedraceae) (9-16:1 = 0.5%, 11-16:1 = 0, 9-18:1 = 20.6, 11-18:1 = 10.8) and from *Dyckia montevidensis* (Bromeliaceae) (9-18:1 = 7.4%, 11-16:1 = 0.5, 9-18:1 = 18.2, 11-18:1 = 18.4), two species outside of the Meliaceae family, also did not fit the line proposed in (12). The presence of small amounts of 11-16:1 in all of these species indicates the possibility that another biosynthetic pathway also could be operational, i.e., a delta-11 desaturase. Indeed, in studies of 11-18:1 biosynthesis this acid is a fairly minor lipid constituent. In seed where large amounts of unusual olefinic unsaturation has been reported, such as in delta-5 [*Limnanthes* (18)] and delta-6 acids [*Umbelliferae* (14)], a specific desaturase has been found. It is quite possible that a delta-11 desaturase is operative in seeds from plants such as *Asclepias* and *Entandraphragma.* This system is not unknown, and has been reported to be active in bacterium, *Leptospira canicola* (19).

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