

GENERAL RESEARCH

Industrial Utilisation of *Celsia coromandeliana* Seed Oil: A Moderate Source of Isoricinoleic Acid

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Celsia coromandeliana, Vahl Syn. *Verbasum coromandelianum*, (Vahl) Kuntze seed oil was found to contain 22.0% 9-hydroxyoctadec-*cis*-12-enoic acid (isoricinoleic acid) previously unknown in the Scrophulariaceae plant family. It also consists of other normal fatty acids such as lauric acid (1.3%), myristic acid (2.6%), palmitic acid (8.2%), stearic acid (3.2%), oleic acid (17.2%), and linoleic acid (45.5%). The identification and characterization were based on UV, FTIR, ^1H NMR, and mass spectra, GLC analysis, and chemical degradations.

Introduction

The seed oils containing hydroxy fatty acids are industrially important as they are used in protective coatings, plastics, urethane derivatives, surfactants, dispersants, cosmetics, plasticizers, lubricant additives, pharmaceuticals, soaps, detergents, textiles, and a variety of synthetic intermediates. The ethoxylated derivatives of seed oils containing hydroxy fatty acids are used as stabilizers of hydrophobic substances in industries such as perfumes and cosmetics, e.g., castor oil. The polyethoxylated hydroxy fatty acids are nonionic surfactants and are included in the formulations for cleaning clothes, dishes, hard surfaces, and metals and in textile processing.

The new and interesting unusual fatty acids present in high concentrations in certain seed oils are being exploited for industrial utilization. These fatty acids of unusual structures are highly important in the production of oleochemicals. The only hydroxylated vegetable oil of commercial use is castor seed oil. The industrial importance attained by this seed oil in numerous applications suggests that additional hydroxylated acid containing seed oils may extend the range of usefulness of this type of compound in industry. In the production of nylon-11, castor oil is transesterified with methanol to form methyl ricinoleate and glycerol. The hydrogenation of castor oil can be performed in a number of ways to produce unique derivatives. The largest use for hydrogenated oil is in the manufacture of multipurpose greases. *Celsia coromandeliana* is a moderate source of hydroxy fatty acid, which shows sufficient promise for its exploitation for industrial utilization. Considering the extensive applications of hydroxy fatty acids isolated from natural oil and fats for industrial uses, an attempt has been made to isolate new and interesting unusual fatty acids.

An exhaustive survey of the literature reveals that no work has been reported about the component fatty

Table 1. Analytical Values of *Celsia coromandeliana* Seed Oil

oil content in seeds	16.0%
unsaponifiable matter	2.2%
iodine value	116.0
saponification value	200.0
direct TLC test	+ve ^a
Halphen test	–ve ^b
Picric-acid TLC test	–ve ^b
2,4-dinitrophenyl hydrazine (2,4-DNPH) TLC test	–ve ^b
infrared spectrum for hydroxyl functional group	3450 cm ^{–1}

^a +ve indicates positive response to the test. ^b –ve indicates negative response to the test.

acids of *Celsia coromandeliana* seed oil. The present investigation describes the occurrence of isoricinoleic acid together with the other normal fatty acids in *Celsia coromandeliana* seed oil as well as in the Scrophulariaceae plant family.

Experimental Section

The air-dried seeds were powdered and extracted thoroughly with light petroleum ether (bp 40–60 °C) in a Soxhlet extractor for 24 h to yield 16.0% of a yellowish oil. The analytical values of oil so obtained were determined according to the standard American Oil Chemists' Society (AOCS) methods⁸ and are listed in Table 1. The direct TLC of the oil revealed the presence of hydroxy fatty acids. This hydroxy fatty acid showed a large spot moving a little lower than the *Ricinus communis* seed oil and with the same mobility as the *Semecarpus kurzi*⁵ and *Wrightia coccinea*⁹ seed oils. The seed oil did not respond to the Halphen test,⁷ Picric-acid TLC test,⁶ or the 2,4-dinitrophenylhydrazine (2,4-DNPH) TLC test,⁴ thereby indicating the absence of cyclopropenoid, epoxy, and keto fatty acids, respectively.

The transesterified methyl esters of *Celsia coromandeliana* seed oil (200 mg) were treated with hexamethyldisilazane and trimethylchlorosilane.³ The silylated methyl esters were subjected to GLC analysis using silylated methyl esters of castor oil as the reference

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Table 2. Composition of Silylated Methyl Esters of *Celsia coromandeliana* Seed Oil

fatty acids	percentage
lauric	1.3
myristic	2.6
palmitic	8.2
stearic	3.2
oleic	17.2
linoleic	45.5
isoricinoleic (C _{18:1} -OTMSi)	22.0

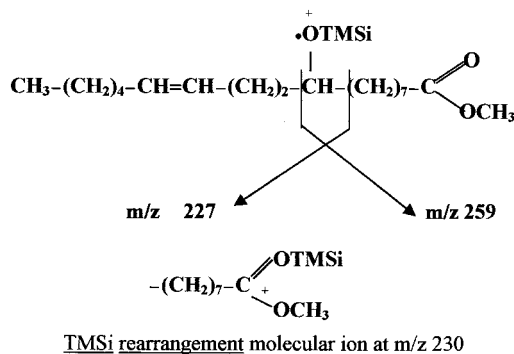
standard. The seed oil of *Celsia coromandeliana* was found to contain isoricinoleic acid (22.0% of total silylated fatty acid methyl esters), along with the other normal fatty acids such as lauric (1.3%), myristic (2.6%), palmitic (8.2%), stearic (3.2%), oleic (17.2%), and linoleic (45.5%), and the results are summarized in the Table 2.

Instrumentation. The UV spectra were taken on a Hitachi 270-30 model instrument using 0.001% concentration of methanol as the solvent. The IR spectra were recorded on a Fourier transform infrared (FTIR) Bomem Michelson Series model instrument as liquid films. The ¹H NMR spectra were recorded on a Varian T-60 model instrument using CDCl₃ as the solvent. The chemical shifts were measured in parts per million (ppm) downfield from internal TMSi at $\delta = 0$. The mass spectra were recorded on a Finnigan Mat instrument with PDP Micro Computer 810, at 70 eV with a source temperature of 150 °C. The GLC analysis was performed on a Perkin-Elmer model Sigma unit using a 15% DEGS column on chromosorb W (354–250 μ m) 45–60 mesh. The temperatures at the injection port, detector port, and oven were 240, 240, and 190 °C, respectively. The nitrogen flow and chart speed were 30 mL/min and 1 cm/min, respectively. The machine recorded directly the weight percent of individual peaks. The peaks were identified by comparing their retention times with those of standard reference samples under similar conditions. The melting points were recorded on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Isolation of Hydroxy Fatty Acid. The saponification of *Celsia coromandeliana* seed oil was effected by stirring the oil overnight at room temperature (27 °C) with 0.8 N alcoholic potassium hydroxide. The material that could not be saponified was removed. The resulting mixed fatty acids were separated into oxygenated and nonoxygenated fractions according to Gunstone's partition method¹ between light petroleum ether (bp 40–60 °C) and 80% methanol. The yield of hydroxy fatty acid was 22.0% of total fatty acids. A concentrate of pure hydroxy fatty acid (21.9%) was obtained by preparative TLC techniques. The elemental analysis (Calcd for C₁₉H₃₄O₃: C, 73.07%; H, 11.53%. Found: C, 73.18%; H, 11.63%) of the hydroxy methyl ester suggested a mono-hydroxy compound.

Results and Discussion

The infrared spectrum of the hydroxy fatty ester showed strong absorption bands at 3450 and 1740 cm⁻¹ for the free hydroxyl and ester carbonyl functional groups, respectively. The infrared spectrum also showed the absorption bands at 715 and 1620 cm⁻¹ for a *cis* double bond. However, the UV and IR spectra showed no evidence for trans unsaturation or the presence of conjugation. The unsaturated hydroxy fatty acid upon hydrogenation¹¹ gave 9-hydroxyoctadecanoic acid (mp

Scheme 1. Mass Spectral Fragmentation of TMSi Derivative of 9-Hydroxyoctadec-*cis*-12-enoate (M⁺ = 384).

and mixed mp 81–82 °C). The chromic acid oxidation¹⁰ of 9-hydroxyoctadecanoic acid gave 9-oxo-octadecanoic acid (mp 79–80 °C). The infrared spectrum of this 9-oxo-octadecanoic acid showed a characteristic absorption band at 1710 cm⁻¹. The reductive deoxygenation² of 9-hydroxyoctadecanoic acid yielded octadecanoic acid (stearic acid), as identified by GLC analysis. The permanganate–periodate¹² oxidation of the unsaturated hydroxy fatty acid afforded hexanoic acid (*p*-bromophenacyl ester, mp 70–71 °C) and γ -lactone. The infrared spectrum of γ -lactone showed a characteristic absorption band at 1775 cm⁻¹. The oxidative cleavage products such as hexanoic and γ -lactone suggest a double bond at C₁₂ and a hydroxyl group at C₉.

The ¹H NMR spectrum of the unsaturated hydroxy fatty ester exhibited signals at δ 5.33 (m, 2H, $-CH=CH-$), 3.6 (s, 3H, $-COOCH_3$), 3.45 (m, 1H, $-CHOH$), 4.2 (m, 1H, $-CHOH$, which disappears upon D₂O addition), 2.2 (m, 6H, overlapping signals ascribable to allylic protons and protons α to the carbonyl function), 1.2 (s, 18H, shielded methylene protons $-(CH_2)_9-$), and 0.88 (t, 3H, terminal $-CH_3$). After the sample was shaken with D₂O, the signals at δ 4.2 disappeared, with a small change in the signal at δ 3.45. The acetylated derivative of the hydroxy fatty ester showed infrared absorption bands at 1730 and 1210 cm⁻¹ for the acetate group, and the ¹H NMR spectrum showed two new signals at δ 5.31 (m, 1H, $-CH-OCOCH_3$) and 2.1 (s, 3H, $-OCOCH_3$).

The mass spectrum of the trimethylsilyl (TMSi) derivative of the hydroxy olefinic ester showed molecular ion peak at m/z 384, indicating a C₁₈ chain with unsaturation. The mass spectrum of the TMSi derivative of hydroxy olefinic ester was identical to that of the TMSi derivative of authentic methyl isoricinoleate. The structure-revealing molecular ions were observed at m/z 227 and 259. The TMSi molecular rearrangement ion at m/z 230 unequivocally established the position of the hydroxy group at C₉ and indicated the double bond at C₁₂ (Scheme 1).

Thus, the conclusive results demonstrated that the isolated hydroxy fatty acid from *Celsia coromandeliana* seed oil can be characterized as 9-hydroxyoctadec-*cis*-12-enoic acid (isoricinoleic acid).

Acknowledgment

This research work is financially supported by the Department of Science & Technology (DST), New Delhi, India 110 016.

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Received for review June 13, 2000

Revised manuscript received August 21, 2000

Accepted September 4, 2000

IE0005809