Cassia siamea Seed Oil: A Minor Source of Vernolic and Cyclopropenoid Fatty Acids

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***Cassia siamea* oil contains palmitic (19.0%), stearic (7.6%), oleic (11.6%), linoleic (42.7%), malvalic (2.0%), sterculic (3.1%) and vernolic (14.0%) acids.**

Cassia siamea Lam., Syn. *Senna siamea* (Lam.) H. Irwin & Barneby, is a large ornamental tree indigenous to India. The flowers are used as a vegetable. The pods and leaves contain toxic alkaloid. This species is used as one of the hosts for the lac insect (1).

The present paper describes the occurrence of vernolic and cyclopropenoid fatty acids along with usual fatty acids. This is the first report on this seed oil.

MATERIALS AND METHODS

Seeds of *Cassia siamea* were powdered and extracted thoroughly with light petroleum ether to yield the oil. The analytical values for the oil and seeds were determined according to AOCS methods (2). The oil responded to Halphen and picric acid thin layer chromatography (TLC) tests (3,4), indicating the presence of cyclopropenoid and epoxy fatty acids, respectively. The infrared spectra of the oil and its methyl esters showed characteristic bands at 1010 cm^{-1} and 825 cm^{-1} for cyclopropenoid and epoxy functional groups, respectively. The Durbetaki titration (5) of oil at 3 and 55 C indicated 14.2% epoxy and 5.2% cyclopropenoid fatty acids, respectively.

Acetolysis of epoxide. A portion of oil (20.0 g) was stirred overnight at room temperature with 80 ml of 10% sulphuric acid in 200 ml of acetic acid, as descirbed by Wilson (6). The mixture was diluted with water and extracted with ether. The combined ether extracts were washed with water, dried over anhydrous sodium sulphate and evaporated in a stream of nitrogen to yield an oil.

The oil was saponified by being left overnight at room temperature with 0.8N alcoholic potassium hydroxide, and nonsaponifiable material was removed by ether extraction. After careful acidification to pH 5 with 0.5N sulphuric acid, the mixed fatty acids were extracted immediately with ether. The ether solution was washed with water until neutral, and the solvent was removed. Separation of these mixed fatty acids into oxygenated and nonoxygenated fractions was accomplished by preparative TLC.

Analytical TLC was performed on plates coated with 0.25- or 0.1-mm layers of silica gel G using 20 or 30% ether in hexane as the solvent. Preparative TLC was effected on 20-cm × 2-cm plates with 1.0-mm layers of silica gel. When the plates were sprayed with dichlorofluorescein, the separated bands were clearly visible under UV light. Acids from silica were extracted with ether.

Infrared (IR) spectra were determined as liquid films or as 1% solution in carbon tetrachloride on a Perkin-Elmer Model 577 instrument. GLC analysis was done on a Perkin-Elmer Sigma unit with a column containing 15% DEGS on Chromosorb W, 45-60 mesh. The temperature at injection port, detector port and oven were 240, 240 and 190 C, respectively. Nitrogen flow and chart speed were 30 ml/min and one cm/min, respectively.

TABLE 1

Analytical Data of Oil

Oil content	7.0 %
Unsaponifiable matter	1.98%
Iodine value	101
Saponification value	197
Halphen test	+
Picric acid TLC test	+
quivalent	
at 3 C	14.2 %
at 55 C	5.2 %
Fatty acids	
Palmitic	19.0 %
Stearic	7.6 %
Oleic	11.6 %
Linoleic	42.7 %
Vernolic	14.0 %
Malvalic	2.0 %
Sterculic	3.1 %

+ Indicates positive response to the test.

The fatty acid methyl esters were prepared by transesterification of the oil with absolute methanol that contained 1% sodium methoxide. The reaction was allowed to proceed by refluxing the solution for 20 min, and methyl esters were extracted with ether.

The methyl esters of nonoxygenated fatty acids (200 mg), prepared as described above, were treated with 60 ml absolute methanol saturated with silver nitrate (7). The reaction was allowed to proceed at room temperature with stirring for 24 hr. The normal methyl esters and the reaction products from cyclopropenoid fatty acids were recovered from the reaction mixture by adding 100 ml of distilled water and extracting them with ether. The extracts were dried over anhydrous sodium sulphate and the solvent was evaporated in a stream of nitrogen.

RESULTS AND DISCUSSION

Results are presented in Table 1. The dihydroxy acid obtained by preparative TLC had an IR absorption at 3450 cm^{-1} for the hydroxyl group, and its weight was equivalent to 14.0% of the total oil. The unsaturated dihydroxy acid on hydrogenation (8) furnished 12,13-dihydroxyoctadecanoic acid (9), m.p. 96–97 C (lit. m.p. 95–96 C). The unsaturated dihydroxy acid was cleaved with permanganate-periodate regent (10). GLC analysis of the resulting products as their methyl esters

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showed that the cleavage fragments were hexanoic and azelaic acids.

The unsaturated dihydroxy acid had the same R_f value as threo 12,13-dihydroxy oleic acid obtained by acetolysis of *Vernonia anthelmintica* seed oil.

The seed oil of *Cassia siamea* thus contains a minor amount of vernolic acid (14.0%). Seed oils containing epoxy acids are of potential interest as stabilizers in plastic formulations and in the preparation of other long-chain compounds (11,12). The seed oil of *Cassia siamea* also contains cyclopropenoid fatty acids (5.1%). Oils containing cyclopropenoid fatty acids have attracted attention owing to their biological effects in animals (13,14) and co-carcinogenic properties (15,16). This seed oil contains an appreciable amount of palmitic acid (19.0%) and a small amount of stearic acid (7.6%). The unsaturated acids are oleic (11.6%) and linoleic (42.7%).

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