Isoricinoleic Acid in *Semecarpus kurzii* Seed Oil

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ABSTRACT

Seed oil of *Semecarpus kurzii* was found to contain 10.5% of 9-hydroxy-*cis*-12-enoic (isoricinoleic) acid along with the usual fatty acids. The identification of the hydroxy acid was made on the basis of chromatographic, spectroscopic and chemical methods, with isoricinoleic acid used as the reference standard.

INTRODUCTION

Semecarpus kurzii, Engler (Anacardiaceae) vern. Bara Bhilwara (Hindi), is a handsome tree, distributed throughout the forests of Andaman and Nicobar (India) islands. The acrid juice causes blisters on skin. The leaves are used for elephant fodder, and the fruits are eaten by pigeons.

This paper details the fatty acid composition of *S. kurzii* seed oil. This is the first report of the occurrence of 9-hydroxy-*cis*-12-enoic (isoricinolic) acid in this family.

EXPERIMENTAL

Oil was extracted from the ground seeds of *S. kurzii* with light petroleum ether (boiling point 40-60 C) in Soxhlet apparatus. Preparation of the mixed fatty acids, methylation, purification of the hydroxy ester and hydrogenation were performed as previously detailed (1).

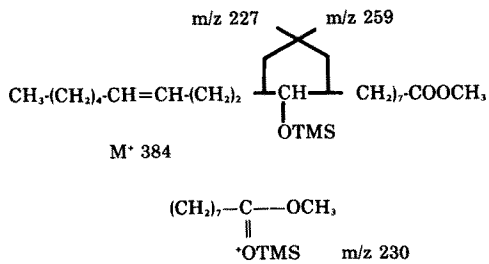
The chromatographic and spectroscopic methods have been described (2). Silylation of the methyl ester was conducted with hexamethyldisilazane and trimethylchlorosilane (3). Oxidative fission and deoxygenation were carried out according to published procedures (4,5); chromic acid oxidation was performed by the procedure of Smith et al. (6). Acetylation of the hydroxy acid was done with AC_2O-pyridine (7). The analytical values of oil and seeds were determined according to AOCS methods (8).

RESULTS AND DISCUSSION

Preliminary screening of the oil revealed the presence of an oxygenated acid (2,9). The presence of *trans* and/or conjugated unsaturation in the oil and its methyl ester were ruled out on the basis of ultraviolet (UV) and infrared (IR) spectra.

The elemental analysis (calcd. for $C_{19}H_{36}O_3$. C, 73.07%, H, 11,53%; found: C, 73.15%, H, 11.6%) of the hydroxy methyl ester suggested a monohydroxy compound. Its R_f, m.p., IR, NMR and MS characteristics were identical to those of authentic methyl isoricinoleate. The IR spectrum showed a broad band at 3400 cm^{-1} indicative of a hydroxyl group. Its NMR spectrum gave characteristic signals at δ 5.31 m(2H, C<u>H</u>=C<u>H</u>), 3,45m (1H, C<u>H</u>-OH) and 4.2m(1H, CH-O<u>H</u>, disappeared upon D_2O addition), along with the usual fatty ester signals (1). Its acetylated derivative showed new IR spectral bands at 1730 and 1210 cm^{-1} for the acetate group, and the NMR spectrum gave two new signals at δ 5.32m(1H, C<u>H</u>-OAc) and 2.07s(3H, OCOC<u>H</u>$_3$).

The mass spectrum of its trimethylsilyl (TMS) derivative (scheme 1) showed peaks at m/z 384(5% M^+), 294(32% M-90), 230 (10%, TMS rearranged ion), 75[50%, $HO^+=Si(CH_3)_2$] and 73 [100%, $(CH_3)_3Si^+$]. The structure revealing peaks at m/z 259 (38%) and 227 (38%) confirmed the position of the hydroxyl group at 9. The formation of these peaks of about equal intensity are characteristic when an OTMS group and double bond are separated by two methylene groups (10).



SCHEME 1

Hydrogenation of the unsaturated hydroxy acid gave 9-hydroxyoctadecanoic acid. It melted at 81-82 C either alone or mixed with authentic 9-hydroxyoctadecanoic acid. Reductive deoxygenation (5) of 9-hydroxyoctadecanoic acid yielded octadecanoic (stearic) acid as identified by GLC. Chromic acid oxidation (6) of this acid gave 9-oxo-octadecanoic acid (melting point 79-80 C, IR: 1710 cm^{-1}). Permanganate periodate[4] oxidation of the hydroxy acid afforded hexanoic acid and a γ-lactone, (IR: 1775 cm^{-1}), thus locating the position of double bond at C_{12} and hydroxyl group at C_9. These results conclusively demonstrated that the hydroxy acid present in the oil was 9-hydroxyoctadec-*cis*-12-enoic (isoricinoleic) acid.

GLC analysis revealed the presence of 10.5% isoricinolic acid along with other usual fatty acids (Table I). The analytical values of seeds and oil are given in Table II.

TABLE I

Fatty Acid Composition (wt%) of *S. kurzii* Seed Oil

14:0	16:0	16:1	18:0	18:1	18:2	18:3	Isoricinoleic acid
0.1	18.3	0.3	12.1	33.4	25.0	0.3	10.5

TABLE II

Analytical Data on Seeds and Oil

Oil %	Protein %	Moisture %	Unsaponifiable %	IV	S.V.	RI D_n^{30}
11.5	0.6	4.1	0.6	87.8	175.6	1.479

IV, iodine value; S.V., saponification value; RI, refractive index.

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