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SHORT REPORTS

A KETO FATTY ACID FROM *LAGERSTROEMIA SPECIOSA* SEED OIL

CHIRAG MAHMOOD JEHAN, D. DAULATABAD* and ABDURRAZZAQUE M. MIRAJKAR

Department of Chemistry, Karnatak University, Dharwad 580003, India

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Key Word Index—*Lagerstroemia speciosa*; Lythraceae; seed oil; keto fatty acid; 9-ketooctadec-*cis*-11-enoic acid.

Abstract—A new keto fatty acid, (9-ketooctadec-*cis*-11-enoic acid), has been isolated from *Lagerstroemia speciosa* seed oil. Identification was made by chemical and spectroscopic methods.

INTRODUCTION

The occurrence of keto fatty acids in natural seed oils is rare, although naturally occurring long chain hydroxy fatty acids are widely distributed in plants [1, 2]. The oil of *Licania rigida* [3] which has attained commercial status, contains 70–86% 4-ketoeleostearic acid. This acid is popular for its drying properties and hence it is used as an ingredient of paints and varnishes. *Lagerstroemia speciosa* which contains *ca* 20% of a hitherto unknown keto fatty acid has now been characterized as 9-ketooctadec-*cis*-11-enoic acid.

Lagerstroemia speciosa is a medium sized decidious tree distributed throughout India. Its leaves are purgative, deobstruent and diuretic, its roots are considered as astrigent, stimulant and febrifuge and its seeds are narcotic [4].

RESULTS AND DISCUSSION

Lagerstroemia speciosa seed oil responded to the DNP test [5], indicating the presence of a keto group. The IR spectrum of the corresponding methyl ester exhibited characteristic double carbonyl peaks at 1740 cm^{-1} for (ester-carbonyl) and 1705 cm^{-1} (chain carbonyl). The IR spectrum also showed a characteristic bands at 715 and 1620 cm^{-1} for the presence of *cis* double bonds. However, IR and UV spectra of the oil showed no *trans* unsaturation or the presence of conjugation.

The ^1H NMR spectrum of the methyl ester exhibited a multiplet at δ6.8 (2H, –CH=CH–) protons and second multiplet at δ3.2 (2H, CH_2-CO) and a singlet at δ2.9 (4H, OC–CH_2 CH_2–CO_2) besides usual protons signals. The unsaturated acid on reduction with Pd/C furnished 9-ketooctadecanoic acid. On oxidation [6] with $KMnO_4$–$NaIO_3$ in *t*-butanol it gave heptanoic acid (*p*-bromophenacyl ester, mp 66–67°) and azelaic acid (mp 106–107°) respectively.

The structure of the keto acid was further confirmed by mass spectrometry. The spectrum showed a $[M]^+$ at *m/z* 310, indicating a C_{18} chain acid with a keto group and unsaturation. An α-cleavage fragment on either side of the keto group gave peaks at *m/z* 185 and 153 (arising from *m/z* 185 by loss of 32 mu) and allylic cleavage at *m/z* 125 and 239 unequivocally established the position of the keto group at C-9 and placed the double bonds at C-11. All these observations showed that the original acid is 9-ketooctadec-*cis*-11-enoic acid. The seed oil of *L. speciosa* contains an appreciable amount of the new keto acid (21.1%) (Table 1).

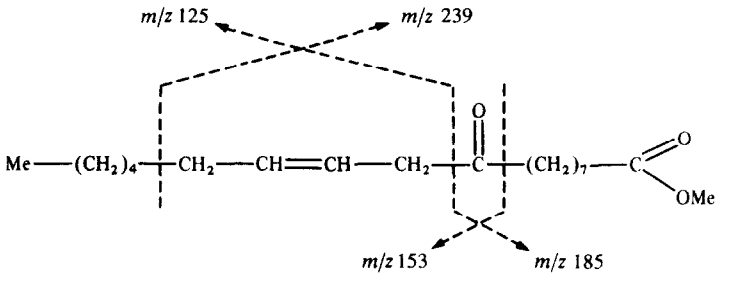
EXPERIMENTAL

IR were recorded in 1% CCl_4 solns. ^1H NMR were run at 60 MHz in $CDCl_3$ with TMS as int. std. Chemical shifts were measured in δppm downfield from TMS. MS were obtained by GC-MS at 70 eV. GC was carried out on 15% DEGS on Chromosorb W. The temp. of inj., det. and oven were 240, 240, and 190° respectively. N_2 flow rate was 30 ml min^{-1}.

Table. 1. Analytical data for seed oil from *Lagerstroemia speciosa*

Oil content	2.7%
Unsaponifiable matter	1.9%
Saponification value	195.5
Iodine value	122.3
DNP Test	+ve
Picric acid test	–ve
Halphen test	–ve
Fatty acids	
Palmitic	9.7%
Stearic	4.6%
Oleic	10.3%
Linoleic	54.3%
Keto acid	21.1%

*Author to whom correspondence should be addressed.



Air-dried seeds were extracted with petrol (40–60°) to yield the oil (2.7%). Analytical data were obtained according to AOCS methods [7]. The oil did not respond to Halphen [8] and picric acid TLC tests [9], indicating the absence of cyclopropoenoid and epoxy functional groups, respectively. However, the oil did respond to the DNP test showing the presence of a keto group. Me esters were prepd by refluxing the oil in MeOH in an acidic medium. Saponification of the oil was achieved by stirring overnight at room temp. with 0.8 M alcoholic KOH. Non-saponifiable matter was removed by extraction with Et_2O.

The mixed fatty acids were partitioned according to the method of ref. [10] between petrol and 80% MeOH. A concentrate of pure oxo acid (20.7%) was obtained by prep. TLC.

Identification of keto acid. Analysis carbon 73.30%, (required 73.52%), Hydrogen 11.12% (required 11.03%), with a molecular formula $C_{19}H_{34}O_3$. IR ν^{CCl_4} cm^{-1}: 1740 (CO_2Me) 1705 (CO), 715 and 1620 for *cis* double bonds. ^1H NMR ($CDCl_3$) δ0.85*s* (3H, terminal Me), δ1.25 *br s* (18 H, $-CH_2-$) δ2.2 *m* (2H, $-CH_2-C=C$), δ2.9 *s* (4H, $OC-CH_2$, CH_2-CO_2), δ3.2 *m* (2H, CH_2-CO), δ3.67*s* (3H, OMe) and δ6.8 *m* (2H, $-CH=CH-$). Hydrogenation was carried out using 10% Pd-c in EtOH (5 ml) to give 9-ketooctadecanoic acid, mp (43–44°). ^1H NMR δ0.85 (3H, Me), 2.3 (6H, $-CH_2-CO-CH_2$,CH_2-CO_2) and 3.67 (3H, OMe). MS, *m/z* 312.

Oxidation of the unsaturated acid was carried out in *t*-BuOH (20 ml). A soln of keto acid in *t*-BuOH (0.25%) was treated with a soln of $NaIO_3$ (200 mg) in 20 ml H_2O and $KMnO_4$ (1 ml) in the presence of K_2CO_3 (60 mg). The mixt. was stirred at room temp. for 24 hr, and the soln then decolourized with $NaHSO_3$ followed by acidification with HCl. The mixed acids were extracted with Et_2O. The Et_2O was removed and the extracts treated with 1% H_2SO_4 in MeOH (20 ml). The mixt. was refluxed for 1 hr and then extracted with Et_2O. The extracts were dried (Na_2SO_4) and the solvent removed under red. pres. GC analysis of the products as Me esters showed that the cleavage fragments were heptanoic and azelaic acids, respectively.

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