Pergamon

PII: S0031-9422(97)00205-7

Phytochemistry, Vol. 46, No. 1, pp. 155–156, 1997

0031-9422/97 $17.00+0.00

A KETO FATTY ACID FROM *AMOORA ROHITUKA* SEED OIL

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(*Received in revised form* 13 *January* 1997)

Key Word Index—*Amoora rohituka*; Meliaceae; seed oil; keto fatty acid; 7-keto-octadec-*cis*-11-enoic acid.

Abstract—7-keto-octadec-*cis*-11-enoic acid has been isolated from *Amoora rohituka* seed oil. Its identification was based on chemical and spectroscopic evidence. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Amoora rohituka is a large evergreen tree, having a straight cylindrical trunk with a heavy crown. The bark is astringent and used for treatment of enlarged glands, and disease of the liver and spleen [1]. The seeds are acrid, refrigerant laxative, anthelmintic and cure ulcers [2]. The present work describes the isolation and identification of a novel keto fatty acid in the seed oil of this species.

RESULTS AND DISCUSSION

Amoora rohituka seed oil responded to the DNPH test [3] indicating the presence of a keto group. The IR spectrum of the corresponding methyl ester exhibited characteristic double carbonyl peaks at 1740 cm^{-1} (ester C=O) and 1705 cm^{-1} (chain C=O). The IR spectrum also showed bands at 715 and 1620 cm^{-1} for *cis*-double bonds; but, at 970–960 cm^{-1} no absorbance for a *trans*-double bond could be detected. The ^1H NMR spectrum of the isolated methyl ester of the keto acid exhibited a multiplet at δ 5.38 (2H, —CH=CH—), a second multiplet at δ 2.25 (2H, $—CH_2—CO_2$) and a third multiplet at δ 2.11 (4H, $—CO—CH_2—$, $—CH_2—CO—$), apart from the usual proton signals. The acid on hydrogenation with Pd-C furnished 7-keto-octadecanoic acid. Oxidation [4] of the unsaturated acid with $KMnO_4$–$NaIO_4$ in *t*-butanol, gave heptanoic acid (*p*-bromophenacyl ester) and pimelic acid (*p*-bromophenacyl ester), respectively.

The structure of the keto acid was further supported by mass spectrometry (Scheme 1). A $[M]^+$ was observed at *m/z* 310 (3.8%), together with ions at *m/z* 157 (11%) and 181 (14%); an α-cleavage fragment on either side of the keto group was also observed at *m/z* 196 (7%) and 172 (13%) (McLafferty cleavage ions on both sides of the keto group). These four ions locate the keto group at C-7. Furthermore, allylic cleavage at *m/z* 239 (81%) and 125 (15%) was observed. Other important ions were observed at *m/z* 153 (10%), 115 (18%), 139 (3%), 101 (15%), 125 (9%), 87 (65%), 111 (16%), 73 (8%), 199 (7%), 43 (52%) and 74 (base peak). All these observations confirmed that the original acid was 7-keto-octadec-*cis*-11-enoic acid.

EXPERIMENTAL

General. IR: 1% CCl_4 soln. ^1H NMR: 90 MHz in $CDCl_3$ with TMS as int. standard; chemical shifts in δ downfield from TMS. MS: GC-MS at 70 eV, source temp. 150°. GC: 15% DEGS with temps at injector, detector and oven at 240, 240 and 190°, respectively; N_2 flow rate 30 ml min^{-1}.

Extraction and isolation. Air-dried seeds were extracted with petrol. Analytical values were determined according to AOCS methods [5] and are listed in Table 1. The oil did not respond to the Halphen [6] and picric acid TLC [7] tests, indicating the absence of cyclopropenoid and epoxy fatty acids, respectively. However, the oil responded to the DNPH test [3], showing the presence of a keto group. Me esters were prepared by refluxing the oil in MeOH in an acidic medium; saponification was carried out by stirring overnight with 0.8 M alcoholic KOH. Non-saponifiable matter was removed by extracting with Et_2O. The mixed fatty acids were partitioned [8] between petrol and 80% MeOH. A sample of pure keto acid was obtained by prep. TLC.

Identification of keto ester. Analysis: carbon 73.35% (requires 73.52%), hydrogen 11.05% (requires 11.03%). Molecular formula $C_{19}H_{34}O_3$. IR: 1740 cm^{-1} ($—CO_2Me$) and 1705 cm^{-1} (chain carbonyl), *cis*-double bond at 715 and 1620 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.90 *s* (3H, Me), 1.28 *br s* (16H, $—CH_2—$chain),

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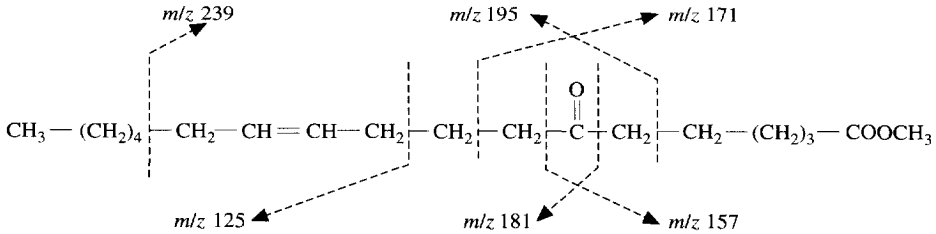

Scheme. 1. Mass spectral fragmentation of keto fatty acid methyl ester.

Table 1. Analytical data and component fatty acids of *Amoora rohituka* seed oil

Oil content	41.4%
Unsaponifiable matter	2.6%
Saponification value	202.3
Iodine value	46.3
2,4-DNPH TLC test	+ve
Picric acid TLC test	−ve
Halphen test	−ve
Fatty acids	*Percentage*
Palmitic	29.6
Stearic	27.8
Oleic	25.5
Linoleic	9.4
Arachidic	1.4
7-Keto-octadec-*cis*-11-enoic	6.3

1.95 *m* (4H, $-CH_2-C\equiv C-CH_2$), 2.11 *m* (4H, $-CH_2-C-C=O-CH_2$), 2.25 *m* (2H, CH_2-CO_2), 3.75 *s* (3H, OMe), 5.38 *m* (2H, $-CH=CH$). MS *m/z* 310 $[M]^+$, see Scheme 1. Hydrogenation was carried out using 10% Pd-C in EtOH (5 ml) to give 7-keto-octadecanoic acid (mp 82–83%). ^1H NMR: δ 0.90 (3H, Me), 2.11 (4H, $-CH_2-CO-CH_2$), 2.25 (2H, CH_2-CO_2), 3.75 (3H, OMe). MS: *m/z* 312 $[M]^+$. α-cleavage fragments at *m/z* 157 and 183.

Position of double bond. Oxidation of the unsaturated acid was carried out in *t*-BuOH (20 ml). A soln of the acid (0.25%) was treated with a soln of $NaIO_4$ (200 mg) in 20 ml of 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 solution then decolorised with $NaHSO_3$ followed by acidification with HCl. The fatty acids were extracted with Et_2O, the solvent removed and the acids obtained treated with 1% H_2SO_4 in MeOH (20 ml) and refluxed for 1 hr and then extracted with Et_2O. The extracts were dried (Na_2SO_4) and solvent removed under red. press. GC analysis showed Me heptanoate and Me pimeleate as products, both having the same R_t as those of authentic samples.

Position of keto group. Hydrogenation and oxidation of the keto acid was carried out as described above. GC analysis showed that Me pimeleate to be one of the products, having the same R_t as that of an authentic sample.

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