Cryptolepis buchnani Seed Oil: A Rich Source of Keto Fatty Acid

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A keto fatty acid (9-oxo-*cis*-12-octadecenoic acid) has been isolated in appreciable amounts (45.9%) from *Cryptolepis buchnani* seed oil. The identification was based on chemical and spectroscopic methods.

KEY WORDS: 9-oxo-*cis*-12-octadecenoic acid, Asclepidiaceae, *Cryptolepis buchnani*, fatty acids, seed oil.

The occurrence of keto fatty acids in natural seed oils is rare (1-5). A survey of the literature reveals that no work has been reported on the seeds of *Cryptolepis buchnani*, which is a climbing plant occurring throughout India (6) and belongs to the Asclepidiaceae plant family. We now report the occurrence of a novel keto fatty acid in *C. buchnani* seed oil as well as in the plant family.

EXPERIMENTAL PROCEDURES

Air-dried seeds (100 g) were extracted with light petroleum ether. The analytical values obtained were determined according to AOCS methods (7) and are listed in Table 1.

TABLE 1

Analytical Data of *Cryptolepis buchnani* Seed Oil

Oil content	8.5%
Unsaponifiable matter	1.7%
Saponification value	190.44
Iodine value	53.28
2,4-D.N.P. Test	+
Picric acid TLC test	−
Halphen test	−
Fatty acid composition (%)	
Palmitic	30.9
Stearic	6.5
Oleic	5.5
Linoleic	7.4
Behenic	0.8
Lignoceric	3.0
Keto acid	45.9

The oil responded to the DNPH test (8) showing the presence of a keto group. The methyl esters (200 mg) were prepared from oil by refluxing the oil in methanol that contained 1% sulfuric acid. Saponification of the oil was carried out by stirring it overnight with 0.8N alcoholic KOH. The non-saponifiable matter was removed by extracting with ether, and fatty acids were isolated after neutralization with dilute hydrochloric acid. The mixed fatty acids were partitioned according to the method of Gunstone (9) between petroleum ether and 80% methanol. A concentrate of pure oxo acid (46.0%) was obtained by preparative thin-layer chromatography.

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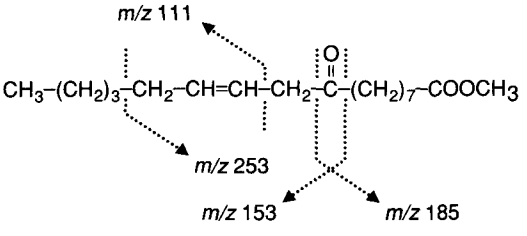
Infrared (IR) spectra were recorded in 1% CCl_4 solution. H^1 nuclear magnetic resonance (NMR) was run at 60 MHz in $CDCl_3$ with TMS as internal standard. The chemical shifts were measured in δ ppm downfield from TMS. Mass spectra were recorded on a Jeol-JMS-D-300 Model instrument, Tokyo, Japan. Gas-liquid chromatography (GLC) was carried out with a Perkin-Elmer Sigma Unit (Norwalk, CT) having a stainless steel column (2 m × 3 mm) coated with 15% DEGS and a flame ionization detector. The temperatures at the injection port, detector and oven were 240°, 240° and 190°C, respectively. Nitrogen carrier flow was 30 mL/min.

RESULTS AND DISCUSSION

The IR spectrum of the keto acid methyl ester exhibited characteristic double carbonyl peaks at 1740 cm^{-1} (ester-C-O) and 1705 cm^{-1} (chain-C-). The IR spectrum also showed bands at 715 and 1620 cm^{-1} for a *cis* double bond. The IR and ultraviolet (UV) spectra of the oil showed no *trans* absorption. The H^1-NMR spectrum indicated an unsaturated keto ester: multiplet at δ 2.13 (6H, $-C\underline{H}_2-C-C\underline{H}_2-$, and $-C\underline{H}_2-C-O-$), another complex multiplet at δ 1.97 (4H, $-C\underline{H}_2-C=C-C\underline{H}_2-$), and a third multiplet at δ 5.45 (2H, $-C\underline{H}=C\underline{H}-$). The other signals were at δ 3.6 (3H, $-OC\underline{H}_3$), δ 1.25 (16H, chain-$C\underline{H}_2-$) and δ 0.85 (3H, $-C\underline{H}_3$).

The structure of the keto fatty acid was further supported by its mass spectrometry behavior. The mass spectrum of the ester gave a molecular ion peak at *m/z* 310 consistent with a C-18 chain with a keto group and a double bond. Alpha cleavage fragments on either side of the keto group gave peaks at *m/z* 185 (32.1%) and 153 (14.3%) and cleavage allylic to the double bond gave *m/z* 111 (16.0%) and 253 (29.2%), establishing the position of the keto group at C-9 and the double bond at C-12 (Scheme 1).



SCHEME 1

The unsaturated keto acid on reduction with Pd/C furnished 9-oxooctadecanoic acid, m.p. 42-43°C (lit. 44-45°C). On oxidation with $KMnO_4/NaIO_4$ in *t*-butanol it gave hexanoic and azelaic acids.

All these observations showed that the original acid is 9-oxo-*cis*-12-octadecenoic acid. Other fatty acids are listed in Table 1.

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