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Unique Occurrence of cyclopropenoid fatty acids in *Asparagus racemosus* seed oil: A rich source of oil and its possible industrial application

Kariyappa S. Katagi[1]* and Kallappa M. Hosamani[2]

1. Department of Chemistry Karnatak University's Science College Dharwad -580 001, **INDIA**
2. P.G. Department of Studies in Chemistry, Karnatak University, Pavate nagar Dharwad-580 003, **INDIA**

Email: kskatagi@gmail.com

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ABSTRACT

The present investigation reveals the occurrence of cyclopropenoid fatty acids (CPFAs) in the seed oil of Asparagus racemosus (AR). These unusual fatty acids were characterized by GC, IR and NMR studies and supported by chemical degradation methods. The iodine value, saponification value are 79 and 215 respectively. Further, the Durbitaki titration assisted the quantification of CPFAs. The detected CPFAs have been characterized as 7-(2-octacyclopropen-1-yl) heptanoic acid and 8-(2-octacyclopropen-1-yl) octanoic acid which are quantified as 3.2% and 2.8% respectively.

Keywords: *Asparagus racemosus* seed oil, fatty acids, cyclopropenoid fatty acid, industrial application.

INTRODUCTION

The vegetable seed oils are intricate mixtures containing triglycerols, diaylglycerols, unusual fatty acids etc. which will differ from source to source based on the varieties of plant so also the growing style. The industrial application of unusual fatty acids are in the manufacture of protective coatings, plastics, urethane derivatives, surfactants, dispersants, cosmetics, lubricants, varieties of synthetic intermediates, stabilizers in plastic formulations, shoe polish, liquid soap, shampoo and in the preparations of other long-chain compounds. The interesting *unusual fatty acids* present in high concentration of certain seed oils are being exploited for the industrial utilization. These fatty acids of unusual structures are highly important to the production of oleo chemicals [1,2]. The cyclopropenoid fatty acids manifest a number of unusual properties including high dipole moment (0.445 D) for a hydrocarbon, high reactivity towards the addition reactions and ring-opening reactions. The main drive that led to the discovery of cyclopropenoid fatty acids came from the food and agriculture industries [3]. The cyclopropenoid fatty acids have been suggested that they play both antifungal [4] and antifeedant [5] roles. The presence of these acids can interfere with fatty acid desaturases in animals that include cotton seed products in their diet [6,7,8] . In poultry, inclusion of cotton seed products in feed causes discoloration of the egg yolk [9,10].

Asparagus racemosus (AR) belongs to Liliaceae plant family which consists of 187 genera and more than 2500 species. It is an extensively and much-branched under shrub. The leaves are long. The flowers are white and fragrant. It is commonly distributed on the ghats of Konkan and Mahabaleshwar. It is said to be tonic and diuretic and useful as galactagogue. The root is largely used in the preparation of medicated oils prescribed for nervous and rheumatic complaints. A mixture of honey and fresh root juice is given as a demulcent in dyspepsia. The root is bitter, sweet, oleaginous, cooling, indigestible, appetizer, alterative,

stomachic, diuretic, demulcent, antispasmodic,tonic, aphrodisiac, laxative, gleet, gonorrhoea, diarrhoeatic, dyspepsia, expectorant, galactagogue, astringent to the bowels and useful in dysentery, tumours, inflammations, in the diseases of the kidney and liver, scalding urine, diseases of the blood and the eye, throat complaints, tuberculosis, leprosy, epilepsy, night blindness [11,12,13]. The present investigation describes unique occurrence of cyclopropenoid fatty acids along with the other normal fatty acids.

MATERIALS AND METHODS

Materials: The seeds of *AR* were collected during winter season in the Western ghats of India. *Sterculia foetida* seeds were collected during summer season from Western Ghats of Karnataka, India. The chemicals were of reagent grade.

Oil extraction: The seeds of *AR* of 100 g were ground, powdered and the oil content extracted by extraction with light petroleum ether (B.P. 40-60 °C) in a Soxhelt extractor for 24 hrs. The organic extract was filtered and dried over anhydrous Na_2SO_4. The petroleum ether was removed under vacuum.

Instrumentation: The UV spectra and IR spectra of seed oil were taken on Hitachi 270-30 and on a Nicolet 5700 FTIR instrument. The ^1H NMR was recorded on Bruker Avance-300 (300 MHz) Model spectrophotometer using $CDCl_3$ as the solvent. The quantification of the methyl esters (MEs) was carried out using GC chromosorb, W 45-60 mesh. The temperature at injection port, detector port and oven were 240ºC, 240ºC and 190ºC respectively. The nitrogen flow and chart speed were 30 mL/min and 1 cm/min, respectively. The machine recorded directly the weight percent of individual peaks. The peaks were identified by comparing their retention times with those of reference standard under similar conditions.

Detection of CPFAs in the seed oil: The analytical results of seed oil so obtained were according to the American Oil Chemists' Society methods [14]. The seed oils of *AF* responded to the Halphen test [15] indicated the presence of CPFA. The seed oil did not respond to direct thin layer chromatography (TLC) test, picric-acid TLC test [16] and 2,4-dinitrophenylhydrazine (2,4-DNPH) TLC test [17] which infers the absence of hydroxy, epoxy and keto functional groups in the fatty acids. No significant indication obtained from the UV spectral studies. The seed oil showed characteristic strong absorption band at 1014 cm^{-1} for cyclopropenoid functional groups. Further, the estimation by Durbetaki titration [18] at 55ºC resulted the percentage of total CPFAs in the seed oil of *AR* is presented in Table-1.

Halphen test for the detection of CPFAs: The 1:1 by volume of seed oil and Halphen reagent were mixed then heated on a water bath at 80ºC until all the carbon disulphide boiled off. This was further heated on oil bath for 1-2 hours at 110-115 ºC. The red color indicated the presence of CPFAs.

Quantification of CPFAs: The strength of commercially available Durbetaki reagent (HBr in acetic acid) was determined using potassium phthalate and 1% crystal violet as the indicator. 300-500 mg of the oil sample was weighed in a 50 mL conical flask and dissolved using 5 mL of distilled benzene. Four to five drops of indicator solution was added. Durbetaki reagent (HBr in acetic acid 0.1N) was taken in a semi-micro burette and was added to the conical flask slowly with constant stirring at 55ºC. The end point was observed by bluish green colour. The amount of HBr reactive fatty acid (s) in the oil sample is estimated the results are given in Table -1.

Table1. Analytical values of seed oil of *Asparagus recemosus*

Oil Content in seeds	14. 0 %
Unsaponifiable matter	2.3 %
Iodine value (mg iodine/g)	79.0
Saponification value (mg KOH/g)	215.0
Refractive index (25 ^{0}C)	1.4835
Specific gravity (25 ^{0}C)	0.8990
Durbetaki titration at 55°C	6.2
IR spectrum for cyclopropenoid functional group	1014 cm^{-1}
^{1}H NMR spectrum for cyclopropene proton	δ= 0.74

Transesterification: The *AR* seed oil was transesterified with 1% sodium methoxide in methanol (50 mL) under reflux for 1 hour. Then, the reaction mixture was diluted with distilled water (25 mL) and extracted with diethyl ether (30 mL). The ether extract was dried over anhydrous Na_2SO_4. The solvent was removed in a stream of nitrogen.

Preparation of CPFA derivatives: The transesterified methyl esters (ME) of *AR* seed oil (200 mg) was treated with 60 mL of absolute methanol saturated with silver nitrate [19] . The reaction was carried out with stirring at room temperature (27ºC) for 24 hours. The normal methyl esters and the cyclopropenoid derivatives were recovered from the reaction mixture separately by adding 100 mL of distilled water and extracted with ether. The ether extract was dried using Na_2SO_4.

CPFAs ether and ketone derivatives: The transesterified ME of seed oil of *AR* (200 mg) was treated with 60 ml of absolute methanol saturated with the $AgNO_3$. The reaction was allowed to proceed at room temperature (27 ^{0}C) with stirring for 24 hours. The normal MEs and the reaction products from cyclopropenoid fatty esters were recovered from the reaction mixture by adding 100 ml of distilled water and extracting with ether. The ether extract was dried over anhydrous sodium sulphate then the solvent was removed in a stream of nitrogen. The GC analysis was carried out using the corresponding methyl esters of seed oil of *Sterculia foetida* as reference standard. The results are summarized in the Table -2**.**

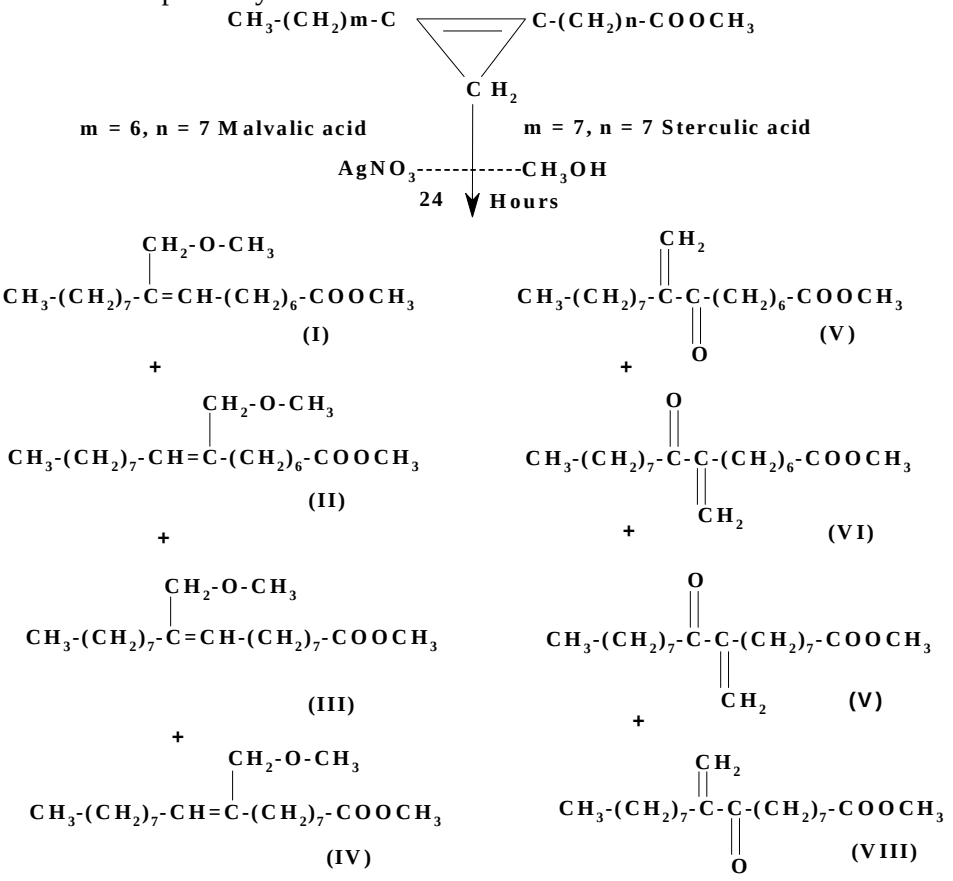
Table 2. Distribution of fatty acids in the seed oil of *Asparagus recemosus*

% Component normal fatty acids	
Myristic	12.0
Stearic	16.7
Palmitic	8.6
Oleic	34.7

Linolenic	22.0
% CPFAs	
Malvalic	3.2
Sterculic	2.8

RESULTS AND DISCUSSION

The individual infrared spectra of seed oil of AR had the characteristic strong absorption band at 1014 cm^{-1} for the cyclopropenoid functional group. The ^1H NMR of seed oils had a typical singlet signal at δ 0.74 for the cyclopropene protons. The CPFAs determined by ether and ketone derivatives. The transesterified ME was converted into ether and ketone (Scheme) derivatives by the interaction of ME with an excess of absolute methanol saturated with silver nitrate. The recovered MEs of the other normal fatty acids and ether and ketone derivatives of CPFAs were submitted to the gas chromatographic analysis using *Sterculia foetida* MEs as a reference standard. Thus, the CPFAs have been detected as 7-(2-octacyclopropen-1-yl) heptanoic acid (malvalic acid) and 8-(2-octacyclopropen-1-yl) octanoic acid (sterculic acid) are estimated by Durbetaki titration and GC data. The scheme for the derivatives of CPFAs depicted. Along with these unusual fatty acids the high percentage of normal fatty acids like stearic acid, linolenic acid and oleic acid 16.7%, 22% and 34.7% respectively.



APPLICATIONS

The proximate analysis, physico chemical characterization and component fatty acid details reveals the possible industrial application of seed oil of *AR.* CPFAs have got their unique applications as mentioned in the introductory part. The rest of the material can be used (based on high saponification value) in the manufacture of shoe polish, liquid soap and shampoo production or biofuel etc [20, 21].

CONCLUSIONS

This research work investigated the occurrence of CPFAs in the seed oil of *AR.* The results of this investigation indicate 7-(2-octacyclopropen-1-yl) heptanoic acid (malvalic acid) and 8-(2-octacyclopropen-1-yl) octanoic acid (sterculic acid). The fatty acid profile reflects the possible application of this seed oil as potential feed stock for the industry.

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