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Occurrence of Cyclopropenoid Fatty Acids in Acacia Farnesiana Seed Oil and its Possible Industrial Utilization

KEYWORDS: Acacia farnesiana, seed oils, fatty acids, cyclopropenoid fatty acid, Industrial utilization

Kariyappa.S.Katagi
Assistant Professor Department of Chemistry Karnatak University's, Karnatak Science College Dharwad -580 001 INDIA

Kallappa. M. Hosamani
Professor of Organic Chemistry P.G. Department of Studies in Chemistry Karnatak University, Pavate nagar Dharwad-580 003, INDIA

ABSTRACT *In this work the presence of unusual fatty acids ; cyclopropenoid fatty acids (CPFAs) in the seed oil of Acacia fernesiana (AF) is detected along with other normal fatty acids. These fatty acids were characterized by spectral support and chemical degradation methods. The CPFAs have been characterized as 7-(2-octacyclopropen-1-yl) heptanoic acid (malvalic acid) and 8-(2-octacyclopropen-1-yl) octanoic acid (sterculic acid) are 5% and 4% respectively. Further, the analytical values like iodine value, saponification value are 76 and 186 respectively. The Durbitaki titration and IR details proved the presence of above mentioned CPFAs in the seed oil of AF.*

INTRODUCTION

The various uses of the plant seed oils can be used to make a strong case for an increase in its production as a vital raw material for the chemical industries. The seed oils containing unusual fatty acids are industrially important as they are used in the protective coatings, plastics, cosmetics, lubricants, varieties of synthetic intermediates, stabilizers in plastic formulations. 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 for the production of oleo chemicals (D.S. Ogunniyi, 2006, Osman et al., 1984).

The CPFAs signify the number of unique properties including high dipole moment (0.445 D), high reactivity towards the addition reactions and ring-opening reactions. The main impetus that led to the discovery of CPFAs came from the food and agriculture industries (Hosamani, 1993). The CPFAs play both antifungal (Schmid and Patterson, 1988) and antifeedant (Binder etal, 1982) role. The presence of these acids can interfere in animals feed that include cotton seed products in their diet (Yang et al., 1999; Quintana et al., 1998 ; Cao et al., 1996). In poultry inclusion of cotton seed products in feed causes discoloration of the egg yolk (Evens et al., 1967; Panigrahi and Plumb, 1996).

Acacia fernesiana (AF) belongs to Leguminosae plant family which consists of about 400 genera and about 6000-7000 species (Cooke. T, 1967). It is a medium-sized thorny bush / small tree. It has now spread throughout India, Burma and Ceylon (Kirtikar, et al, 1933). The flowers are fragrant and deep yellow, bark is acrid, astringent, used to cure blood related diseases, itching, bronchitis, leucoderma, ulcers, inflammations, erysipelas. The plant yields sweet gum, a tonic and aphrodisiac useful inconfectionery. The tender leaves used in the treatment of gonorrhea (Wealth of India CSIR 1948 New Delhi). The earlier workers have reported normal fatty acids.

The present investigation reported the occurrence of CPFAs along with the other normal fatty acids in the seed oil of Acacia farnesiana.

MATERIALS AND METHODS

The seeds of AF were collected during winter season in the Western ghats of India. Sterculia foetida seeds were collected during summer season in the Botanical garden of Karnatak University , Dharwad, India. The reagents and chemicals were of reagent grade.

Oil extraction

The seeds of AF of 100 g were ground , powdered and extracted the oil content by extraction with light petroleum ether (B.P. 40-60 °C) in a Soxhlet 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 were taken on Hitachi 270-30 but no significant observed. IR spectra of oil was recorded on a Nicolet 5700 FTIR instrument as liquid films. The 1H NMR was recorded on Bruker Avance-300 (300 MHz) Model spectrophotometer using CDCl3 as the solvent. The quantification of the MEs was carried out using GC chromosorb, W, 45-60 mesh. The temperature at injection port, detector port and oven were 240°C, 240°C and 190°C 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 (Link, 1973). The seed oils of AF responded to the Halphen test (Halphen, G., 1897) indicated the presence of CPFAs. The seed oils did not respond to direct thin layer chromatography (t.l.c) test , picric-acid t.l.c test (Fioriti, & Sims, 1968) and 2,4-dinitrophenylhydrazine (2,4-DNPH) t.l.c test (Davis, et al 1969) shows absence of hydroxy, epoxy and keto functional groups in the fatty acids. The seed oil showed characteristic strong absorption band at 1011 cm-1 1 for cyclopropenoid functional groups. Further, the estimation by Durbetaki titration (Harris, Magne, & Skau, 1963) at 55°C resulted the percentage of total CPFAs in the seed oil of AF is presented in Table-1.

Halphen test for the detection of CPFAs

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

Estimation 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. About 300-500 mg of the oil sample was weighed in a 50 mL conical flask and

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dissolved in 5 mL of distilled benzene. Four to five drops of crystal violet 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 (Table-1 about here).

Transesterification

The FA 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 AF seed oil (200 mg) was treated with 60 mL of absolute methanol saturated with silver nitrate (Schneider et al, 1968). The reaction was carried out with stirring at room temperature (27°C) 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 using Na_2SO_4.

CPFAs ether and ketone derivatives

The transesterified ME of seed oil of AF (200 mg) was treated with 60 ml of absolute methanol saturated with the $AgNO_3$ (Schneider, et al., 1968). 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 Na_2SO_4 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 about here).

RESULTS AND DISCUSSION

The individual infrared spectra of seed oil had the characteristic strong absorption band at 1012 cm^{-1} for the cyclopropenoid functional group. The ^{1}H NMR of seed oils had a typical singlet signal at δ 0.73 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 characterized as 7-(2-octacyclopropen-1-yl) heptanoic acid (malvalic acid) and 8-(2-octacyclopropen-1-yl) octanoic acid (sterculic acid) are quantified 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 palmitic acid (29.4 %) and olieic acid (33.6 %) are reported.

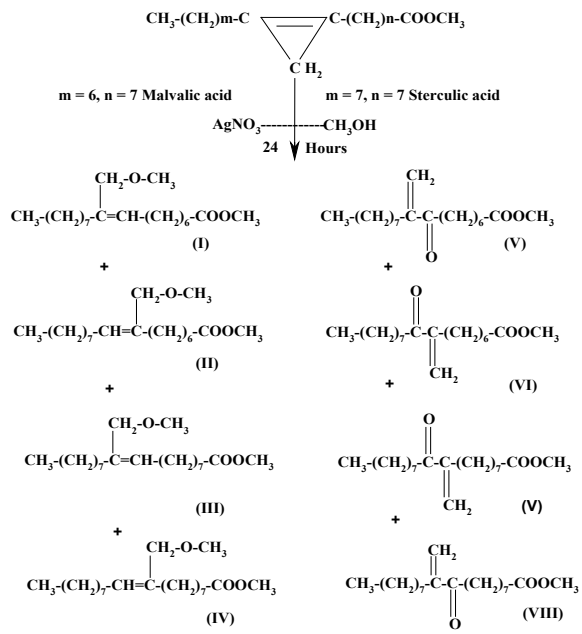
Table. 1
Analytical values of seed oil of Acacia fernesiana

Oil Content in seeds	6.0 %
Unsaponifiable matter	2.2 %
Iodine value (mg iodine/g)	76.0
Saponification value (mg KOH/g)	187.0
Refractive index (25 ^{0}C)	1.4835
Specific gravity (25 ^{0}C)	0.9361
Durbetaki titration at 55°C	9.2
Infrared spectrum for cyclopropenoid functional group	1013 cm^{-1}

Table – 2.
Component fatty acids in the seed oil of Acacia fernesiana

% Component normal fatty acids	
Myristic	8.7
Stearic	7.3
Palmitic	29.4
Oleic	33.6
Linoleic	-
Linolenic	12.0
% CPFAs	
Malvalic	5.0
Sterculic	4.0

Scheme: Ether and ketone derivatives of CPFAs



CONCLUSION

The present study reported the CPFAs distribution in the seed oil of Acacia farnesiana . 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 suggest the possible application of this oil as potential industrial resources.

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