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FATTY ACIDS OF INDIGENOUS RESOURCES FOR POSSIBLE INDUSTRIAL APPLICATIONS

Part IX. The Seed Oil of *Euphorbia helioscopia* Linn.

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Euphorbia helioscopia seeds contain 28% of fixed oil whose composition, as determined by gas chromatography is lauric acid, 2.85%; myristic acid, 5.49%; palmitic acid, 9.88%; stearic acid, 1.13%; oleic acid, 15.80%; linoleic acid, 22.14%; linolenic acid, 42.71%. The use of this oil in paints, varnishes and alkyd resins and the possibility of *E. helioscopia* as a potential seed crop are discussed.

INTRODUCTION

Euphorbia helioscopia, (N.O. Euphorbiaceae) locally known as *ganda buti* is a common field weed in winter crops. The plant, 30-50 cm. in height, is widely distributed in Pakistan, India, Iran and many other parts of the world [1]. The plant bears seeds which mature around April. The seeds contain an oil which reportedly possesses certain biological properties. Earlier works have described only the physico-chemical constants of the seed oil [2]. The present work was, therefore, undertaken to determine the fatty acid composition of this oil and also to assess its uses for industrial purposes.

MATERIALS AND METHODS

Mature plants were collected from the Laboratories campus and dried in shade. The seeds were separated from the plant matter and then ground in a pestle and mortar. All chemicals were of laboratory grade. The solvents were redistilled before use.

The crushed seeds (135g) were placed in a soxhlet thimble and extracted with hexane for 24 hr. The extract was dried, (anhydrous sodium sulphate) filtered and the solvent removed by distillation on a water bath. Final traces of the solvent were removed under vacuum. A brownish red oil (37.79g, i.e. 27.97%) was obtained.

Spectroscopic analysis of oil. Infrared spectrum of the oil was recorded by pressing the oil sample between sodium chloride plates. The spectrum showed peaks at 3020 cm^{-1}, 2920 cm^{-1} 2860 cm^{-1} 1740 cm^{-1} and 1170 cm^{-1}.

Thin layer chromatography of the oil. The oil, cotton seed oil, octacosanol and β-sitosterol were charged to a thin layer plate (silica gel, 20x5 cm x 0.1 mm) and the plate developed in hexane-ether (90:10). The spots were visualised by spraying with a solution of ceric sulphate (1%) in sulphuric acid (10%) and heating in an oven at 105° for 5 min.

Saponification of the oil. The oil (33 g) was refluxed with 0.5N methanolic potassium hydroxide for 2 hr. Methanol was removed by distillation and the residue taken in distilled water (500 ml). The soaps were extracted thrice with ether (200 ml). The etherial layers were combined, washed with water, dried over anhydrous sodium sulphate and evaporated to give an unsaponifiable product (0.49 g, 1.48%).

Liberation of fatty acids. The soap solution was acidified with 2N H_2SO_4. The liberated acids were extracted with ether, dried and ether evaporated to give reddish brown coloured acids.

Esterification of fatty acids. The acids (2.4 g) were esterified by refluxing with methanol containing 0.5% hydrochloric acid (10 ml). The mix was diluted with water and extracted with ether. The slightly coloured esters formed were passed over a small silica gel column to remove the colouring matter. The yield was 2.4 g.

Gas chromatography of methyl esters. Gas chromatographic analysis was performed on a Pye Unicam Series 204. A wall coated open tubular column SP 1000 (25m) was used for the separation. The other conditions were: column temp. 196°; detector, 300°; injector, 250°; carrier

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gas, hydrogen, 1 ml/min, split ratio 1:100. The peaks were registered and integrated by a Spectraphysics recorder. The concentration of individual components was calculated as the percentage area under each peak.

Column chromatography of the unsaponifiable matter. The unsaponifiable (1.1 g) was refluxed with hexane (10 ml) and then allowed to stand overnight. The supernatant was charged to a column of silica gel, (Kieselgel 60, 230-400 mesh ASTM, E.Merck, 40g, h=46cm, ϕ 1.5 cm). The residue (450 mg, 41%) which remained in the flask was only partially soluble in chloroform. The column was eluted with hexane and hexane-ether. The pure class compounds which could be isolated were hydrocarbons (130 mg, 12%), fatty alcohols (75 mg, 7%) and sterols (108 mg, 10%). The resinous mass (170 mg, 15%) was eluted finally with methanol-chloroform.

RESULTS AND DISCUSSIONS

The Physico-chemical constants of the oil have been compared with the values reported in earlier work [2]. The yield of oil is somewhat lower than reported. This may be due to the ecological conditions like temperature, humidity, soil conditions, etc. The yield may be improved if the species is reared as a regular crop.

The density of the oil as determined is lower than the reported one. However, the variation is quite minor (1.8%).

The refractive index was determined at 34° due to limitations of the apparatus used. The value found is lower than the reported one. This can be easily explained by considering the dependence of refractive index on density which in turn is related to temperature.

The iodine value, which is an index of unsaturation, is the same in both the cases. The saponification value which has been found to be higher in the present case may be due to the presence of some lower fatty acids.

Euphorbiaceae seed fats show large variation in their chemical compositions [3]. Some species, *Aleurites moluccana, Colliguaya intergessima, Euphorbia calycina, E. erythraeae, E. marginata, and Hevea brasiliensis,* contain linolenic, linoleic and oleic acids as the major part and only small quantities of saturated fatty acids. Some other species such as *Aleurites cordata, A. fordii, A. montana,* etc. contain the conjugated isomer of linolenic acid commonly known as eleostearic acid (9, 11, 13-octadecatrienoic acid) as the major component. Ricinoleic (12-hydroxyoctadec-9-enoic) acid is also present upto 90% in *Ricinus* spp. *(R. communis* or castor seed and *R. zanzibarinus).* The presence of diene C_{10} or C_{12} acids has been reported in *Sapium sebiferum* and *S. discolor.*

Thin layer chromatography and infrared analysis did not indicate the presence of hydroxy acid derivative in this oil. The presence of unsaturation could, however, be observed by the peaks at 3020 cm^{-1} and 920 cm^{-1}. The region around 1600 cm^{-1} was quite clear providing an indication of the lack of conjugated unsaturation.

The fatty acids were isolated by the saponification of the oil and subsequent esterification of the acidic fraction. The purified esters were analysed by gas chromatography. The fatty acids ranged from C_{12} to C_{18}. The saturated fatty acids which formed only 19.35% of the total acids were lauric (2.85%), myristic (5.49%), palmitic (9.88%), and stearic (1.13%). The major components of this oil were C_{18} unsaturated acids which were oleic acid (15.80%), linoleic (22.14%), and linolenic acid (42.71%). This composition is nearly the same as that of linseed oil.

The unsaponifiable matter in this oil is about double than what had been reported in literature [2]. This unsaponifiable was resolved into class compounds. The major portion of the unsaponifiables (56%) was a resinous mass which could partially be charged to the column. The resinous mass might have been present in the oil or is formed by the action of alkalis on various diterpene compounds having multifunctional groups e.g. euphoscopins [4] or heliocopinolides [5].

The yield of oil from *E. helioscopia* is 28%. This yield is higher than in cottonseed oil (11.6-24%), soybean oil (15-20.1%) but lower than linseed oil (45%). Among Euphorbia species, *Euphorbia lathyris* seeds contain 40% of an oil which is quantitatively triglyceride in nature [6]. *Jatropha curcas* is another species which has been investigated in Thailand. The yield of seeds/plant/year is reported to be 2 kg. Experiments in Thailand have proved its use as a substitute for diesel in driving farm machinery [7].

Table 1. Physico-Chemical Characteristics of the Oil.

Characteristic	Observed	Literature
Yield	27.97%	32.61%
Colour	Brownish red	Pale yellow
Density	0.9179	0.9346
Refractive index at 34°C	1.4692	1.4821*
Iodine value		
Vijs (1 hr.)	203.82	204.4
Saponification value (2 hr. reflux)	207.0	191.1
Unsaponifiable	1.48%	0.70%

*at 22°C.

The use of *E. helioscopia* for producing hydrocarbons either through the extraction of latex or by destructive distillation does not seem feasible as the total hexane extract of the dried plant is only 2.8% [8]. However, the plant seed may become a potential source of oil as anticipated for *Euphorbia lathyris* or *Jatropha curcas* if the plants are cultivated for the purpose of seeds.

Table 2. Fatty Acid Composition of the Oil.

Acid	Percentage
Lauric acid	2.85
Myristic acid	5.49
Palmitic acid	9.88
Stearic acid	1.13
Oleic acid	15.80
Linoleic acid	22.14
Linolenic acid	42.71
Saturated acid	19.35

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