Preparation of Surface Active Agents from Non-edible Oils and their Protein Isolates

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Abstract
Surface active agents play important role in household and personal care products. These also find application in enhancing industrial utility of textile, paper and leather products. Attempt has been made in the present study to find alternative to known sulphated oil substitute (e.g. TRO) from non-edible oils of Tectona grandis and Pithecellobrium dulce Preparation of surface active agents from protein isolates of these have also been tried to utilise these as value added products since protein based surface active agents are skin compatible and biodegradable.

1. Introduction

The study was undertaken to analyse non-traditional seed oils which after evaluation may find utility for industrial purposes.

The forests of Madhya Pradesh are rich sources for some of such non- traditional raw materials which have not been properly screened.

The chosen raw materials for the present study include: *Pithecellobrium dulce, Tectona grandis, Annona squamosa and Balanites aegyptiaca*

Pithecellobrium dulce (Leguminosae)[1,2] is a cultivated tree distributed in Central Madhya Pradesh. Two saponins from *P. saman*[3,4] a triterpenoid glycoside from *P. arborecum* and *P. cubense*[5] and chemical composition of *P. multiflorum*[6] have been reported.

Tectona grandis (Verbenaceae)[7-9] is a tree, distributed in Madhya Pradesh and Rajsthan. In Madhya Pradesh, the most important forests are Hosangabad and Betul.[10] The nut has a hard testa.[11] Relation between chemical and physical properties of soil to the growth rate of teak has been studied.[12,13] Some active constituents of the genus have been reported.[14]

Annona squamosa (Annonaceae)[15-17] is a tree, found throughout Madhya Pradesh.[18]

Alkaloids have been isolated by several workers for various species e.g. *A. montana, A. cristalensis, A. squamosa and A. glabra.*[19-22.] A ketone and alcohol have been isolated from the leaves.[23] Recently antibacterial activity of seed extracts against some pathogenic bacteria, have been carried out.[24]

Balanties aegytica (Simarubaceae)[25-27] is found in black cotton soil. It is the Indian species of the genus. It is small spiny tree with bifoliate leaves. Sesquiterpene[28], saponin[29] and alkaloid[30] have been reported. The roots have been shown to possess molluscicidal activity.

Surface active agents (Surfactants) is a term applied to organic compounds which, when present at low concentration in a system, have a tendency to adsorb onto the surface or interfaces of the system and of altering the surface or interfacial free energies of those interfaces to a marked degree. “Interface” indicats a boundary between two immiscible phases, “Surface” denotes an interface where one phase is usually air Surface active agent, after adsorbing at the interface changes the amount of work requite to expand the interfaces.

Surface active agents play an important role in personal care and household products, apart from their use in textile and leather industries[34].

Naturally occurring fatty acids are suitable as raw materials (oleo chemicals) for preparation of surface active agents[35].

An attempt has been made in this study to use the above extracted non-traditional oils in making of surface active agents.

2. Related Work

The study was undertaken to analyse non-traditional seed oils which after evaluation may find utility for industrial purposes.

The forest of Madhya Pradesh are rich sources for some of such non- traditional raw materials which have not been properly screened.

The chosen raw materials for the present study include: *Pithecellobrium dulce, Tectona grandis, Annona squamosa and Balanites aegyptiaca.*

(A) Fatty Acid Profile

Pithecellobrium dulce (Yield 19%)- Myristic acid (14:0), Palmitic acid (16:0), Stearic acid (18:0), Oleic acid (18:1) and Linoleic acid (18:2)

Tectona grandis (Yield 7%) - Stearic acid (18:0), Oleic acid (18:1) and Linoleic acid (18:2)

Annona squamosa (Yield 15%)- Lauric acid (12:0), Palmitic acid (16:0), Palmitoleic acid (16:1), Oleic acid (18:1) and Linoleic acid (18:2) *Balanites aegyptiaca* (Yield 22%) - Palmitic acid (16:0), Palmitoleic acid (16:1), Stearic acid (18:0), Oleic acid (18:1) and Linoleic acid (18:2).

(B) Determination of Surface Active Properties

Out of several methods available for preparing fat based surfactants, sulphation represents a basic industrial process. Surface active properties e.g. surface tension, wetting power foaming power, and dispersing power of the sulphated contents of above metioned oil were determined.

Highest value for surface tension was observed in the sample of *Balanites aegyptiaca*. Wetting power of a surfactant is determined in terms of sinking time. Lesser the sinking time. *(Pithecellobrium dulce)*, greater is the utility as wetting agent. Foaming power is determined in terms of initial foam height and foam decay. Initial foam height is better in the test simple where surface tension is low *(Pithecellobrium dulce* and *Tectona grandis*). Dispersing power is determined in terms of suspension. Higher the dispersed content, more efficient would be surface active agent *(Pithecellobrium dulce).* This also correlates with low surface tension of *Pithecellobrium dulce*.

3. Experiment, Result and Discussion

The raw materials were collected from nearby forests and authenticated at the Botany Department of the University. These were extracted with petroleum ether (60-80°) in a Soxhlet. The oils were saponified in presence of alkali[33]. The saponified mixed fatty acids were converted to methyl esters (FAME) with methanol/ H_2SO_4 and analysed by GLC using. OV 101 column with N_2 as carrier gas (flow rate

10ml/min) F.1. Detector, chart speed of 4mm/min and 1µl sample injection. The results were compared with standards (Fatty acid standards kit from Sigma) and by spiking. Fig V/1 to V/4 show the GLC profiles of the oils.

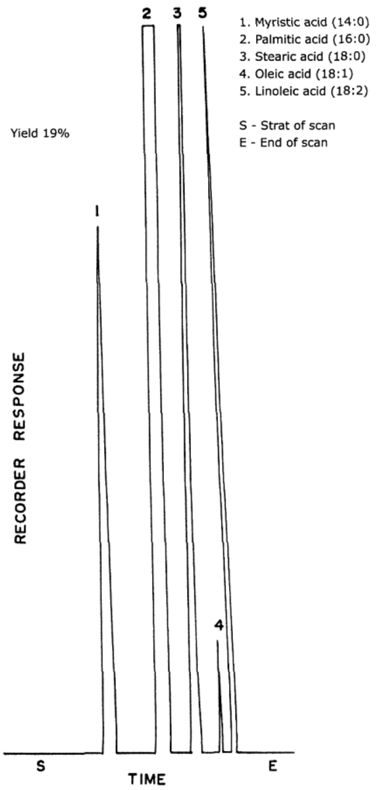

Fig. V/1 : GLC of the mixed fatty esters of *Pithecellobrium dulce* seed oil

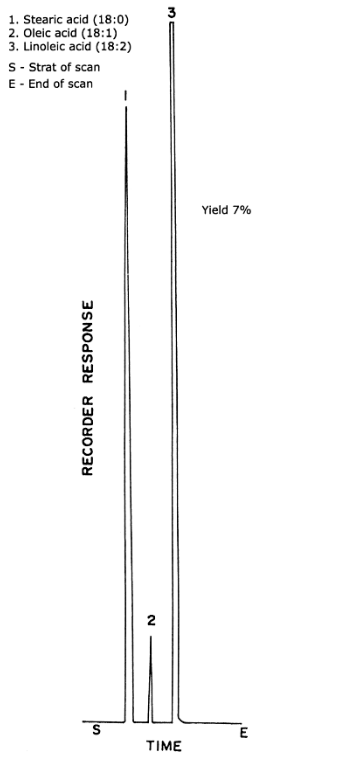

Fig. V/2 : GLC of the mixed fatty esters of *Tectona grandis* seed oil

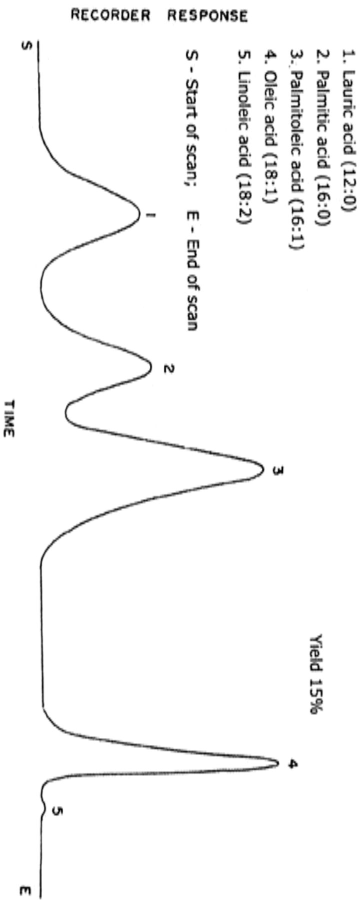

Fig. V/3 : GLC of the mixed fatty acid esters of *Annona squamosa* seed oil

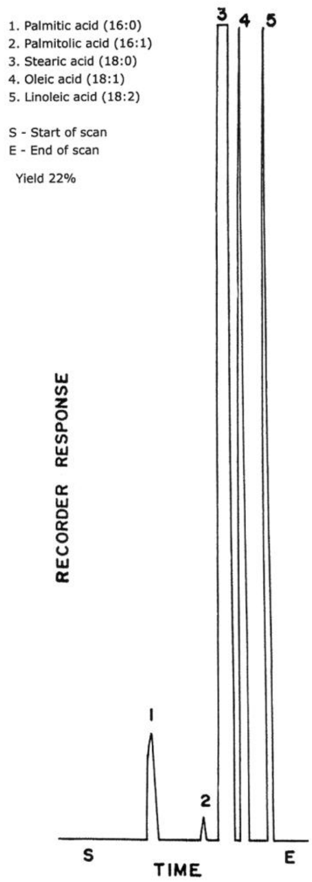

Fig V/4 : GLC of the mixed fatty esters of *Balanites aegyptiaca* seed oil

Out of several methods available for preparing fat based surfactants, sulphation represents a basic industrial process[36].

For a typical sulphation process, specific amount of oil (10 g) was taken in a glass beaker, placed in a trough of water at room temperature and concentrated sulphuric acid was added (6ml) dropwise from a burette with stirring. The temperature was kept at around 30°C. Acid was dropped for the first two hours and stirring was continued for another two hours, finally the container was kept overnight for completion of the reaction. Then the sulphated mass was washed with distilled water and NaCl solution to remove unused acid. The sulphated content separated from the aqueous layer, was transferred to a beaker and neutralised with 20% NaOH to pH of around 7.

Surface active properties:[35]

(i) Surface tension:

Surface tension of different concentrations of sulphated mass (0.25, 0.50, 0.75, and 1%) in distilled water.

(ii) Wetting power:

Cylinder (500ml), copper hook (1.5g), anchor (40g), skein (5g, two ply), stopwatch and different concentrations of sulphated mass (0.25, 0.50, 0.75 and 1%) in distilled water.

The hook, anchor and skein were taken to the graduated cylinder containing the test solution. The hook was dipped into the solution fallowed by dropping of skein and the stopwatch started simultaneously. The sinking time is attained when the hook reaches the level of anchor. The watch was stopped and time noted. Same process was repeated for different concentrations. The wetting power is given in terms of sinking time.

(iii) Foaming power:

2% concentration of sulphated mass was prepared, 50ml of this solution was taken in 500ml measuring cylinder provided with a stopper. The cylinder was inverted and restored about 50 times in minimum possible time (1 min). Foam volume was noted from the bottom of the cylinder. This is initial foam height. The height measurement was again taken after 1 minute, 2.5 minutes and 5 minutes. This gives the foaming power in terms of foam decay for the test sample.

(iv) Dispersing power:

Different concentrations (0.25, 0.50, 0.75 and 1%) of the sulphated mass are prepared. In a graduated cylinder (250ml) (for each sample) 2g of carbon black, 5ml of liquid paraffin and 50 ml of test sample was taken. The volume was made upto 100 ml with water. After 2 hrs, 5ml solution was pipetted out from each cylinder and transferred to a previously weighed Petridish. The solutions in different dishes were evaporated to dryness (oven) to yield a constant weight. On subtraction of the empty weight of Petridish, the actual weight (mg) of dispersed content from each sample can be found out.

Results and Discussion

The observations are shown in Tables and Figs. Highest value for surface tension was observed in the sample of *Balanites aegyptiaca.* Surface tension decreases with increase in concentration of the test sample.

Wetting power of surfactant is determined in terms of sinking time. Sinking time decreases with increase in concentration of the test sample. Lesser the sinking time of a surface active agent, grater is its utility as a wetting agent. The tested samples may replace or at least relieve pressure on castor oil which is in demand for preparation of value added products in dying of textiles.

Foaming power has been determined in term of initial foam height (0 min) and foam decay. Foam decays gradually with increase in surface activity of surface active agent. Initial foam height is better in the test sample where surface tension is low (*P. dulce and T. grandis)*

Dispersing power of the test samples is determined in terms of suspension (mg) after 2 hours. Higher the dispersed content, more efficient would be the surface active agent *(P. dulce).* This correlates with low surface tension of *P. dulce*.

Table 1 : Surface Tension of Tested Samples

Concentration of Sulphated mass (%)	Surface tension (25°c) of oils (Dyne/cm)			
	P. dulce	T. grandis	A. squamosa	B. aegyptiaca
0.25	36	34.6	33.9	42.1
0.50	33	33.1	33.4	40
0.75	31	31.8	31	38
1.0	30	30.1	30	37.5

Table 2 : Wetting Power in Terms of Sinking Time of Tested Oils

Concentration of Sulphated mass (%)	**Sinking time (Sec) of samples**			
	P. dulce	T. grandis	A. squamosa	B. aegyptiaca
0.25	***94.2***	***153.2***	***125***	***315.2***
0.50	***39.2***	***73.7***	***86.2***	***130.3***
0.75	***35***	***38.5***	***41.5***	***90.2***
1.0	***30***	***30.5***	***30.2***	***82***

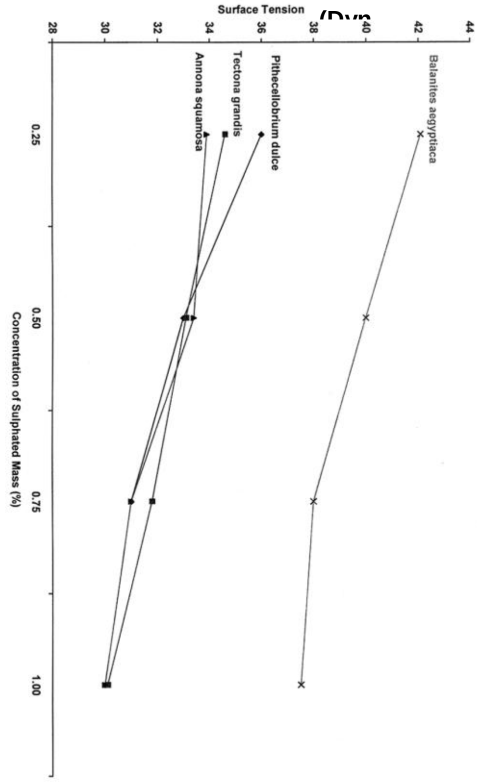

Fig V/5 : Surface active properties : Surface Tension of tested oils

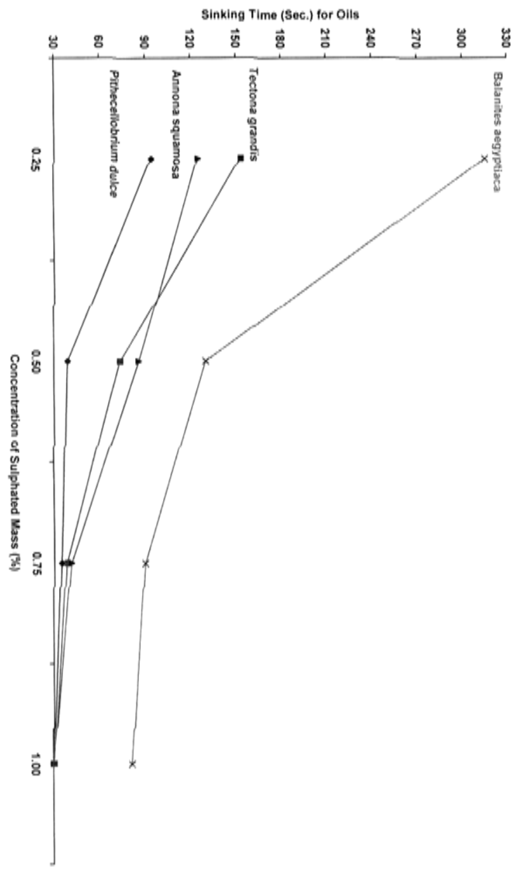

Fig V/6 : Surface active properties : Wetting Power (in terms of sinking time) of tested oils

Table 3 : Foaming Power in Terms of Foam Decay of Tested Oils

Decay time (Min)	Foam decay (ml) of 2% samples			
	P. dulce	T. grandis	A. squamosa	B. aegyptiaca
0	*230*	*240*	*210*	*90*
1	*170*	*59*	*180*	*52*
2.5	*70*	*53*	*165*	*51*
5.0	*58*	*51*	*158*	*51*

Table 4 : Dispersion Power in Terms of Suspension of Tested Oils

Concentration of Sulphated mass (%)	Dispersion (mg) after 2 hrs of samples			
	P. dulce	T. grandis	A. squamosa	B. aegyptiaca
0.25	*18.7*	*12.3*	*15.6*	*8.2*
0.50	*35.3*	*27.2*	*31.3*	*20.3*
0.75	*48.4*	*41.3*	*40.2*	*25.6*
1.0	*54.6*	*46.6*	*45.3*	*32.3*

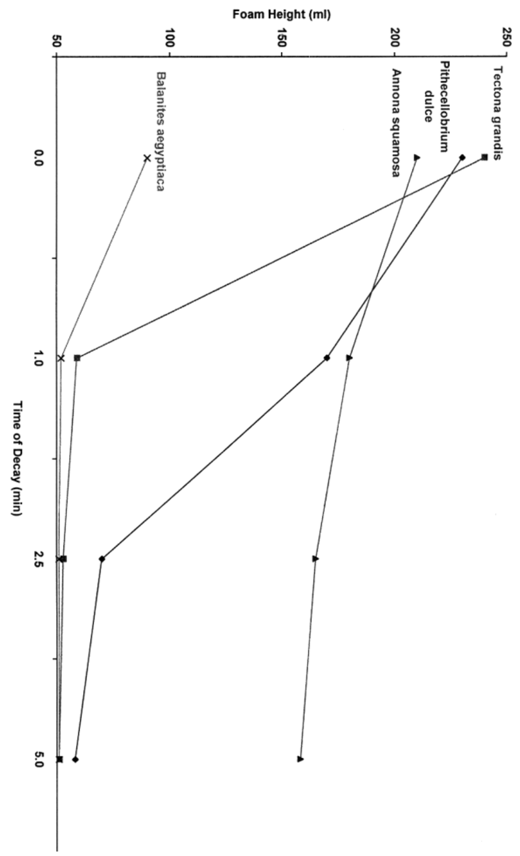

Fig V/7 : Surface active properties : Foaming Power (in terms of foam decay) of tested oils

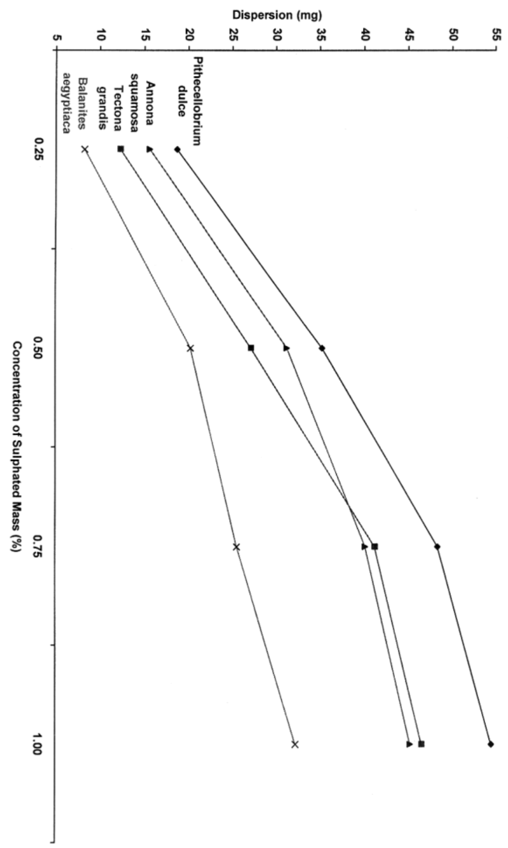

Fig V/8 : Surface active properties : Dispersion Power (in terms of suspension) of tested oils

4. Conclusion

In this research has been implemented of studies of surface active agents from some non edible oils in the presence of Madhya Pradesh forest seeds, pithecellobrium dulce, tectona grandis have rich, sources of surface active activity in the result of GLC methods from non-edible oils of Tectona grandis and Pithecellobrium dulce Preparation of surface active agents from protein isolates of these have also been tried to utilise these as value added products since protein based surface active agents are skin compatible and biodegradable.

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