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Studies on Nonconventional Oil Seeds: A New Source of Edible and Industrial Oils

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The seeds of *Pithecellobium dulce* belonging to *Leguminoseae* family obtained from forest origin were examined for their fatty oil constituents and some applications of oils to edible as well as industrial purposes.

INTRODUCTION

A subacute study was carried out on albino rats to study the nutritive value of the fatty oils extracted from dried and powered seeds by solvent extraction. The oils were also tested for some oil modified alkyds and nitro alkyds by polymerization at 275°C and co-polymerization of glycerylated oil with phthalic and nitrophthalic anhydrides. Oil modified azo alkyd dyes were also attempted from modified nitro alkyds by reducing the nitro group, diazotization and coupling with various phenolic compounds. The shades of dyes were tested by applying these on nylon, polyester and wool fabrics.

The seeds of *P. dulce* were found to contain pale yellow coloured oil in 16.0% yield. Oil shows maximum weight growth in tested albino rats without any toxic effects during nutritional studies. The oil polymerizes within 5 hrs at 275°C and alkyd resin of the oil shows excellent properties. Azo alkyd dyes show good exhaustion, fixation and fastness properties for tested fabrics.

The results show that *P. dulce* seed oils have both nutritional and industrial applications. These oils may be helpful in solving the international problem of scarcity of oils.

In the present work the seed oils of *Pithecellobium dulce* (N.O. Leguminoseae)[1,2] have been examined chemically, with a view of find out new oils for nutritional and/or industrial purposes.

EXPERIMENTAL

(A) Chemical Study of Fatty Oil

The dried and powered *P. dulce* seeds were extracted with petroleum-ether (60–80°) in soxhlet apparatus. The physico-chemical properties of the oil are determined. The fatty acid composition of the oil was found out by GLC analysis of the methyl esters of mixed fatty acids.

(B) Nutritional Study of Fatty Oil

Twenty albino rats of either sex approximately 80 gms in weight were used

for this study. Ten rats were randomly selected that had free access to the basic diet mixed with 10% (v/w) *P. dulce* oil. The experiment was continued for 60 days. The animals were weighed after every 5 days and examined for abnormal signs like change in weight, loss of hairs, scaly tail, etc. At the end of 60 days all surviving animals were sacrificed. Blood was collected by heart puncture and liver was perfused with saline via the portal vein to remove as much of the trapped blood as possible and excised. The excised liver was quickly immersed in chloroform : methanol (2 : 1) mixture. Cholesterol of blood serum and liver was extracted by appropriate method and determined quantitatively by colorimetric estimation.

(C) Polymerization Study of Fatty Oil

Thermal polymerization of *P. dulce* seed oil at different temperatures and for different time durations was carried out in a three necked flask fitted with a thermometer, a mechanical stirrer, a condenser and a CO_2 gas inlet tube. Heating was done on a heating mantle with temperature control. Continuous stirring and bubbling of CO_2 gas were maintained. The density, refractive index, iodine value, intrinsic viscosity and number average molecular weight of oil samples obtained at different temperatures and heating durations are determined (Table 1). From this data, 275°C temperature was chosen for polymerization reaction. 15 Ml samples were drawn at different stages and all the above parameters were determined (Table 2). The progress of polymerization was also determined from IR spectra of each oil sample.

TABLE 1
THERMAL POLYMERIZATION OF *P. DULCE* OIL FOR DIFFERENT TIME AND TEMPERATURE

Sl. No.	Temperature °C	Heating time in hrs.	R. index at 30°C	I. value	Density at 30°C	$[\eta]$ dl/gm in CCl_4	$\overline{M}_n$ in DMF by VPO
1.	Room Temp.	00.0	1.4630	81.52	0.9407	0.044	485
2.	250	16.0	1.4773	41.32	0.9502	0.070	750
3.	260	10.0	1.4737	44.10	0.9480	0.066	708
4.	270	10.0	1.4750	41.93	0.9518	0.074	790
5.	275	06.0	1.4790	40.00	0.9530	0.075	806
6.	285	04.0			gel		

(D) Preparation of Oil-modified Alkyd Resins[3]

Preparation of alkyd resins was carried out in two stages, i.e. glycerolysis of oils and transesterification with phthalic and 3-nitrophthalic anhydrides. The various properties of prepared alkyd resins were determined, which are given in Table 3 and alkyd resins were characterized from their IR spectra.

TABLE 2
THERMAL POLYMERIZATION OF *P. DULCE* OIL AT 275 ± 2°C

Sl. No.	Heating time in hrs.	R. index at 30°C	Density at 30°C	I. value	[η] dl/gm in CCl_4	K. value	Average K	$\overline{M}_n$ in DMF by VPO
1.	0.0	1.4630	0.9407	81.52	0.044	—		485
2.	2.0	1.4653	0.9452	51.23	0.054	0.0007		582
3.	4.0	1.4676	0.9476	48.58	0.063	0.0005	0.0006	678
4.	6.0	1.4692	0.9530	40.00	0.075	0.0006		806
5.	8.0	1.4738	0.9573	38.37	0.090	0.0005		1063
6.	After 8.0				gel product			

Indications: I. value: Iodine value; R. index: Refractive index; [η]: Intrinsic viscosity; $\overline{M}n$: Number average molecular weight.

TABLE 3
PROPERTIES OF ALKYD MODIFIED WITH *P. DULCE* OIL

Sl. No.	Properties	A	B
1.	Appearance of the resin	Yellowish Brown	Brown
2.	Nature of the film	Transparent	Transparent
3.	Acid value	12.2	9.0
4.	Iodine value	48.2	46.8
5.	Refractive index, $\eta_D^{28°}$	1.4916	1.4936
6.	Intrinsic viscosity [η] dl/gm	0.098	0.106
7.	Average molecular weight ($\overline{M}_n$)	1160	1280
8.	Drying time of the film (hrs)	> 48	> 48
9.	Effect of water for 24 hours	No effect	No effect
10.	Effect of 2% H_2SO_4 for 30 minutes	No effect	No effect
11.	Effect of 5% NaOH for 30 minutes	Totally dissolved	Totally dissolved
12.	Effect of CCl_4 for 10 minutes	Totally dissolved	Totally dissolved
13.	Effect of acetone for 5 minutes	Totally dissolved	Totally dissolved
14.	Effect of xylene for 5 minutes	Totally dissolved	Totally dissolved

(E) Preparation of 3-Azo Alkyd Dyes

The 3-nitro alkyd resins obtained in above preparation were separated in sodium bicarbonate soluble and insoluble parts. Insoluble part was reduced with sodium hydrosulphite to 3-amino alkyd resin. Then the dyes were prepared by diazotizing with sodium nitrite and coupling with alkaline phenolic compounds like α-/β-naphthol and 8-hydroxyquinolene in ice-cold condition.

The 3-azo alkyd dyes thus obtained were applied on polyester and nylon fabrics as disperse dyes using Tween-80 as a dispersing agent[4,5]. The exhaustion and fixation rate of the dyes were also determined (Table 4). The dyes also successfully tested for wool yarns.

TABLE 4
EXHAUSTION AND FIXATION STUDY OF 3-AZO ALKYD DYES

Sl. No.	Coupling component and colour of the dye	Fabric used (1 gm)	Qty. of dye left in dye bath (a) (mg)	Amount of dye exhausted from dye bath b = (10 – a) (mg)	% of dye exhausted from dye bath 100 × b/10 (%)	Qty of dye fixed on 1 gm. of dyed fabric (C) (mg)	% of dye fixed on the fabric C × 100/b (%)
1.	α-napthol Light coffee	Nylon	4.20	5.80	58.0	5.68	97.93
2.	β-napthol Light coffee	Nylon	4.10	5.90	59.0	5.82	98.64
3.	8-hydroxyquino-lene Ivory	Nylon	4.70	5.30	53.0	5.18	97.73
4.	α-napthol Light coffee	Polyester	4.32	5.68	56.8	5.32	93.66
5.	β-napthol Light coffee	Polyester	4.20	5.80	58.0	5.70	98.27
6.	8-hydroxyquino-lene Ivory	Polyester	5.10	4.90	48.0	4.75	96.94

RESULTS AND DISCUSSION

The dried and powered *P. dulce* seed on solvent extraction yields 16.0% pale yellow coloured fixed oil having specific gravity at 30°C is 0.9407, refractive index at 30°C is 1.4630, acid value 12.151, saponification value 186.768, iodine value 91.523, acetyl value 6.90 and unsaponifiable matter 0.5%. The GLC analysis of the methyl esters of mixed fatty acids shows the presence of 19.928% palmitic, 3.410% palmitoleic, 12.602% stearic, 58.026% oleic, 1.279% linoleic, 3.171% linolenic, 0.99% arachidic and 0.586% behenic acids. The unsaponifiable matter was found to contain β-sitosterol, stigmasterol, lupeol and unidentified hydrocarbons. The oil is rich in oleic acid.

Examination of animals in the test group failed to show any abnormal signs such as loss of hair or scaly skin/tail. The consumption of water and food of the test group was similar to that of control group. Thus one can conclude that in this 60 days period of observation no toxic effects for the *P. dulce* oil were seen. The weight gain of the two groups was also seen to be identical. The cholesterol content of blood serum as well as liver is also identical in both the groups. Since there is no elevation in blood cholesterol value one can safely use *P. dulce* seed oil as a source of dietary fat.

From the data of Table 1, 275°C temperature was chosen for polymerization

reaction. The observation of Table 2 clearly shows that the density, refractive index, intrinsic viscosity and number average molecular weight increases straightforwardly and unsaturation decreases with increase in reaction time upto 8.0 hrs and after that the oil is converted into the gel form, which indicates the formation of three-dimensional polymer resulting from crosslinking.

The IR spectra of thermally polymerized oil at 275 ± 2°C for different time intervals reveal decrease in the intensity of ethylenic C=CH bands at 3015 cm^{-1} and progressive increase in the intensity of the methylene band[6] at 2930 cm^{-1} indicating decrease in the number of *cis*-double bonds and hence progressive polymerization is observed with increase in treatment time. The adsorption band observed in the region 1465–1460 cm^{-1} is attributed to the C—H bending vibrations of the methylene (—CH_2) group. As polymerization proceeds, this band becomes more and more intense. The weakest absorption at 918 cm^{-1} observed in the oil is due to isolated cis C=C as well as conjugated *trans-trans* (–C=C–C=C–) which is evident from clear absorption at 955 cm^{-1} and 988 cm^{-1} respectively. The absorption band at 725 cm^{-1} is due to —CH_2 rocking vibrations. The intensity of this band increases progressively as the polymetrization proceeds.

The IR spectra[7] of *P. dulce* oil modified 3-nitro alkyd resin shows the symmetrical and asymmetrical stretching vibrations of C–NO_2 group at round 1540 cm^{-1} and 1345 cm^{-1} respectively as strong bands. The strong intensity of these bands proves that in the alkyd resin, the nitrophthalic acid units are incorporated repeatedly.

The observation of Table 3 shows that the oil-modified alkyd and 3-nitro alkyd resin forms transparent film and number average molecular weights are 1160 and 1280 respectively by VPO in CCl_4 solvent at 35°C. Both the alkyds take more than 48 hrs for drying. The water and acid resistance is good but resistivity against alkali and some organic solvents is not satisfactory. These alkyds may find use in paints, varnishes and such type of surface coating materials.

The IR spectra of reduced product of 3-nitro alkyd resin (sodium bicarbonate insoluble part) shows medium broad band due to bonded —NH_2 at around 3450 cm^{-1} on acetylation of the amino group, this band has been weakened. The reduction of nitro group was again tested from the remarkable feature of amino alkyds. The alcoholic solution of amino alkyds shows slight fluorescence in UV light. The corresponding acetyl derivatives do not show fluorescence. The IR spectra of 3-azo alkyd dyes show stretching vibrations at around 1630, 1600 and 1512 cm^{-1}, which were not seen in the case of amino and N-acetylated amino alkyds. Again characteristic frequencies of oil in the region 1000–900 cm^{-1} are observed due to *cis-trans* isomerism.

The 3-azo alkyd dyes obtained from *P. dulce* oil modified 3-nitro alkyd resin

by reduction, diazotization and coupling with alkaline solution of phenolic compounds like α-/β-napthol and 8-hydroxyquinolene in ice-cold condition have decent shades like light coffee and ivory respectively. The dyes have been used as disperse dyes using Tween-80 as a dispersing agent on nylon and polyester fabrics. Dyed fabrics maintained their fastness on exposure to sunlight. From the observations of Table 4 the dyes have good exhaustion and fixation for both the fabrics. The dyes were also successfully used for wool yarns.

Conclusion

The seeds of *Pitecellobium dulce* were found to contain pale yellow coloured semidrying fixed oil in 16.0% yield. Oil shows maximum weight growth in tested albino rats without any toxic effects during nutritional studies. The oil polymerizes within 8.0 hrs at 275°C and alkyd resins obtained by co-polymerization of phthalic and nitrophthalic anhydrides with oil glycerides show excellent properties. 3-azo alkyd dyes show good exhaustion, fixation and fastness properties for tested nylon, polyster fabrics and wool yarns.

The results show that *P. dulce* seed oil has nutritional and industrial applications. The oil may be helpful in solving international problem of scarcity of oils.

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