Cephalaria syriaca Seed Oil

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ABSTRACT

Cephalaria syriaca shrad., in Turkish pelemir, grows predominantly in the southeastern district of Turkey as a weed in cereal fields. Pelemir seeds are sometimes used for extraction of their oil, as an improver of baking value of wheat, and as an antistaling agent for bread. The seeds contain 7.8% moisture; their chemical composition on a dry basis is: crude fat, 25.3%, crude protein, 15.9%; N-free extract, 40.4%; crude fiber, 11.9%; crude ash, 6.5%. Characteristics of the seed oil are: specific gravity at 25 C, 0.9229; refractive index at 25 C, 1.4706; saponification value, 192; iodine value, 88.4; thiocyanogen value, 58.8; Reichert-Meissl value, 0.36; Polenske value, 0.25; unsaponifiable matter, 1.24%; hydroxyl value, 20.9. The fatty acid components are: lauric acid, 1.5%; myristic acid, 19.5%; palmitic acid, 9.4%; stearic acid, 2%; oleic acid, 23.0%; linoleic acid, 36.9%. The chemical composition of extracted cakes on a dry basis is: crude protein, 20.4%; crude fat, 0.8%; N-free extract, 50.5%; crude ash, 6.4%; crude fiber; 14.4%%; saponin, 7.5%. The oil contains 7.8% epoxy acid, calculated as epoxy oleic acid, which makes its use as an edible oil rather difficult but renders it usable in industries using epoxidized oils. Due to its high content of myristic acid, the oil is very suitable for soapmaking as well.

INTRODUCTION

Syrian scabious, *Cephalaria syriaca* Schrad. or *Scabiosa syriaca* L. (in Turkish pelemir), belongs to the plant family Dipsacaceae. It is a perennial plant and grows as a weed in wheat fields, predominantly in southeastern Turkey. In certain regions, like Kayseri and Erzincan, pelemir is specifically grown for its seeds, which are added to wheat in order to ameliorate its baking value and to delay staling. Sometimes they extract oil from the seeds as well. Considering the seed's less exacting character, the Turkish Ministry of Agriculture made some field trials with pelemir to replace wheat in the arid and less productive areas of southeastern Turkey. An average of 1500 kg of pelemir seeds was produced per hectare, the ratio of the amount of seeds sown to the amount harvested being between 1:25 and 1:80. This ratio is very high when compared to that of wheat from these less productive soils. Pelemir also gives satisfactory results as an oil plant. Oil yield of pelemir seeds per hectare, even in those arid areas, amounts to 375 kg.

TABLE I

The Physical and Chemical Analysis of Pelemir Seeds

	Kayseri 1973	Diyarbakir 1974
1000 Kernel weight, g	14.2	14.0
Hectoliter weight, kg	59.3	60.2
Kernel size, average, mm	5.9	6.4
Kernel width, average, mm	2.0	2.1
Water, %	6.4	9.2
Fat, % (dry basis)	24.9	25.8
Protein, % (dry basis)	14.8	16.9
Ash, % (dry basis)	7.8	5.3
Crude fiber, % (dry basis)	11.9	11.8
N-free extract, % (dry basis)	40.6	40.2

Pelemir (45 tons) was processed for oil extraction in Gaziantep in 1974. The seeds were bought for 10 cents per kg, and the oil was sold to soap manufacturers for 60 cents per kg. The residual seed cakes were sold for 9 cents per kg to be used as animal feedingstuff.

Pelemir has for some time been subject to study by various research workers, and earlier literature on the subject is given under references (1-7). The present study was undertaken to provide further detailed information on the composition of the oil and seed as to its fatty acid components and saponin.

EXPERIMENTAL PROCEDURES

Materials

Pelemir seeds were brought from Kayseri in 1973 and from Diyarbakir in 1974. Analyses were done on the seeds, their oil, and seed cake.

Methods

The physical and chemical properties of pelemir seeds were determined according to the "Official and Tentative Methods of the American Oil Chemists' Society" (8).

The seeds were extracted in a Soxhlet apparatus with petroleum ether (bp 40-60 C). Pelemir oil was analyzed later for determination of its characteristics as well as its chemical composition.

The oils were saponified by the usual procedure, and the resulting fatty acids were esterified using BF_3-methanol reagent (8). The methyl esters were analyzed by a gas chromatograph (Varian, Model 2100) equipped with a flame ionization detector. The column (6 ft x 1/4 in.), packed with 10% diethylene glycol succinate on 100/120 mesh Chrom G, was operated at 220 C, with a carrier gas flow of 60 ml N/min. A strip chart recorder, Model A-25, was used, and recorder speed was kept at 20 cm/hr.

The detector and injector temperatures were both kept at 225 C. The hydrogen and air flow rates were 40 and 60 ml/min, respectively.

The peaks were identified by their relative retention times and by using reference fatty acid esters where required. The percentage of each component was calculated from the ratio of each peak area to the sum of the areas under all of the component peaks and reported as percent by weight.

The high hydroxyl value of pelemir oil suggested the presence of an oxygenated fatty acid, the nature of which was determined by thin layer chromatography because oils containing triglycerides of epoxy and hydroxy acids show very characteristic chromatographic patterns. The adsorbent layer was Silica Gel G. A solution (1%) of pelemir oil in chloroform was prepared, as well as of castor oil which is known to contain a hydroxy acid, and of olive oil which is known to contain neither epoxy nor hydroxy acid. The solvent system used was petroleum ether (bp. 40-60 C)-diethyl ether-acetic acid (70:30:2). Visualization was affected by carbonization by heating after spraying with a 5% solution of potassium dichromate in 40% sulfuric acid (9).

Later, to see whether this epoxy component was saturated or unsaturated, the chromatogram was sprayed with a 1% solution of α-cyclodextrin and developed with iodine vapors (10). The spots corresponding to epoxy

TABLE II

Comparison, of Oil Yield per Hectare for Various Turkish Oilseeds

	Area sown (hectares)	Production (tons)	Seed yield per hectare, kg	% Of oil in seed	Oil yield per hectare, kg
Cottonseed	670,000	736,000	1,110	23	255
Sunflower	355,000	390,000	1,078	40	431
Sesame	67,000	40,000	603	58	349
Linseed	13,000	9,000	636	40	254
Hempseed	8,600	3,000	337	35	118
Soybean	8,000	11,000	1,465	19	278
Safflower	1,300	1,060	790	28	221
Rapeseed	400	4,500	1,086	35	380
Pelemir	---	---	1,500	25	375

components became dark, showing unsaturation. The quantitative determination of the epoxy component was made by first determining the oxirane oxygen, which is the oxygen contained in the —— C —— C —— grouping by
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titrating with hydrobromic acid (8). The result was confirmed by gas chromatography according to the method of Kleiman et al. (11). The epoxy component was converted to a methoxy-hydroxy derivative after esterification with BF_3 and was subjected to gas chromatography using a nonpolar column, 125 cm long, packed with 1% Apiezon L on Chromosorb G. It eluted as a single peak with a longer retention time than methyl ricinoleate.

The seed cakes after oil extraction are bitter in taste. Various research workers have indicated that a glycoside is the reason for this bitterness. A small amount of the seed cake, when shaken in a test tube with water, foamed. This was also observed by Klimmer (6) and was taken as an indication for the presence of saponins. Saponins have a more or less hemolyzing effect on blood erythrocytes, and we used this property as a qualititative confirmation test for their presence in the pelemir seed cake (9). We later extracted this foaming element using the Roberts and De Silva method (12) for saponin extraction.

The saponins thus obtained were subjected to acid hydrolysis, and KBr discs of the dry hydrolysate were studied with a Perkin Elmer Model 177 Infrared-Spectroscope.

During hydrolysis of the saponins, the glycosidic linkage was broken, and the carbohydrate moiety was separated from the sapogenin part by extracting the sapogenin part with ether. The carbohydrate moiety that remained in the aqueous phase was chromatographed on Silica Gel G in 0.2 M sodium acetate, using the solvent system n-butanol-acetic acid-water (60:20:20), development distance being 15 cm. After drying, the plate was sprayed with aniline-diphenyl amine reagent (4 g:4 ml) in 80% phosphoric acid and kept 10 min at 85 C. The R_f values of sample sugars were compared with those of standards.

The pelemir seed cakes, after extraction of saponins, are perfectly palatable as animal feedstuffs. In order to have an idea of its nutritive value, the amino acid components were determined by a Beckman Multichrom Liquid Column Chromatograph, Model 4255.

RESULTS AND DISCUSSION

The Seeds

The physical and chemical properties of pelemir seeds are summarized in Table I. As stated above, pelemir is usually a weed in cereal fields, and it is difficult to separate pelemir seeds from wheat kernels because of their similarity in shape and length. But there is a rather big difference in width; wheat kernels are much wider than pelemir seeds.

It will be seen from Tables I and II that pelemir seeds are a rather rich source of oil when compared to oil yield per hectare of other oilseeds. The percentage of oil in pelemir is higher than soy and cottonseed, and the oil yield per hectare of pelemir comes third after sunflower and rapeseed. We should take into consideration that this figure for pelemir represents the yield from dry and arid soils where commercial cultivation of the established oilseeds is almost impossible. A much higher yield per hectare is to be expected if pelemir were planted in the rich and productive soils used for other oilseed crops.

TABLE III

	Kayseri 1973	Diyarbakir 1974
Refractive index, 25 C	1.4702	1.4711
Specific gravity, 25 C	0.9241	0.9217
Saponification value	190.0	193.6
Iodine value (Hanus)	89.0	87.8
Thiocyanogen value	58.4	59.2
Hydroxyl value	22.2	19.7
Reichert-Meissl index	0.33	0.38
Unsaponifiables, %	1.28	1.19
Lauric acid (12:0, %	1.4	1.6
Myristic acid (14:0), %	18.4	20.5
Palmitic acid (16:0, %	8.8	10.0
Stearic acid (18:0), %	1.9	2.0
Oleic acid (18:1), %	25.5	20.6
Epoxy acid, as epoxy oleic, %	7.8	7.7
Linoleic acid (18:2), %)	36.3	37.6

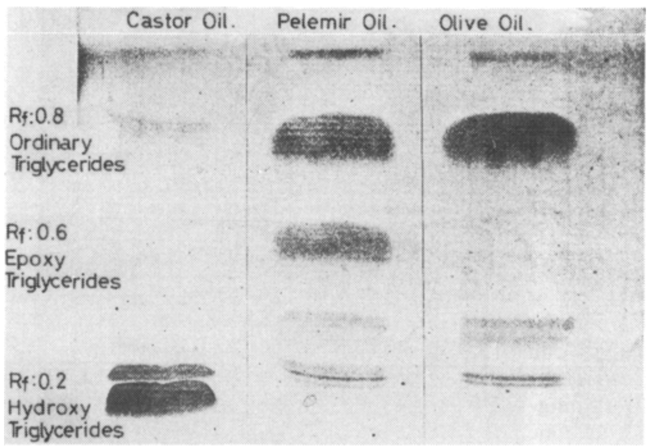

FIG. 1. Comparison of pelemir triglycerides with castor and olive oils by TLC.

The Oil

The results of analyses of pelemir oil are shown in Table III. Pelemir seed oil, with an iodine number 88, can be classified as a nondrying oil. When spread on a glass surface, it was observed that the oil was still fluid even after several months.

The unexpectedly high specific gravity, viscosity, and

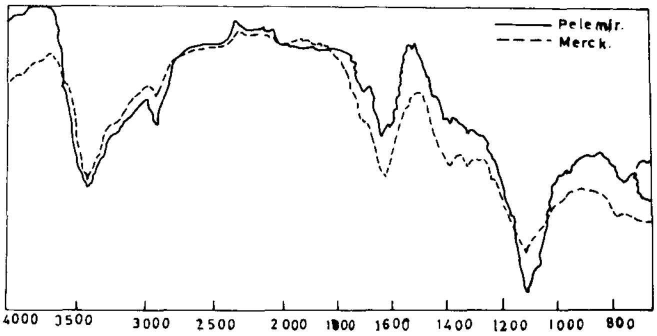

FIG. 2. IR spectra of pelemir and Merck sapogenins (KBr discs).

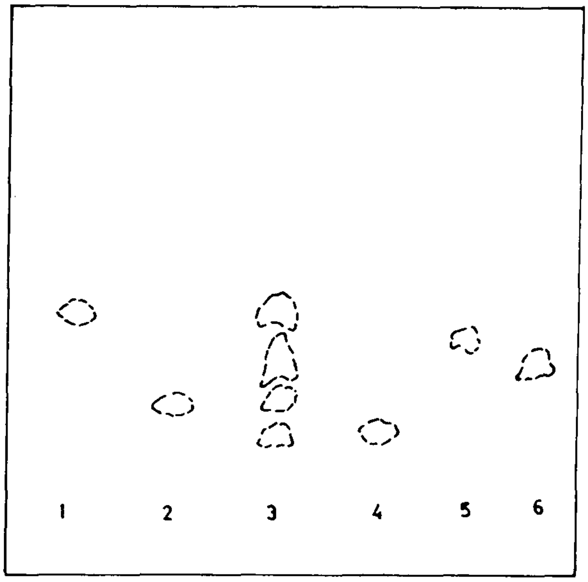

FIG. 3. TLC of carbohydrate moiety of hydrolized pelemir saponin. 1. xylose, 2. mannose, 3. pelemir sugars, 4. galaktose, 5. glucose, 6. galacturonic acid.

especially high hydroxyl values were taken to indicate the presence of an oxygenated fatty acid. By use of thin layer chromatography, it was confirmed that the oil contained an epoxy constituent, since pelemir triglycerides appeared clearly at the R_f distances characteristic for epoxy-acid-containing triglycerides (Fig. 1). As stated under Methods, it was concluded that the epoxy constituent of pelemir oil was unsaturated. Later, this epoxy component was determined quantitatively by HBr titration and by gas chromatography to be 7.8% as epoxy-oleic acid. This is in agreement with Earle's review (13) which states that oils from the Dipsacaeea family and genus cephalaria have been shown definitely to contain vernolic acid up to values of 10%.

The fatty acid components, as determined by GLC are also shown in Table III. The oil contains appreciable amounts of myristic and lauric acids which are characteristic of the plant families lauracea, myristicaceac, and palmae. Myristic and lauric acids are useful for soapmaking. Soap made in the laboratory was of good character and had a high foaming capacity.

In recent literature (14), the presence of an epoxy group is indicated to be hazardous to human health and possibly has a carcinogenic effect. Therefore, we cannot risk using it as an edible oil. In Turkey about 25,000 tons of edible oil is being used annually for soapmaking and for other industrial purposes. We could replace this with pelemir oil and use our edible oils for food.

TABLE IV

Analysis of Pelemir Cakes

	After extraction of oil	After extraction of oil and saponin
Water, %	6.8	3.0
Protein, % (dry basis)	20.4	21.8
Fat, % (dry basis)	0.8	0.9
Ash, % (dry basis)	6.4	6.9
Crude fiber, % (dry basis)	14.4	15.2
Saponin, % (dry basis)	7.5	---
N-free extract, % (dry basis)	50.5	55.2

TABLE V

The Amino Acid Composition of the Pelemir and Sunflower Cakes without Oil and Saponin (Essential Amino Acids are Marked "+")

	(mg Amino acid/100 g seedcake)	
	Pelemir	Sunflower
+ Isoleucine	946	1736
+ Leucine	1375	2553
+ Lysine	1007	1403
Cystine	1423	2169
+ Phenylalanin	99	1804
Tyrosine	562	898
+ Threonine	1065	1378
Arginin	1501	3323
Histidine	464	867
Alanine	1101	1468
Aspartic acid	1968	3531
Glutamic acid	3501	9181
Glycine	1783	2137
Proline	1004	1722
Serine	964	2222

Also, in PVC manufacture, synthetically epoxidized oils are being added to procure plasticity. Pelemir oil, which naturally contains this epoxy group, can readily be used as a precursor for plasticizing PVC. Pelemir oil is being used in the leather industry as well for rather a long time in the Kayseri region (15,16).

The Cakes

The bitter principle of the pelemir cake after oil extraction was shown to be a saponin, as explained under Methods, and the saponin yield was 7.5% by weight. This increases the commercial value of the cake because saponin itself is an expensive material and has use in many industrial fields.

The infrared spectrum of pelemir saponin implied it was of triterpenoid nature, after comparison with the spectrum of Merck saponin which is known to be triterpenoid (Fig. 2). Its carbohydrate moiety isolated after hydrolysis consisted mainly of xylose, mannose, and galactose, as determined by thin layer chromatography (Fig. 3).

The seed cake, after extraction of oil and saponins, was analyzed and the results are shown in Table IV. The significantly high protein content makes it suitable for animal feeding. Its amino acid composition, as determined by liquid column chromatography, is given under Table V. Though it will be observed that it is poorer than sunflowerseed cake, almost all the biologically essential amino acids are present in significant amounts. Therefore, it probably can be used as a base for the preparation of animal feeds.

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