• TECHNICAL

Seed and Seed Oil of *Pistacia Terebinthus* and *P. Lentiscus*

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Abstract

Seeds of *Pistacia Terebinthus L.* and *P. Lentiscus L.* were collected from Greek Islands and their composition was determined.

Seed oil was taken through various processes and the determination of its physical constants and chemical characteristics was carried out. The maximum and minimum of all the values obtained as well as mean values are given. From iodine and thiocyanogen values the glyceride composition of Pistacia oil was also calculated. Average values are also tabulated.

Introduction

Among the Greek kinds of Pistacia, more interesting from the point of view of the oil content of their seeds are *Pistacia Terebinthus L.* (Turpentine-tree) and *P. Lentiscus L. (Lentisk)* because both are abundant in Greece (1–3). *P. Vera L.* which is also abundant gives edible seeds, while *P. Mutica F. et M.* is much less abundant.

The composition of some kinds of Pistacia seeds is given in the literature (3–5). Also, some earlier papers (5–11), give the constituents and the properties of Pistacia seed oil; but the determination of the composition and properties of the oil of the Greek varieties of Pistacia has not been given yet.

Since Greece has multiple uses for an abundance of Pistacia, this work concerns the determination of the composition of Pistacia seed and oil and the examination of the properties of the latter.

Experimental

Pistacia Seed Composition

Seeds of *Pistacia Terebinthus L.* and *P. Lentiscus L.* were collected from the Greek islands Chios and Patmos where the mentioned kinds are very abundant. The age of all samples examined was two and four months.

The composition of the seeds was determined for various samples according to the following known methods:

Water-content: In electrical oven at 105C.
Oil content: Extraction with Petroleum ether (b.p. 40–60C).
Protein-content: After Kjeldahl.
Crude-fiber: After König.
N-free extract: Calculated from the difference.

The gross structural characteristics of the seeds and the average composition of the samples are given in Table I.

Pistacia Seed Oil Examination

1) *Physical Properties and Chemical Characteristics.* The examination of Pistacia seed oil was carried out on a variety of samples taken through the following processes:

a) Laboratory extraction with petroleum ether.
b) Laboratory pressing in a small model press.
c) Breaking of the seeds and pressing within special sacks.
d) Breaking of the seeds and boiling with water.

The two latter are in use by the inhabitants at the places of production.

Six samples in each of the above four groups were analysed, three for *P. Terebinthus L.* and three for *P. Lentiscus L.* Samples of groups "a" and "b" were processed in the author's laboratory while those of groups "c" and "d" were produced by home industry.

The age of the samples was between one month and two years. The oldest were stored in dark bottles in a refrigerator at 0C in the author's laboratory.

All samples were clear, with a slightly sweet taste and the special sharp odor of Pistacia oils. The color for *P. Terebinthus* samples was yellow to brown and for *P. Lentiscus*, deep green.

The specific gravity and the refractive index as well as the chemical characteristics of the samples were determined according to the recognised methods (12–13). For the experimental determination of the average mol wt of the fatty acids, the latter were isolated and examined. Free fatty acid (FFA) content was calculated on the assumption that the average mol wt of the FFA is ca. 278, as it was extracted from the experimental data.

In Table II, mean values of 12 samples from each kind of Pistacia oil, taken as above, are reported.

2) *Composition of Pistacia Oil.* For the composition of Pistacia oil, the UV absorption technique of analysis (14) was applied on two samples. Results obtained for these two samples are as follows: Conjugated diene %: 0.6; 0.9. Conjugated triene, tetraene, pentaene: 0; 0. Linoleic acid %: 22.6; 21.5. Linolenic acid %: 0.2; 0.33. Oleic acid %: 51.4; 52.6. Saturated acids %: 20.8; 20.3.

From these results, the composition in hypothetically pure triglycerides was calculated and compared with the composition in hypothetically pure triglycerides calculated (13) by the iodine and thiocyanogen values which were found respectively: I.V.: 88.81; 88.70, T.V.: 68.82; 69.60.

The results are tabulated in the Table III. In this table, all conjugated and nonconjugated diene triglycerides are reported as "linolein."

Though the occurence of linolenic acid is in agreement with the literature (15–16), it should be noticed that the linolenic content determined as above falls within the limits of error of the method. Since the results obtained by the two methods were in agreement, no other samples were run by isomerization, but their composition was calculated by iodine and thiocyanogen values. Maxima and minima of the values obtained, as well as mean values, are tabulated in the Table II.

TABLE I
Average composition of Pistacia Seed

Constituent	Whole seed average composition %	
	P. Terebinthus L.	*P. Lentiscus L.*
Shape	Spherical	Spherical or spheroidal
Average diam	6 mm	3 mm
Color	Blueish green to deep green	Yellowish red to black or to redish black
Average 100-seed wt	20.0 gr	3.0 gr
Moisture	8.4	15.5
Oil	38.2	31.2
Protein (N × 6.25)	9.2	8.7
N-free extract	15.0	16.5
Crude fiber	27.0	24.7
Ash	2.16	3.23
Ash basic constituents (as K_2CO_3)	1.14	1.59

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TABLE II
Physical Constants and Chemical Characteristics of Pistacia Seed Oil
(Mean values of 12 samples of each species)

Determination	*P. Terebinthus L.*			*P. Lentiscus L.*		
	Max	Mean	Min	Max	Mean	Min
Specific gravity at 25C	0.9141	0.9115	0.9081	0.9165	0.9094	0.9023
Refractive Index at 40C	1.4627	1.4619	1.4619	1.4631	1.4622	1.4613
Free fatty acid %	18.3	6.5	2.2	17.3	9.7	2.1
Unsaponifiable matter %	0.75	0.66	0.60	0.88	0.79	0.70
Saponification value	195.1	192.3	191.8	193.5	193.4	193.3
I.V. (Hanus)	90.2	89.2	88.7	88.9	87.2	85.5
Thiocyanogen value	70.5	69.9	69.3	69.5	69.4	69.3
Titer of fatty acids (°C)	27.2	26.9	26.7	30.8	30.3	30.1
Saponification value of fatty acids	202.5	202.2	202.0	202.3	202.0	201.4
Avg mol wt of fatty acids	277.7	277.4	277.0	278.6	277.8	277.3
Glycerides composition %						
Olein	58.8	56.3	53.4	60.9	57.7	55.5
Linolein	24.8	23.6	22.7	23.8	21.7	19.6
Saturated and unsaponifiable	21.7	20.1	18.1	20.7	20.6	19.5

TABLE III
Composition of Pistacia oil in hypothetically pure triglycerides

Sample No.	1		2	
Method	Cd 7-58	Cd 2-38	Cd 7-58	Cd 2-38
Linolenin	0.2		0.3	
Linolein	24.2	24.4	23.4	23.3
Olein	53.7	54.1	54.9	56.2
Saturated and unsaponifiable	21.9	21.5	21.4	20.5

As the chemical characteristics of the oils analysed show, the Greek Pistacia oils have the same composition as those reported from other areas.

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Dimer Acid Structures. The Dehydro-Dimer from Methyl Stearate and Di-Tertiary-Butyl Peroxide[1]

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Abstract

Previous work by Sutton, and by Harrison, McCaleb and Wheeler has shown that methyl stearate is converted to dimers plus higher polymers by the action of di-*t*-butyl peroxide. The latter suggested that in the dimer, there was considerable linkage at carbon 2, the carbon α- to the $COOCH_3$ group, since the dimer ester was incompletely saponified by the usual procedures.

Further proof of α-linkage is now presented. A fraction which is predominantly α-,α'-linked dimer was isolated as the nonpolymeric cyclic anhydride (α-,α'-dicetyl succinic anhydride) by molecular distillation from the linear polymeric non-α-linked polyanhydride. The isolated cyclic anhydride appeared identical with a synthetic α-,α'-dicetyl succinic anhydride, whose synthesis is described.

The original dimer ester, the α-,α'-cyclic anhydride fraction, and the dimethyl ester derived from it, were examined by mass spectrometry. The expected mol wt were confirmed by the parent ion peaks. Fragmentation patterns indicated appreciable α-linkage in the original dimer ester, and almost exclusive α-linkage in the ester from the isolated cyclic anhydride. Aside from preference for the α-position, joining appears to be randomly distributed.

Introduction

THE DIMERIZATION of methyl oleate by the action of di-*t*-butyl peroxide (dehydro-dimerization) has been studied (1), and the dimer structure was shown to be predominantly the result of joining of two moles of methyl oleate at carbons 8,9,10 and 11, with a small amt (5–10%) of joining at the 2 position (α- to $COOCH_3$). The mechanism was considered to be that of hydrogen abstraction by the *t*-butoxy radical from the CH_2's at carbon 8 and carbon 11 adjacent to the double bond, followed by coupling of the free radicals at C_8 and C_{11}, as well as the limiting resonance forms with free radicals at C_{10} and C_9. The dimerization was essentially stoichiometric, one mole of dimer resulting from one mole of di-*t*-butyl peroxide and producing 2 moles of *t*-butanol. The ratio of dimer to higher polymers was rather high (3:1).

The dimerization of methyl linoleate (2,3) and methyl linoelaidate (2) by di-*t*-butyl peroxide has also been studied. The dimer, which contained 4 double bonds, showed considerable amt (ca. 50%) of conjugated dimer. This was explained as resulting from coupling of limiting (conjugated) resonance forms of the free radicals resulting from hydrogen extraction from the active CH_2 at C_{11} between the two double bonds at C_9 and C_{12}.

Dehydrodimerization of methyl stearate has also been reported by Sutton (3), but no structural evidence was given.

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