ther aging showed good toughness and hardness without embrittlement. This was compared with an ester made by the peroxide polymerization of vinyl oleate (8), from which unreacted monomer was removed. The polymerized vinyl oleate ester did not dry hard or tough but remained soft or "cheesy," and did not compare favorably with the product made by direct esterification of the polyvinyl alcohol. This observation apparently verifies the fact that in the polymerized vinyl oleate, the molecular size (degree of polymerization) was not as great as that obtainable by direct esterification.

From work on the preparation and evaluation of the polyvinyl fatty acid esters certain facts are concluded, thus:

a) a better method of synthesis is to be desired in order to increase the yield; and

b) the performance data indicate that the final product has ultimate properties which are equal to or better than standard oleoresinous varnishes and alkyd resins.

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Spectrophotometric Studies of the Composition of Lespedeza Seed Oil

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METHODS of isolation of lespedeza seed oil and a preliminary description of the properties of the oil have been reported in previous papers from this laboratory (1, 2). The oil has an iodine number of approximately 150, which is reflected in its drying properties and indicates the presence of a significant fraction of unsaturated acid glycerides. In this communication we wish to report data obtained on analysis of the ultraviolet absorption spectra of the oil before and after alkali isomerization in terms of the nature and relative quantities of various types of unsaturation present.

Experimental

Isolation of the oil. The seeds used in this study were obtained from the Ross Seed Company and from the Louisville Seed Company, both of Louisville, Kentucky. Dehulling was accomplished by filling a one-quart capacity pebble mill one-third full with pebbles (average size 1") and then adding just enough seeds barely to cover the pebbles. The mill was run for one hour, the hulls were blown out with an air stream, and this treatment was repeated except that the mill was run for only 30 minutes. After this treatment the seeds were approximately 90% hulled. The remaining seeds with hulls were removed manually. The grinding operation in all cases consisted of charging the mill with seeds and pebbles and running the mill until the seeds were ground to a fine powder. This powder was transferred to a 500-ml. Soxhlet extractor and extracted with petroleum ether, b.p. 60-80°C., until the circulating solvent was colorless. After extraction most of the solvent was removed by distillation on a water bath at about 80°C., and the last traces of solvent were removed under vacuum. Stainless steel balls were used to grind a few of the *L. stipulacea* seed samples as described in the discussion. Some of the *L. stipulacea* seed were not separated from the hulls prior to grinding. Operations under nitrogen were done as previously described (2).

Isomerization of the oil. The procedure of Mitchell, Kraybill, and Zscheille (3) was employed except that 95% ethanol checked for optical purity was substituted for 98% ethanol as a solvent. All measurements were made in duplicate and rechecked by different investigators working independently. Standardized sample weights, alkali concentration, and procedural details were used to make the measurements clearly comparable with one another. The original constants (3) were used in the calculations.

Ultraviolet absorption. Measurements were made, using a Beckman Model DU quartz spectrophotometer with 1.00-cm. cells.

Iodine numbers (Wijs). Iodine numbers were found, using the procedure described in A.O.C.S. Official Method Cd. 1-25.

Isolation of the white solid from the hulls. The hulls were ground and extracted as described above for the seeds. The white solid also separates from

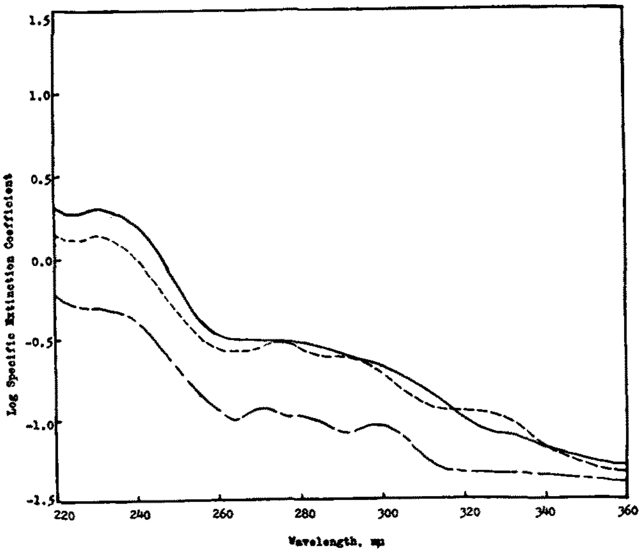

FIG. 1. Ultraviolet absorption spectra of lespedeza seed oil and linseed oil as isolated.

Kobe – – – – – –
Sericea ————————
Linseed—— – —— – —— –

the oil from seeds ground with hulls on evaporation of the solvent. This solid was collected on a filter, washed with acetone, and recrystallized from acetone, m.p. 81°C.

Discussion

Ultraviolet absorption curves have been obtained for the oil isolated from three different species of lespedeza seeds. The curves for the oil obtained from *L. cuneata* (sericea) and *L. striata* (common Kobe) are shown in Figure 1 in comparison with the curve for linseed oil. They are in general similar.

The absorption curves for the oils isolated from seeds of *L. stipulacea* (Korean) are given in Figure 2. Absorption similar to that observed with the oils of other strains was observed when isolated from hull-free seeds ground with either pebbles or stainless steel balls or from the seed-hull mixture ground with pebbles. In contrast, a marked absorption at 270 mμ., corresponding to 1.3% of a conjugated triene structure, was observed when the oil was isolated from the seed-hull mixture ground with stainless steel balls. The possibilities that this absorption was caused by a contaminant introduced with the hulls, or by metal-catalyzed isomerization of a non-conjugated triene structure in the oil uncontaminated with the hulls (4, 5), or by oxidation (6), whether metal-catalyzed or not, were eliminated by carefully standardized and checked control experiments which gave the oils showing no triene absorption in Figure 2.

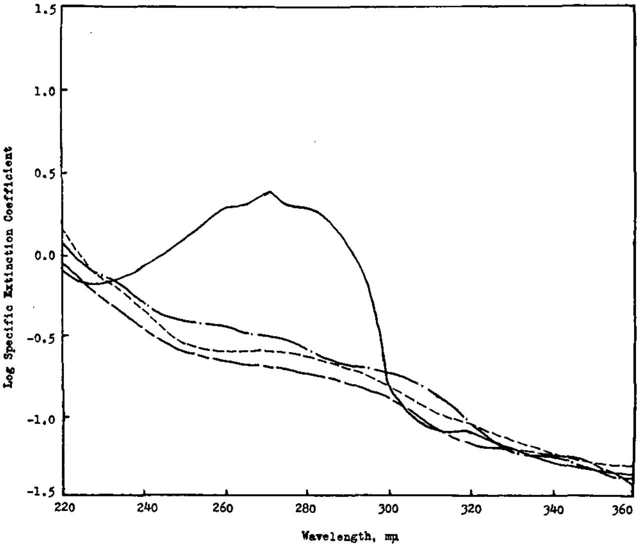

FIG. 2. Ultraviolet absorption spectra for various samples of Korean lespedeza seed oil as isolated.

Seeds with hulls ground with stainless steel balls ————
Hulled seeds ground with stainless steel balls —— · —— ·
Seeds with hulls ground with pebbles —— – —— –
Hulled seeds ground with pebbles – – – – – –

The possibility that the maximum at 270 mμ. came from a constituent of the hulls under the specific conditions of the isolation was eliminated. A sample of the hulls alone was ground with stainless steel balls and extracted. A white solid, m.p. 81°C., was deposited on evaporation of the solvent. This white solid has the same melting point as, and shows no depression of melting point with, a sample of a white solid which separates immediately from the oil extracted from seed-hull mixture on removal of the solvent. This does not appear to be the same solid previously observed (1) to separate from the oil on long standing. A saturated solution of this solid in 95% ethanol gave no absorption over the 220-360 mμ. range. The solid (1 mg.) was only very slightly soluble in 25 ml. of alcohol. The solid is being further characterized.

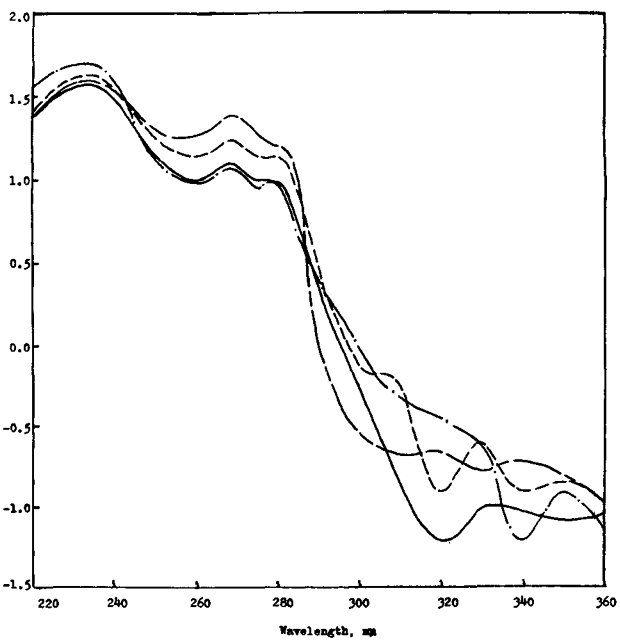

FIG. 3. Ultraviolet absorption spectra of isomerized oils.

Korean – – – – – –
Kobe ————
Sericea —— · —— ·
Linseed —— – —— –

The possibility that the absorption was caused by oxidation during isolation is eliminated because the oil samples isolated in the three other procedures, all under carefully standardized similar conditions, showed no such absorption (Figs. 1 and 2). Had oxidation occurred, such absorption should have been observed in the oils obtained by each of the four isolation procedures or, if necessarily catalyzed only by metals, at least in the oil from hull-free seeds ground with stainless steel balls. Careful exclusion of atmospheric oxygen during all operations (2) also gave an oil from the seed hull mixture ground with stainless steel balls which showed the absorption at 270 mμ.

The remaining possibility is that of some metal-catalyzed reaction taking place in the oil-hull mixture. This may be isomerization of non-conjugated triene structures catalyzed by metal apparently activated by the hulls. Metal-catalyzed isomerizations are known (3, 4) to take place at elevated temperatures, but the specific influence of other materials, such as observed here, have apparently gone unrecognized. It should be noted that the shape of the curve in the 270-mμ. range is not characteristic of triene absorption in this region.

Using a previously described procedure (3) under carefully standardized conditions, the three oil samples were isomerized by heating with alkali. The ultraviolet absorption spectra of the isomerized oils, along with that for alkali isomerized linseed oil run as a control, are shown in Figure 3. From these data and the iodine numbers of the oils, given in Table I, the composition of the oil in terms of mono-, di-, and tri-unsaturated and saturated acid constituents of the glycerides was computed. The results are stated in Table I. Comparison with the data for linseed oil shows that, consistent with the somewhat lower iodine

TABLE I

Percentage Composition and Iodine Numbers of Alkali Isomerized Lespedeza Oils

	Iodine No. (Wijs)	Triene (%)	Diene (%)	Monoene (%)	Saturated (%)
Korean	150.9	28.1	30.3	21.5	20.2
Kobe	149.7	23.1	26.5	42.9	7.5
Sericea	153.8	22.2	41.8	19.4	16.6
Linseed	181.8	44.0	13.8	35.4	6.8

numbers, there is less triene and more diene structure present in each. For the three oils the amounts of mono- and di-unsaturation vary over a wider range than the amounts of triene structure. Of the three the sample of oil from the Kobe species most nearly resembles linseed oil. The wide differences in percentage of saturated acids in view of small differences in iodine value of the oils do not fit the pattern for other oil seeds and should be confirmed by additional determinations before final acceptance.

Summary

The ultraviolet absorption spectra of the oils obtained from lespedeza seeds of three species show an absorption similar to that of linseed oil. The spectra for the alkali isomerized lespedeza seed oils show triene conjugation equivalent to that which would be produced by the presence of 22-28% of a triunsaturated nonconjugated acid (such as linolenic acid) and 26-42% of a diunsaturated nonconjugated acid (such as linoleic acid). The presence of conjugated triene structure in the oil as extracted from a seed-hull mixture ground with stainless steel balls was indicated by an absorption maximum at 270 mμ. Elimination of other possibilities suggest that this absorption is caused by a metal-catalyzed isomerization or other reaction taking place only in the mixture.

Acknowledgment

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Studies of Waxes. III. The Alcohols of Carnauba Wax[1]

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In a review of previous work on composition of carnauba wax Koonce and Brown (1) concluded that it was probable the wax contained straight chain alcohols of even carbon number from C_{26} to C_{34}—the higher alcohols dominating—and a dihydric alcohol, possibly $C_{23}H_{46}(CH_2OH)_2$. The monohydric alcohols however had never been isolated in a pure condition. Later, in their work, Koonce and Brown (2) fractionally distilled the alcohols and from the melting points of the alcohols and their derivatives concluded that the alcohols C_{28}, C_{30}, and C_{32} had been isolated in a purity of approximately 95%, C_{32} being the major constituent. They used the customary helix-packed column at a pressure of 0.28-1 mm. and reported serious decomposition of the charge, due no doubt to the high pressure drop through this type of column.

This paper describes an investigation of the composition of the non-saponifiable portion[2] of carnauba wax using a modified spinning band column developed in this laboratory (3). This column has a very low pressure drop and a high efficiency at low operating pressures and has proved very suitable for the fractionation of such high boiling material.

Saponification of the Wax and Acetylation of the Wax Alcohols

A sample of high grade carnauba wax (Flores Yellow No. 1) was filtered while molten through a heated sintered glass funnel and was found to be almost free from dirt. The cleaned wax (200.0 g.) was saponified by boiling with alcoholic KOH (50 g. in 1 litre 97% alcohol) and petroleum ether (b.p. 80-100°C., 500 ml.) for 24 hr. Water (600 ml.) was then added and the petroleum ether layer separated while hot. The aqueous alcoholic layer was further extracted twice with petroleum ether, the extracts being combined with the first petroleum ether extract and then washed twice with hot 40% aqueous alcohol. These alcoholic washings were extracted three times with petroleum ether. All the petroleum ether extracts were then combined and washed twice with hot 30% aqueous alcohol. The solvent was removed by heating on a steam bath, first under slightly reduced pressure, and finally at 1 mm. The recovered alcohols were pale yellow, melted from 84.8 to 85.5°C. and weighed 107.0 g. or 53.5% of the wax. They were free from acids and unsaponified esters (acid value, 0; saponification value, 0).

The acids were recovered from the combined aqueous alcoholic layer and washings by acidification with HCl and hot extraction with petroleum ether. They weighed 86.8 g. or 43.4% of the wax. Alcohols and acids recovered represent 96.9% out of an expected yield, calculated from the saponification number, of 102.5%. A further 4.6% of a brown resinous material, probably resin acids, was recovered from the acidified aqueous alcoholic liquors, after removal of the acids, by concentrating them to half volume and extracting with ethyl acetate.

The alcohols (91.5 g.) were acetylated by boiling with acetic anhydride (180 g.) for 6 hr., and removing excess anhydride under vacuum at 100°C., finally

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[1] Part II of this series: H. H. Hatt, P. H. A. Strasser, W. J. Troyahn, Proc. Queensland Soc. Sugar Cane Tech. 17th Conference, p. 61.

[2] For convenience hereafter referred to as the wax alcohols.