surized (air, 1 atm.) column (20 x 100 mm.) of powdered anhydrous $MgSO_4$. The addition of benzene containing 1% ethanol eluted a well-defined band of pomiferin. A second zone, remaining near the top of the column, was eluted with a mixture of equal volumes of benzene and ethanol (Fraction C). Fraction A was thus separable into pomiferin (80–85%, by weight) and an unknown substance, Fraction C (15–20%, by weight). Fraction C was a highly active antioxidant substance, which also responded synergistically with pomiferin (Table IV).

TABLE IV

Effects of Chromatographic Fractions on Stability of Lard

Preparation	Induction Period
	hrs.
1. Unprotected lard (control)	2
2. 0.10% Fraction C	23
3. 0.30% Fraction C	72
4. 0.10% pomiferin	30
5. 0.10% pomiferin + 0.10% Fraction C	82

Subsequent experiments have shown Fraction C to be further separable into a number of components by chromatography on $MgSO_4$ with smaller increments of ethanol to the benzene. Three major and several minor bands were separated on the column with 2% ethanol in benzene, and two of the major bands (Nos. 4 and 6) were eluted from the column with this solvent. These constituted 25 and 10% (by weight) of Fraction C and both were light green in color. A third major band (No. 8), constituting 45% of Fraction C, was eluted with 4% ethanol in benzene; it was reddish-brown in color.

In stability tests with lard all of the three major bands showed strong antioxidant activity. Induction periods were 20 to 50% longer than that produced with an equal amount of pomiferin. Peroxide accumulation during the induction period (prooxidant effect), typical of pomiferin, NDGA, and other primary antioxidants, was also less pronounced (Figures 2).

The characterization of the three additional primary antioxidants has not been completed. These were separated chromatographically but were not obtained in a crystalline state. However their ultraviolet absorption spectra, with maxima at 273 (band 6) and 274.5 mμ (bands 4 and 8), were very similar to those of pomiferin and osajin, suggesting a close structural relationship to these compounds. Each of the three gave a positive ferric chloride test for phenols and a positive Wilson (5) boric test for flavones and iso-flavones.

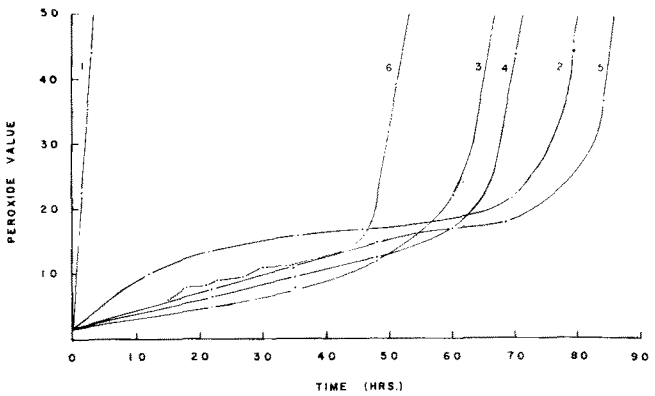

FIG. 2. Peroxide development in lard containing compounds of Fraction C.

1. Control
2. 0.30% NDGA
3. 0.30% band 8
4. 0.30% band 6
5. 0.30% band 4
6. 0.30% pomiferin

Summary

The fruit of the osage orange tree (*Maclua pomifera* [Raf.] Schneider) was shown to contain at least four pigments with antioxidant activity. Pomiferin was present as 3 to 4% of the dry fruit and, as a primary antioxidant, was responsible for 20–25% of the activity exhibited by methanol extracts. An unidentified substance was also present which reacted synergistically with pomiferin, increasing its contribution to the overall activity to approximately 75%. The three new pigments, totalling 0.5% to .75% of the dry fruit, all showed antioxidant activity exceeding that of pomiferin when tested at equal concentrations.

A chromatographic procedure, employing anhydrous magnesium sulfate, was developed and applied successfully in separating mixtures of several iso-flavone pigments.

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Alcoholic Extraction of Vegetable Oils. II. Solubilities of Corn, Linseed, and Tung Oils in Aqueous Ethanol[1]

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IN AN EARLIER communication (1) the need for the study of ethanol as a solvent for vegetable oils was discussed, and complete solubility data on cottonseed, peanut, sesame, and soybean oils in aqueous alcoholic solutions were presented. A literature search revealed no similar data for corn, linseed, and tung oils.

[1] Presented at the Philadelphia fall meeting, American Oil Chemists' Society, October 11, 1955.

Experimental

Unrefined commercially produced oils were used in each case. Their characteristics are given below:

Oil	Acid value	Iodine value (Wij's)	Saponification value
Corn Oil[a]	1.52	120.2	189.7
Linseed Oil	1.48	182.5	191.3
Tung Oil	1.52	168.7	192.5

[a] From wet-milled germs.

The various aqueous solutions of alcohol were obtained by diluting the absolute alcohol. The concentrations of the alcoholic solutions were determined from the densities by the pycnometer method. All values are reported as weight percentage.

The apparatus and the method of solubility determination were the same as previously described (1).

Results

Solubility Data. The solubility data for corn are presented in Figure 1. It is observed that in all cases the solubility of the oil increases steadily until the critical solution temperature is reached. At the critical solution temperature the solubility curves become parallel to the Y axis, indicating that any amount of oil can be dissolved at that temperature, *i.e.*, oil and alcohol are miscible in all proportions at or above that temperature. It is seen from the figure that with 99.9, 98.0, and 95.4% alcohols, the miscibility is attained at 65°, 75°, and 90°C., respectively, while the maximum solubility with 91.5% alcohol even at 90°C. is only 13.7%.

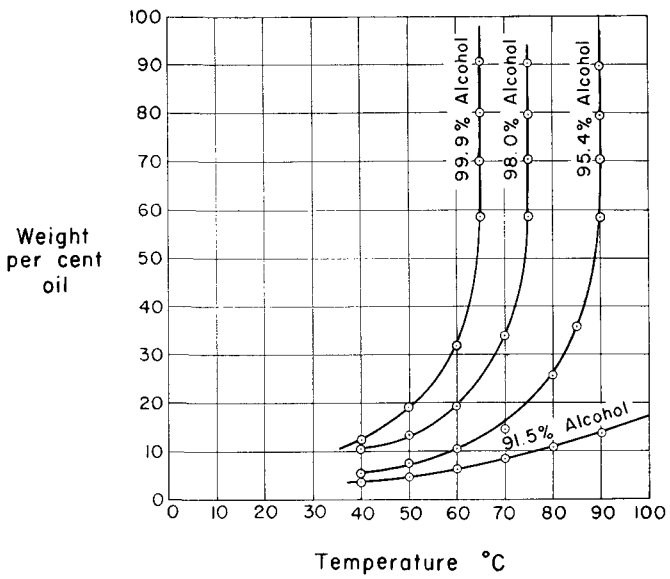

FIG. 1. Solubility curves for corn oil in aqueous ethanol.

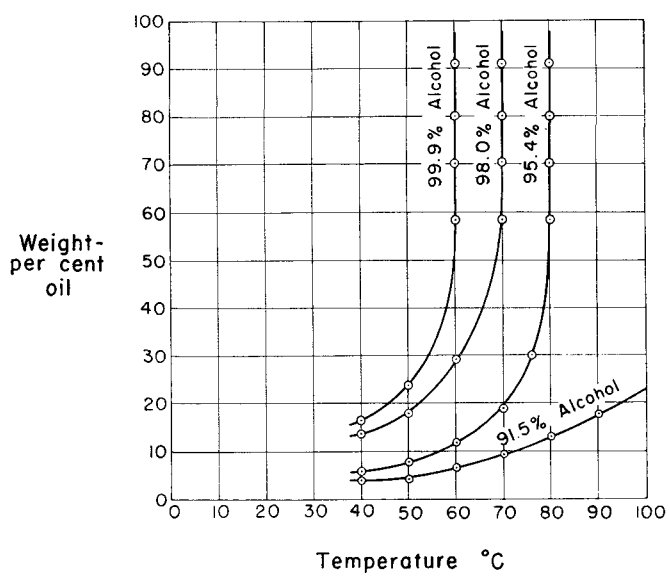

FIG. 2. Solubility curves for linseed oil in aqueous ethanol.

The corresponding data for linseed oil are shown in Figure 2. The curves follow the same general pattern as corn oil. In this case with 99.9, 98.0, and 95.4% alcohols, miscibility is attained at 60°, 70°, and 80°C., respectively, while with 91.5% alcohol the solubility, even at 90°C., is only 17.5%.

The data for tung oil are presented in Figure 3 and indicate that in this case with 99.9, 98.0, and 95.4% alcohols, miscibility is attained at 75°, 85°, and 95°C., respectively, while the solubility with 91.5% alcohol at 90°C. is only 8.5%.

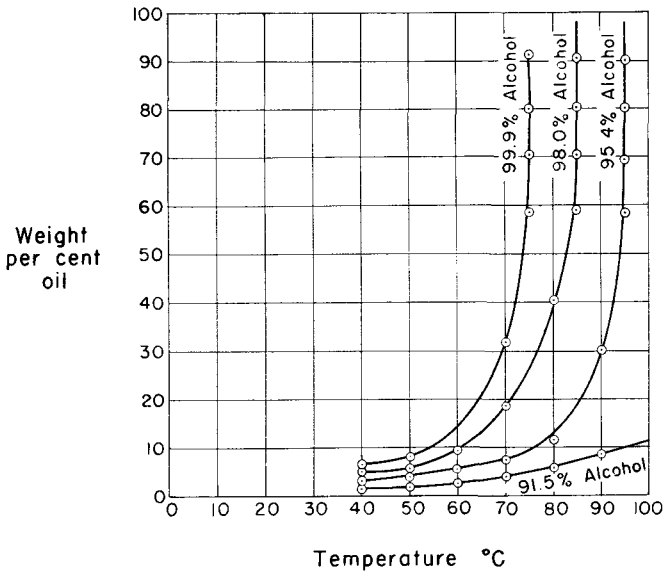

FIG. 3. Solubility curves for tung oil in aqueous ethanol.

Critical Solution Temperature. The critical solution temperature *versus* alcohol composition data for the three oils are presented in Figure 4. It is observed that in all cases the critical solution temperature increases with the water content of alcohol and that the relationship is linear.

Pressure in the System. The pressures developed in the apparatus, which are made up of the atmospheric pressure and the vapor pressures of aqueous ethanol at different temperatures, were read directly from the pressure gauge attached to the apparatus. The pressure gauge readings recorded for different alcoholic

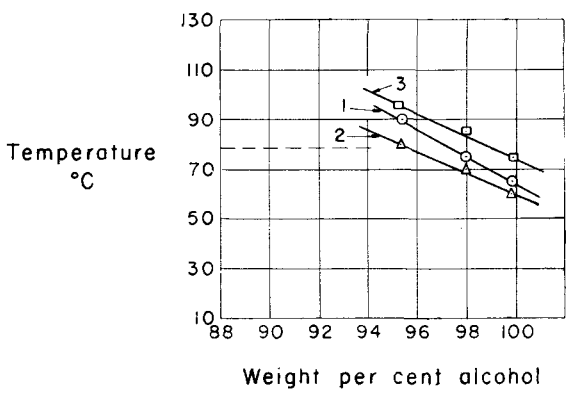

FIG. 4. Variation of critical solution temperature of the three oils with alcohol composition. 1. Corn Oil. 2. Linseed Oil. 3. Tung Oil. Broken line indicates the boiling point of pure ethyl alcohol.

concentrations at various temperatures are given below in pounds per square inch.

Concentration of Alcoholic Solution in Percentage	Pressure, psig					
	Temperatures °C.					
	50	60	70	80	90	95
95.4	2	4	8	15	17	20
98.0	2	4	8	15	18	
99.9	2	4	10	15		

It is seen therefore that the pressure in the vessel increases with the temperature. However all the three concentrations have practically the same gauge readings. Since their boiling points differ very slightly, the different concentrations produce variations in vapor pressure too small to be recorded by the pressure gauge.

The data obtained show that the maximum pressure to be used even with 95.4% alcohol is about 20 p.s.i.g.

Summary

Solubilities of corn, linseed, and tung oils in aqueous alcoholic solutions at various temperatures have been determined by a direct and simple method. The solubility curves for the three oils in aqueous alcoholic solutions are presented.

The critical solution temperature *versus* alcohol composition data have been plotted for the three oils. It is observed that the critical solution temperature increases with the water content of the alcohol and that the relationship is linear in each case. Similar results were obtained for cottonseed, peanut, sesame, and soybean oils previously (1).

The pressure in the system, increases with temperature; the maximum is approximately 20 p.s.i.g.

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ABSTRACTS . . . . . R. A. Reiners, Editor

• Oils and Fats

S. S. Chang, Abstractor
Sini'tiro Kawamura, Abstractor
Dorothy M. Rathmann, Abstractor

Isolation and characterization of some products associated with oxidized flavor. R. R. Riel(Chemistry Division, Science Service, Ottawa), and H. H. Sommer. *J. Dairy Sci.* **38**, 1215–1224 (1955). The limited oxidation of milk phospholipids yielded material which reproduced the typical oxidized flavor in milk. Isolation and characterization of the major oxidized flavor compounds showed that they are predominantly carbonyl compounds. Five different carbonyl compounds were evidenced by chromatography. The empirical formulae calculated for three compounds were $C_{15}H_{26}O_3$, $C_{11}H_{22}O$, $C_{22}H_{38}N_8O_2$ (as bis-hydrazone) and $C_{10}H_{18}N_2O$ (as monohydrazone). There was indication that the C_{15} was a di-unsaturated ketone without conjugation. The C_{11} was presumably undecanal.

Determination of fat in cocoa products. J. Kleinert(Lindt & Sprungli, A.-G., Kilchberg /ZH, Switz.). *Rev. intern. chocolat.* **10**, 302–12(1955). Methods are reviewed for the determination of fat in cocoa products. Cocoa kernels, cocoa powder, bitter milk, and gianduja chocolate were analyzed by the standard international method, the percolation method, the centrifuge method, and the Leithe-Heintz refractometer method and the results compared. Leithe's method was modified and improved by introducing a constant. (*C. A.* **49**, 16260)

The detection of substitute fats in ice cream. M. Keeney(Univ. of Maryland, College Park). *Rept. Proc. Ann. Conv. Intern. Assoc. Ice Cream Manufrs., Production and Lab. Council* **49**, 46–9(1953). The behavior of fat in a mixture of ethyl alcohol (55 volumes) and *iso*-propyl alcohol(45 volumes) at 25–26°F. is used to determine character of the isolated fat. (*C. A.* **49**, 15111)

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Rapid determination of oil in fish meal. G. M. Dreosti and R. P. van der Merwe(Fishing Ind. Research Inst., Cape Town, S. Africa). *Fishing Ind. Research Inst., Progr. Rept. No.* **18** (1955). A refractometric method for determining oil in avacados was adapted to fish meal. The oil is completely extracted from the meal by monochloronaphthalene and the amount of oil in the extract is found by measuring the refractive index of the solution. The results obtained from analyses of 35 meals showed that the refractometric method was more reproducible than the Soxhlet method. (*C. A.* **49**, 16254)

Antioxidants from biological sources for preventing rancidity in fats. E. S. Tatarenko, A. E. Sobol, and Z. N. Novikova (Ukr. Research Inst. Food Ind. Sci., Kharkov). *Mikrobiologiya* **24**, 217–22(1955). The fungus *Naumoviella oleaginosa* can accumulate up to 52% lipoids (calculated on dry weight); its optimum conditions are temperature 25–6°C., pH 5–6, 0.2–1% KH_2PO_4 in the nutrient medium. *N. humicola* and a *Mortierella* species are nearly as active in storing lipoids, which contain 1–18% unsaponifiables of which one component at a concentration of 0.01% increases the rancidity resistance of edible fats 3.5-fold. (*C. A.* **49**, 16253)

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