

Summary

1. The crude oils studied contained from 0.00 to 0.04% gossypol.

2. Much of the gossypol added to crude cottonseed oils disappeared in one hour.

3. The disappearance of gossypol from refined, bleached, and deodorized cottonseed oil, from highly purified tripelargonin, and from ethyl acetate is demonstrable after the lapse of one hour.

4. It is suggested that the initial reaction of gossypol in the oils is an ester exchange reaction.

5. It is further suggested that secondary reactions result in the production of a red coloration product that is not removable from the oil by the standard refining and bleaching methods.

Acknowledgment

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Alcoholic Extraction of Vegetable Oils. Part IV. Solubilities of Vegetable Oils in Aqueous 2-Propanol¹

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IN ASIATIC COUNTRIES, such as India, China, and Japan, the prices of conventional petroleum solvents are abnormally high because of heavy import taxes hence there is considerable scope for the use of lower aliphatic alcohols, which are known to be solvents for oils. The Japanese have reported the use of ethanol as a solvent for the batch extraction of soybeans in a plant at Darien, Manchuria (5, 11). Beekel and coworkers developed a continuous non-distillation process, using ethanol as a solvent while Harris and coworkers found 2-propanol² an excellent solvent for extracting cottonseed (2-4, 6-9). Work is in progress regarding the feasibility of using ethanol as a solvent for extracting cottonseed (15).

The most important and fundamental data necessary in studying the suitability of the solvents for extracting oils are the solubility data of the oils in different concentrations of these solvents. Recently comprehensive data on the solubilities of vegetable oils in aqueous ethanol solutions have been reported (13, 14, 16). A literature search revealed that while some data have been published on the miscibility of cottonseed oil in aqueous 2-propanol solutions, no information is available for other oils. Hence the need for this investigation.

Review of Previous Work

Harris and coworkers (6) have published data on the miscibility of cottonseed oil in 91% (by volume) 2-propanol, based on the cloud-point titration method. Magne and Skau (10) have reported the basic-phase, equilibrium data pertaining to the extraction of cottonseed oil with various concentrations of aqueous 2-propanol, based on work using the static, sealed-tube method. Thus data are available for cottonseed

oil only and were obtained by the static method only, from which critical solution temperature *versus* 2-propanol composition data for use in design of the extraction equipment can be deduced by only an indirect method such as the one suggested by Okamoto (11). The aim of the present investigation was to obtain the basic solubility and critical solution temperature *versus* 2-propanol composition data by a direct method while also getting an idea of the working pressures developed by different concentrations of 2-propanol at various extraction temperatures.

Experimental

The apparatus (Figure 1) and the solubility determination method were the same as previously described (16). The various aqueous solutions of 2-propanol were obtained by diluting pure 2-propanol. The concentrations of the solutions were determined by the pycnometer method. All values are reported as weight percentage. Unrefined and commercially produced oils were used. Their characteristics are given in Table I.

TABLE I
Constants of Oils Used

Oil	Acid value	Iodine value (Wij's)	Saponification value
Babassu.....	2.8	12.8	248.6
Coconut.....	2.8	8.8	257.6
Corn ^a	1.5	120.2	189.7
Cottonseed.....	4.6	105.6	194.6
Linseed.....	1.5	182.5	191.3
Olive.....	1.1	84.6	190.4
Palm.....	3.4	53.9	199.6
Peanut.....	2.7	94.6	194.6
Rapeseed.....	2.7	105.6	171.6
Safflower.....	3.8	145.2	189.8
Sesame.....	2.5	112.7	191.4
Soybean.....	1.0	129.6	192.2
Sunflowerseed.....	1.7	123.8	190.8
Tung.....	1.5	168.7	192.5

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² Isopropanol or isopropyl alcohol.

^a From wet-milled germs.

TABLE II
 Solubilities of Oils in Aqueous 2-Propanol at Various Temperatures

Oil	Concentration of aqueous 2-propanol	Solubility %												
		30°C.	35°C.	40°C.	45°C.	50°C.	55°C.	60°C.	65°C.	70°C.	75°C.	80°C.	85°C.	90°C.
Coconut	99.9	M												
	98.0	M												
	95.2	M												
	90.5	13.60	M											
Babassu	99.9	M												
	98.0	M												
	95.2	M												
	90.5	9.96		13.75	M									
Linseed	99.9	M												
	98.0	M												
	95.2	29.74	M											
	90.5	9.82		12.58		24.24	29.92	M						
Palm	99.9	M												
	98.0	M												
	95.2	21.56	28.59	M										
	90.5	9.12		12.16		16.44		29.01	M					
Cottonseed	99.9	M												
	98.0	39.10	M											
	95.2	15.30		33.02	M									
	90.5	8.66		11.18		15.58		26.58	33.36	M				
Corn	99.9	M												
	98.0	38.71	M											
	95.2	14.58		30.56	M									
	90.5	7.41		10.96		14.36		25.42	32.65	M				
Sunflowerseed	99.9	M												
	98.0	32.72	M											
	95.2	14.11		28.78	M									
	90.5	6.24		8.94		13.12		23.10	27.62	M				
Sesame	99.9	M												
	98.0	30.10	M											
	95.2	13.94		27.71	M									
	90.5	5.82		8.16		12.32		17.32	22.59	M				
Safflower	99.9	M												
	98.0	29.32	M											
	95.2	12.65		26.62	M									
	90.5	5.63		7.95		10.81		16.67	20.26	M				
Soybean	99.9	M												
	98.0	28.78	M											
	95.2	13.54		25.78	M									
	90.5	5.41		7.76		9.78		15.81	19.01	M				
Peanut	99.9	M												
	98.0	26.85	M											
	95.2	13.01		23.39	M									
	90.5	5.28		6.31		8.60		13.20	18.21	M				
Olive	99.9	M												
	98.0	25.32	M											
	95.2	12.55		22.67	M									
	90.5	4.90		5.87		7.51		12.81		33.36	M			
Rapeseed	99.9	17.35	20.99	M										
	98.0	7.99		14.75	23.90	M								
	95.2	5.50		8.38		14.80		34.20	M					
	90.5	2.54		3.48		5.12		7.82		13.62		26.10	38.21	M
Tung	99.9	8.90		16.52	29.46	M								
	98.0	6.39		12.25		24.52	M							
	95.2	4.51		8.12		14.02		29.30	38.12	M				
	90.5	2.31		3.16		4.81		7.61		12.75		24.98	36.11	M

M—Miscible.

Results

The solubility data for the oils are presented in Table II. If the temperature *versus* solubility percentage data from Table II are plotted, solubility curves, similar to those shown in Figure 2 for a typical oil, result. Similar curves were also obtained with aqueous ethanol (13, 14, 16). It is observed, as with ethanol, that the solubility of the oil increases steadily until the critical solution temperature is reached, at and above which the oil and solvent are miscible in all proportions. These data are in excellent agreement with those of Magne and Skau (10), using the static, sealed-tube method as well as those of Harris and Hayward (9).

Pressure in the System

The pressures developed in the apparatus, which are made up of the atmospheric pressure and the vapor pressures of aqueous 2-propanol solutions, at different temperatures were read directly from the pressure gauge attached to the apparatus and are given in Table III.

 TABLE III
 Pressures of Solutions at Various Temperatures

Concentration of 2-propanol solution	Pressure p.s.i.g.				
	50°C.	60°C.	70°C.	80°C.	90°C.
99.9%	2				
98.0%	2	4			
95.2%	2	4	8		
90.5%	2	4	8	15	18

It is seen therefore that the pressure in the vessel increases with temperature. However all the four 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. These data were determined for use in extraction-equipment design and operation rather than as accurate vapor pressure values.

Discussion

If we arrange these oils according to the classification of Bailey (1) together with their critical solution temperatures as in Table IV, some interesting

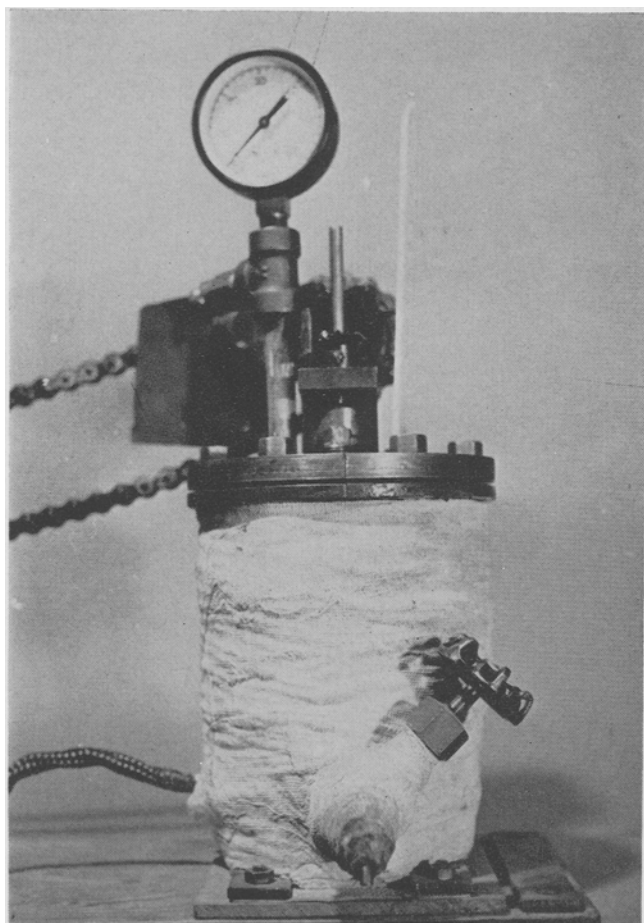


FIG. 1. Solubility determination apparatus.

observations may be made. The high lauric acid oils, coconut and babassu, are the most soluble of the group investigated, closely followed by linseed oil of the linolenic acid group.

All oils in the oleic-linoleic group, excepting palm and olive oils and including soybean oil from the linolenic group, have identical solution temperatures. Palm and olive oil vary only slightly. Rapeseed oil, rich in erucic acid, and tung oil, containing a high α -eleostearic acid content, are the least soluble.

Critical solution temperatures of these oils in ethanol, as compiled in Table V from previous work in this laboratory (13, 14, 16), show the same general pattern although they are less soluble than in the less polar 2-propanol. From the data it appears

TABLE IV
Critical Solution Temperatures for Oils in 2-Propanol

Group and Oil	Critical Solution Temperature °C.			
	Concentration of Aqueous 2-Propanol			
	99.9%	98.0%	95.4%	91.5%
I. Lauric				
Coconut oil.....	M	M	M	35
Babassu oil.....	M	M	M	45
II. Linolenic				
Linseed oil.....	M	M	40	65
III. Oleic-linoleic				
Palm oil.....	M	M	40	65
a) Cottonseed, corn, sunflower, sesame, safflower, soybean, and peanut oils....	M	35	45	70
b) Olive oil.....	M	35	45	75
IV. Erucic acid				
Rapeseed oil.....	40	50	65	90
V. Conjugated acid				
Tung oil.....	50	55	70	90

TABLE V
Critical Solution Temperatures for Oils in Ethanol

Group and Oil	Critical Solution Temperature °C.			
	Concentration of Aqueous Ethanol			
	99.9%	98.0%	95.4%	91.5%
I. Lauric				
Coconut oil.....	28	35	55	75
Babassu oil.....	30	45	60	85
II. Linolenic				
Linseed oil.....	60	70	80
III. Oleic-linoleic				
a) Cottonseed, palm, corn sunflowerseed, sesame, and safflower ^a	65	75	90
Soybean oil.....	67	78	90
b) Peanut and olive oils.....	70	80	95
IV. Conjugated acid				
Tung oil.....	75	85	95
V. Erucic acid				
Rapeseed oil.....	85	95

^a Data on safflower were not reported earlier as they were determined for this paper. Ramalingam and Chari (12) report the following values: 70°, 80°, and 90°C. with 99.94%, 98.0%, and 95.75% ethanol, which also fall within the range of this group.

that there is a general relationship between fatty acid content of an oil and its solubility in an alcohol. It is hoped that a further study may be made of this relationship.

Summary

Solubilities of 14 vegetable oils in four different concentrations of aqueous 2-propanol at various temperatures were determined by a direct and simple method. Comprehensive solubility data of these oils and the critical solution temperature *versus* 2-propanol composition data are presented in tabular form. Solubility of each oil in aqueous 2-propanol increases with temperature until the critical solution temperature is reached, at and above which oil and the solvent are miscible in all proportions. Further the critical solution temperatures of all the oils with aqueous 2-propanol solutions increased with the increase in water content of 2-propanol solutions. There appears to be a general relation between fatty acid contents of the oils and critical solution temperatures which needs further study.

Cottonseed oil

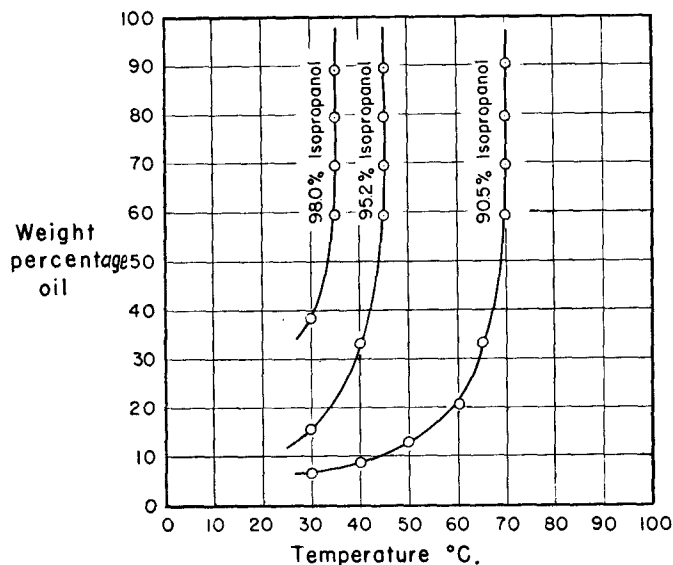


FIG. 2. Solubility curves for cottonseed oil in aqueous 2-propanol.

Acknowledgment

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Antioxidant Activity of Phenols as Related to Effects of Substituent Groups¹

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IN A RECENT COMPARISON of alkyl phenols as antioxidants for lard (1) it was observed that compounds having alkyl groups in the 2 position invariably showed some activity and that compounds with alkyl groups in both the 2 and 6 positions showed substantially higher activity. Similar observations were made with gasoline (2) and lubricating oils (3) as substrates. Since the alkyl groups provide some steric hindrance in the region of the phenolic group, the term "hindered phenols" has sometimes been applied to such compounds. However the thought that antioxidant activity is not attributable solely to a steric effect was suggested by the observation (1) that the comparatively large nitro-, bromo-, or iodo-groups imparted no such antioxidant activity to the phenol molecule.

The purpose of the present work was to learn more about the nature of substituents which can impart antioxidant activity to phenols, especially substituents in the 2 and 6 positions.

Experimental

Materials and Procedure. Few of the desired substituted phenols were available from commercial sources, and it was necessary therefore to synthesize most of them. The compounds, some of their properties, and their sources are indicated below. Melting points are not corrected.

2,6-di-*tert*-butyl-4-methylphenol, m.p. 69.5°C. (The Dow Chemical Company and Koppers Company Inc.). Recrystallized three times from aqueous ethanol.

2,6-di-bromo-4-methylphenol, m.p. 47-48°C. Prepared as reported by Ruderman (4).

2,6-di-iodo-4-methylphenol, m.p. 60.5°C. Iodination performed as reported by Datta and Prosad (5).

2,6-di-nitro-4-methylphenol, m.p. 78.5°C. Synthesized in manner of Monti and Cianetti (6).

2,6-di-benzoyl-4-methylphenol, m.p. 163-164°C. Procedures of Newman and Pinkus used in the synthesis (7, 8, 9).

2,6-di-methoxymethyl-4-methylphenol, b.p. 124°C., 1-2 mm. Hg. This phenol was prepared by acetolysis of 2,6-di-acetoxymethyl-4-methylphenylacetate as reported by Barthel (10). The

2,6-di-acetoxymethyl-4-methylphenylacetate (b.p. 180-187°C. approx. 1 mm. Hg.) was prepared from 2,6-di-(di-methylaminomethyl)-4-methylphenol as Bruson *et al.* (11) prepared 2,4,6-tri-acetoxymethylphenylacetate from 2,4,6-tri-(dimethylaminomethyl)phenol.

2,6-di-hydroxymethyl-4-methylphenol, m.p. 129°C. The synthesis was performed as reported by Granger (12).

2,6-di-(dimethylaminomethyl)-4-methylphenol, b.p. 132-135°C., approx. 1 mm. Hg. Synthesized in the manner reported by Bruson and MacMullen for synthesis of 2,4,6-tri-(dimethylaminomethyl)phenol (11). The compound 4-methylphenol was used as starting material instead of phenol. Auwers (13) has shown that formaldehyde adds to the 2,6 positions of 4-methylphenol and that this reaction is involved in the synthesis.

2,6-di-methoxyphenol, m.p. 54.5-55.5°C. (Eastman Organic Chemicals).

2,6-di-methoxy-4-propylphenol. Synthesized as reported by Hunter and Hibbert (14), who used the procedure of Hurd and Fowler (15). Because of low yield the compound was purified by molecular distillation. A light yellow oil was obtained.

2,6-di-methoxy-4-propionylphenol, m.p. 106.5-108°C. Prepared as reported by Hunter and co-workers (16) in the manner of Coulthard *et al.* (17).

2,6-di-*tert*-butyl-4-methylphenylbenzoate, m.p. 168-169°C. Synthesized in the manner of Stillson *et al.* (18).

2,6-di-methoxyphenylpropionate, b.p. 127-133°C., approx. 1 mm. Hg. Esterification was performed as reported by Hunter *et al.* (16), who used the procedure developed by Miller and co-workers (19).

3,5,3',5'-tetra-*tert*-butylstilbene-4,4'-quinone, m.p. 308°C. Synthesized in manner of Cook *et al.* (20).

1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethane, m.p. 169°C. Prepared by reduction of preceding quinone in the manner of Yoke and co-workers (21). Purified by passing heptane solution through activated clay³ and then crystallizing from aqueous acetone.

The substrate used was a bleached, deodorized, and dried lard which had very little, if any, antioxygenic material present. The method for its preparation and the method for testing antioxidant effectiveness have been reported previously along with an explanation of the term *catechol index* used to express relative effectiveness (4). All of the compounds were tested at a concentration of one micromole per gram of lard except Compound XIV, which was tested at 0.5 micromole per gram of lard. All of the compounds were either recrystallized or distilled until a constant antioxidant activity was obtained.

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