ratios. In no case do the points deviate from the best average curves by more than $\pm 0.3\%$ O_2 absorbed.

c) The non-reproducible deposition of oil on solid: That the oil-silica gel samples were consistently prepared is obvious from the discussion of point (b). Reproducibility was not noticeably improved when continuous magnetic stirring was substituted for occasional swirling during the pentane evaporation step.

Summary

The rate of oxygen uptake of purified soybean oil was determined as a function of the dispersion of the oil on the surface of highly porous silica gel. The most rapid consumption of oxygen took place at well-defined oil/solid ratios characteristic of the specific surface areas of the adsorbents. At these critical concentrations it was shown that the oil constituted a closely packed monomolecular layer. The existence of such critical ratios was regarded as further substantiation of the radical chain mechanism of autoxidation.

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A Test for Dehydrated Castor Oil Involving the Formation of 10,12-Octadecadienoic Acid Upon Alkali-Isomerization [1]

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ALONG with linseed and tung oil the dehydration product of castor oil (DCO) is rated today as a highly important drying oil for the paint, varnish, and related industries. It is produced and marketed under a variety of trade names. There are also various other "synthetic" drying oils containing a substantial proportion of conjugated fatty acid glycerides, and it will frequently be necessary to decide by analysis whether an oil sample from unknown sources is a DCO or some other product. The customary analytical methods alone will usually be inadequate to decide this question.

A typical analysis of a laboratory product compared with the castor oil from which it was prepared by the Ufer process (20) is given in Table I. Com-

TABLE I
Analytical Constants Before and After Dehydration

	Castor oil	DCO
Viscosity, 25°C. (Poise)	6.6	1.2
Refractive index, 25°C.	1.4770	1.4819
Spec. gravity, 25°C.	0.9610	0.9315
Spec. refraction, 25°C.	0.294	0.306
Acid value	0.2	2.2
Saponification value	178.7	191.2
Hydroxyl value	166.1	16.0
Total iodine value (11)	88.9	153.6
Partial iodine value (11)	87.9	128.8
Woburn diene value (11)	1.0	24.8
Diene value [Kaufmann-Baltes (6)]	0.6	15.7
Optical rotation (NaD, 200 mm.)	+8.8°	+4.9°

mercial oils will often have lower total iodine or higher hydroxyl values than those listed, indicating less complete dehydration (13, 14). Except for the positive optical rotation, similar constants might equally be found on other partially conjugated products or on mixtures of natural conjugated with nonconjugated oils. It should be pointed out that all DCO's tested, including those made by the Scheiber process involving distillation (15), have been found

to show considerable optical rotation. This value is, in fact, much higher than would be expected, considering the extent of dehydration achieved. Nevertheless optical rotation cannot serve as a characteristic for distinguishing DCO from other oils. On the one hand, distilled DCO fatty acids that are used in the preparation of alkyd resins may show no rotation while, on the other, some natural oils, such as sesame, are also dextro-rotatory.

On the other hand, DCO contains a chemical constituent which, as far as we know today, is unique and permits an unquestionable identification of this oil. This constituent is an isomer of ordinary linoleic acid (by reasoning given below the cis-trans isomer), which is readily distinguished from the other isomers by its behavior upon alkali-isomerization. As has been shown (9), DCO upon treatment with excess of aqueous alkali (21) yields solid 10,12-octadecadienoic acid (m.p. 57°), which can be isolated from the fatty-acid product by crystallization. Similar treatment of natural oils containing linoleic acid does not produce a high-melting conjugated product although both 9,11- and 10,12-octadecadienoic acid isomers of lower melting points are formed.

Constitution and Isomerism of DCO. The principal chemical reaction taking place upon dehydration of castor oil, involving the splitting-off of the OH-group in ricinoleic acid together with a neighboring H-atom is well known and needs not be discussed here in detail. Only the question as to which carbon of the fatty acid chain supplies the hydrogen atom has caused some controversy.

While it had originally been thought (1, 16)—and Scheiber (17) still holds this view today—that a hydrogen on the 11th carbon is involved, leading to the exclusive formation of conjugated octadecadienoic acids, Priest and von Mikusch (13) and also Steger and van Loon (19) concluded on the basis of diene values that non-conjugated isomers predominate in the product.

Later spectrometric absorption methods (4) gave somewhat higher results than the maleic anhydride addition values, but some uncertainty exists as to the correct evaluation of absorption values if unknown isomers are present. Similarly the Woburn method of determining diene value by subtracting partial from total iodine value gave higher figures for conjugation than the direct diene value would indicate; and von Mikusch and Frazier (11) concluded on the basis of maleic anhydride addition values obtained at high temperature that under ordinary conditions maleic anhydride does not add to all conjugated constituents.

A recent study of the stearic aspects of the diene synthesis shows that trans-trans conjugated double bonds should add maleic anhydride more easily than the cis-trans or trans-cis isomers and that the cis-cis compound may not react at all or possibly only after a change in configuration (2).

The correctness of this hypothesis has been demonstrated experimentally in the meantime, and the use of a definite amount of iodine to catalyze the addition of maleic anhydride to the inactive cis-isomers has been proposed (10). The "pandiene values" thus obtained indicate that DCO contains about 35% of conjugated constituents or roughly one-half of the newly formed unsaturation. Thus a substantial proportion of both conjugated and isolated linoleic acid isomers are formed upon dehydration.

Assuming on the basis of physico-chemical data (3) that the double bonds of oleic, linoleic, and ricinoleic acids all have the cis-structure,[2] dehydration may result in two conjugated and two non-conjugated linoleic-acid isomers, all having a cis-double bond between the 9th and 10th carbon atoms:

> 9-cis,11-cis octadecadienoic acid.
> 9-cis,11-trans octadecadienoic acid.
> 9-cis,12-cis octadecadienoic acid.
> 9-cis,12-trans octadecadienoic acid.

That the cis-double bond already present in ricinoleic acid is, as a rule, not elaidinated during catalytic dehydration is shown by the fact that trans, trans-9,11-octadecadienoic, melting at 54°C., which is found in the distillation product of ricinelaidic acid (7), is not produced to an appreciable extent upon dehydrating castor oil or ricinoleic acid. Thus the free fatty acids of a catalytically dehydrated oil, upon storing at 0-3°C. for a week, yielded only 0.7% of solids, consisting chiefly of saturated fatty acids. Under similar conditions an elaidinated product or the dehydration product of ricinelaidic acid would completely solidify and give a good yield of the solid conjugated acid.

For the present purpose we are concerned only with the non-conjugated 9,12-octadecadienoic acids. The cis-cis isomer is identical with the ordinary linoleic acid contained in most natural drying oils. The only 9,12-linoleic acid isomer therefore which can be contained in DCO and is not present in natural oils is then the cis-trans compound.

Characteristic Behavior of 9-Cis,12-Trans Linoleic Acid. In order to show that the non-conjugated portion in DCO is actually responsible for the formation of the solid 10,12-acid upon alkali treatment, the conjugated acids were removed from the distilled DCO
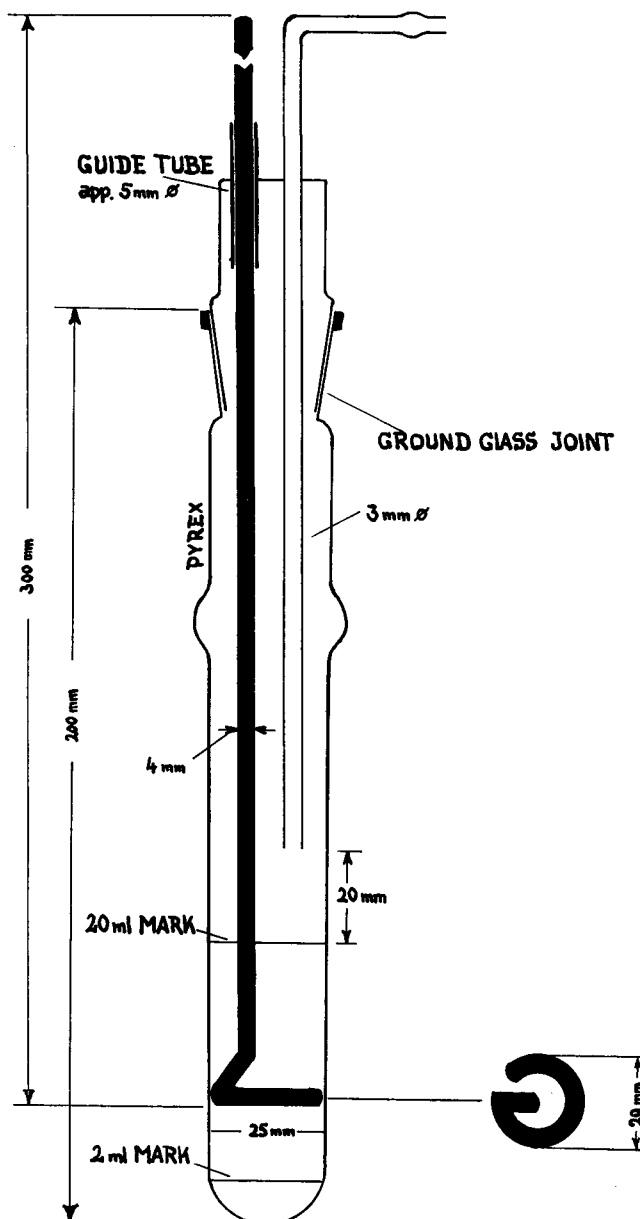

FIG. 1. Reaction tube for isomerization.

fatty acids by treating them with an excess of maleic anhydride and extracting the addition products with petroleum ether, in which they are nearly insoluble. The soluble portion, containing chiefly non-conjugated or 9,12-acids, was treated with alkaline diethylene glycol in the manner described below. The product upon crystallization at low temperature yielded up to 37% of solid conjugated acid, which after three recrystallizations melted at 54-57°C. and showed no melting point depression with a pure 10,12-octadecadienoic acid specimen obtained directly from DCO.

Hence, since it can be shown that the non-conjugated fraction of DCO acids upon alkali isomerization gives rise to a solid 10,12-linoleic acid isomer, which is not formed from any natural oil containing linoleic acid, it may be concluded:

a) That the 9-cis,12-trans octadecadienoic acid contained in DCO is responsible for the formation of the solid conjugated acid upon alkali isomerization and

b) That natural oils (which do not yield the solid acid upon alkali isomerization) do not contain cis-trans linoleic acid.

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[2] The cis-cis-structure of linoleic acid can be demonstrated by purely chemical means making use of the behavior of its alkali-isomerization products towards maleic anhydride [vide (10) and unpublished data].

Directions for the Test

It follows then that the formation of solid 10,12-octadecadienoic acid upon alkali-isomerization is a specific property of cis-trans linoleic acid and that this property may serve to test unknown oils or fatty acids (e.g., those isolated from an alkyd resin) for the presence of dehydrated castor oil or its acids. The test is best carried out as described below.

a) *Preparation of the Fatty Acids.* Using the known procedure of saponifying the oil and acidifying the soaps, the free fatty acids are prepared. In order to remove any polymeric or oxidized material the fatty acids are taken up in an ample amount of petroleum ether, filtered if insolubles are present, and the solvent removed in vacuo.

b) *Isolating the Liquid Fatty Acids.* The soluble fatty acids are chilled to —40° in five to six volumes of methanol. This is carried out in an alcohol-dry-ice bath contained in a large Dewar flask. Provided the fatty acids are chilled slowly and allowed to reach equilibrium for a few hours, the solid acids present will separate out in well-defined crystals that can be filtered off quickly. The solvent is evacuated from the filtered liquid in vacuo.

c) *Alkali-Isomerization.* A reagent suitable for the isomerization is prepared by heating 20 g. of NaOH (or KOH) with 100 ml. of diethylene glycol to above 200°C. in a beaker or porcelain dish to drive off any water present. Approx. two ml. of the liquid fatty acids are made up to 20 ml. with this solution. Figure 1 shows a reaction tube best suited for this purpose. It carries markings at 2 and 20 ml. An inlet tube for inert gas ends slightly above the level of the liquid. A glass rod of 4 mm. diameter bent to a ring at the bottom is manipulated through a piece of glass tubing of slightly larger diameter, which, like the inlet tube, is sealed to the ground glass top. A slow stream of hydrogen or nitrogen is passed through to replace the air, the space between stirrer and guide tube serving as gas outlet. The reaction tube containing the alkali reaction mixture is lowered into an oil bath at a temperature of 200°C. in such a manner that the surface of the bath is at least 2 cm. above the surface of the reaction mixture (Figure 2). During the first five minutes, in which the mixture acquires the temperature of the bath and is saponified, thorough mixing is effected by raising and lowering the stirring rod. After a total of 20 minutes the isom-

erization is complete and the reaction tube is removed from the oil bath and allowed to cool while still passing inert gas into the tube. The warm and liquid soap is washed into a separatory funnel with hot water and acidified by adding HCl and shaking. After some further cooling the fatty acids are taken up with petroleum ether, the ether layer filtered over anhydrous sodium sulphate and freed from solvent in vacuo or under carbon dioxide.

d) *Separating the Solid Conjugated Acid.* The isomerization product (approx. 2 ml.) is dissolved in 15 ml. of methanol and the solution chilled to —40°, repeating the procedure used for separating the saturated fatty acids. After rapid filtration through a Gooch crucible (chilled to —40°), the crop of crystals is rinsed twice without delay, using 2 ml. of chilled methanol each time.

To provide for slow cooling of the solution in the dry-ice bath and ensure formation of well-filterable crystals, the use of a double-walled evacuated flask, similar to a Shukoff freezing point flask, may be recommended.

As an alternative, if a deep-freeze chest is available, the isomerized fatty acids are frozen out overnight from 5 volumes of 75% ethanol at —20°C. and the crystals filtered off and washed with some of the chilled solvent.

Using either of these procedures with dehydrated castor oil, the yield of the solid acid will be up to 22% of the conjugated product, and the melting point may be somewhere between 45 and 50°C. After one further recrystallization from 40 vols. of 75% ethanol at 0°C., or from 25 vols. of petroleum ether (b.p. 50-70°C.) at —40°, the product will melt between 50 and 55°C.

e) *Identification of the 10,12-Octadecadienoic Acid.* While a crude product melting around or above 50°C. is sufficient to demonstrate the presence of DCO in the substance under investigation, it may be desirable to test the identity of the crystals obtained by checking their mixed melting point with genuine 10,12-octadecadienoic acid. This is prepared by purifying the crude acid obtained from DCO as indicated above. Several recrystallizations from alcohol and petroleum ether will give a sharp melting point of about 57°C. The observed analytical constants of a sample thus prepared were as follows (Table II).

Interference by Other Acids

Other fatty acids contained in the known drying oils will not interfere with this test with the possible
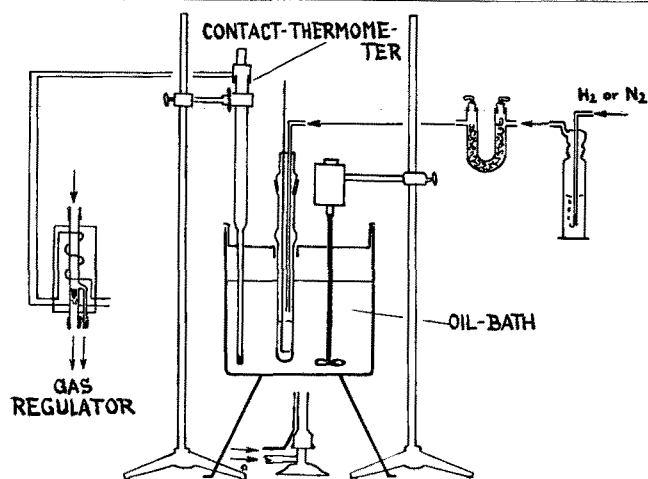

FIG. 2. Set-up for alkali-isomerization.

TABLE II

Analytical Data for 10,12-Octadecadienoic Acid

Melting point	56.4-57.5°C.
Refractive index, n_D^{60}	1.4692
Partial iodine value (11)	91.8
Diene value [Kaufmann-Baltes (6)]	89.9
Pandiene value (10)	89.5[1]
Thiocyanogen value	91.3; 91.8

Some previously reported constants (9)

Acid value	199.6
n_D^{60}	1.4689
n_D^{70}	1.4656
Density, d_4^{70}	0.86857
Molar refraction	89.36
Exaltation	+3.43

[1] With trans,trans-isomers there is practically no difference between diene and pandiene value since such isomers add maleic anhydride equally well without the use of a catalyst.

exception of linolenic acid, which upon alkali isomerization yields the high-melting pseudo-elaeostearic acid (12, 5). This may be recognized however by its much higher refractive index and, if purified, its higher melting point. If the presence of much linolenic acid becomes apparent, the isomerization of a new sample should be carried out at 220°C. Under these conditions the isomerized trienoic acids, which are less stable than the conjugated dienoic acids, are largely polymerized.

TABLE III

Examination of Various DCO Samples

Sample	Original solid acids %	Rise in n_D^{25} upon isomerization	Solid conjugated product			Mixed m.p.
			%	m.p.°C	n_D^{50}[1]	
Lab. 1	3.1	0.0034	21.9	47	1.4742	
			12.0	53	1.4730	+
Lab. 2	3.7	0.0048	19.3	48		
			10.1	52	1.4731	+
"Isoline"	1.6	0.0040	21.5			
			11.5	49	1.4722	+
"Dienol"	2.5	0.0036	20.0	45		
			8.5	52	1.4725	+
"Synourin oil"	Trace		17.7	43	1.4708	+
"Pythrinol"	2	0.0043	20.0	38	1.4705	+
DCO : Linseed oil 1 : 3	15.2	0.0061				
			0.6	46		+

[1] Corrected by 0.00035 units per degree if measured above 50°C.

Results Obtained with Various Oils

a) *DCO Samples.* A number of commercial and laboratory samples of DCO were tested in the manner described. The oils from the trade showed considerable variations in their analytical constants; the total iodine value of Pythrinol, for instance, was only 115.3, and the Synourin oil, which had been stored for over 10 years without precaution, contained much oxidized material. Nevertheless all products yielded from 17 to 22% of crude 10,12-octadecadienoic acid, which showed no depression of melting point when mixed with a pure sample of this acid (Table III). After one recrystallization (shown in the second line for each sample in the table) the refractive indices at 50°C. were between 1.4722 and 1.4731.

A mixture of one part of DCO with three parts of linseed oil also gave a positive test although the yield was small, indicating considerable solubility of the solid conjugated acid in the refrigerated solution of the isomerization mixture.

b) *Other Oils.* The results obtained on various conjugated and non-conjugated oils are listed in Table IV, which shows also the refractive indices of the original fatty acids and the solid acids removed prior to isomerization.

Solid conjugated products were obtained only with linseed and cameline (German sesame) oils, both of which contain much linolenic acid. With linseed oil an isomerization temperature of 220°C. caused the yield of solid conjugated acid, which melted at a much lower temperature than that found from DCO, to be negligible. The crystals obtained from cameline seed oil were shown to be pseudo-elaeostearic acid both by the refractive index, which was approx. 0.0150 units higher than that of the 10,12-acid, and by the melting point after recrystallization.

The other oils could easily be distinguished from DCO because of the absence of solid isomerization products. By means of the proposed test it is possible also to differentiate between various types of oils, such as natural or artificial conjugated or non-conjugated products or mixtures of them. The conjugated oils, for instance, that had been prepared by alkali or catalytic isomerization made themselves known in the test by showing no rise in refractive index during the treatment with alkaline glycol. Where a rise was observed, such as with "Conjulin," the conjugation treatment had not been a complete one. (The sample tested was drawn from an early commercial batch and does not necessarily represent later production.)

TABLE IV

Examination of Other Oils

Oil	Fatty acids n_D^{50}	Removed solid acids		Isomerization	
		%	n_D^{50}	Change in n_D	% solid products
Sesame	1.4568	33.5	1.4350	+0.0084	0
Poppyseed	1.4578	21.6	1.4345	+0.0064	0
Tobacco seed	1.4565	15.8		+0.0090	0
Corn	1.4552	44.1	1.4510	+0.0053	0
"Drisoy"	1.4582	19.0	1.4458	+0.0063	0
Linseed	1.4588	15.9	1.4472	+0.0070	< 1[1]
Cameline seed	1.4610	25.0	1.4352	+0.0073	6.5[2]
Conjugated soya	1.4556			+0.0002	0
Conjugated-sunflower	1.4650	2.2	1.4535	—0.0002	0
Conjugated linseed	1.4722	20.7	1.4418	—0.0003	0
"Conjulin"	1.4752	7.8	1.4448	+0.0033	0
Tung+sunflower, 1:2	1.4702	32.4	1.4770	+0.0042	0
Castor (n_D^{25})	1.4717	2.2		—0.0008	0
Tall oil (n_D^{25})	1.4960	0		+0.0010	0
Boleko (n_D^{20})	1.5000	12[3]	1.4947	0.00	0

[1] m.p. approx. 25°.

[2] $n_D^{50} = 1.4872$; m.p. recrystallized $=79°$ (pseudo-elaeostearic acid).

[3] Liquid at room temperature.

The non-conjugated drying and semi-drying oils deposited variable amounts of saturated acids, characterized by low refractivity. Upon isomerization these oils showed a rise in refractive index exceeding that of DCO. Mixtures of natural conjugated with non-conjugated oils deposited solid unsaturated acids of high refractivity during the preliminary treatment. Tung oil alone will not give a rise in n_D during the alkali treatment, but mixtures with non-conjugated oils will do so.

Boleko oil, which contains acetylenic linkages, behaves like a natural conjugated oil in that it shows no rise in refractive index and deposits solid unsaturated acids. The tall oil investigated was a sample of the distilled product with the solid abietic acid removed; it yielded no solid constituents either before or after treatment and contained only little material that responded to alkali isomerization as shown by the small change in refractivity.

Conclusions

The proposed method of using the formation of solid 10,12-octadecadienoic acid as a test for DCO appears well suited for differentiating this oil from other conjugated material, such as artificially isomerized products or natural drying oils of the tung oil type. If the refractive indices are determined on the various intermediary fractions, it is also possible to

differentiate between "synthetic" and natural conjugated and non-conjugated oils or fatty acids.

Linolenic acid is the only other constituent occurring in drying oils that may cause interference through the formation of a solid conjugation product. The yield of pseudo-elaeostearic acid is small however, and it can hardly be mistaken for the solid dienoic acid.

For determining the presence of DCO fatty acids in alkyd resins Stafford and Williams (18) have recommended the use of UV-spectrometry. Since the spectrometer however allows no distinction between DCO on the one hand and a conjugated dienoic product on the other, the use of the chemical method here proposed is offered as an analytical tool for investigating alkyds.

The method might well be adapted for quantitative determination. A definite solubility of the solid 10,12-acid in the alcoholic solution at low temperature however will have to be taken into consideration. A reference curve for pure 9,12-cis,trans-linoleic acid, showing the yields of 10,12-octadecadienoic acid obtained therefrom with varying percentages present in a mixture would be desirable. Cis,trans-linoleic acid, an isomer yielding no solid bromides, has not as yet however been isolated in a pure form.

Limitation. The laboratory samples of DCO investigated here have in all cases been prepared by a catalytic procedure (20). It is not likely that all the commercial samples tested have been made with catalysts of the same type. Until the products from all industrially used processes of castor oil dehydration have been tested in this fashion however, the proposed method should be considered limited to DCO obtained by any procedure employing an acidic catalyst.

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Spectrophotometric Analysis of Tall Oil Rosin Acids

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TALL OIL is a by-product of the kraft paper industry which has found extensive use in protective coatings and industrial soaps for it is essentially a mixture of unsaturated fatty and rosin acids containing a small percentage of higher alcohols (28). There is annually available about 130,000 tons of the whole tall oil, and this figure is steadily growing with the expanding kraft paper industry. Depending upon demand, 40 to 60% of the whole tall oil is refined by distillation or acid refining (27).

The fatty acid and unsaponifiable fractions of tall oil have been investigated and their compositions clarified to some extent. The fatty acid portion of the whole tall oil contains approximately 45% oleic, 48% linoleic, and 7% palmitic acid (1). In the unsaponifiable portion substantial quantities of β-sitosterol and lignoceryl alcohol have been identified (19).

Investigation of the rosin acid fraction of tall oil has been retarded by the confusion which has existed until recently in the chemistry and composition of the rosin acids. It has lately been demonstrated that the rosin acids in gum and wood rosin are composed of a mixture of eight different rosin acids, whose structures are shown in Figure 1. Their approximate proportions have been found to be 30-40% abietic, 10-20% neoabietic, 14% dihydroabietic, 14% tetrahydroabietic, 5% dehydroabietic, 16% of the isomeric dextropimaric acids, and less than 1% of levopimaric acid (12). Of these acids the most significant are abietic and neoabietic acids, which are interconvertible, and which are responsible for the oxidation of rosin and the reaction of rosin with maleic anhydride in resin formation. These two acids disproportionate when subjected to heat and catalysts to yield the stable dehydrogenated and hydrogenated abietic acids.

While most of the investigations of tall oil rosin acids have been conducted on the acids crystallizing from distilled tall oil, some information has been collected on those in whole tall oil. By selective esterification Dittmer (9) isolated the total rosin acids from Swedish whole tall oil as brown crystals. Recrystallization from methanol yielded yellow crystals, which melted at 161-166°C. and analyzed for $C_{20}H_{30}O_2$, the same as abietic acid. Hasselstrom (20) likewise formed abietic acid (m.p. 164.5-165.5°C.; $[a]_D$ — 53.9°C.) by the action of glacial acetic acid on the material crystallizing from American whole tall oil. In neither case was any yield given. Pyhala (24, 25) isolated crystalline rosin acids from whole Finnish tall oil