The Fat Acids of American Tall Oil[1]

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Introduction

TALL OIL represents a large potential source of fat acids and rosin acids in the United States. A recent survey (1) indicates that in 1942 the production was 178,000 pounds per day and that 816,000 pounds per day might be produced if all of the potentially available tall oil were recovered. This survey also points out that tall oil in the United States is produced only by the southern paper mills, where the greatest volume of pine wood is processed by the sulfate process, from which tall oil can be recovered. The average composition of a number of crude tall oils was reported to be 58% rosin acids, 36% fat acids and 6% unsaponifiable. Apparently, most of the tall oil produced in the United States is used as such either crude or refined, without separation of the rosin and fat acids. A booklet (2) published by one of the large producers of tall oil lists a number of uses such as in asphalt emulsions, soaps for laundries and textile scouring, metal cleaning, emulsions, flotation agents, cutting oils, etc.

In spite of the large industrial use of tall oil very little information is available concerning the composition of the fat acids which constitute one-third or more of the oil. This is especially true of tall oil from American sources. The booklet previously mentioned (2) states that, "the fatty acids present are nearly all unsaturated 18 carbon acids, some oleic and principally linoleic acid." The most complete examination of the fat acids of a tall oil appears to have been made by Niessen (3). He examined a sample of tall oil obtained from Michael Bartel and Company of Regensburg. The fat acids were isolated as methyl esters by means of the well-known preferential esterification process, (4) followed by removal of free rosin acids with alkali and distillation of the methyl esters. The recovered fat acids showed no saturated acid content by the Twitchell lead salt alcohol method. They had an I. V. of 166 (Kaufmann) and a T. V. of 96 (Kaufmann). The calculated composition was reported to be: oleic acid, 22.7%; linoleic acid, 71.3%; linolenic acid, 6.0%. If revised empirical constants (5) were used instead of Kaufmann's theoretical thiocyanogen values, the calculated composition would have been about 5% lower in oleic, 10% higher in linoleic, and 5% lower in linolenic acid content.

In view of the lack of published data on American tall oil the following results on the fat acid composition of representative samples are presented. Five different crude and one refined tall oil were obtained from different producers in the southern United States. The fat acids were isolated as methyl esters by a method similar to that employed by Niessen (3) and were analyzed by two independent methods. One method was by determination of I. V. and T. V. The other method was based on the spectral method of Mitchell (6).

Experimental

THE samples of tall oil were analyzed for approximate rosin and fat acid content by the method of preferential esterification and double titration described by Hastings (7) with the results shown in Table I. Sample A is a refined oil, and the others are crude tall oils. The values for the crude tall oils lie within the range of accepted composition except that rosin acid content is slightly lower than average.

TABLE I
Analyses of Tall Oil Samples

Sample	Fat Acid %	Rosin Acid %
A	61	32
B	42	44
C	45	46
D	38	46
E	36	41
F	45	38

The fat acids were separated as methyl esters by the following procedure: 150 gms. of tall oil were mixed with 100 gms. of absolute methanol containing 5 gms. of sulfuric acid. The mixture was refluxed for 60 minutes, cooled, and diluted with water. The mixture of rosin acids and fat esters was extracted with ethyl ether, and the ether solution was washed with an excess of 5% NaOH solution to remove most of the rosin acid. The solution was washed several times with water and again with caustic, and finally several times with water. After drying over Na_2SO_4 and evaporation of ether, the crude methyl esters were distilled at a constant pressure of 2 mm. through a five-inch lagged Vigreux column.

The esters distilled at a temperature corresponding essentially to 18 carbon methyl esters, leaving a considerable residue of high boiling material which appeared to consist of unsaponifiable matter and polymerized acids. The distilled esters were saponified, the soap solutions were extracted with ether to remove unsaponifiable matter, and the free acids were recovered. They were analyzed for iodine value (rapid Wijs method) (8), thiocyanogen value (24 hrs., 0.2 N) (9) and saturated acids by the low temperature method of Earle and Milner (10). Spectrophotometric measurements were made on the acids before isomerization, and on the acids after alkali isomerization according to the spectral analysis method of Mitchell (6), using a Beckman quartz spectrograph.

Table II is a summary of the analytical data thus obtained. The constants for the various samples fall within a fairly narrow range. The yields of distilled ester are 80-90% of those expected from the fat acid content of the tall oils, except sample C, where excessive loss was caused by bad emulsions during the alkali washing to remove rosin acid.

The absorptions at 2680 Å before isomerization correspond to 0.3 to 0.6% of conjugated linolenic acid, using Kass' constant of 215 (11) for the specific α of a pure conjugated linolenic acid. However, alkali isomerization conditions did not change the value appreciably. Furthermore, the absorption at 2900 Å and at 3000 Å was usually slightly higher than at 2680 Å. These facts would indicate that the absorption at 2680Å was no doubt due to a trace of some

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TABLE II

Analytical Data on Fat Acids of Tall Oil

Sample	Yield, dist. ester, % of oil	Non-sap. in dist. ester %	N_d^{30}	I.V.	T.V.	Determ. % sat.	Specific alpha, 1 gm./1000 ml. 1 cm.			
							At 2340 Å		At 2680 Å	
							Before isom.	After isom.	Before isom.	After isom.
A	60	....	1.4596*	129.0	91.4	7.0	10.8	39.2	0.7	0.6
B	36	2.9	1.4692	132.0	92.0	6.4	11.8	40.8	1.3	1.1
C	31	3.2	1.4685	132.0	89.0	7.8	13.5	43.1	1.5	1.2
D	33	3.7	1.4670	128.3	88.0	6.5	13.3	42.9	0.8	0.6
E	33	4.4	1.4694	133.1	91.0	6.7	15.2	45.5	0.8	0.7
F	39	4.6	1.4683	123.2	87.3	7.0	10.9	39.0	0.7	0.6
Methyl linoleate			1.4583*	172.5*	92.8*	....	0.68†	87.0†	0.2†	0†

* Values for methyl ester, all other values for free acid.
† Values determined on methyl ester and calculated to free acid.

absorptive impurity and not due to linolenic acid. In view of these considerations it appears most reasonable to consider linolenic acid to be absent.

The absorptions at 2340 Å before isomerization correspond to a content of 9 to 13% of conjugated linoleic acid (Table II), using Kass' constant of 115 for the specific α of a pure conjugated linoleic acid. The conjugated linoleic acid was undoubtedly formed by the action of the alkali and heat during the cooking of the wood from which the tall oil was derived, resulting in a partial isomerization of the linoleic acid.

IN calculating the total linoleic* acid from spectral data, two different methods may be used. In the first method, the total linoleic acid is calculated directly from the specific α at 2340 Å after isomerization (using the constant 87.1, of Mitchell). In the second method the content of normal linoleic acid is calculated from the difference in absorption before and after isomerization (using the 87.1 constant), and to this is added the conjugated linoleic acid (calculated from absorption value before analytical isomerization) to give total linoleic acid content.

The second method is apparently a more direct and strict interpretation of the data, since it assumes only that the absorption before isomerization is due to conjugated linoleic acid and that the increase in absorption upon isomerization is due to normal linoleic acid.

The authors feel, however, that the first method probably gives a more accurate estimation of total linoleic acid, based on the following considerations: it is reasonable to suppose that the conjugated linoleic acid found in the fat acids was caused by a partial isomerization of normal linoleic acid originally present, due to the action of alkali and heat during the cooking. This amount of isomerization corresponds to only about two minutes of the 25 minutes used in the analytical isomerization, and from the nature of the time-reaction curve (6) of the analytical isomerization, this amount of additional time would have very little effect on the analytical method. The difference of 3% to 4% of linoleic acid between methods 1 and 2 lies in the following facts: As Kass has pointed out (11), when normal linoleic acid is alkali isomerized, it attains a constant maximum of about 75% conversion to conjugated linoleic acid, while the 25% which remains unconjugated is not identical with the original linoleic acid but is probably geometrically isomerized. The isomeric linoleic acid thus formed in 25% yield is certainly not a polymerization product since alkali isomerized linoleic acid is distillable with negligible residue if excessively long or intense heating is avoided. Furthermore, Von Mikusch (12) has shown that total unsaturation remains essentially unchanged during alkali isomerization. This altered linoleic acid represents an isomer (or isomers) which would not be detected by spectral analysis if it were present in the original mixture before analytical isomerization, since it does not rearrange to a conjugated form upon treatment with hot alkali.

If, in fact, the 9 to 13% of conjugated linoleic acid found in the fat acids of tall oil was due to a partial alkali isomerization of normal linoleic acid present in the wood, then a corresponding amount of altered linoleic acid would be present which would not be included in method 2 of calculation but would be included in method 1. Therein lies the explanation of the 3-4% higher values for linoleic acid by method 1. Method 1 assumes that the same ratio of altered to conjugated linoleic acid was formed in the partial isomerization which occurred during cooking, as is formed in the analytical method, and that the two forms survived in the same ratio during isolation of the acids.

Oleic acid content was calculated from the spectral data by two methods. In the first method (column 3), it was obtained by the difference between 100 and the sum of % total linoleic (method 1) plus % saturated acids determined. In the second method (column 5), oleic acid content was calculated from I. V. and total linoleic acid as determined by spectral analysis (method 1), using the formula given by Mitchell (6). In this case, saturated acids were determined by difference (column 6).

In calculating the composition from I. V., and T. V., linolenic acid was assumed to be absent, in view of previous considerations. The presence of some conjugated linoleic acid makes questionable the exact application of this method since I. V. and T. V. of conjugated linoleic acid have not been established.

THE compositions of the fat acids, shown in Table III, are reported to the nearest whole percentage in view of the previously considered possible sources of error involved in any treatment of the analytical data. The compositions calculated by the different methods show appreciable variations for a given sample but perhaps not more than might be expected from the nature of the mixture.

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* The term linoleic acid is used to designate any octadecadienoic acid; normal linoleic acid to designate the 9.13 linoleic acid found in the usual vegetable oils, and conjugated linoleic acid to designate the conjugated octadecadienoic acids (10, 12 or 9, 11). Altered linoleic acid is used to designate the non-conjugated linoleic acid which is formed in about 25% yield when normal linoleic acid is alkali conjugated to the maximum degree, and which is not identical with the original or the conjugated linoleic acid (see discussion in text).

TABLE III

Calculated Composition of Tall Oil Fat Acids

Sample	From Spectrophotometric Analysis						From I.V. & T.V., Assuming no Linolenic		
	1	2	3	4	5	6	7	8	9
	% conj. linoleic	linoleic	% oleic by diff.	% sat. detd.	% oleic by I.V.	% at. by diff.	% linoleic	% oleic	% sat. by diff.
A	9	45 (1) 42 (2)	48 51	7	53	2	44	54	2
B	10	47 (1) 44 (2)	47 50	6	53	0	47	52	1
C	12	49 (1) 46 (2)	43 46	8	47	4	50	46	4
D	12	49 (1) 46 (2)	44 47	7	44	8	47	47	6
E	13	52 (1) 48 (2)	41 45	7	43	5	50	48	2
F	9	45 (1) 42 (2)	48 51	7	47	8	42	52	6
Ave	11	48	45	7	....	....	....	....	....

It is the opinion of the authors that the compositions shown in the first four columns of figures (method 1) in Table III are probably the most reliable representation of the actual composition of the fat acids. The variation in composition between various samples is relatively small, and the average compositions of the fat acids of tall oil is seen to be 48% linoleic, 45% oleic, and 7% saturated acids.

Sample D was chosen as a representative sample for a more detailed examination by fractional distillation. Six hundred and sixty grams of the crude oil were esterified and made free of rosin acid in a manner similar to that previously described. The crude methyl ester (330 gms.) was subjected to fractional distillation through a Podbielniak Hypercal column with the results shown in Table IV. The I. V., T. V., and spectrophotometric data were all measured on the fat acids which had been made free of unsaponifiable matter with the exception of fractions 4, 5, and 6, each of which had a low content of unsaponifiable matter. Samples 4, 5, and 6 were analyzed as methyl esters and for uniformity the results were calculated to free acid and reported as shown. Fractions 1 through 7 were taken at a constant regulated pressure of 5 mm. with a reflux ratio of 6 to 1 (20 to 1 setting).

At this point, the pot temperature had reached 295° C., so the pressure was decreased, and fraction 8 was collected without reflux. Fraction 9 was obtained by distillation of the residue (after fraction 8) in the small flask with a short Vigreux column. The cut-off on the previous distillations (Table II) corresponded approximately to a point including fraction 8, where the yield of distilled ester, based on original tall oil, is 34.4%, compared to 33% for the same tall oil in Table II.

Inspection of Table IV indicates that there is present in fraction 1 a high percentage of a low-boiling unsaponifiable material, amounting to a little over 1% of the total crude esters. This material was liquid, and appeared to be of a terpene nature. Fraction 2 corresponds to methyl palmitate in boiling point and in equivalent weight of the isolated fat acids. The melting point of the fat acids of fractions 1 and 2, after recrystallization, confirmed the presence of palmitic acid and indicated that it was the principal fat acid component. Fractions 3, 4, and 5 represent intermediate fractions between C_{16} and C_{18} methyl esters. The break between C_{16} and C_{18} esters was not as sharp as was usually obtained with this column on normal mixtures. This may have been caused in part by the presence of an unsaponifiable component which is seen gradually to decrease to a minimum of 1.0% in fraction 6, which is the main C_{18} fraction as shown by boiling point and equivalent weight. All of the fractions through 6 contain little conjugated linoleic acid, as indicated by the absorption before isomerization.

Fraction 7 shows a slightly higher boiling point than the main C_{18} fraction, and it also has a higher content of unsaponifiable matter and of saturated acids, and considerable conjugated linoleic acid. The equivalent weight of the acids is still quite close to

TABLE IV

Data on Fractions From Distillations of Tall Oil Esters

Fraction No.	B. P. °C.	Pr. mm.	% Wt. of total	Sum % wt.	Unsap. %	Eq. wt.* acids	I. V. acids	T. V. acids	% sat. acids	Sp. a acids 2340 Å	
										Before isom.	After isom.
1	81-162	5	2.3	2.3	60.0	250	31.0	23.7	......	2.9	3.2
2	162-167	5	3.8	6.1	9.2	254	11.1	11.0	79.0	0.5	0.7
3	168-176	5	1.3	7.4	6.0	269	40.7	20.6	70.4	2.7	17.6
4	176-182	5	2.5	9.9	2.8	277	113.0	75.5	20.3	2.7	39.7
5	182-186	5	7.6	17.5	1.4	279	139.2	93.6	0.4	1.0	48.0
6	186	5	42.8	60.3	1.0	280	127.1	90.4	2.0	1.2	36.7
7	186-190	5	2.5	62.8	7.4	282	112.0	86.7	10.5	29.2	37.5
8	190-175	5-2	6.1	68.9	10.0	291	127.3	95.0	2.0	68.3	72.5
9	180	.35	6.2	75.1	24.2	338	151.1	108.0	9.2	26.9	41.8
10 Res	......	....	24.9	100.0	39.0	315	106.2	51.6	....	6.6	14.3

* Eq. wt. of first six fractions detd. on dist. methyl esters and corrected for unsap. content of fraction. Unsap.-free fatty acids of last four fractions used for eq. wt. detn.

C_{18}. Apparently the C_{18} conjugated esters are higher boiling than the C_{18} non-conjugated esters. The accumulation of stearic acid in this fraction following the main C_{18} fraction is to be expected. Fraction 8, which was collected with much less effective fractionation has an equivalent weight of acids considerably above that of C_{18} acids, indicating an appreciable contamination with higher molecular weight acids. This fraction is remarkable in that the conjugated linoleic acid is highly concentrated in it, with relatively little normal linoleic (compare absorption before and after isomerization).

Fraction 9 is still higher boiling, has higher unsaponifiable content, but is lower in apparent conjugated acids. The equivalent weight indicates acids at least as high as C_{22}. A more detailed examination with refractionation would be necessary to establish the nature of these higher acids. Fractions 7, 8, and 9 all gave negative qualitative tests for rosin acid. The residue is quite high in unsaponifiable matter. The acids of the residue free of unsaponifiable matter, were quite viscous, and are apparently a mixture of polymerized acids and high molecular weight monobasic acids. The low equivalent weight compared to fraction 9 would also indicate an appreciable amount of dimerized and trimerized linoleic acid (eq. wt. 280).

The calculated compositions of the fractions from the distillation are shown in Table V. The calculated linoleic content of fraction 1 is probably meaningless but is small enough to be of no great significance. On fraction 2 the % saturated acids determined is about 9% lower than that calculated from spectral analysis or from I. V. and T. V. with the result that the oleic content by difference is 9% higher than by the other two methods. The calculated oleic content (which varies from 10.5 to 20.2% according to method of calculation) is probably due to palmitoleic acid since the oleic content of the next fraction is much lower. If the iodine number of palmitoleic acid were used in calculating the oleic content of this fraction, the calculated oleic value would be 1 to 2% lower. On fraction 3 the results of the various methods of calculation are in somewhat better agreement, but the % saturated acids determined is about 4% lower than that calculated by the two methods where it is obtained by difference. On fractions 4, 5, and 6 the compositions calculated by the various methods are in good agreement. These three fractions make up about 53% of the total sample of crude esters, 70% of the total distilled esters, or 77% of the distilled esters up to and including C_{18} esters (through fraction 8).

In fractions 1 to 6 inclusive, the amount of conjugated linoleic acid is so small as to make little difference whether method 1 or method 2 is used to calculate total linoleic acid content. Method 1 was actually used. Fractions 7, 8, and 9 are quite high in conjugated linoleic acid, and considerable differences are shown when their compositions are calculated by the two methods.

ACTUALLY, unpublished data from this laboratory indicate that the altered linoleic acid ester distills with the conjugated acid ester at a temperature above ordinary C_{18} esters. This fact would make the total linoleic acid calculated by method 1 the more accurate determination of total linoleic acid.

The calculations on fraction 7 involving I. V. (columns 5 and 6) and I. V. and T. V. (columns 7, 8, 9) are at wide variance with those obtained directly from spectral data. The calculations on subsequent fractions from I. V. and T. V. gave meaningless values which are not recorded. This is to be expected in view of their very high content of conjugated linoleic acid. The calculations on fraction 9 and residue are of doubtful significance since the equivalent weight indicates the presence of a large amount of acids of high molecular weight of unknown identity.

As was previously mentioned, the cut-off on the distillation of the esters described in Tables II and III corresponded approximately to a point including fraction 8. It is evident from equivalent weights in Table IV that this corresponds quite closely with complete removal of C_{18} esters. A calculated composition of the composite of fractions 1 to 8 inclusive should, therefore, agree with the composition of this oil (D) shown in Table III. The composite of fractions 1 to 8 inclusive, calculated from data in Tables IV and V (method 1) has a fat acid composition as

TABLE V

Calculated Composition of Fractions of Distilled Esters

Fraction No.	Analysis by Spectral Method						Analysis by I. V. & T. V.		
	1	2	3	4	5	6	7	8	9
	% conj. lin.	% total lin.	% oleic diff.	% sat. det.	% oleic I. V.	% sat. diff.	% lin.	% oleic	% sat. diff.
1	2.5	3.7	......	......	27.0	69.1	8.5	17.3	74.2
2	0.4	0.8	20.2	79.0	10.5	88.7	0	12.0	88.0
3	2.3	21.2	8.4	70.4	4.9	73.9	24.9	0	75.1
4	2.3	45.0	34.7	20.3	35.0	20.0	44.2	37.0	18.8
5	0.9	52.7	46.9	0.4	47.1	0.2	52.9	46.3	0.8
6	1.1	42.6	55.4	2.0	55.4	2.0	42.8	55.0	2.2
7	25.4	43.1 (1) 35.0 (2)	46.4 54.5	10.5	(37.8)	(19.1)	(29.6)	(65.2)	(5.2)
8	59.3	83.3 (1) 66.1 (2)	14.7 31.9	2.0	......	......	......	......	......
9	23.4	48.0 (1) 40.5 (2)	42.8 50.3	9.2	......	......	......	......	......
10	5.7	16.4 (1) 14.5 (2)	......	......	......	......	......	......	......

follows: saturated acids 9.0% (7% in Table III); oleic acid 46.5% (44% in Table III); total linoleic acid 44.3% (49% in Table III); conjugated linoleic acid 6.8% (12% in Table III). The fact that conjugated linoleic acid recovery and also total linoleic acid recovery is about 5% low is probably due to polymerization of this amount of the conjugated ester during the longer period of heating at the higher pot temperatures involved in the detailed fractional distillation. The agreement of the two sets of figures as given above is fairly good and is even closer if allowance is made for the loss of 5% of conjugated linoleic acid by polymerization.

The main points which the fractional distillation reveals are that saturated acids are mostly palmitic, that there may be approximately 1% of palmitoleic acid, and that the conjugated linoleic ester is somewhat higher boiling than the normal C_{18} esters and can be separated and concentrated by fractional distillation. The detailed fraction distillation essentially confirmed the previously determined composition of the fat acids of tall oil.

Summary

The composition of the fat acids of six samples of American tall oil has been determined. They are all quite similar in fat acid composition. The average values were: linoleic acid 48%; oleic acid 45%; saturated acids 7%. There is present approximately 11% of conjugated linoleic acid, probably formed by the action of alkali and heat during the cooking of the pulp from which the tall oil was formed.

Detailed fractional distillation of a sample of the methyl esters of the fat acids showed that the saturated acids are mostly palmitic, that there may be about 1% of palmitoleic, and that the conjugated linoleic acid present can be separated and concentrated by fractional distillation.

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Report of the Soybean Analysis Committee 1944-45

THIS Committee carried out collaborative analyses for oil on seven samples during the past year. In addition, several members of the Committee carried on extensive investigations of the various factors influencing the determination of oil. The results of the collaborative tests are listed in Table 1. These analyses for oil content were carried out in accordance with the amplified official A.O.C.S. method as published in Oil & Soap, *21*, 306 (1944). Samples Nos. 11, 12, 13, and 1945-1 were whole soybeans which each collaborator ground in his own laboratory. Portions of Sample 1945-1 were dried, ground in a hammer mill at one laboratory, and then sent to each collaborator. The results are shown in columns 6, 7, and 8 of Table 1.

The standard deviation between collaborators ranges from 0.18 to 0.09 for the four samples of whole soybeans. This indicates very good reproducibility of the method in the hands of these seven laboratories. When the variables introduced by grinding and regrinding are eliminated, however, the standard deviation for a 2-gram sample is 0.07 and for a 5-gram sample is 0.04. This latter value is a goal to aim for. Consideration of the results in Table 1 led one of the Committee, F. I. Collins of the U. S. Regional Soybean Laboratory, to carry out some experiments on grinding which are summarized in Table 2. Most of these results represent the average of 16 separate oil determinations (four samples of each of four varieties of soybeans). The results in Table 2 indicate again the importance of fine initial grinding, and show that good regrinding is essential for coarsely ground soybeans. Table 2 also shows that if the initial grinding is sufficiently fine, regrinding may not be necessary.

Elimination of the regrinding operation would speed up the determination of oil, reduce greatly the labor involved, and, as shown by Table 1, improve the reproducibility of results, especially if 5-gram samples were used for extraction. Although repeated efforts have been made, it has been impossible to devise a method of specifying objectively the fineness of initial grinding necessary to eliminate regrinding. As Table 2 shows, any one of several types of mills will grind satisfactorily, but these samples were ground by those skilled in the adjustment and operation of the various mills used. Of these mills, only the Wiley and hammer types require no adjustment by the operator. The Wiley mill does not grind suffi-

TABLE 2

Per Cent Oil Content (14% Moisture Basis) as Affected by Grinding and Regrinding

Mill	Strokes Regrinding		No Regrind
	200	100	
Wiley (2-mm.)	18.99	18.82	....
Wiley (1-mm.)	18.90	18.78	....
Wiley (35-mesh)	19.02	18.92	....
Hammer	19.08	19.04	18.87
Bauer	19.06	19.02	18.88
Arcade	19.12	19.11	19.10