

Gas Chromatographic Analysis of Tall Oil Fractionation Products After Methylation with *N,N*-Dimethylformamide Dimethylacetal

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Abstract

Tall oil fractionation products such as tall oil fatty acids, distilled tall oil, and tall oil rosin are routinely analyzed by gas chromatography (GC) after derivatization with diazomethane or esterification with methanol using boron trifluoride as a catalyst. An alternative derivatizing reagent, *N,N*-dimethylformamide dimethylacetal, has been investigated for the preparation of methyl esters of fatty acids and resin acids in tall oil fractionation products prior to GC analysis. This reagent provides a safe, rapid, and reproducible means of derivatization that eliminates the need to isolate the methyl esters from the derivatization reaction mixture.

Introduction

Tall oil is a natural product of pine trees that is derived as a byproduct from the Kraft pulping process. Characteristically, the two main chemical structures in crude tall oil are resin acids and fatty acids. The resin acids are diterpene carboxylic acids based on an alkyl-substituted perhydrophenanthrene ring structure. The fatty acids are predominantly 18-carbon, straight-chain mono- or diunsaturated fatty acids. Exact chemical composition varies with the age, pine species, and geographical location of the coniferous trees. Essentially all of the crude tall oil produced today is refined by fractional distillation to produce tall oil fatty acids, tall oil rosin, distilled tall oil, tall oil heads, and tall oil pitch. Each of these tall oil fractionation products is used in a wide variety of applications. For many applications, it is necessary to know the level of the individual fatty acids and resin acids present in these products.

Chromatographic procedures have been developed for the analytical separation of the volatile acid components of crude tall oil (1-5), distilled tall oil (3,5), and tall oil rosin (6). All of these procedures rely heavily on capillary gas chromatography

(GC) after derivatization of the fatty acids and resin acids to the methyl esters. However, all of these methods employ the use of diazomethane, a highly explosive gas, for derivatization. Furthermore, exposure to diazomethane at selected concentrations can cause severe lung damage, skin burns, and eye damage.

Alternative methods have been produced by the American Society for Testing and Materials (ASTM) for resin-acid composition in tall oil rosin (ASTM D 3008-90) and fatty-acid composition in tall oil fatty acids (ASTM D 1983-90) (7). These methods and other standard methods, such as the method developed by the American Oil Chemists' Society (AOCS) for fatty acids (AOCS Ce 1-62) (8), employ alternative derivatizing reagents. In ASTM D 3008-90, a portion of the sample is prepared by esterifying it with diazomethane or converting it to the tetramethylammonium (TMAH) salt. The TMAH salt is subsequently pyrolyzed to the methyl ester in the hot injection port of the GC. However, TMAH may induce an alkaline isomerization of the nonconjugated diunsaturated fatty acids to conjugated fatty acids, thus leading to inaccurate results.

Both the ASTM D 1983-90 method and the AOCS Ce 1-62 method are based on esterification of fatty acids with methanol using boron trifluoride as a catalyst. The methyl esters are extracted with ethyl ether and recovered by evaporation of the ether. However, Shantha et al. found that boiling conjugated linoleic acid (CLA) samples for 2 min with 12.5% BF₃-methanol reagent resulted in a 3% loss in the *cis*-9,*trans*-11 CLA isomer and a 3% loss in the *trans*-10,*cis*-12 CLA isomer. Furthermore, the method resulted in an increase in the *trans,trans*- CLA isomers and the formation of an unknown artifact (9). The authors caution that the choice of methylating reagent is critical in the analysis of conjugated fatty acids as fatty acid methyl esters.

Since their introduction as derivatizing reagents, *N,N*-dimethylformamide dialkylacetals (DMF dialkylacetals) have been applied to a wide range of compounds (10,11). The DMF dimethylacetals have been used to convert fatty acids to methyl esters (10), amino acids to *N*-dimethylaminomethylene methyl

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ester derivatives (11), phenols to methyl ethers (12), and certain diols to epoxides (13). Christophersen and Rasmussen (14) have used DMF dimethylacetal reagent to analyze barbiturates. In all cases, the reactions were rapid with accurate results and good reproducibility.

Based on these investigations, we have examined the applicability of using DMF dimethylacetal as a derivatizing reagent in the analysis of tall oil fractionation products. Three samples, representing a tall oil fatty acid (TOFA), a distilled tall oil (DTO), and a tall oil rosin (TOR), were derivatized with a commercially available DMF dimethylacetal, and the resulting mixtures were separated on a capillary column with a polar stationary phase.

Experimental

The three tall oil fractionation products, a tall oil fatty acid (Xtol tall oil fatty acid), a distilled tall oil (Acintol distilled tall oil), and a tall oil rosin (Lytol tall oil rosin) were obtained from Arizona Chemical (Panama City, FL) and Georgia-Pacific (Crossett, AR). The *N,N*-dimethylformamide dimethylacetal derivatizing reagent was obtained from Pierce (Rockford, IL) as a 2-mEq/mL solution in pyridine under the commercial trade name Methyl-8 reagent and was used as received.

The samples were derivatized by adding 1 mL of Methyl-8 reagent to a 50-mg sample containing 15 mg of margaric acid (purity > 99%) (Fluka Chemie AG, Buchs, Switzerland) as an internal standard. Holmbom has shown (5) that heptadecanoic acid (margaric) occurs in negligible amounts in samples of wood extractives and tall oil. The samples were heated for 30 min in sealed vials to 85°C to ensure complete dissolution and derivatization and allowed to cool to room temperature prior to injection into the GC.

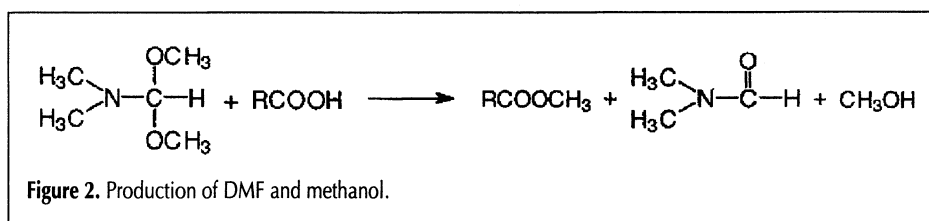
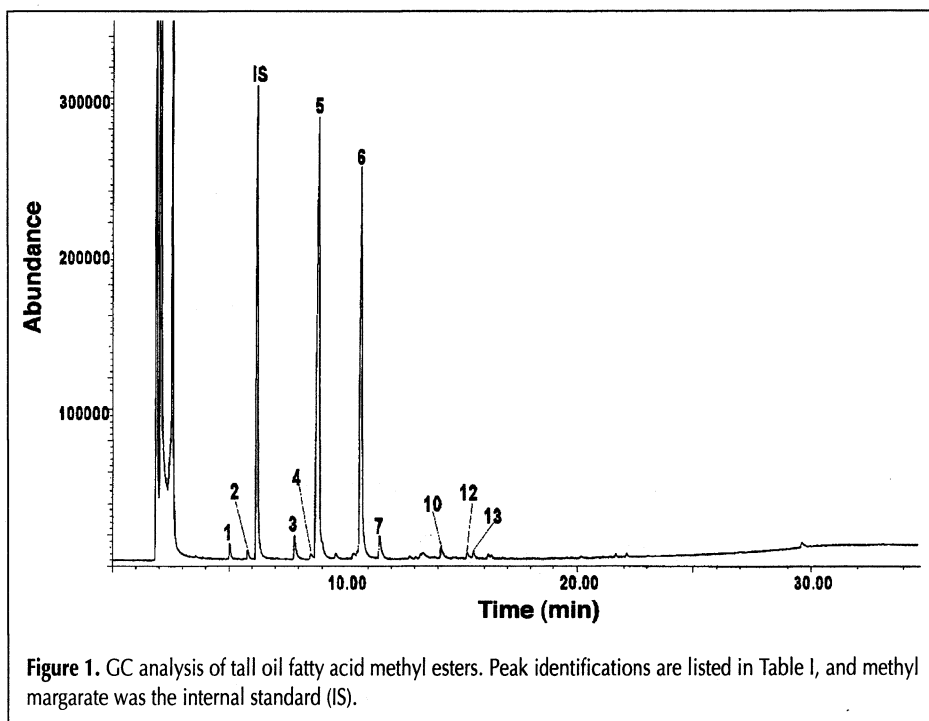
GC analyses were performed with a Varian model 3700 GC (Varian Associates, Florham Park, NJ) equipped with a flame-ionization detector (FID) supplied with high-purity air and hydrogen (Air Products, Allentown, PA). A 0.1- μ L aliquot of the resulting methyl esters was separated using an SP-2380 (90% bis-cyanopropyl-10% phenylcyanopropyl polysiloxane) fused-silica capillary column (30 m \times 0.25-mm i.d., 0.20- μ m film thickness) (Supelco, Bellefonte, PA). High-purity helium (Air Products, Allentown, PA) carrier gas was used with an average linear velocity of 27.5 cm/s at an

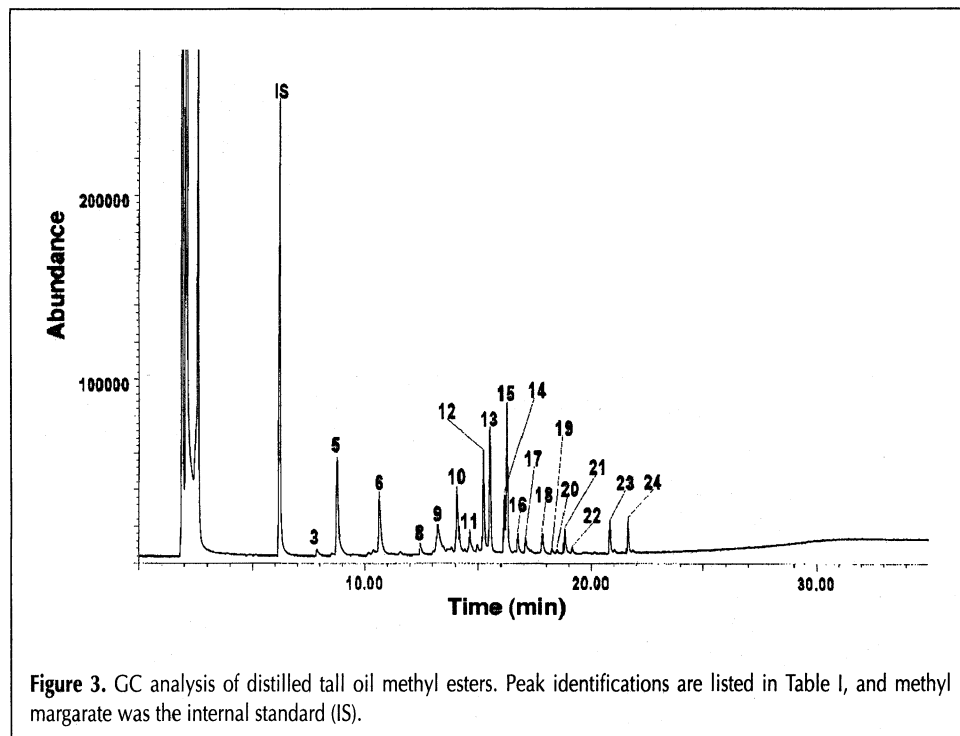
oven temperature of 150°C and a split ratio of 100:1. The inlet injection temperature and detector temperature were both 250°C. The GC oven temperature program consisted of the following sequence: an initial hold at 150°C for 10 min followed by a 5°C/min increase to 250°C and a hold at 250°C for 20 min. Data were collected using a Technivent (St. Louis, MO) Vector Two data system.

Peak identifications were made by GC-mass spectrometry (GC-MS) using a Hewlett-Packard model 5890A GC (Hewlett-Packard, Wilmington, DE) directly interfaced to a Trio 1 MS (Fisons Instruments, Beverly, MA), with an interface temperature of 280°C. Chromatographic conditions were as above. Electron-impact mass spectra between 10 and 1000 Daltons were recorded every second at an electron energy of 70 eV.

Results and Discussion

Figure 1 shows the chromatographic profile obtained from the GC-FID analysis of a typical tall oil fatty acid sample (Xtol tall oil fatty acid) after conversion to methyl esters via the DMF dimethylacetal reagent. The early eluting peaks (between 1.5 and 3 min) included the solvent (pyridine), unreacted *N,N*-dimethylformamide dimethylacetal, and two reaction byproducts, methanol and *N,N*-dimethylformamide (DMF). The DMF and methanol were produced as shown in Figure 2. This





sample is typical of tall oil fatty acid (TOFA) products with the main components being *cis*-9-octadecenoic acid (oleic acid), *cis*-9,*cis*-12-octadecadienoic acid (linoleic acid), and lesser amounts of other fatty acids such as hexadecanoic (palmitic), octadecanoic (stearic), *cis*-9,*cis*-12,*cis*-15-octadecatrienoic (linolenic), and linoleic isomers (15). All of the major peaks were well-resolved in a relatively short analysis time. Table I shows the relative FID area percent composition and relative retention times of the principal peaks from the chromatogram.

Figure 3 shows the chromatogram obtained from the analysis of the methyl esters of a distilled tall oil (Acintol distilled tall oil). The designation *distilled tall oil* (DTO) generally refers to a high-resin-acids fraction usually taken as a bottoms product in the final fatty acid fractionation column or as a side stream between fatty acid and rosin cuts. Because this is an intermediate distillation fraction, DTO is a mixture of fatty acids and resin acids that can vary from as little as 23% fatty acids and 77% resin acids to 68% fatty acids and 32% resin acids by weight (16). The relative FID area percentage composition and relative retention times of the principal peaks are listed in Table I.

The tall oil distillation process often causes substantial isomerization of the resin acids. This is illustrated by the dominating resin acids Δ^8 -isopimaric and Δ^8 -pimaric. Also, the 7(8)-15pimaradienoic acid is formed during distillation because this resin acid has not been found to occur naturally.

Finally, Figure 4 shows the chromatogram ob-

Table I. Composition and Relative Retention Times of Principal Components in Tall Oil Fractionation Products

GC peak number*	IUPAC† name	Common name	t_r^{\ddagger}	Amount (%)§		
				TOFA	DTO	TOR
1	Hexadecanoic acid	palmitic	0.807	1.1		
2	14-Methyhexadecanoic acid		0.935	0.7		
3	Octadecanoic acid	stearic	1.259	2.3	0.9	
4	<i>trans</i> -9-Octadecenoic acid	elaidic	1.373	0.6		
5	<i>cis</i> -9-Octadecenoic acid	oleic	1.427	48.2	11.1	
6	<i>cis</i> -9, <i>cis</i> -12-Octadecadienoic acid	linoleic	1.719	35.9	7.9	
7	<i>cis</i> -9, <i>cis</i> -12, <i>cis</i> -15-Octadecatrienoic acid	linolenic	1.849	2.3		
8	Eicosanoic acid	arachidic	2.005		1.4	
9	Octadecadienoic acid		2.131		5.0	
10	Octadecadienoic acid		2.274	1.4	7.8	
11	11,14-Eicosadienoic acid		2.359		3.3	
12	<i>cis</i> -5, <i>cis</i> -11, <i>cis</i> -14-Eicosatrienoic acid		2.455	0.6	9.3	
13	8(9),15-Isopimaradien-18-oic acid	Δ^8 -isopimaric	2.501	0.6	11.2	1.7
14	2 α -[2'(m-Isopropylphenyl)ethyl]-1 β ,3 α -dimethylcyclohexanecarboxylic acid	secodehydroabietic	2.603		4.1	1.8
15	8(9),15-Pimaradien-18-oic acid	Δ^8 -pimaric	2.621		12.0	1.9
16	2 β -[2'(m-Isopropylphenyl)ethyl]-1 β ,3 α -dimethylcyclohexanecarboxylic acid	secodehydroabietic	2.704		1.9	
17	8(14),15-Pimaradien-18-oic acid	primaric	2.756		2.5	2.0
18	7(8),15-Pimaradien-18-oic acid		2.877		1.9	
19	8,13-Abietadien-18-oic acid	palustric	2.945		0.6	9.3
20	?-Abietadien-18-oic acid		2.982		0.4	1.9
21	7,15-Isopimaradien-18-oic acid	isopimaric	3.035		2.3	6.5
22	?-Abieten-18-oic acid	dihydroabietic	3.089		0.5	3.1
23	7,13-Abietadien-18-oic acid	abietic	3.357		2.5	40.3
24	8,11,13-Abietawien-18-oic acid	dehydroabietic	3.488		3.0	17.2
25	8(14),13(15)-Abietadien-18-oic acid	neoabietic	3.519			4.0

* As methyl esters.

† International Union of Pure and Applied Chemistry.

‡ Retention time relative to methyl margarate.

§ Relative percentage uncorrected for the amount of nonvolatile materials present.

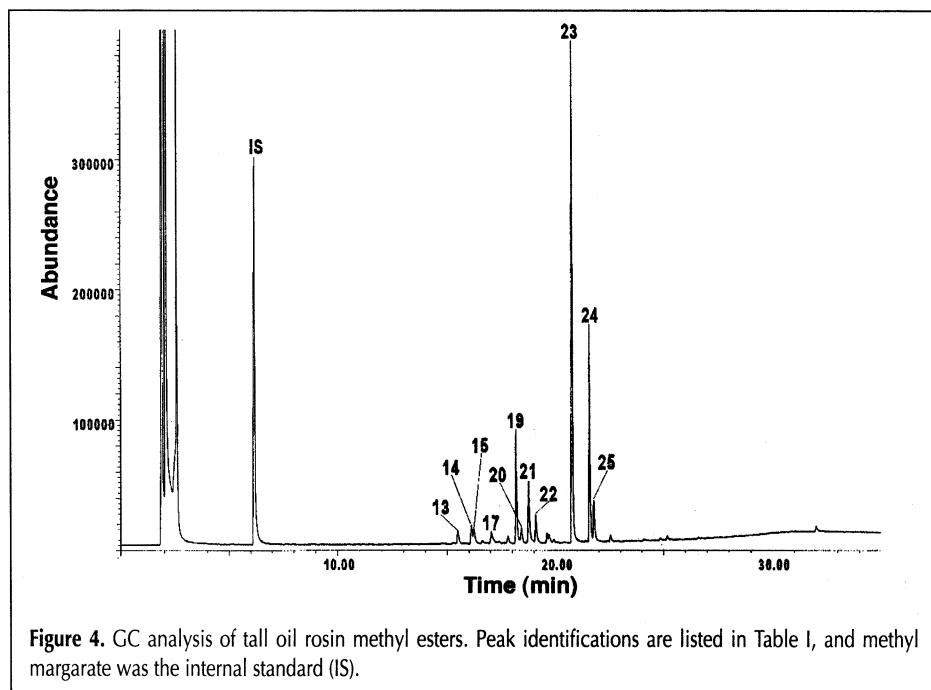


Figure 4. GC analysis of tall oil rosin methyl esters. Peak identifications are listed in Table I, and methyl margarate was the internal standard (IS).

Table II. Standard Deviations from Replicate Derivatizations

Analyte	Average peak area*	
	Current work	Previous work†
TOFA		
Methyl stearate	2.15 ± 0.18	2.32 ± 0.17
Methyl oleate	46.52 ± 1.45	47.17 ± 1.82
Methyl linoleate	35.27 ± 0.71	35.20 ± 0.61
DTO		
Methyl stearate	0.91 ± 0.07	1.01 ± 0.33
Methyl oleate	10.98 ± 0.23	10.85 ± 0.97
Methyl linoleate	8.05 ± 0.30	7.80 ± 0.44
Methyl abietate	2.44 ± 0.16	2.97 ± 0.35
Methyl dehydroabietate	2.41 ± 0.39	2.72 ± 0.45
TOR		
Methyl abietate	40.68 ± 0.94	42.81 ± 1.43
Methyl dehydroabietate	15.89 ± 0.81	16.18 ± 1.54

* Relative percent uncorrected for the amount of nonvolatile materials present.
† ASTM Research Report D01-1101.

tained from the analysis of a typical tall oil rosin sample (Lytor tall oil rosin) after conversion to methyl esters. Table I lists the relative FID area percentage composition and relative retention times of the major components in this sample.

Generally, most TOR samples contain less than 3% fatty acids and 3–7% neutral materials. These neutral species, often referred to as unsaponifiables, include fatty alcohols, resin alcohols, resin aldehydes, esters, diterpene hydrocarbons, and steroids (17). The unsaponifiable content of rosin is typically determined by an extraction method after saponification, such as ASTM D1065-82 (7).

Repeatability of the derivatization procedure was investigated by taking six different portions of each tall oil fractionation product, derivatizing each portion, and injecting each derivatized portion into the GC once. Relative area percentages

were determined for the methyl esters of three fatty acids (stearic, oleic, and linoleic) and the methyl esters of two resin acids (abietic and dehydroabietic). Table II shows the standard deviations obtained from these replicate analyses. The results indicate that for components present at levels less than 3%, the maximum standard deviation was 0.38% absolute, whereas the maximum standard deviation for major components was 1.37% absolute. These values are typical of the precision criteria used for judging the acceptability of within-laboratory results obtained when employing the ASTM methods D3008-90 and D1983-90. Also included in Table II are precision data from an inter-laboratory study conducted in 1995 by ASTM subcommittee D01.34 on naval stores of the capillary GC determination of fatty and rosin acids

in these same three samples by nine laboratories (18). The participating laboratories employed various derivatizing reagents, including diazomethane and trimethylphenylammoniumhydroxide. Our results agree quite favorably with those obtained in the interlaboratory study.

Conclusion

The derivatizing reagent *N,N*-dimethylformamide dimethylacetal has been shown to be an effective methylating derivatizing agent for the preparation of methyl esters of fatty acids and resin acids in tall oil fractionation products prior to GC analysis. This reagent provides a safe, rapid, and reproducible means of derivatization that can replace more classical and potentially hazardous methods, such as the use of diazomethane.

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