found that the temperature change did not affect the recovery significantly.

Soybean and sunflower oils, at various stages of refinement, were analyzed by this method and the results are presented in Table I. Crude and degummed oils presented no problems during the analysis; however, care must be exercised with refined oils in the extraction and concentration stages to obtain reproducible results.

The main advantage of the proposed method is that ashing or digestion of the oil, prior to the colorimetric phosphorus analysis, is unnecessary. The proposed extraction procedure is simple and inexpensive.

ACKNOWLEDGMENTS

R. Bagnari made the phosphorus determinations.

TABLE I

Phospholipid Content of Oils

Sample	% Phospholipids[a]	Coefficient of variation (%)
Soya oil		
Crude	1.17 ± 0.05[b]	4.3
Degummed	(2.37 ± 0.120) × 10^{-2}	5.1
Refined	(1.49 ± 0.01) × 10^{-4}	0.7
Sunflower seed oil		
Crude	(2.48 ± 0.15) × 10^{-1}	6.0
Degummed	(1.24 ± 0.07) × 10^{-2}	5.6
Neutralized	(9.24 ± 0.68) × 10^{-4}	7.4
Winterized	(6.91 ± 0.60) × 10^{-4}	8.7
Refined	(5.83 ± 0.42) × 10^{-4}	7.2
Glycerol trioleate PC solution	1.53 ± 0.07	4.6

[a] Mean of 10 replicates.
[b] Standard deviation.

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Oxidation of Unsaturated and Hydroxy Fatty Acids by Ruthenium Tetroxide and Ruthenium Oxyanions

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ABSTRACT

The reactions of ruthenium VIII tetroxide (RuO_4) and the ruthenium VII and VI oxyanions, perruthenate (RuO_4^-) and ruthenate ($RuO_4^{=}$) with hydroxy substituted and unsaturated fatty acids have been studied. At a 1:1 molar ratio, ruthenium tetroxide (RuO_4) and both oxyanions (RuO_4^- and $RuO_4^{=}$) oxidized 12-hydroxystearic acid to 12-ketostearic acid. With 9,10-dihydroxystearic acid, the type of oxidation products obtained depended on the amount of ruthenium oxidant used. At high ratios of oxidant to substrate, cleavage to pelargonic and azelaic acids occurred whereas at lower ratios, partial oxidation to diketo and acyloin derivatives predominated. The oxidation of oleic acid with excess ruthenium tetroxide (RuO_4) or perruthenate anion (RuO_4^-) gave the cleavage products pelargonic and azelaic acid through the intermediate formation of dihydroxy and diketo intermediates. Ruthenate anion ($RuO_4^{=}$) did not react with the double bond of oleic acid.

INTRODUCTION

Ruthenium tetroxide (RuO_4) is recognized as one of the more potent oxidizing agents of organic substrates (1-6). In practice, RuO_4 is conveniently generated from a catalytic amount of ruthenium dioxide and a large excess of an oxygen donor such as sodium meta-periodate or sodium hypochlorite (5); these oxidants also regenerate RuO_4 from any RuO_2 product formed during the oxidation of the organic substrate. The latter reoxidation procedure with RuO_2 has been successfully used for the oxidation of cyclobutanols to cyclobutanones (1), substituted benzene compounds to alicyclic carboxylic acids (1), alkynes to α-diketones or carboxylic acids (3), cycloalkanes to cycloalkanones or carboxylic acids (5), and cycloalkenes to aldehydes (7). In a previous study, we reported a procedure for the oxidative cleavage of monounsaturated fatty acids using ruthenium dioxide and sodium hypochlorite (8,9). The use of sodium hypochlorite as the cooxidant required that the reaction be done under basic conditions to prevent the formation of chlorine-containing compounds. However, ruthenium tetroxide is reported to be stable only below pH 7 (10). Under alkaline conditions (pH 7-12), ruthenium tetroxide is reduced to perruthenate anion (RuO_4^-) and at pH greater than 12, the perruthenate anion is further reduced to ruthenate anion ($RuO_4^{=}$) (10). When catalytic amounts of ruthenium dioxide together with large amounts of sodium hypochlorite are used for the oxidation of unsaturated fatty acids under alkaline conditions, it is unclear which ruthenium species are formed and which ones are oxidizing the unsaturated fatty acid. To better understand the reaction pathway of the oxidation and to identify the

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true ruthenium oxidant in this reaction, this paper describes the oxidative behavior of the ruthenium species when reacted with unsaturated fatty acids, hydroxy fatty acids and hydroxy unsaturated fatty acids, respectively.

EXPERIMENTAL PROCEDURES

Materials

Oleic acic (98%) and ricinoleic acid (98%) were obtained from Applied Science Labs (State College, PA). 12-Hydroxystearic acid was obtained by catalytic hydrogenation of ricinoleic acid. *erythro*-9,10-Dihydroxystearic acid was obtained by $KMnO_4$ oxidation of oleic acid (8).

Sodium salts of fatty acids were prepared by reacting the fatty acid with an equivalent of sodium hydroxide in 90~95% aq ethanol. The soaps were recrystallized from ethanol. Methyl esters of fatty acids were prepared using BF_3/methanol reagent. Ruthenium dioxide ($RuO_2 \cdot xH_2O$, 53% metal) was purchased from Engelhardt Ind., (Newark, NJ) and potassium perruthenate ($KRuO_4$) was purchased from Alfa Products (Danvers, MA).

Gas liquid chromatography (GLC) was conducted with a Hewlett Packard Model 7620 chromatograph equipped with dual flame ionization detectors. Separations were obtained on 8 ft × 1/8 in. silanized stainless steel columns packed with 7.5% EGA + 2% H_3PO_4 on 90-100 mesh Anakron ABS or 3% SP-2100 DOH on 100/120 Supelcoport. Quantitation of peak areas were obtained with a Consolidated Scientific Industries Supergrator-2-integrator and all have been expressed as area % using methyl palmitate as an internal standard.

Preparation of ruthenium tetroxide (RuO_4) solution.. An excess of sodium periodate (4 g) and 25 mL of H_2O were placed into a 200-mL round-bottom flask equipped with a magentic stirring bar and condenser. Ruthenium dioxide ($RuO_2 \cdot xH_2O$, 1 g) and 50 mL of carbon tetrachloride were added to the flask. The reaction was stirred 1 hr at room temperature and the carbon tetrachloride layer was separated from the aq layer. The water layer was extracted with 20 mL of carbon tetrachloride and the combined carbon tetrachloride solutions were stored over aq periodate solution in the refrigerator. The ultraviolet (UV) spectrum of this RuO_4 solution agreed with the published spectrum and the concentrations were determined using known extinction coefficients for the maxima at 385 nm and 310 nm (11).

Preparation of sodium ruthenate. A solution of sodium ruthenate (50 mL, 0.037 M) was prepared by stirring equal volumes of 1.0 M aq sodium hydroxide solution with a solution of ruthenium tetroxide in carbon tetrachloride for 2 hr at ambient temperature. The 2 layers were separated and the aq layer was extracted with 50 mL of carbon tetrachloride to remove unreduced ruthenium tetroxide. The aq layer was allowed to stand at room temperature for 2 days. During this time, ruthenium tetroxide is first reduced to perruthenate ion (RuO_4^-) and then to ruthenate ion ($RuO_4^=$).

The UV-visible spectrum of this $RuO_4^=$ solution was identical to the published spectrum and the concentration of $RuO_4^=$ was determined using absorption maxima at 465 nm and 385 nm (11).

Preparation of potassium perruthenate solution. Because of the difficulty of stabilizing perruthenate solutions under basic conditions, we purchased potassium perruthenate from Alfa Chemicals (Danvers, MA). The UV-visible spectrum in an aq alkaline solution was identical to the published spectrum and the concentrations were determined using absorption maxima at 385 and 310 nm (11).

Procedures

Oxidation of methyl 12-hydroxystearate by ruthenium tetroxide. Methyl 12-hydroxystearate (0.314 g, 1.0 mmol) and 30 mL of carbon tetrachloride were placed into a 250-mL 3-necked round-bottom flask equipped with thermometer, addition funnel, condenser and magnetic stirrer. All other experiments were run using the same apparatus. Distilled water (30 mL) was added to the homogeneous solution, then 27.0 mL (0.037 M, 1.0 mmol) of ruthenium tetroxide in carbon tetrachloride was added by drops to the flask over a 15-min period at room temperature. After the reaction mixture was stirred for 2 hr, isopropanol was added to destroy excess RuO_4, and the 2 layers were separated. The aq layer, after 1.0 M aq sodium hydroxide solution was added to pH above 12, was filtered through Celite to remove suspended RuO_2. The filtrate was acidified with conc HCl to pH 2 and extracted with ether (3 × 50 mL). The carbon tetrachloride layer was filtered through Celite. Both organic layers were washed with H_2O, dried over $MgSO_4$, the 2 organic layers were combined, and the solvent was removed in vacuo to give 0.342 g of product. The oxidation product, after esterification with BF_3/CH_3OH, was analyzed by GLC and thin layer chromatography (TLC), then identified by comparison with a standard.

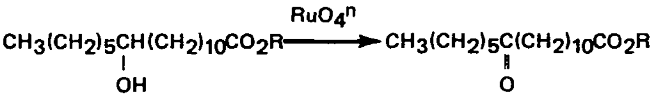
Oxidation of sodium 12-hydroxystearate by potassium perruthenate. Sodium 12-hydroxystearate (0.2415 g, 0.75 mmol) was dissolved in 50 mL of distilled water. To this stirred solution was added 50 mL of 0.015 M $KRuO_4$ solution (0.75 mmol) over a 15-min period at room temperature. After 2 hr, isopropanol was added to the flask until the starch-iodide test was negative, then 1.0 M aq NaOH solution was added to pH above 12. The mixture was then filtered through Celite to remove suspended solid RuO_2. The clear filtrate was acidified with conc HCl to pH 2 and extracted with ether (3 × 50 mL). The combined ether extracts were washed with H_2O, dried over $MgSO_4$, and the solvent was removed in vacuo to give 0.24 g or product. The oxidation product, after esterifying with BF_3/CH_3OH, was analyzed by GLC and TLC, then identified by comparison with a standard.

Oxidation of sodium 12-hydroxystearate by sodium ruthenate. Sodium 12-hydroxystearate (0.2415 g, 0.75 mmol) was dissolved in 50 mL of 1.0 M NaOH aq solution. To this homogeneous solution was added 15.86 mL of 0.0473 M Na_2RuO_4 solution (0.75 mmol) by drops over a 15-min period at room temperature. After the mixture was stirred for 2 hr at room temperature, isopropanol was added until the starch-iodide test was negative. The mixture was then filtered through Celite to remove suspended solid RuO_2. Isolation and identification of oxidation products were made by the previously described procedure. A series of similar oxidation reactions were also done with the 3 ruthenium oxidants using 9,10-dihydroxystearic acid, oleic acid and ricinoleic acid, as well as their methyl esters as the substrates. Product distribution was studied by varying the molar ratios of oxidant to substrate.

RESULTS AND DISCUSSION

As noted previously, aq solutions of ruthenium tetroxide (RuO_4) are unstable at pH >7 (10). When alkaline sodium hypochlorite is used to generate RuO_4, the latter rapidly disproportionates to a mixture of ruthenium oxyanions. On the other hand, chlorocarbon solutions of RuO_4 are reported as being stable for long periods of time at 5 C (12). In the present study, therefore, we carried out the oxidation of the organic substrate with carbon tetrachloride solutions of RuO_4. To facilitate the removal of the ruthenium dioxide (RuO_2) formed by reduction, it was necessary to have a mixed aq-CCl_4 reaction medium because RuO_2 readily forms an insoluble hydrate which is easily removed from the reaction by filtration. In the absence of water, the spent oxidant absorbed the reaction products and led to poor recovery of products. Reactions of the 2 oxyanions perruthenate, RuO_4^-, and ruthenate, $RuO_4^{=}$, with fatty acid substrates were done in alkaline solutions of the oxyanions at controlled pH. Both ruthenium oxyanions are stable under the conditions used.

Our initial studies were concerned with the oxidation of monohydroxy fatty acids. Lee et al. (13) had previously reported that secondary alcohols, e.g., cyclohexanol, are oxidized exclusively to ketones with either RuO_4 or $RuO_4^{=}$. We chose 12-hydroxystearic acid **1a** and its methyl ester **1b** as a model for hydroxy substituted fatty acids. As shown in Equation I, the hyroxy acid **1a** was converted to 12-ketostearic acid derivative **2a** (>95% yield) by either ruthenium oxyanion $RuO_4^{=}$ or RuO_4^- at a 1:1 molar ratio of reactants. A similar result was also obtained when the methyl ester **1b** was oxidized to the keto derivative **2b** by ruthenium tetroxide. In no case could we detect the presence of any cleavage products with these ruthenium oxidants, even when a large excess of the oxidants was used.



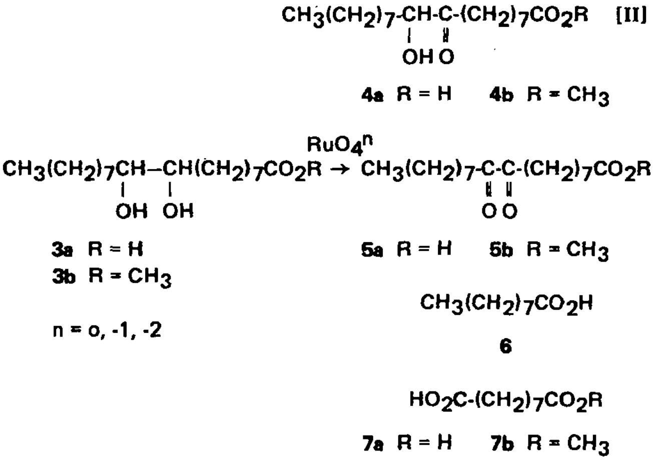
$$\mathrm{CH_3(CH_2)_5\underset{\displaystyle OH}{\underset{|}{C}}H(CH_2)_{10}CO_2R \xrightarrow{RuO_4^{n}} CH_3(CH_2)_5\underset{\displaystyle O}{\underset{\|}{C}}(CH_2)_{10}CO_2R}$$

1a R = H　　**2a** R = H　[I]

1b R = CH_3　　**2b** R = CH_3

n = 0, -1, -2

The reaction of vicinal dihydroxy compounds with ruthenium oxidants was studied using the model fatty acid derivatives *erythro*-9,10-dihydroxystearic acid **3a** and the corresponding methyl ester **3b** (Equation II). In this instance, the types of oxidation products formed were the same with all 3 ruthenium oxidants; however, the distribution of oxidation products was dependent on the molar ratio of oxidant used. For example, when each of the 3 ruthenium oxidants was used at a molar ratio of 2:1 (oxidant to dihydroxy compound) the oxidation mixture was composed of ketol **4** (43%), a mixture of positional isomers, diketone **5** (22%) and the cleavage products **6** (17%) and **7** (13%). Complete cleavage at the 9,10-position occurred at a stoichiometry of 4:1 (oxidant to diol) for both perruthenate anion and ruthenium tetroxide whereas the ruthenate anion required a stoichiometry of 8:1 in order to obtain a quantitative conversion of **3** to cleavage products **6** and **7**.



$$\mathrm{CH_3(CH_2)_7\text{-}\underset{\displaystyle OH}{\underset{|}{C}}H\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}(CH_2)_7CO_2R}\quad [II]$$

4a R = H　**4b** R = CH_3

$$\mathrm{CH_3(CH_2)_7\underset{\displaystyle OH}{\underset{|}{C}}H\text{–}\underset{\displaystyle OH}{\underset{|}{C}}H(CH_2)_7CO_2R \xrightarrow{RuO_4^{n}} CH_3(CH_2)_7\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}(CH_2)_7CO_2R}$$

3a R = H　　**5a** R = H　**5b** R = CH_3

3b R = CH_3

n = 0, -1, -2

$CH_3(CH_2)_7CO_2H$

6

$HO_2C\text{-}(CH_2)_7CO_2R$

7a R = H　**7b** R = CH_3

The reaction of oleic acid, **8a**, and methyl oleate **8b** with the ruthenium oxidants was also studied. This is shown in Equation III. Previously we had used the sodium hypochlorite-RuO_2 reoxidation procedure for the oxidative cleavage of oleic acid to acids **6** and **7** (9). In that study, a catalytic amount of RuO_2 was used in conjunction with a molar ratio of hypochlorite to oleic acid of 6:1. In the present work, we used molar equivalents of the ruthenium oxidants to study the mode of oxidation of oleic acid and of methyl oleate. At a molar ratio of 4:1 (oxidant:double bond) both the perruthenate anion, RuO_4^-, and ruthenium tetroxide, RuO_4, quantitatively cleaved the double bonds of **8a** and **8b** to give acids **6** and **7a** or **7b**, respectively (9). At lower molar ratio of reactants (2:1, the partial oxidation products **3** (17%), **4** (24%) and **5** (15%) were formed together with the cleavage products **6** (23%) and **7** (19%). On the other hand, the ruthenate oxyanion, $RuO_4^{=}$, did not react with the double bond of oleic acid at all. This result was in agreement with the earlier work of Schroder et al. who reported that the ruthenate anion did not react with the double bond of cyclohexene (14).

$$\mathrm{CH_3(CH_2)_7CH = CH(CH_2)_7CO_2R \xrightarrow{RuO_4^{n}} \mathbf{3a,b} + \mathbf{4a,b} + \mathbf{5a,b} + \mathbf{6} + \mathbf{7a,b}}$$

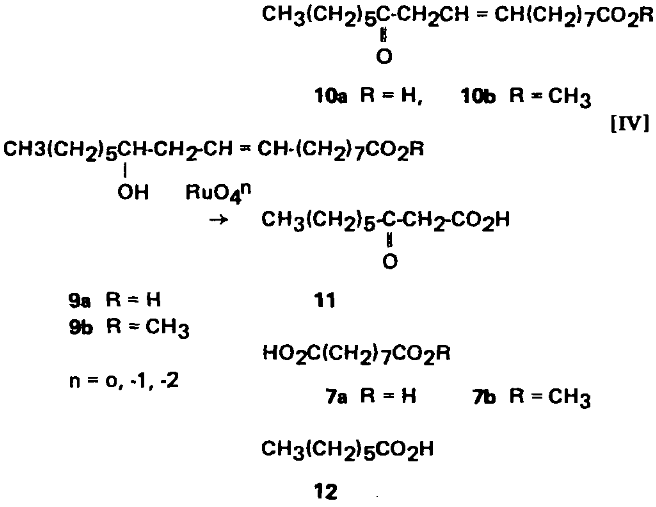
8a R = H　[III]

8b R = CH_3

n = 0, -1

From the foregoing results, the following may be concluded. When the alkaline sodium hypochlorite-RuO_2 reoxidation procedure is used to oxidize unsaturated fatty acids (9), the actual ruthenium oxidant involved is the perruthenate oxyanion, RuO_4^-, and not the ruthenate oxyanion, $RuO_4^{=}$, or ruthenium tetroxide, RuO_4. This conclusion is based on the knowledge that: (a) the ruthenate anion does not attack carbon-carbon double bonds, and (b) ruthenium tetroxide is rapidly reduced to the perruthenate anion at pH >7 (10). Furthermore, as the $RuO_4^{=}$ anion did oxidize hydroxy acids **1a** and cleave dihydroxy acid **3a**, the first step in the oxidation of oleic acid is most probably the formation of the vicinal dihydroxy derivative **3a**. The vicinal diol **3a** then undergoes further oxidation to the acyloin **4a**, then the diketone **5a**, and finally the cleavage acids **6** and **7a**.

In view of the noted difference in oxidative reactivity between the perruthenate and ruthanate oxyanions, we decided to study the oxidation of ricinoleic acid, **9**, with the ruthenium oxidants. The ruthenate anion, $RuO_4^{=}$, was expected to only oxidize the 12-hydroxy group of **9a** to ketoacid **10a** whereas the perruthenate anion would attack both the hydroxy and double bond functionalities of **9a** to give acids **11** and **7a** (Equation IV). In reality, however, the reaction of acid **9a** with RuO_4^- at a molar ratio of 1:6



$$\mathrm{CH_3(CH_2)_5\underset{\displaystyle O}{\underset{\|}{C}}\text{-}CH_2CH = CH(CH_2)_7CO_2R}$$

10a R = H,　**10b** R = CH_3

[IV]

$$\mathrm{CH_3(CH_2)_5\underset{\displaystyle OH}{\underset{|}{C}}H\text{-}CH_2\text{-}CH = CH\text{-}(CH_2)_7CO_2R \xrightarrow{RuO_4^{n}} CH_3(CH_2)_5\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}CH_2\text{-}CO_2H}$$

9a R = H　　**11**

9b R = CH_3

n = 0, -1, -2

$HO_2C(CH_2)_7CO_2R$

7a R = H　**7b** R = CH_3

$CH_3(CH_2)_5CO_2H$

12

yielded, in addition to the expected products **7a** and **11**, large amounts of heptanoic acid, **12** (Equation IV). The formation of **12** could result from cleavage of the C_{11}-C_{12} bond of **10a** or by subsequent oxidation of ketoacid **11** by the perruthenate anion. When RuO_4 was used to oxidize the methyl ester **9b** in organic solvent, a similar product mixture was obtained with the exception that, under these so-called neutral conditions, ~20% of the ketoacid **11** decarboxylated to 2-octanone.

Surprisingly, when ruthenate anion, $RuO_4^{=}$, was allowed to react with acid **9a** at a 1:1 stoichiometry, minor amounts (~25%) of the cleavage acids **11**, **7a** and **12** were also formed in addition to the expected ketoacid **10a**. At higher molar ratios of oxidant to substrate, more of the cleavage products **11** and **7a** predominate (>80% yield). The acids **7a** and **11** seemed to form after the formation of 12-keto-oleic acid **10a**; therefore, the ruthenate anion may attack the enolate anion of acid **10a** with subsequent cleavage of the $C_{11,12}$ and $C_{9,10}$ bonds. This result was unexpected because $RuO_4^{=}$ did not attack isolated double bonds and smoothly converted 12-hydroxystearate to 12-ketostearate.

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New Esterification Method for Resin Acids

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ABSTRACT

The reaction of tetraalkylammonium salts of resin acids using dehydroabietic acid as the model with various alkyl polychlorides was studied as a method for preparing new ester derivatives of rosins. Of the alkyl halides investigated, methylene chloride, 1,1-dichloroethane, 1,2-dichloroethane, trichloroethylene and 1,2,3-trichloropropane reacted with tetrabutylammonium dehydroabietate at moderate temperatures in short reaction times. A number of new esters were identified by NMR, IR and CI-MS. Although many of the primary products were the anticipated monoesters and diesters, some dehydrochlorinated esters were also obtained. The reaction with trichloroethylene resulted in appreciable amounts of dehydroabietic acid anhydride.

INTRODUCTION

Esterification of rosin is difficult because of the hindered tertiary carboxylic acid group of the component diterpene resin acids. Thus, most commercial rosin esters are produced by the reaction of rosin with polyols at high temperature. Such ester formation is energy-intensive and the products are limited to esters of a few available polyols.

The reaction of alkyl monohalides with alkali salts of rosin acids is well known (1,2). However, it is difficult to find a solvent which will dissolve these salts and the alkyl halide without decomposition of reagents and reaction products. Thus, this type of reaction has been of little commercial importance.

Holmberg and Hansen (3) found that the reaction of tetrabutylammonium salts of carboxylic acids with dichloromethane is a convenient method for the preparation of esters of many carboxylic acids. Methylenebisdiesters were obtained in 80% or greater yields by reacting for 4 days in refluxing methylene chloride. These yields were obtained even for such hindered acids as trimethylacetic acid. Application of the tetrabutylammonium salt-alkyl halide procedure to rosins has a potential for energy-conserving preparation of new rosin esters.

EXPERIMENTAL

Reaction

Tetrabutylammonium dehydroabietate (TBA-DeAb) was prepared by mixing 500 mg (1.67 mM) dehydroabietic acid (purity 99+%) dissolved in 10 mL diethyl ether with 2.27 g (1.67 mM) of 19% aq tetrabutylammonium hydroxide. The ether and water were removed with a vacuum evaporator. Other tetralkylamine salts of dehydroabietic acid were prepared in a similar manner.

Reaction of the dehydroabietic acid amine salts with polychloro-compounds was done in reaction vials placed in a constant temperature bath. For example, a 0.6-mL reaction vial containing 20 mg (0.037 mM) of TBA-DeAb and 0.5 mL methylene chloride was placed in the water bath at 40 C for 5 hr. The solution was then transferred to a 10-mL separatory funnel with 5 mL of ether and treated with 2 mL of 5 N H_2SO_4 to quench the reaction. The ether layer was washed with water until neutral, and then dried over $MgSO_4$ After the solvent was removed, the product was analyzed by appropriate methods.

Analysis

Several methods including gas liquid chromatography (GLC), high pressure liquid chromatography (HPLC), infrared (IR) and ultraviolet thin layer chromatography (TLC-UV) were investigated for analyzing the reaction products. The reaction product of TBA-DeAb and methylene chloride was used to evaluate the different methods.

Samples were methylated with ethereal diazomethane