

Published 1/1 2004

Method for Characterization of Gum Rosin by Capillary Gas Chromatography

1. Scope

1.1 These test methods cover the determination of the amounts of certain rosin acids in gum rosin using capillary gas chromatographic separation of the volatile methyl esters of these acids.

1.2 Three methods for forming the methyl esters are described. The classic method for the formation of methyl esters is through the use of diazomethane, but diazomethane is a hazardous and toxic material, and so is no longer the preferred reagent. Methyl esters may be formed through the use of tetramethylammonium hydroxide (TMAH), trimethylphenylammonium hydroxide (TMPAH), or N,N-dimethylformamide dimethyl acetal (DMF-DMA).

1.3 This method is primarily for the identification of gum rosins from specific species of pine trees. It is not designed for the quantitative analysis of gum rosin mixtures. If such analyses are required the internal standard technique described in ASTM Method D5974 should be used.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

D 509 Test Methods of Sampling and Grading Rosin

D 804 Terminology Relating to Naval Stores, Including Tall Oil and Related Products

D 5974 Fatty and Rosin acids in Tall oil fractionation Products by Capillary Gas Chromatography

3. Significance and Use

3.1 Gum rosins are important commercial materials, primarily composed of rosin acids, but also containing some neutral material. For many applications, it is necessary to know the level of the individual rosin acids present in these products. Gas chromatography has proven to be a useful tool for such determinations (see ASTM Test Methods D 509), and capillary chromatography, described in these test methods, is considered to be the most effective gas chromatographic technique currently available.

3.2 Due to hydrogen bonding, unmodified rosin acids cannot be volatilized at atmospheric pressure without undergoing decomposition. So, it is necessary to convert the free acids to the more volatile and more stable methyl esters, prior to chromatographic separation.

3.3 These test methods describe three ways to prepare methyl esters. The classic method is through the use of diazomethane, but diazomethane is a hazardous and toxic material, and so is no longer the preferred agent.

3.3.1 TMPAH or TMAH are satisfactory methylating agents as both produce results that are very similar to those of diazomethane, but without the hazards that are associated with diazomethane.

3.3.2 DMF-DMA gives results comparable to TMPAH and TMAH and is easy and safe to use. However, the reagent is moisture sensitive, requiring samples to be free of any significant levels of water.

PREPARATION OF METHYL ESTERS

4. Conversion By Means of Tetramethylammonium Hydroxide (TMAH)

4.1 Apparatus

4.1.1 Standard Laboratory Equipment

.

4.2 Reagents and Materials

4.2.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2.2 *Tetramethylammonium Hydroxide Solution*, 24 % in methanol, CAS No. 75-59-2.

4.2.3 *Tetramethylammonium Hydroxide Solution*, 6 % (v/v) in methanol. Dilute 25 mL of the reagent described in 4.2.2 with 75 mL of methanol.

4.2.4 *Phenolphthalein Solution*, 1 % (w/v) in methanol.

4.2.5 *Diethyl Ether*, anhydrous.

4.2.6 *Methanol*, anhydrous.

4.2.7 *Acetic Acid*, 5 % volume/volume (v/v) in methanol.

4.2.8 *Toluene*, optional.

4.3 Procedure:

4.3.1 Dissolve the sample from 9.1 in 0.5 to 3.0 mL of a 50:50 ether/methanol mixture, add 2 to 3 drops of phenolphthalein indicator solution, and titrate to a pH of 7.8 to 8.1 or to the very first permanent pink color, with the 6 % solution of TMAH. If the solution is overtitrated, it can be back titrated with the acetic acid in methanol solution to the end point. When the solution is injected into the heated injection port of the chromatograph, the tetramethylammonium salts are pyrolyzed to methyl esters.

NOTE 1—For solid rosin 2 to 3 drops of toluene may be added to the vial prior to the addition of TMAH, to assist in dissolving the sample.

5. Conversion By Means of Trimethylphenylammonium Hydroxide (TMPAH)

5.1 Apparatus:

5.1.1 Standard Laboratory Equipment.

5.2 Reagents and Materials:

5.2.1 *Purity of Reagents*, see 4.2.1.

5.2.2 *Trimethylphenylammonium Hydroxide Solution*, 0.2 M or 0.1 M in methanol, CAS No. 1899-02-1.

5.2.3 *Diethyl Ether*, anhydrous.

5.2.4 *Methanol*, anhydrous.

5.2.5 *Toluene*, optional

5.3 Procedure:

5.3.1 Add 0.5 to 3.0 mL of a 50:50 ether/methanol, to the sample from 9.1. Add 2 to 3 drops of phenolphthalein indicator solution and titrate to the very first permanent pink color with the TMPAH in methanol solution. When the solution is injected into the heated injection port of the chromatograph, the trimethylphenylammonium salts are pyrolyzed to their respective methyl esters.

NOTE 2—For rosins that are difficult to dissolve, 2 to 3 drops of toluene may be added to the vial prior to the addition of TMPAH, to assist in dissolving the sample.

6. Conversion by Means of N,N-Dimethylformamide Dimethyl Acetal (DMF-DMA).

6.1 Apparatus:

6.1.1 *Standard Laboratory Equipment* .

6.2 Reagents and Materials:

6.2.1 *Purity of Reagents*, see 4.2.1.

6.2.2 *N,N-Dimethylformamide dimethyl acetal (DMF-DMA)*, CAS No. 4637-24-5.

6.2.3 *Methanol*, anhydrous.

6.2.4 *Toluene*.

6.3 Procedure:

6.3.1 Place the sample from 9.1 in an appropriate anhydrous vial, and dissolve with approximately 0.5 mL of either methanol or toluene. Add approximately 1 mL of DMF-DMA, mix well, and maintain the sample at 30–40°C for 15 minutes

7. Apparatus

7.1 *Gas Chromatograph*— An instrument equipped with a flame ionization detector (FID) that can be operated at conditions given in 10.1.

7.2 *Column*— The recommended (referee) column is a fused silica BDS column 25 m in length, 0.32 mm internal diameter, with a 0.20 µm film thickness, and provides separations equivalent or better than that displayed in Fig. 1 - 3. Other suitable columns are high resolution columns between 15 and 60 m in length, 0.25 to 0.53 mm internal diameter, with a 0.20-µm film thickness of biscyanopropylsiloxane type liquid phase.

7.3 *Analytical Balance*, accurate to 0.1 mg

8. Reagents and Materials

8.1 *Purity of Reagents*—See 4.2.1

8.2 *Rosin*— Rosin should be sampled following the procedures described in publications such as the Chinese National Standard, GB 8145-87, ASTM Test Method D 509 or the Naval Stores Act of 1923 (42 Stat 1435.7 USC-91-99) as amended in 1951.

NOTE 3—Rosin samples need to be freshly broken from a larger mass to ensure the results are not affected by air oxidation of the rosin.

9. Procedure

9.1 *Preparation of Test Sample*—Weigh approximately 50 mg of sample into a suitable vial, and convert to methyl esters or substituted ammonium salts as described in Sections 4, 5, or 6.

10. Set-up of Gas Chromatograph (GC)

10.1 Set the GC conditions so that they are approximately (see Note 4) as follows:

Column temperature; Isothermal	195°C
Injection port temperature	300°C
Injection port liner	glass split
Detector temperature	280°C
Carrier gas	Hydrogen or Helium
Linear gas velocity	40 cm/s
Split ratio	40 to 1
Detector	FID
Hydrogen	50 kPa
Air	100 kPa

NOTE 4—These are the typical operating conditions for the instrument using the BDS column. The individual instrument should be adjusted in accordance with manufacturer's instructions to optimize desired performance. Ongoing adjustments in operating temperature and flow rate may be necessary to maintain optimum performance of the column due to aging. If other columns are used (see 7.2) operating conditions should be used to give separations equivalent or better than that displayed in Fig. 1 - 3. In the US suitable BDS columns can be obtained from Restek Corporation (800 356 6801) and in Europe from HNU Nordion (358 9 565 7240).

11. Analysis

11.1 Inject 0.5 to 1.0 μL of the test sample prepared in 9.1.

NOTE 5—Dilution of the sample with additional solvent may be necessary to obtain injections that do not overload the column or detector.

12. Calculation

12.1 Sum all the areas of the individual peaks, exclusive of the solvent peak, to obtain the total peak area.

12.2 Calculate the relative percent of each rosin acid methyl ester present, uncorrected for the amount of polymeric materials present, as follows:

$$\text{Rosin acid \%} = (A \times 100) / TA$$

where:

A = peak area for rosin acid methyl ester being determined, and
 TA = sum of areas of all rosin acid methyl ester peaks.

NOTE 6—See Fig. 1-3 for typical chromatograms of selected gum rosins and Table 1 for their compositions estimated from these chromatograms

13. Report

13.1 Report the area percent of the individual rosin acids to the nearest 0.1 %

13.2 By comparison with the data in Table 1 and Fig. 1, 2 and 3, establish the identity of the gum rosin

Table 1 *Typical Composition of Characteristic Resin Acids in Gum Rosins from some Pine Species*

Resin Acid	Pinus Massoniana (%)	Pinus Merkusii (%)	Pinus Elliottii (%)	Relative Retention
Communic	0	0	5	0.588
Palustric	25	20	19	0.634
Isopimaric	2	15	17	0.664
Abietic	35	35	23	0.967
Dehydroabietic	4	5	5	1.000
Neoabietic	16	5	20	1.092
Mercusic	0	7	0	1.514

NOTE 7—Capillary Gas Liquid Chromatography (GLC). Conversion of Rosin resin acids to their methyl derivatives by means of tetramethylammonium hydroxide (TMAH) procedure. Column fused silica BDS, l = 25m, d = 0.32mm, film = 0.2µm. T = 195°C isotherm, column flow = 50 kPa H₂

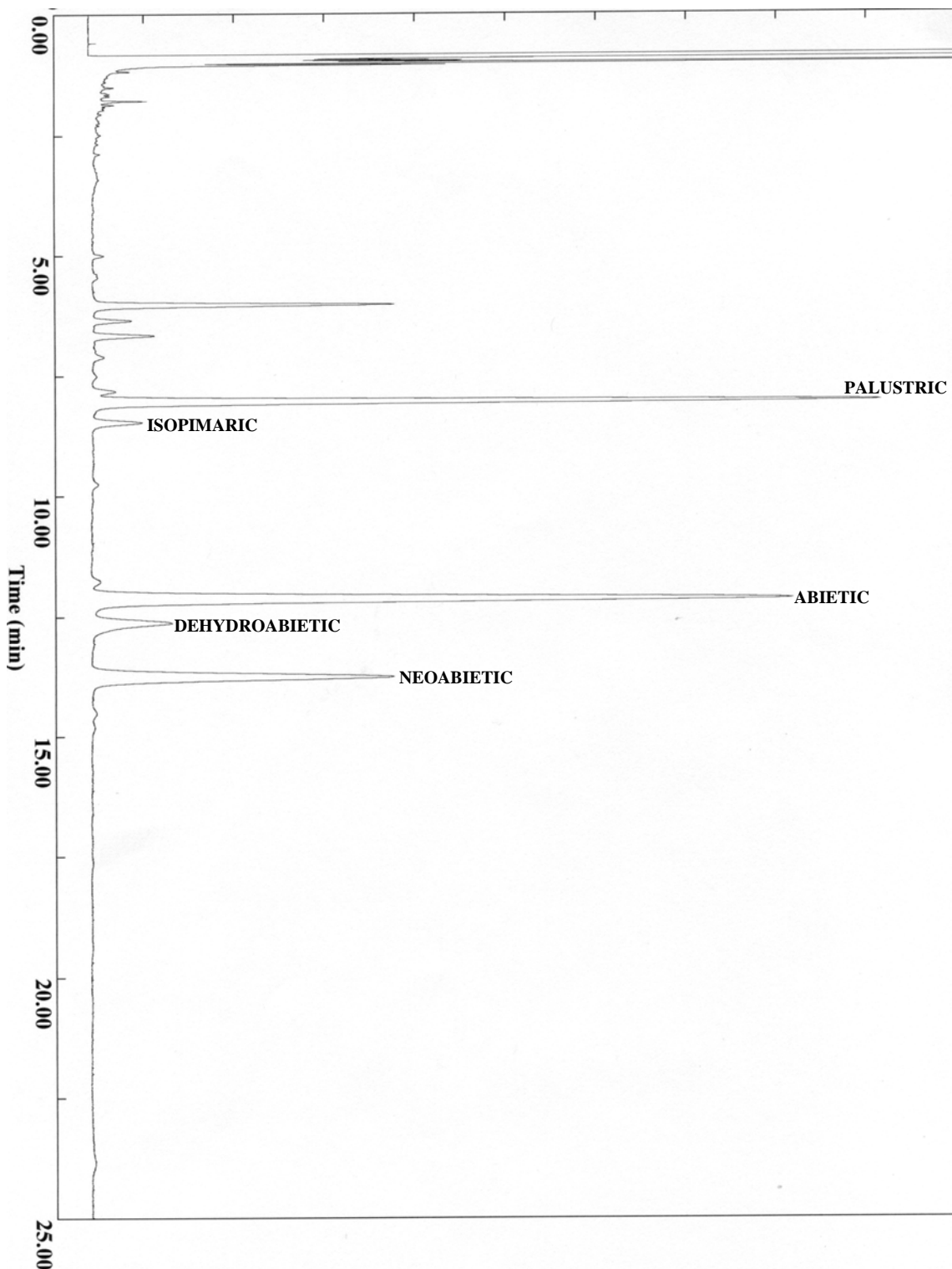


Figure 1 *Chromatogram of Resin Acid Methyl Esters from Pinus Massoniana Rosin*

NOTE 9—Capillary Gas Liquid Chromatography (GLC). Labeled peaks are eluted as methyl esters. Conversion of resin acids to their methyl derivatives by means of tetramethylammonium hydroxide (TMAH) procedure. Column fused silica BDS, l = 25m, d = 0.32mm, film = 0.2 μ m. T = 195°C isotherm, column flow = 50 kPa H₂.

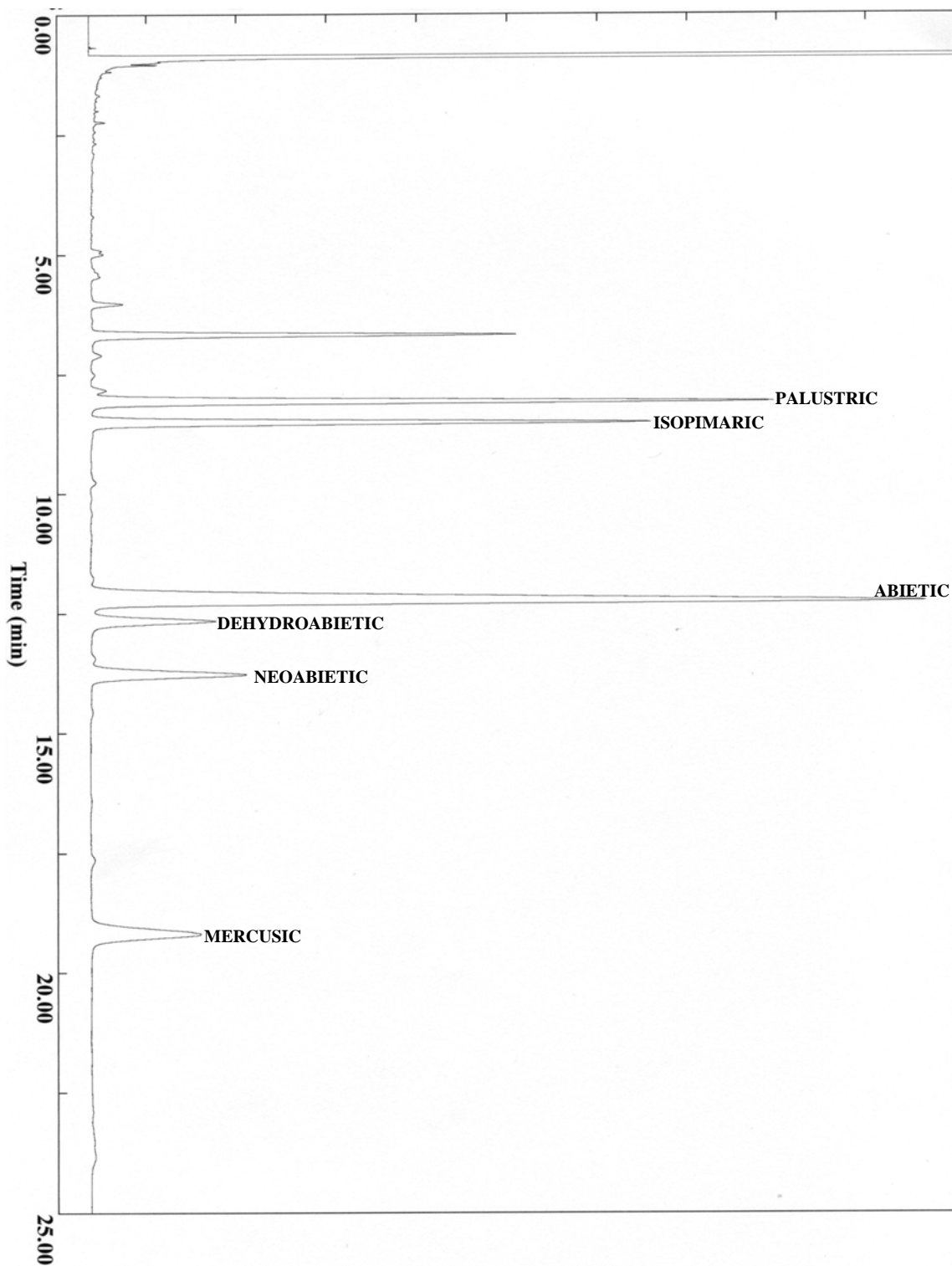


Figure 2 *Chromatogram of Resin Acid Methyl Esters from Pinus Merkusii Rosin*

NOTE 10—Capillary Gas Liquid Chromatography (GLC). Labeled peaks are eluted as methyl esters. Conversion of resin acids to their methyl derivatives by means of tetramethylammonium hydroxide (TMAH) procedure. Column fused silica BDS, l = 25m, d = 0.32mm, film = 0.2 μ m. T = 195°C isotherm, column flow = 50 kPa H₂.

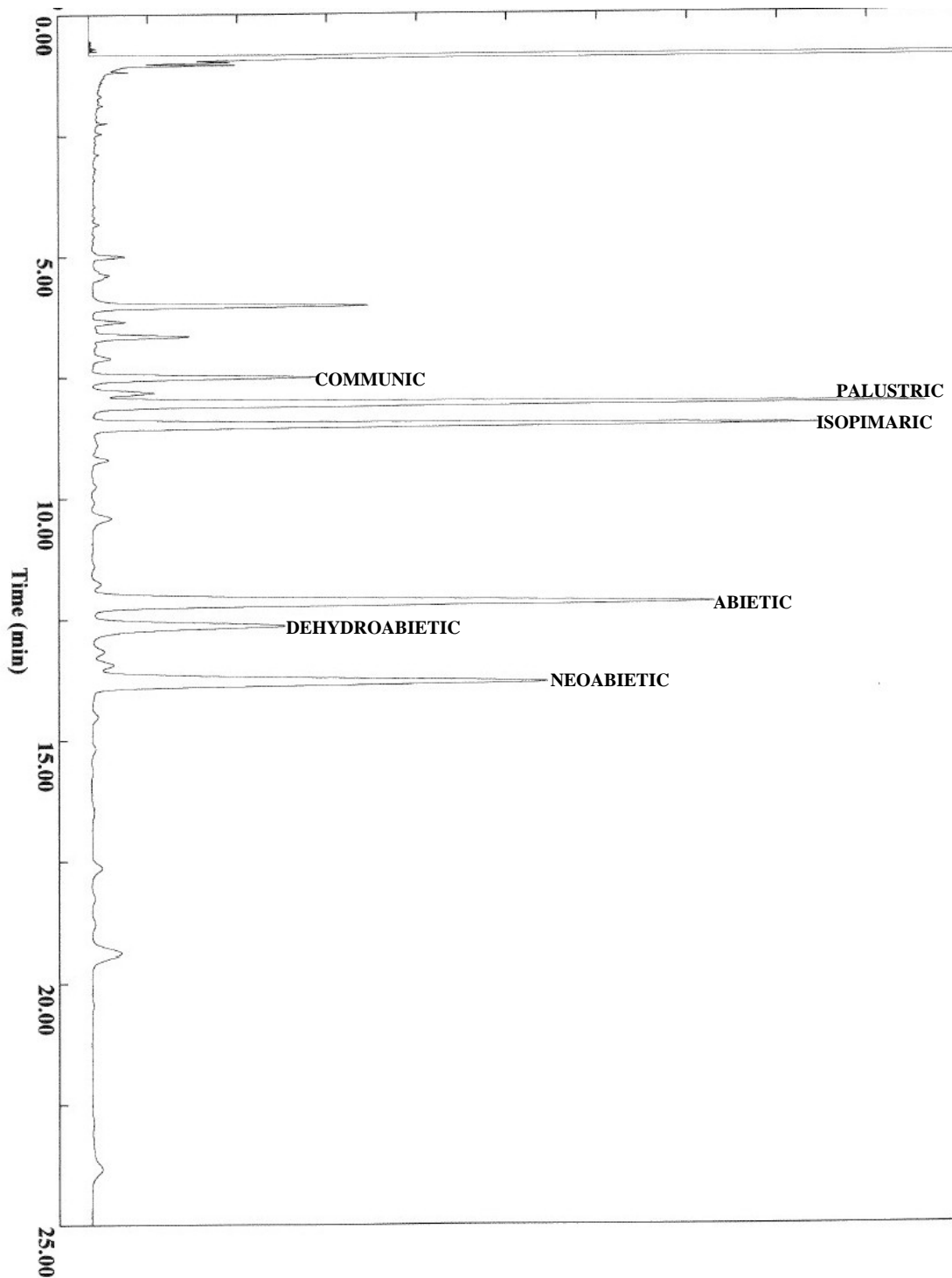


Figure 3 *Chromatogram of Resin Acid Methyl Esters from Pinus Elliottii Rosin*

NOTE 11—Capillary Gas Liquid Chromatography (GLC). Labeled peaks are eluted as methyl esters. Conversion of resin acids to their methyl derivatives by means of tetramethylammonium hydroxide (TMAH) procedure. Column fused silica BDS, $l = 25\text{m}$, $d = 0.32\text{mm}$, film = $0.2\mu\text{m}$. $T = 195^\circ\text{C}$ isotherm, column flow = 50 kPa H_2 .