H4R CONSORTIUM

Reference Document on the Identification of Rosin and Rosin Derivatives

Sponsored by the H4R Consortium[1]

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Executive Summary

The different analytical techniques commonly used in regulatory fora have been reviewed for their utility in determining the identification and composition of rosin and its derivatives.

There is no single analytical technique available that identifies the chemical nature of the rosin or rosin derivatives. Only by combining techniques and also knowing the chemical process applied, can the identity and composition be established to the maximum extent possible.

From this review the following analyses are recommended.

Table 1 - Overview of analyses

Rosin Category / Information	Section	Rosin, hydrogenated rosin and their salts	Rosin esters	Rosin adducts and rosin adducts salts	Rosin adduct esters
Infra-Red	2.1	+	+	+	+
UV-VIS	2.2	+	+	+	+
^{1}H-NMR	2.3	+	+	+	+
^{13}C-NMR	2.4	-	-	-	-
Chromatography					
GC	2.4.1	+	-	+	-
HPLC	2.4.2	-	-	-	-
SEC	2.4.2	-	+	-	+
Mass spectrometry*					
LCMS	2.5	+	+	-	+
Fragmentation MS		-	-	+	-
MALDI / Electrospray		-	-	-	-

*Not a routine technique for these types of substances

This document gives reference values and also an example of good practice when reporting the data.

Contents

Executive Summary 1

1. Introduction 3

2. Review of analytical techniques for rosin and rosin derivatives 5

2.1 Infra-Red spectroscopy 5

2.2 UV-VIS 8

2.3 ^{1}H-NMR 11

2.4 ^{13}C-NMR 21

2.5 Chromatography 23

2.5.1 Gas chromatography (GC) 23

2.5.2 Liquid Chromatography 25

2.6 Mass spectrometry 28

2.7 Acid value 37

3. Manufacturing: 38

3.1 Rosin 38

3.2 Hydrogenated rosin 38

3.3 Rosin esters 38

3.4 Rosin adducts & Rosin adduct salts 38

3.5 Rosin adduct, esters 41

3.5.1 Rosin, formaldehyde adduct 41

4. Conclusions 41

Appendix 1 - Reference IR Spectra 43

Appendix 2 - Reference Spectra UV-VIS 47

Appendix 3 – NMR 48

Appendix 4 - Mass spectra for specific rosin acid methyl esters 104

1. Introduction

Rosin is obtained from pine trees and consists of hundreds of components. The variation in the ratio of the components is caused, amongst others, by geographical as well as climatic differences (see Table 1 below). For this reason rosin and its derivatives from industrial processes based on rosin are UVCB's.

The question arises as to how to demonstrate that the substance used in testing (phys/chem, tox and ecotox) is indeed the substance that has been registered.

As we will see below, there is no single analytical technique available that identifies the chemical nature of the rosin or rosin derivatives. Only by combining techniques and also knowing the chemical process applied, can the identity and composition be established to the maximum extent possible.

This document is intended to give guidelines on the identification of rosin and rosin derivatives.

Table 2Principal Resin Acids

Principal Resin Acids in Typical Pine Oleoresins and Some Commercial Gum Rosins[1]

Samples	*Pimaric*	*Sandara-copimaric*	*Communic*	*Levo-pimaric/ Palus-tric*	*Iso-pimaric*	*Abietic*	*Dehydro-abietic*	*Neo-abietic*
OLEORESIN				*Per Cent of Acid in Acid Fraction*				
P. elliottii var. elliottii	5.1	1.8	3.1	37	21	9.7	3.7	16
P. elliottii var. densa	3.8	1.9	3.1	38	21	12	3.7	16
P. palustris	5.4	1.1	0	52	10	9.4	8.3	13
P. taeda	8.7	2.2	0	64	T	8.6	6.3	9.5
P. ponderosa	7.6	2.9	0	40	15	11	8.2	11
P. halepensis	0	1.2	0	39	10	37	1.5	9.7
P. brutia	0	1.2	0	44	10	32	2.5	10
P. pinaster	8.0	2.0	0	39	12	14	4.2	18
P. caribaea	4.2	2.2	0	49	8	10	8.6	16
P. peuce	1.8	1.0	0	12	32	35	0.8	14
ROSINS								
American	5.1	1.8	2.8	25	17	22	5.7	20
American[2,3]	5.4	1.8	1.8	20.3(1.4)	14.2	27.9	7.1	16.3
Brazilian[2]	4.7	1.7	3.2	11.4(.3)	18.2	36.3	5.4	
Burmese	7.9	3.0	0	44	8.3	30	6.0	2.2
Chinese	9.2	2.7	0	22	1.5	44	4.3	15
French	10	2.2	0.3	22	7.0	36	4.9	17
Greek	0	1.9	0	14	11	50	4.5	13
Honduran	9.6	2.2	0	21	17	22	12	15
Indian	9.2	1.5	0	11	20	38	2.0	18
Mexican[2,4]	6.8	1.2	0	9.8(0.3)	12.9	53.3	7.8	6.1
Portuguese	8.8	1.9	0.7	30	5.3	32	5.1	16
Portuguese[2]	8.3	1.4	0	20.4(11.7)	4.5	27.7	5.8	17.2
Russian	7.8	2.4	0	27	5.6	35	5.3	17
Spanish	8.7	1.5	0	27	0	36	1.9	24
Turkish	0	1.3	0	24	13	41	5.1	15

[1]Data from ref. *31*. This table also appears in Chapter 4 as Table 1.
[2]D.F. Zinkel, Private communication. Palustric values given first; levopimaric values are in ().
[3]Also contains small amounts of imbricataloic acid, as well as imbricatoloic and isocupressic acids and their acetates (*32*).
[4]A distilled rosin.

Source: Naval Stores, 1989, editors Duane F. Zinkel and James Russell, ISBN 0-9600416-2-5

2. Review of analytical techniques for rosin and rosin derivatives

2.1 Infra-Red spectroscopy

IR spectroscopy can be used to provide an overview of some functional groups and has specific profile dependent upon the rosin derivative.

Analysis of the IR spectrum shows some items that are noteworthy:

- The O-H stretch vibration at ~3500 cm^{-1} is only visible in the esters, not in rosin or hydrogenated rosin. The intensity of the peak could be caused by excess alcohol or incomplete esterification of the polyol (ratio of mono-, di-, tri- and/or tetra-ester may vary).

- The O-H stretch vibration of the acid group is visible as a very broad band from 3500 – 2500 cm^{-1} (dotted, curved line in the spectra below) with two weak absorptions at 2652 and 2528 cm^{-1}, which do not appear in any of the spectra of the esters.

- The C=O stretch vibration in the acid group absorbs at a lower wavenumber (1690-1700 cm^{-1}) than in the esters (1715-1735 cm^{-1}).

  The C=O stretch vibration region for the metal salts of rosin acids need special attention. Remarkable are the two absorptions in the regions in the range of 1520 – 1550 (strong) and 1620 – 1650 cm^{-1} (medium). The frequency of these absorptions seems to be depending on the water or hydroxide content of the test sample. Rosin monovalent salts (e.g. Na, K) are hygroscopic; divalent salts (e.g. Ca, Mg, Zn) are not hygroscopic, but may contain hydroxide.

- The complex region below 1500 cm^{-1} is the so-called fingerprint area. In general it is difficult to assign absorption to specific vibrations. Comparison of the spectrum of the test sample with reference spectra can give information on the substance identity.

IR characteristics of different rosin derivatives are given in Table 2

Reference spectra (See Appendix 1)

It is noted that the commonly available published spectra were prepared over 20 years ago. It is unclear as to the quality of the samples used, as well as the calibration of the spectrometer. For this reason H4R organised a new reference set in 2011.

Conclusion: Infrared spectra can give indications on the nature of the substance. However, it is only possible to identify a substance by comparing carefully the spectra of rosin and rosin derivatives with reference spectra.

Recommendation to Registrants

a) Include the reference set of spectra used in registration dossier

b) Include in section 1.4 one spectrum of the legal entity's registered substance.

c) Draw a conclusion on the identity by comparison to the reference spectra.

Table 3 Infra-red Absorption of Rosin and some derivatives

absorption (cm^{-1})	Vibration	Comment	Rosin	Rosin, Disproportionated	Rosin, Disproportionated, K-salt	Rosin, Disproportionated, Na-salt	Rosin, Disproportionated, Ca-salt	Rosin, Disproportionated, Ca/Zn-sal	Rosin, Disproportionated-sal	Rosin, hydrogenated	Rosin, glycerol esters	Rosin, pentaerythritol esters	Rosin, triethylene glycol esters	Rosin, hydrogenated, glycerol esters	Rosin, hydrogenated, pentaerythritol esters	Rosin, fumarated	Rosin, fumarated, pentaerythritol ester (acid number 4 - 8)	Rosin, fumarated, pentaerythritol ester (acid number 143)	Rosin, fumarated, decyl ester (acid number 62)
± 2300 - 3600 (acid)	O-H stretch (acid)	peak intensity can vary	+	+	-	-	-	-	-	+	-	-	+	-	-	+	-	+	+
± 3514	O-H stretcvh alcohol	peak intensity can vary	-	-	-	-	-	-	-	-	+	+	+	+	+	-	+	+	-
± 3354 (high acid number fumarated PE-ester																			
3360	O-H stretch (water)	strong / broad	-	-	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-
2866 + 2925	C-H stretch (alkanes)	strong	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2652	C-H stretch (acidic substances)	weak	+	+	-	-	-	-	-	+	-	-	-	-	-	+	-	-	-
2528	C-H stretch (acidic substances)	weak	+	+	-	-	-	-	-	+	-	-	-	-	-	+	-	-	-

absorption (cm^{-1})	Vibration	Comment	Rosin	Rosin, Disproportionated	Rosin, Disproportionated, K-salt	Rosin, Disproportionated, Na-salt	Rosin, Disproportionated, Ca-salt	Rosin, Disproportionated, Ca/Zn-salt	Rosin, Disproportionated-salt	Rosin, hydrogenated	Rosin, glycerol esters	Rosin, pentaerythritol esters	Rosin, triethylene glycol esters	Rosin, hydrogenated, glycerol esters	Rosin, hydrogenated, pentaerythritol esters	Rosin, fumarated	Rosin, fumarated, pentaerythritol ester (acid number 4 - 8)	Rosin, fumarated, pentaerythritol ester (acid number 143)	Rosin, fumarated, decyl ester (acid number 62)
± 1780 (anhydride)	C=O stretch	strong	-	-	-	-	-	-	-	-	-	-	-	-	-	+	-	+	+
± 1730 (esters)	C=O stretch	strong	-	-	-	-	-	-	-	-	+	+	+	+	+	-	+	+	+
± 1690 (acid)	C=O stretch	strong	+	+	-	-	-	-	-	+	-	-	-	-	-	+	-	+	+
± 1602 - 1530 (salt)	C=O stretch	strong (salt: medium - broad)	-	-	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-

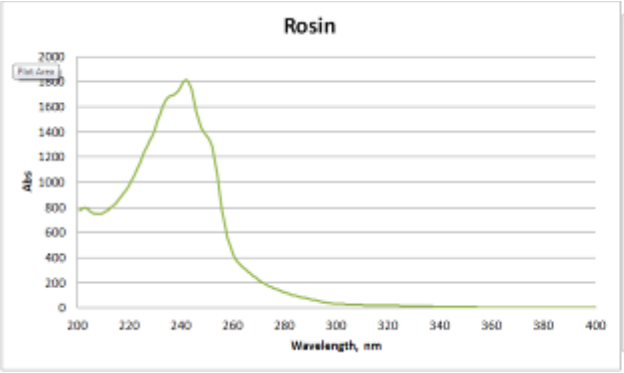
Reference Infrared spectra have been developed[2] on Rosin and 15 derivative derivatives and these spectra are available in Appendix 1.

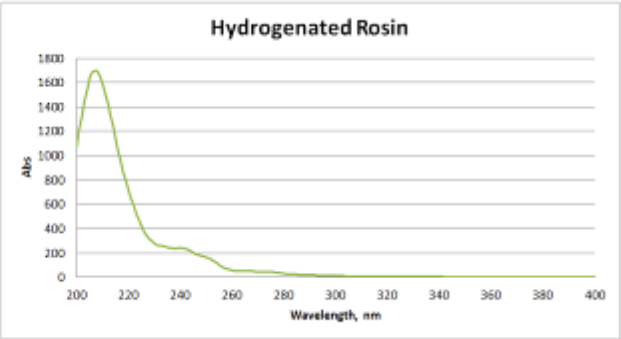
[2] Harlan Laboratories (2011)

Report - CAS No's 8050-09-7, 9007-13-0, 61790-50-9, 61790-51-0, 68334-35-0, 68440-56-2, 8050-25-7, 8050-26-8, 8050-31-5, 8050-28-0, 65997-04-8, 95009-65-7, 160901-14-4, 92202-14-7, 94581-15-4 and 91081-53-7: Determination of Infrared Spectra. Study Number: 41104486

2.2 UV-VIS

Rosin and rosin derivatives are typically amber coloured. In the visible part of the spectrum there is no absorption and it is only in the UV spectrum that absorption is seen. Rosin has two absorptions: 205 nm and a stronger absorption at 240 nm (see figure). Upon hydrogenated the absorption at 240 nm diminishes:





The absorption at 240 nm is linked to conjugated double bonds in resin acids. It should be noted that upon esterification a certain amount of disproportionation takes place as a natural process. This is clearly visible in the spectra of the esters. The hydrogenated versions of the esters show an even further reduction of the absorption at 240 nm.

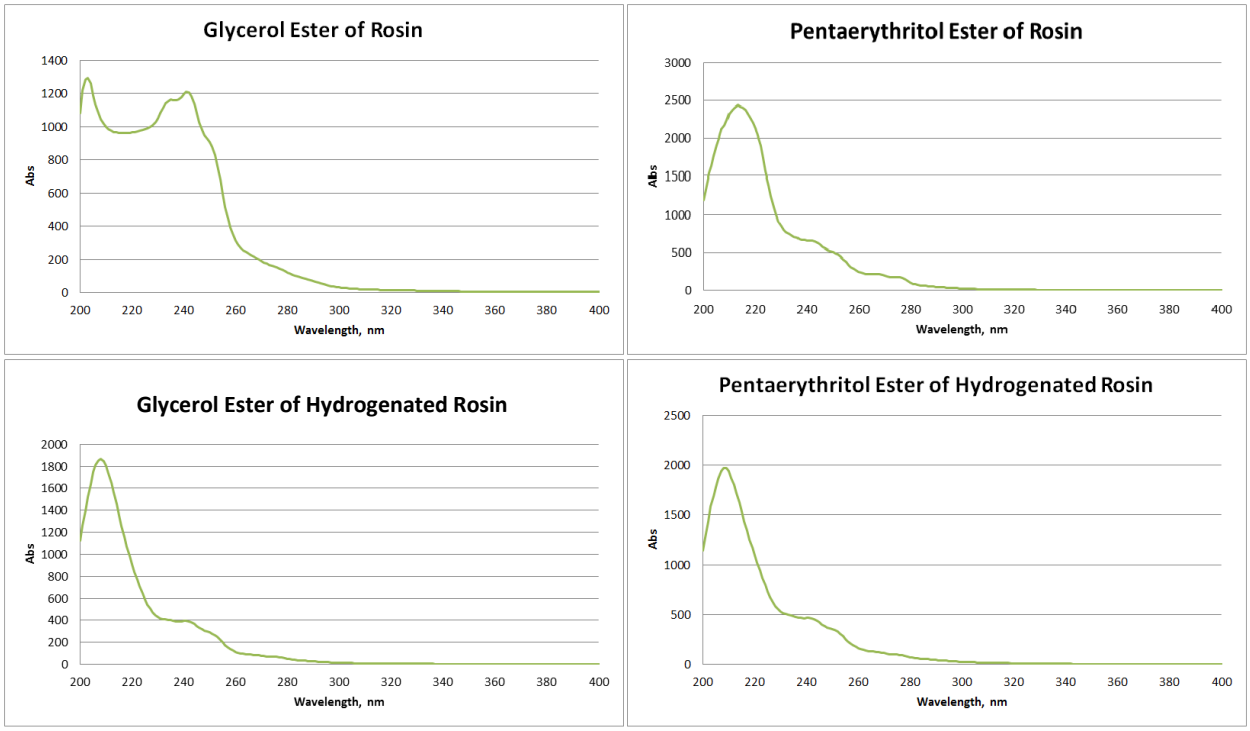
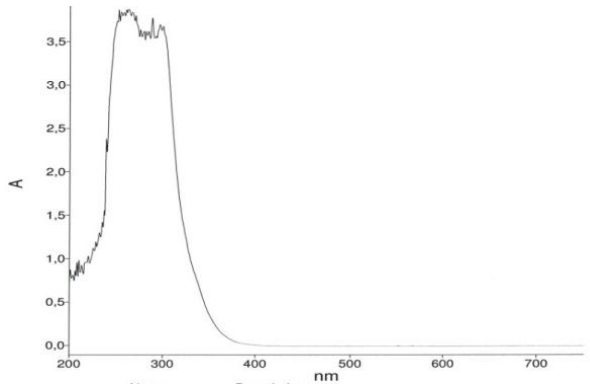


Figure Pentaerythritol Ester of Fumarated Adduct of Rosin



Solubility is an important issue as rosin and rosin derivatives do not dissolve in water at pH 2 or 7. At pH 10 only those resins that may form salts will be soluble, thus excluding most rosin derivatives (including esters). Heptane is a commonly used solvent.

Clearly, the UV-VIS spectra do not contribute to the identification of a substance.

Recommendation for registrants

- UV/VIS spectra have to be recorded in an organic solvent

- Record the region 200 – 800 nm

Reference spectra – See Appendix 2

2.3 ^{1}H-NMR

The proton NMR spectra show several regions that can help to define functionalities in the test substance:

carboxylic acid (9-11 ppm)

- aromatic (7-7½ ppm)
- olefinic (4½ - 6 ppm)
- ester (~4 ppm)
- aliphatic (0.8 – 3 ppm)

Interpretation

It is by definition very difficult to assign certain absorptions to specific chemical substances. Rosin is a UVCB and its derivatives are even more complex than their parent substance. Skakovskii et al (Journal of Applied Spectroscopy, ***75***, No 3, pages 439-443 [2008]) have assigned the peaks of aromatic and olefinic absorptions to individual resin acids.

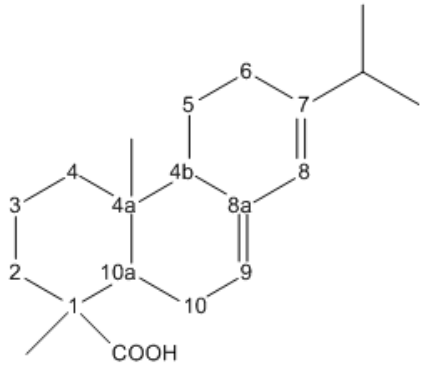
^{1}H-NMR spectra can be calculated. The simulated spectra in this document have all been generated by use of ChemDraw Ultra, version 11.0. By combining calculated spectra, one can simulate the spectrum of rosin.

Comparison of the simulated spectrum of all resin acids with the spectrum recorded by Skakovskii et al shows the limitations of a simulated spectrum. Nevertheless, simulated spectra show where to look for peaks that are specific for specific rosin derivatives.

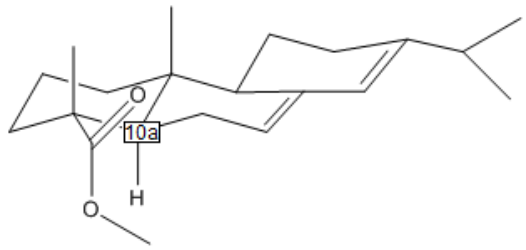
The phenomena in ^{1}H-NMR are always local, i.e. the chemical shift is determined by the type of chemical bond (single bond or double bond) and the type of atoms/groups in the direct vicinity of the proton in question. E.g., the proton at position 10a absorbs at 1.76 ppm in abietic acid and at 2.07 in the methyl

For rosin derivatives the most important are in the ^{1}H-NMR lies between 3.5 and 6 ppm. E.g., the protons ìn the ethylene group next to position 7 in (iso)pimaric acid, absorb at 5.0 ppm. No other absorptions are observed at 5 ppm. Upon hydrogenation, this absorption will disappear. So, the absorption at 5.0 ppm can be used as a marker for hydrogenation.

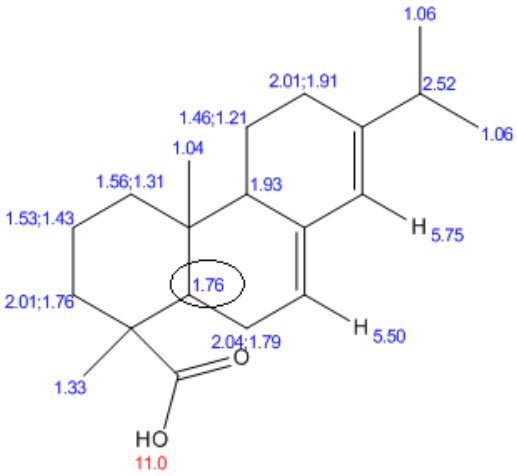
Also, the hydrogen atoms in the alcohol show absorptions that are characteristic. The table below shows the most important (calculated) peaks. In the Annex the real spectrum as well as the calculated spectrum is shown.



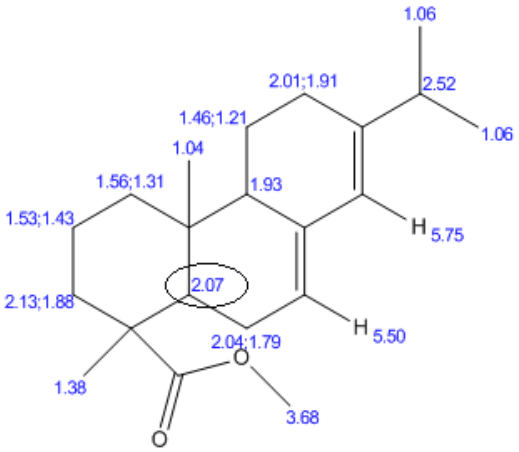
Phenanthrene-based numbering system



Steric proximity of the ester group to the hydrogen atom at position 7



1H-NMR chemical shifts in abietic acid



1H-NMR chemical shifts in methylabietate

Table 4 Characteristic absorptions in (iso)pimaric acid

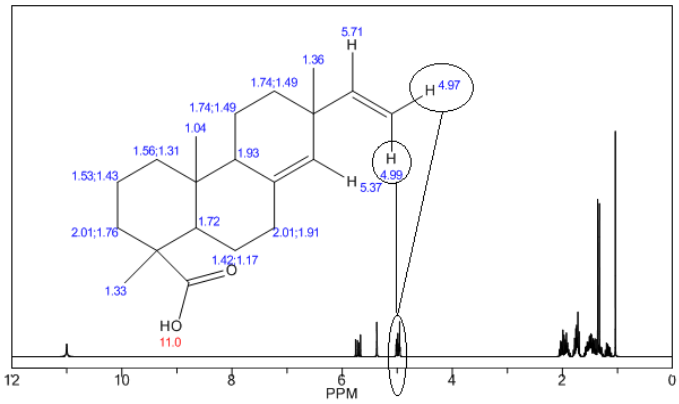
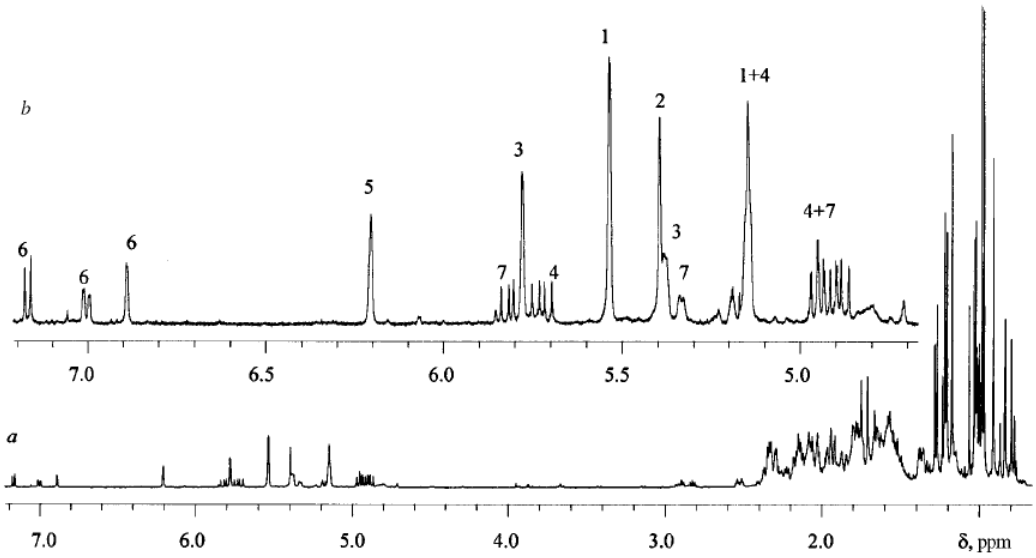


Table 5 Characteristic absorptions in calculated 1H-NMR spectra

	substance	alcohol OH	C-H adjacent to ester	C-H adjacent to ether	C-H adjacent to alcohol
Category 2	abietic acid, methyl ester	-	3.68	-	-
	abietic acid, methyl ester (Landucci*)	-	3.37	-	-
	abietic acid, triethylene glycol di-ester	-	4.25	3.65	-
	abietic acid, triethylene glycol mono-ester	3.65	4.25	3.54, 3.56, 3.65	3.44
	abietic acid, pentaerythritol tetra-ester	-	4.00	-	-
	abietic acid, pentaerythritol mono-ester	3.65	4.00	-	3.45
	abietic acid, glycerol tri-ester	-	4.32, 5.15	-	-
	abietic acid, glycerol 1,2-di-ester	3.65	4.20, 4.45, 4.64	-	3.65, 3.90
	abietic acid, glycerol 1,3-di-ester	3.58	4.23	-	4.41
	abietic acid, glycerol 1-mono-ester	3.58, 3.65	4.11, 4.36	-	3.56, 3.81, 3.90
	abietic acid, glycerol 2-mono-ester	3.65	4.13	-	3.59
	abietic acid, neopentylglycol di-ester	-	4.00	-	-
	abietic acid, neopentylglycol mono-ester	-	4.00	-	3.45
	abietic acid, trimethylolpropane tri-ester	-	4.00	-	-
	abietic acid, trimethylolpropane di-ester	3.65	4.00	-	3.45
	abietic acid, trimethylolpropane mono-ester	3.65	4.00	-	3.45

Figure 1 1H-NMR spectrum of rosin as published by Skakovskii et al (Journal of Applied Spectroscopy, 75, No 3, pages 439-443 [2008]).



^{1}H NMR spectrum of a $CDCl_3$ solution of balsam from pine resin collected in the vicinity of Gomel: a) total spectrum, b) aromatic and olefin proton region. The numbers indicate the lines belonging to the corresponding resin acids.

Chemical Shifts (δ, ppm) of Signals Used for Quantitative Analysis in the ^{1}H NMR Spectra of Resin Acids (solutions in $CDCl_3$).

Acid		Number of the carbon atom								
number	name	5	6	8	9	11	12	13	14	15
1	Levopimaric acid		5.11	5.49		1.13	0.87		0.94	0.93
2	Palustric acid			5.40		1.21	1.03		1.07	1.04
3	Abietic acid			5.78	5.38	1.26	0.84		1.03	1.01
4	Pimaric acid			5.15		1.24	0.78	5.72	4.95	1.00
									4.91	
5	Neoabietic acid			6.21		1.22	0.80		1.75	1.71
6	Dehydroabietic acid	7.20	7.04	6.92		1.32	1.25		1.26	1.26
7	Isopimaric acid				5.33	1.27	0.87	0.91	5.81	4.93
										4.87

Figure 2 Simulated 1H-NMR spectrum of all resin acids combined. Note that the spectrum is obtained by adding up the spectra of all resin acids in equal ratios, which does not reflect rosin as used by industry. Also, neutral species, i.e. components without a car

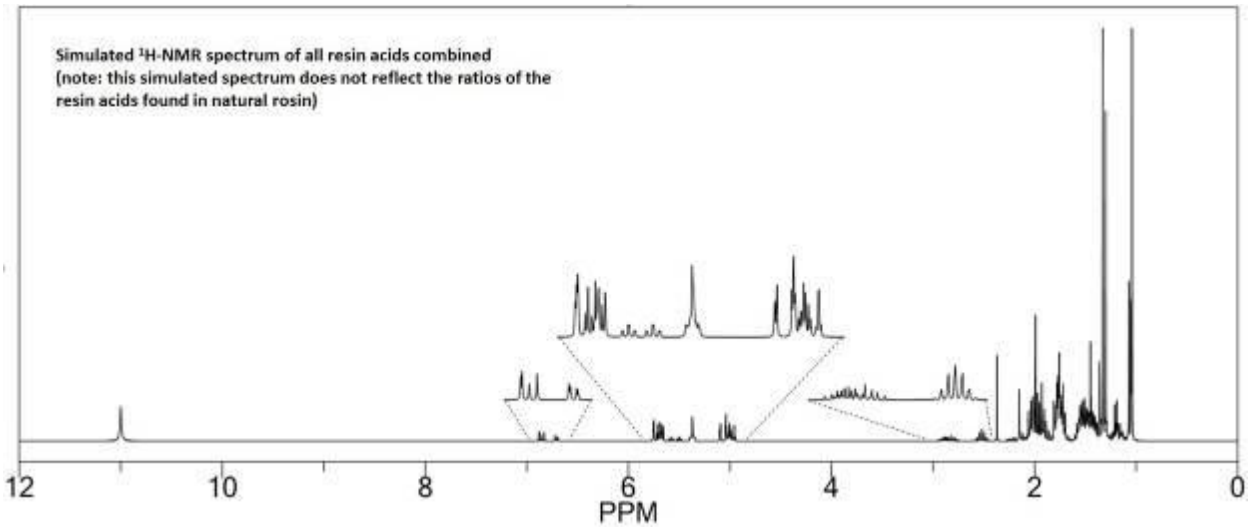
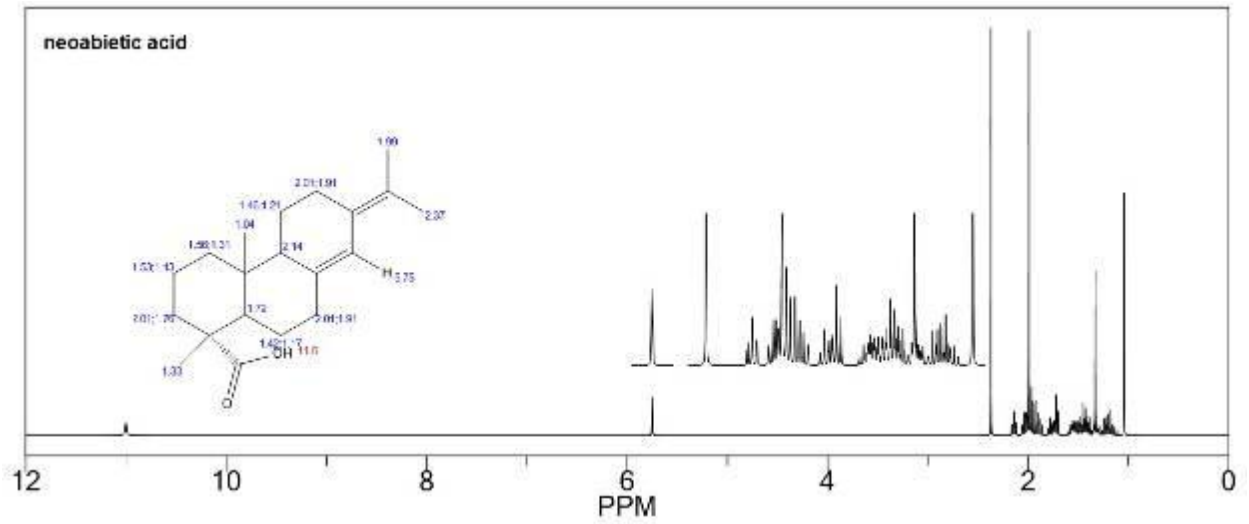
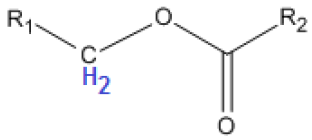


Figure 3 The simulated spectrum of Neoabietic acid. Note the characteristic peak at 5.8 ppm. In the spectrum of Skakoskii this peak can be found at 6.21 ppm, showing the limitations of simulated spectra.

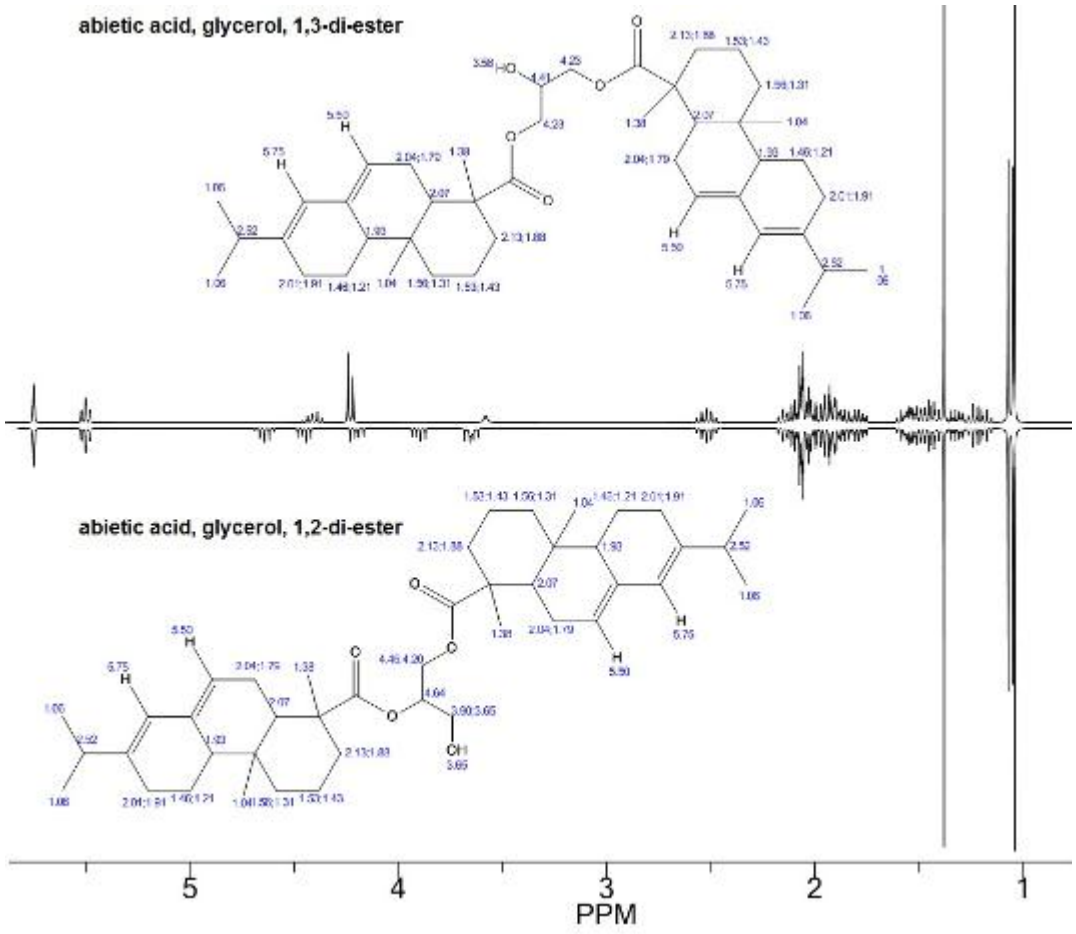


The following observations are very useful in the identification of rosin derivatives:

- the olefinic peaks should decrease or disappear upon hydrogenation, disproportionation or adduct formation. Special attention should be given to the absorption of the olefinic protons in the ethylene group in (iso)pimaric acid. This absorption lies at 5.0 ppm
- the proton of the acid group (10 – 11 ppm) should disappear upon esterification or salt formation. Note that the peak of the proton in the carboxylic acids group is usually extremely broad, making it almost always invisible.
- the aromatic peaks give an indication on the degree of disproportionation, more aromaticity implies greater disproportionation
- protons of the alcohol next to carboxylic function in esters are very specific [~4 ppm])



As the coupling of protons is dependent on the distance to other protons, one may safely assume that upon derivatisation of rosin acids, the chemical shifts for the tricyclic diterpene protons will not shift significantly. The simulated spectra demonstrate that the assumption is realistic in a model. For example, the di-ester of abietic acid with glycerol knows two types: glycerol-1,2-diabietate and glycerol-1,3-diabietate. The change in the spectra is dramatic in the 3.5 – 5 ppm region. The protons in the abietic acid skeleton do not change. It is only the protons near the center of reaction (in this case the ester functionality) change their chemical shifts.


abietic acid, glycerol, 1,3-di-ester
abietic acid, glycerol, 1,2-di-ester
5
4
3
2
1
PPM

It goes without saying that the real spectrum is spectacularly more complex as all moieties are present. In total, for the glycerol ester there are 8,000 isomers for the tri-ester, 800 for the di-ester and 400 for the mono-ester, totalling 9,200 isomers. Nevertheless, it will be demonstrated that a substance can be identified by specific absorptions in the 3.5 – 6.5 ppm region (see table).

Figure 4 Combined real world spectra, and the simulated spectrum of abietic acid

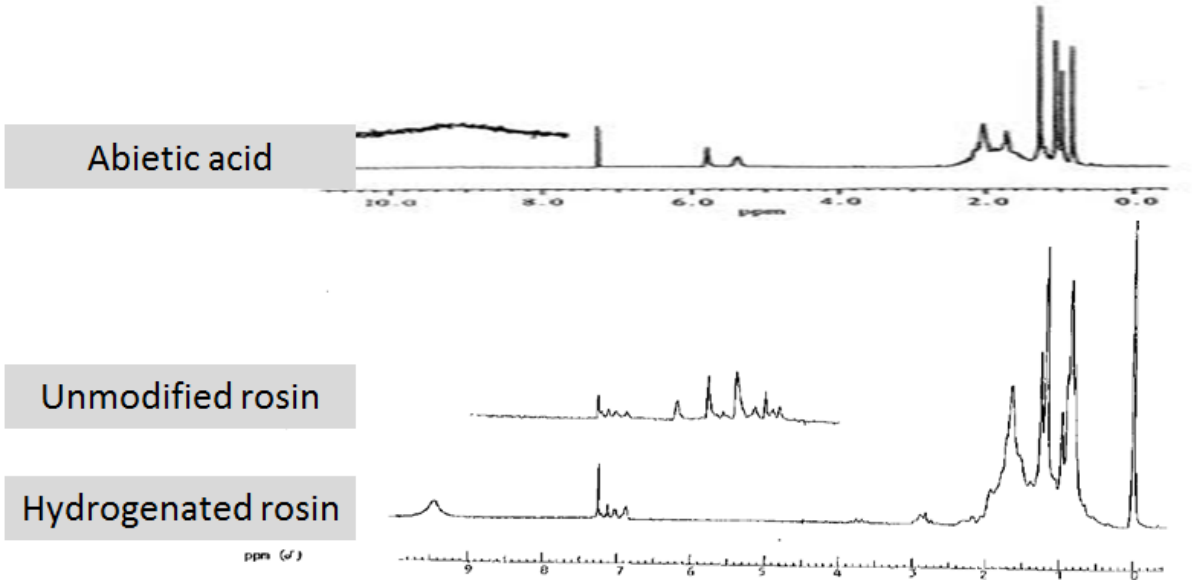
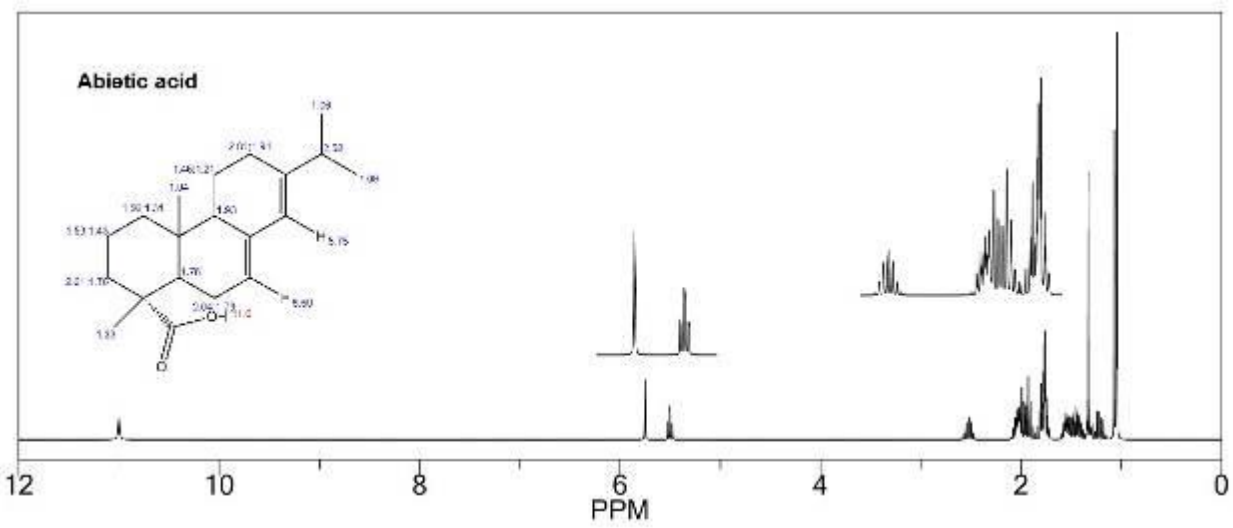


Figure 5 1H-NMR spectra of pure abietic acid, unmodified rosin and hydrogenated rosin (



Note the peak at 7.26 ppm, which is attributable to the solvent chloroform). At the bottom the simulated ^{1}H-NMR spectrum of abietic acid. The peaks in the aromatic region are attributable to dehydrogenated rosin, a result from an unavoidable disproportionation reaction.

Figure 6 The simulated 1H NMR spectrum of a pure abietic acid, fumarated, esters with pentaerythritol.

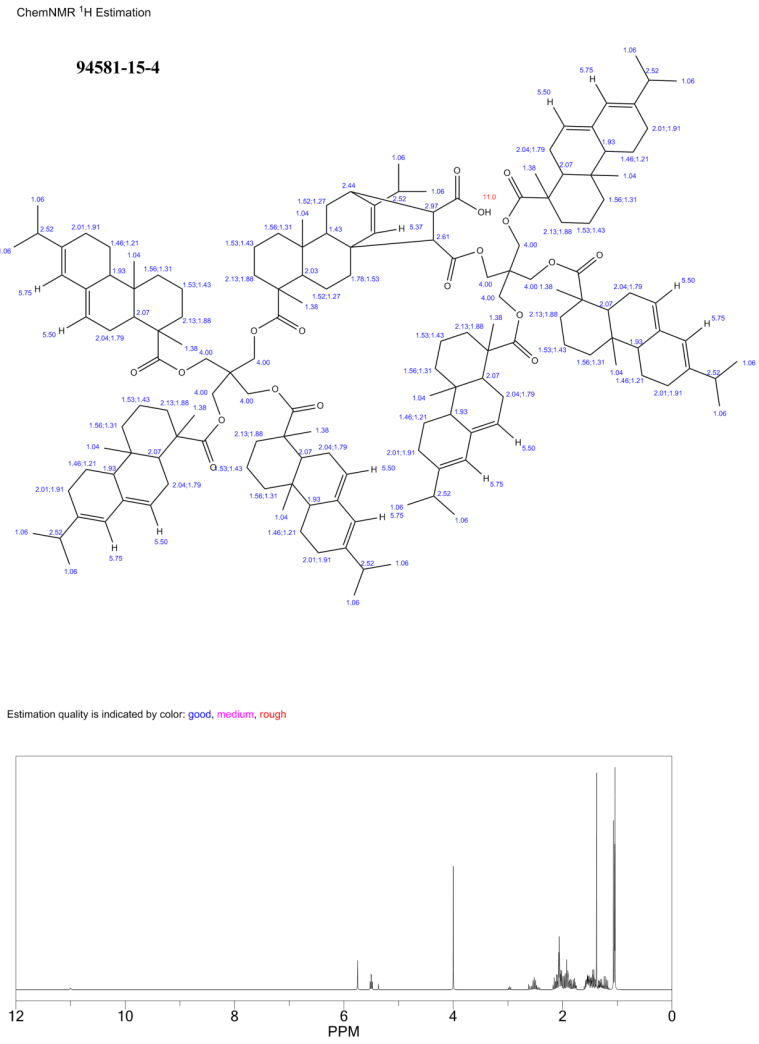
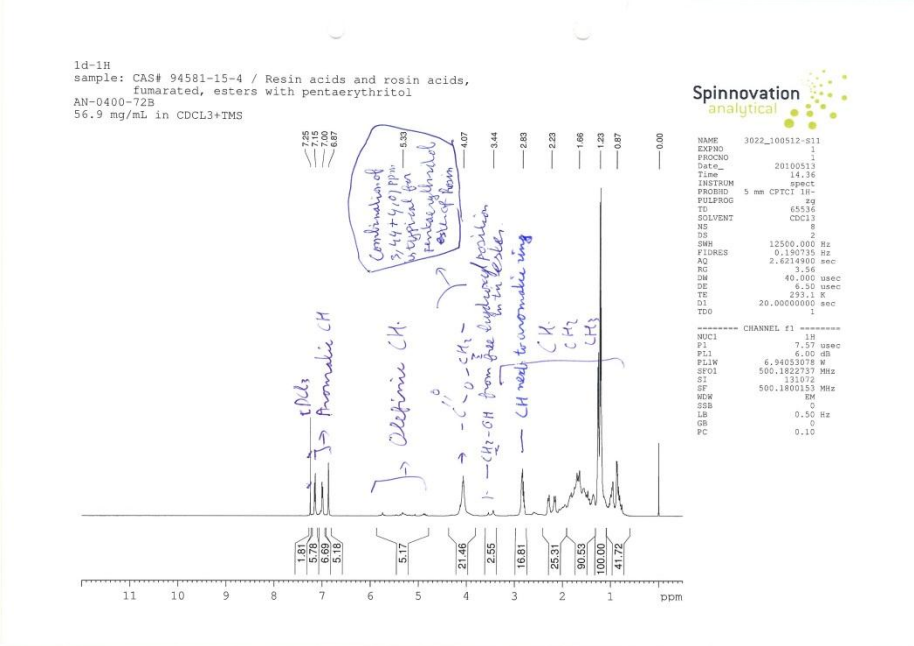


Figure 7 1H-NMR spectra of resin acids and rosin acids, fumarated, esters with pentaerythritol



(Note the peak at 7.25 ppm, which is attributable to the solvent chloroform). The peaks in the aromatic region are attributable to disproportionation reaction, which is catalytically performed in situ with the rosin ester formation as well to improve oxidative stability of the rosin ester product.

Reference spectra - See Appendix 3

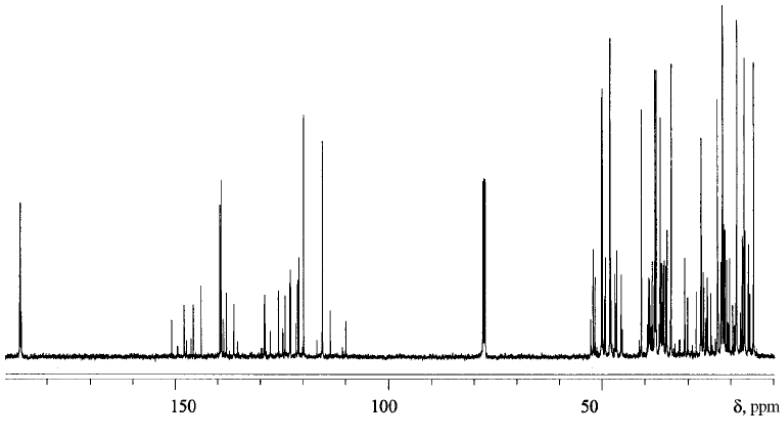
2.4 ^{13}C-NMR

^{13}C-NMR has the disadvantage that the surface area of a peak is not proportional to the abundance of a particular type of carbon atom. E.g., quaternary carbon atoms have a much lower response than a primary carbon atom in a methyl group. However, a peak with a low surface area/peak height can mean two things (a) it is a quaternary carbon atom of an abundant species of molecule, or (b) it is a primary carbon atom of a molecule with low abundancy. Below a 13C-spectrum of rosin is given.

Simulation of ^{13}C-NMR spectra gives a spectrum where all carbon atoms have the same intensity. An example for abietic acid is given below.

All in all, ^{13}C-NMR without the availability of pure isomers is not a useful tool for the identification of a rosin resin.

Figure 8 13C NMR Spectrum of a CDCL3 solution of balsam from pine resin collected in the vicinity of Komarin

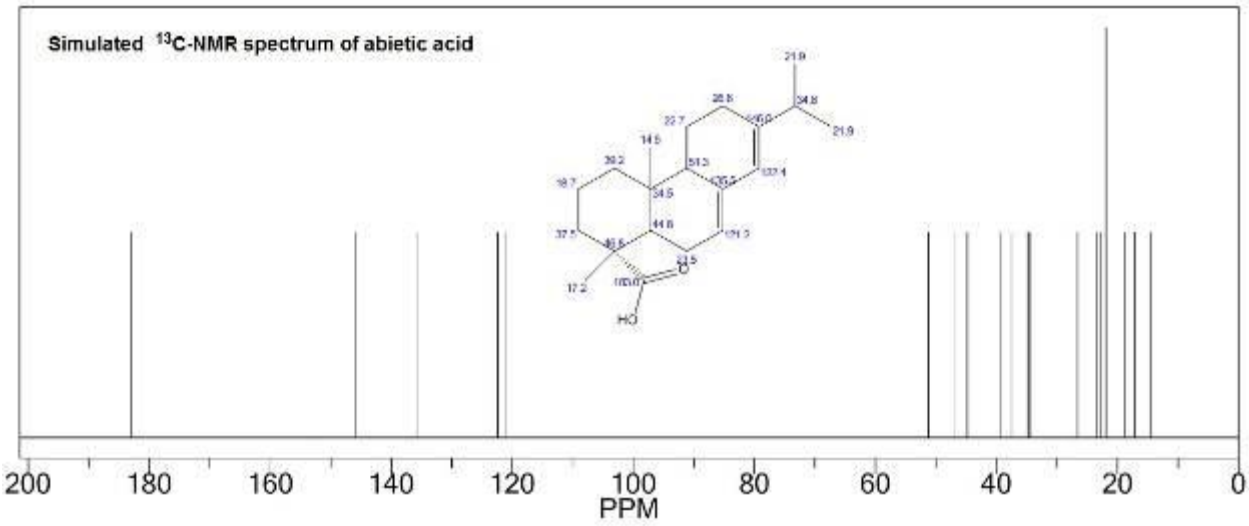


^{13}C NMR spectrum of a $CDCl_3$ solution of balsam from pine resin collected in the vicinity of Komarin.

Chemical Shifts (δ, ppm) of Signals Used for Quantitative Analysis in the ^{13}C NMR Spectra of Resin Acids (solutions in $CDCl_3$).

Acid		Number of the carbon atom											
number	name	4b	5	6	7	8	8a	9	11	12	13	14	15
1	Levopimaric acid			115.5	139.5	119.8	139.2		17.0	14.8		22.1	22.0
2	Palustric acid	125.7			144.0	120.9	138.0		21.4	16.7		21.9	21.7
3	Abietic acid				136.2	121.2	145.9	123.1	17.4	14.7		22.1	21.5
4	Pimaric acid					129.5	138.3		17.5	15.9	147.9	113.3	30.2
5	Neoabietic acid				124.2	122.8	139.1		17.5	16.0	128.9	21.0	20.4
6	Dehydroabietic acid	147.4	124.6	124.8	146.4	127.6	135.4		25.8	16.9		24.7	24.7
7	Isopimaric acid						136.3	121.6	17.8	16.0	22.2	151.0	110.0

Figure 9 Simulated 13C-NMR spectrum of abietic acid



2.5 Chromatography

None of the substances involved, including rosin itself are sufficiently volatile to be analysed with GC. Only the methyl ester of rosin is sufficiently volatile for GC analysis.

It is assumed that rosin, hydrogenated rosin, disproportionated rosin and formaldehyde adduct can be derivatised to the methyl ester with diazomethane without extensive isomerisation. Therefore, these resins can be analysed by GC as well. Methods have been published; see ISO 19334[3], ASTM D 5974 and Pine chemicals Association PCTM 27[4].

Rosin salts can be converted into the free acid by acidification, followed by methylation after which GC analysis is feasible. It is assumed that in these reactions the composition doesn't alter significantly. This would yield the spectra of the starting material.

ll other rosin derivatives are not volatile enough and only liquid chromatography remains as a feasible technique.

2.5.1 Gas chromatography (GC)

The order of the peaks may be different with different techniques. Assignment of the peaks is based on ISO 19334. Following the method used in this standard, the elution order is

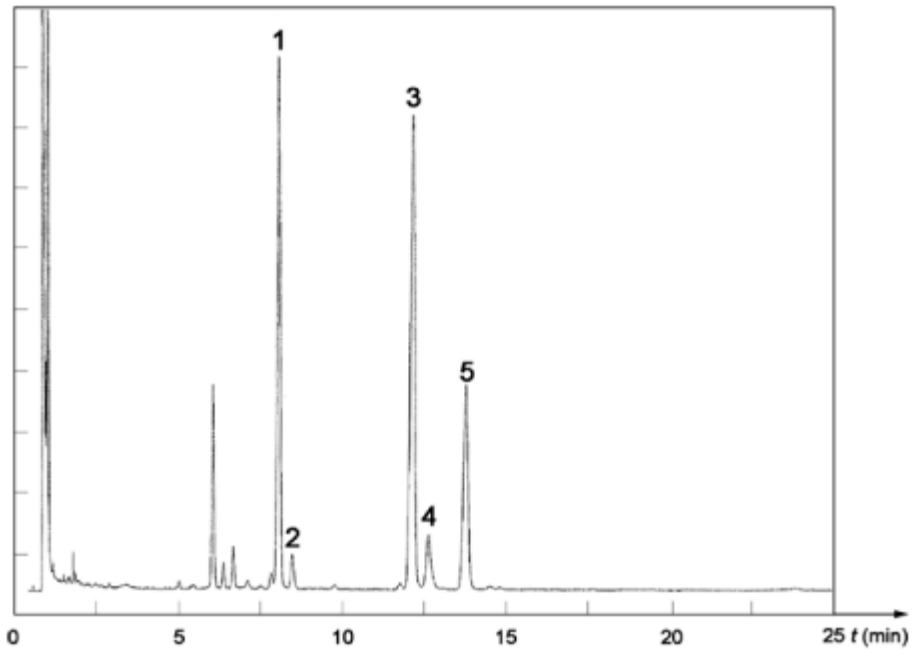
1. communic acid
2. palustric acid
3. isopimaric acid
4. abietic acid
5. dehydroabietic acid
6. neoabietic acid

The ratio of the individual components varies, amongst others, due to geographical as well as climatic variations. An extensive comparison on composition can be found in Table 1.

[3] http://www.iso.org/iso/catalogue_detail.htm?csnumber=39051

[4] PCA—TEST METHOD PCTM 27 Published 1/1 2004 Method for Characterization of Gum Rosin by Capillary Gas Chromatography

Table 6 GC traces of Rosin, methyl ester

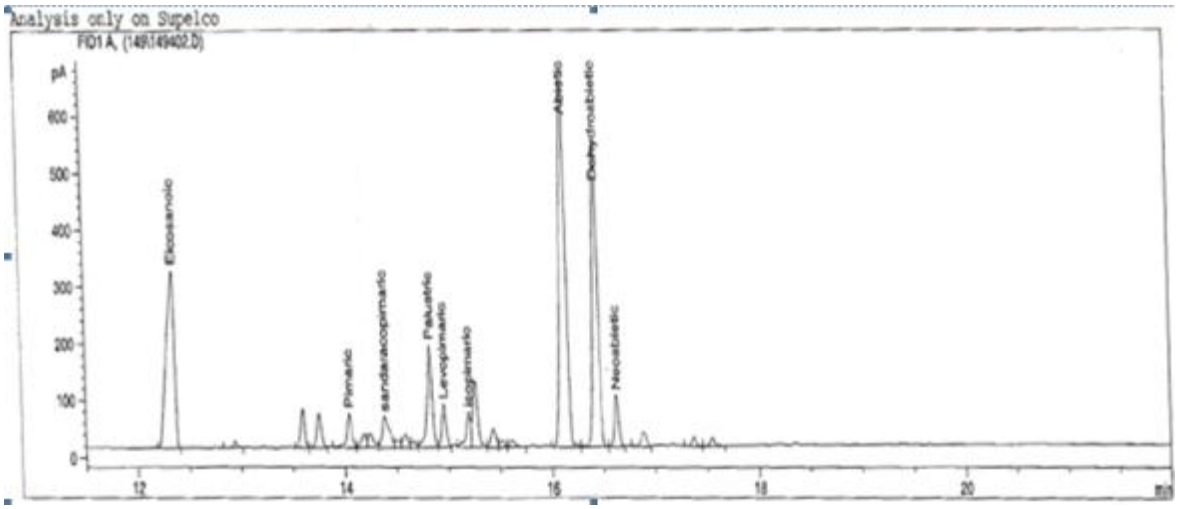


Key

1 palustric acid
2 isopimaric acid
3 abietic acid
4 dehydroabietic acid
5 neoabietic acid

Unpublished protocol

Figure 10 Order of peaks - Rosin, methyl ester



Note that the order of the peaks is different between the two techniques.

Recommendation for the registrant - by using a standard techniques, - ISO 19334[5] and PCA—TEST METHOD PCTM 27 - it is possible to identify the main constituents and their concentrations.

2.5.2 Liquid Chromatography

For the non-volatile rosin esters liquid chromatography is the only means to separate the individual constituents. For the non-esterified rosin resins, i.e. the rosin resins with free carboxylic acid groups that can be derivatised to the methyl ester, liquid chromatography is not the preferred method. GC is by far the better method for these resins, because of the superior separation of the constituents, which necessary for identification and quantification.

In principle two techniques can be used to separate the constituents, through interaction with a liquid phase (HPLC) or by separation based on hydrodynamic volume (size exclusion chromatography [SEC], also called gel permeation chromatography [GPC]). Due to their similarity, separation of isomers is impossible in LC.

As the Guidance Document states “A chromatogram that can be used as a fingerprint shall be given to characterise the composition of the substance. If applicable, also other valid constituent separation techniques might be used.” The best method to characterise the composition of the substance is by its reference substances, i.e. the mono-, di-, tri- and/or tetra-esters, GPC is the preferred method as a fingerprint.

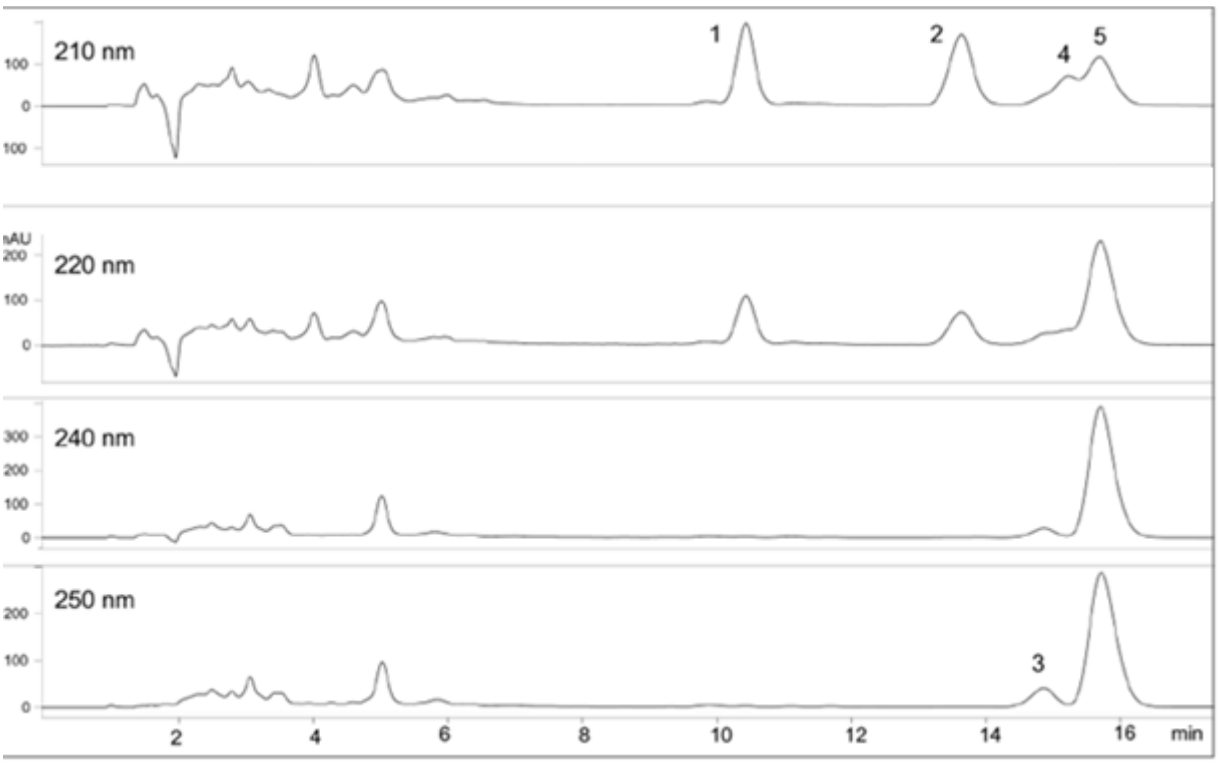
GPC separates on hydrodynamic volume, thus molecular weight in case of similar molecules. This way mono-, di-, tri- and tetra-esters can be separated. No further separation into isomers is possible, as isomers will have very similar hydrodynamic volumes. In combination with MS the peaks in the GPC can be assigned unambiguously to the mono-, di-, tri and/or tetra-esters.

The peaks in GPC have to be integrated and the relative surface areas have to be determined for quantification purposes. Even though there is no complete peak separation, the peaks are close to being Gaussian, so it is acceptable to assume that ratio of the areas of the peaks can be determined by drawing the line from the “valley” between peaks perpendicular to the base line. Better methods than this do not seem to be available, but suggestions are welcomed.

Conclusion

As can be seen in the figures below HPLC does not give sufficient information on the identity of the test substance The GPC, Figure , give information of the ratio of mono-, di- ,tri-, and possible tetra- esters. It can therefore be possible to differentiate between the esters and to quantify between the degree of esterification of the polyol. It is demonstrated that it is of no value to identify the individual constituents of esters.

Figure 11 HPLC chromatogram of rosin at various wavelengths



Peak assignment: 1 = dehydroabietic acid, 2 = internal standard (eicosapentaenoic acid), 3 = unknown, 4 = pimaric acid, 5 = abietic acid.

Source: U. Nilsson et al, J. Sep. Sci. 2008, 31, 2784-2790

Figure 12 GPC trace of rosin, pentaerythritol esters

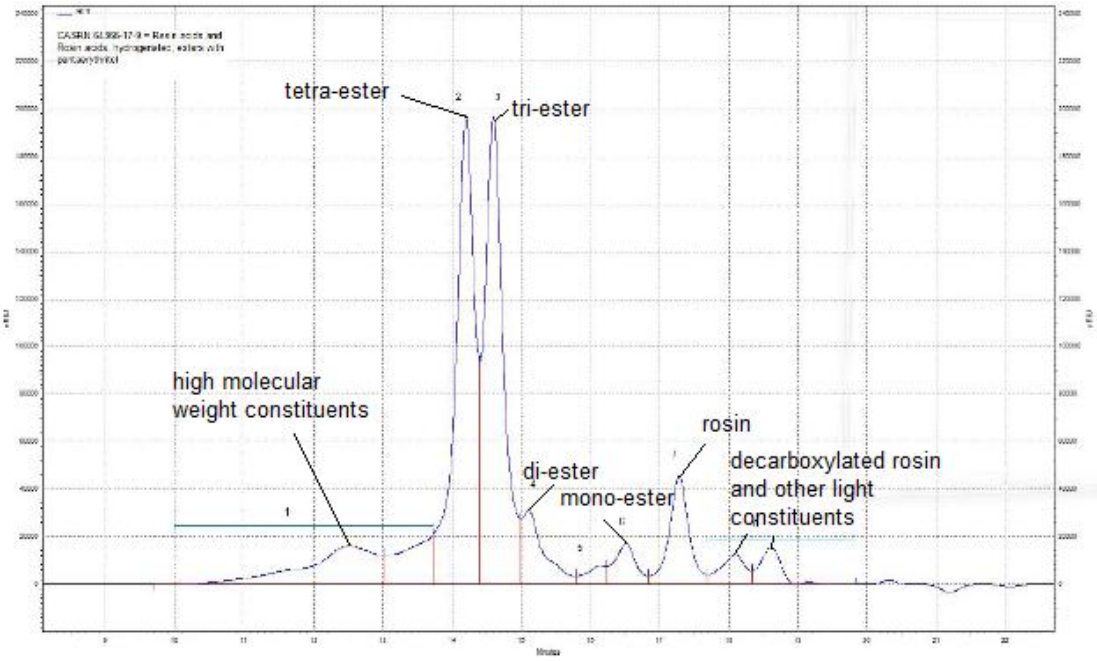
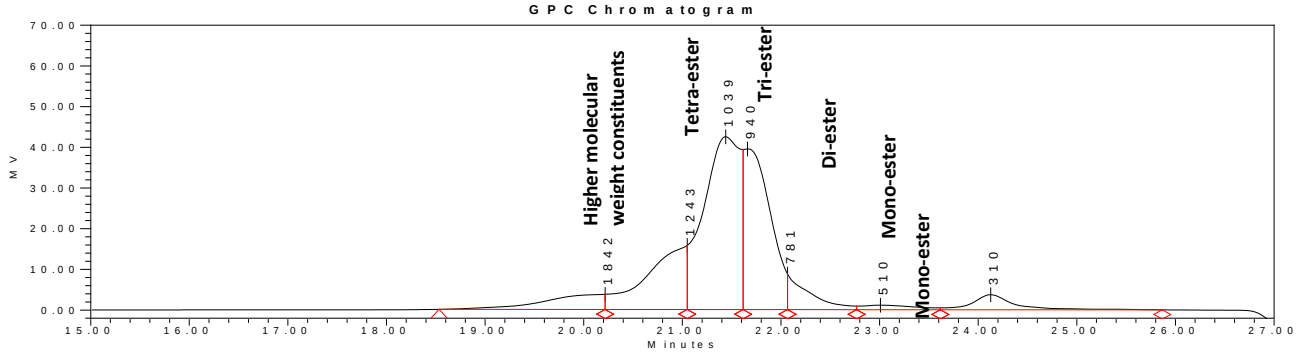


Figure 13 GPC trace of resin acids and rosin acids, fumarated, esters with pentaerythritol



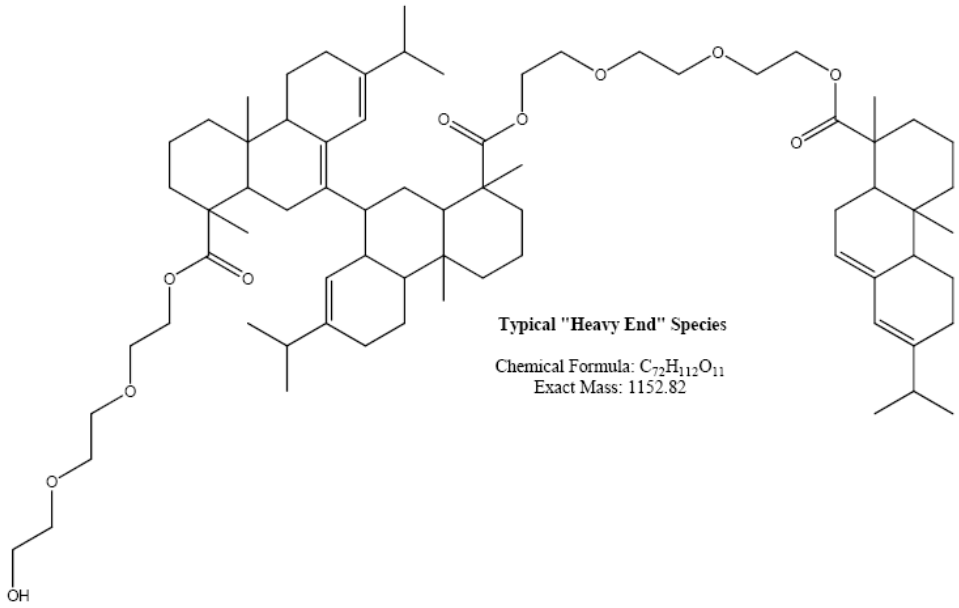
2.6 Mass spectrometry

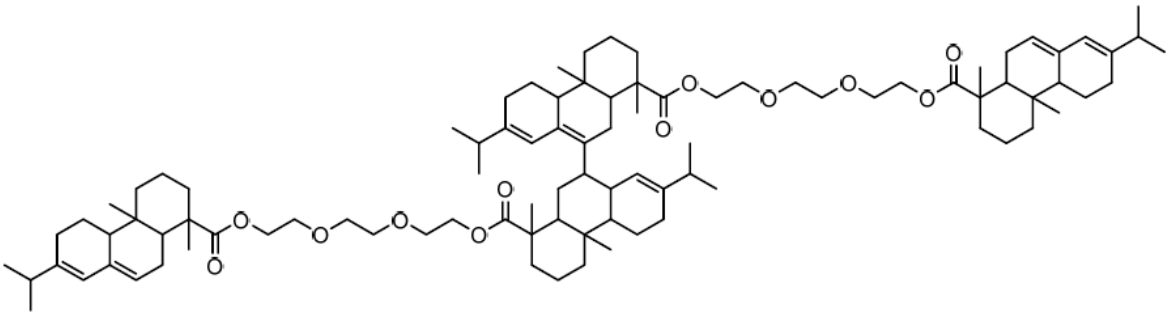
Because of the complexity of rosin and its derivatives, liquid chromatography has only limited capabilities. Even with HPLC the overlap of peaks is such that assignment of individual isomers is not possible. The only possible technique is making using of gel permeation chromatography coupled with mass spectrometry.

In mass spectrometry the method of ionisation is critical to the information obtained. In case of complex mixtures, electrospray is the method to use (ESI). This way the accurate mass of the molecules is obtained without fragmentation of the parent ion.

With this technique it is possible to have a best scientific guess on the nature of the constituents in these substances. E.g., all rosin derivatives contain so-called “heavy ends”, species with a high molecular weight originating from so-called rosin dimers. Examples are given in the figures below.

Figure 14 structures for species found in the triethylene glycol ester of rosin

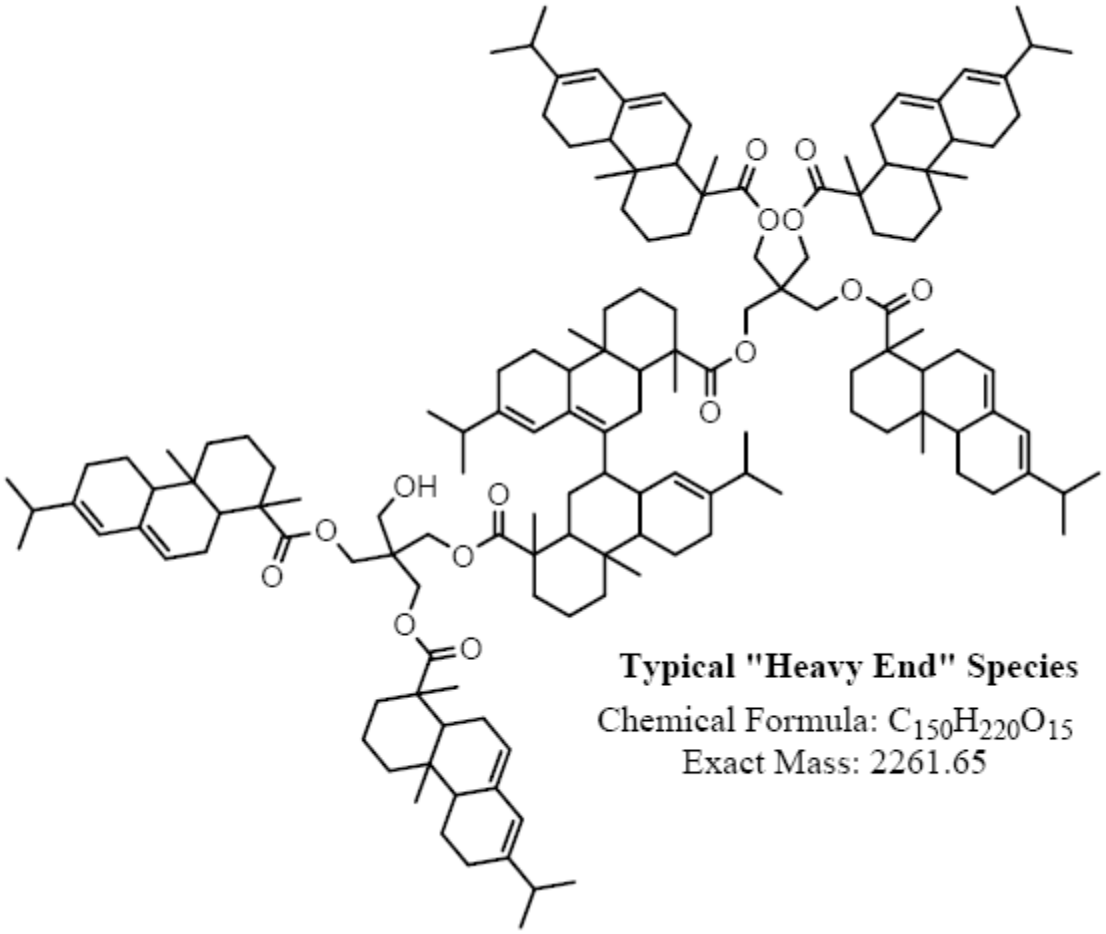




Typical "Heavy End" Species

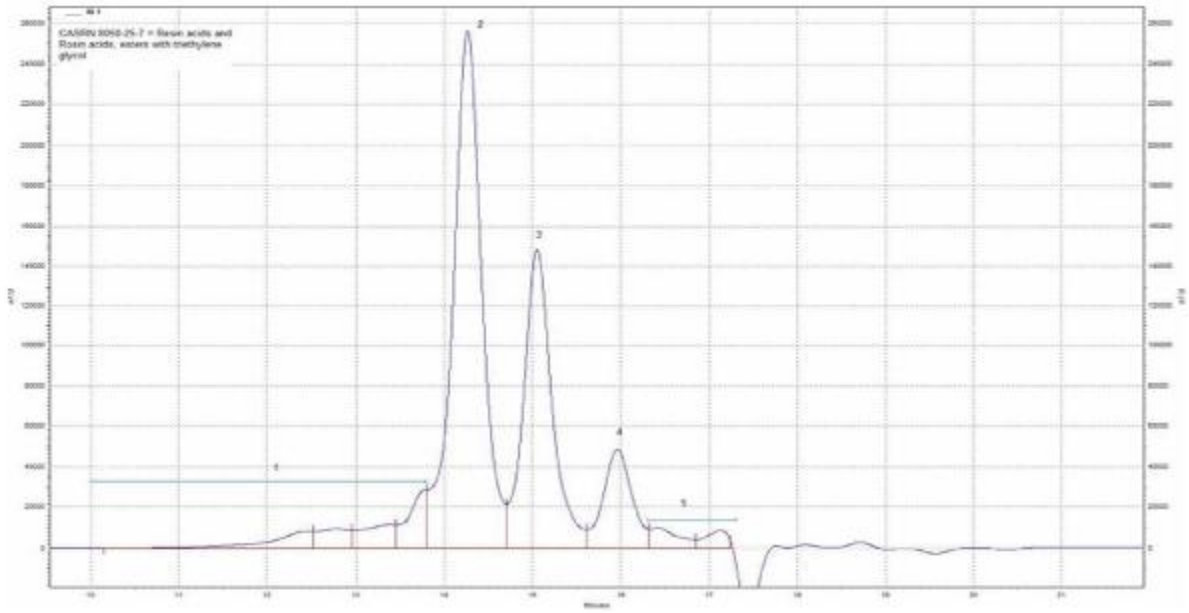
Chemical Formula: $C_{92}H_{140}O_{12}$
Exact Mass: 1437.03

Figure 15 A possible structure for species found in the pentaerythritol ester of rosin



In Figure 16a typical chromatogram is presented for the triethylene glycol ester of rosin. It should be borne in mind that the peaks for the di- and the mono-ester consist all possible isomers and combinations of resin acids with tri-ethylene glycol. Below the chromatogram the MS traces for the di- and the mono-esters are given.

Figure 16 GPC trace of the tri-ethylene glycol ester of rosin



Peak number	Component	Constituent	Triethylene glycol ester of Rosin Area%
1	Heavy ends	Complex mixture of dimerized esters	10.19
2	Di- ester	Resins acids, di esters with triethylene glycol	49.45
3	Mono ester	Resins acids, mono esters with triethylene glycol	27.86
4	Rosin Acids	Resins acids	9.32
5	Rosin light ends	Mono- and sesquiterpenes	3.18
		Total	100

Figure 17 MS trace for the triethylene glycol ester of rosin. Note the presence of dehydro, dihydro and tetrahydro species

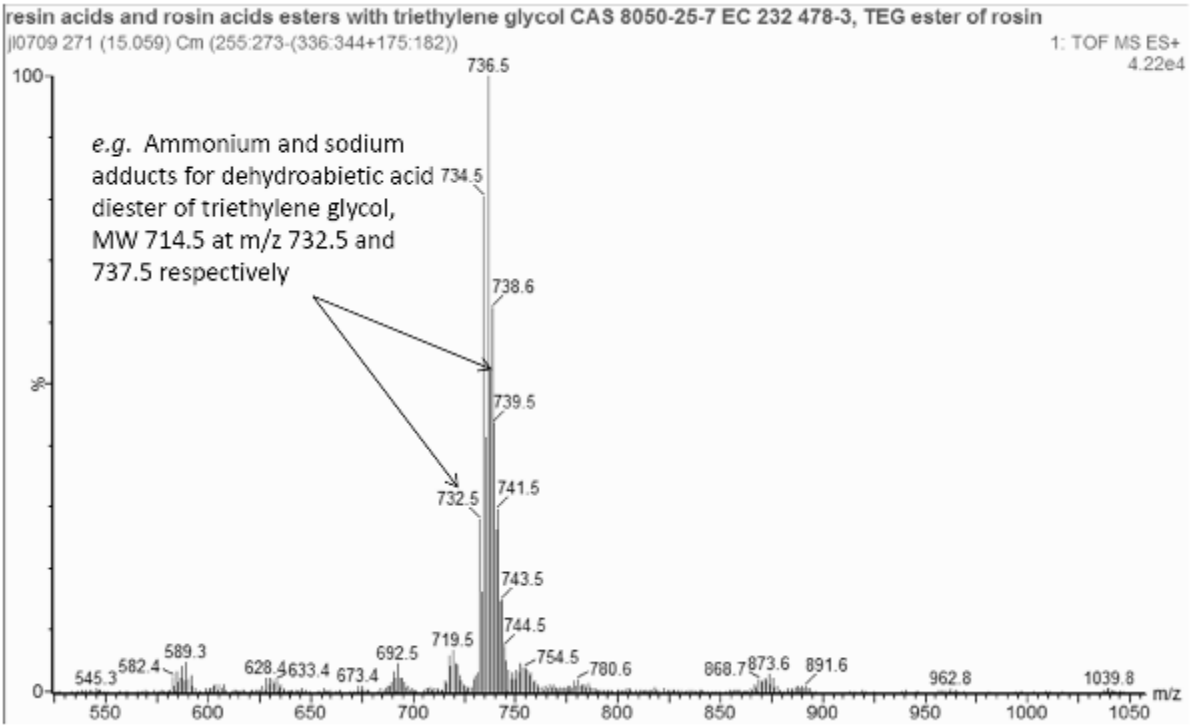


Figure 18 MS trace for the monotriethylene glycol ester of rosin. Note the presence of dehydro, dihydro and tetrahydro species.

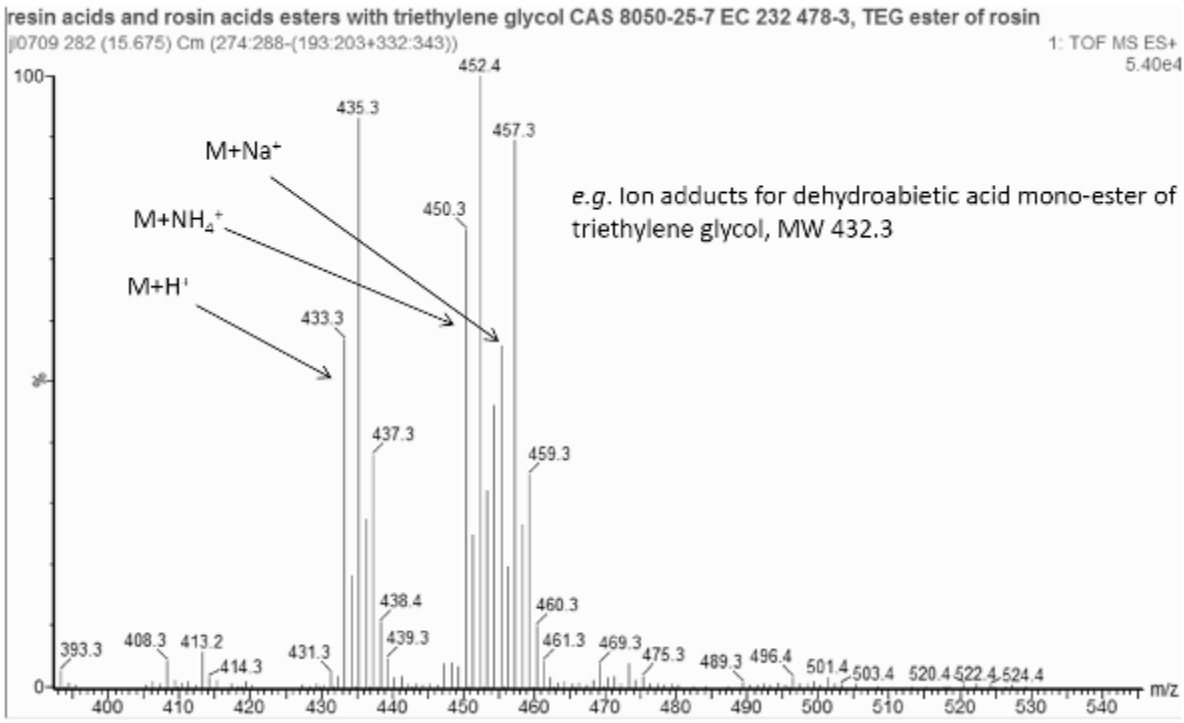


Figure 19 MS trace for the "heavy ends in the triethylene glycol ester of rosin

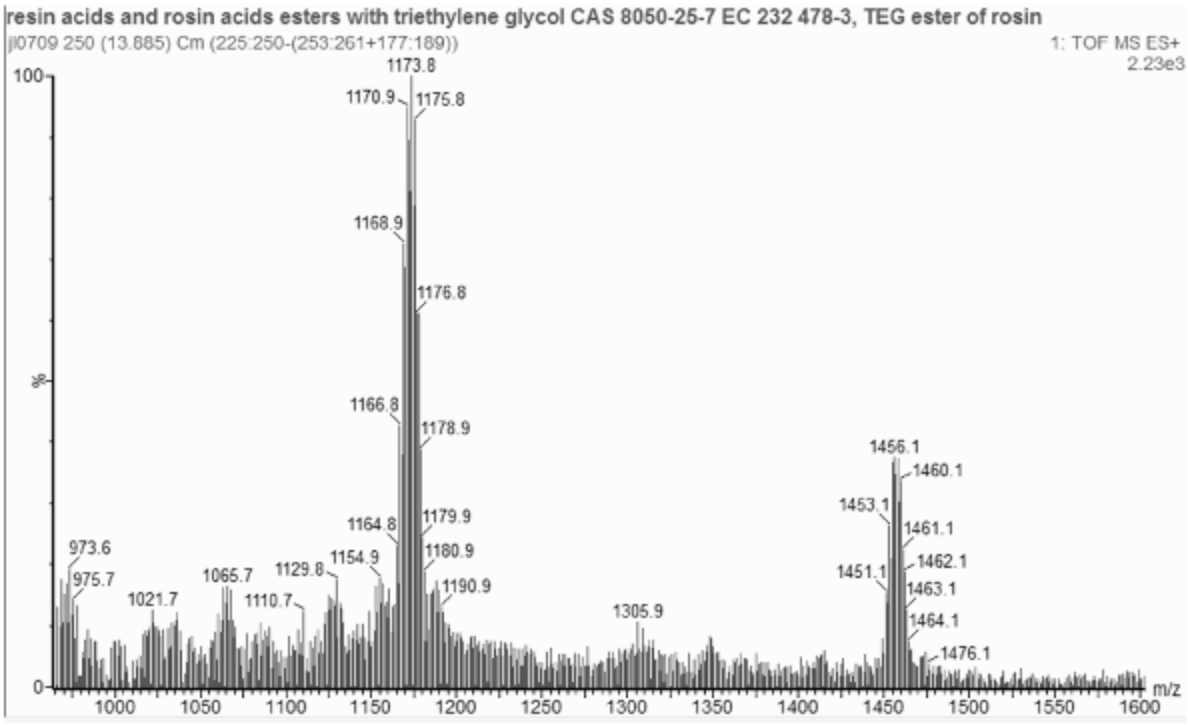


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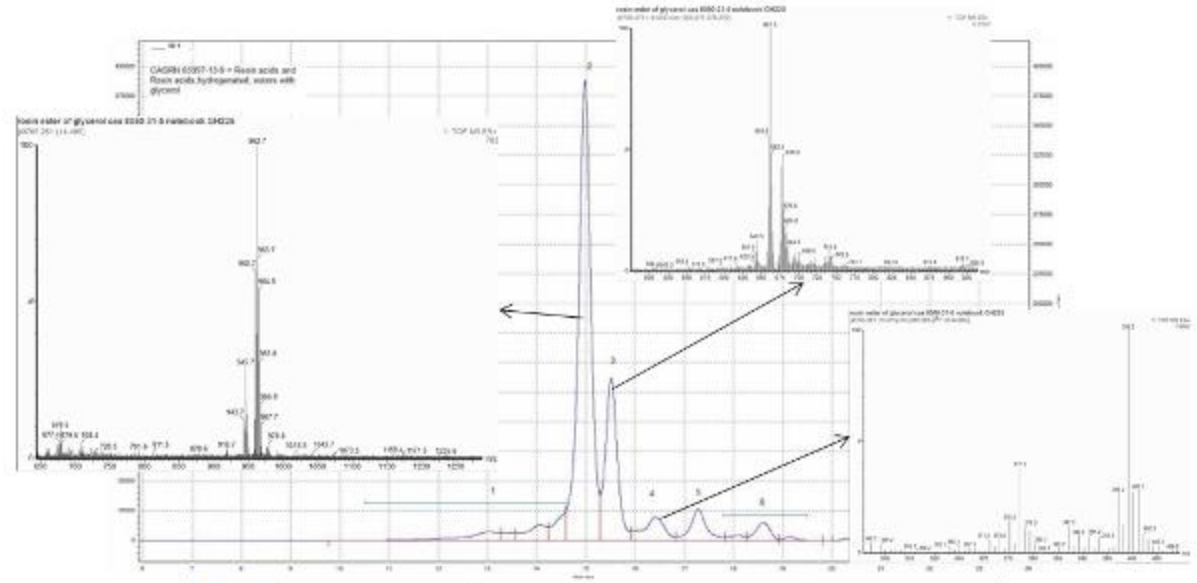
Figure 20 GPC trace for the glycerol esters of rosin with the mass spectra included



Peak number	Component	Constituent	Glycerol Ester of hydrogenated rosin Area%
1	Heavy Ends	Unidentified complex mixture of dimerized esters, acids and polyol	10.49
2	Tri-Ester	Resins acids, hydrogenated, tri esters with glycerol	56.39
3	Di-Ester	Resins acids, hydrogenated, di esters with glycerol	19.11
4	Mono-Ester	Resins acids, hydrogenated, mono ester with glycerol	4.96
5	Rosin Acids	Resin acids, hydrogenated	5.04
6	Rosin light ends	Mono- and sesquiterpenes	4.01
		Total	100

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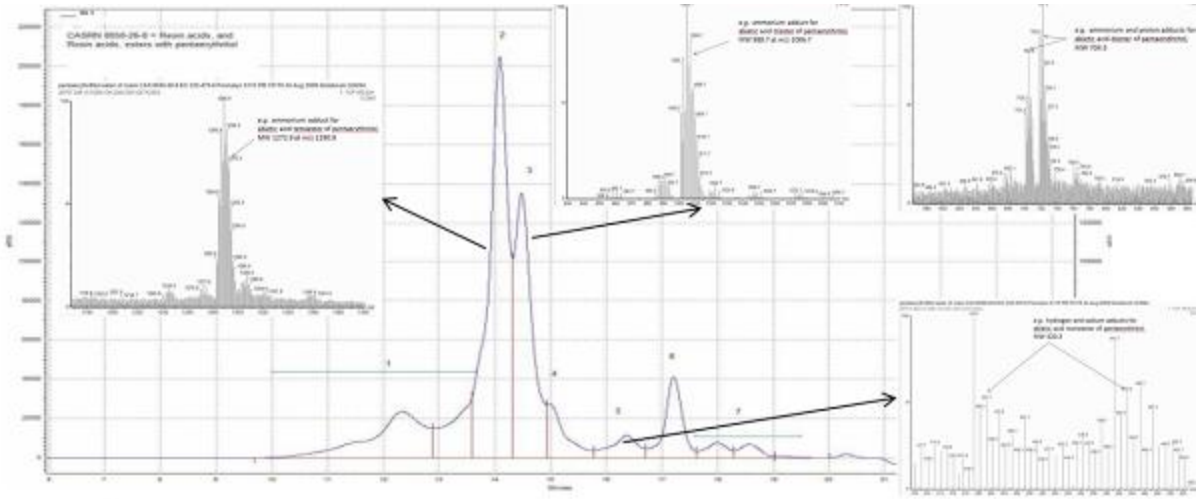
Figure 21 GPC trace for the pentaerythritol esters of rosin with the mass spectra included.



Peak number	Component	Constituent	Penta Ester of Rosin Area%
1	Heavy Ends	Unidentified complex mixture of dimerized esters, acids and polyol	19.20
2	Tetra-Ester	Resins acids, tetra esters with pentaerythritol	38.92
3	Tri-Ester	Resins acids, tri esters with pentaerythritol	23.42
4	Di-Ester	Resins acids, di esters with pentaerythritol	4.90
5	Mono-Ester	Resins acids, mono ester with pentaerythritol	3.09
6	Rosin Acids	Resin acids	7.18
7	Rosin light ends	Mono- and sesquiterpenes	3.29
		Total	100%

Conclusion:

Using GPC-ESI-MS gives proof of the identity of a test substance. Also, it gives proof that in a GPS the constituents with the highest molecular weight and thus highest hydrodynamic volume, elute fastest.

Recommendation to registrants

The GPC-MS traces given in the appendices should be used to determine the elution pattern of the registrant's GPC trace used for quantification.

2.7 Acid value

Since rosin consists mainly of organic acids the determination of the acid value or acid number has traditionally been one of the most applied identification and specification techniques for rosin and rosin derivatives.

The acid value is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of a chemical substance or in this case rosin or a rosin derivative. The acid value is a measure of the amount of carboxylic acid groups present.

The acid value determination is done by titration with KOH of a solution of rosin in a suitable solvent using an indicator to determine the endpoint and is for instance described in ASTM method D 465-05(2010).

For pure abietic acid the acid value can be calculated using the following molecular weight numbers:

KOH 56.1 Dalton

Abietic Acid 302 Dalton

Acid Value Abietic Acid: 1/302 * 56.1 * 1000 = 185.8 mg KOH/gr AA

Depending on the origin and the processing of rosin typically a range of acid values can be found in the literature. As reference a table with values for rosin from different geographical regions is given below. The data were published by the FAO on their website
http://www.fao.org/docrep/V6460E/v6460e0b.htm

Table 7 Some trade specifications for gum rosin

Origin	Softening point (°C)	Acid value
China, PR	70-85	162-175
Portugal	min 70	165-171
Brazil	70-78	155-170
Indonesia	75-78	160-200

3. Manufacturing:

Information on the manufacturing process gives further indication of the nature of the substance. Obviously, if one adds glycerol to the reactor, one does not have to expect to synthesise the pentaerythritol ester. Below some details of the manufacturing progress of various rosin derivatives are given.

3.1 Rosin

Rosin can be obtained from pine trees in three different ways and each method needs its own refinement technique:

- Tapping a live tree yields so-called oleoresin, a mixture of terpenes and rosin. Terpenes are removed by distillation, yielding gum rosin as the residue.
- Pulping pine trees for paper-making, yields so-called tall oil, mainly consisting of fatty acids and rosin. The fatty acids are removed by distillation to yield rosin as the residue.
- After cutting the tree, the stumps may reside in the soil for an extended period of time. Over time the terpenes will have volatilised. The stumps are shredded and extracted with a solvent to yield rosin.

3.2 Hydrogenated rosin

Rosin is molten, after which hydrogen gas is added under pressure, elevated temperature and a catalyst. The degree of hydrogenation can be monitored by UV absorption.

3.3 Rosin esters

Esterification of rosin usually is a batch process, in which rosin is molten and heated to temperatures exceeding 150 °C. The alcohol is added, after which the esterification commences. As esterification is an equilibrium reaction, water has to be removed continuously. The time to achieve complete esterification exceeds 6 hours.

The degree of esterification is monitored by determining the acid number (mg KOH to neutralise 1 g of rosin). Rosin has a typical acid number value of about 160. Most rosin esters have an acid value not exceeding 16, thus a conversion rate of at least 90 %.

3.4 Rosin adducts & Rosin adduct salts

Manufacturing of adducted rosin; fumarated or maleated rosin

Rosin can be reacted in a Diels-Alder reaction with either maleic anhydride, maleic acid or the stereoisomer fumaric acid (4 – 12 parts per 100 parts rosin, w/w). Reaction temperature varies from 175 - 250 °C depending upon the reactivity of the dieneophile of choice.

Fumarated rosin:

Reaction products, that are obtained at 190 - 230 °C, are the fumaropimaric tricarboxylic acid (trans-maleopimaric tricarboxylic acid) and even maleopimaric acid anhydride. Reaction temperature, time and molar ratio have effect on the yield of the components.

Since fumaric acid is used in substoichiometric amounts, conversion is complete within 2 hours at 190 °C. Non reacted fumaric acid can be analyzed in an aqueous extract of the final product. Main properties, which are controlled by reaction conditions, are ratio fumaro-/maleo adduct (GC), acid number and softening point

Maleated rosin:

Primary reaction products obtained at 175 – 190 °C, are the maleopimaric acid anhydride and the (cis-) maleopimaric tricarboxylic acid .

Since maleic acid and maleic acid anhydride are used in substoichiometric amounts, conversion is complete within 2 hours at 190 °C. Non reacted maleic acid can be analyzed in an aqueous extract of the final product. Main properties are amount of maleo adduct (GC), acid number and softening point

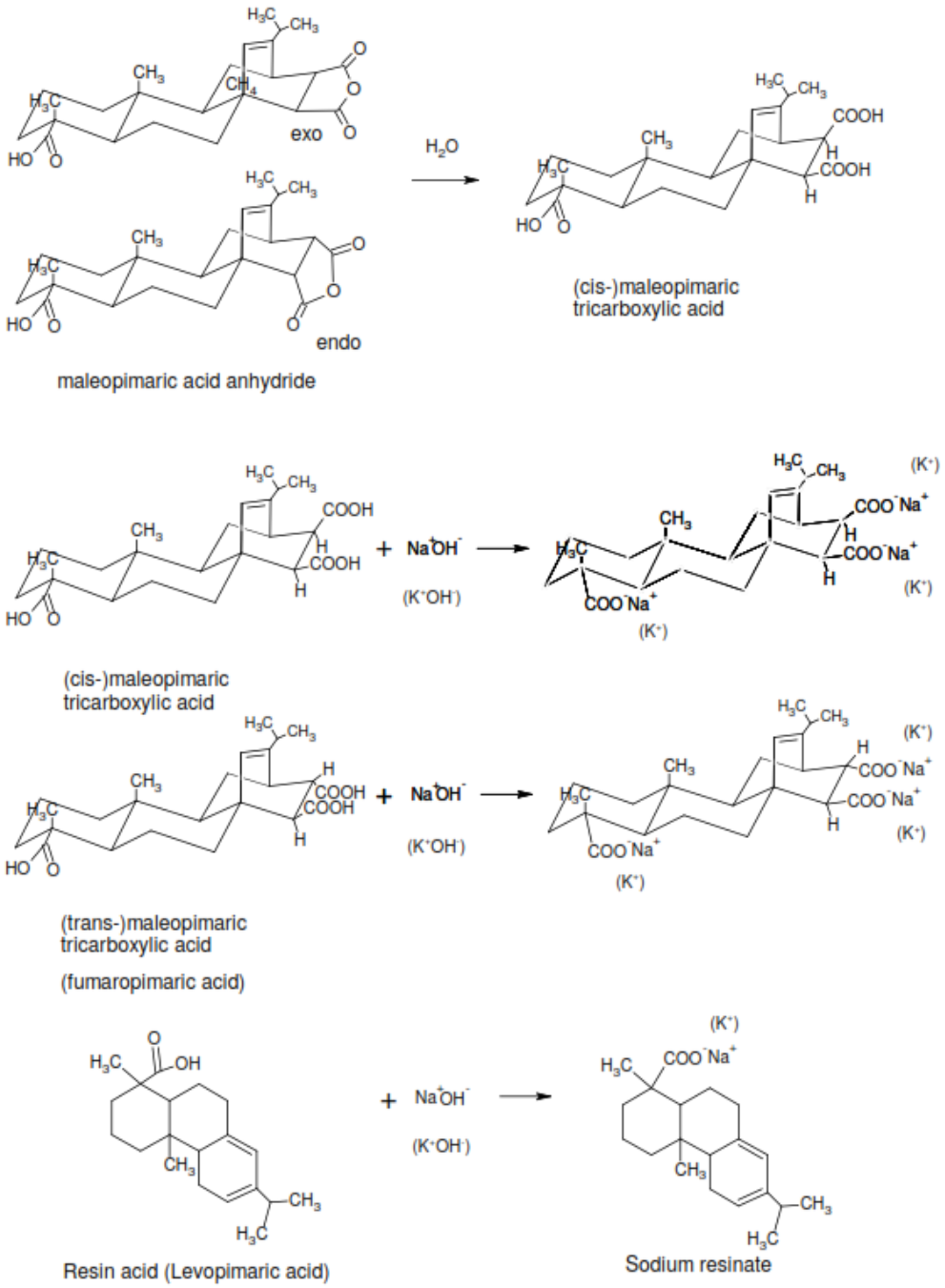
Rosin adduct salts:

Molten adducted rosin is added in either a batch or continuous process with hot solution of sodium (or potassium, calcium) hydroxide in water in pre-determined proportions, typically 1:1 stoichometrically. It is stirred or agitated until a solution is formed.

The result of the blending passes to a storage tank for subsequent packaging or bulk shipment. Usually no attempt is made to evaporate the water of sodium or potassium salts: the commercial product is usually provided to Downstream Users as a solution of the rosin salt in water at a pre-determined concentration. The Downstream Users use it as supplied.

Figure 22

Sodium and Potassium salt formation of maleated or fumarated Rosin



3.5 Rosin adduct, esters

The commercial production of rosin adduct esters is either starting from rosin adduct or as a two-step process.

When starting with rosin adduct, the substance is molten, after which the alcohol is added. The progress of the reaction is monitored by e.g. establishing the "acid number" (mg KOH to neutralise 1 g of product) until it has reached to the required specification.

In the two-step process, the first step involves the production of the Diels-Alder adduct with fumaric acid or maleic anhydride. This involves heating the two reactants together above 150 °C in a closed reactor with stirring. The progress of the reaction is monitored using GC or GPC techniques on samples extracted periodically until the required specification has been reached.

The second step involves the charging of the alcohol - usually a polyol such as pentaerythritol - to the reactor and continuing to heat and stir at elevated temperatures. As water is generated from the esterification reaction the reactor must be so designed to allow this to escape otherwise the conversion rate would be low. The progress of the reaction is monitored by e.g. establishing the "acid number" (mg KOH to neutralise 1 g of product) until it has reached the required specification. Other control parameters can be used for this, such as "softening point". By adjusting the process and reaction conditions the formation of polymeric components can be controlled.

3.5.1 Rosin, formaldehyde adduct

Rosin is reacted with formaldehyde at elevated temperatures (above the softening point of rosin) in a closed reactor with stirring. Typical reaction conditions are a temperature in the range of 140 - 200 °C and a reaction time of 2 - 6 hours. Under acidic conditions mainly methyl dehydro resin acids are formed.

3.4.3 Rosin Salts

Rosin is molten and added in either a batch or continuous process with hot solution of sodium (or potassium) hydroxide in water in pre-determined proportions, typically 1:1 stoichometrically. It is stirred or agitated until a solution is formed.

The result of the blending passes to a storage tank for subsequent packaging or bulk shipment. Usually no attempt is made to evaporate the water: the commercial product is usually provided to Downstream Users as a solution of the rosin salt in water at a pre-determined concentration. The Downstream Users use it as supplied.

4. Conclusions

There is no single analytical technique available that identifies the chemical nature of the rosin or rosin derivatives. Only by combining techniques and also knowing the chemical process applied, can the identity and composition be established to the maximum extent possible.

Appendix 1 - Reference IR Spectra

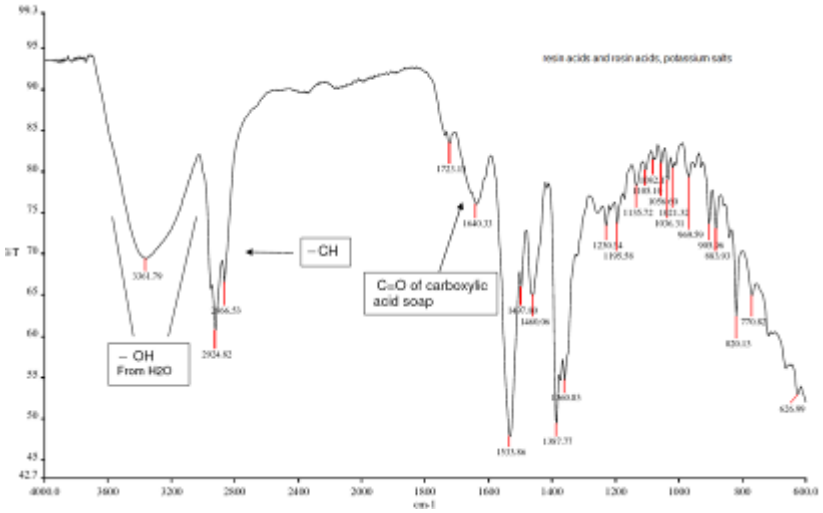
Reference Spectra for Rosin and derivatives have recently been determined by Harlan L:aboratoies. Their report is attached

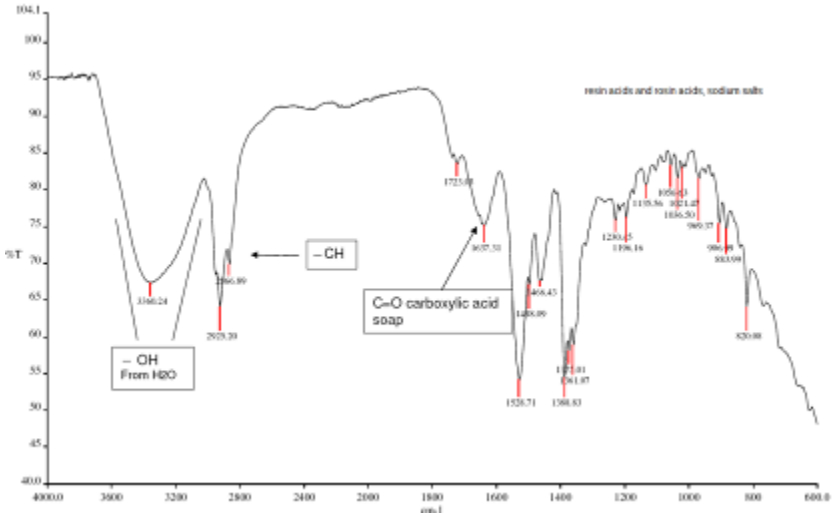
Reference

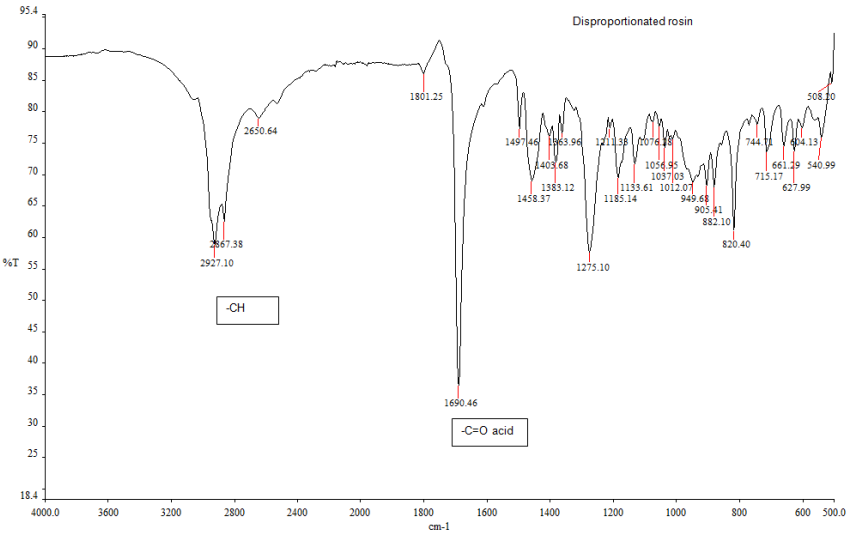
Harlan Laboratories Ltd (2010) CAS No's 8050-09-7, 9007-13-0, 61790-50-9, 61790-51-0, 68334-35-0, 68440-56-2, 8050-25-7, 8050-26-8, 8050-31-5, 8050-28-0, 65997-04-8, 95009-65-7, 160901-14-4, 92202-14-7, 94581-15-4 and 91081-53-7: Determination of Infrared Spectra. Report to H4R Consortium

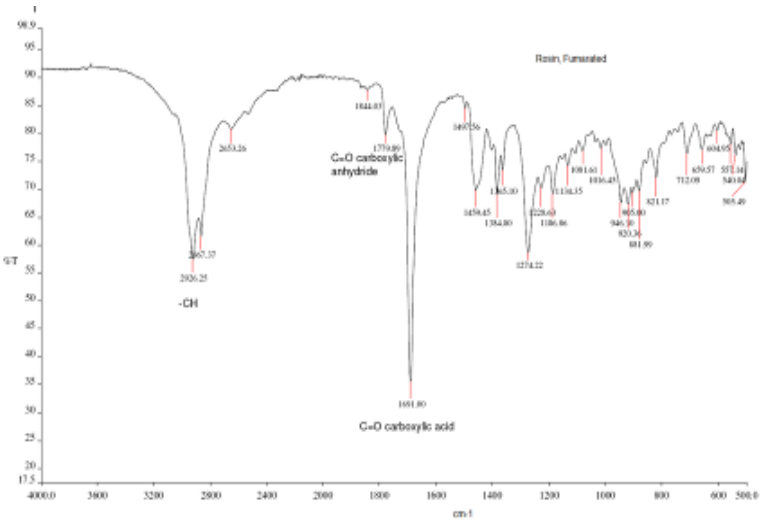
Harlan 2020 IR reference FINAL.PDF

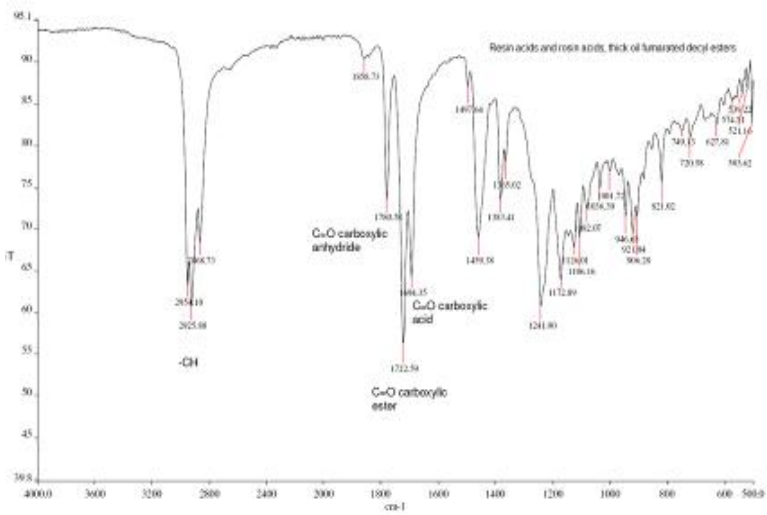
Reference IR Spectra for some Rosin derivatives

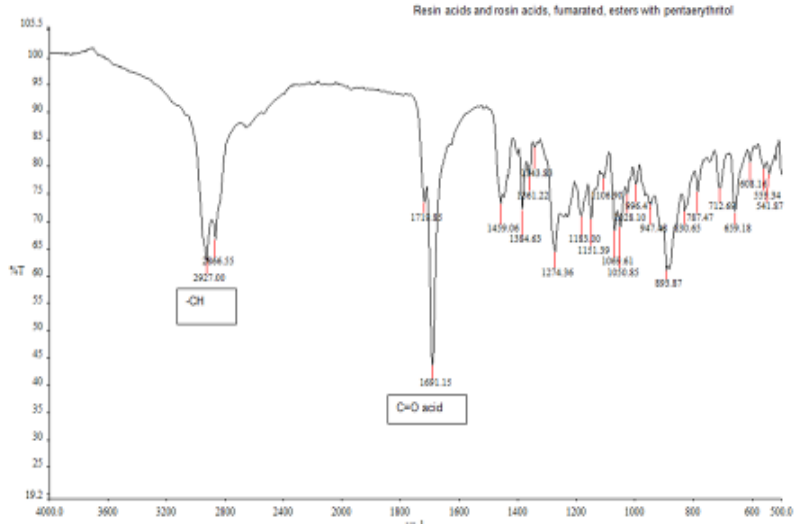


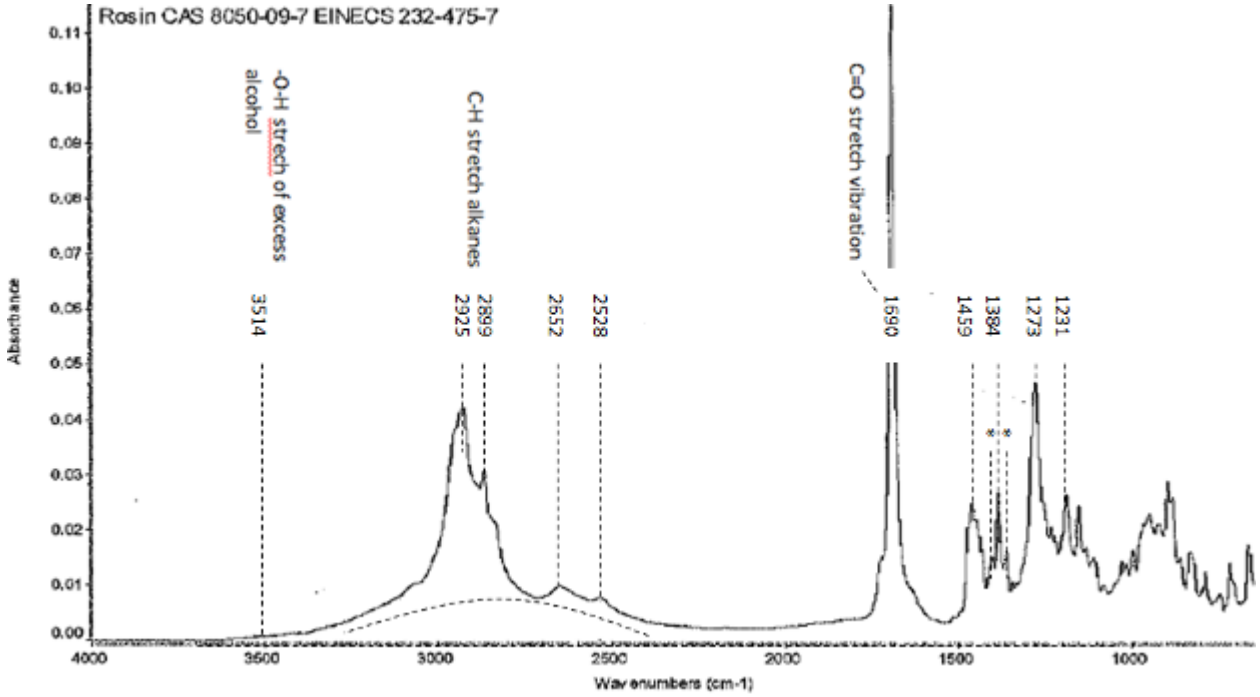


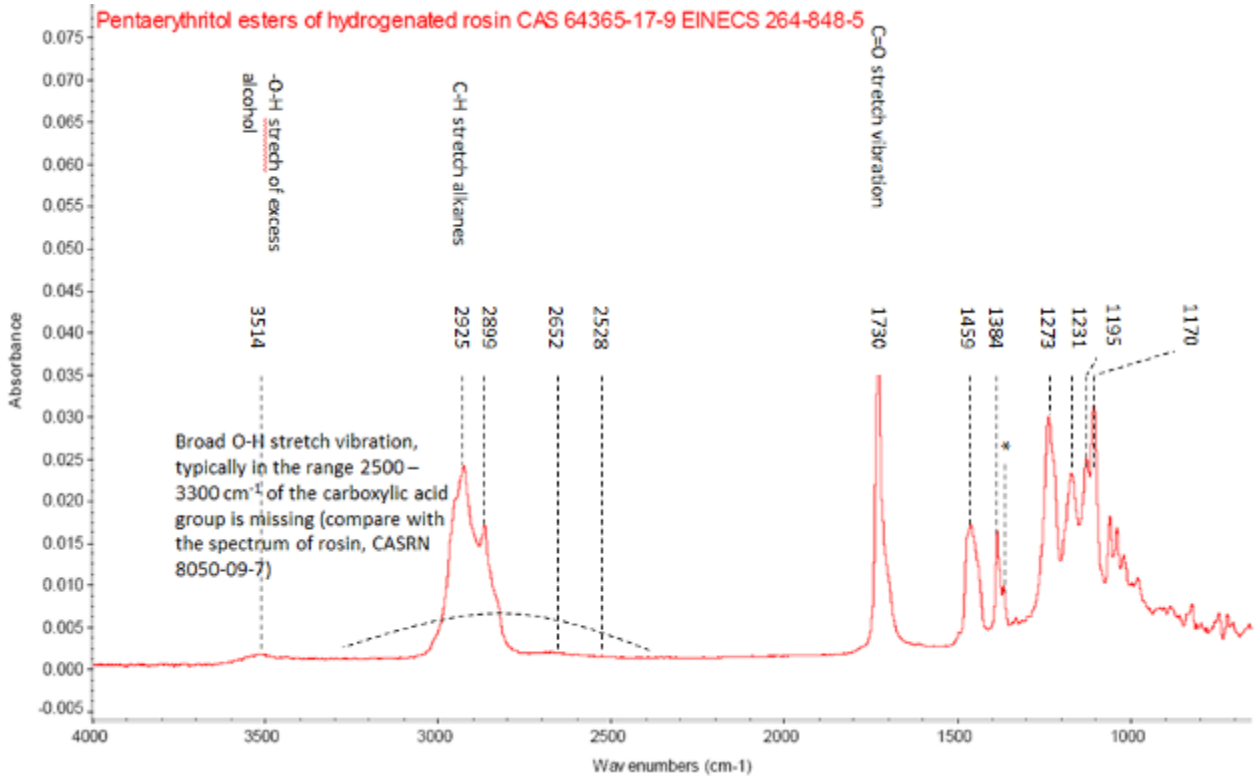



Rosin, Fumarated
C=O carboxylic anhydride
C=O carboxylic acid
-CH
%T
cm-1

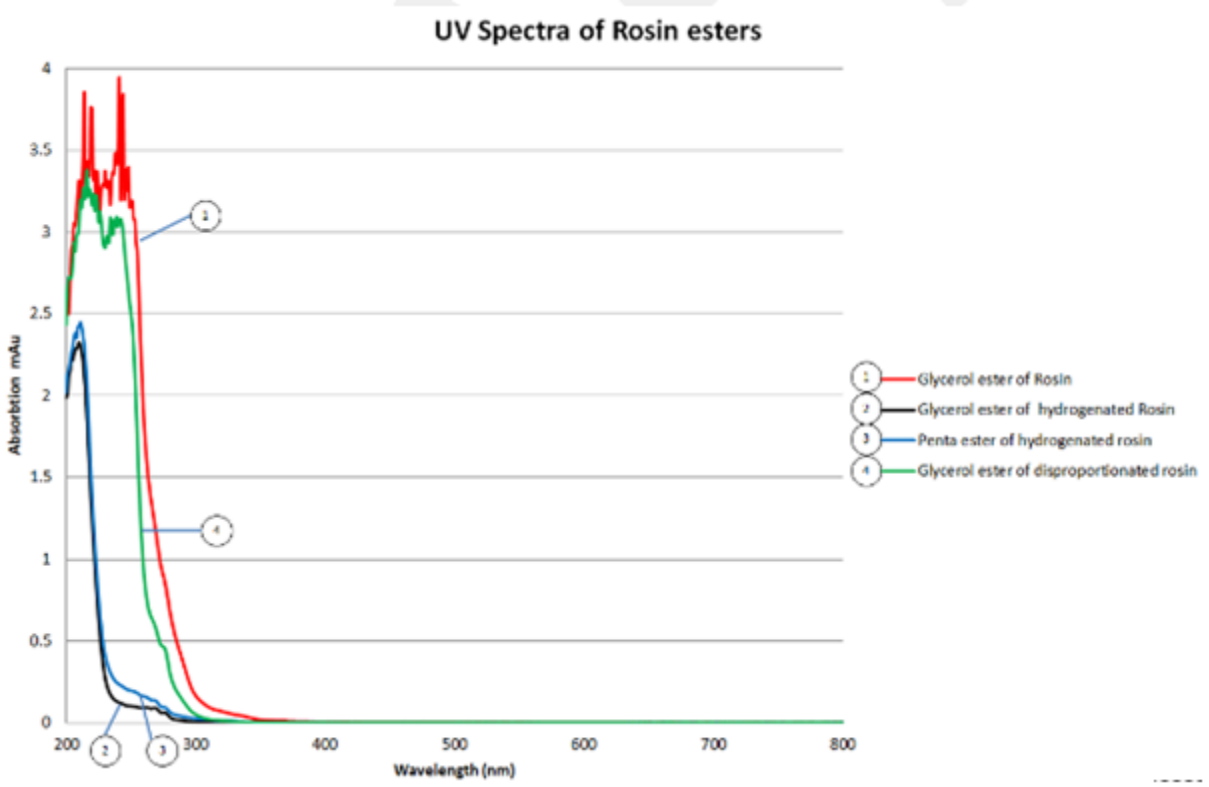

Resin acids and rosin acids, thick oil fumarated decyl esters
C=O carboxylic anhydride
C=O carboxylic acid
C=O carboxylic ester
-CH
%T
cm-1


Resin acids and rosin acids, fumarated, esters with pentaerythritol
-CH
C=O acid
%T


Rosin CAS 8050-09-7 EINECS 232-475-7
-O-H strech of excess alcohol
C-H stretch alkanes
C=O stretch vibration
3514
2899
2925
2652
2528
1690
1459
1384
1273
1231
Absorbance
Wavenumbers (cm-1)


Pentaerythritol esters of hydrogenated rosin CAS 64365-17-9 EINECS 264-848-5
-O-H strech of excess alcohol
C-H stretch alkanes
C=O stretch vibration
3514
2899
2925
2652
2528
1730
1459
1384
1273
1231
1195
1170
Broad O-H stretch vibration, typically in the range 2500–3300 cm-1 of the carboxylic acid group is missing (compare with the spectrum of rosin, CASRN 8050-09-7)
Absorbance
Wavenumbers (cm-1)

Appendix 2 - Reference Spectra UV-VIS



Source - Eastman Chemical Middelburg (2011) Solvent n-Heptane

Appendix 3 – NMR

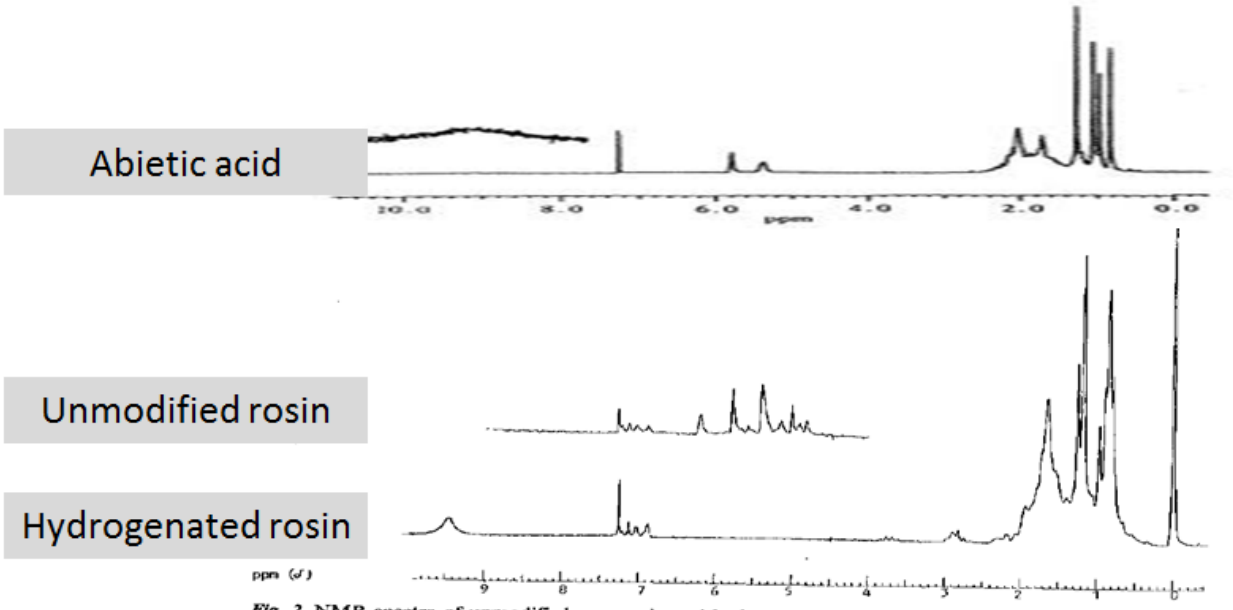


Fig. 2. NMR spectra of unmodified gum rosin and hydrogenated gum rosin.

Simulated Spectra

The following indicative spectra were produced using the ChemDraw software for ^{1}H- and ^{13}C-NMR spectra:

Individual resin acids

Hydrogenated rosin

Dehydrogenated rosin

Esters: glycerol, pentaerythritol, triethylene glycol

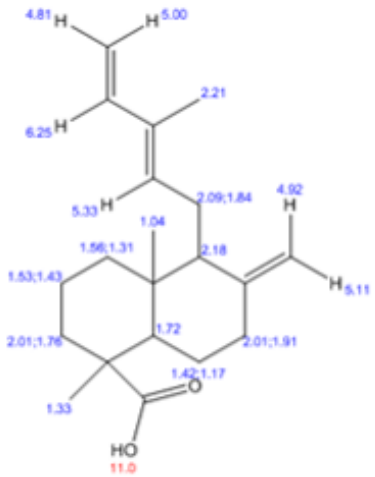
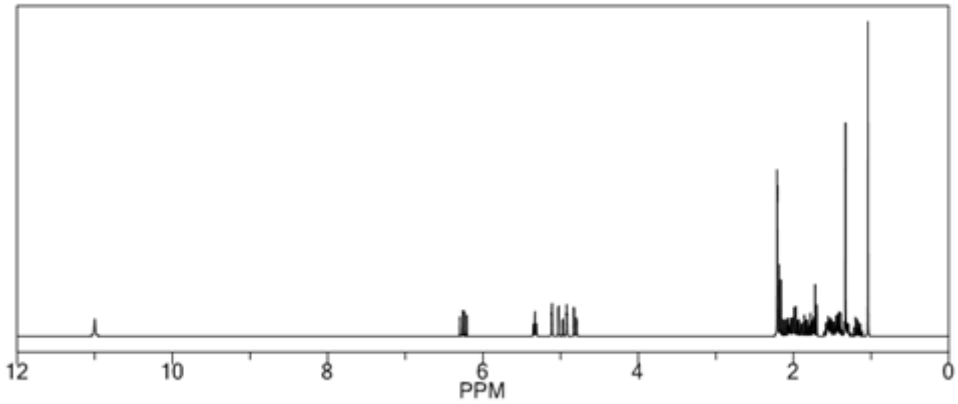
Salts

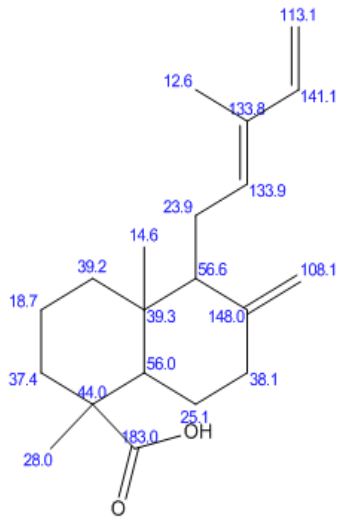
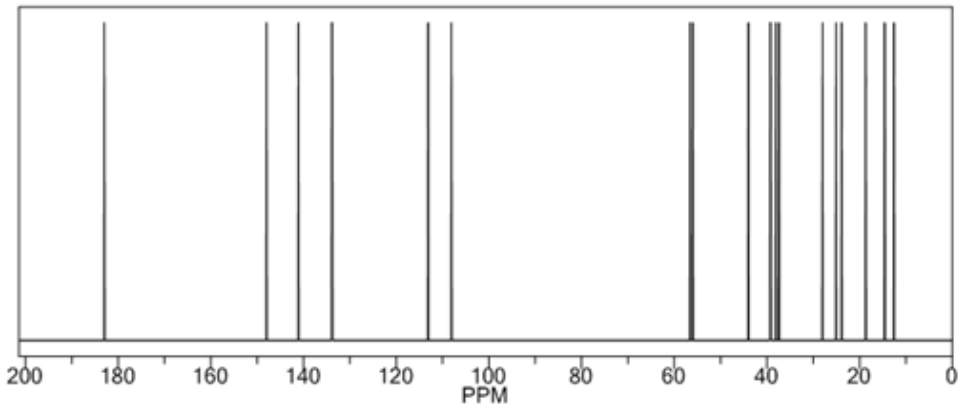
Adduct acid and anhydride

Adduct esters fumaric penta

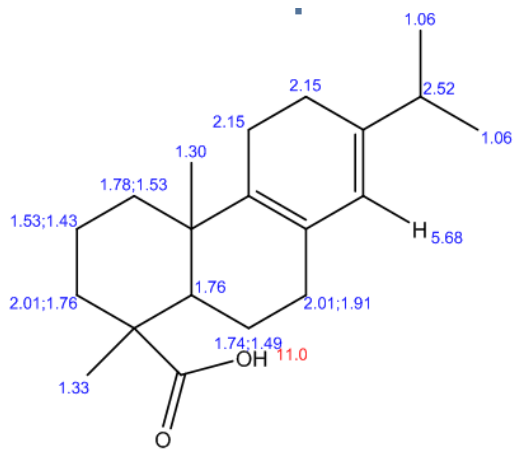
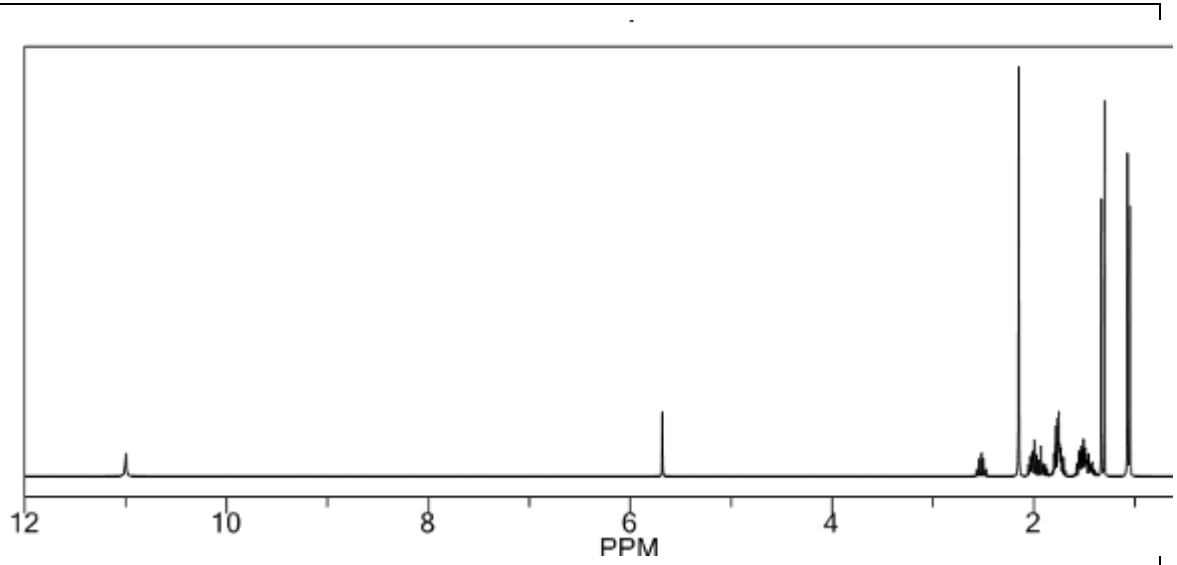
Formaldehyde adduct

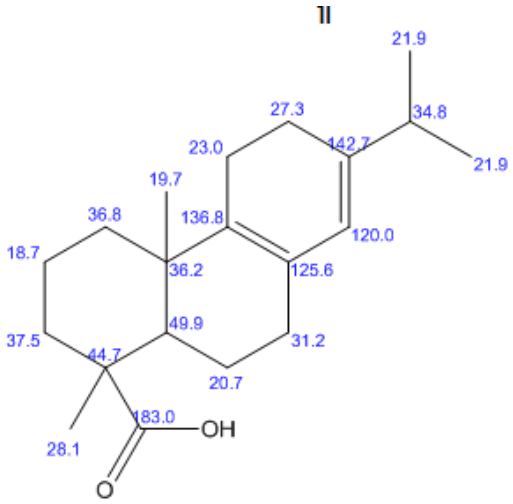
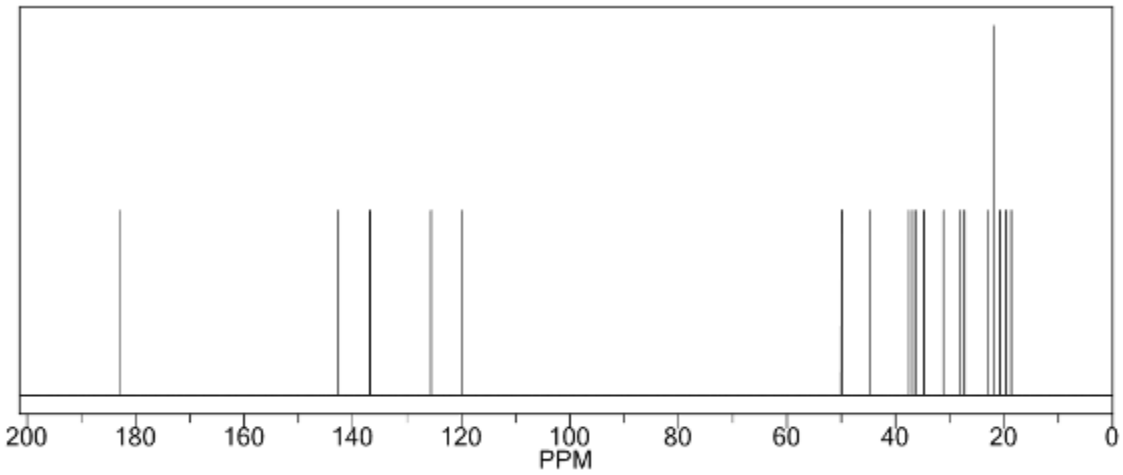
Estimation quality is indicated by color: good, medium, rough

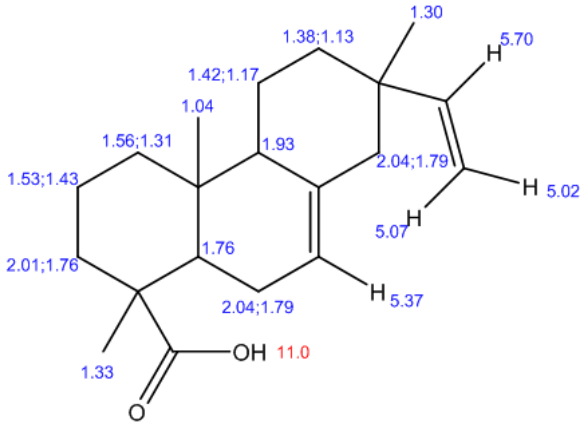
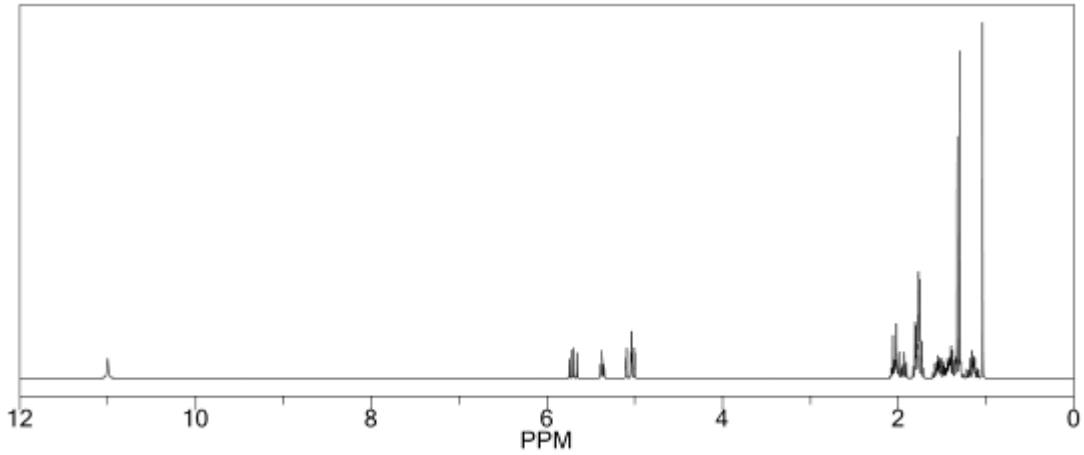
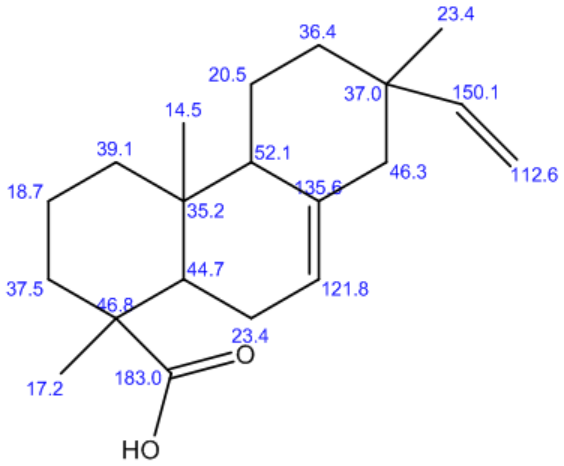
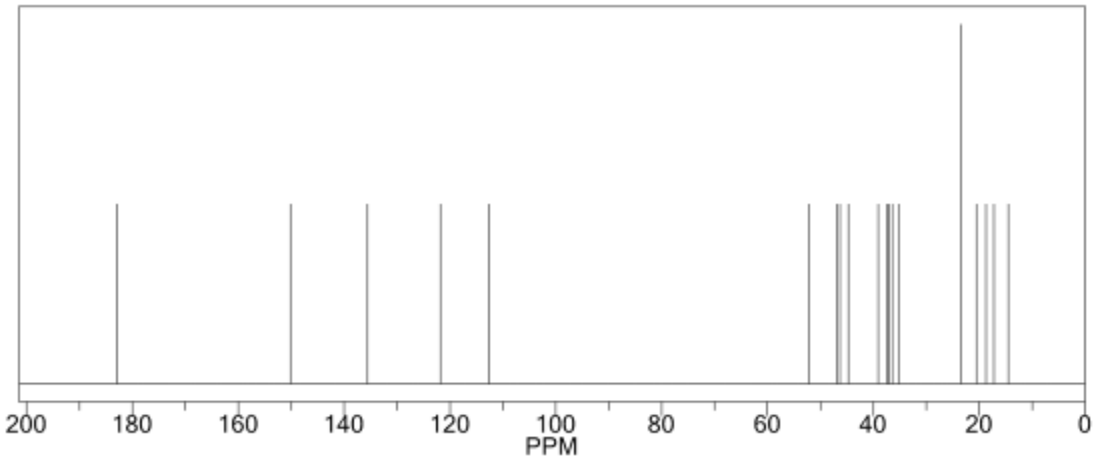
Communic acid simulated spectrum		
^{1}H-NMR		

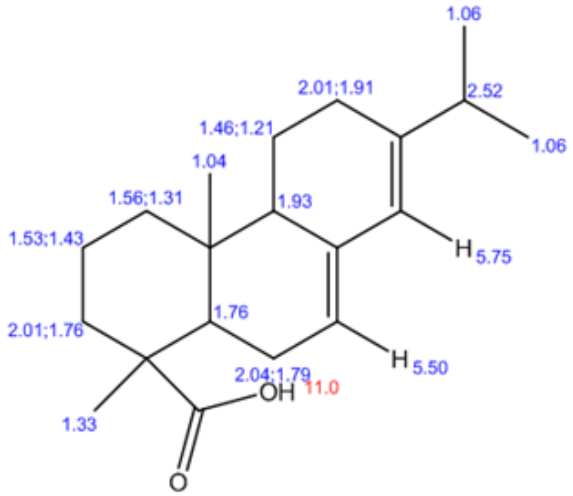
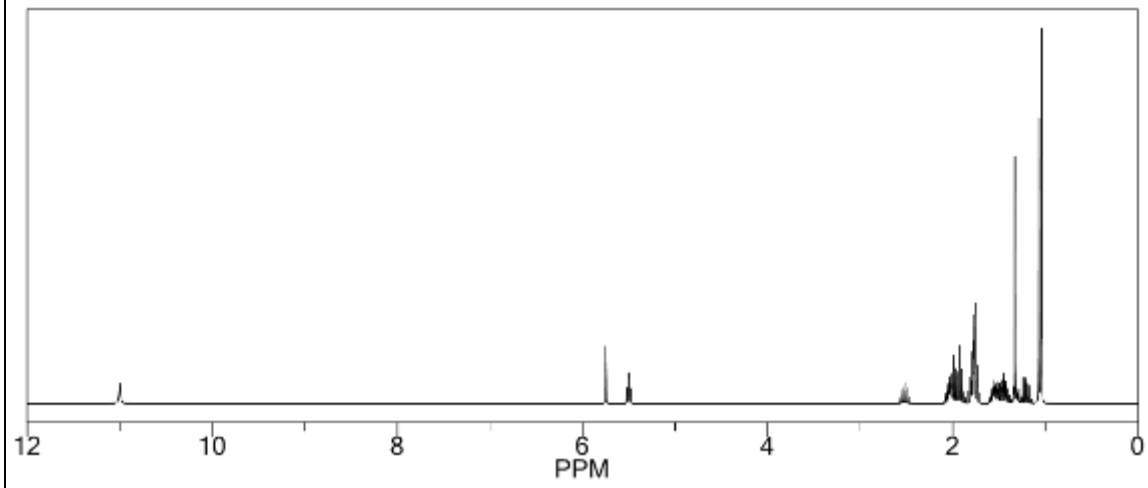
NMR 13C		

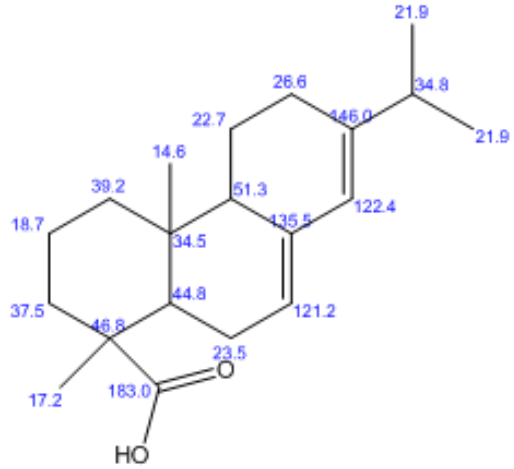
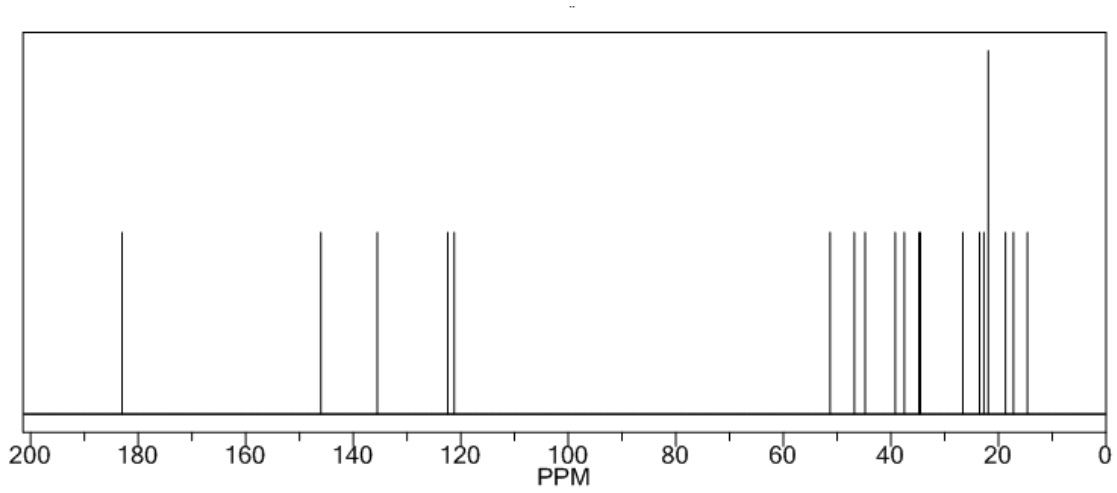
Palustric acid simulated spectrum

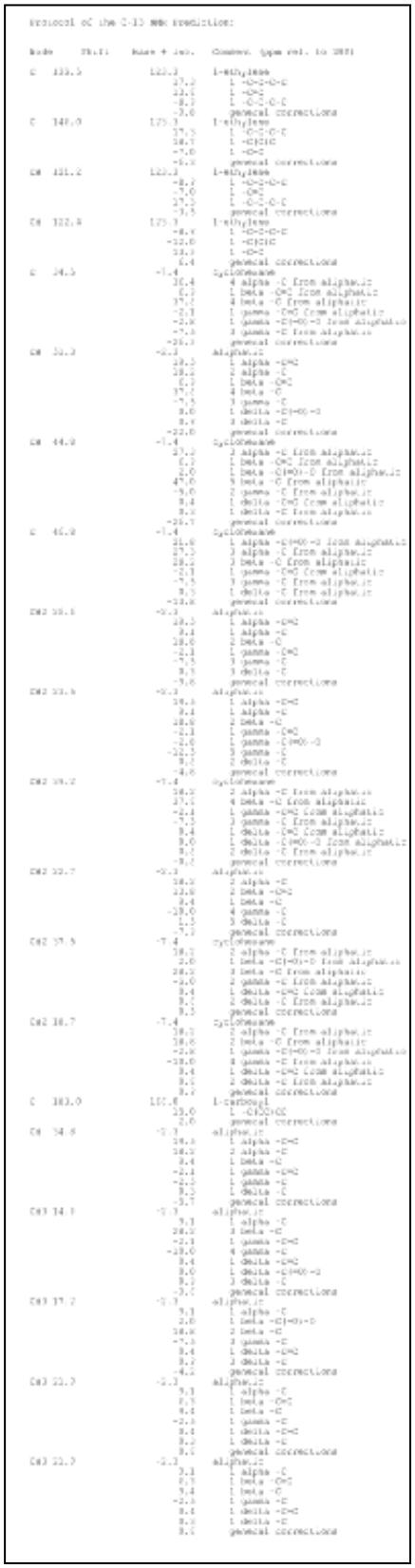
^{1}H-NMR	 1.06 2.15 2.52 2.15 1.06 1.30 1.78;1.53 1.53;1.43 H 5.68 1.76 2.01;1.76 2.01;1.91 1.74;1.49 OH 11.0 1.33 O	 12 10 8 6 4 2 PPM

NMR 13C		
Isopimaric acid simulated spectrum		

^{1}H-NMR		
NMR 13C		

Abietic acid simulated spectrum		
^{1}H-NMR		

NMR 13C	 21.9 26.6 34.8 22.7 146.0 21.9 14.6 39.2 51.3 122.4 18.7 135.5 34.5 44.8 37.5 121.2 46.8 23.5 O 17.2 183.0 HO	 200 180 160 140 120 100 80 60 40 20 0 PPM



Protocol of the C-13 NMR Prediction:

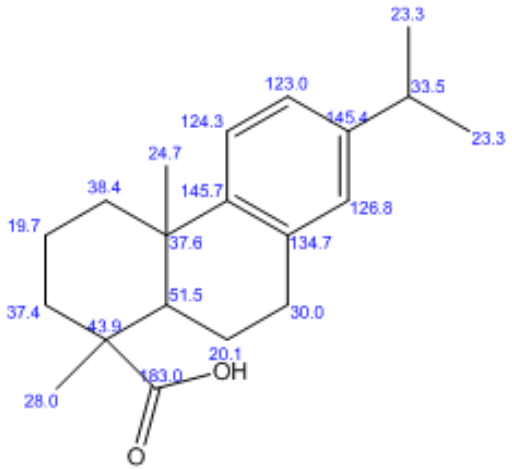
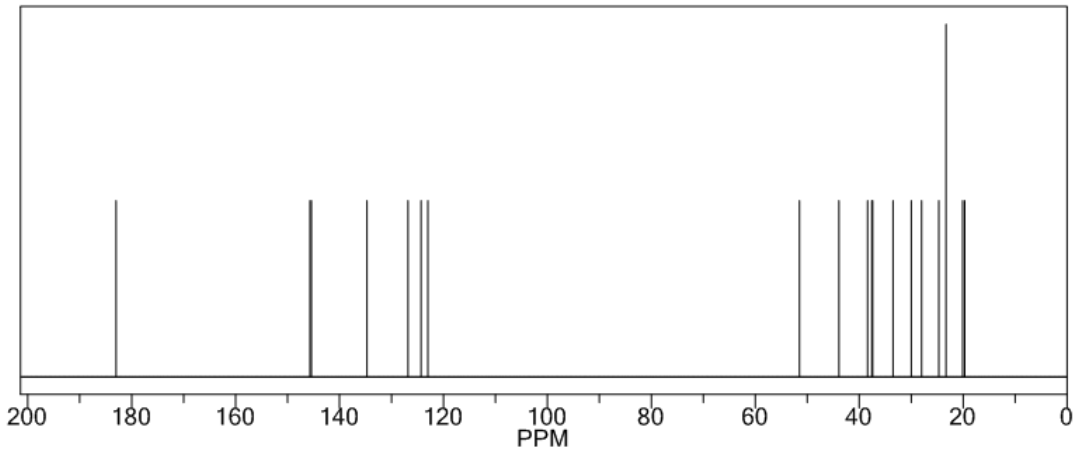
Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
C 133.5		123.3	1-ethylene
		17.2	1 -C-C-C-C
		12.5	1 -C=C
		8.2	1 -C-C-C-C
		-3.6	general corrections
C 148.0		123.3	1-ethylene
		17.5	1 -C-C-C-C
		18.7	1 -C=C(C)C
		-7.6	1 -C=C
		-6.4	general corrections
CH 121.2		123.3	1-ethylene
		-8.2	1 -C-C-C-C
		-7.6	1 -C=C
		17.5	1 -C-C-C-C
		-3.5	general corrections
CH 122.8		123.3	1-ethylene
		-8.4	1 -C-C-C-C
		-22.6	1 -C(C)=C
		13.3	1 -C=C
		5.4	general corrections
C 24.5		-1.4	cyclohexane
		20.4	4 alpha -C from alpha,c
		6.3	1 beta -C=C from aliphatic
		17.2	4 beta -C from aliphatic
		-2.1	1 gamma -C=O from aliphatic
		-2.8	1 gamma -C(=O)-O from aliphatic
		-7.6	3 gamma -C from alpha,c
		-25.2	general corrections
CH 32.3		-2.3	alpha,c
		19.5	1 alpha -C=C
		28.2	2 alpha -C
		6.3	1 beta -C=C
		37.5	4 beta -C
		-7.5	3 gamma -C
		9.6	1 delta -C(=O)-O
		9.4	3 delta -C
		-22.6	general corrections
CH 44.9		-1.4	cyclohexane
		21.6	1 alpha -C(=O)-O from aliphatic
		27.5	3 alpha -C from alpha,c
		28.2	3 beta -C from aliphatic
		-2.1	1 gamma -C=O from aliphatic
		-7.5	3 gamma -C from alpha,c
		9.5	1 delta -C from alpha,c
		-23.8	general corrections
CH2 30.6		-2.3	alpha,c
		19.5	1 alpha -C=C
		9.1	1 alpha -C
		28.6	2 beta -C
		-2.1	1 gamma -C=O
		-7.5	3 gamma -C
		9.5	3 delta -C
		-9.6	general corrections
CH2 33.6		-2.3	alpha,c
		19.5	1 alpha -C=C
		9.1	1 alpha -C
		28.6	2 beta -C
		-2.1	1 gamma -C=O
		-2.8	1 gamma -C(=O)-O
		-22.5	3 gamma -C
		9.5	2 delta -C
		-4.6	general corrections
CH2 39.2		-7.4	cyclohexane
		18.9	2 alpha -C from alpha,c
		37.5	4 beta -C from aliphatic
		-2.1	1 gamma -C=O from aliphatic
		-7.5	2 gamma -C from alpha,c
		9.4	1 delta -C=O from aliphatic
		9.6	1 delta -C(=O)-O from aliphatic
		9.5	2 delta -C from alpha,c
		-9.6	general corrections
CH2 33.7		-2.3	alpha,c
		18.9	2 alpha -C
		33.6	2 beta -C=C
		9.4	1 beta -C
		-19.0	4 gamma -C
		1.5	3 delta -C
		-7.2	general corrections
CH2 37.5		-7.4	cyclohexane
		18.1	2 alpha -C from alpha,c
		2.6	1 beta -C(=O)-O from alpha,c
		28.2	3 beta -C from aliphatic
		-2.0	2 gamma -C from alpha,c
		9.4	1 delta -C=C from aliphatic
		9.5	2 delta -C from alpha,c
		9.3	general corrections
CH2 38.7		-7.4	cyclohexane
		18.1	2 alpha -C from alpha,c
		28.6	2 beta -C from aliphatic
		-2.8	1 gamma -C(=O)-O from aliphatic
		-18.0	4 gamma -C from alpha,c
		9.4	1 delta -C=C from aliphatic
		9.5	2 delta -C from alpha,c
		9.2	general corrections
C 183.0		181.8	1-carbonyl
		19.0	1 -C(C)=CC
		2.0	general corrections
CH 34.8		-2.3	alpha,c
		19.5	1 alpha -C=C
		18.2	2 alpha -C
		9.4	1 beta -C
		-2.1	1 gamma -C=C
		-2.5	1 gamma -C
		9.5	1 delta -C
		-3.7	general corrections
CH3 14.1		-2.3	alpha,c
		9.1	1 alpha -C
		28.2	2 beta -C
		-2.1	1 gamma -C=C
		-19.0	4 gamma -C
		9.4	1 delta -C=C
		9.6	1 delta -C(=O)-O
		9.3	3 delta -C
		-3.7	general corrections
CH3 17.2		-2.3	alpha,c
		9.1	1 alpha -C
		2.6	1 beta -C(=O)-O
		28.6	2 beta -C
		-7.5	3 gamma -C
		9.4	1 delta -C=C
		9.3	3 delta -C
		-4.2	general corrections
CH3 22.9		-2.3	alpha,c
		9.1	1 alpha -C
		9.5	1 beta -C=C
		9.4	1 beta -C
		-2.5	1 gamma -C
		9.4	1 delta -C=C
		9.3	1 delta -C
		9.1	general corrections
CH3 22.9		-2.3	alpha,c
		9.1	1 alpha -C
		9.5	1 beta -C=C
		9.4	1 beta -C
		-2.5	1 gamma -C
		9.4	1 delta -C=C
		9.3	1 delta -C
		9.1	general corrections

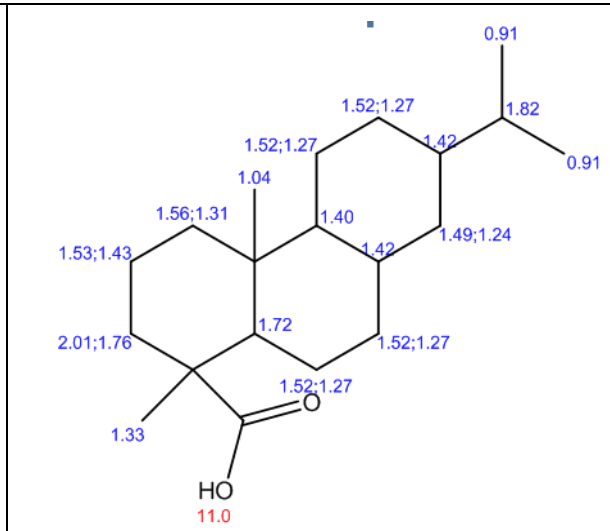
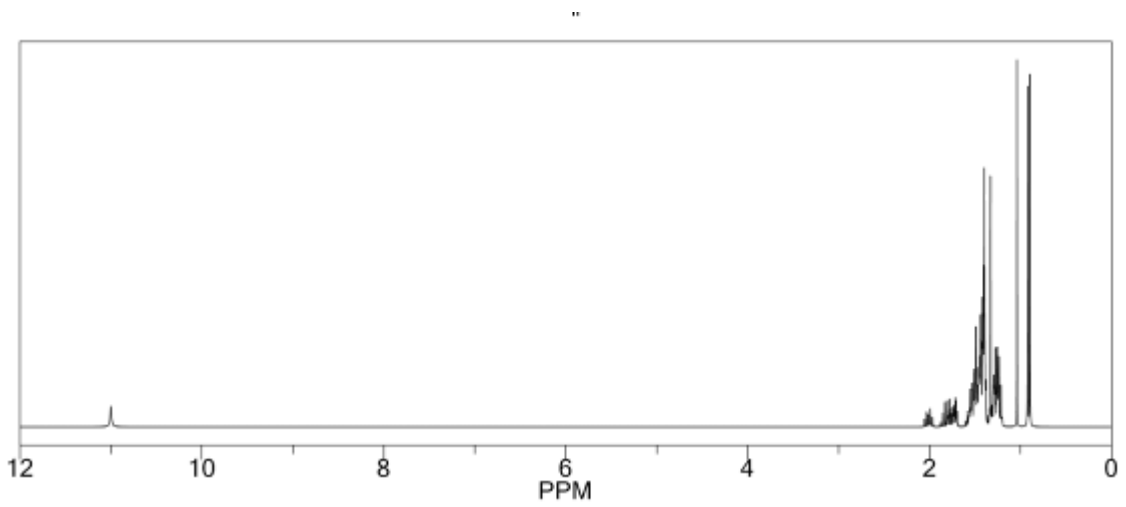
Protocol of the H-1 NMR Prediction:

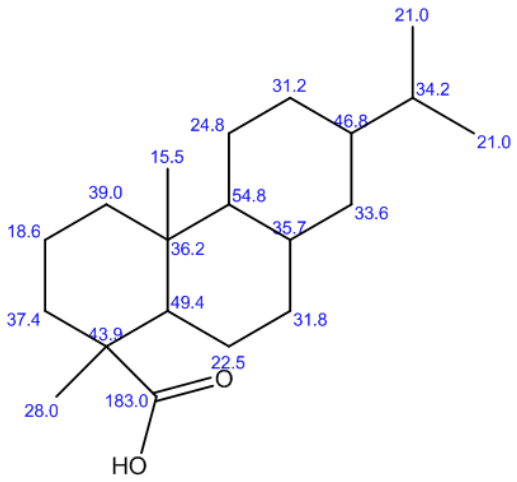
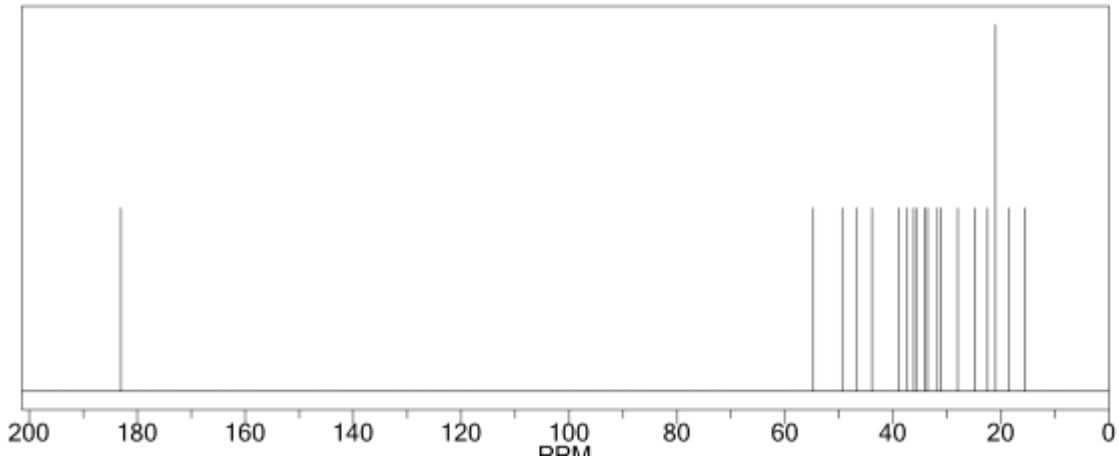
Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
OH 11.0		11.00	carboxylic acid
CH 1.93		1.96	cyclohexene
		-0.02	2 beta -C from methine
		-0.01	1 beta -C from methine
CH 1.76		1.44	cyclohexane
		-0.02	2 beta -C from methine
		0.32	1 beta -C(=O)-O from methine
		-0.01	1 beta -C from methine
		0.03	1 beta -C=C from methine
CH2 2.01;1.910000		1.37	methylene
		0.63	1 alpha -C=C
		-0.04	1 beta -C
CH2 2.04;1.795000		1.96	cyclohexene
		-0.04	1 beta -C from methylene
CH2 1.56;1.315000		1.44	cyclohexane
		-0.08	2 beta -C from methylene
		0.08	general corrections
CH2 1.46;1.205000		1.37	methylene
		0.00	1 beta -C=C
		-0.04	1 beta -C
		0.00	1 beta -C=C
CH2 2.01;1.765000		1.44	cyclohexane
		0.23	1 beta -C(=O)-O from methylene
		-0.04	1 beta -C from methylene
		0.26	general corrections
CH2 1.53;1.430000		1.44	cyclohexane
		0.04	general corrections
CH 2.52		1.50	methine
		0.34	2 alpha -C
		0.68	1 alpha -C=C
CH3 1.04		0.86	methyl
		0.30	3 beta -C-R
		-0.12	general corrections
CH3 1.33		0.86	methyl
		0.23	1 beta -C(=O)-O
		0.20	2 beta -C-R
		0.04	general corrections
CH3 1.06		0.86	methyl
		0.20	1 beta -C=C
		0.05	1 beta -C
		-0.05	general corrections
CH3 1.06		0.86	methyl
		0.20	1 beta -C=C
		0.05	1 beta -C
		-0.05	general corrections
H 5.50		5.59	cyclohexene
		-0.09	1 -C=C cis from 1-ethylene
H 5.75		5.25	1-ethylene
		-0.50	2 -C c + t
		1.00	1 -C=C gem

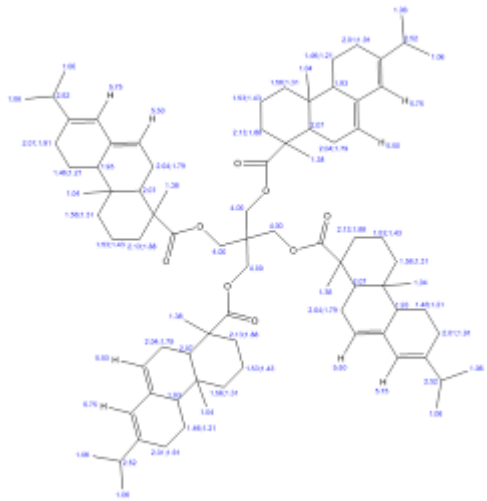
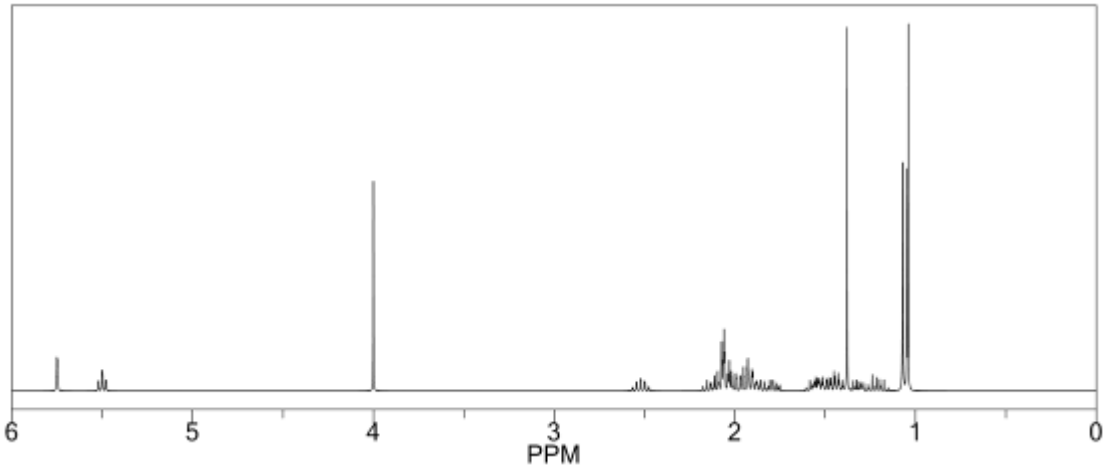
1H NMR Coupling Constant Prediction

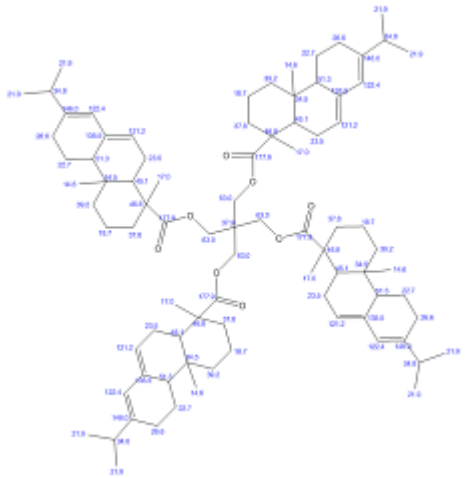
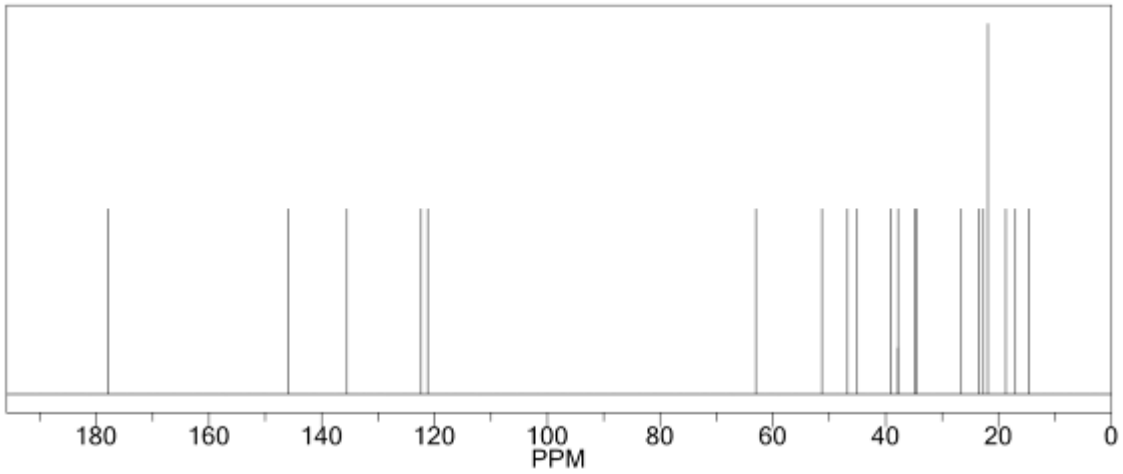
shift	atom index	coupling partner, constant and vector
11.0	22	
1.93	10	
		14 7.0 H-C-CH-H
		23 -1.0 H-C>C=C>H
1.76	4	
		7 7.0 H-C-CH-H
1.96	13	diastereotopic -12.4 H-C-H
		14 7.1 H-CH-CH-H
		24 -1.0 H-CH>C=C>H
1.92	7	diastereotopic -12.4 H-C-H
		23 6.2 H-CH-C(sp2)-H
		4 7.0 H-CH-C-H
1.44	6	diastereotopic -12.4 H-C-H
		1 7.1 H-CH=CH-H
1.33	14	diastereotopic -12.4 H-C-H
		10 7.0 H-CH-C-H
		13 7.1 H-CH-CH-H
1.89	2	diastereotopic -12.4 H-C-H
		1 7.1 H-CH=CH-H
1.48	1	diastereotopic -12.4 H-C-H
		6 7.1 H-CH=CH-H
		2 7.1 H-CH-CH-H
2.52	17	
		18 6.8 H-C-CH2-H
		19 6.8 H-C-CH2-H
		24 -1.0 H-C>C=C<H
1.04	15	
1.33	16	
1.06	18	
		17 6.8 H-CH2-C-H
1.06	19	
		17 6.8 H-CH2-C-H
5.50	23	
		7 6.2 H-C(sp2)-CH-H
		10 -1.0 H>C=C>C=H
5.75	24	
		13 -1.0 H>C=C>CH-H
		17 -1.0 H>C=C<C-H

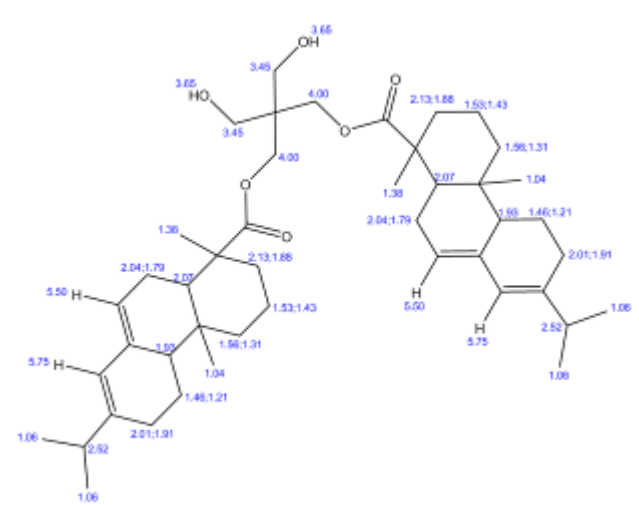
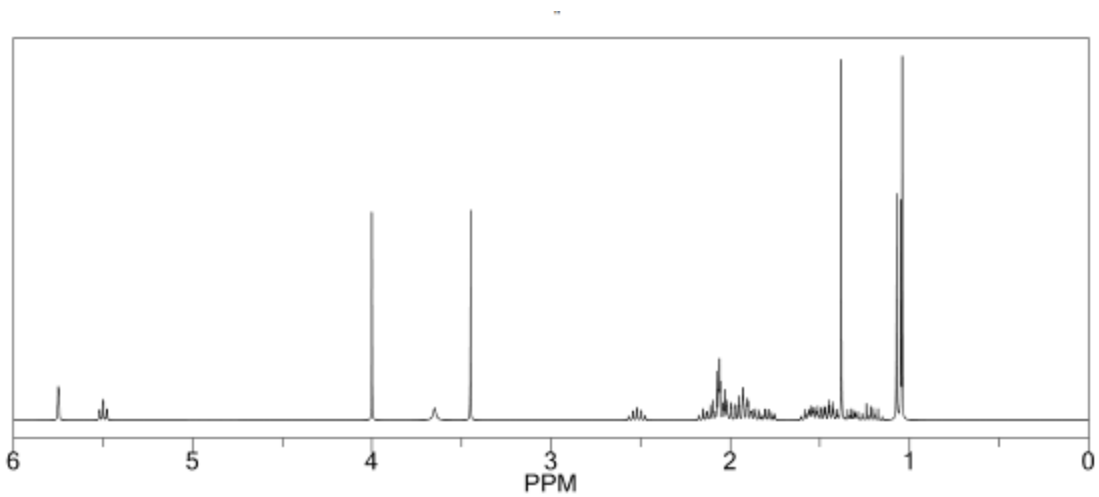
Dehydroabietic acid simulated spectrum		
^{1}H-NMR		
NMR 13C		

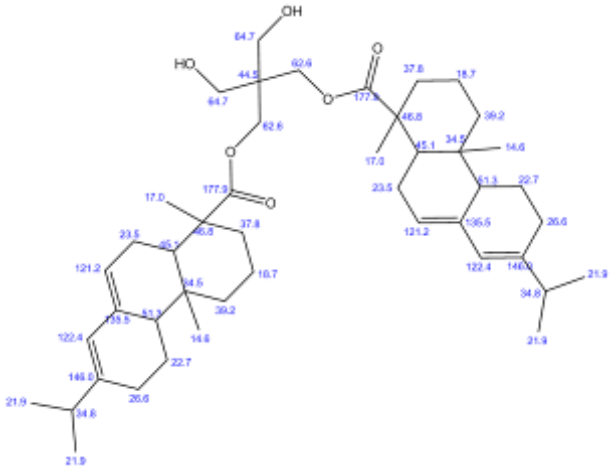
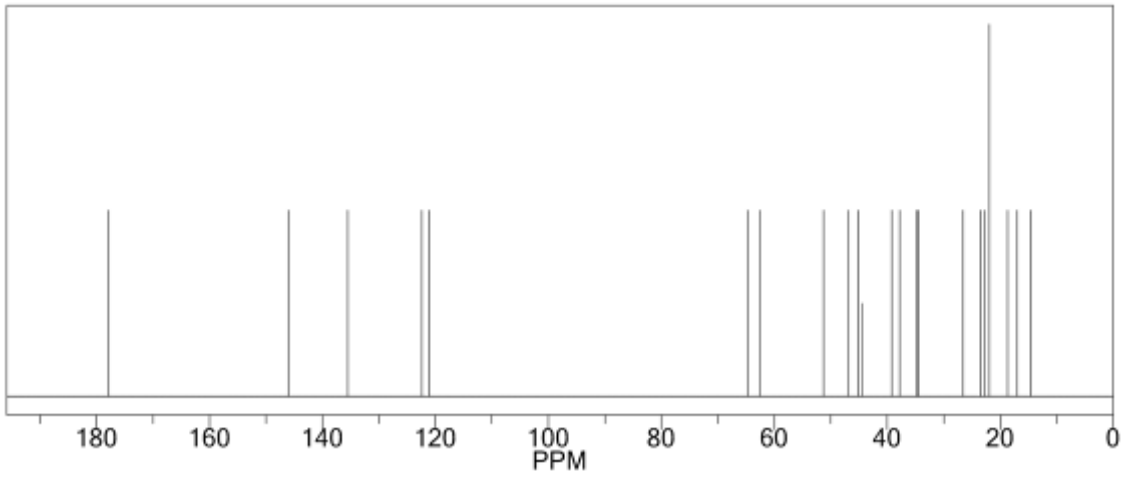
Tetrahydro abietic simulated spectrum		
^{1}H-NMR		

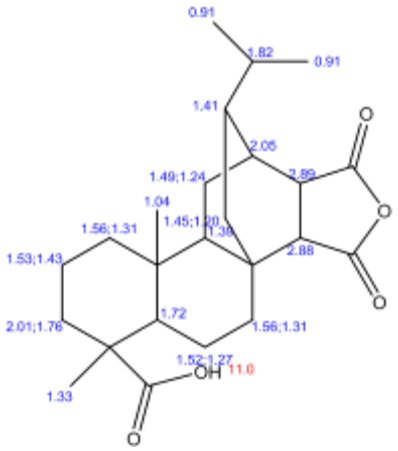
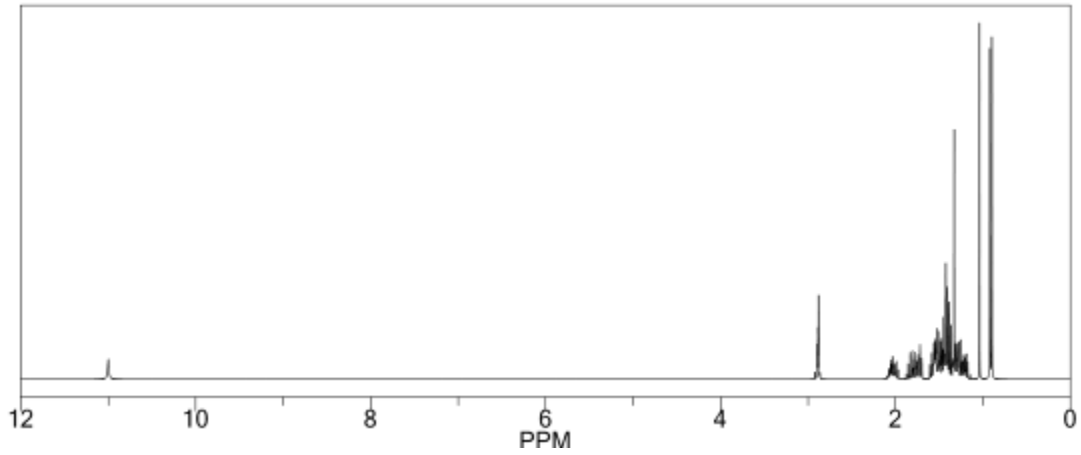
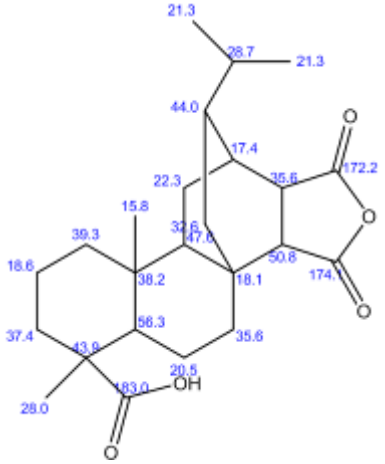
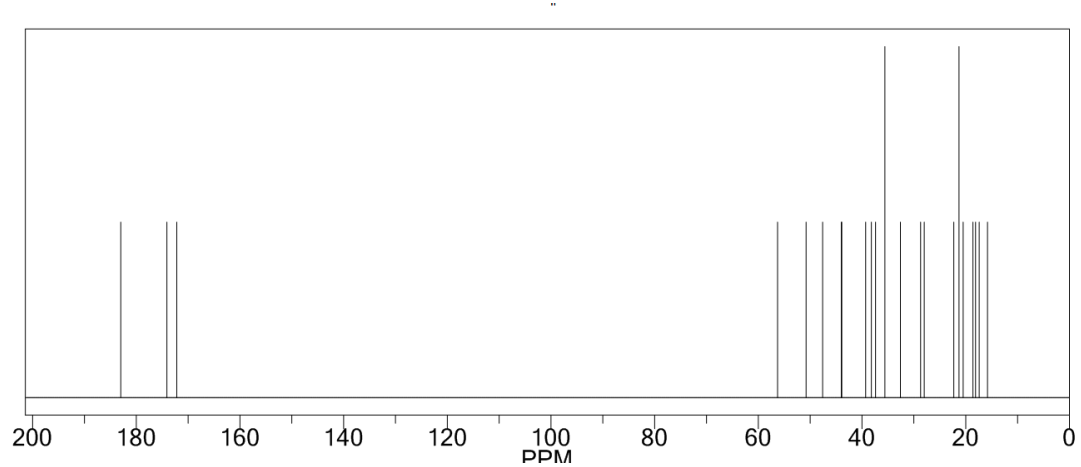
NMR 13C	 21.0 31.2 34.2 24.8 46.8 21.0 15.5 39.0 54.8 33.6 18.6 35.7 36.2 49.4 37.4 43.9 31.8 22.5 O 28.0 183.0 HO	 200 180 160 140 120 100 80 60 40 20 0 PPM

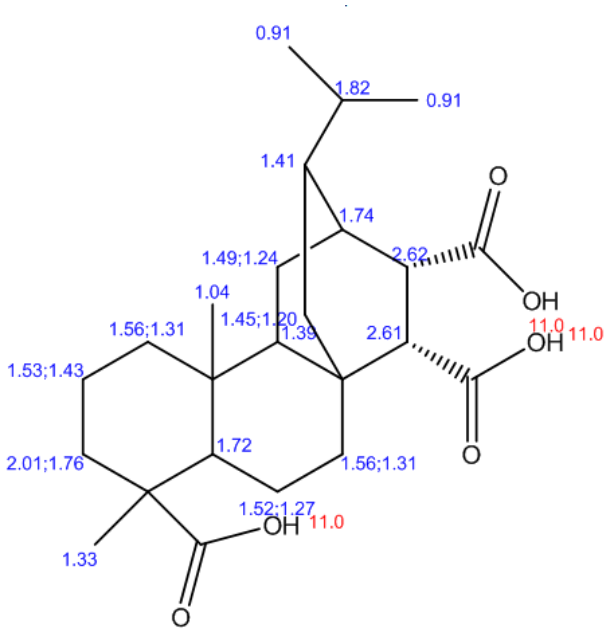
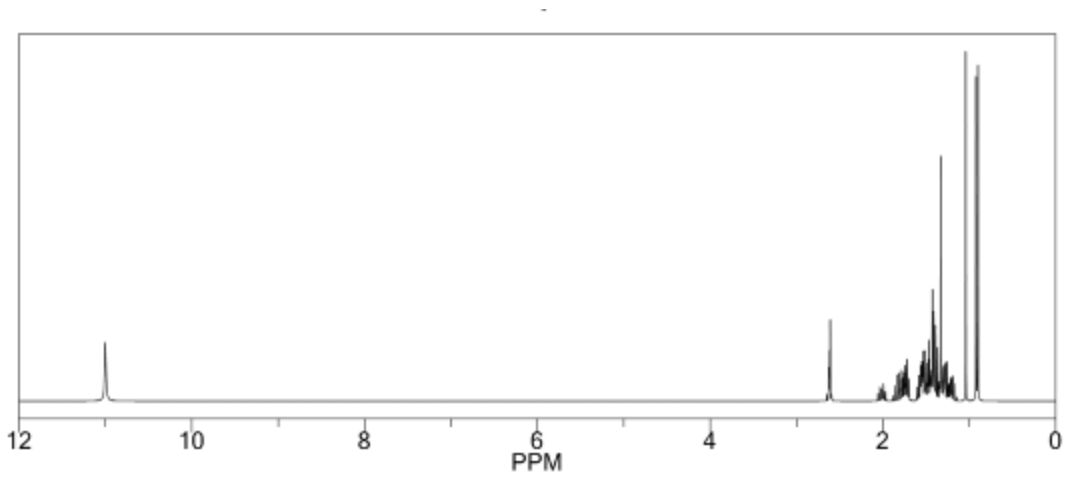
Pentaerythritol tetra-ester of abietic acid simulated spectrum		
^{1}H-NMR		

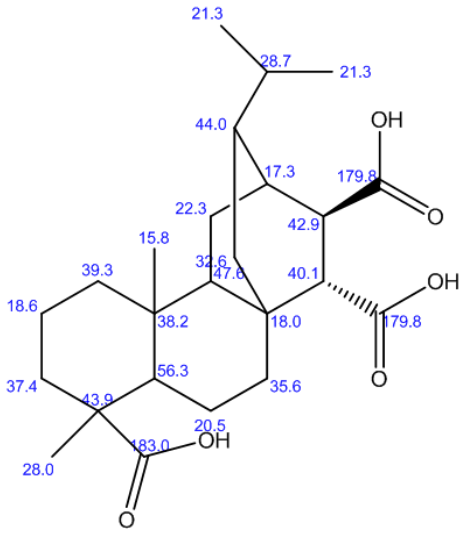
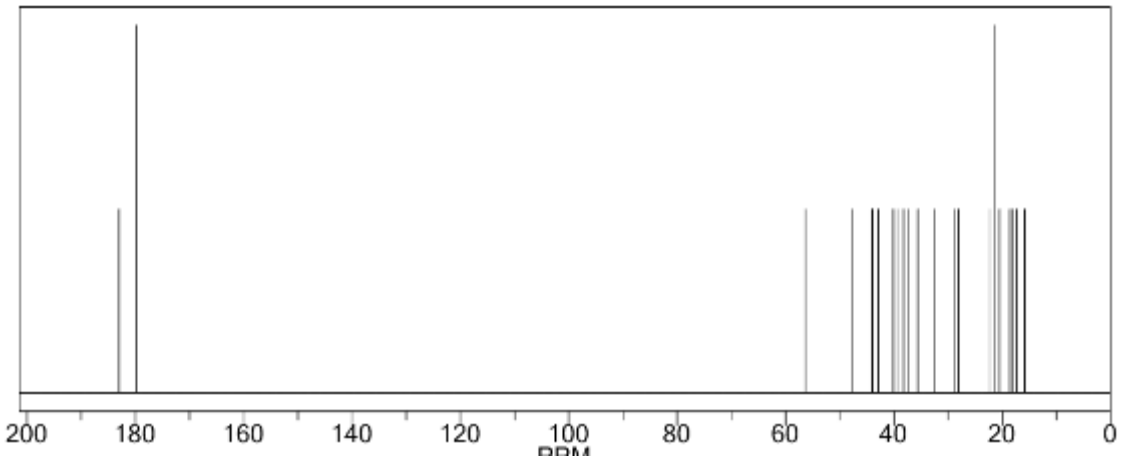
NMR 13C		

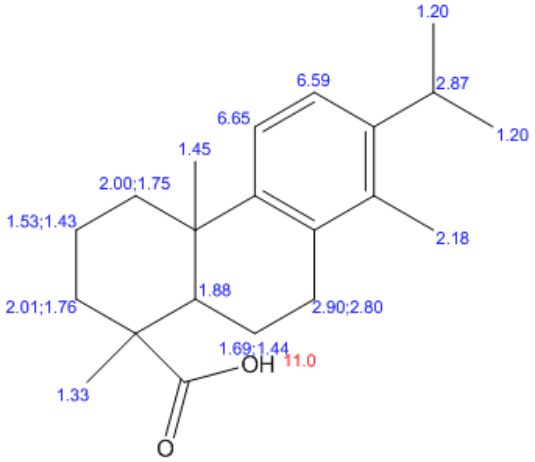
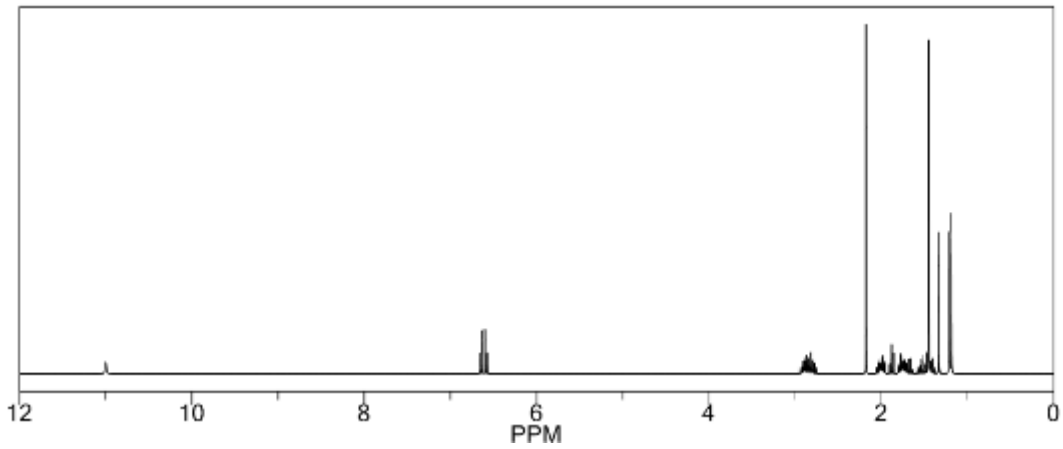
Simulated NMR Spectra of the pentaerythritol di-ester of abietic acid		
^{1}H-NMR		

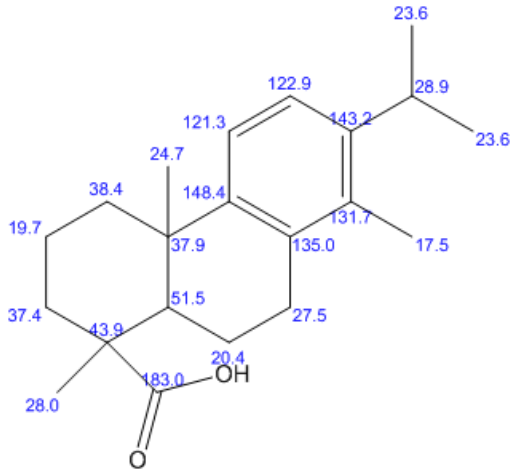
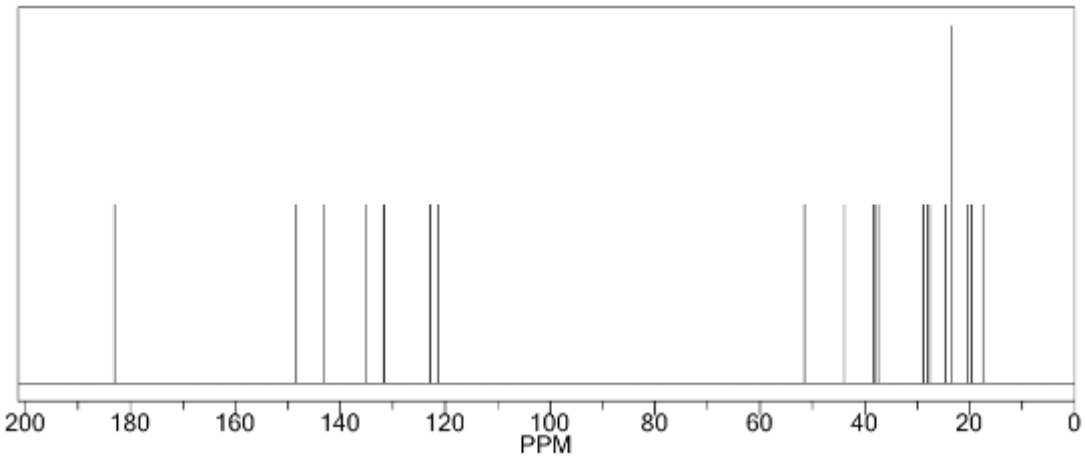
NMR 13C		

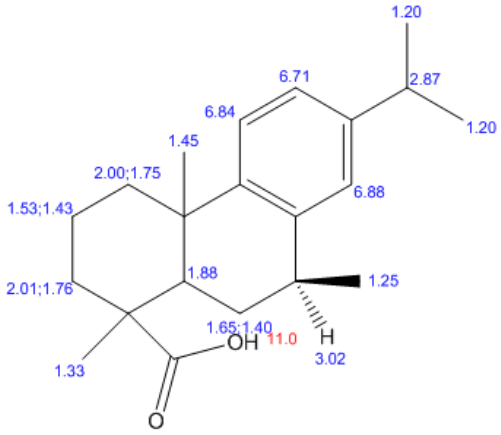
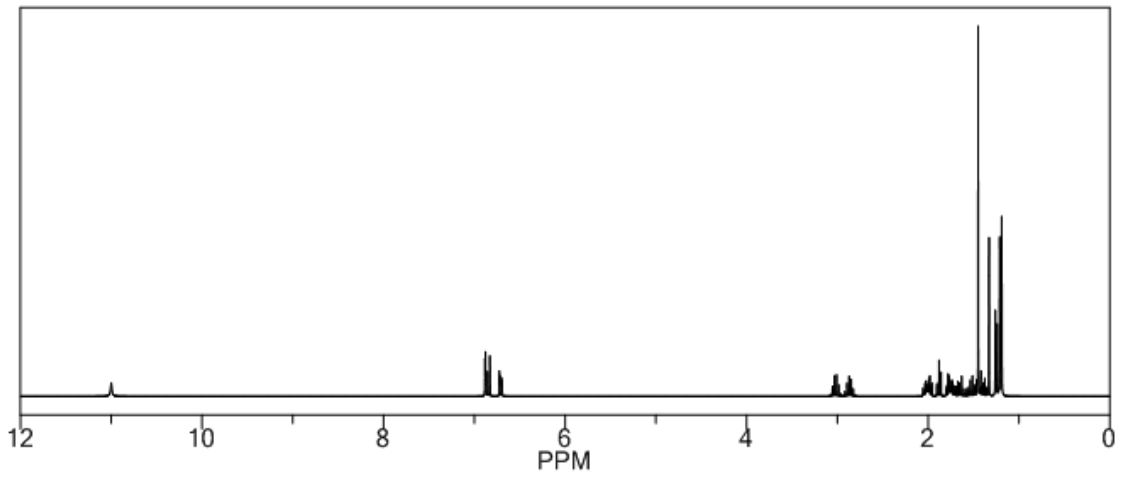
Simulated NMR Spectra of the maleic anhydride adduct of rosin		
^{1}H-NMR		
NMR 13C		

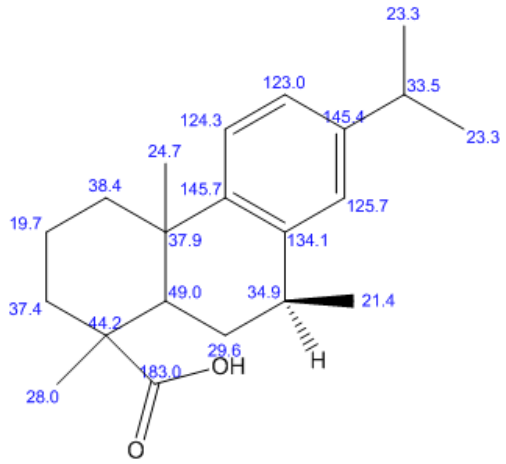
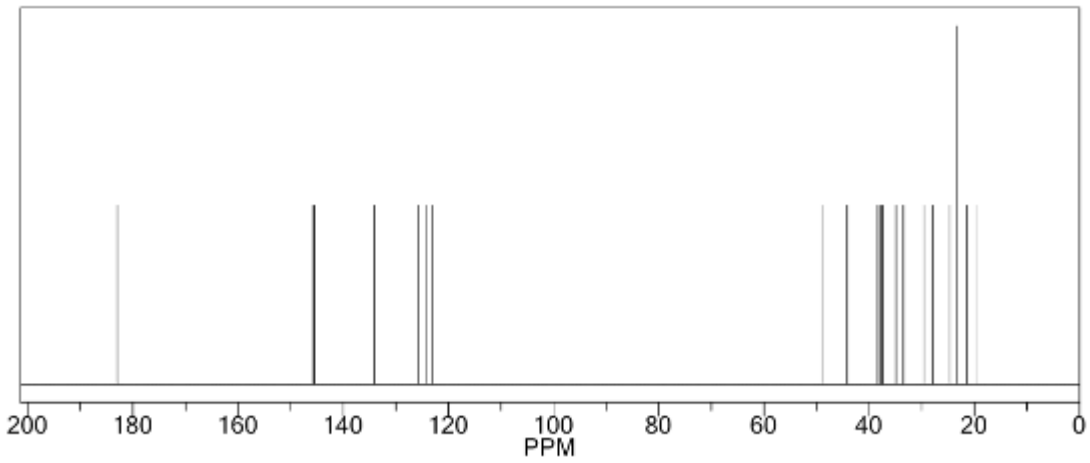
Simulated NMR Spectra of the maleopimaric acid endo-endo isomer		
^{1}H-NMR		
NMR 13C		

Simulated NMR Spectra of maleopimaric acid endo-exo isomer		
^{1}H-NMR		
NMR 13C		

Simulated NMR Spectra of the formaldehyde adduct of rosin 14-methyldehydroabietic acid		
^{1}H-NMR		

NMR 13C	 23.6 122.9 28.9 121.3 143.2 23.6 24.7 38.4 148.4 19.7 131.7 37.9 135.0 17.5 51.5 37.4 27.5 43.9 20.4 183.0 OH 28.0 O	 200 180 160 140 120 100 80 60 40 20 0 PPM

Simulated NMR Spectra of the formaldehyde adduct of rosin 7(S)-methyldehydroabietic acid		
^{1}H-NMR		

NMR 13C	 23.3 123.0 33.5 124.3 145.4 23.3 24.7 38.4 145.7 125.7 19.7 37.9 134.1 49.0 34.9 21.4 37.4 44.2 29.6 183.0 OH H 28.0 O	 200 180 160 140 120 100 80 60 40 20 0 PPM

Simulated NMR Spectra of the formaldehyde adduct of rosin 7(R)-methyldehydroabietic acid

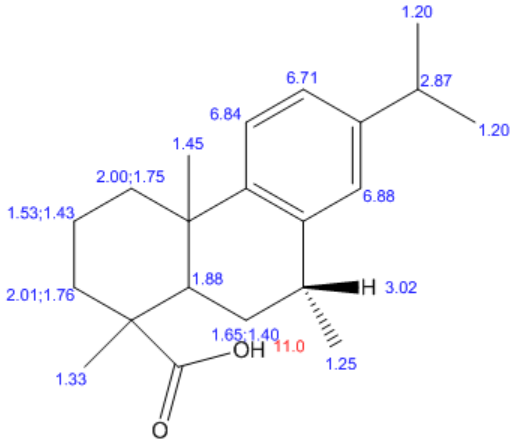
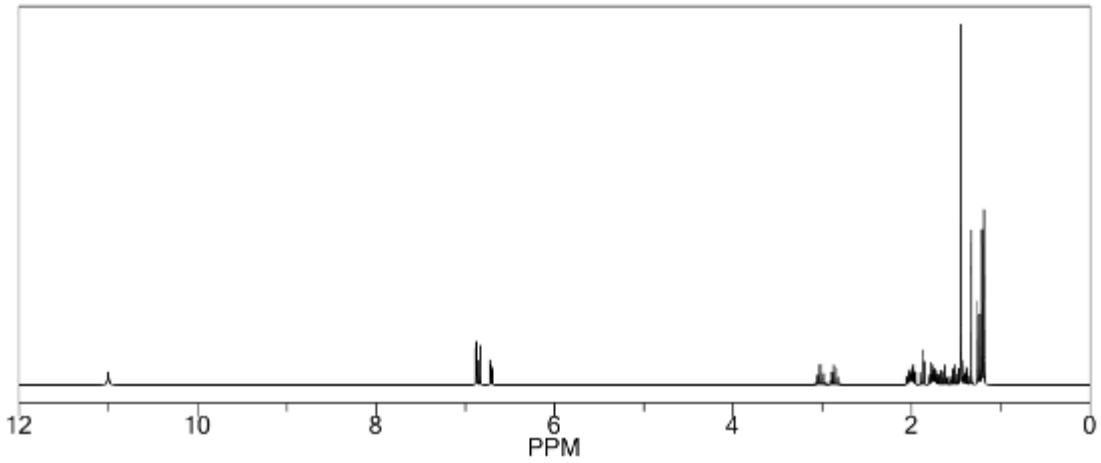
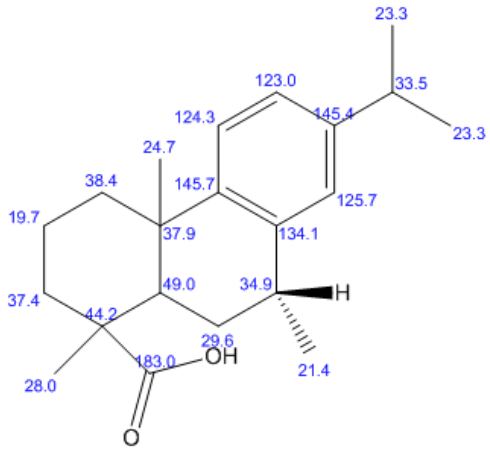
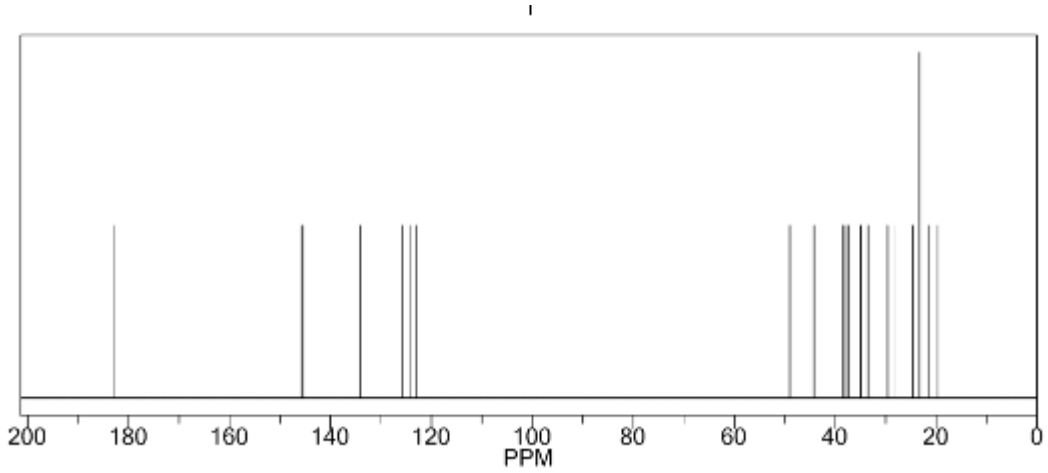
^{1}H-NMR		
NMR 13C		

Table 8 Simulated 1H-NMR spectra of rosin esters

	R_2-C**H**-OH	R-C$\mathbf{H_2}$-OH	R'-C$\mathbf{H_2}$-O-R	R_2'-C**H**-O-R	R-O**H**	R'-O-C$\mathbf{H_2}$-R	R'$_2$-C**H**-COO-R	R'$_2$-C**H**-COOH	spectrum N^o
gly, mono-ester, position 1	3.90	3.56; 3.81	4.11; 4.36	-	3.58; 3.65	-	-	-	1
gly, mono-ester, position 2	-	3.59	-	4.13	3.65	-	-	-	2
gly, di-ester, position 1,3	4.41	-	4.11; 4.36	-	3.58	-	-	-	3
gly, di-ester, position 1,2	-	3.65; 3.90	4,20; 4.45	4.64	3.65	-	-	-	4
gly, tri-ester	-	-	4,20; 4,45	5.15	-	-	-	-	5
penta, mono-ester	-	3.45	4.00	-	3.65	-	-	-	6
penta, di-ester	-	3.45	4.00	-	3.65	-	-	-	7
penta, tri-ester	-	3.45	4.00	-	3.65	-	-	-	8
penta, tetra-ester	-	-	4.00	-	-	-	-	-	9
diethyleneglycol, mono-ester	-	3.44	4.25	-	3.65	3.56; 3.65	-	-	10

diethyleneglycol, di-ester	-	-	4.25	-	-	3.65	-	-	11

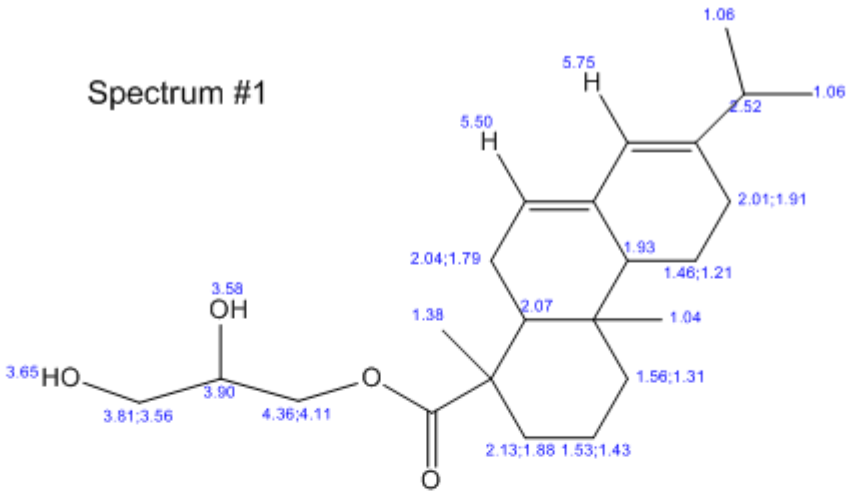
triethyleneglycol, mono-ester	-	3.44	4.25	-	3.65	3.54; 3.56; 3.65	-	-	12
triethyleneglycol, di-ester	-	-	4.25	-	-	3.54; 3.65	-	-	13

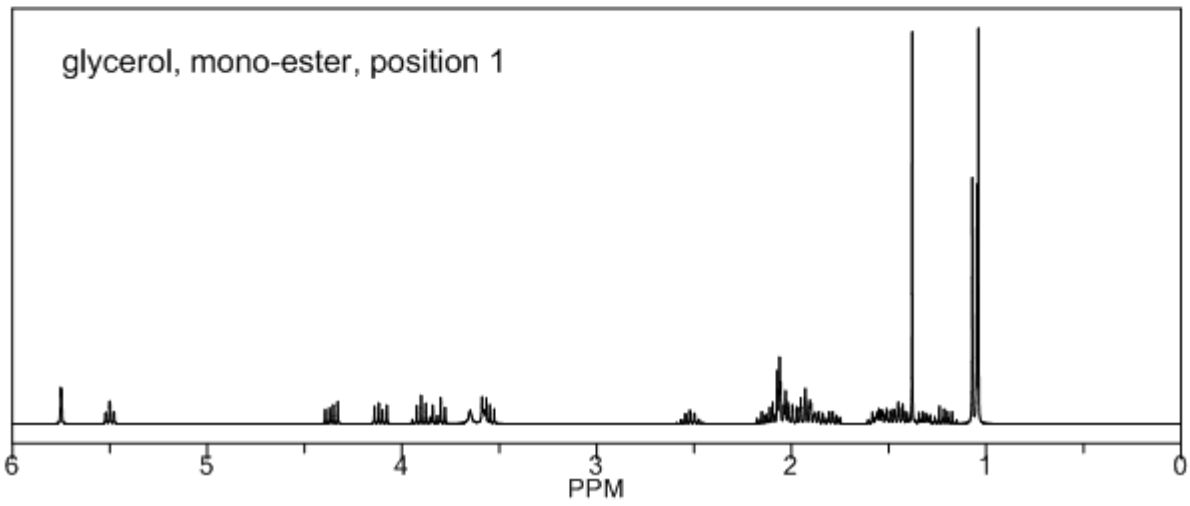
trimethylolpropane, mono-ester	-	3.45	4.00	-	3.65	-	-	-	14
trimethylolpropane, di-ester	-	3.45	4.00	-	3.65	-	-	-	15
trimethylolpropane, tri-ester	-	-	4.00	-	-	-			16

neopentylglycol, mono-ester	-	3.45	4.00	-	3.65	-	-	-	17
neopentylglycol, di-ester	-	-	4.00	-	-	-	-	-	18

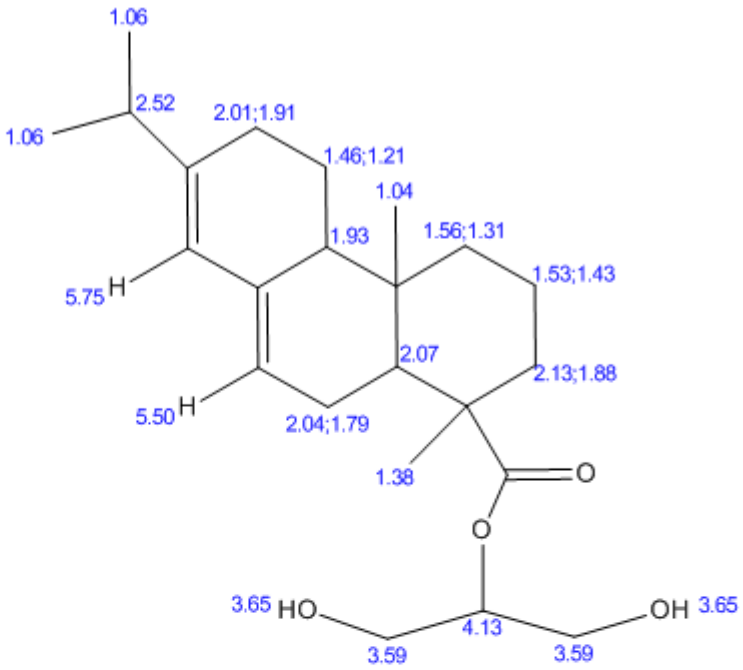
maleic adduct, glycerol-1 mono-ester, esterified at isopropyl side	3.90	3.56; 3.81	4.11; 4.36	-	3.58; 3.65	-	2.58	2.92	19
maleic adduct, glycerol-1 mono-ester, esterified at bridge side	3.90	3.56; 3.81	4.11; 4.36	-	3.58; 3.65	-	2.57	2.93	20

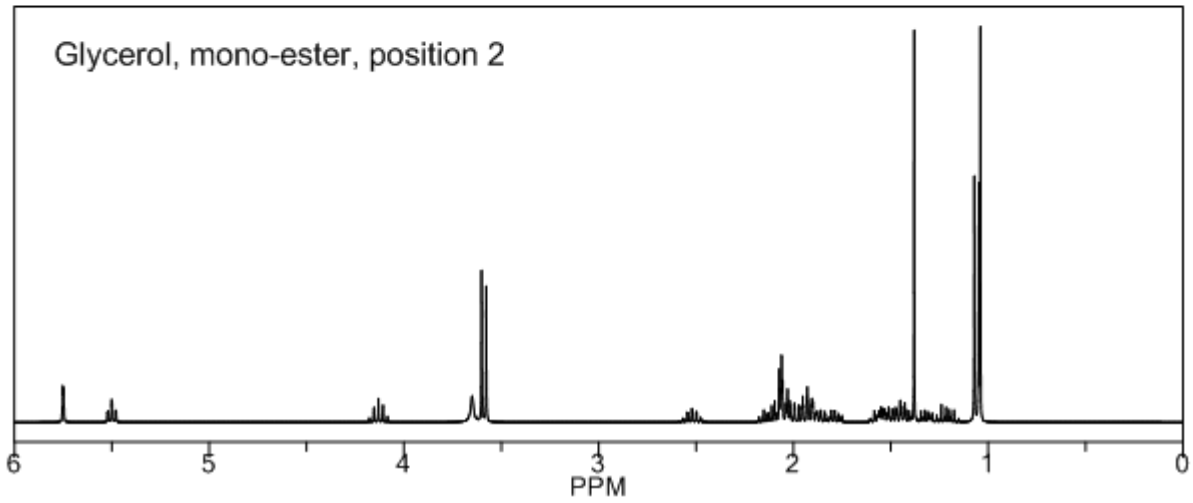
maleic adduct, glycerol-1 mono-ester, esterified at abietic side	3.90	3.56; 3.81	4.11; 4.36	-	3.58; 3.65	-	-	2.61; 2.62	21
maleic adduct, glycerol-2 mono-ester, esterified at isopropyl side	-	3.59	-	4.13	3.65	-	2.58	2.92	22
maleic adduct, glycerol-2 mono-ester, esterified at bridge side		3.59	-	4.13	3.65	-	2.57	2.93	23
maleic adduct, glycerol-2 mono-ester, esterified at abietic side	-	3.59	-	4.13	3.65	-	2.57	2.61; 2.62	24
maleic adduct, glycerol-1 di-ester, esterified at bridge side	3.90	3.56; 3.81	4.11; 4.36	-	3.58; 3.65	-	2.88; 2.89	-	25
maleic adduct, glycerol-1 di-ester, esterified at bridge side and abietic side	3.90	3.56; 3.81	4.11; 4.36	-	3.58; 3.65	-	2.57	2.93	26
maleic adduct, glycerol-1,2 di-ester, esterified at bridge side	-	3.65; 3.90	4.20; 4.45	4.64	3.65	-	2.88; 2.89	-	27
Fumaric adduct, pentaerythritol tetra-ester	-	-	4.00	-	-	-	2.61	2.97	28
Fumaric adduct, pentaerythritol tri-ester	-	3.45	4.00	-	3.65	-	2.61	2.97	29

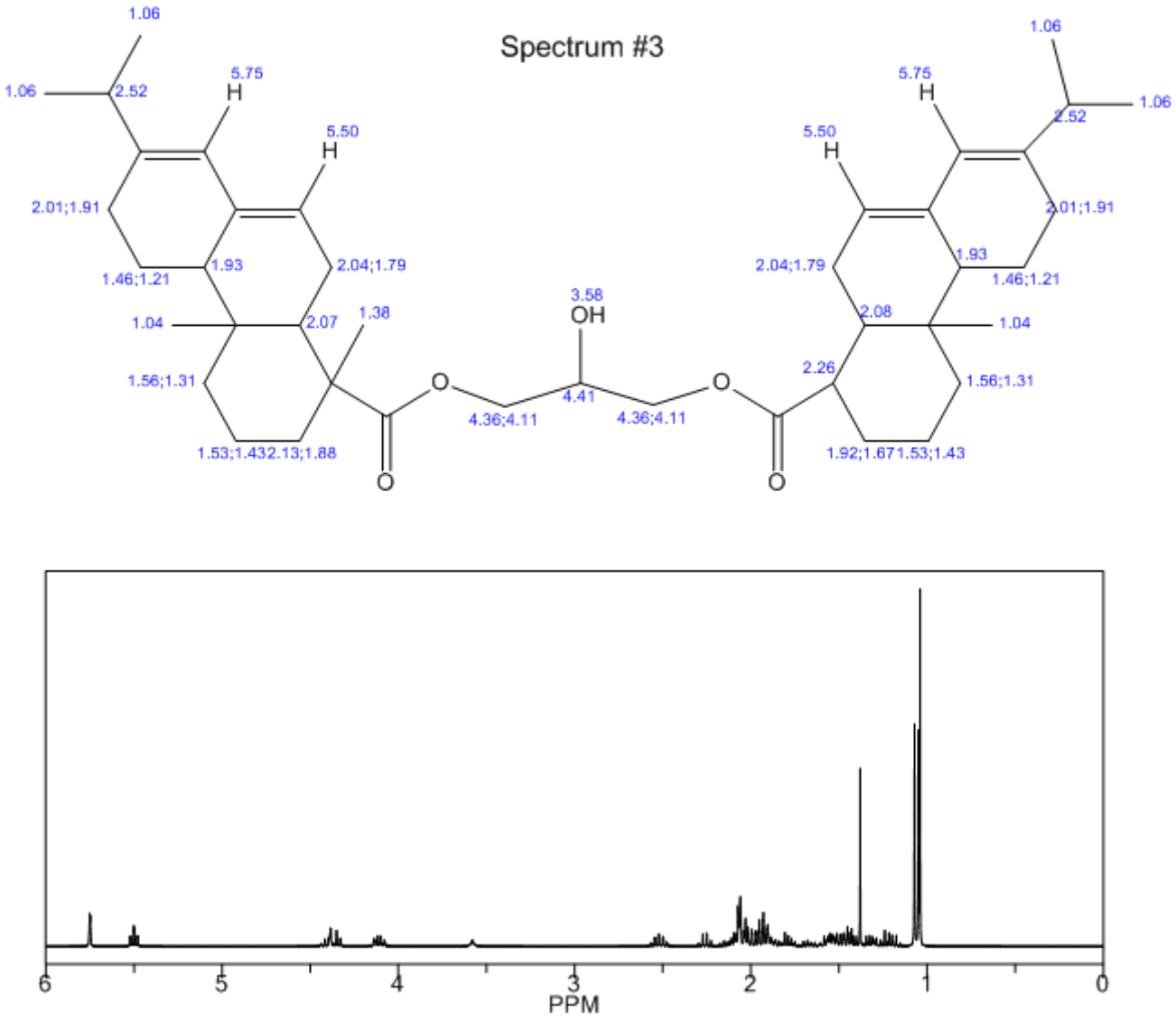

Spectrum #1
1.06
5.75
H
1.06
2.52
5.50
H
2.01;1.91
2.04;1.79
1.93
1.46;1.21
3.58
OH
1.38
2.07
1.04
3.65 HO
O
1.56;1.31
3.90
3.81;3.56
4.36;4.11
2.13;1.88 1.53;1.43
O

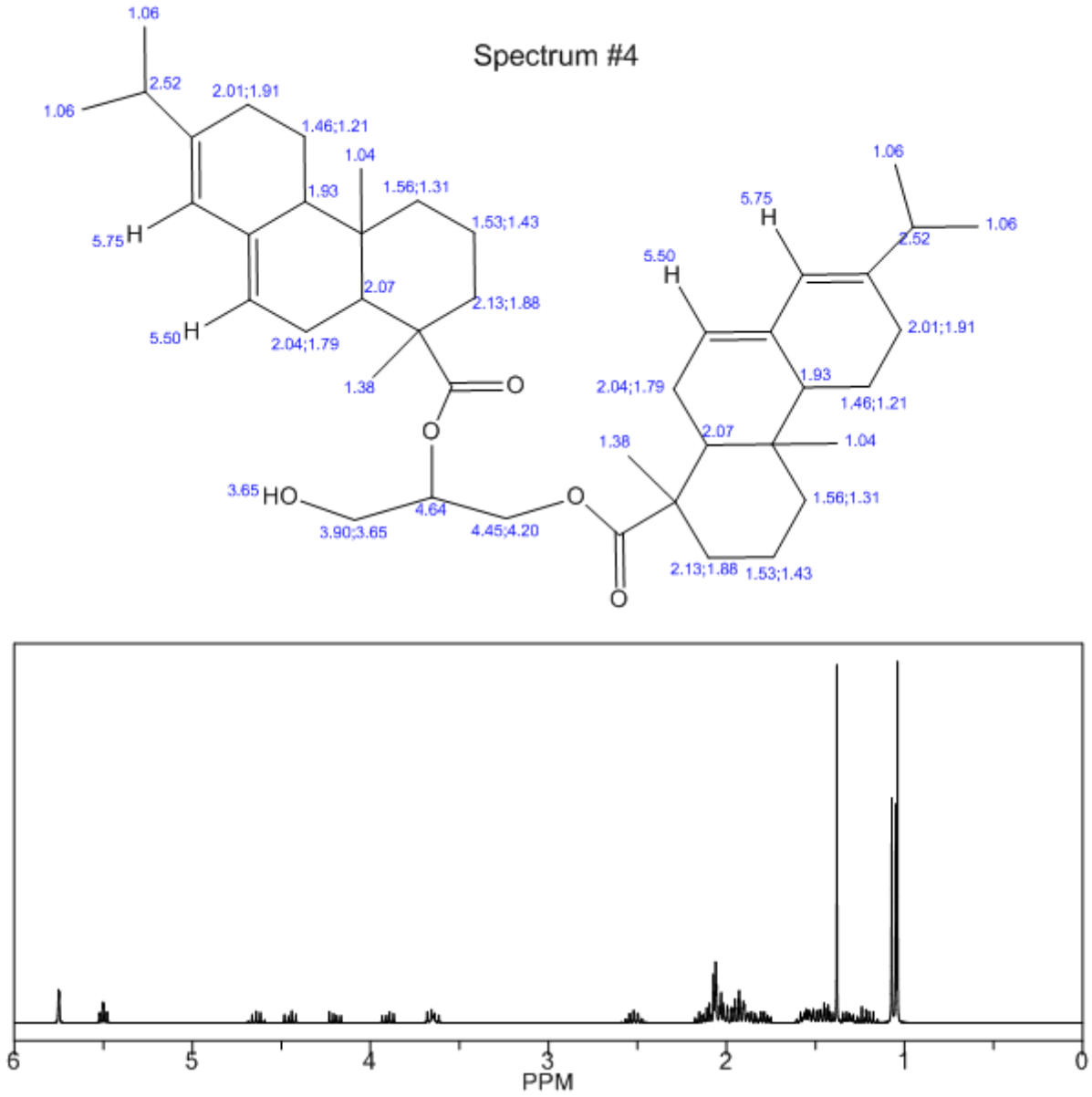

glycerol, mono-ester, position 1
6
5
4
3
2
1
0
PPM

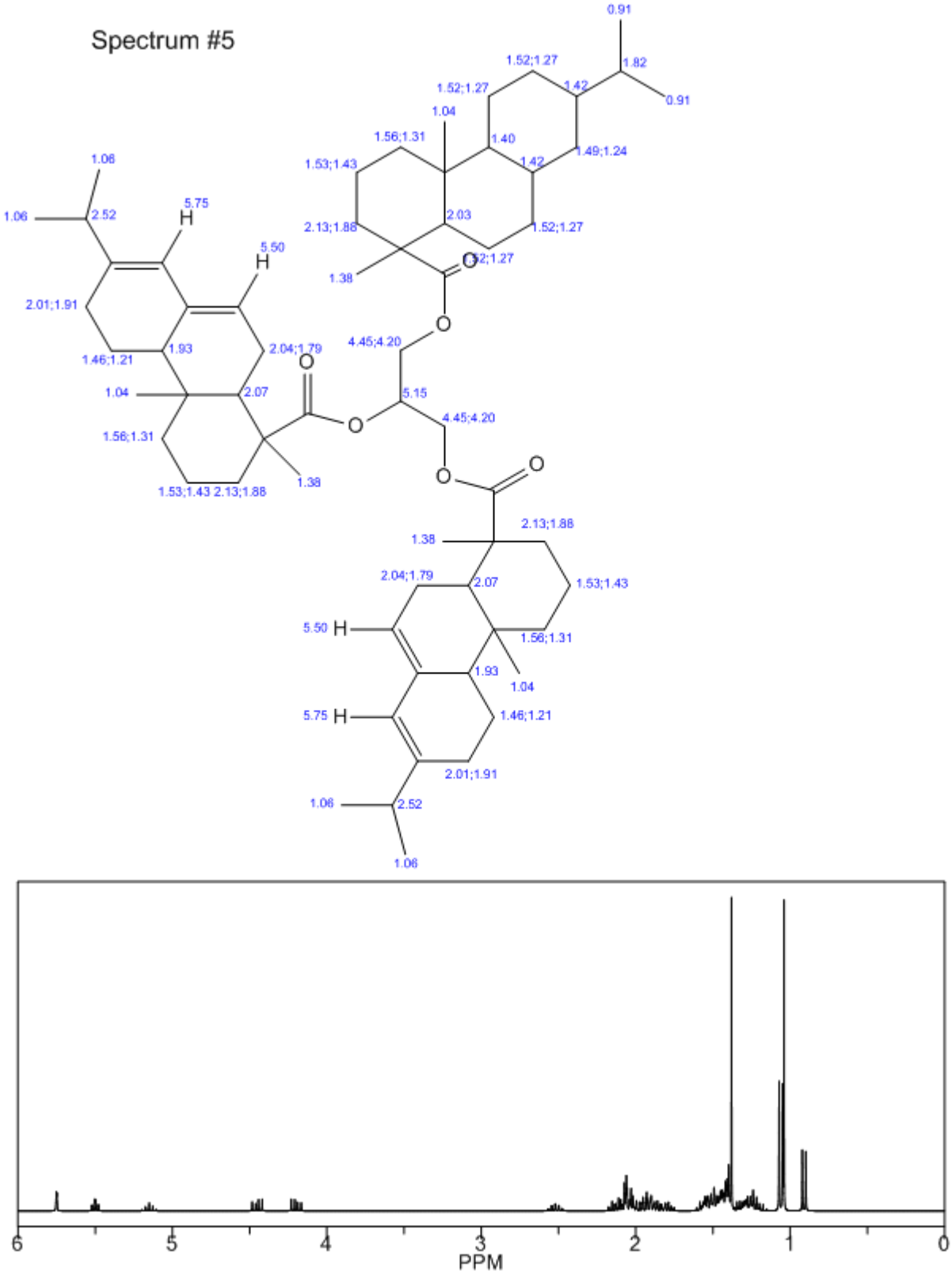
Spectrum #2

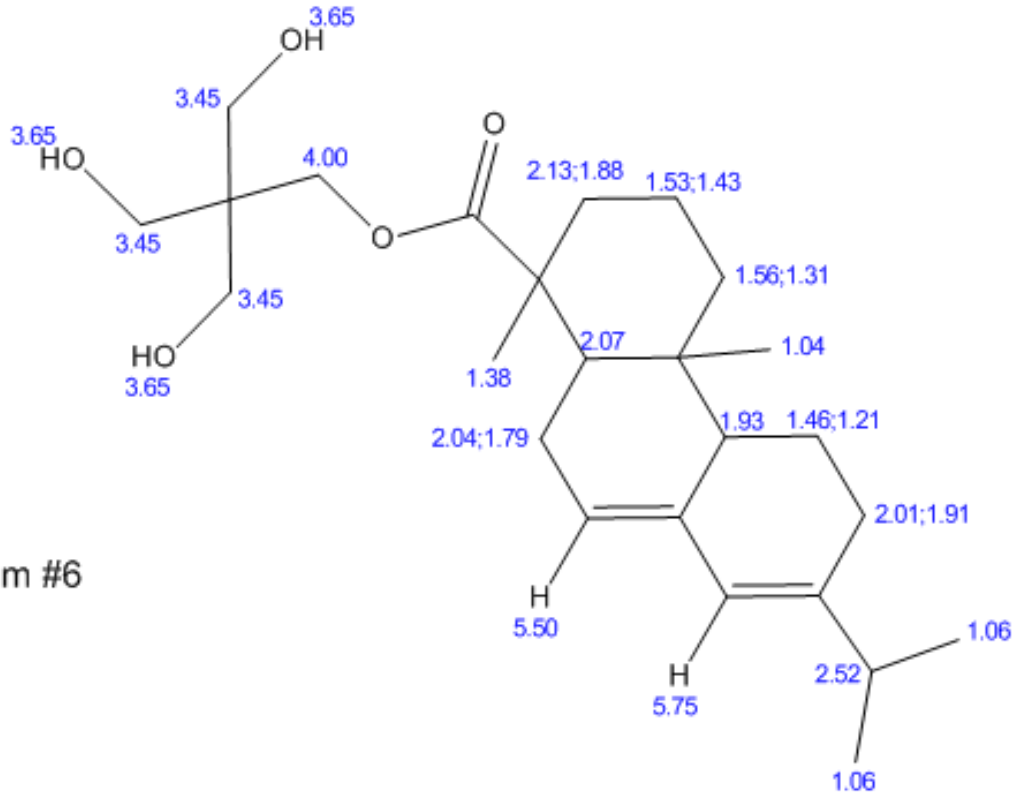

1.06
2.52
1.06
2.01;1.91
1.46;1.21
1.04
1.93
1.56;1.31
1.53;1.43
5.75 H
2.07
2.13;1.88
5.50 H
2.04;1.79
1.38
O
O
3.65 HO
4.13
OH 3.65
3.59
3.59


Glycerol, mono-ester, position 2
6
5
4
3
2
1
0
PPM

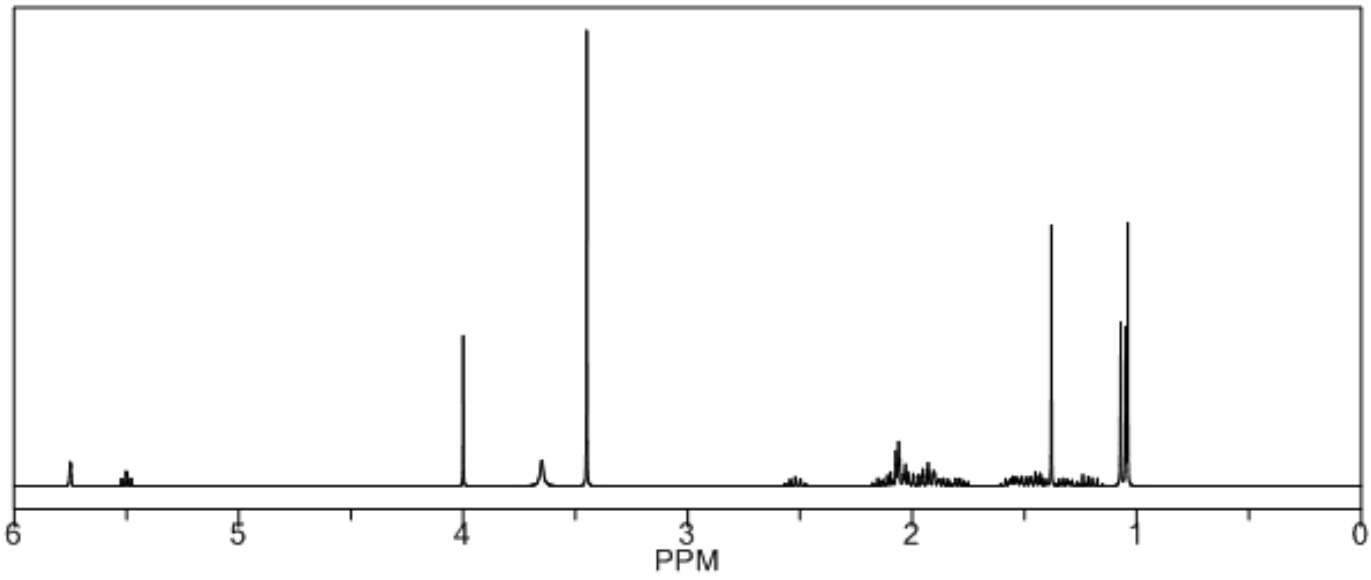

Spectrum #3
1.06
1.06
2.52
5.75
H
5.50
H
2.01;1.91
1.46;1.21
1.93
2.04;1.79
1.04
2.07
1.38
1.56;1.31
1.53;1.43
2.13;1.88
O
3.58
OH
4.41
4.36;4.11
4.36;4.11
O
O
2.26
2.08
1.04
1.93
2.04;1.79
1.46;1.21
2.01;1.91
1.56;1.31
1.92;1.67
1.53;1.43
1.06
2.52
1.06
5.75
H
5.50
H
6
5
4
3
2
1
0
PPM

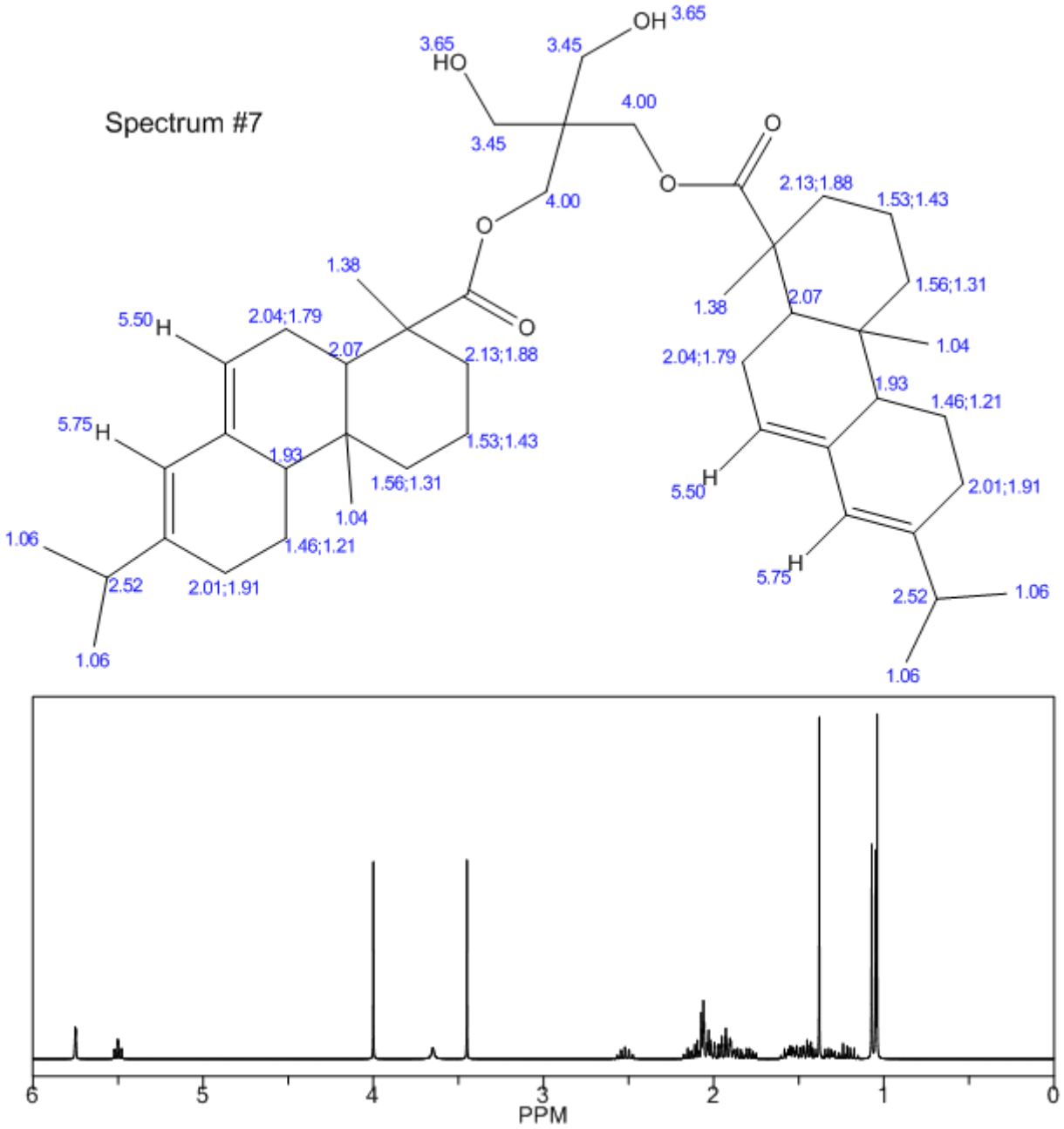

Spectrum #4
1.06
2.52
1.06
2.01;1.91
1.46;1.21
1.04
1.93
1.56;1.31
1.53;1.43
5.75 H
2.07
2.13;1.88
5.50 H
2.04;1.79
1.38
O
O
3.65 HO
4.64
3.90;3.65
4.45;4.20
O
O
1.06
5.75
H
2.52
1.06
5.50
H
2.01;1.91
1.93
2.04;1.79
1.46;1.21
2.07
1.04
1.38
1.56;1.31
2.13;1.88
1.53;1.43
6
5
4
3
2
1
0
PPM

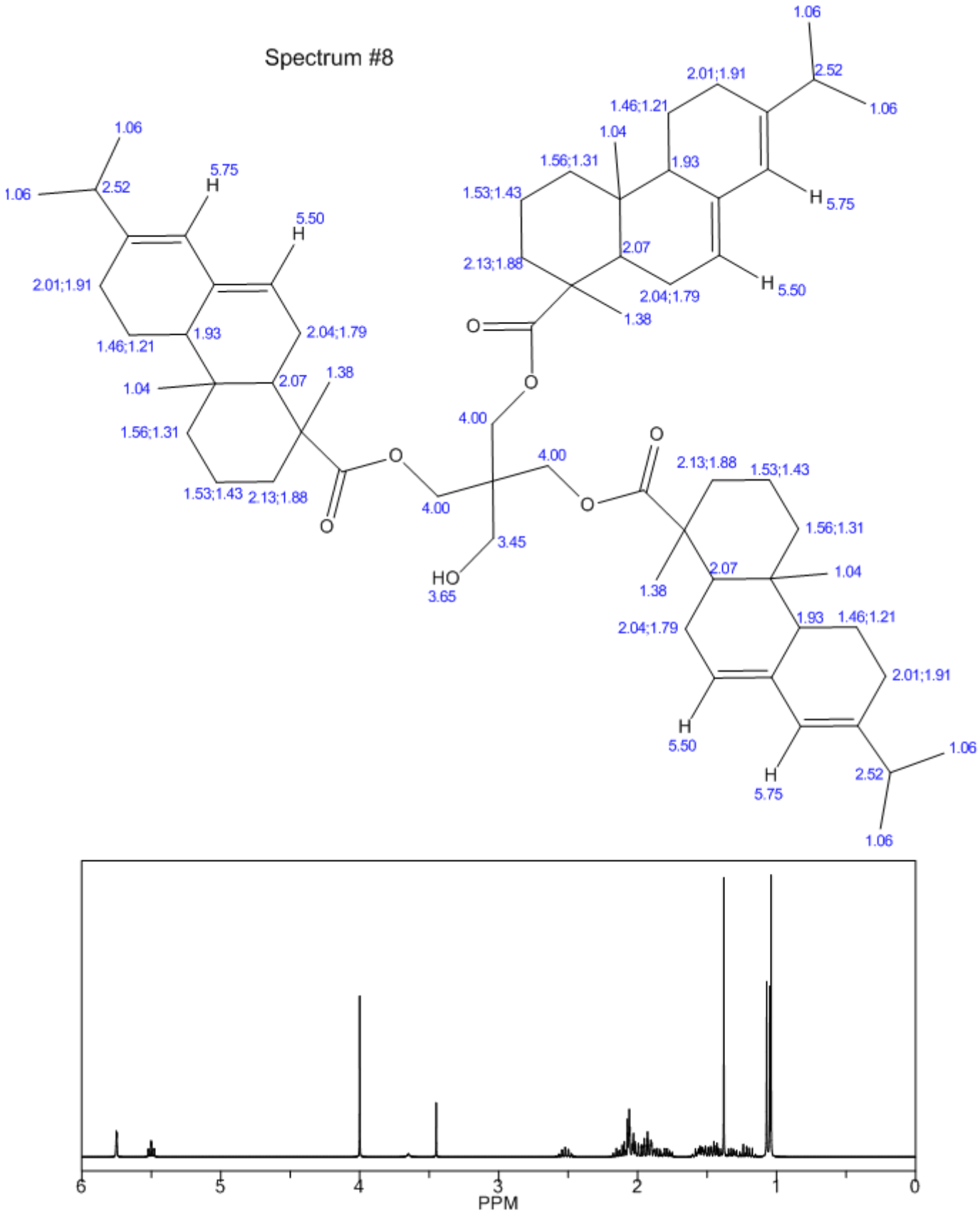

Spectrum #5
PPM
6
5
4
3
2
1
0

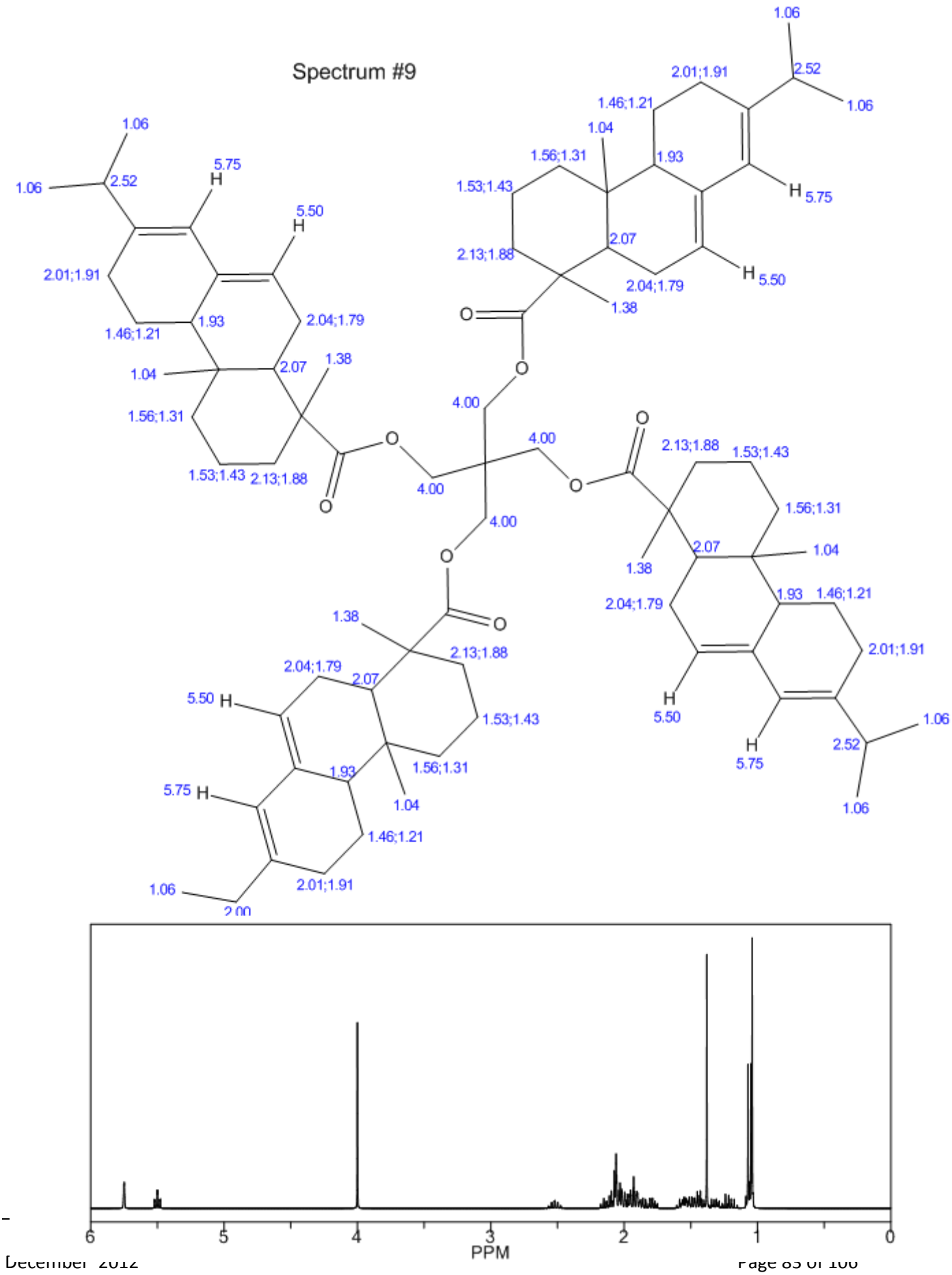

3.65
OH
3.45
3.65
HO
4.00
O
O
2.13;1.88
1.53;1.43
3.45
1.56;1.31
3.45
2.07
1.04
HO
3.65
1.38
1.93
1.46;1.21
2.04;1.79
2.01;1.91
H
5.50
1.06
H
5.75
2.52
1.06

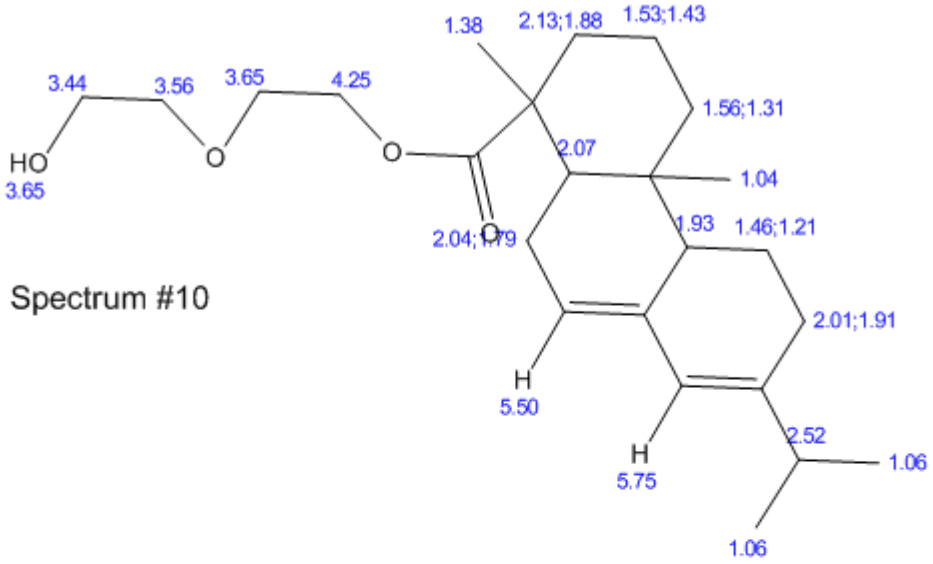
Spectrum #6

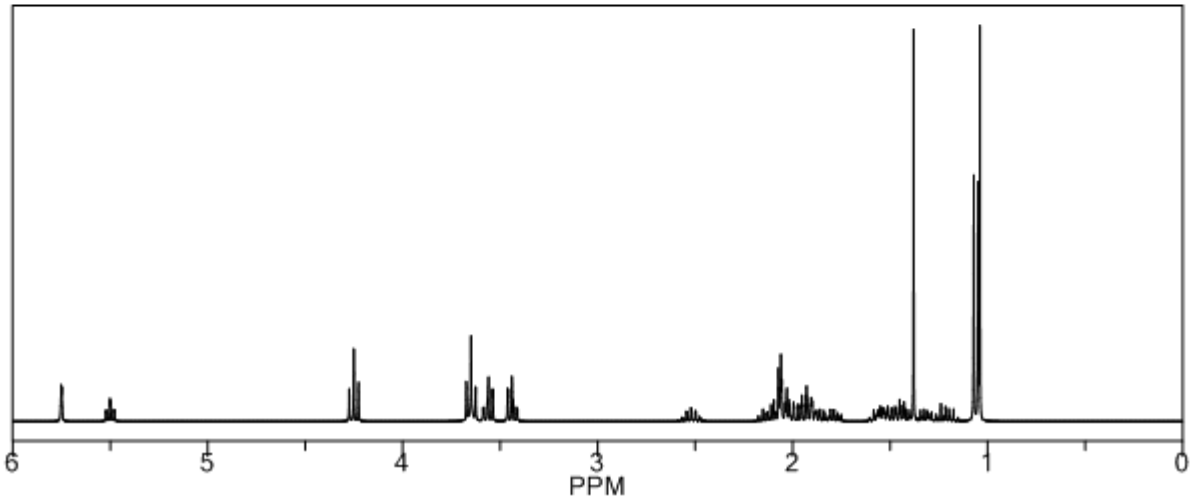

6
5
4
3
2
1
0
PPM

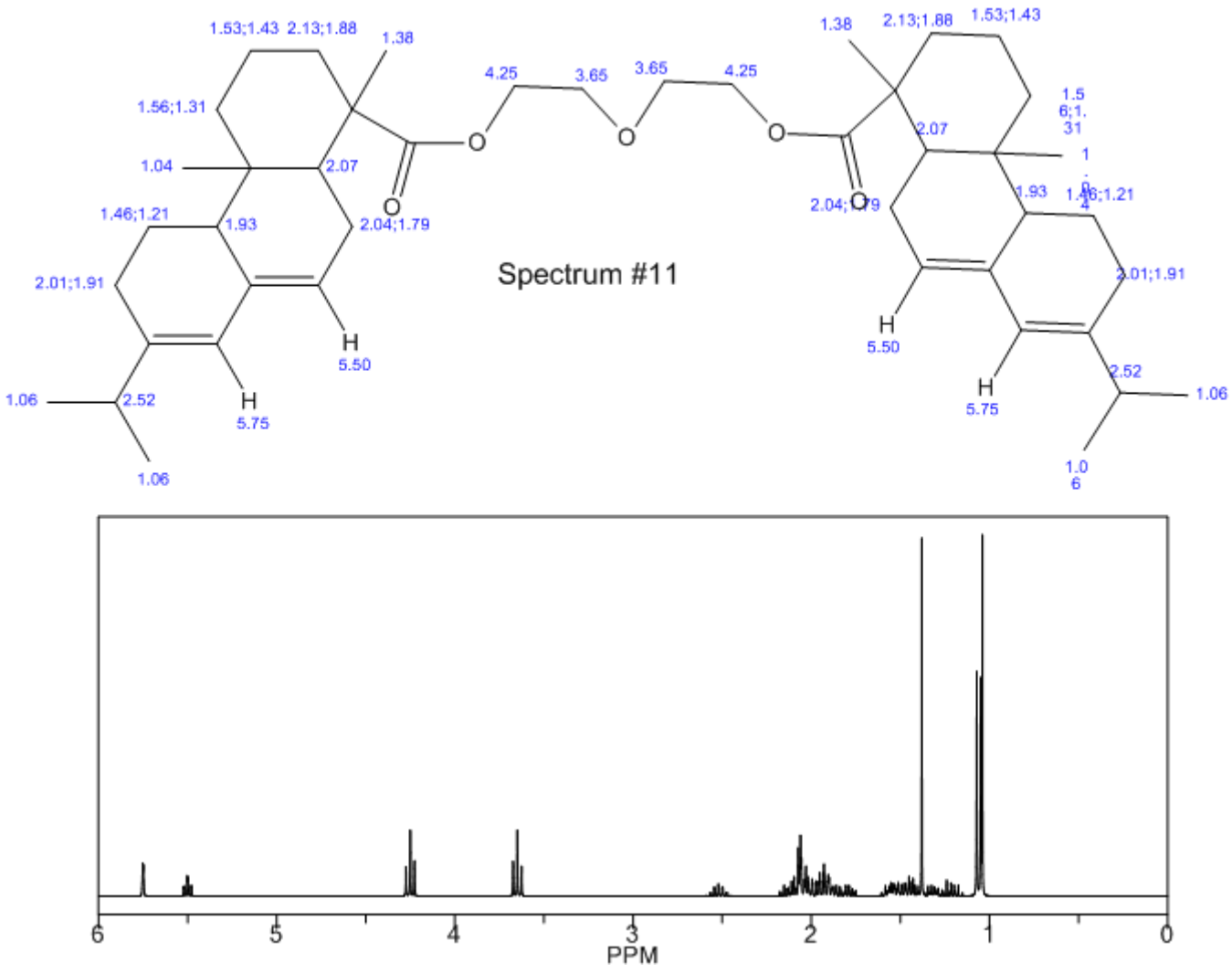

Spectrum #7
OH 3.65
3.65
HO
3.45
4.00
3.45
O
4.00
O
O
2.13;1.88
1.53;1.43
1.38
O
1.56;1.31
5.50 H
2.04;1.79
2.07
2.13;1.88
1.38
2.07
1.04
2.04;1.79
1.93
1.46;1.21
5.75 H
1.53;1.43
1.93
1.56;1.31
1.04
5.50 H
2.01;1.91
1.06
1.46;1.21
2.52
2.01;1.91
5.75 H
2.52
1.06
1.06
1.06
6
5
4
3
2
1
0
PPM

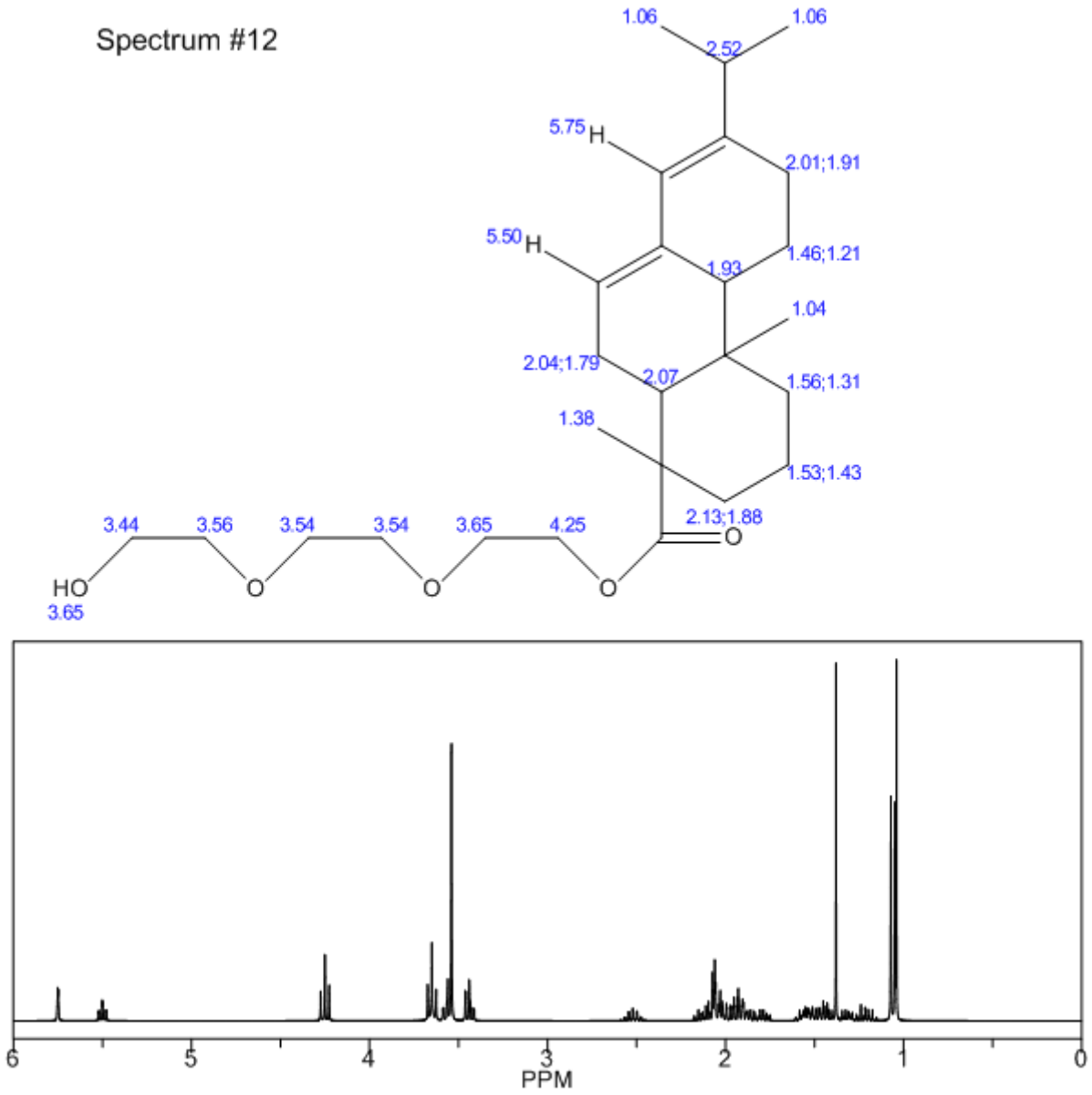

Spectrum #8
1.06
2.52
1.06
5.75
H
5.50
H
2.01;1.91
1.46;1.21
1.93
2.04;1.79
1.04
2.07
1.38
1.56;1.31
1.53;1.43
2.13;1.88
O
4.00
3.45
HO
3.65
2.13;1.88
1.53;1.43
1.56;1.31
2.07
1.04
1.38
2.04;1.79
1.93
1.46;1.21
2.01;1.91
H
5.50
H
5.75
2.52
1.06
1.06
6
5
4
3
2
1
0
PPM

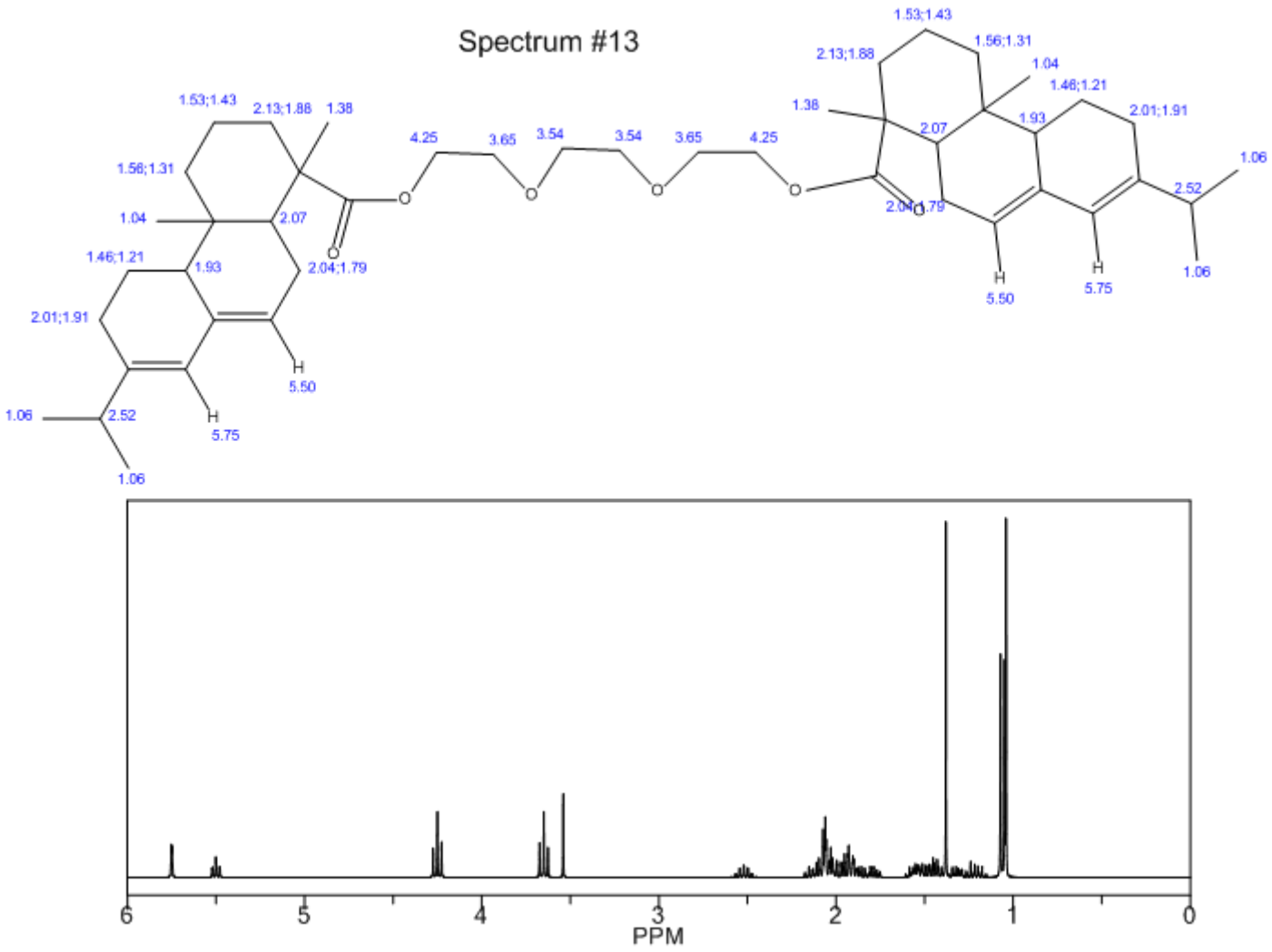

Spectrum #9
PPM
6
5
4
3
2
1
0

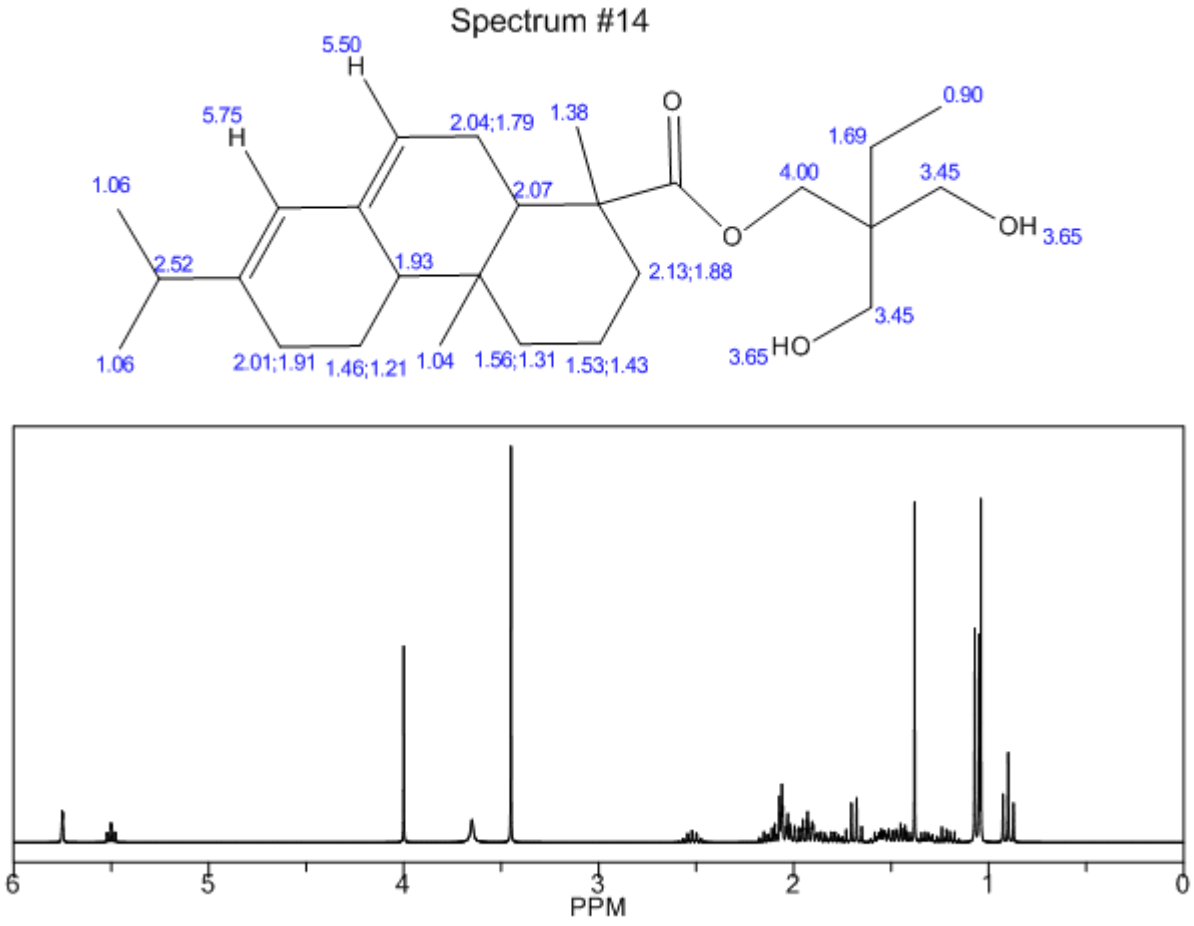

1.38
2.13;1.88
1.53;1.43
3.44
3.56
3.65
4.25
1.56;1.31
HO
3.65
O
O
2.07
1.04
O
2.04;1.79
1.93
1.46;1.21
Spectrum #10
2.01;1.91
H
5.50
H
5.75
2.52
1.06
1.06

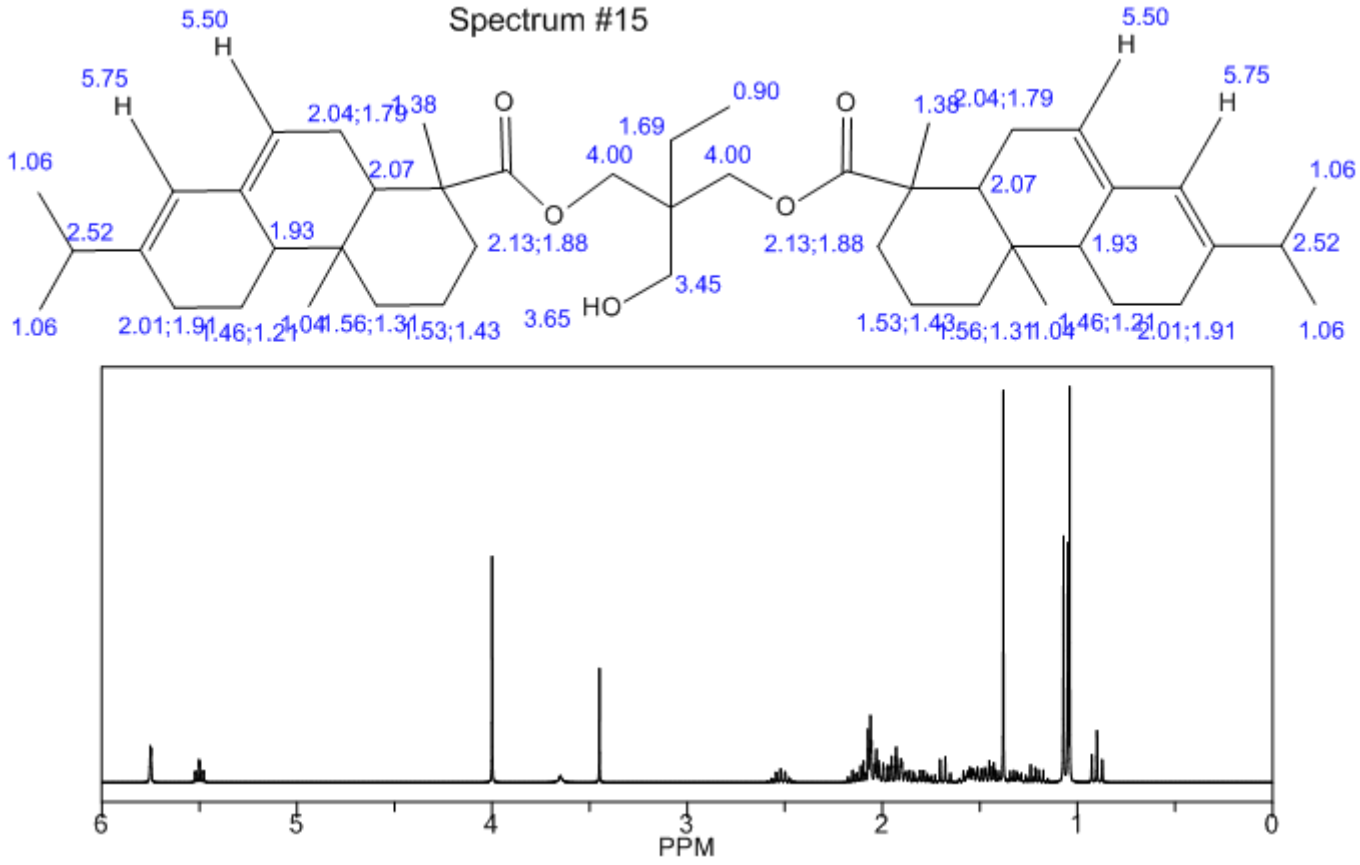

6
5
4
3
2
1
0
PPM

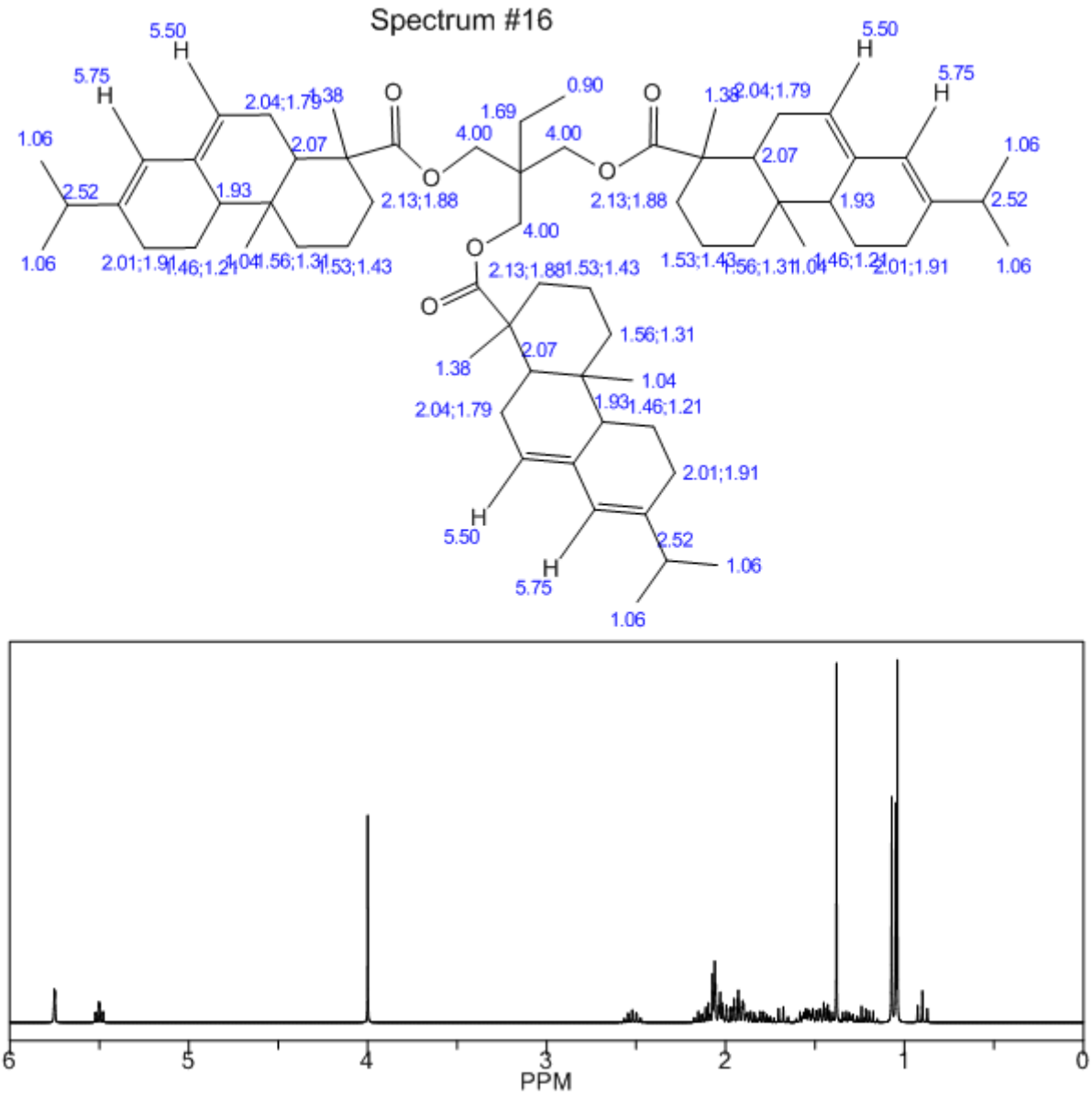

Spectrum #11
PPM
6
5
4
3
2
1
0

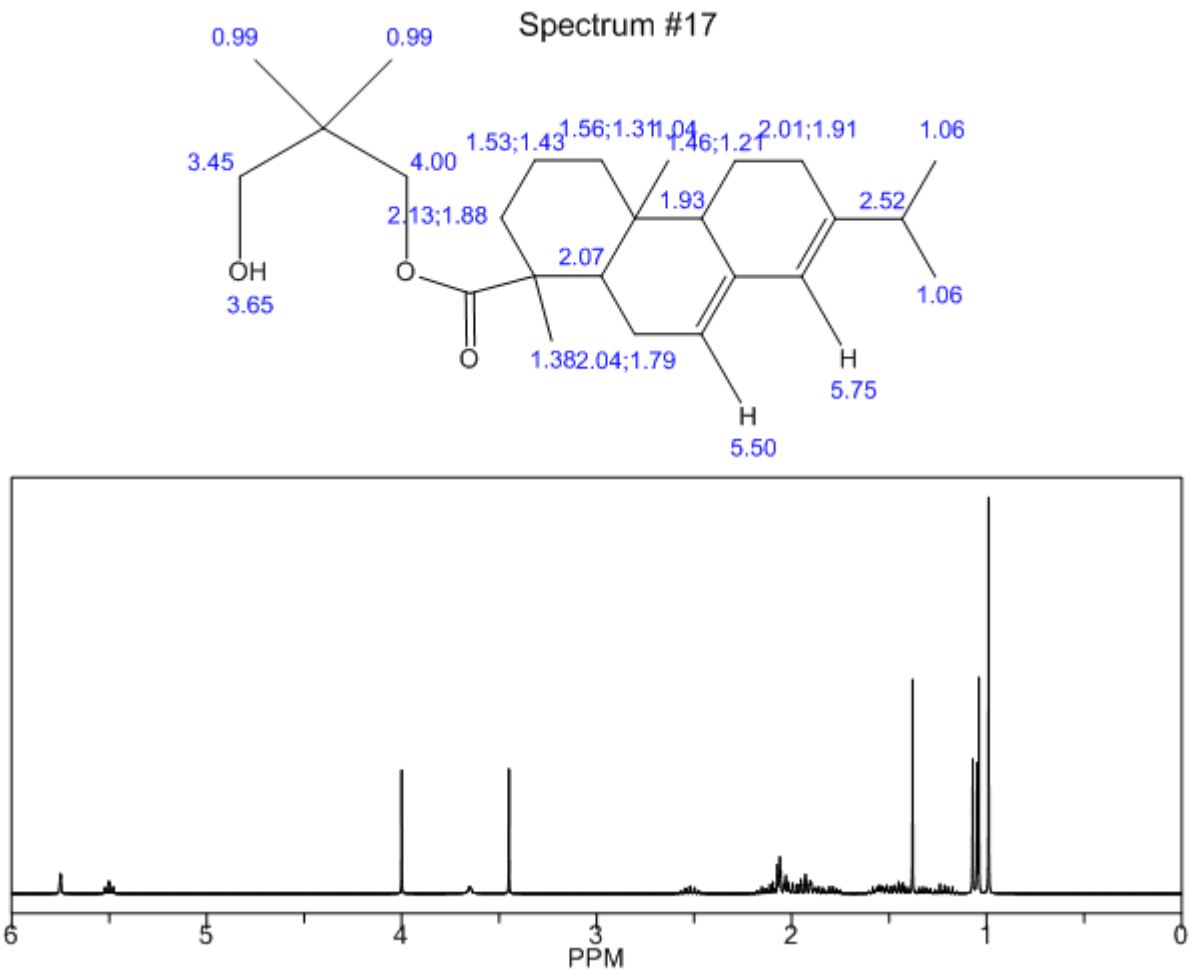

Spectrum #12
1.06
1.06
2.52
5.75
H
2.01;1.91
5.50
H
1.46;1.21
1.93
1.04
2.04;1.79
2.07
1.56;1.31
1.38
1.53;1.43
3.44
3.56
3.54
3.54
3.65
4.25
2.13;1.88
O
HO
3.65
O
O
O
6
5
4
3
2
1
0
PPM

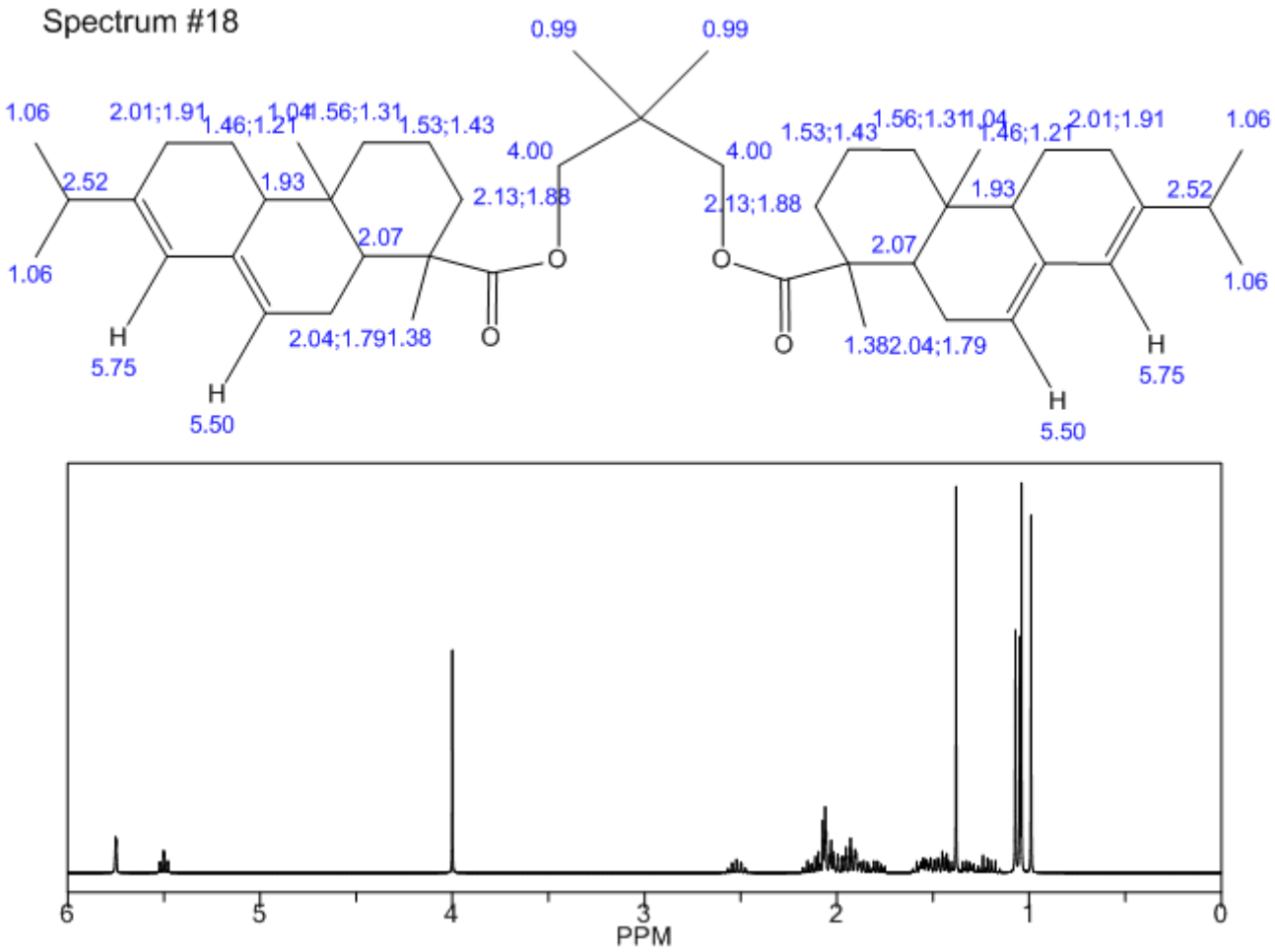

Spectrum #13
1.53;1.43
2.13;1.88
1.38
1.56;1.31
1.04
1.46;1.21
1.93
2.07
2.01;1.91
2.04;1.79
4.25
3.65
3.54
3.54
3.65
4.25
1.06
2.52
5.50
5.75
PPM
6
5
4
3
2
1
0


Spectrum #14
5.50
H
5.75
H
2.04;1.79
1.38
O
0.90
1.69
4.00
3.45
OH
3.65
1.06
2.07
O
2.52
1.93
2.13;1.88
3.45
3.65
HO
1.06
2.01;1.91
1.46;1.21
1.04
1.56;1.31
1.53;1.43
6
5
4
3
2
1
0
PPM

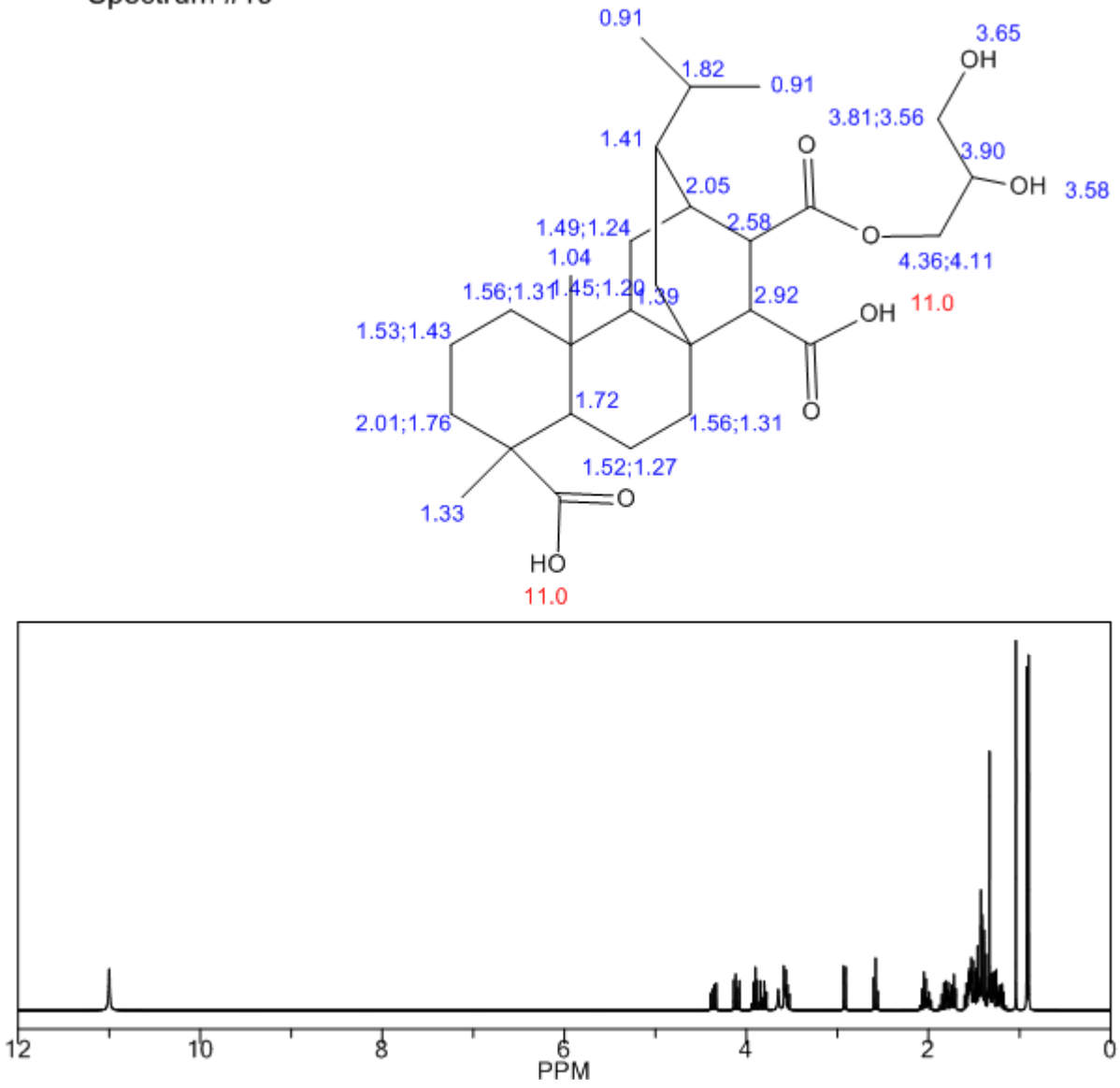

Spectrum #15
5.50
H
5.75
H
2.04;1.79
1.38
O
0.90
1.69
4.00
4.00
O
1.38
2.04;1.79
5.50
H
5.75
H
1.06
2.07
2.13;1.88
O
2.13;1.88
2.07
1.06
2.52
1.93
1.93
2.52
3.45
3.65
HO
1.06
2.01;1.91
1.46;1.21
1.04
1.56;1.31
1.53;1.43
1.53;1.43
1.56;1.31
1.04
1.46;1.21
2.01;1.91
1.06
6
5
4
3
2
1
0
PPM

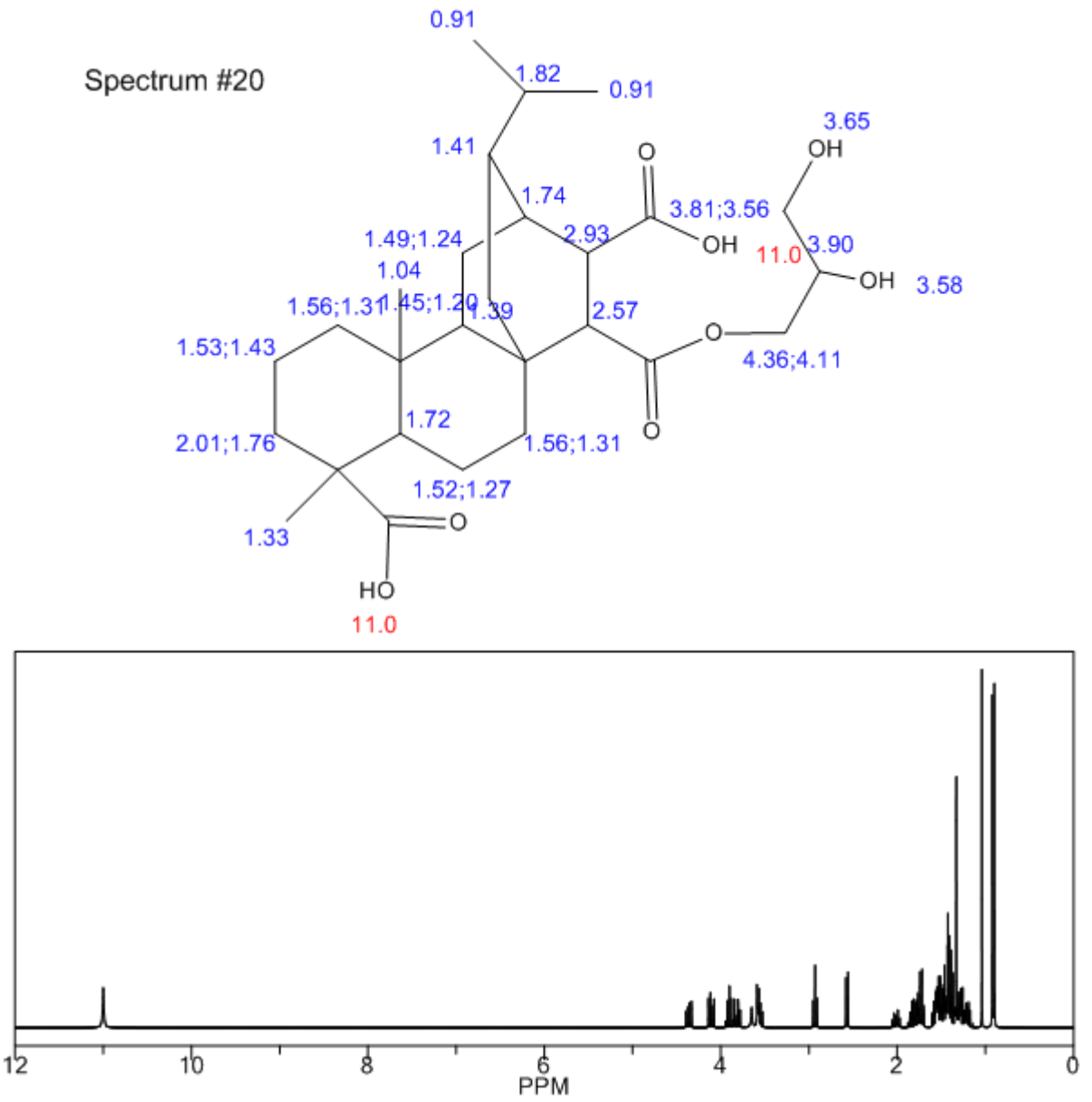

Spectrum #16
PPM
0
1
2
3
4
5
6


Spectrum #17
0.99
0.99
3.45
4.00
OH
3.65
2.13;1.88
O
O
1.53;1.43
1.56;1.31
1.04
1.46;1.21
2.01;1.91
1.06
1.93
2.52
2.07
1.06
1.382.04;1.79
H
5.75
H
5.50
6
5
4
3
2
1
0
PPM

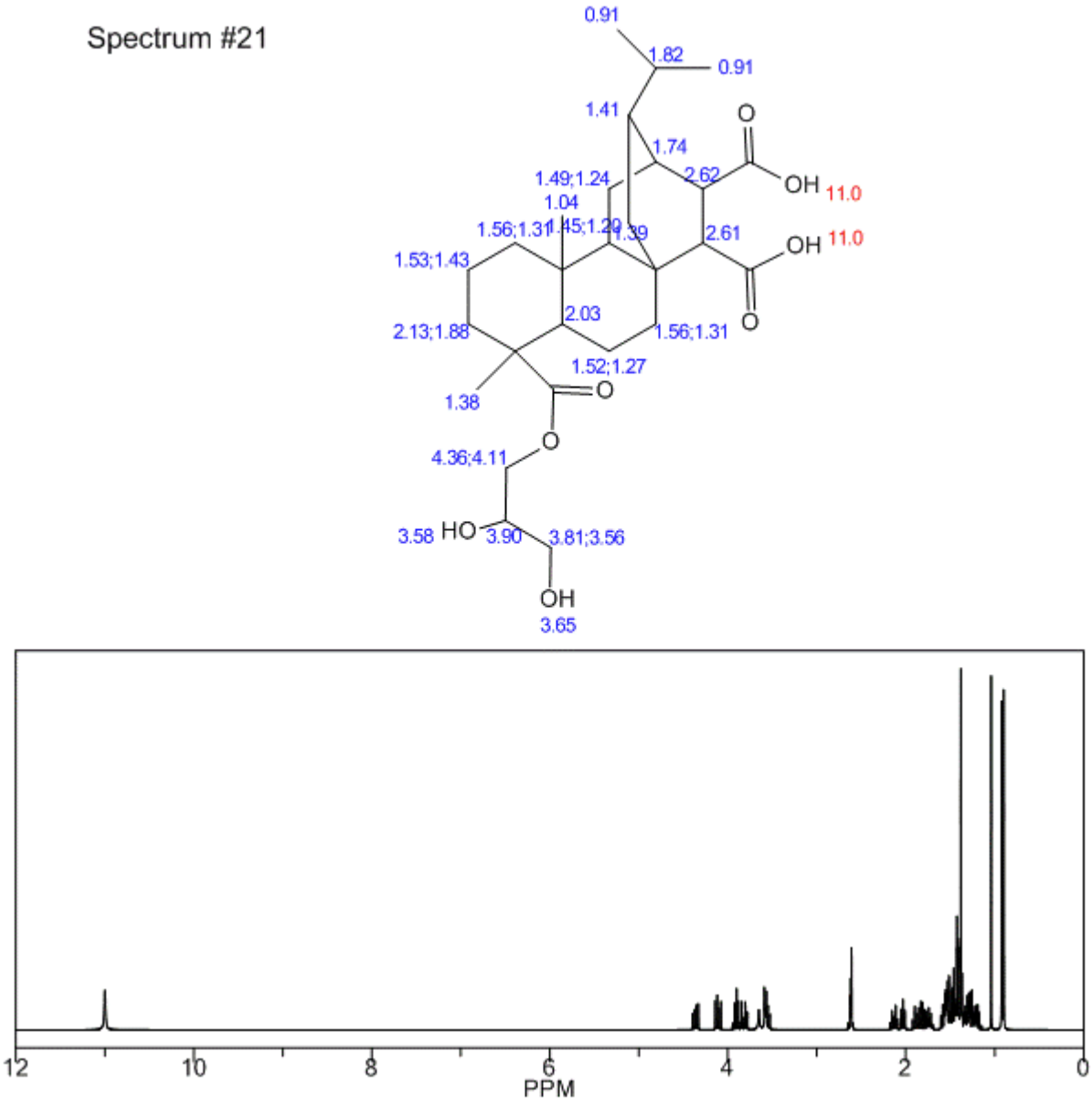

Spectrum #18
0.99
0.99
1.06
2.01;1.91
1.46;1.21
1.04
1.56;1.31
1.53;1.43
4.00
4.00
2.52
1.93
2.13;1.88
2.13;1.88
2.07
1.06
O
O
H
5.75
2.04;1.791.38
O
H
5.50
1.53;1.43
1.56;1.31
1.04
1.46;1.21
2.01;1.91
1.06
1.93
2.52
2.07
1.06
O
1.382.04;1.79
H
5.75
H
5.50
6
5
4
3
2
1
0
PPM

Spectrum #19

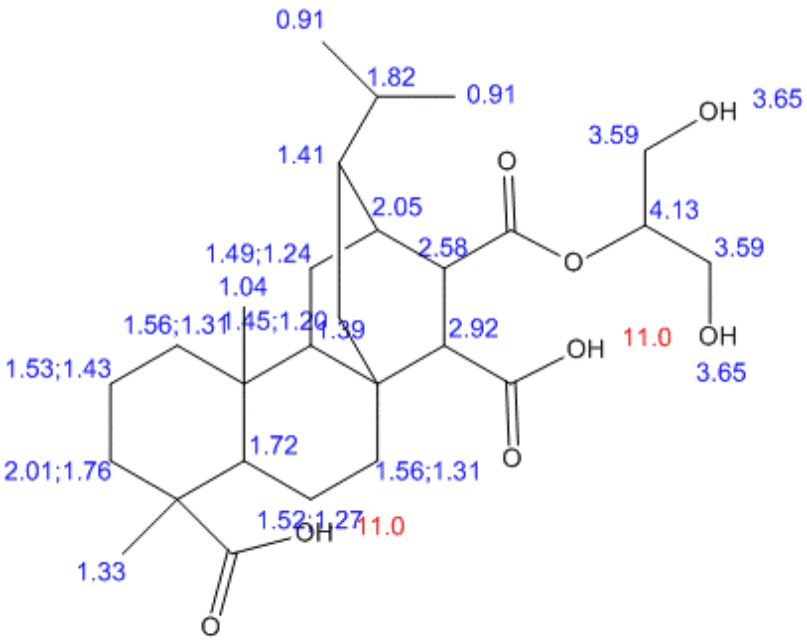

0.91
1.82
0.91
1.41
2.05
1.49;1.24
1.04
1.56;1.31
1.45;1.20
1.39
1.53;1.43
2.58
2.92
OH
11.0
1.72
2.01;1.76
1.56;1.31
1.52;1.27
1.33
HO
11.0
O
O
O
O
3.65
OH
3.81;3.56
3.90
OH
3.58
4.36;4.11
12
10
8
6
4
2
0
PPM

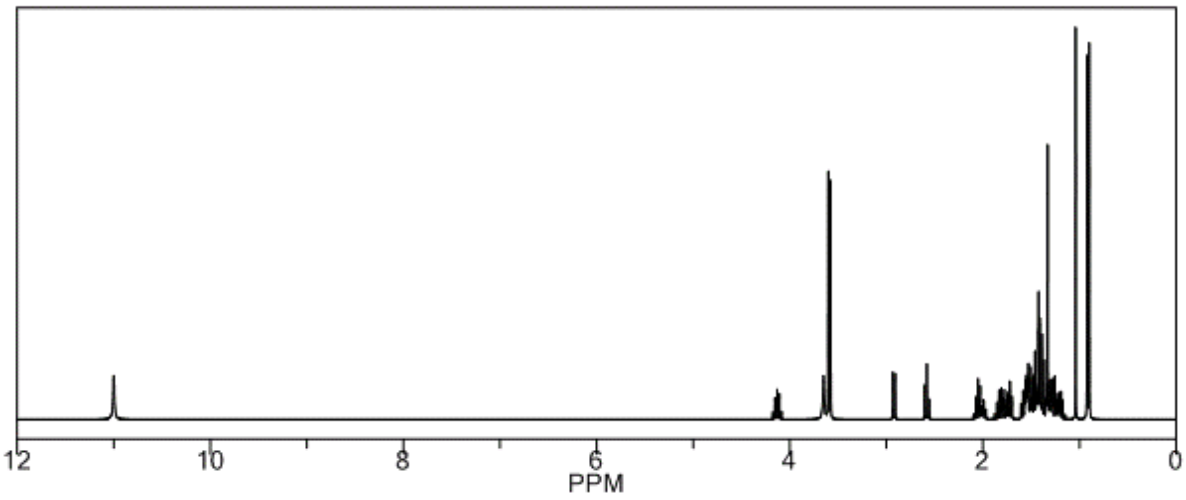

Spectrum #20
0.91
1.82
0.91
1.41
3.65
OH
O
1.74
3.81;3.56
1.49;1.24
2.93
OH
11.0
3.90
1.04
OH
3.58
1.56;1.31
1.45;1.20
1.39
2.57
O
1.53;1.43
4.36;4.11
1.72
O
2.01;1.76
1.56;1.31
1.52;1.27
O
1.33
HO
11.0
12
10
8
6
4
2
0
PPM

Spectrum #21

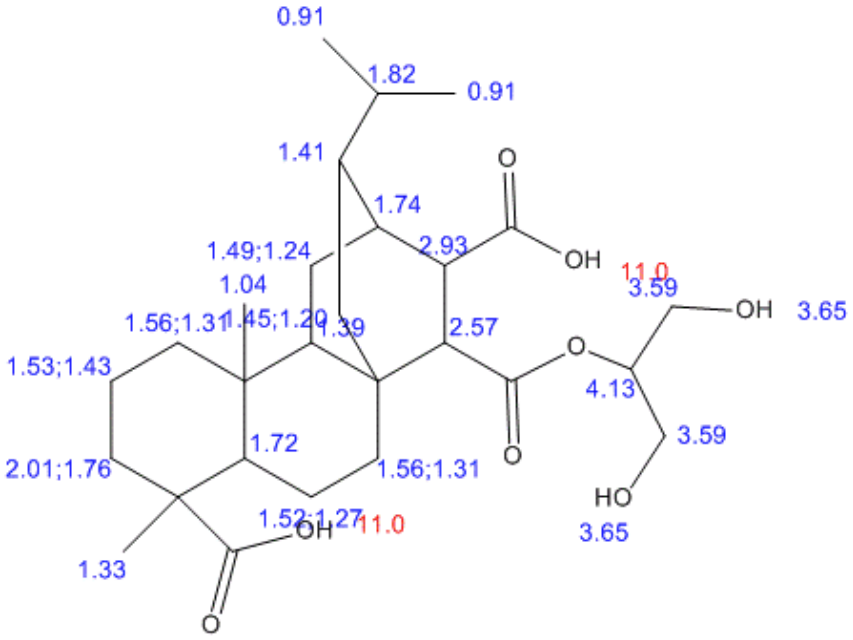

0.91
1.82
0.91
1.41
O
1.74
2.62
OH
11.0
1.49;1.24
1.04
1.56;1.31
1.45;1.29
1.39
2.61
OH
11.0
1.53;1.43
2.03
O
2.13;1.88
1.56;1.31
1.52;1.27
1.38
O
O
4.36;4.11
3.58
HO
3.90
3.81;3.56
OH
3.65
12
10
8
6
4
2
0
PPM

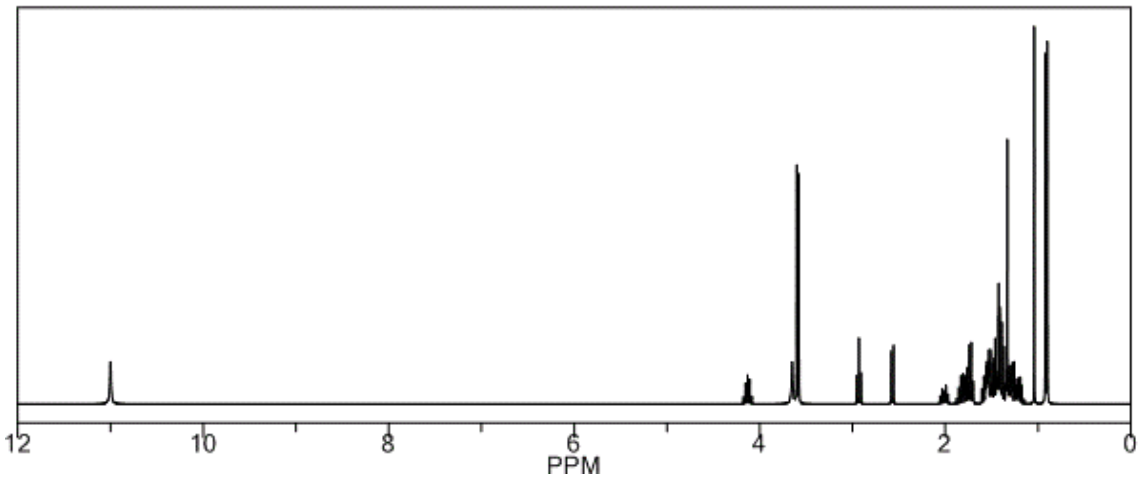
Spectrum #22


0.91
1.82
0.91
OH
3.65
3.59
1.41
O
2.05
4.13
1.49;1.24
2.58
O
3.59
1.04
1.56;1.31
1.45;1.29
1.39
2.92
OH
11.0
OH
1.53;1.43
3.65
1.72
2.01;1.76
1.56;1.31
1.52;1.27
OH
11.0
1.33
O

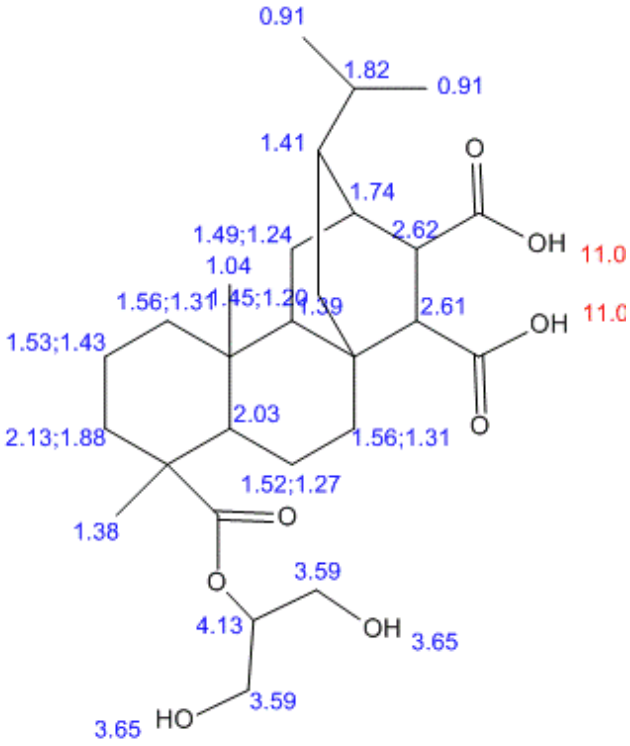

12
10
8
6
4
2
0
PPM

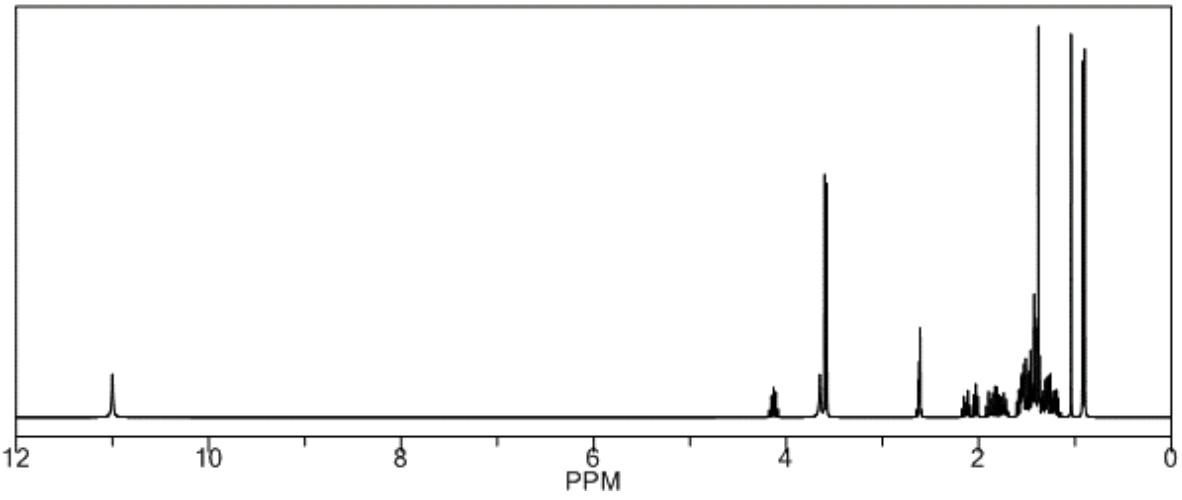
Spectrum #23

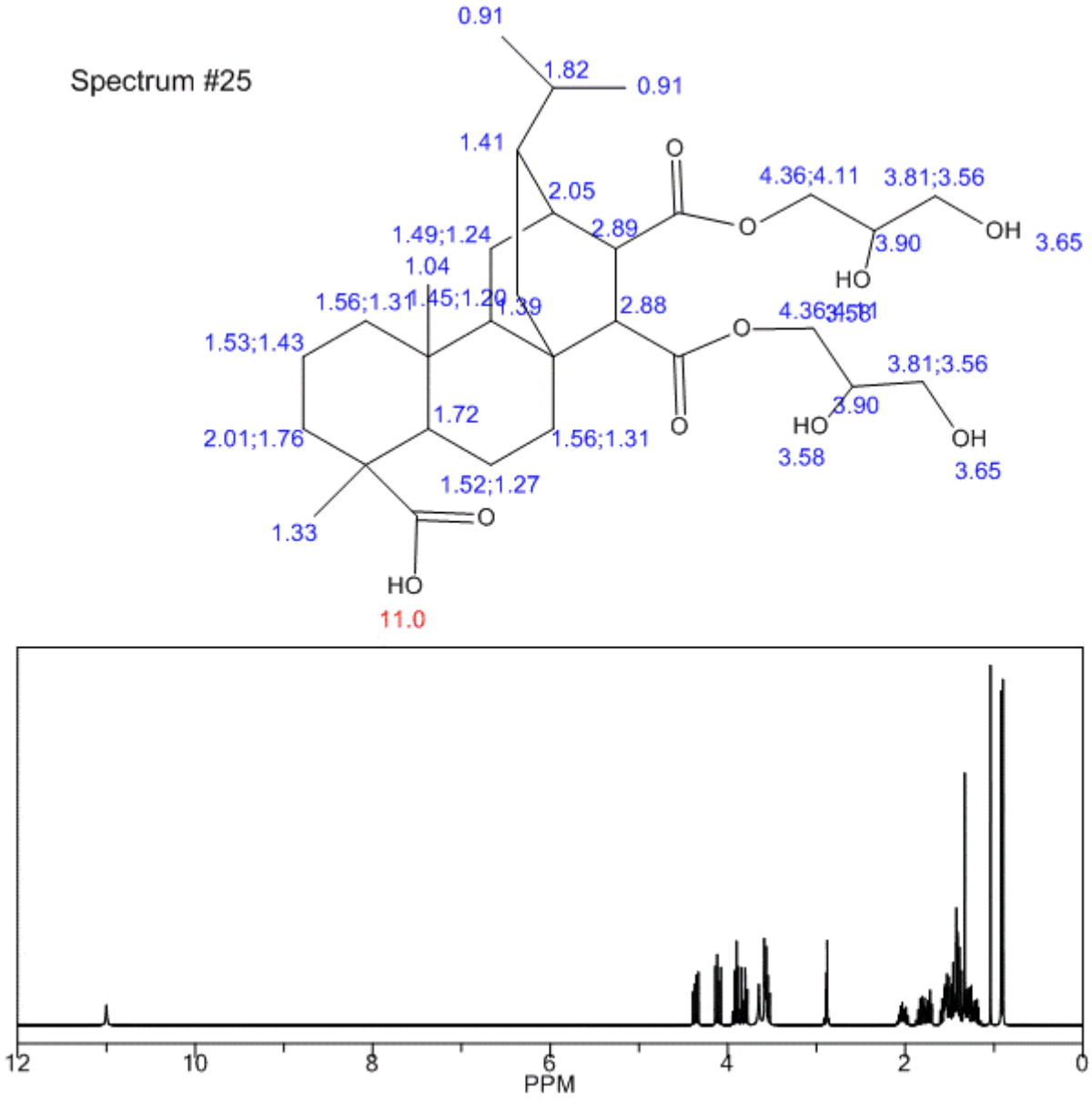

0.91
1.82
0.91
1.41
1.74
1.49;1.24
2.93
1.04
1.56;1.31
1.45;1.20
1.39
2.57
1.53;1.43
1.72
2.01;1.76
1.56;1.31
1.52;1.27
1.33
OH
11.0
3.59
OH
3.65
4.13
3.59
HO
3.65
O

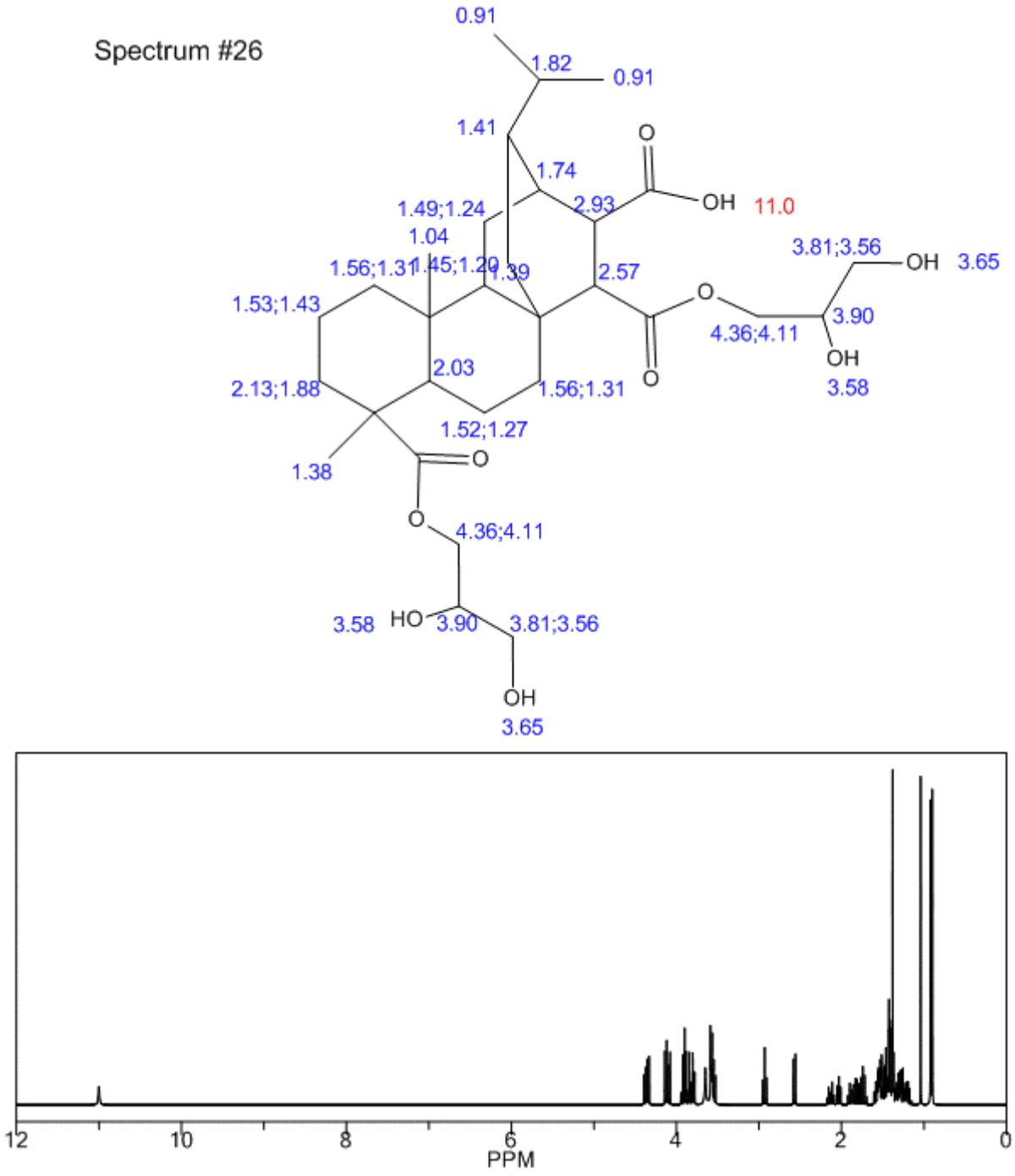

12
10
8
6
4
2
0
PPM

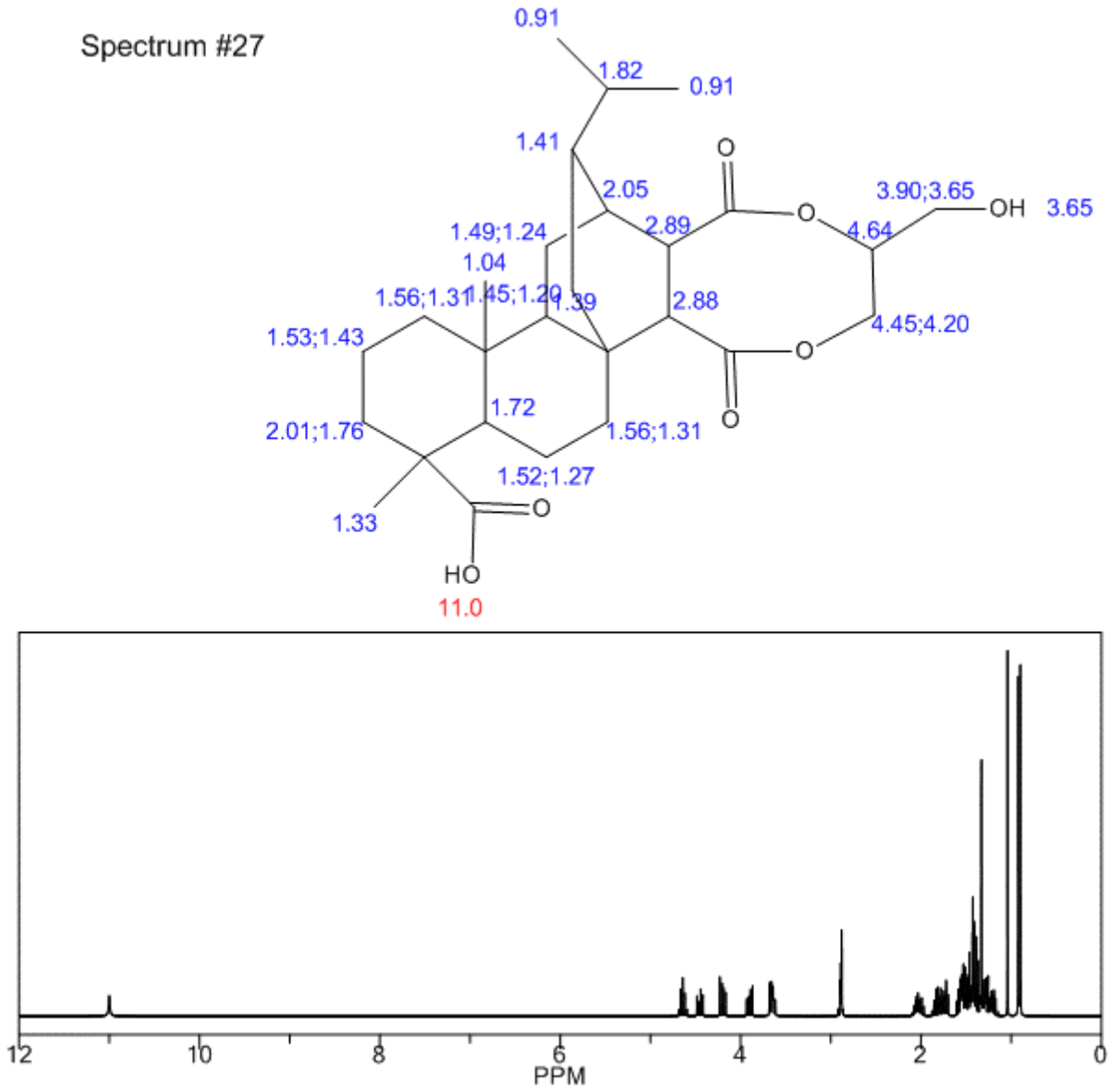
Spectrum #24


0.91
1.82
0.91
1.41
1.74
1.49;1.24
2.62
OH
1.04
1.56;1.31
1.45;1.29
1.39
2.61
OH
1.53;1.43
2.03
2.13;1.88
1.56;1.31
1.52;1.27
1.38
O
O
3.59
4.13
OH
3.65
3.59
3.65
HO


12
10
8
6
4
2
0
PPM

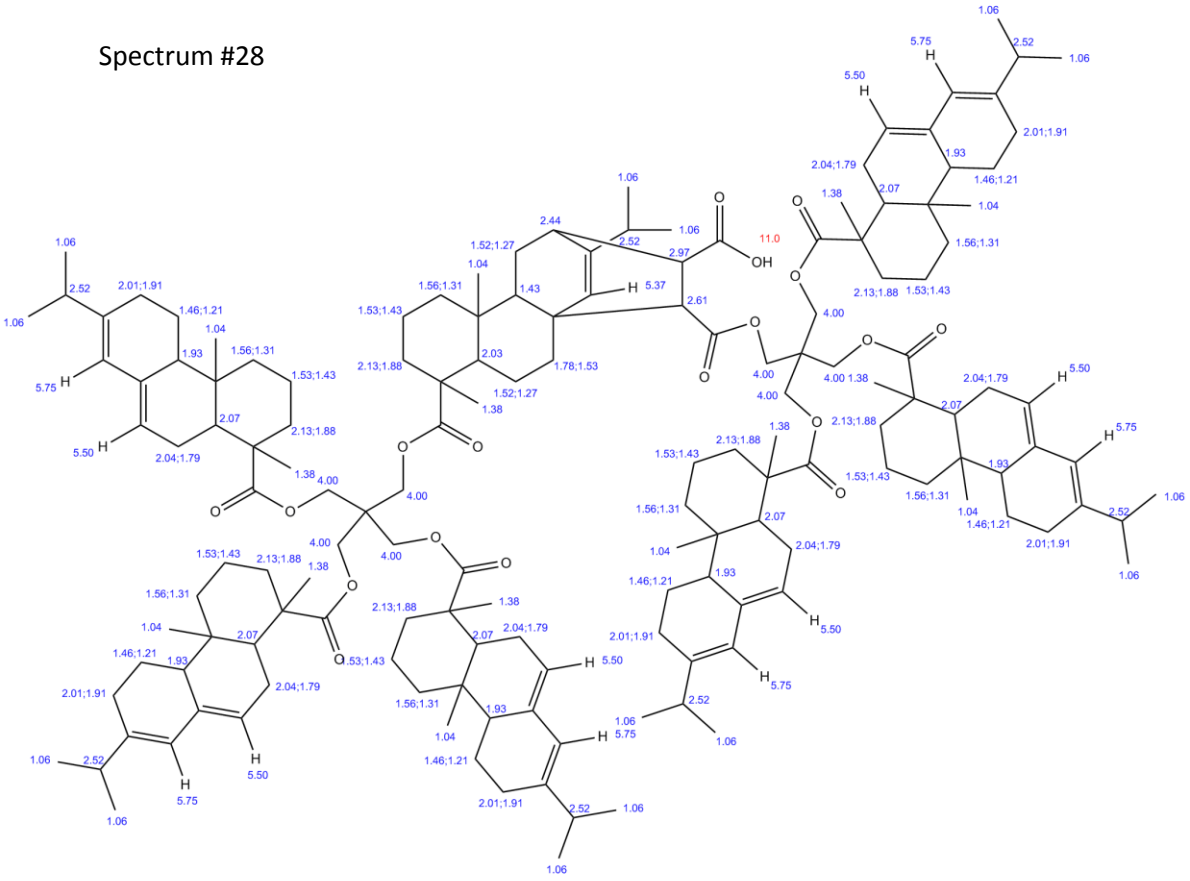

Spectrum #25
0.91
1.82
0.91
1.41
2.05
1.49;1.24
2.89
1.04
1.56;1.31
1.45;1.20
1.39
2.88
1.53;1.43
1.72
2.01;1.76
1.56;1.31
1.52;1.27
1.33
HO
11.0
O
4.36;4.11
3.81;3.56
3.90
OH
3.65
HO
4.36;4.11
3.81;3.56
3.90
HO
3.58
OH
3.65
12
10
8
6
4
2
0
PPM


Spectrum #26
0.91
1.82
0.91
1.41
1.74
1.49;1.24
2.93
OH
11.0
1.04
3.81;3.56
OH
3.65
1.56;1.31
1.45;1.20
1.39
2.57
1.53;1.43
3.90
4.36;4.11
OH
3.58
2.03
2.13;1.88
1.56;1.31
1.52;1.27
1.38
4.36;4.11
3.58
HO
3.90
3.81;3.56
OH
3.65
12
10
8
6
4
2
0
PPM

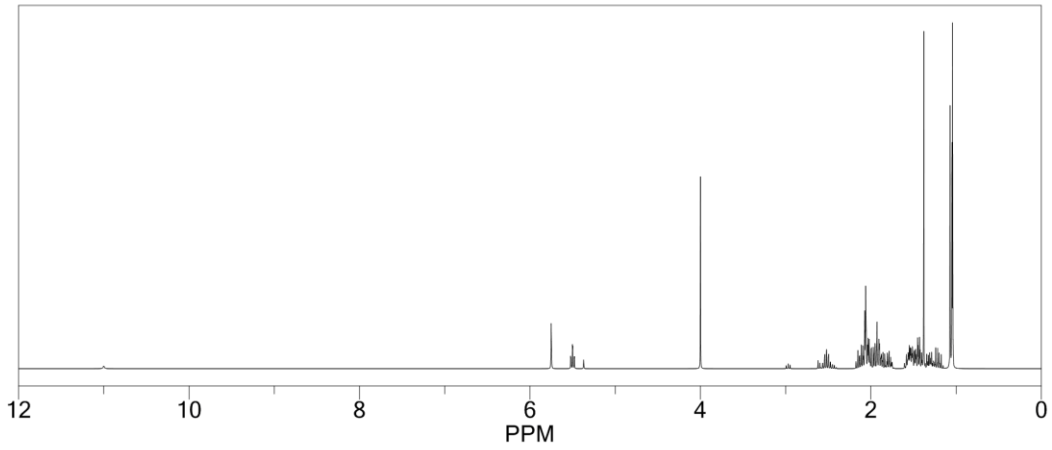

Spectrum #27
0.91
1.82
0.91
1.41
2.05
3.90;3.65
OH 3.65
1.49;1.24
2.89
4.64
1.04
1.56;1.31
1.45;1.20
1.39
2.88
4.45;4.20
1.53;1.43
1.72
2.01;1.76
1.56;1.31
1.52;1.27
1.33
HO
11.0
12
10
8
6
4
2
0
PPM

ChemNMR ^{1}H Estimation

Spectrum #28

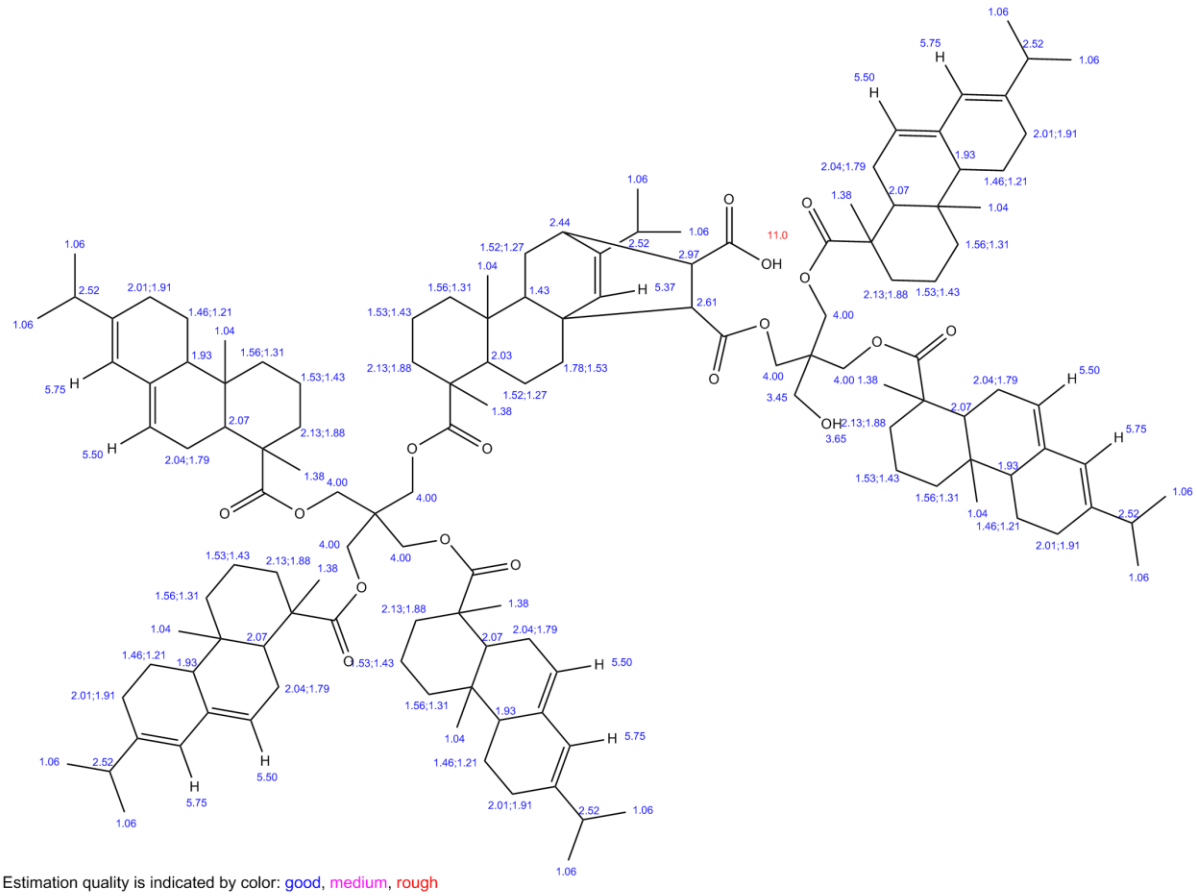


Estimation quality is indicated by color: good, medium, rough

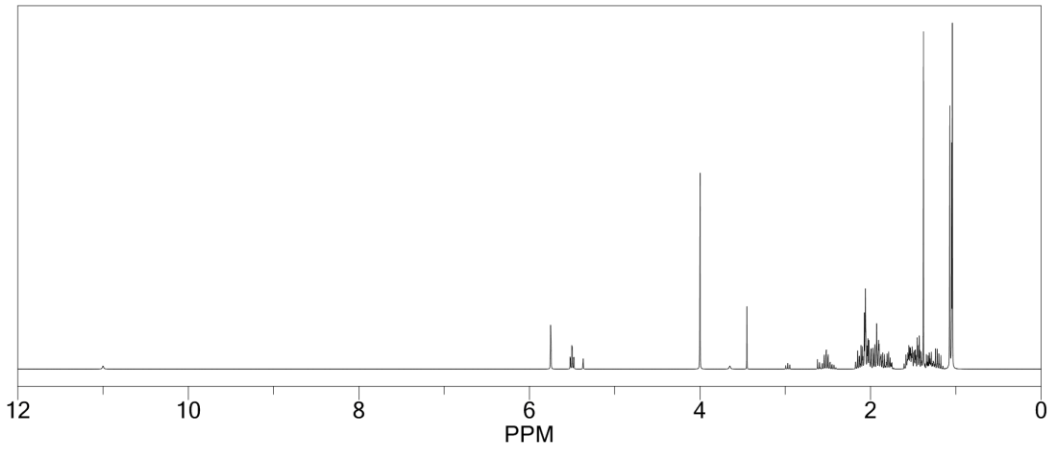


ChemNMR ^{1}H Estimation

Spectrum #29

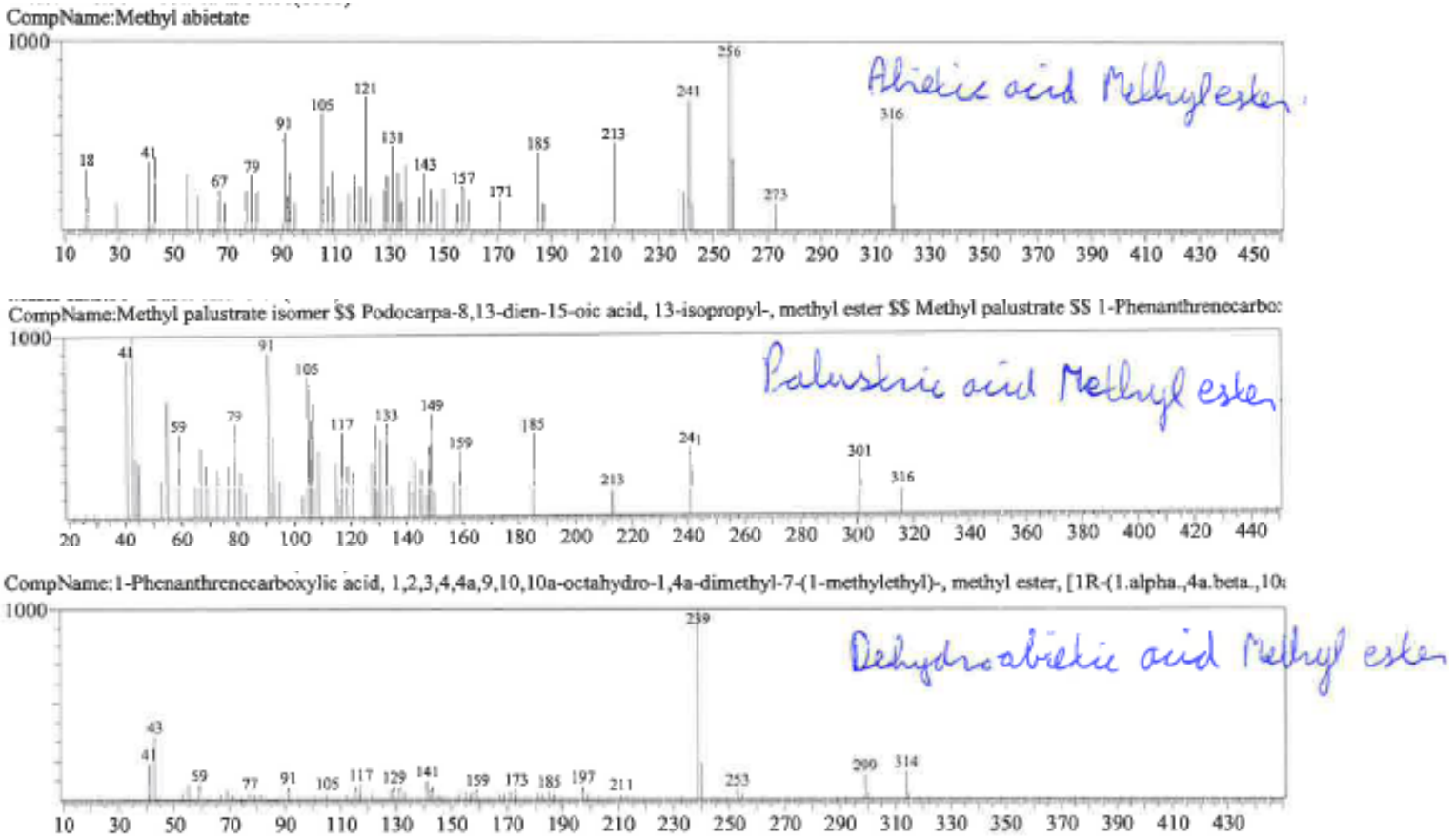


Estimation quality is indicated by color: good, medium, rough



Appendix 4 - Mass spectra for specific rosin acid methyl esters

(Source: NIST library)



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