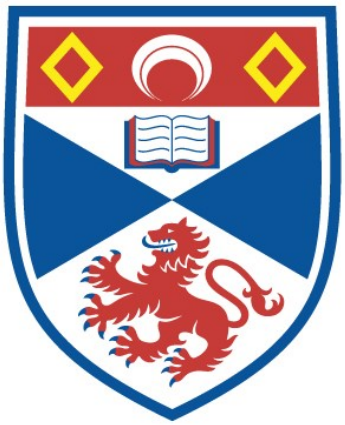
STUDIES OF THE INTERACTIONS OF RESIN ACIDS WITH PIGMENT YELLOW 13

Roger A. Spark

A Thesis Submitted for the Degree of MPhil
at the
University of St Andrews



1996

Studies of the interactions of resin acids with Pigment Yellow 13

being a thesis by

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Submitted for the degree of
Master of Philosophy
in the Faculty of Science of the
University of St Andrews

21st November 1995

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Declaration

I, Roger A. Spark, hereby certify that this thesis, which is approximately 20,000 words in length, has been written by me, that it is a record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

I was admitted as a research student in October, 1994 and as a candidate for the degree of Master of Philosophy in October, 1994; the higher study for which this is a record was carried out in the University of St Andrews between 1994 and 1995.

Signed 21st November 1995

Certification

I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate for the degree of Master of Philosophy in the University of St Andrews and that the candidate is qualified to submit this thesis in application for that degree.

Signed . 21st November 1995

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There are a few people I would like to say "Thank You" to for making this possible. Firstly, my heartfelt thanks to Dr Frank Riddell, without whose belief in me I would not be where I am today. I have learnt a lot about NMR, chemistry and myself under his guidance.

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And, of course, to Claire.

ABSTRACT

The surface interaction between Pigment Yellow 13, a classical diarylide pigment, and abietic acid type resin acids, used commercially to coat pigment products, was investigated by the joint techniques of solid-state ^{13}C CP/MAS NMR and powder X-ray diffraction. The initial objective of the study was to synthesise ^{13}C labelled resin acid analogues to provide a handle for the NMR study.

Attempts were made to label the carboxylic acid carbon of abietic acid, *via* a Barton reaction and subsequent Grignard reaction and carboxylation. Esterification of various resin acid substrates with ^{13}C labelled diazomethane was also attempted. These routes proved difficult, due to the sterically hindered nature of the acid substrates. Labelled adducts were formed from ^{13}C-maleic anhydride and isomerised abietic acid, but were found to be lost from the pigment during resination. Attempts to form a more stable adduct with *N*-methylmaleimide were unsuccessful.

A series of experiments was carried out to coat Pigment Yellow 13 with incremental amounts of abietic acid, maleopimaric acid and dihydroabietic acid. The maleopimaric acid was lost during processing. The pigment samples resinated with abietic acid and dihydroabietic acid were analysed by the techniques mentioned previously.

The presence of resin acids during pigment processing was found to enhance the crystallinity of the pigment particles, as opposed to the heat treatment during processing which promotes particle size. The resin acids were found to be more amorphous than the starting resin when reprecipitated on the pigment particles. ^{13}C CP/MAS NMR shows that there is no chemical interaction between the pigment molecule and the carboxylic acid of the resin.

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Project description

Various natural resins of the abietic acid type are used commercially by Ciba-Geigy to coat many of their pigment products. Applying resin to the pigment crystals serves to enhance certain properties or characteristics of the pigment. Resination has been used commercially for many years, but to this point, the mechanism of the action of the resin on the pigment is not fully understood. The purpose of this project then was to try to define more fully the exact role of the resin acids when added to the pigment.

A technique which suggests itself as being applicable to the investigation of the interaction between abietic type resin acids and the surface of pigment crystals is the solid-state NMR technique known as cross-polarisation / magic angle spinning NMR: or more conveniently CP/MAS NMR.

In the ^{13}C CP/MAS NMR spectrum of abietic acid there are three well separated chemical shift regions of interest; the carboxylic acid carbon, the olefinic carbons and the alicyclic carbons. Because of the low concentrations of abietic acid typically used in pigment preparation, it would seem advisable to attempt to insert a ^{13}C label to facilitate the NMR investigation. It would be desirable to label the carboxylic acid carbon which is well separated in chemical shift from the other carbons.

The ^{13}C CP/MAS NMR spectra will potentially show a variety of features of the interaction between the resin acid and the pigment e.g. chemical shift, line width and relaxation times. Multiple occupancy sites for the acid grouping will show as a series of chemical shifts. If there is a single site occupied then a single resonance should be observed. Several sites will lead either to the observation of several lines or to a 'smearing out' of the carboxylic acid resonance. Line widths can also give a good indication of the degree of crystallinity, or order, of the molecules in a solid.

Powder X-ray diffraction (XRD) studies can be used to supplement the NMR data. The resolution, or sharpness, of the diffraction patterns obtained for resinated pigments can again give an indication of crystallinity. Also, by comparing the

scattering angles of the peaks observed, the likelihood of any chemical interaction having taken place can be assessed.

Studies within this project were carried out using Pigment Yellow 13 (P.Y.13), a classical diarylide pigment. P.Y.13 has three separate methyl environments, and so gives a useful pattern when analysed by ^{13}C CP/MAS NMR, as opposed to P.Y.12 which only has one methyl environment. The resin acids used in the study were abietic acid, maleopimaric acid (commercial Ennesin MU4 resin) and dihydroabietic acid (commercial Staybelite resin).

1 LITERATURE SURVEY

1.1 C-13 NMR of Pigment Yellow 12 and Pigment Yellow 13

MSc. Thesis, University of St Andrews (1992)

K. S. Cameron.

A range of recrystallised diarylide yellow pigments, as well as the corresponding monoazo pigments, were analysed by ^{13}C CP/MAS NMR on a Bruker 500MSL spectrometer operating at 125.758MHz. Many of the resonances for Pigment Yellow 12 and Pigment Yellow 13 were reported[1] (Table 1.1).

A diarylide yellow pigment has a basic structure (Figure 1.1) that contains a minimum of 32 carbons and so can be expected to give a complex solid-state ^{13}C NMR spectrum. The information gained for the monoazo precursors made it possible to identify and assign most of the resonances for the diarylide pigments.

Since the molecule is symmetrical, half of the molecule is numbered and each ^{13}C resonance accounts for at least two carbons.

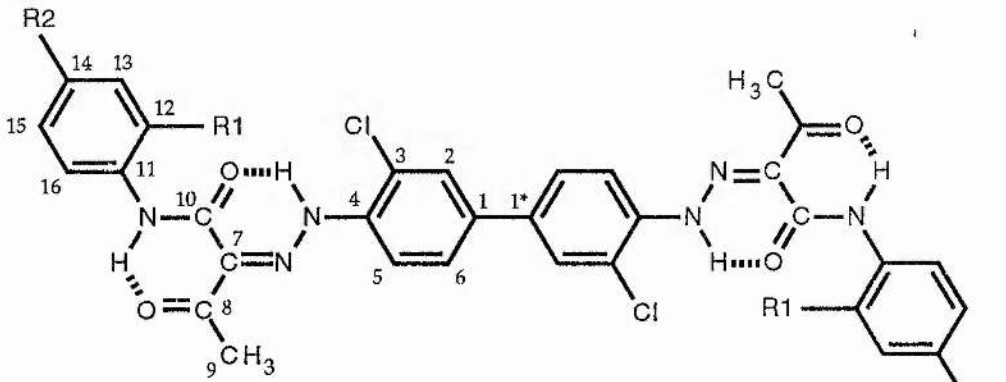


Fig. 1.1 Diarylide Yellow pigment structure.

Where there is no assignment made for a resonance, this is because the peak could not be assigned to a particular carbon. The only carbons not assigned are the aromatic carbons with a hydrogen substituent, since these peaks tend to overlap and so individual peaks are obscured.

Table 1.1 Solid-state C-13 resonances for P.Y.12 and P.Y.13

	P.Y.12 δ_C	P.Y.13 δ_C
C-1	134.3 135.0ppm	131.7ppm
C-2		
C-3	120.4 123.4	118.9 123.0
C-4	138.2	138.7
C-5		
C-6		
C-7	127.0	126.7
C-8	199.0 199.9	199.4
C-9	26.7	26.8
C-10	162.2	161.4
C-11	138.2	135.8
C-12		126.7
C-13		
C-14		131.7
C-15		
C-16		
R-1		20.2
R-2		22.8

The diarylide pigments in general give very similar ^{13}C chemical shifts to those obtained for the corresponding monoazo compounds, indicating similar environments in both classes of pigment. The main differences in the spectra are the C-1 peaks and the splitting of C-8 in Pigment Yellow 12.

1.2 Crystal structure of Pigment Yellow 13

PhD Thesis, Heriot-Watt University (1990)

J. E. Monteith.

The crystal structures of diarylide yellow pigments, including Pigment Yellow 12 and Pigment Yellow 13, were solved[2] using intensity data measured on a STOE Stadi-2 two-circle diffractometer.

Pigment Yellow 13 was synthesised by coupling tetrazotised 3.3'-dichlorobenzidine with acetoacet-*m*-xylidine at 5°C. Intensely coloured, orange, triclinic shaped crystals were grown by slowly cooling a hot 1,2,4-trichlorobenzene solution of the boiled pigment.

Good quality single crystals were analysed, and the data gained were used to determine cell parameters and the space group. Several methods were used to achieve this; structure factor calculations, least-squares refinement and mosaic spread. Computation of the data was performed following a FORTRAN program, to calculate bond lengths and angles, torsion angles, intermolecular contacts and least-squares best planes.

Crystal data $C_{36}H_{34}N_6O_4Cl_2$ M.W. 685

triclinic a=8.363 (4), b=12.512 (8), c=8.743 (7) Å, β=105.70 (8), γ=104.04 (4) °, V=823.5 Å^3, Space group P1, Z=1, Dx=1.35Mgm^{-3}, Dc=1.41Mgm^{-3}, λ (Mo Kα)=0.07103Å, μ (Mo Kα)=0.250mm^{-1}.

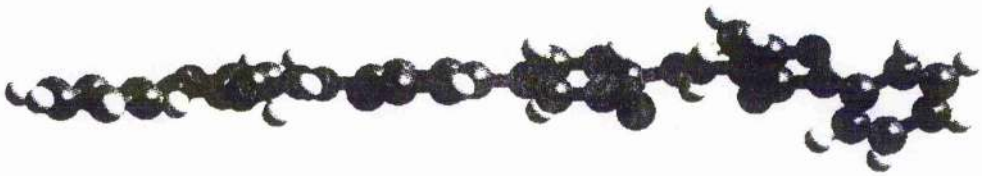
Approximate crystal dimensions 0.5 x 0.5 x 0.5mm.

The two halves of P.Y.13 are related by a crystallographic centre of symmetry at the midpoint of C-1 - C-1'. As a result, the two central chloro-substituted benzene rings must be parallel and also coplanar. There is weak hydrogen bonding present which may be responsible for the planarity of the molecule. Bond length information suggests a degree of localisation of π-electrons within the molecule.

The molecules pack in a two-dimensional interleaved arrangement and the inclination of the normal to the molecular plane relative to the stacking direction is 47.78°. The distances between the plane of the ketohydrazone group in one molecule and the equivalent planes in molecules above and below are 3.36 and 3.23Å respectively.

Pigment Yellow 12 differs from Pigment Yellow 13 by having no methyl groups on the extreme benzene rings. This change affects the end-to-end molecular packing, and consequently significantly changes the angle of rotation around C-1 - C-1'. This dramatic change is well illustrated in Figure 1.2.

Pigment Yellow 13



Pigment Yellow 12

Fig. 1.2 Structures of P.Y.13 and P.Y.12 derived from XRD data.

1.3 C-13 NMR of abietic acid

A Org. Magn. Res., **11** (1978) 427-8

W. B. Smith.

Commercial grade abietic acid was purified by several recrystallisations of the diamylamine salt. The ^{13}C NMR spectrum was recorded on a JEOL FX-60 spectrometer operating at 15MHz in $CDCl_3$ solution. The assignment of lines in the ^{13}C spectrum was achieved[3] by using carbon T_1 relaxation time values and lanthanide induced shift effects (Table 1.2).

B Magn. Reson. Chem., **28** (1990) 443-7

C. Kruk, N. K. de Vries, G. van der Velden.

Abietic acid was purified from the diamylamine salt. Two-dimensional (2D) INADEQUATE ^{13}C NMR was recorded on a Bruker WM250 spectrometer operating at 62.89MHz in $CDCl_3$ solution. The information gained was used to establish the carbon-carbon connectivities in abietic acid, and allowed unambiguous assignment for all 20 carbons[4] when considered with other 1D and 2D NMR techniques (Table 1.2). Proton assignment was established via ^{1}H-^{13}C heteronuclear chemical shift correlation and NOE-difference experiments.

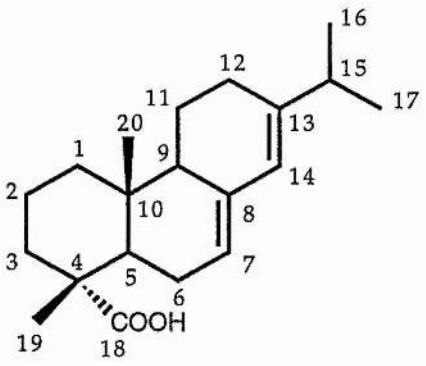


Fig. 1.3 Abietic acid.

Table 1.2 C-13 resonances for abietic acid

	A	B
	δ_C	δ_C
C-1	38.3ppm	38.37ppm
C-2	18.1	18.11
C-3	37.2	37.27
C-4	46.3	46.40
C-5	44.9	45.01
C-6	25.6	25.66
C-7	120.5	120.48
C-8	135.5	135.56
C-9	51.0	51.05
C-10	34.5	34.54
C-11	22.5	22.55
C-12	27.5	27.49
C-13	145.1	145.12
C-14	122.5	122.54
C-15	34.8	34.90
C-16	20.9	20.89
C-17	21.4	21.42
C-18	185.4	185.20
C-19	16.7	16.71
C-20	14.0	14.05

The T_1 for C-15 is just over twice that for the ring methines and indicates the rotational freedom of the isopropyl sidechain at C-13.

1.4 C-13 NMR of maleopimaric acid

Magn. Reson. Chem., **28** (1990) 443-7

C. Kruk, N. K. de Vries, G. van der Velden.

As for abietic acid, 2D INADEQUATE ^{13}C NMR, plus several 1D and 2D NMR techniques, was used to gain unambiguous assignments for the 24 carbons in maleopimaric acid[4] (Table 1.3).

Purified maleopimaric was obtained from the crude reaction mixture by dissolving in toluene and precipitating the adduct by the addition of n-heptane. The structure of maleopimaric acid can be seen in Figure 1.4.

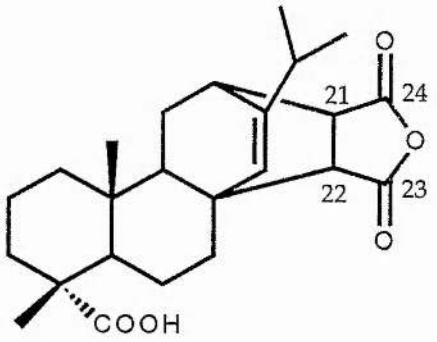


Fig. 1.4 Maleopimaric acid.

Although the reaction between levopimaric acid (isomerised abietic acid) and maleic andydride can theoretically lead to four isomers, only one isomer is formed in high yield.

An NOE-difference experiment using the multiple irradiation technique was performed to establish the isomer formed. Observed NOE effects confirmed the dominant isomer is the one which is formed when the dienophile, maleic anhydride, attacks the diene from below, with the anhydride ring pointing upwards (Figure 1.5).

Table 1.3 C-13 resonances for maleopimaric acid

	δ_C		δ_C
C-1	37.97ppm	C-13	148.07ppm
C-2	16.89	C-14	125.12
C-3	36.74	C-15	32.69
C-4	46.77	C-16	19.91
C-5	49.05	C-17	20.50
C-6	21.62	C-18	184.86
C-7	34.76	C-19	16.40
C-8	40.37	C-20	15.42
C-9	53.25	C-21	45.58
C-10	37.51	C-22	53.03
C-11	27.18	C-23	172.64
C-12	35.64	C-24	170.87

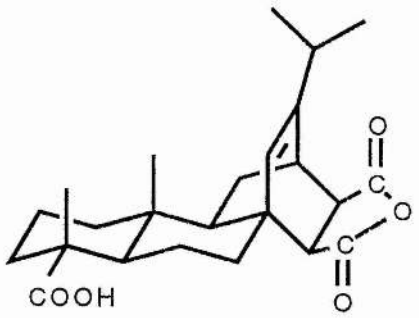


Fig. 1.5 Major isomer of maleopimaric acid.

1.5 Crystal structure of abietic acid

Bull. Chem. Soc Jpn., **67** (1994) 807-15

K. Okada, S. Takekuma.

The crystal and molecular structures of abietic acid have been determined by single-crystal X-ray diffraction analysis[5]. Crystals of abietic acid were recrystallised as colourless prisms from aqueous ethanol by slow evaporation. M.p.159-168°C. $[\alpha]_D$ -104.4" (c=0.5, EtOH). Data were collected at room temperature.

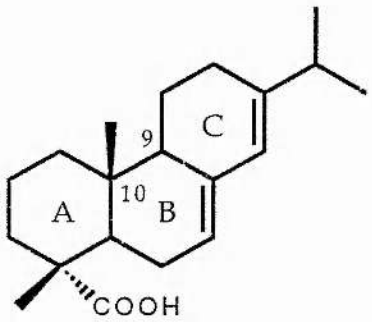


Fig. 1.6 Abietic acid.

The crystallographic asymmetric unit cell contains two independent molecules with similar geometries and planar conformations. In each molecule (Figure 1.6) cyclohexane ring A has a typical chair form. Cyclohexane rings B and C have half-chair conformations. The relative stereochemistry for both molecules is *trans* fusion for the A/B ring junction, and *anti* between H-9 and C-10 methyl.

Crystal data $C_{20}H_{30}O_2$ M.W. 302.46

monoclinic a=14.058 (2), b=11.911 (1), c=11.753 (2) Å, β=111.73 (1) °, V=1828.1 (6) $Å^3$, Space group $P2_1$, Z=4, Dx=1.099gcm^{-3}, λ (Cu Kα)=1.5148Å, μ (Cu Kα)=5.01cm^{-1}.

Approximate crystal dimensions 0.2 x 0.2 x 0.2mm.

1.6 The structure of an abietic acid dimer

J. Chem. Soc., Chem. Commun., (1986) 1038-9

B. Gigante, R. Jones, A. M. Lobo, M. J. Marcelo-Curto, S. Prabhakar, H. S. Rzepa, D. J. Williams, D. F. Zinkel.

The first X-ray structural determination of an acid-catalysed dimer of abietic acid is reported[6]. The dimer was isolated from toluene-*p*-sulphonic acid-catalysed dimerisation of methyl levopimarate in chloroform at room temperature.

A single-crystal X-ray analysis reveals that only one new C-C bond, between C-7 and C-7', has been formed. The two monomer fragments are orientated to each other in a way which brings H-7 and H-14' close together (2.01Å). This conformation is confirmed by ^1H NMR by the observation of a strong nuclear Overhauser enhancement between H-7 and H-14'.

Two new chiral centres are created during dimerisation, at C-7' and C-13', and one is lost at C-9'. The structure of the abietic acid dimer is seen in Figure 1.7.

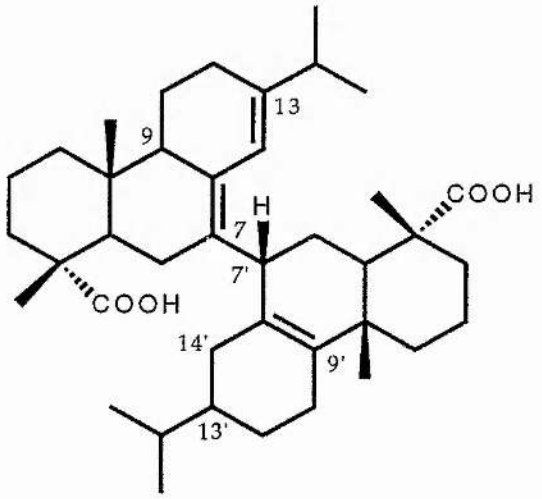


Fig. 1.7 Structure of an abietic acid dimer.

2 INTRODUCTION

2.1 CIBA-GEIGY - a brief history

Previous to 1970, CIBA and GEIGY were two independent companies, both involved in the manufacture of pigments and pigment preparations. CIBA had manufacturing facilities in Switzerland and concentrated on high performance pigments. J.R. GEIGY produced high performance pigments in Switzerland too, but had also acquired a classical organic pigments company earlier in the century. This was the Glasgow firm of James Anderson Colours Ltd. which was later moved to Paisley. Both businesses grew from the Swiss chemical industries' large involvement in the development and manufacture of synthetic organic dyestuffs.

Competition existed between the two, although CIBA's main business was in plastics and fibres while Geigy targeted mainly inks and paints. At the time of the merger, therefore, a good synergy existed between their product ranges and many of those original products are still produced today.

After the initial merger the first major change to take place was in 1979 when the business of Hercules Inc. was acquired, with manufacturing facilities in the United States. This allowed the company to become a major supplier of inorganic pigments, including lead chromates, cadmiums, iron blue, chromium oxide green and ceramic pigments. This acquisition also included Ten Horn of Holland who produced lead chromate pigments and some speciality organic pigments.

In 1980 a joint venture was set up with Daihan Colours of South Korea to manufacture classical pigments. This served primarily to expand CIBA-GEIGY's presence in the Far East but since then Daihan Swiss products have become international products and are now sold throughout the world.

The last major addition to the business came about in 1983 when the quinacridone business was acquired from Du Pont Chemical of the United States. These products complemented the existing range of high performance pigments.

In 1987 the decision was taken to close the inorganic and organic pigments plant at Glens Fall in the United States, originally part of Hercules Inc.. Organic pigment production from Glens Fall was transferred to Paisley.

CIBA-GEIGY is now a multiple production site operation and makes the business very much a global and international enterprise with a broad range of products on offer.

2.2.1 **Light and colour**

Light is a form of energy. Our main source of light is the sun, kept at a fierce temperature by a series of chemical and nuclear reactions. The energy released by these reactions is also felt by us as heat. Heat and light are produced in the same process: they are different manifestations of energy and form part of a large series of electromagnetic radiations.

Energy is radiated in waves, alternating between maximum and zero intensity; the crests and troughs of the waves. All electromagnetic radiations move at the same high velocity through air or vacuum (the speed of light). They differ, however, in frequency. The frequency is the number of waves that move past a fixed point in one second. Since all radiations move at the same velocity and the frequency may differ, then the wavelength must vary also. The wavelength is the distance from trough to trough or crest to crest.

For electromagnetic radiations, the wavelengths vary from less than 0.1nm for gamma rays to up to 20km for radiowaves. Visible light, with a wavelength of 400 to 700nm, is the only electromagnetic radiation which affects the eye in such a way as to transmit signals to the brain, which the brain then interprets as a picture.

2.2.2 Colour

If two rays of visible light differ slightly in wavelength, they will have different effects on the eye i.e. they will appear to be a different colour or shade.

Throughout the visible range of the electromagnetic spectrum. there is a gradual change in colour from violet at about 400nm, through blue, green, yellow and orange, to red at about 620nm. However, the colours merge smoothly into each other throughout and so cannot be counted. Sunlight contains all the wavelengths as a mixture and the eye registers the mixture as the colour white. White light can be separated into its component colours by a prism and the range of colours produced is a spectrum. The principle colours in a spectrum are Red-Orange-Yellow-Green-Blue-Indigo-Violet.

When a coloured object is illuminated by white light, it absorbs some of the wavelengths and transmits others. The eye receives the transmitted wavelengths and interprets them as one colour. This colour is dominated by the main wavelength transmitted, and modified by undertones of the other wavelengths, which give an individual shade.

There are, for example, many red shades, some are dark, some are bright, some have a yellow undertone (e.g. scarlet) and some have a blue undertone (e.g. magenta). A truly black object absorbs all the wavelengths and a truly white one none of them.

A fundamental aspect of colour chemistry (and thus pigment chemistry) is how much and at what wavelengths original white light is retransmitted by an object.

2.2.3 Colour chemistry

Among organic compounds, it is evident that coloured chemicals usually contain certain groups, which are called chromophores, and are found as part of aromatic molecules. Typical chromophores include the azo group, the nitro group, the carbonyl group, the thio group, the nitroso group and the ethenyl group.

These coloured molecules have their colour intensified or modified by certain other groups known as auxochromes. Typical auxochromes include the amino group, the hydroxyl group, the methoxy group and the iodo, bromo and chloro groups.

This phenomenon can be explained to some extent by saying they create within the molecule highly localised electronic disturbances. These "areas" absorb electromagnetic radiations and, depending on the visible wavelengths absorbed, the colour is determined. Colourless compounds absorb only in regions outside the visible spectrum.

2.3 **Pigments**

The word pigment is derived from the Latin word PINGERE, to paint, and was originally restricted to those solid materials added to a medium to give a paint with the desired consistency, covering power and appearance. This definition has long since been extended to include materials used for similar purposes in inks, rubber, plastics and many other media.

Industrially, a pigment is any finely divided insoluble black, white or coloured solid material, a major function of which is to improve the appearance of or give colour to the medium in which it is to be used. Incorporation is always by physical mixing of pigment and medium, and it is this feature that distinguishes a pigment from a dyestuff.

Pigments and dyes are often derived from the same basic building blocks - the difference being dyes are soluble in the media they are incorporated into and pigments are not. Ciba-Geigy at Paisley is concerned solely with the manufacture of pigments.

Pigments used for industrial purposes can be classified as:

Natural or Synthetic

Organic or Inorganic.

It is unlikely that there is any organic pigment of which the naturally occurring form is still in industrial use today. Many inorganic pigments, however, are still dug

out from the earth's crust. Frequently there is a synthetic equivalent - apparently the same chemically, but often with quite different properties.

Organic pigments, as in general chemistry, are those products which are based on carbon chains and carbon rings. However, organic pigments can also include metallic elements in their structure, as in the phthalocyanines, which help stabilise the properties of the organic component.

It is interesting to note that the average particle size of inorganic pigments is significantly greater than that for organic pigments. This means that the specific surface area of organic pigments is much bigger. The larger surface area for organic pigments gives products with much higher colour strength, although their dispersibility in media is usually poorer.

The optimum particle size to achieve maximum light scattering (leading to opacity) is between 400 and 800nm (wavelength of visible light). Inorganic pigments have particle sizes nearer to this optimum than organic pigments, which tend to be much smaller. This is a primary reason why most organic pigments are considered transparent and most inorganic pigments are considered opaque.

2.3.1 Organic pigments

Organic pigments can be fundamentally divided into classical pigments and high performance pigments. It is normally the performance criteria which determine whether an organic pigment is defined as classical or high performance. The division between high performance pigments and classical pigments relates also to historical development. Most common classical pigments were developed before the Second World War; it is only since then that the more complex chromophoric structures of the high performance pigments have been commercially available products.

It is a sound principle that as the molecular weight of a pigment, and by implication its complexity, is increased, so its solvent fastness properties improve. The increase in molecular weight of monoazo pigments (340-400) to diazo pigments (600-830) to azo condensation pigments (900-1200) shows this trend quite clearly.

Molecular weight consideration is often not the most important factor, for it is easily obscured by the influence of groups which either prevent close packing because of their bulk and shape or, because of their electronic state, tend to induce repulsion between individual pigment molecules.

Groups which are widely used to confer insolubility in pigments are carbonyl and amino groups, which may occur together as an amide group or can be situated in different parts of the molecule. Through the strategic placing of CO and NH groups, virtual insolubility can be achieved in all common solvents. Increased intermolecular forces such as hydrogen bonding also raise the melting point and hence increase the range of applications in which a pigment may be used.

It is often the case that, to achieve these more stable types of molecule, the whole manufacturing procedure is much more complicated.

2.3.2 Classical organic pigments

Some of these product structures date back to the earliest development of synthetic dyestuffs in the mid 1800's. By far and away the most common classical pigments are the azo compounds (compounds which include the chromophore N=N). Many different azo structures exist which give rise to a whole range of yellow, orange and red pigments. A fundamental split can be made between monoazo compounds (containing one N=N group) and diazo compounds (containing two N=N groups).

2.3.2.1 Monoazo pigments

All azo compounds are manufactured by diazotising an aromatic amine to form a diazo base which is then coupled with a suitable coupling component. For example, a substituted aniline can be diazotised then coupled with beta-naphthol. By controlling the type of coupling component used, a division between yellow and orange/red pigments is achieved. For yellow pigments, the diazo base is coupled with an aceto-acetarylamide to form the generically known group of arylamide Yellow Pigments, often known as "Hansa Yellows".

In the case of the simpler red pigments, the coupling component is beta-naphthol, giving rise to the generic name "Beta-Naphthol Reds". Both pigments use the same diazo base: 3-nitrotoluene-4-diazonium chloride (from 3-nitro-4-aminotoluene).

2.3.2.2 Diazo pigments

This group of pigments overcome some of the deficiencies of the monoazo group, namely fastness to heat and solvents. The basic starting point for most pigments of this type is 3,3'-dichlorobenzidine which is tetrazotised and coupled with an aceto-acetarylamide to form diarylide Yellow Pigments (Figure 2.1).

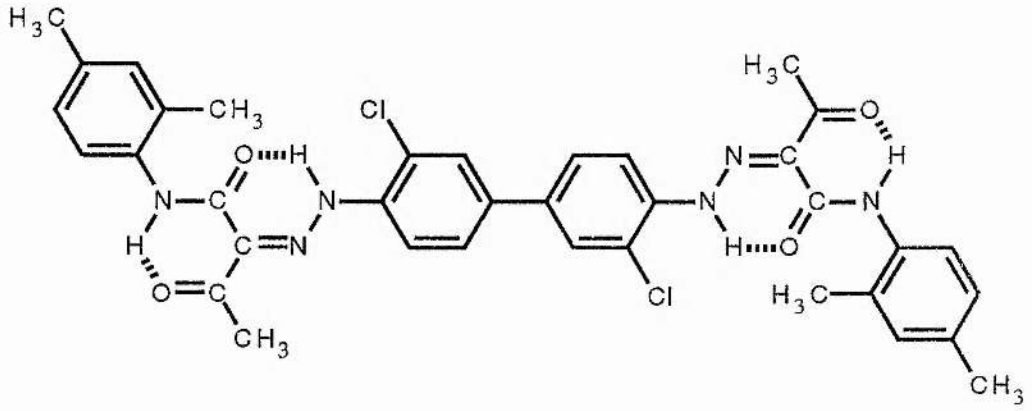


Fig. 2.1 Pigment Yellow 13.

Tetrazotised 3,3'-dichlorobenzidine, coupled with acetoacet-*m*-xylidine.

By varying the coupling component, namely to use pyrazolone derivatives, orange and red pigments are produced.

2.3.2.3 Diarylide Yellow pigments

(most common products: Pigment Yellow 12, 13, 14, 17, 55, 83)

The Diarylide Yellows are characterised, by virtue of their larger molecular size, as having good heat and solvent resistance and excellent colour strength. They vary in lightfastness from very poor (P.Y.12) to good (P.Y.83). The range of products offered by diarylide yellows is sufficient to meet virtually all requirements of most printing processes. The products are widely used in the plastics industry, although they are generally not recommended at low concentrations as the migration resistance is not sufficient.

2.3.3 Colour Index

With the extremely large number of pigments available, it is useful to have a system of classification. Such a system is "The Colour Index", as drawn up by the Society of Dyers and Colourists (U.K.) and the American Association of Textile Chemists and Colourists.

The system classifies each commercially available pigment firstly as C.I. Pigment. Each product has a C.I. Generic Name and Number described in terms of properties e.g. C.I. Pigment Yellow 12. In addition, where the chemical constitution of the pigment has been disclosed, a 5 figure C.I. Constitution Number is allocated e.g. C.I. No.44045.

This means that the broad chemical constitution may refer to a number of Generic Names, depending on whether the final conversion is to basic dye, pigment etc.. Each product has a C.I. Generic Name but not necessarily a C.I. Constitution Number. In the pigments business, the C.I. Generic Name is most useful in that all the products of Ciba-Geigy and its competitors are classified in the same way.

Throughout this thesis, pigment products will be named either, for example, Pigment Yellow 13 or P.Y.13.

2.4 **Property requirements of pigments**

A pigment has already been defined as an insoluble material used to improve the appearance or provide colour to the medium in which it is being used. To achieve this, certain fundamental properties are required of pigments.

A fundamental aspect common to all usages of pigment is that the product has to be incorporated into the medium for which it is intended. This is known as dispersion of pigments.

2.4.1 Dispersion

The smallest pigment particles are formed in discrete units, or primary particles. These primary particles may be cubes, spheres, rods, needles etc. and, owing to their high surface energy, randomly join together to form aggregates. During subsequent processing (filtration and drying), these aggregates and other primary particles lump together to form what are known as agglomerates. Thus, the sold product is a mixture of agglomerates and aggregates.

As these aggregates are formed, so the surface area of the pigment is reduced and since it is the surface of the pigment particles which impart colour, then less colour will be delivered. Therefore, to obtain maximum value, these large particles must be broken down to increase surface area - by dispersion. The effect on this increase in surface area is very dramatic as particle size is reduced.

2.4.1.1 Optimum particle size

As the pigment is dispersed and the particle size reduced, so the colour strength is increased, but how far can this be reduced to achieve the optimum size? Firstly, individual particles must not be visible to the naked eye. The resolving power of the human eye is 50-70μm, so any particle larger than this will be visible.

Secondly, as dispersion is increased and more surface area is made available, then it follows that the fluidity of the medium is reduced and viscosity is increased.

There may then come a point where the forces required to manoeuvre the medium are too great and at high pigmentation levels there is a limit to the particle size reduction.

Thirdly, achievement of opacity and transparency is important. A pigment displays maximum hiding power when its particle size corresponds to the wavelength of visible light. Maximum hiding power is therefore obtained in the particle size range 0.2-1μm; below 0.1μm, the higher the transparency.

Finally, the economics need to be considered, since pigment dispersion in a medium requires time and energy. Colour strength increase in relation to particle size reduction is not linear, and to achieve a significant further increase in colour strength after a set period of time, a disproportionately high level of energy and time is used. Therefore, for economic reasons pigments are rarely dispersed to their full extent.

From these factors, the optimum particle size can be estimated to be up to 50μm, and in practice between 0.1 and 0.5μm. In reality, however, it is usual for there to be a spread of particle sizes, with small numbers of particles of much larger and much smaller size.

2.4.1.2 Principles of dispersion

Dispersion, the broad term for incorporation of pigments in a medium consists of four processes:

wetting out (of the pigment surface)
breaking down (of the agglomerates)
distribution (of the particles uniformly in the substrate)
stabilisation (of the dispersion obtained).

Wetting can be described as the spreading of a liquid on the surface of powder pigment and the elimination of the pigment-air interface. It can also be thought of as the softening of the powder pigment agglomerates by means of a liquid. Wetting, therefore, depends on the affinity of the pigment surface to the medium and also the

steric interaction between the molecules of the medium and the structure of the pores of the agglomerates.

The affinity for absorption of a medium by a pigment is dependent on a number of factors; the type of pigment being used, particle size and size distribution, particle shapes and surface characteristics.

The achievement of good wetting is the first step to achieving good dispersion, and the lower the viscosity of the medium, the better the chances of achieving good wetting. In paints and inks, for example, viscosity is reduced by "thinning" the medium down with solvents, which serves to improve wetting.

The agglomerates and remaining aggregates are broken down into the primary particles and distributed throughout the medium. The breaking of the agglomerates is achieved under shear conditions and by impact/attrition. It is clear then that to achieve maximum effectiveness at this stage, the shear forces and/or the probability of crushing must be at a maximum. This may be achieved by the correct selection of the dispersion equipment, depending on the viscosity, and type of medium to be pigmented.

Once a pigment has been dispersed into the medium, stabilisation is required to maintain the pigment as primary particles. In media with low viscosities, the attraction forces between the dispersed pigment particles cause the particles to contract and come together again. This is known as flocculation or reagglomeration, and to reduce this tendency the particles must be stabilised.

There are two actions of stabilisation to consider:

i) Steric stabilisation. Particle separation, due to the adsorbed layer of carrier medium on the pigment particle surface, which interferes with the close approach of other particles. For effective steric hindrance, there must be a sufficient thickness of adsorbed layer to extend far enough around the particle to counteract the natural attractive forces between particles.

ii) Charge stabilisation. Repulsive forces between particles owing to electrical charges maintain the deflocculated state only if the particles are sufficiently far apart for the repulsive forces to counteract and exceed the attractive forces that exist between the particles.

Charge stabilisation occurs when an ionisable material from the medium allows a negative or positive ion to be adsorbed on the pigment surface, the opposite charge diffusing into the medium. Thus the particles acquire a like charge. The ability to achieve sufficient stabilisation is dependent on the surface chemistry of both the pigment and the medium.

Inability to achieve stabilisation, such that flocculation occurs, leads to a number of problems:

- extreme viscosity (sometimes leading to gelation) and poor flow
- lower colour strength
- lower gloss
- colour differences on application
- poor dispersion level in general.

In addition to the fundamental requirement of dispersion, the following important characteristics of pigments in use need to be considered and defined:

lightfastness
weatherfastness
flocculation
heat stability
opacity / transparency / hiding power
colour strength
chemical resistance
solvent resistance
rheology
gloss properties.

2.4.2 Lightfastness is defined as the resistance of the product, within a given medium, to colour change when exposed to daylight. The radiation within daylight that is most damaging is the Ultra Violet radiation. Testing for lightfastness is a useful way of determining reasonably quickly whether a product will have sufficient durability for a given application.

When measuring lightfastness, there is no definitive result which can be measured directly. The quoted result is comparative to an accepted standard, after exposure to light for a set period of time, under a standard set of conditions and in a given medium.

2.4.3 The ultimate test of durability for a coloured system is for weatherfastness, actual exposure to outside weather conditions. Exposure during weathering is influenced by more than just visible light: high energy U.V. radiation, heat, moisture and impurities in the atmosphere. Tests for exterior exposure are carried out at locations selected for their aggressive conditions. One of the well known testing stations in the world is in Florida - particularly for automotive paint applications.

Weatherfastness data can only be compared when the climatic conditions during testing are constant and well known. Artificial weathering equipment may be used to accelerate the assessment. The equipment is capable of providing water spray (for rain), temperature changes, light (and dark) and varying levels of humidity.

2.4.4 During dispersion the aim is to surround the pigment particles with sufficient resin, such that particle to particle contact is then avoided. On occasions this process is reversed and reagglomeration or flocculation occurs.

Reagglomeration means that pigment particles stick together, and the contact surfaces between the particles contain no binder material. Flocculation differs in that the particles do not lose their surrounding binder material. Flocculates are weakly linked particles which may be easily separated by low shear forces.

Flocculation of a pigment leads to problems like loss of colour strength, gloss and transparency. The tendency to flocculate is based on the interaction of the pigment surface and constituents of the medium. Flocculation may be prevented by the addition of small amounts of suitable amounts of additives into the application medium.

2.4.5 Heat stability is defined as the resistance of the pigment to change brought about by exposure to high heat conditions, either during dispersion or application of the medium. Many applications of pigment products require that the material is exposed to high heat conditions. High heat conditions cause colourants to degrade and in the plastics industry, processing temperatures are pushing the limits of stability of many compounds. Heat stability is not merely a case of noting the temperature at which a pigment product degrades, but the total time that the product is subjected to that high temperature must also be considered.

2.4.6 Opacity / transparency / hiding power. Light passing through a transparent medium will either pass straight through or be reflected from the substrate without substantial alteration. Light entering an opaque medium, however, will not penetrate and will either be absorbed or reflected.

Transparency is an important requirement in certain pigment applications. It is not strictly correct to describe pigments in terms of transparency or opacity. A pigment should instead be described by its ability to impart a degree of hiding (hiding power), or reduction of the transfer of light in a particular medium. Pigmented media achieve hiding power by one of two mechanisms; absorption of light and scattering of light.

As previously discussed, black absorbs all light, colours absorb selected wavelengths and white absorbs no light but scatters the light very effectively. White and black pigments, therefore, have excellent hiding power, whereas coloured pigments rely on selective absorption of light and degree of scattering to achieve hiding power.

Two important parameters influence the degree to which light scattering occurs:

.i) Refractive index. When light moves from a low density medium into a high density medium, the change in direction which the light experiences is called refraction. The Refractive Index is the ratio of the angle of incidence to the angle of refraction. Refraction at an irregular surface causes scattering of the light crossing the boundary, and the greater the difference in refractive index between the two sides of a boundary, the greater the scattering.

ii) Particle size. The particle size of the pigment also determines the level of scattering that occurs when light enters a pigmented medium. The nearer the particle size of the pigment to the wavelengths of light, the more the light will be interfered with. In the yellow colour area, where less light is absorbed, the predominant mechanism for achieving hiding power is light scattering. Inorganic pigments such as Chrome Yellow have a significantly higher hiding power potential than organic pigments. Blending with inorganic pigments such as Titanium White is probably the best known technique for achieving hiding power. However, other pigments offer the potential to reduce light penetration by the mechanism of absorption.

2.4.7 Colour strength relates to the amount of a particular colourant that is required to produce any given colour intensity. Pigments in a medium absorb and scatter light, and the degree to which these phenomena occur determine the colour strength of the pigment. There are several ways colour strength may be assessed. One technique uses the ability of a coloured pigment to absorb light, and thus change the colour of an opaque white pigment when the two are mixed together.

Similarly, for any given level of coloured pigment, the amount of white pigment required to give a particular colour intensity is a measurable assessment of the colour strength. Another technique used is a comparison of the tinting power of one pigment versus another. In other words, the number of parts of one pigment that equate to one hundred parts of another.

2.4.8 Chemical resistance. Pigment products are often likely to come into contact with chemicals which react with and so adversely affect the characteristics of the product. The most common form of chemical attack is from acidic or alkaline media. For example, in industrial atmospheres sulphur dioxide is present, which forms sulphurous acid and subsequently sulphuric acid with water. This can attack pigmented systems and is particularly important when considering applications for long term exposure e.g. automotive paint finishes.

2.4.9 Solvent resistance. Many applications of pigmented media will come into contact with organic solvents during their useful life. It is thus an important requirement that pigments should be as insoluble as possible in organic solvents.

It was mentioned previously that increasing the complexity of the chemical structure of organic pigment molecules imparts a much higher degree of solvent resistance. Therefore, it is mainly with classical organic pigments that problems of poor solvent resistance occur. Pigment products are tested against a broad range of solvents for resistance to chemical reaction and degradation.

2.4.10 Rheology is the study of flow and deformation of matter. The incorporation of a pigment into a medium will invariably alter its rheological properties. The most common term used when discussing rheology is the viscosity of the medium, but many other factors contribute.

Fluids which show ideal fluid behaviour are known as Newtonian. Many fluids behave in a Newtonian manner, including water and mineral oil. As we would expect, however, many fluids show deviations from ideal Newtonian behaviour.

2.4.11 Gloss. Part of the light incident on a surface is reflected, and the rest of the light penetrates the surface and, after scattering and multiple reflection beneath the surface, is re-emitted in a nearly diffuse state.

Light reflected at the surface is composed of two parts: the specular reflection (mirror gloss) and the diffuse reflection (haze). For specular reflection, the incident rays are reflected directly off the pigmented surface and the undercoat surface. Diffuse reflection is made up of point scattering and absorption within the pigment layer.

Gloss deficiency of a surface may be due to:

- poor level of dispersion and presence of very large pigment particles or agglomerates
- insufficient dispersion stability which leads to flocculation
- pigment concentration which is too high
- unfavourable rheology which leads to a poor levelling of the wet film.

There is also a close relationship between the gloss behaviour of a pigmented film and the crystal shape of pigment particles. Pigments with pronounced angular crystal shape often prevent the formation of a sufficiently smooth film surface. This can be largely overcome and the gloss improved if the pigment needles are broken perpendicular to their length.

2.5 **Resins and the resination**

Resins are only one of a number of additives which are employed industrially to change pigment characteristics in some way, and this thesis is concerned with the interaction between the pigments and the resins. Other additives include fatty acids, oligomeric and polymeric acids, aliphatic amines, pigment functional derivatives and surfactants. The additives which are used are carefully selected to influence the pigment characteristics in order to suit the chosen application. These additives can be responsible for controlling the size of pigment particles, enhancing the crystal structure, altering crystal surface and shape and improving processing. Pigment characteristics to be enhanced by such additives include rheology, gloss, colour strength, dispersibility, transparency and heat stability.

2.5.1 Influence of resins

The resins themselves can be utilised to influence certain well defined pigment characteristics. Pigment resination serves to:

- control crystal growth, influencing transparency and dispersibility
- reduce aggregation and agglomeration in finishing, drying and grinding, so improving dispersibility. The resin finish rounds off sharp corners on the pigment crystals and covers defects
- reduce interfacial tension, which positively influences the dispersibility due to the improved wettability. Wetting is improved because the resins applied to the pigment particles are often soluble in the solvent media.

Not only the amount of resin, but when it is added, is an important factor. Addition of resin during the early part of pigment synthesis means that the resin is adsorbed by the crystal nuclei, thereby preventing unlimited crystal growth. The resultant small particles give rise to certain improved pigment characteristics:

- colour strength
- gloss
- transparency
- purity.

Even additions of 40% resin (especially with diarylide pigments) scarcely affect the colour strength because now the particles are protected from aggregation and agglomeration, are optimally coated and can contribute fully to the colour strength.

When the resin is applied to the fully developed larger particles, after synthesis is completed, then other characteristics are positively influenced:

- dispersibility
- rheology
- opacity.

2.5.2 The abietic-type resin acids

Resin acids are monocarboxylic acids of alkylated hydro-phenanthrene nuclei. The two-double-bond acids have the formula $C_{20}H_{30}O_2$ and the abietic type resin acids are characterised by the isopropyl group at C-13. The two double bonds may be located as illustrated in Figure 2.2.

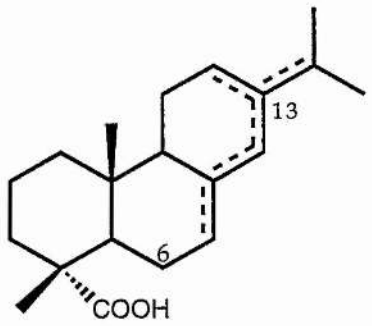


Fig. 2.2 Abietic-type resin acid structure.

The three rings of the resin acids are fused together to form relatively rigid structures which means they possess relatively high melting points. Also, some of their unique properties arise from their hydrophobic skeleton and hydrophilic carboxylic acid group which contributes to their excellent solubility in the correct solvent media.

The carboxylic acid group is attached to a tertiary carbon atom and is so closely surrounded by other groups that it is highly hindered. In particular, it is hindered by the methylene group at C-6 which can be appreciated with a molecular model.

The abietic-type acids are readily susceptible to isomerisation by heat, acid or atmospheric oxygen. Migration of the whole diene system to an adjacent position should be expected when the resin acids are heated above their melting point.

There are three abietic-type acids which will be utilised during these studies:

abietic acid itself,

maleopimaric acid (commercial Ennesin MU4 resin)

and dihydroabietic acid (commercial Staybelite resin).

2.5.3 Abietic acid

Abietic acid is the most common of the resin acids by virtue of its ready formation by acid-catalysed isomerisation of rosin.

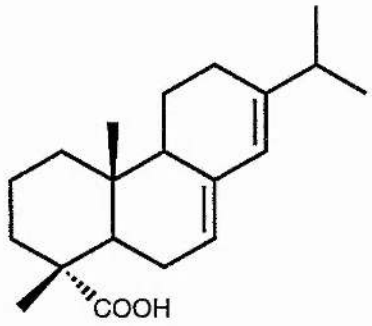


Fig. 2.3 Abietic acid.

The literature survey has already detailed much information about abietic acid. The structure and conformation of abietic acid solved by single crystal X-ray diffraction were reported[2], as were the ^{13}C NMR data[3,4], including a full assignment for all 20 carbons. The structure of an abietic acid dimer was also reported[6].

Over many years there has been much research carried out by a great deal of people to isolate and characterise abietic acid, the main component of oleorosin obtained from pine trees. Abietic-type acids are found to isomerise easily under certain conditions, which made characterisation of abietic acid difficult due to the shifting of the double bonds. Since it has been possible to isolate abietic acid, it has been the subject of many types of chemical reactions, due to its availability and its many commercial applications. An excellent account of the isolation and characterisation of abietic acid, as well as an extensive review of its chemistry are reported by Simonsen and Barton[7].

Abietic acid is difficult to purify to its full extent by conventional methods. However, this can be achieved by first isomerising the rosin to abietic acid, then forming a diamylamine salt of the acid[8]. The diamylamine salt is a convenient way to store the acid, since it may be susceptible to atmospheric oxidation as the free acid.

Abietic acid is regenerated from the pure salt by decomposition with a weak acid such as acetic acid.

Abietic acid used in these studies was twice recrystallised from Aldrich technical grade material (~70 %) using aqueous ethanol (m.p. 131-134°C).

2.5.4 Maleopimaric acid

Maleopimaric acid is the main chemical component of the commercial resin Ennesin MU4.

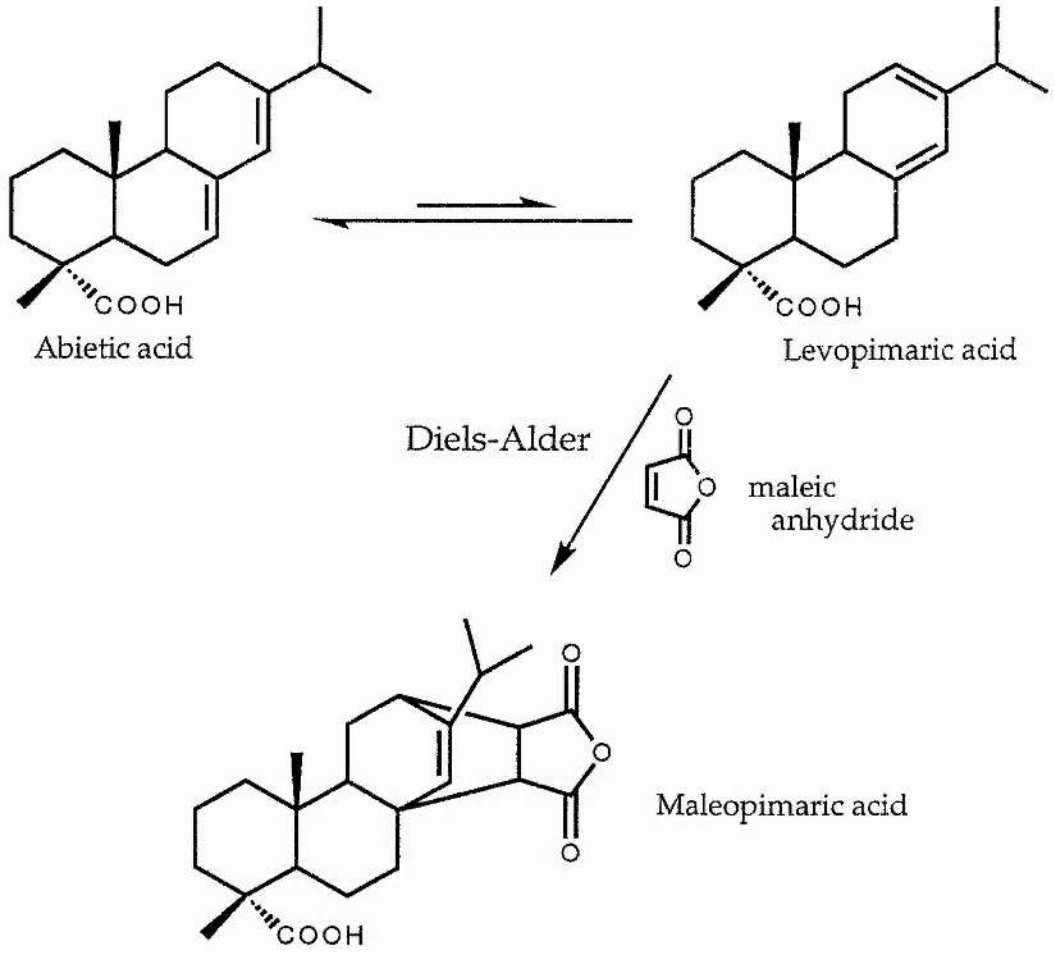


Fig. 2.4 Synthesis of maleopimaric acid by a Diels-Alder reaction.

Maleopimaric acid is the condensation product of the reaction between levopimaric acid, an isomerisation product of abietic acid, and maleic anhydride by a

Diels-Alder type reaction (Figure 2.4). ^{13}C NMR data for the adduct and configuration of the molecule have been reported in the literature survey[4], and further structural information is reported[9,10,11,12].

It has been reported[9,10] that abietic acid only forms addition products with maleic anhydride at temperatures over 100°C. Elevated temperatures serve to isomerise the abietic acid to the diene, levopimaric acid, in trace quantities. The trace of levopimaric acid reacts with maleic anhydride to displace the equilibrium, until eventually all of the abietic acid has been converted to the Diels-Alder adduct.

The isopropyl bearing ring in levopimaric acid is skewed in such a way that the β face is shielded by the methyl group at C-10, while the α face is free for attack by the dienophile. This would indicate a back-side approach by the dienophile in the Diels-Alder reaction.

Generally, in Diels-Alder reactions, the original geometry in the dienophile is retained. When a cyclic diene and a dienophile are allowed to react via the Diels-Alder reaction, the *endo* isomer is generally favoured. The anhydride moiety of maleopimaric acid has been shown[11] to be *cis* to the double bond. It has been confirmed[12] that the anhydride group is in the *endo* position, as represented in Figure 2.5. It should also be noted that the carbonyls in the anhydride ring shown are orientated differently; one is close to the isopropyl group and the other is remote.

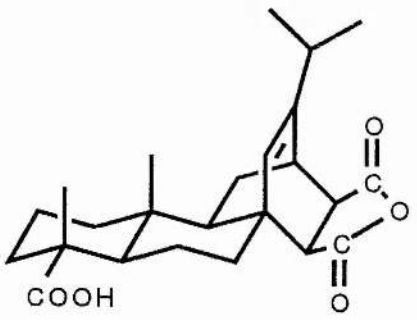
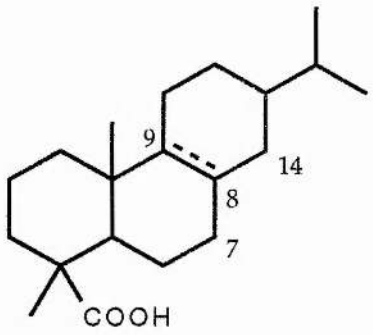


Fig. 2.5 Major isomer of maleopimaric acid.

2.5.5 Dihydroabietic acid

Dihydroabietic acid is the main chemical component of the commercial resin Staybelite.



- - - probable position of double bond

Fig. 2.6 Dihydroabietic acid.

Dihydroabietic acid (Figure 2.6) is a product of the partial hydrogenation of abietic acid. The process of hydrogenation, however, leads to isomerisation of the double bond, and it is uncertain where the double bond resides. The double bond will be in one of three positions: from C-8 to either C-7, C-9 or C-14. It is thought most likely to reside between C-8 and C-9, although a mixture is probable in which this structure is the main component.

The solution NMR of Staybelite resin seems to confirm the presence of a mixture, because of the many lines present in the spectrum compared to what we would expect from a pure sample.

No NMR or crystal data for dihydroabietic acid have been reported to my knowledge, which makes assignment of ^{13}C NMR signals very difficult.

2.6 Nuclear Magnetic Resonance (NMR)

Atomic nuclei observable by NMR have a nuclear spin quantum number (I) which makes them behave in a similar way to tiny bar magnets when subjected to a magnetic field, B_0. The magnetic moments of each nucleus can align themselves in (2I+1) ways. ^1H and ^{13}C both have I=1/2, so they can align themselves in one of two ways; in the direction of the magnetic field (low energy state), or against the direction of the field (high energy state). The precessional frequency of the nuclei in the external field is ω_0 (the Larmor frequency) and is directly proportional to the strength of the external field, B_0:

$$\omega_0 = \gamma B_0$$

where, B_0= strength of external field

γ= magnetogyric ratio (constant for a given nucleus)

The vector sums of the millions of nuclear magnets give rise to a net nuclear magnetisation parallel to the magnetic field (Figure 2.7).

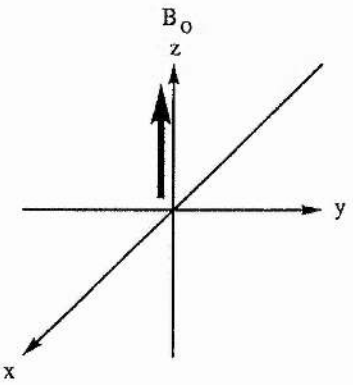


Fig. 2.7 Nuclear magnetisation parallel to B_0.

A powerful radiofrequency (RF) pulse is then applied close to the Larmor frequency, the effect being to excite some of the nuclei. The RF pulse serves to generate an electromagnetic field along the x-axis and to tip the magnetisation towards the xy plane. The magnetisation now precesses in the xy plane at the Larmor frequency.

However, the excited nuclei lose their extra energy and relax back along the z-axis. A receiver coil picks up the resultant oscillation of magnetisation in the xy plane during what is called the acquisition period, and gives a complicated wave pattern called the free induction decay (FID). The FID contains frequency information about all of the nuclear spins. The FID is converted into a frequency spectrum by Fourier transform, which is a mathematical conversion of the interference pattern.

Our analysis involves gathering information on the compounds by ^{13}C NMR spectroscopy in the solid state. Historically, huge problems have had to be overcome to make these techniques more common in the modern laboratory.

2.6.1 Carbon-13 NMR

Carbon-13 NMR has several advantages over proton NMR in terms of its power to elucidate organic structures[13]. First, ^{13}C NMR provides information about the backbone of the molecule rather than the periphery. In addition, the chemical shift range for ^{13}C in a number of compounds is about 200ppm, compared with only up to about 15ppm for ^{1}H; less overlap of peaks is the consequence. Because the natural abundance of ^{13}C is only about 1.1%, spin-spin coupling between carbon nuclei does not occur since chances of having two ^{13}C adjacent in the same molecule are negligible, and ^{13}C-^{12}C coupling does not occur because I=0 for ^{12}C. Finally, good methods exist for decoupling the interaction between ^{13}C and ^{1}H, giving carbon spectra consisting of only single lines.

Analysis of the ^{1}H nucleus is relatively easy because of its high abundance (99.98%) and high sensitivity. Carbon-13 accounts for only 1.1% of carbon nuclei,

and the small magnetogyric ratio, which is about 0.25 that of the proton, combine to make ^{13}C NMR about 6000 times less sensitive than ^{1}H NMR.

The most important developments in ^{13}C signal enhancement include high field strength magnets, Fourier transform instruments, and ^{1}H decoupling by double resonance techniques. Without these developments, the method would be restricted to the study of highly soluble low-molecular weight solids, neat liquids and isotopically enriched compounds.

2.6.2 Solid-state C-13 NMR[14]

NMR of solid materials is still a less popular spectroscopic technique than high resolution solution NMR. It is interesting to note that the very first NMR experiments were carried out on both liquids and solids, in fact the first ^{1}H observation was on paraffin wax. However, it soon became evident that conventional high resolution techniques were not possible for solids.

The main difference between the liquid and solid-state is the timescale involved and the geometry of the molecular motions. These affect the signal by modulating interactions between the spins and their environment. There are three principal reasons why high resolution spectra are difficult to achieve for solids:

i) dipolar couplings. Heteronuclear dipolar couplings between ^{13}C and ^{1}H, which are of the order of a few kHz, produce severe line broadening because they are dependent on the angle between the ^{1}H-^{13}C vector and the magnetic field. Whilst isotropic tumbling averages out these interactions in solution, this cannot happen in a normal solid. Strong homonuclear dipolar couplings between ^{13}C spins can be neglected due to the low natural abundance of ^{13}C (~1.1%). In such diluted spin systems the heteronuclear dipolar interactions between ^{1}H and ^{13}C are dominant.

ii) chemical shift anisotropy (CSA). The orientation dependent magnetic shielding of the nuclear spins, which give rise to the CSA, typically lead to a broadening of the ^{13}C resonance of about 10kHz at a magnetic field of 4Tesla. Different molecular orientations give rise to many lines for each resonance on the NMR spectrum, which

is observed as severe line broadening. Rapid molecular motion for solutions again averages out the effect to zero.

iii) long spin-lattice relaxation times (T_1) for C-13. Molecular motions in solids are reduced when compared to liquids and so the dipolar relaxation produced as a result of molecular tumbling in liquids is virtually absent.

The dependence of ^{13}C NMR spectra on the distribution of orientations, as well as on the slow motions of the molecules, provides the main applications of NMR spectroscopy. It is useful to investigate samples in the solid-state since their physical properties are of more interest than their chemical structure. In addition, the chemical structure can be analysed using "liquid-like" solid-state NMR spectra which can be generated by special experimental techniques.

Difficulties posed by reduced molecular motions in solids can be overcome by ^1H high power decoupling, and the techniques collectively known as CP/MAS NMR (cross-polarisation magic angle spinning).

2.6.2.1 CP (cross-polarisation)

The strong magnetic moment and high abundance of the ^1H nucleus can be utilised to enhance the signal intensity of the ^{13}C spins. Utilisation of this technique to observe ^{13}C is called cross-polarisation.

A 90° ^1H pulse is first applied along the x'-axis. The phase of the ^1H transmitter is then shifted 90° along the y'-axis to spin lock the ^1H magnetisation, and the ^{13}C transmitter is turned on so that both RF fields meet the Hartman-Hahn condition:

$$\gamma_C B_{1C} = \gamma_H B_{1H}$$

Under these conditions, the magnetisation from the large ^1H reservoir is transferred into the ^{13}C spin system.

After use of the dipolar couplings between ^{1}H and ^{13}C for cross-polarisation, the couplings become a nuisance as they give rise to line broadening. The broadening can be removed by applying a particularly intense dipolar decoupling (DD) field (typically 100W) on the ^{1}H channel during acquisition of the ^{13}C signal, for which a specially designed probe is essential. However, the signals are still broadened by chemical shift anisotropy.

2.6.2.2 MAS (magic angle spinning)

The chemical shift anisotropy broadening, and also the dipolar coupling, are proportional to $(3\cos^2\theta-1)$ where θ is the angle between the magnetic field and the solid sample. This term vanishes at 54.7°, the "magic angle", where the sample is observed to imitate the motions of the molecules in a liquid.

$$\text{i.e. when } (3\cos^2\theta-1) = 0$$

$$\theta = 54°44' \qquad (54.7°)$$

If the entire sample is mechanically rotated at this angle with a frequency higher than the chemical shift anisotropy, then the CSA vanishes from the spectrum. At lower spinning speeds a series of spinning sidebands, whose intensity is similar to the CSA pattern, is observed.

For MAS, the solid sample is placed inside a small turbine called a rotor which is air-borne and driven by a stream of gas. This limits the speed of rotation to typically 10kHz, although nowadays supersonic turbines and probes are available. The spectrum consists of centre bands and sidebands which occur at multiples of the spinning frequency. These sidebands can be removed either by higher spinning speeds or by a total suppression of spinning sidebands (TOSS) pulse sequence.

When combining these techniques, the acquisition of high resolution ^{13}C spectra for solids is now made possible.

The following diagram (Figure 2.8) makes clear the effect each of these techniques has in improving the resolution of ^{13}C spectra obtained in the solid-state:

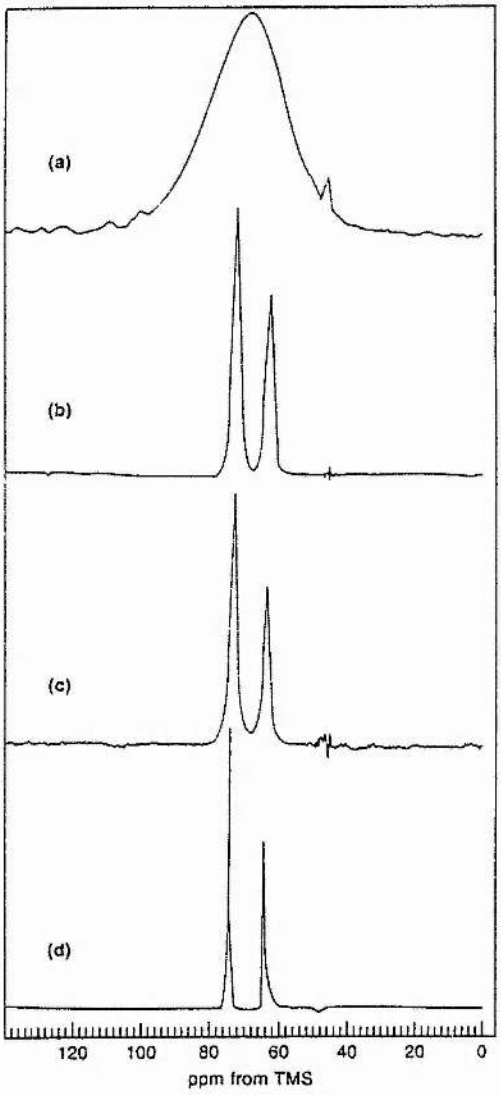


Fig. 2.8 Carbon-13 spectra of crystalline adamantane:

a) nonspinning and no proton decoupling,

b) nonspinning with dipolar decoupling and CP,

c) with MAS but no dipolar decoupling or CP,

d) with MAS, dipolar decoupling and CP.

Figure 2.8 reproduced from *Principles of Instrumental Analysis*, D. A. Skoog and J. J. Leary, (1992).

2.7 **Powder X-ray diffraction (XRD)**

X-ray diffraction is a technique which can be used to solve crystal structures and conformations of crystalline solids. Although this is normally achieved through analysis of single crystals. Which have well defined crystal domains. it is also possible when analysing crystalline powders, which have many crystals at random orientations. The information gained. namely scattering angle, 2θ, and scattering intensity, is processed in a complex but methodical manner to obtain well defined crystal parameters.

However, our study is not interested in solving crystal structures. Instead, we are to consider the diffractograms obtained as "fingerprints", with characteristic patterns of peaks for each pigment and resin sample. Since we are looking for some indication of a chemical interaction taking place during resination of the pigment, we are to compare the diffractograms obtained for the pigment and the resin acid with the resultant diffraction pattern for the resinated pigment.

If new peaks are seen to emerge or initially peaks are totally diminished in the diffractogram of the resinated sample, then this would presumably indicate the presence of a new species in the sample, and not just the starting pigment and resin acid. If all the peaks in the diffractogram of the resinated pigment can be ascribed to either the starting pigment or resin acid, or both, then this could indicate that chemical interaction during resination has not taken place.

Information on crystallinity, or degree of order, in the pigment crystals can also be obtained from the diffractograms. Increased crystallinity is inferred when the diffraction pattern for a pigment sample is sharper and better resolved when compared with the pattern for a similar sample.

2.8 **Proposed chemistry**

The synthesis of ^{13}C labelled resins would be most attractive for studying the interaction between pigments and resins. This would allow ready observation by solid-state ^{13}C NMR of particular atoms in the resin coating the pigment. at reasonably low concentrations, and could also facilitate relaxation time measurements to probe motions of the resin molecules in the resinated pigment.

2.8.1 The Barton reaction

It would be desirable to label the carboxylic carbon of abietic acid with ^{13}C because of its distinctive chemical shift. If the ^{12}C carboxylic acid group could be converted to the bromide, then the labelled carboxylic acid could be obtained *via* the Grignard and $^{13}CO_2$ (from ^{13}C labelled barium carbonate of which we have a supply).

The traditional method of generating the bromide from the acid is by the Hunsdiecker reaction, seen in Figure 2.9, where the silver salt of the acid is heated with bromine in CCl_4 to facilitate a radical reaction.

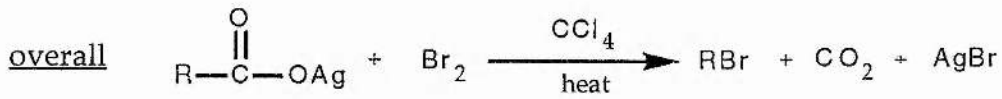
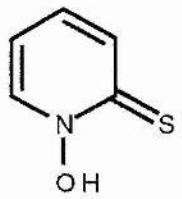
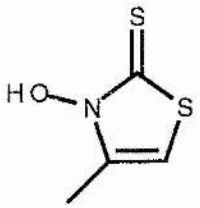


Fig. 2.9 The Hunsdieker reaction.

Labelling by this method is difficult, however, but is thought to be readily achieved by use of the Barton reaction followed by a Grignard and $^{13}CO_2$. Both Leo Paquette (leading American synthetic chemist) and John Walton (our internal expert on radical reactions) believed this route would work.

The Barton reaction is a very versatile reaction involving a radical mechanism and is driven by aromatisation of the starting reagent. Many variants of the starting reagent have been used, and two are shown in Figure 2.10.





N-hydroxypyridine-2-thione 3-hydroxy-4-methylthiazole-2-(3H)-thione

Fig. 2.10 Two possible reagents for Barton reaction.

Paquette carried out an investigation[15] of several bromodecarboxylation options for the conversion of cycloalkanones to vinyl bromides. The most reliable and effective intermediate found was the thiohydroxamic ester (Figure 2.11), from the thiazole reagent above.

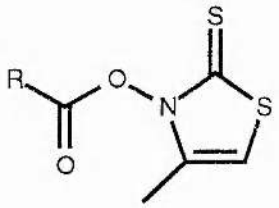


Fig. 2.11 Thiohydroxamic ester intermediete.

It is reported by Barton[16] that carboxylic acid esters derived from *N*-hydroxypyridine-2-thione react with bromotrichloromethane in a radical chain reaction to give the corresponding nor-alkyl bromides in high yield. It is reported that high yields of primary, secondary and tertiary bromides can be obtained in a reaction which tolerates ester and ketonic functionality.

A general scheme for the reaction is outlined in Figure 2.12.

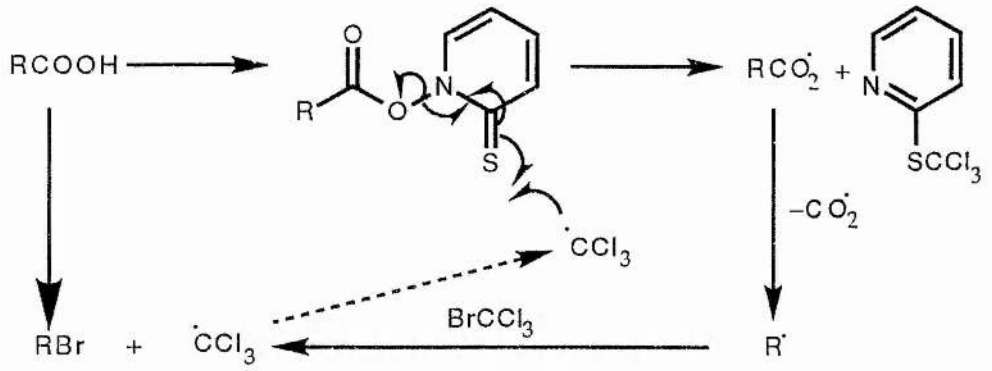


Fig. 2.12 General scheme for the Barton reaction.

2.8.2 A model reaction system - cyclohexanone

In order to check the feasibility of this chemistry, it was proposed to employ a model reaction system, using cyclohexanone to generate a quaternary carbon centre with both bromine and methyl substituents, as required for abietic acid. The model scheme is given in Figure 2.13.

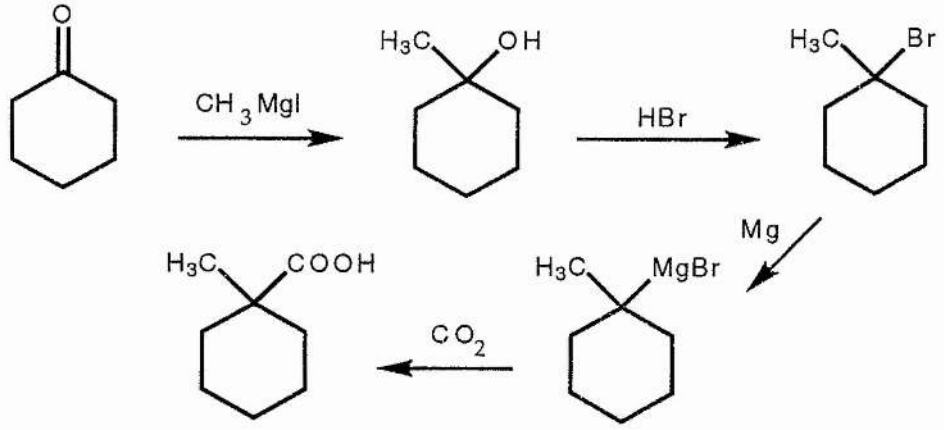


Fig. 2.13 Reaction scheme for model compound.

The tertiary bromide, mimicking the bromide formed from abietic acid after the Barton reaction, may then be used to generate the Grignard reagent when reacted with magnesium. The tertiary carboxylic acid could then be formed by reaction of the Grignard reagent with CO_2. Labelled CO_2 could be used to form the labelled carboxylic acid.

3 DISCUSSION

3.1 The model reaction system

A scheme for the model reaction system is outlined in Figure 2.13.

The Grignard reagent in the first step was formed from methyl iodide and magnesium and was used immediately to make the tertiary alcohol from previously distilled cyclohexanone. An acid work-up allowed isolation of the alcohol. Purification by distillation yielded a colourless product which freezes at around room temperature.

Preparation of the bromide was accomplished by the straightforward addition of hydrobromic acid to facilitate bromination, with water as a by-product. Purification by distillation gave the tertiary bromide, a clear colourless liquid.

The next two steps were combined in one reaction. A Grignard reagent was prepared from the bromide and magnesium, and several attempts were made to form the carboxylic acid with CO_2. Initially the Grignard was poured onto an excess of solid carbon dioxide, but the isolated product was not the desired acid, as confirmed by spectroscopic means (IR and ^1H NMR). Gutt reported[17] a similar reaction and stated very poor yields, with substantial amounts of methylcyclohexane, methylenecyclohexane and 1-methylcyclohexene formed (Figure 3.1).

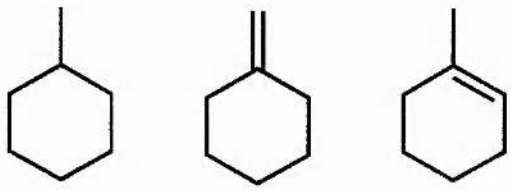


Fig. 3.1 Products of the model reaction.

After scrutiny of the ^1H NMR spectra of the product mixture, all three species were positively identified. Further experiments were carried out using gaseous CO_2 bubbled through the Grignard solution, since $^{13}CO_2$ generated from the labelled

barium carbonate would be most conveniently delivered in this way. However these experiments and other variations with solvents (various quantities of ether and THF) proved unsuccessful. This may be due to the tertiary nature of the intended carboxylic acid, but carboxylation of modified abietic acid would be even more difficult due to the additional steric hindrance encountered from substituents of the adjoining ring.

The desired acid was made, however, following a method by Haaf[18] (Figure 3.2). Acid treatment of methylcyclohexanol gives a cationic intermediate which rearranges to give a more stable species which yields the acid on addition of formic acid.

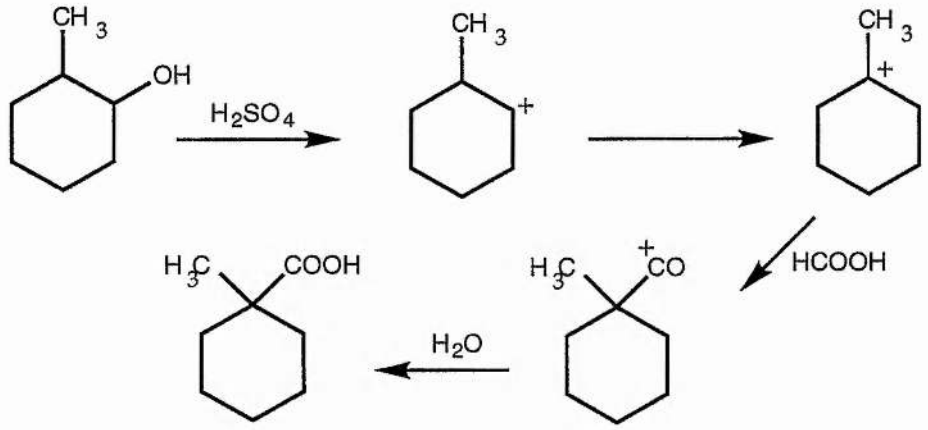


Fig. 3.2 Alternative synthesis of model compound.

This in itself is not a useful means of introducing a ^{13}C label, since the carboxylic acid carbon in the product is incorporated from the formic acid, but it was thought the acid could be used as a substrate for a trial Barton reaction. However, since the final stage does not yield the desired model acid, this route is not worth pursuing further.

An alternative route, though not studied here, could be by introduction of a bromide by a Barton reaction, as initially intended, followed by reaction with a ^{13}C labelled cyanide and subsequent hydrolysis of the nitrile to the labelled carboxylic acid.

3.2 **Resinations of Pigment Yellow 13**

Next, it was necessary to consider the resin acids and their application in coating pigments. The pigment to be used throughout this study was Pigment Yellow 13 (P.Y. 13), which was one of the pigments prepared and studied by Ken Cameron during his MSc.

3.2.1 Synthesis of Pigment Yellow 13

While at Paisley sufficient P.Y.13 aqueous slurry was prepared, as described in the Experimental Section, for a series of resination experiments.

The synthesis (Figure3.3) involved the controlled coupling of DCB tetrazo with 2 equivalents of the amide coupling component, AAMX. The formation of the yellow pigment was observed immediately upon addition of the DCB tetrazo.

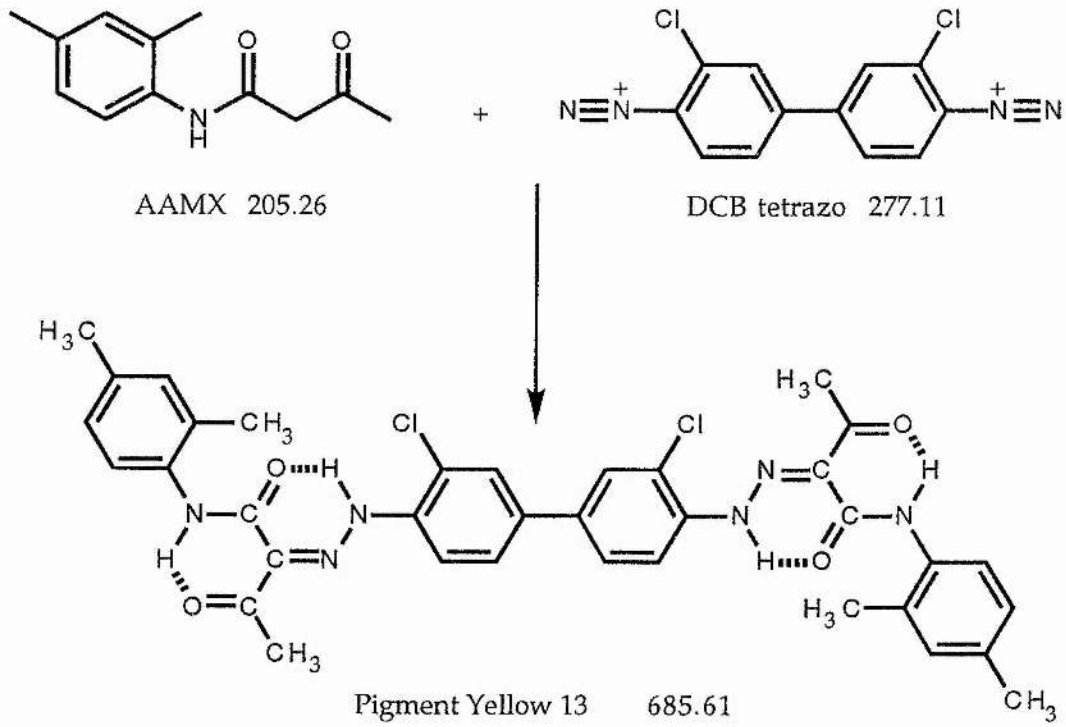


Fig. 3.3 Synthesis of Pigment Yellow 13.

AAMX = acetoacet-*m*-xylidine

DCB tetrazo = 3,3'-dichlorobenzidine tetrazo

The Pigment Yellow 13 was stored, for use in the resinations, as an aqueous slurry at pH6.0.

3.2.2 Resination procedure

Resinations of Pigment Yellow 13 were carried out using incremental amounts of each resin acid i.e. abietic acid, Ennesin MU4 and Staybelite. It was proposed to apply 10%, 20%, 30% and 40% by weight of resin acid in each case, with respect to P.Y.13 weight.

A general procedure for the resinations is given in the Experimental Section.

The P.Y.13 aqueous slurry is adjusted to pH10 before adding the resin solution, to maintain the resin in solution. After raising the temperature to 95°C, the pH is adjusted to 7.0 to precipitate the resin. Stirring is continued at 90-95°C for 30 minutes; the "heat treatment". After cooling to 70°C, the resinated product is filtered, washed with water and dried at 70°C overnight.

The yields of the resinated pigments are reported in Table 3.1. Each resinated pigment sample was analysed at Paisley for total resin content, and the results of these analyses can be seen in Table 3.2.

A sample of P.Y.13 was isolated in the absence of any resin, as a standard.

3.2.3 Results of resination experiments

Table 3.1 Yields of resinated P.Y.13 samples

% Resin added	YIELDS (g) Abietic acid	Ennesin MU4	Staybelite
10%	10.04	9.84	10.57
20%	10.74	10.00	8.27*
30%	11.65	10.05	12.21
40%	11.86	10.06	13.23

* physical losses!

Table 3.2 Resin contents of resinated P.Y.13 samples

% Resin added	% RESIN Abietic acid	Ennesin MU4	Staybelite
10%	6.9	1.6	7.7
20%	11.7	2.1	15.3
30%	19.9	2.8	20.1
40%	24.5	3.3	26.0

During the resinations, the resin acids were dissolved in alkali, and so were in solution as the sodium salt. The P.Y.13 resinated with maleopimaric acid (Ennesin MU4 resin) would seem to retain little of the acid during the resination procedure. During the resination procedure, exposure to alkali would presumably cause ring opening of the anhydride moiety (Figure 3.4), resulting in the modified tri-acid being washed away by the water. Throughout this study, it was noted that the pH of the prepared resin solution was often higher than 12, which is a harsh environment for these acid anhydrides.

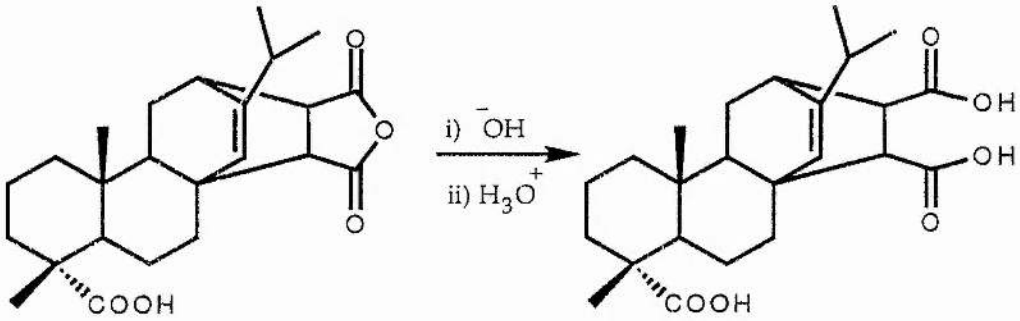


Fig. 3.4 Base induced anhydride ring opening.

3.3 C-13 labelling experiments

The failure of the initial approach suggested that alternative ways of introducing ^{13}C labels to the resin acids should be examined. There are two ways which would seem appropriate:

i) the use of labelled maleic anhydride as a dienophile for the Diels-Alder reaction with isomerised abietic acid,

ii) the use of labelled Diazald to provide a ^{13}C labelled methylene group for esterification of carboxyl groups.

First, we need to look at the possibility of reacting abietic acid and maleic anhydride to form maleopimaric acid, with a view to using ^{13}C labelled maleic anhydride.

3.3.1 Diels-Alder reaction of abietic acid with maleic anhydride

Isomerisation of abietic acid to levopimaric acid is necessary to provide a suitable diene for the Diels-Alder reaction with maleic anhydride. The use of heat or acid is required for this isomerisation. It has already been mentioned that the resin acids isomerise at temperatures approaching their melting points[10]. It was therefore decided to perform the reaction (Figure 3.5) at raised temperatures to achieve a molten reaction mixture where solvents are not a concern.

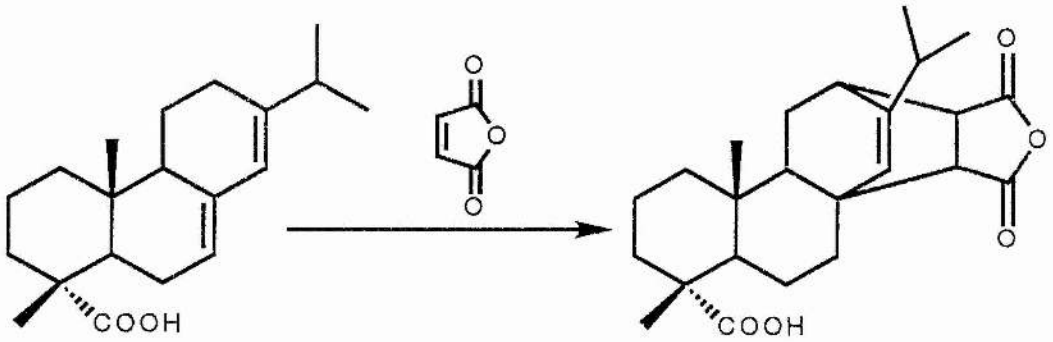


Fig. 3.5 Diels-Alder reaction of abietic with maleic andydride.

Levopimaric acid is known to be formed in only trace quantities from isomerisation of abietic acid[9,10], but the continual reaction of this diene with maleic anhydride drives the reaction to completion. It was initially unknown how long was necessary for complete reaction, so a series of test-tube reactions were set up at 150°C and taken off sequentially each hour. Traces of impurities were still present after 2 hours by solution ^{13}C NMR, but reaction was clean after this. Samples of maleopimaric acid were then prepared optimally at ~160°C for 2.5 hours with 1.1 equivalents of maleic anhydride. Yields were consistently around 85-95%, and it was observed that at temperatures of ~170°C the maleic anhydride was observed to sublime to some extent.

A temperature of ~160°C is sufficient to achieve a molten reaction mixture and the product is a glassy amber coloured solid when allowed to cool. After dissolving in ether, washing with water and evaporating the ether, a crispy off-white solid is

obtained. Acetic acid seemed to be the only suitable solvent for recrystallisation but is not desirable. A preferred recrystallisation from toluene/n-heptane was reported[4], but was found to be unsatisfactory.

It was then agreed with Ciba-Geigy to purchase two 250mg samples of ^{13}C labelled maleic anhydride (Figure 3.6).

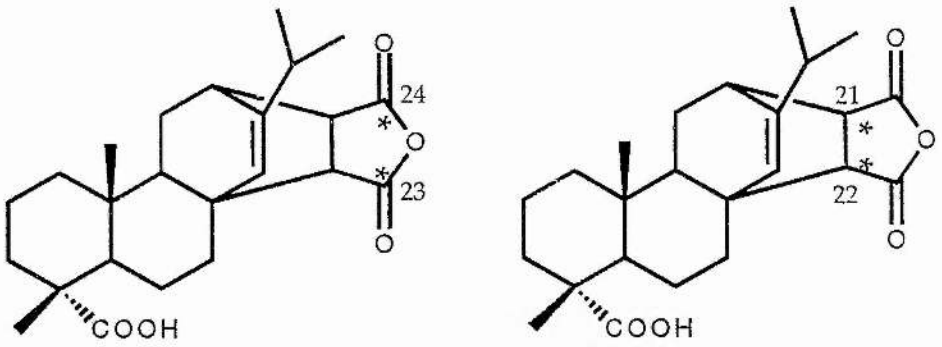
1,4-$^{13}C_2$ 2,3-$^{13}C_2$

Fig. 3.6 C-13 labelled maleic anhydride.

It was considered sufficient to apply the label at 10% loading i.e. applied along with 90% normal maleic anhydride. The labelled maleopimaric acids (Figure 3.7) were prepared at ~160°C for 2.5 hours in expected yield. Solution ^{13}C NMR showed enhanced signals for the relevant carbon frequencies. 'Triplets' were observed for both cases due to coupling.

For 1,4-$^{13}C_2$ maleic anhydride, the resonances enhanced for the subsequent adduct are 172.6 and 170.9ppm for C-23 and C-24 respectively.

For 2,3-$^{13}C_2$ maleic anhydride, the resonances enhanced for the subsequent adduct are 45.6 and 53.0ppm for C-21 and C-22 respectively.



23,24-$^{13}C_2$ 21,22-$^{13}C_2$

Fig. 3.7 C-13 labelled maleopimaric acids.

These prepared ^{13}C labelled maleopimaric acids were then used in resination experiments to coat P.Y.13. These were carried out as described earlier, but on one-tenth scale. 10 and 20% loadings were prepared for each label. Unfortunately. we now know that little of this adduct is retained during resination and this was confirmed when yields of the resinated pigment products were similar to the weight of the starting pigment.

The problem of retention of the maleopimaric during resination needs to be addressed, or an alternative approach is needed.

3.3.2 Use of *N*-methylmaleimide as the dienophile

Since the maleic anhydride moiety of Ennesin MU4 resin ring opens during the caustic dissolution prior to resination, an alternative approach would be to use an analogue more resistant to alkaline hydrolysis. A suitable compound to try may be maleimide, or an *N*-alkylated maleimide to confer stability on the system. *N*-Methylmaleimide (Figure 3.8) would appear to be a good target compound since it is more stable to ring opening than maleimide itself, and is more suitable than *N*-phenylmaleimide, for example, since molecular packing in the crystal will not be significantly disrupted when compared with the maleic anhydride adduct.

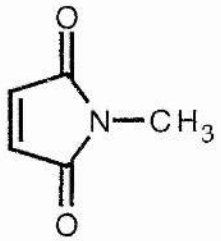


Fig. 3.8 *N*-Methylmaleimide.

In order to incorporate a label, it would be necessary to utilise labelled maleic anhydride in a reaction with methylamine to form the subsequent *N*-methylmaleimide (Figure 3.9). The first step involves reaction of maleic anhydride with methylamine to yield the maleic acid monomethylamide, a method for which is reported[19].

The second stage involves loss of water to allow ring closure of the amide to yield the *N*-methylmaleimide. Two methods for this reaction have been reported. The first method[20] reacts the maleic acid monomethylamide with acetic anhydride and sodium acetate at 100°C for 1 hour. An alternative method[21] merely heats the amide to 160°C, to drive off water and allow ring closure.

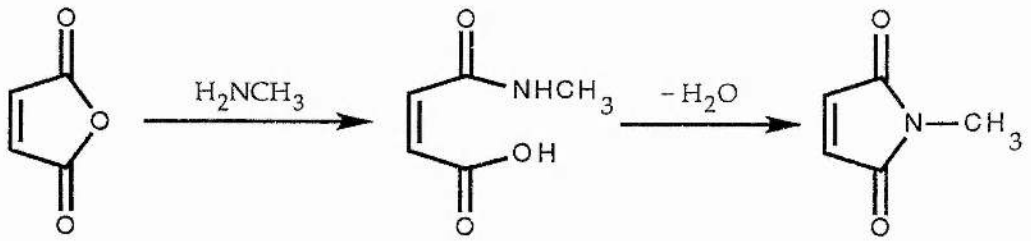


Fig. 3.9 Synthesis of *N*-methylmaleimide from maleic anhydride.

Formation of the maleic acid monomethylamide was carried out by reacting maleic anhydride in ether with 1.5 equivalents of ethanolic methylamine solution. Initially this reaction was cooled in an ice-water bath, but the maleic anhydride was observed to come out of ether solution. Later reactions were carried out at room temperature, where solution was maintained until the methylamine was added. An off-white precipitate was formed immediately upon addition of the methylamine.

Precipitation was promoted by stirring with ice-water cooling, before filtering the product. Two solvents were used for recrystallisation; ethanol yielded a white crystalline product in 30.6% yield, and acetone yielded a similar product in 11.5% yield. The acetone solution which this product was isolated from quickly degraded to a deep brown colour.

Reaction of the amino acid with sodium acetate and acetic anhydride at 100°C was found to be very inefficient. During distillation of the organic mixture, a clear liquid product was collected which proved to be acetic anhydride. However, a crystalline solid was observed to form in the arm of the Vigreux distillation flask, and was collected. This product, which had a characteristic sharp irritating odour, proved to be *N*-methylmaleimide by NMR.

Reaction of the amino acid at 160°C for 2 hours yielded a brown residue in the bottom of the test-tube. A crystalline deposit was collected separately from near the mouth of the test-tube, and had the same characteristic odour as before. Conversion to *N*-methylmaleimide was poor at 8.7%.

The yields of these reactions needed to be optimised, especially since labelled maleic anhydride is proposed to be used. In the meantime, the formation of the adduct from isomerised abietic acid and *N*-methylmaleimide (Figure 3.10) needed to be assessed.

We had hoped that the reaction would be as efficient as the corresponding formation of maleopimaric acid discussed earlier.

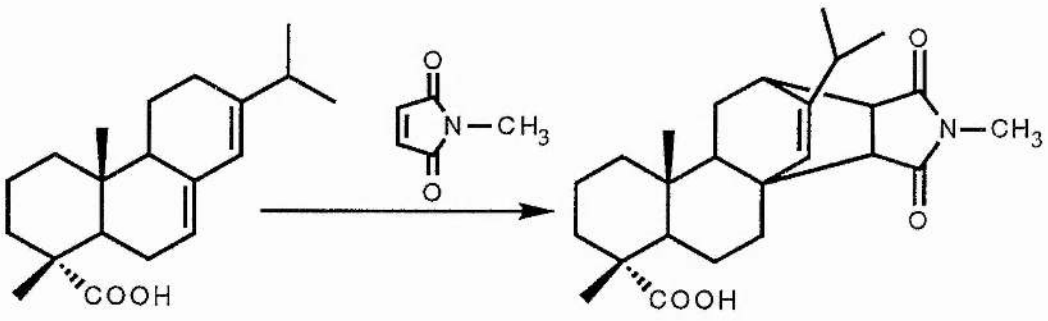


Fig. 3.10 Diels-Alder reaction of abietic acid with *N*-methylmaleimide.

Abietic acid and 1.1 equivalents of *N*-methylmaleimide were reacted at 160°C in a quickfit test-tube for 2 hours. The resultant glassy residue did not dissolve in ether, so the precipitate was filtered and dried under vacuum. ^{13}C NMR of the precipitate showed many more peaks than expected. Since peaks corresponding to abietic acid were not present, they were probably due to decomposition products, even though there may have been an insignificant conversion to the adduct.

Subsequent attempts to form the adduct were hindered to some extent by the evaporation of the *N*-methylmaleimide at elevated temperatures. Reacted residues which were obtained were analysed and the NMR spectra were highly complex, indicating a mixture of components, as suggested previously.

The formation of the *N*-methylmaleimide proved to be more difficult than expected. Because of the poor conversions of the two reactions to form the *N*-methylmaleimide and the apparent decomposition during attempts to form the adduct, this route is seen as an unsuitable means of introducing a label.

An alternative possibility is the use of a higher *N*-substituted maleimide, namely *N*-phenylmaleimide (Figure 3.11). The higher molecular weight should ensure it is less volatile at elevated temperatures, and remains in a molten state during reaction. However, molecular packing in the crystal may be affected by the introduction of a bulky phenyl group, and constraints on time meant this route could not be investigated further.

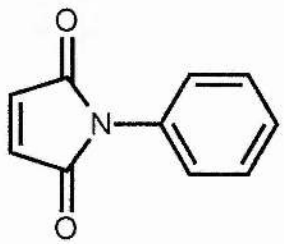


Fig. 3.11 *N*-Phenylmaleimide.

3.3.3 Diazald esterification

N-methyl-*N*-nitroso-*p*-toluenesulphonamide, otherwise known as Diazald, is the precursor to diazomethane, a useful reagent for the preparation of methyl esters. When Diazald is subjected to base, diazomethane is generated (Figure 3.12) and distilled across in ethereal solution ready for application to the carboxylic acid substrate.

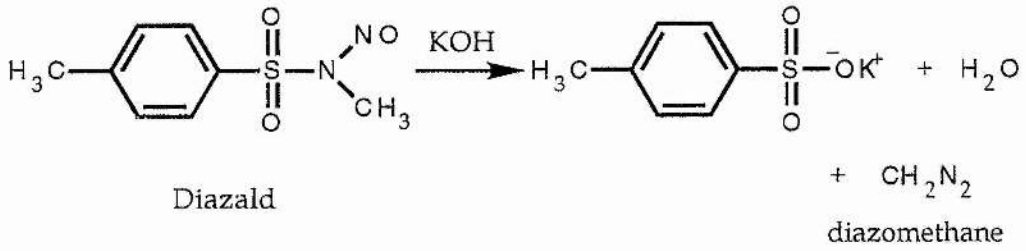


Fig. 3.12 Generation of diazomethane from Diazald.

It was proposed to use ^{13}C-labelled Diazald, which is obviously a source of a ^{13}C labelled methylene group, for the generation of ^{13}C labelled methyl esters. It was hoped that Diazald esterification would provide a useful route to an enhanced handle for ^{13}C NMR.

Attempts to incorporate a labelled ester into resin acid analogues, via diazomethane, concentrated on the study of Ennesin MU4 resin and abietic acid itself.

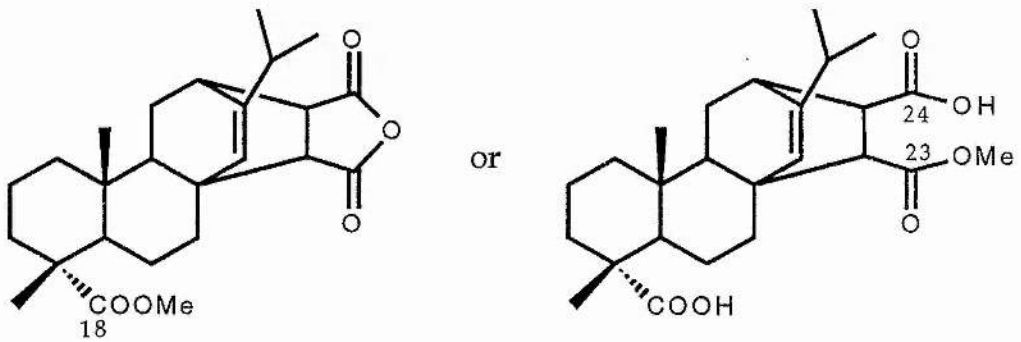


Fig. 3.13 Possible esterification products of Ennesin MU4.

Esterification of the Ennesin MU4 resin was expected to be complicated (Figure 3.13), since it is probably readily converted to the tri-acid in the presence of base. Esterification at C-18 alone depends on the anhydride moiety staying intact. However, esterification at C-23 or C-24 may be useful, or indeed esterification at a mixture of the three.

Esterification of Ennesin MU4 proved unsuccessful, with complex spectra and no evidence of a characteristic ester resonance by solution ^{13}C NMR. It is known that esterification of the tertiary carboxyl group at C-18 is difficult, due to steric hindrance, and requires elevated temperatures with other esterification reagents.

Esterification of abietic acid would appear to be a simpler proposition (Figure 3.14), but steric hindrance at C-18 is still a problem.

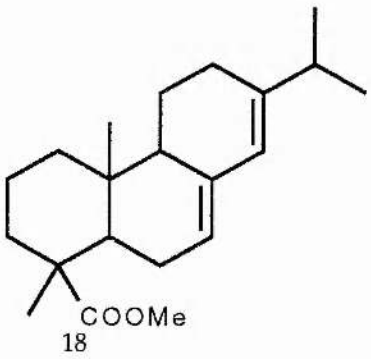


Fig. 3.14 Esterification of abietic acid.

Of course a consequence of esterification of abietic acid is the loss of the free acid for solubility in alkali. Also, the carboxylic acid group, which it is believed may take part in some chemical interaction with the pigment, would be modified, which is undesirable for the subsequent study. However, esterification of abietic acid may be followed by addition of maleic anhydride to form maleopimaric acid methyl ester with free acid potential for formation of the sodium salt.

Attempts were made to synthesise methyl abietate, but in each case ^{13}C solution NMR gave complex spectra with many lines, indicating a mixture of products, which

may only contain a very small amount of methyl abietate. if any. Column chromatography would have proved impractical with such a mixture.

Difficulty of esterification of the carboxyl group may again be explained by steric hindrance.

3.4 Investigation of the form of resin acids during resination

The form of each resin acid when it actually coats the pigment needed to be investigated. In order to evaluate this, each acid was subjected to the so called 'heat treatment' process, but in the absence of any P.Y.13. This involved adding the hot resin solution to water adjusted to pH10. The solution was then heated to 95°C at which point the pH was adjusted to 7.0 to precipitate the resin. The mixture was then stirred at 90-95°C for a further 30 minutes. After cooling, filtration. washing and drying each resin acid was isolated, presumably in the form which coats the pigment.

Solution ^{13}C NMR indicated that the abietic acid and Staybelite remained essentially unchanged after the process, while the maleopimaric acid underwent a marked change. Although the exact nature of this is not certain, some ring opening mechanism to the tri-acid seems inevitable. Recovery of this modified maleopimaric acid was difficult in any quantity.

Abietic acid and Staybelite resin which were isolated were unchanged chemically, by solution NMR, but were physically lumpy and off-white in appearance. They may be more amorphous than the initial acids when re-precipitated during the resination, but analyses by solid-state ^{13}C NMR and powder X-ray diffraction should prove conclusive.

4 SOLID-STATE NMR STUDIES

Solid-state ^{13}C NMR spectra were recorded on a Bruker 500MSL spectrometer, operating at 125.758MHz, utilising the CP/MAS (cross-polarisation magic angle spinning) technique to optimise ^{13}C spectra. The spectra were recorded at a spinning speed of ~7.5kHz unless otherwise stated, and a different spinning speed was used, where appropriate, to identify spinning sidebands. Spinning sidebands are denoted +.

4.1 Pigment Yellow 13

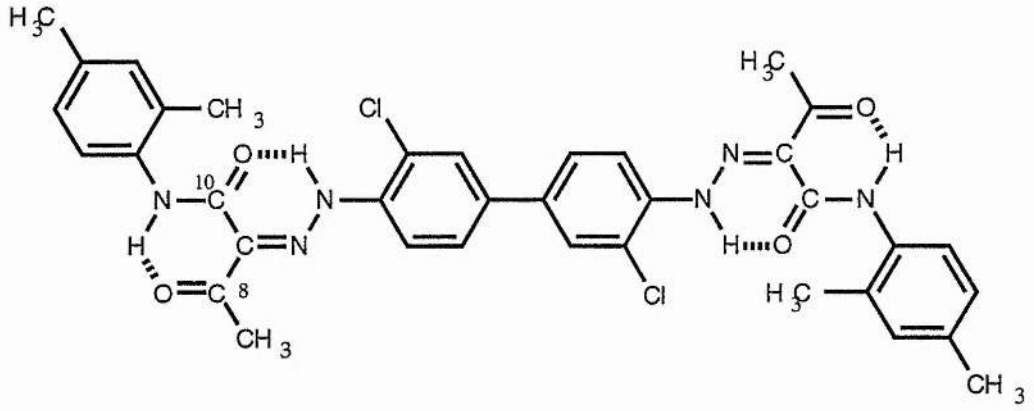


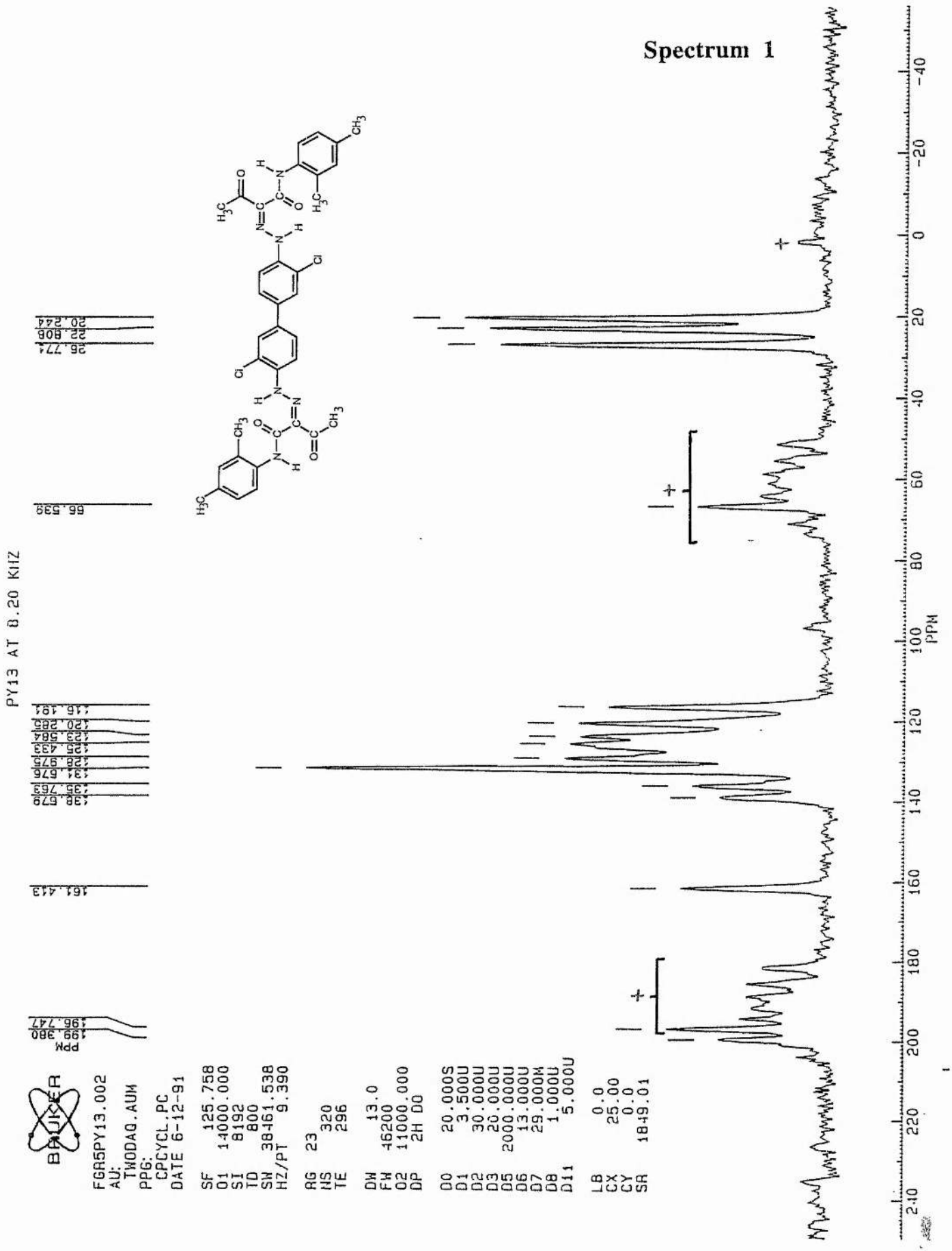
Fig. 4.1 Pigment Yellow 13.

Solid-state ^{13}C CP/MAS NMR spectra for Pigment Yellow 13 have been previously reported[1], as discussed in the literature survey.

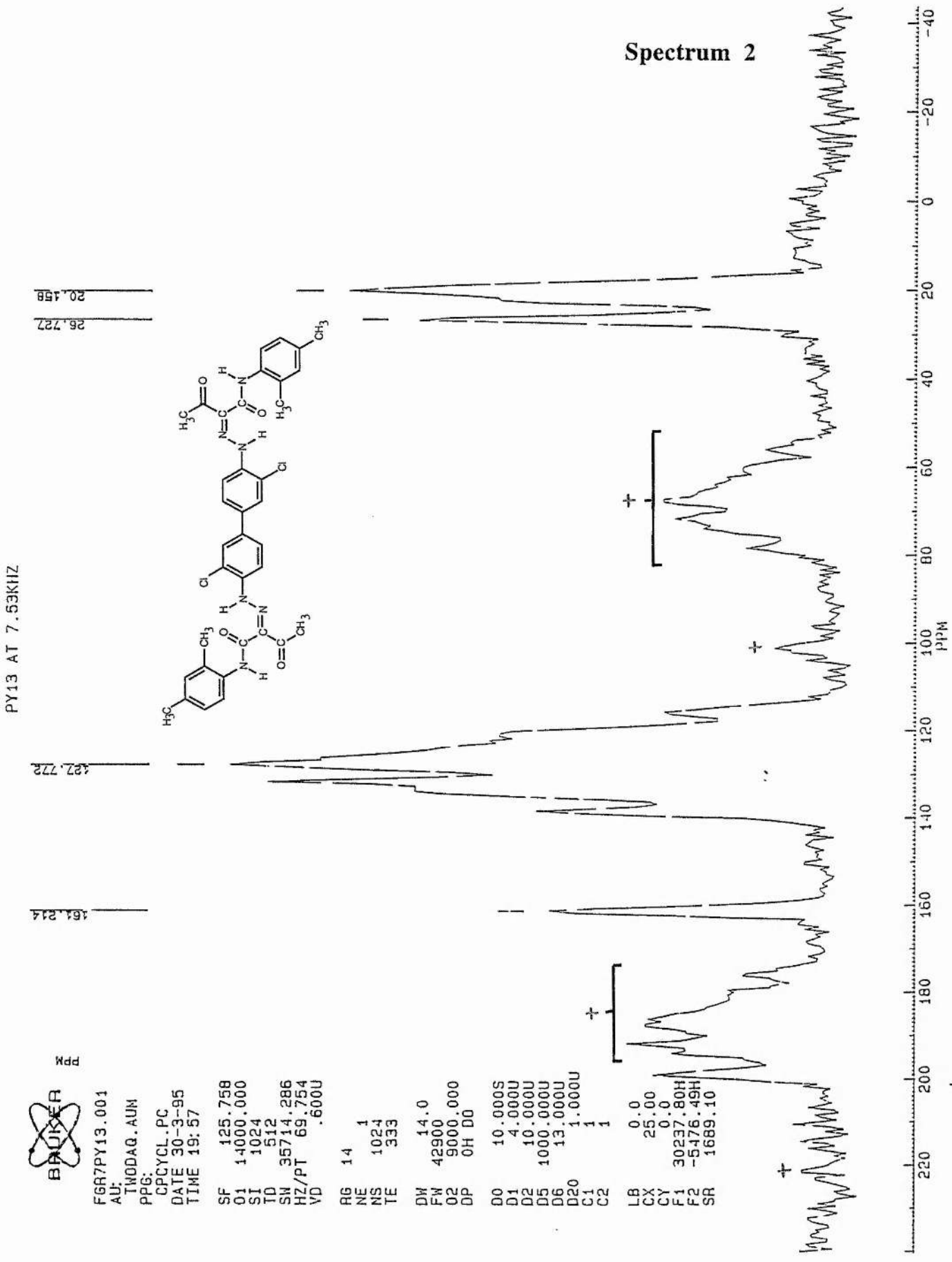
Spectrum 1 shows a sample of P.Y.13 synthesised previously within the group and recrystallised from 1,2,4-trichlorobenzene. The three methyl environments for P.Y.13 are well resolved between 20 and 27ppm. There is a broad region from 110 to 140ppm containing carbon resonances for cyclic parts of the molecule. Spinning sidebands are observed at equal frequencies either side of this region.

The C-10 carbonyl resonance is observed at 161.4ppm, and the other carbonyl resonance, for C-8, is at 199.4ppm but partially obscured by sidebands. The C=N resonance (126.7ppm) is obscured by the cyclic part of the spectrum.

Spectrum 1


PY13 AT 8.20 KHZ
FGR5PY13.002
AU: TWODAQ.AUM
PPG: CPCYCL.PC
DATE 6-12-91
SF 125.758
O1 14000.000
SI 8192
TD 800
SW 38461.538
HZ/PT 9.390
RG 23
NS 320
TE 296
DW 13.0
FW 46200
O2 11000.000
DP 2H D0
D0 20.000S
D1 3.500U
D2 30.000U
D3 20.000U
D5 2000.000U
D6 13.000U
D7 29.000M
D8 1.000U
D11 5.000U
LB 0.0
CX 25.00
CY 0.0
SR 1849.01
PPM
PPM

Spectrum 2


PY13 AT 7.53KHZ
20.158
26.727
127.722
161.214
PPM
FGR7PY13.001
AU: TWODAQ.AUM
PPG: CPCYCL.PC
DATE 30-3-95
TIME 19:57
SF 125.758
O1 14000.000
SI 1024
TD 512
SW 35714.286
HZ/PT 69.754
VD .600U
RG 14
NE 1
NS 1024
TE 333
DW 14.0
FW 42900
O2 9000.000
DP OH DO
DO 10.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 30237.80H
F2 -5476.49H
SR 1689.10

Spectrum 2 shows a sample of crude P.Y.13 isolated as a standard for the resinations (which has undergone the heat treatment in the absence of resin). The sample is more amorphous than the recrystallised sample, as can be seen from the broader lines throughout. The three methyl resonances are poorly resolved and appear as two broad peaks, one of which has a pronounced shoulder.

The heat treatment alone is known to promote increased crystal size, but it appears crystallinity is not enhanced.

4.2 **Abietic Acid**

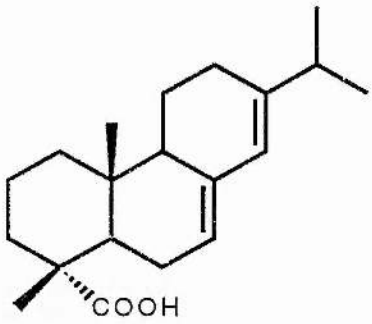


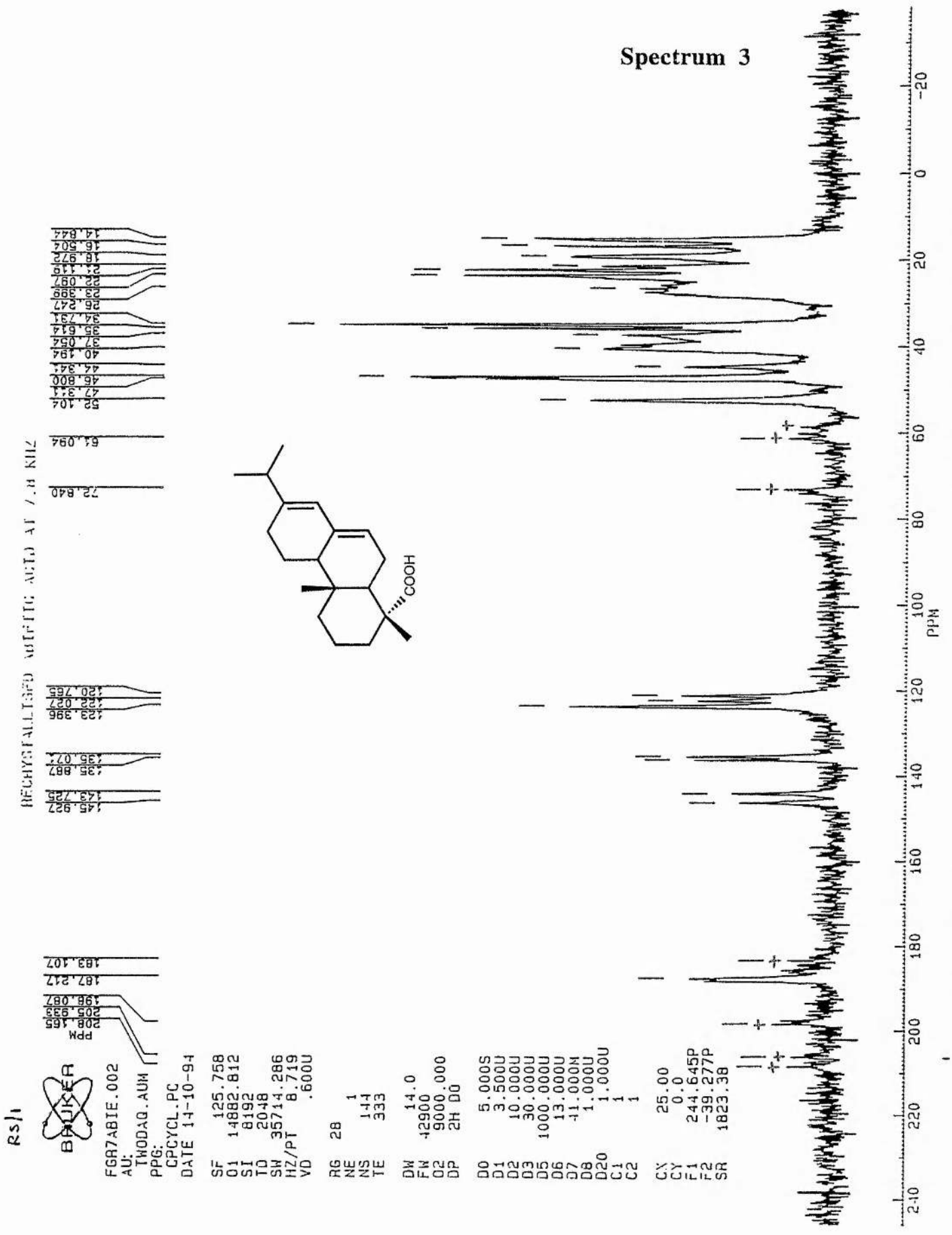
Fig. 4.2 Abietic acid.

Spectrum 3 shows a solid-state spectrum of abietic acid recrystallised twice from aqueous ethanol. There are three main regions in the spectrum. The region from 15 to 55ppm contains the aliphatic resonances. The four olefinic carbons are observed between 120 and 145ppm, while the carboxylic acid resonance is seen at 187.2ppm. A full assignment is detailed in the literature survey.

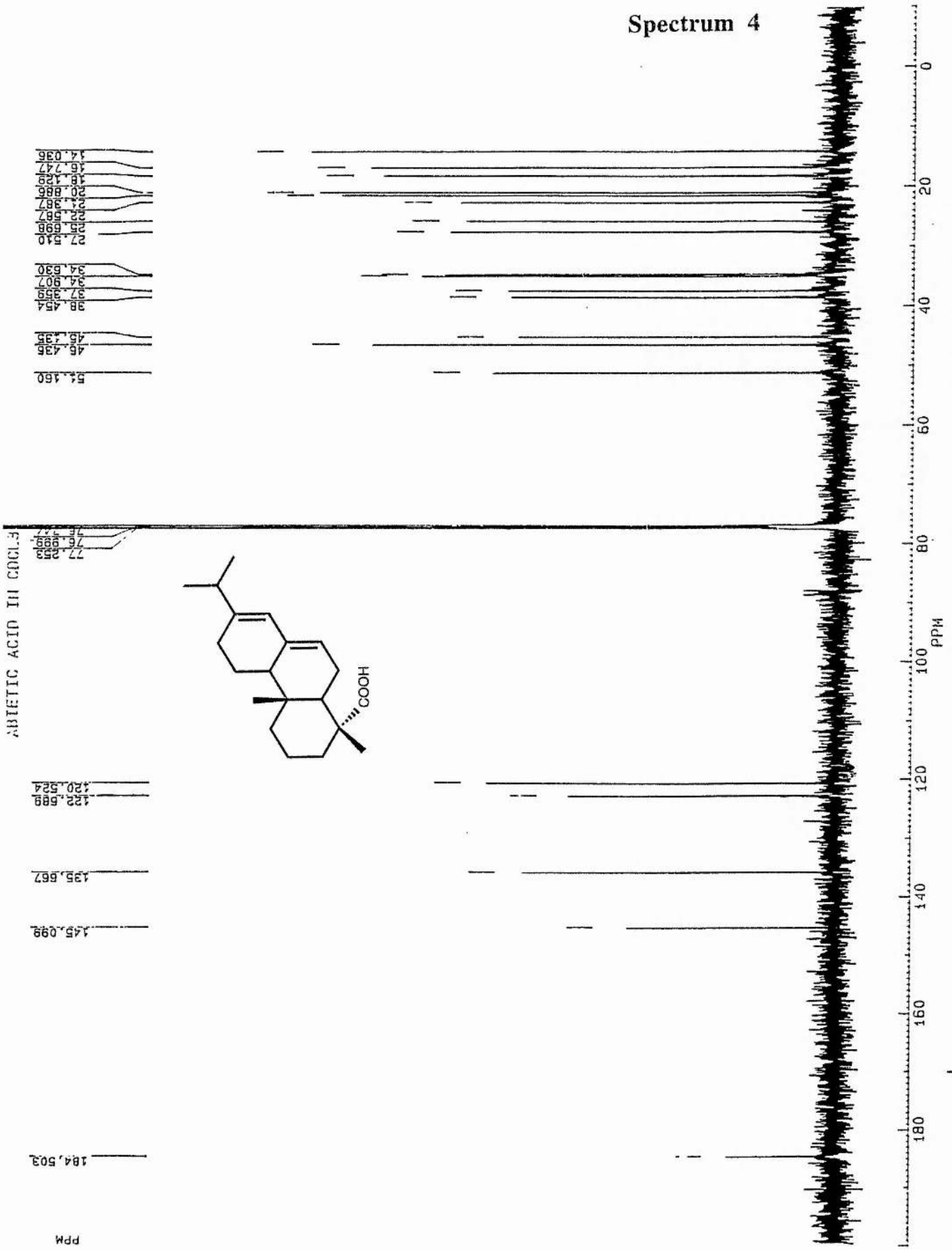
The resolution of the spectrum in the solid-state is sufficient to show many of the signals as doublets, especially evident for the olefinic carbons, reflecting the presence of two independent molecules in the asymmetric unit cell.

Spectrum 4 shows the same sample in $CDCl_3$ solution recorded on the Bruker 500MSL for comparison. Spectrum 5 is provided as a direct comparison of the two techniques.

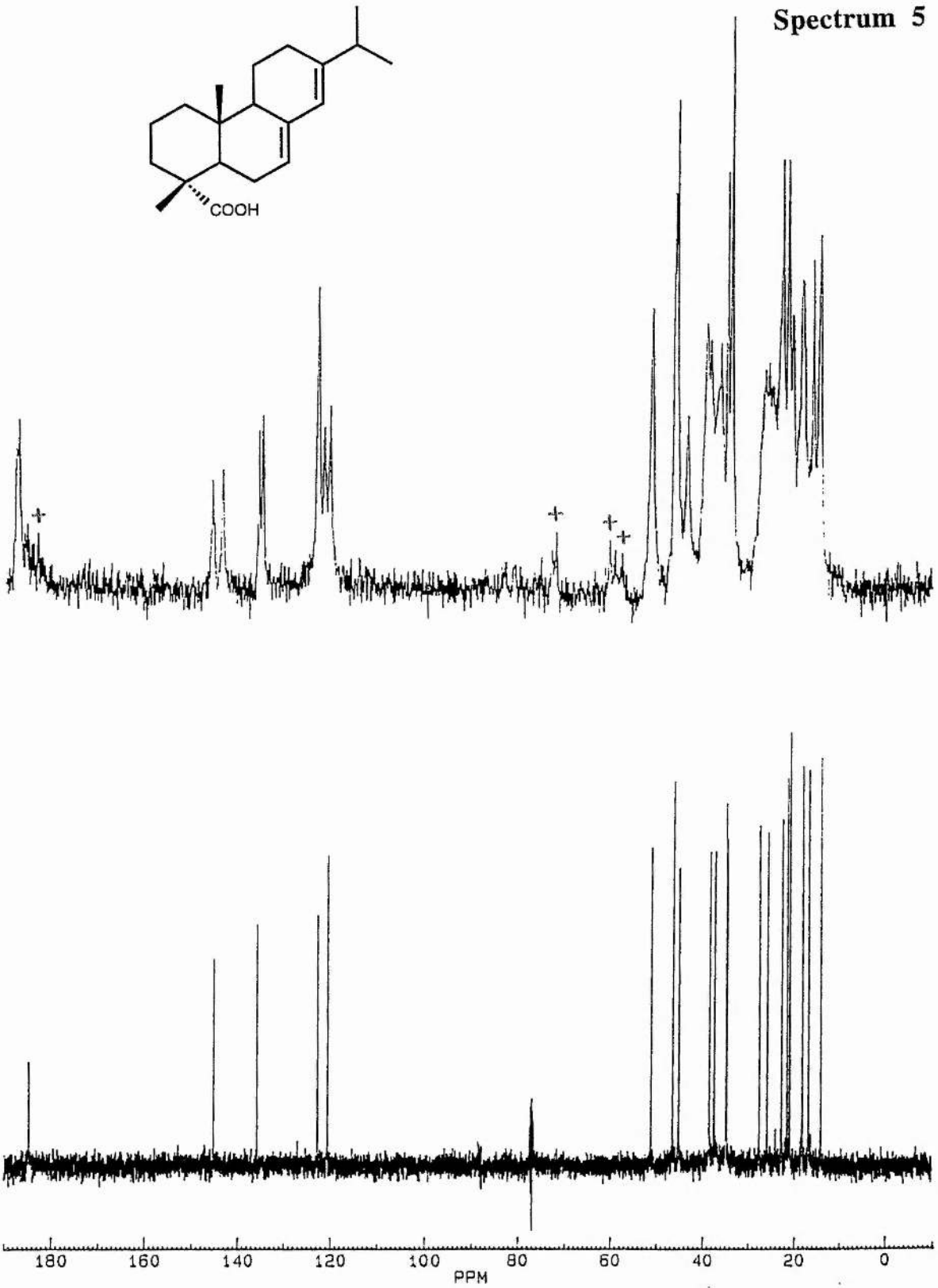
Spectrum 3



Spectrum 4


ABIETIC ACID IN CDCL3
14.036
16.247
18.129
20.886
24.387
22.587
25.698
27.540
34.530
37.359
34.907
38.454
46.435
45.135
54.160
77.253
76.989
120.524
122.588
135.667
145.099
184.503
COOH
PPM
0
20
40
60
80
100
120
140
160
180

Spectrum 5



4.3 Maleopimaric acid (Ennesin MU4 resin)

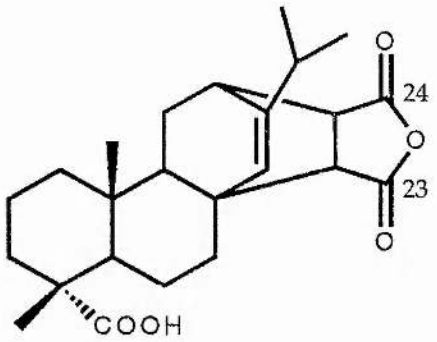
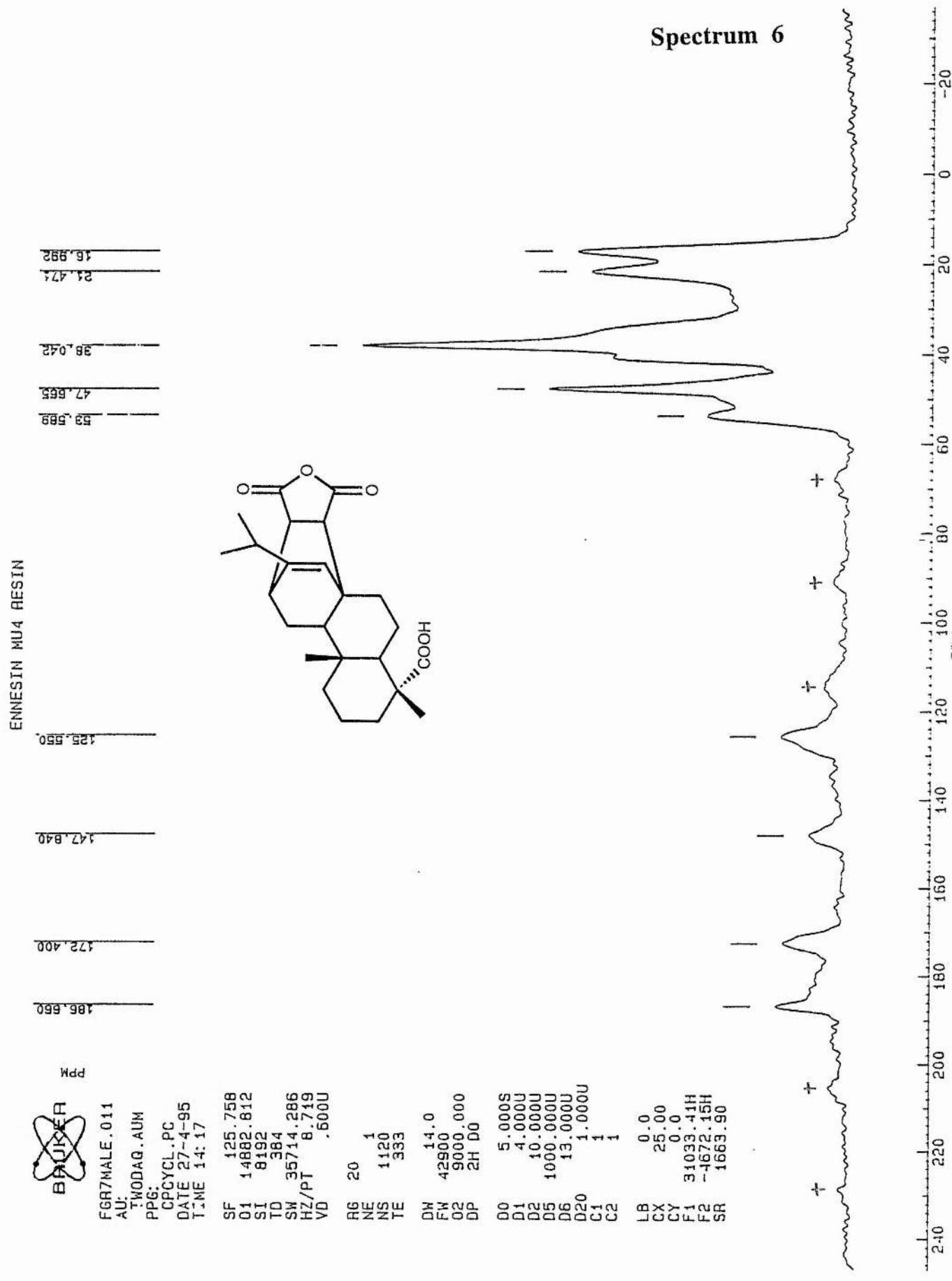


Fig. 4.3 Maleopimaric acid.

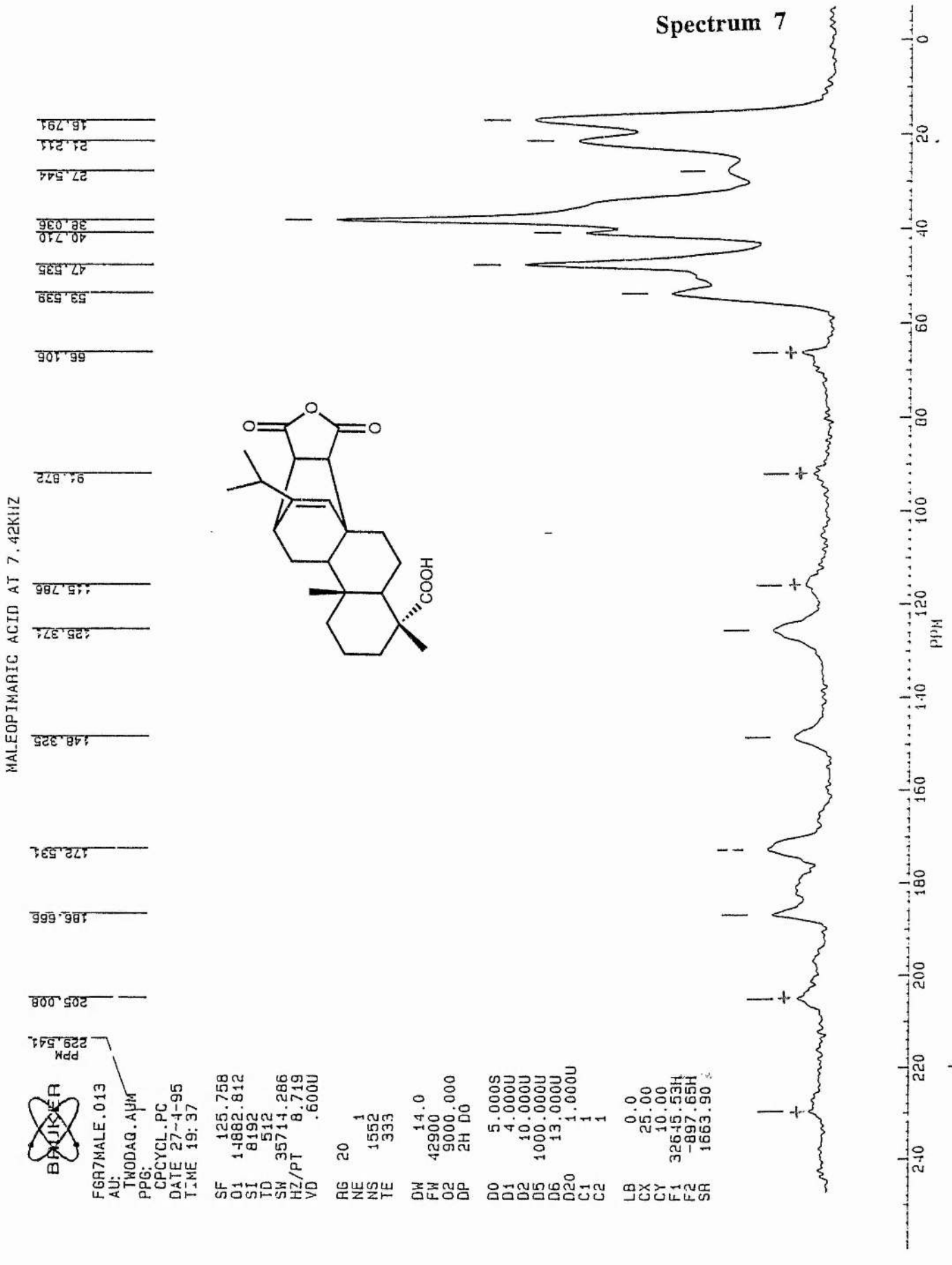
The commercial grade adduct, Ennesin MU4 resin, is seen in Spectrum 6, while the lab. synthesised compound, maleopimaric acid, is seen in Spectrum 7. They are similar in appearance, each having a broad amorphous region between 15 and 55ppm. Spectrum 6 shows four signals further down field. The resonances at 125.6 and 147.8ppm are from the two olefinic carbons. The broad signal at 172.4ppm accounts for both carbonyl resonances of the anhydride moiety of the adduct, while the carboxylic acid carbon is seen at 186.5ppm. Additional peaks in Spectrum 7 are due to spinning sidebands.

A marked difference is observed for the maleopimaric acid in Spectrum 8, which was recrystallised from acetic acid. Much greater resolution and hence crystallinity is reflected by the emergence of discrete peaks. The resonances for the carbonyl carbons, C-23 and C-24, are now well resolved at 174.5 and 172.4ppm respectively. The presence of five peaks around 180ppm instead of the three we would expect is presumably due to acetic acid of recrystallisation, although this was not checked further.

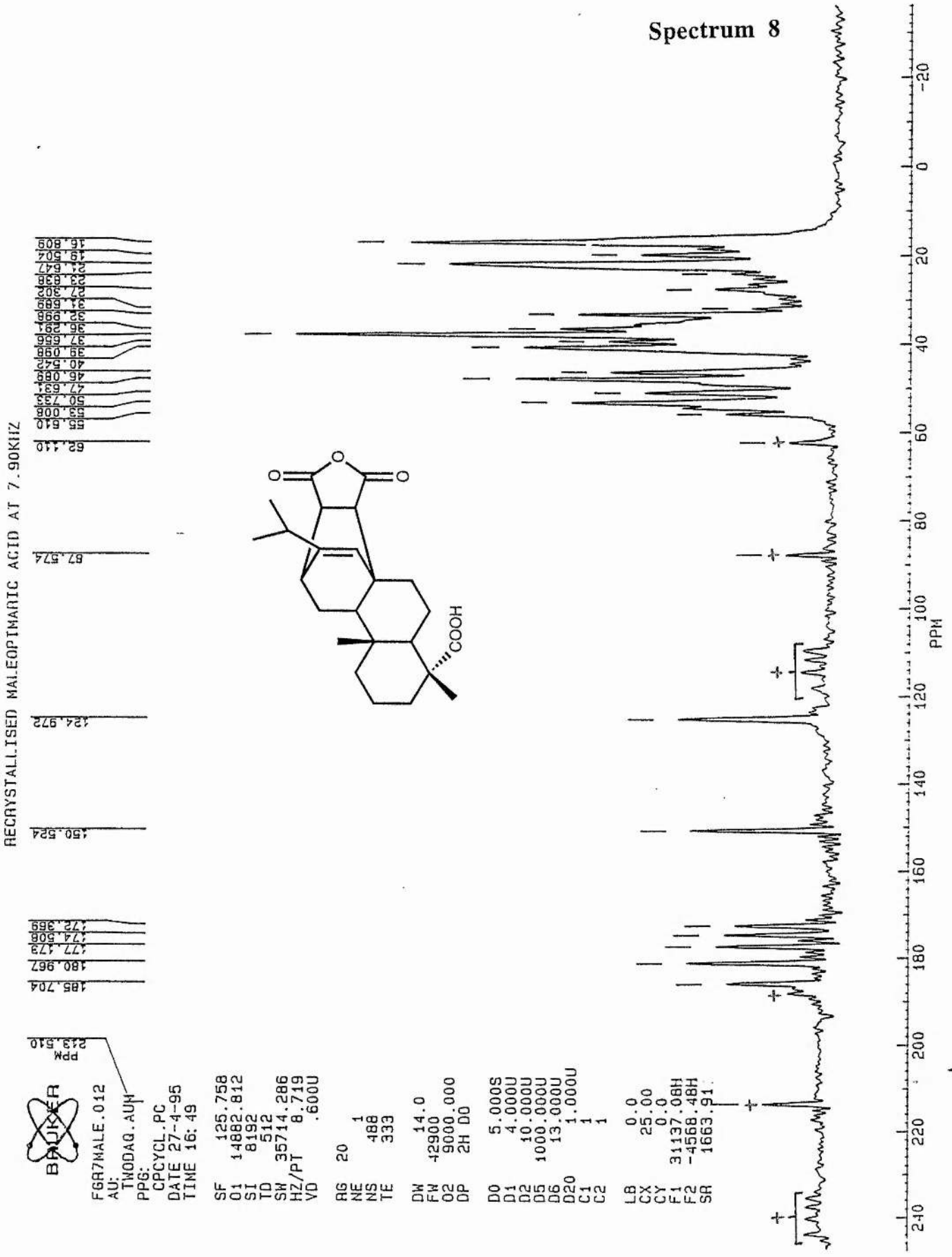
Spectrum 6


ENNESIN MU4 RESIN
BRUKER
PPM
FGR7MALE.011
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 27-4-95
TIME 14:17
SF 125.758
O1 14882.812
SI 8192
TD 384
SW 35714.286
HZ/PT 8.719
VD .600U
AQ 20
NE 1
NS 1120
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DO
DO 5.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 31033.41H
F2 -4672.15H
SR 1663.90
186.660
172.400
147.840
125.550
53.589
47.665
38.042
24.474
16.992
COOH
PPM

Spectrum 7


MALEOPIMARIC ACID AT 7.42KHZ
BRUKER
FGR7MALE.013
AU: TWODAQ.AUM
PPG: CPCYCL.PC
DATE 27-4-95
TIME 19:37
SF 125.758
O1 14882.812
SI 8192
TD 512
SW 35714.286
HZ/PT 8.719
VD .600U
RG 20
NE 1
NS 1552
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H D0
D0 5.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 10.00
F1 32645.53H
F2 -897.65H
SR 1663.90
PPM
229.541
205.008
186.666
172.591
148.325
125.372
115.786
94.872
66.106
59.539
47.535
40.710
38.036
27.544
21.211
16.791
COOH
PPM

Spectrum 8


RECRYSTALLISED MALEOPIMARIC ACID AT 7.90KHZ
BRUKER
FGR7MALE.012
AU: TWODAQ.AUM
PPG: CPCYCL.PC
DATE 27-4-95
TIME 16:49
SF 125.758
O1 14882.812
SI 8192
TD 512
SW 35714.286
HZ/PT 8.719
VD .600U
RG 20
NE 1
NS 488
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H D0
D0 5.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 31137.08H
F2 -4568.48H
SR 1663.91
213.510
185.704
180.967
177.173
174.506
172.369
150.524
124.972
87.574
82.410
55.610
55.008
50.733
47.631
46.089
40.542
39.098
37.656
36.291
32.998
31.589
27.302
23.838
21.647
19.504
16.809
COOH
PPM

4.4 Dihydroabietic acid (Staybelite resin)

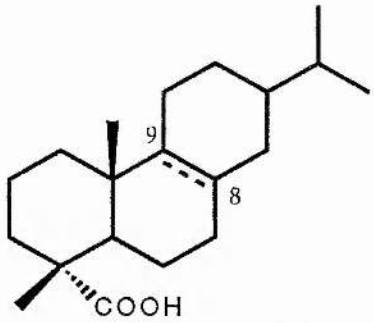


Fig. 4.4 Dihydroabietic acid.

Spectrum 9 shows the commercial product, Staybelite resin, which is crude and so the signals are understandably broad. The three signals seen down field are due to the carboxylic acid carbon (186.7ppm) and the two olefinic carbons. The presence of two olefinic signals, although broad, may indicate that there is only one principal double bonded species responsible for dihydroabietic acid, most likely between C-8 and C-9.

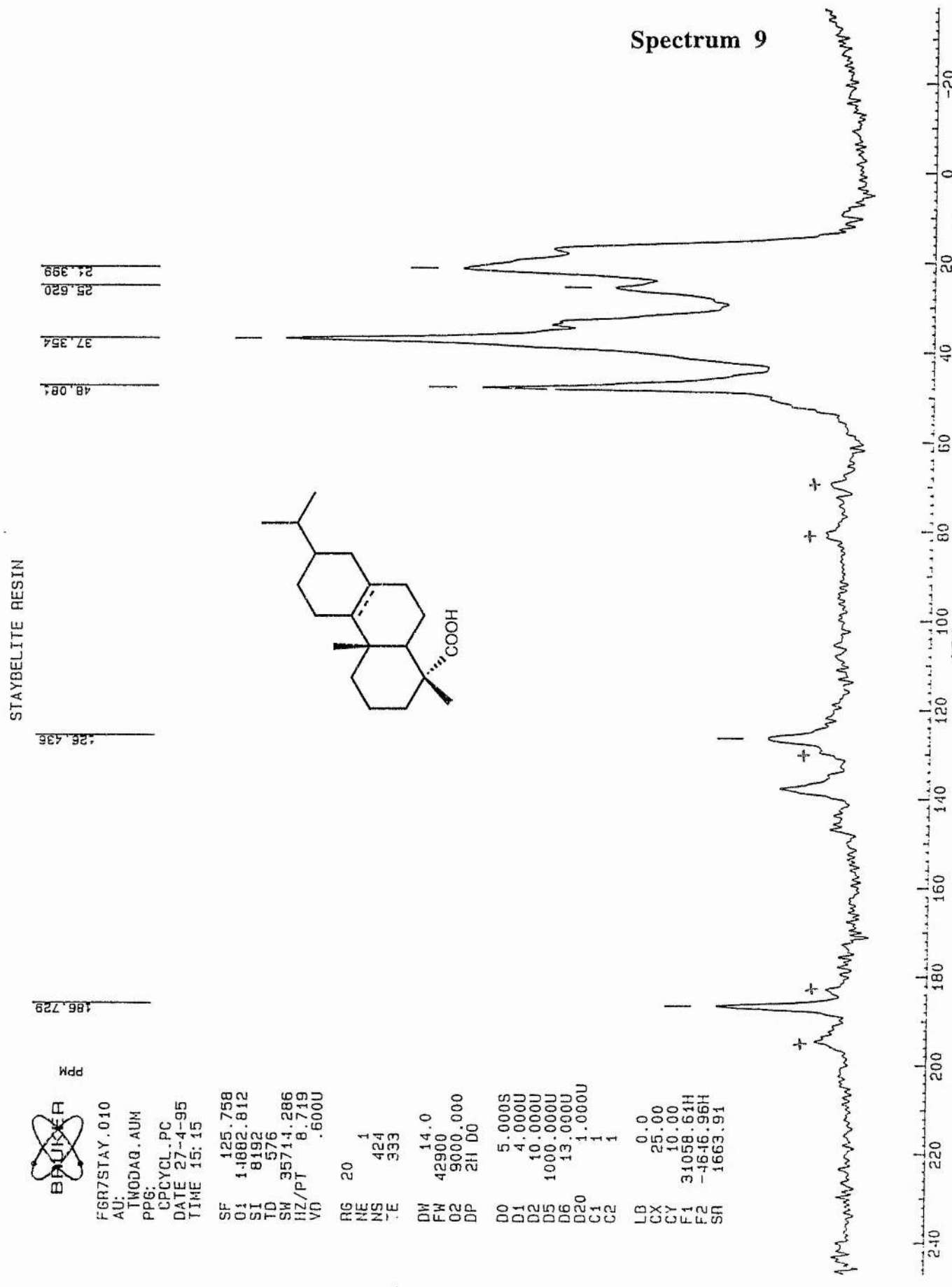
The Resinated Pigments

Each sample was recorded twice, at two different spinning speeds. ~7.5kHz and ~10kHz. This allowed the identification of spinning sidebands, since the position of the sidebands moves with varying spinning speed.

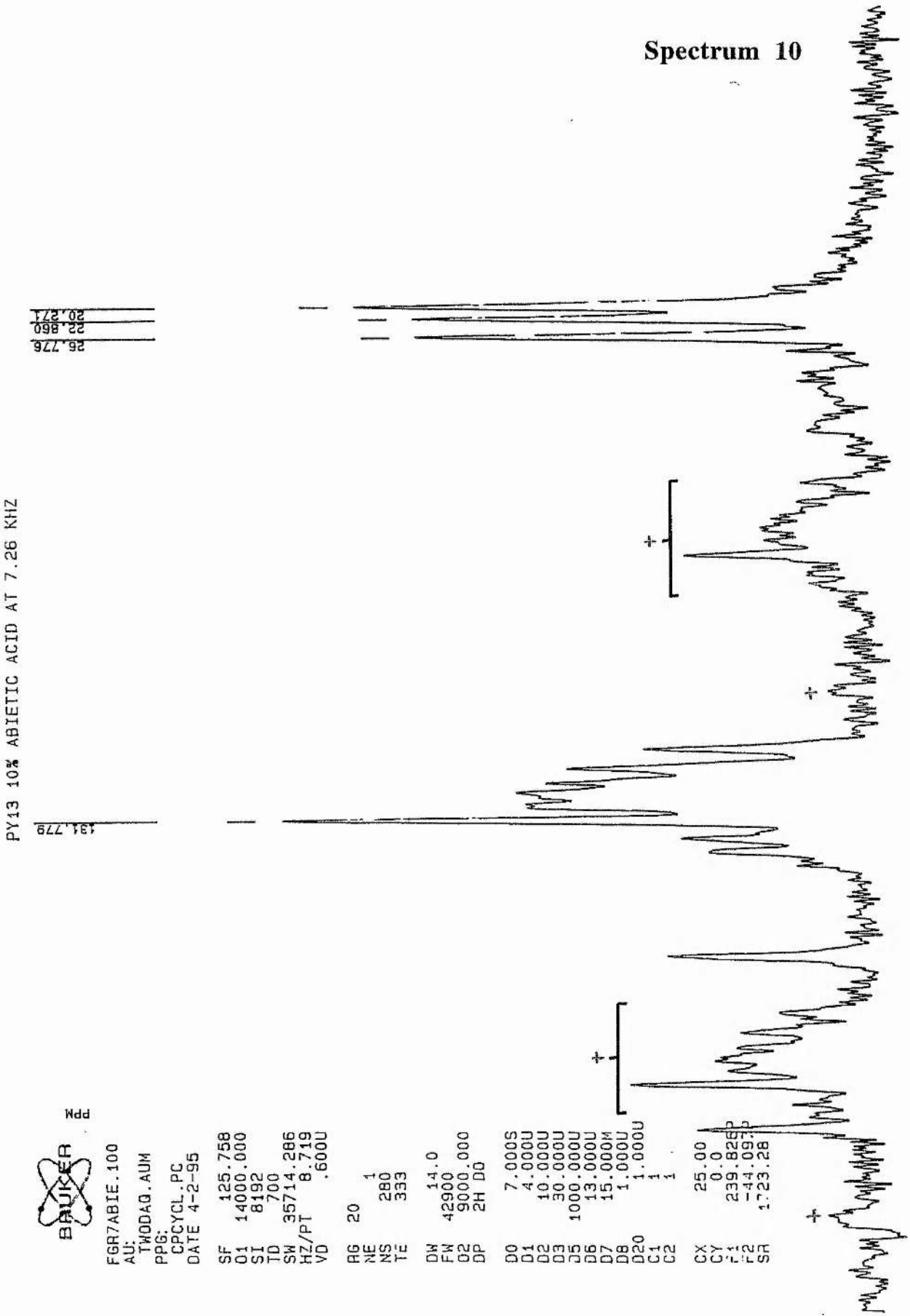
4.5 Pigment Yellow 13 / abietic acid

Spectra 10 to 13 relate to Pigment Yellow 13 resinated with 10-40% recrystallised abietic acid. Spectrum 14 is a stacked plot of these spectra, from 10 to 70ppm, provided for comparison purposes.

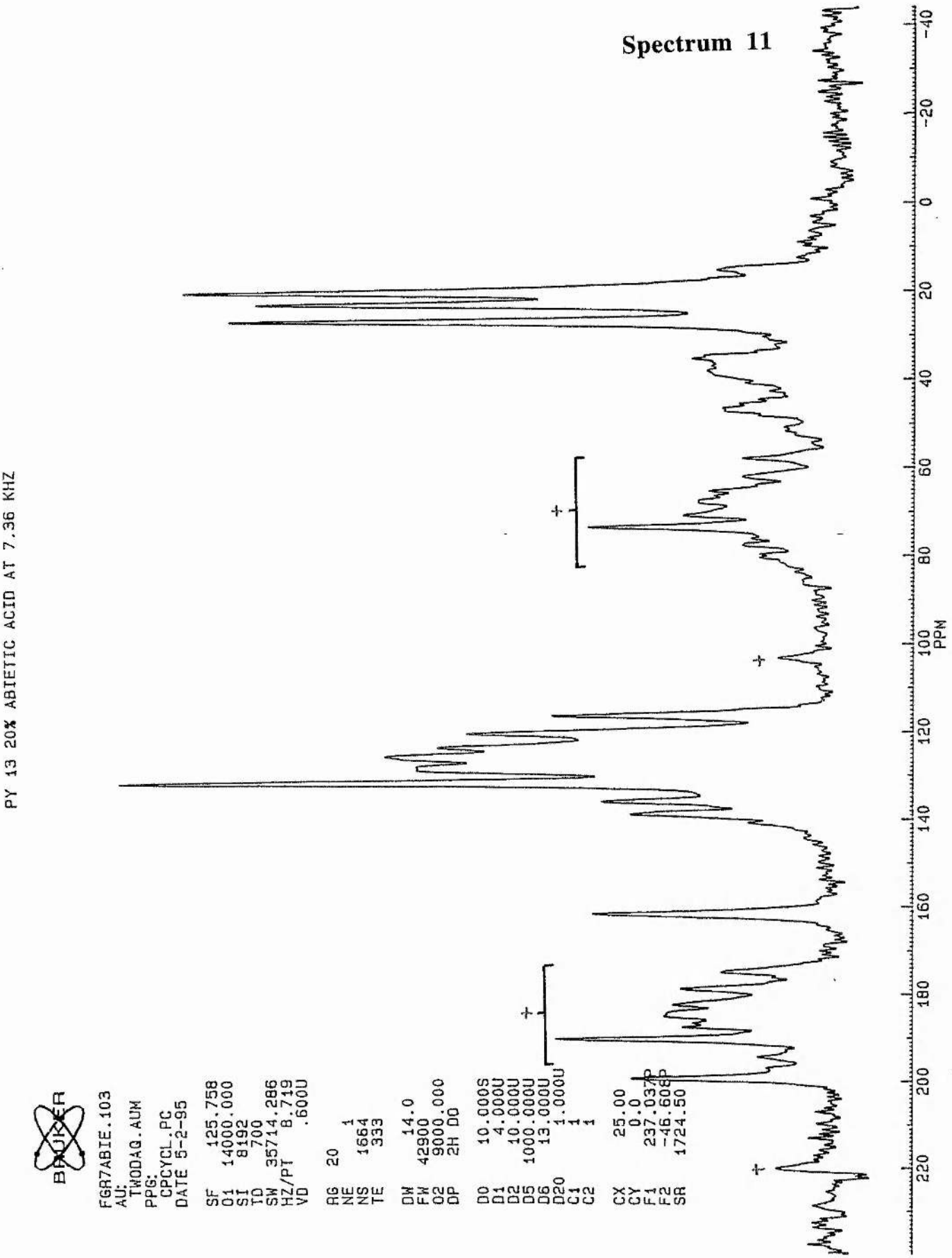
Spectrum 9


STAYBELITE RESIN
FGR7STAY.010
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 27-4-95
TIME 15:15
SF 125.758
O1 14882.812
SI 8192
TD 576
SW 35714.286
HZ/PT 8.719
VD .600U
RG 20
NE 1
NS 424
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H D0
D0 5.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 10.00
F1 31058.61H
F2 -4646.96H
SR 1663.91
186.729
126.436
48.084
37.354
25.620
24.399
COOH
PPM

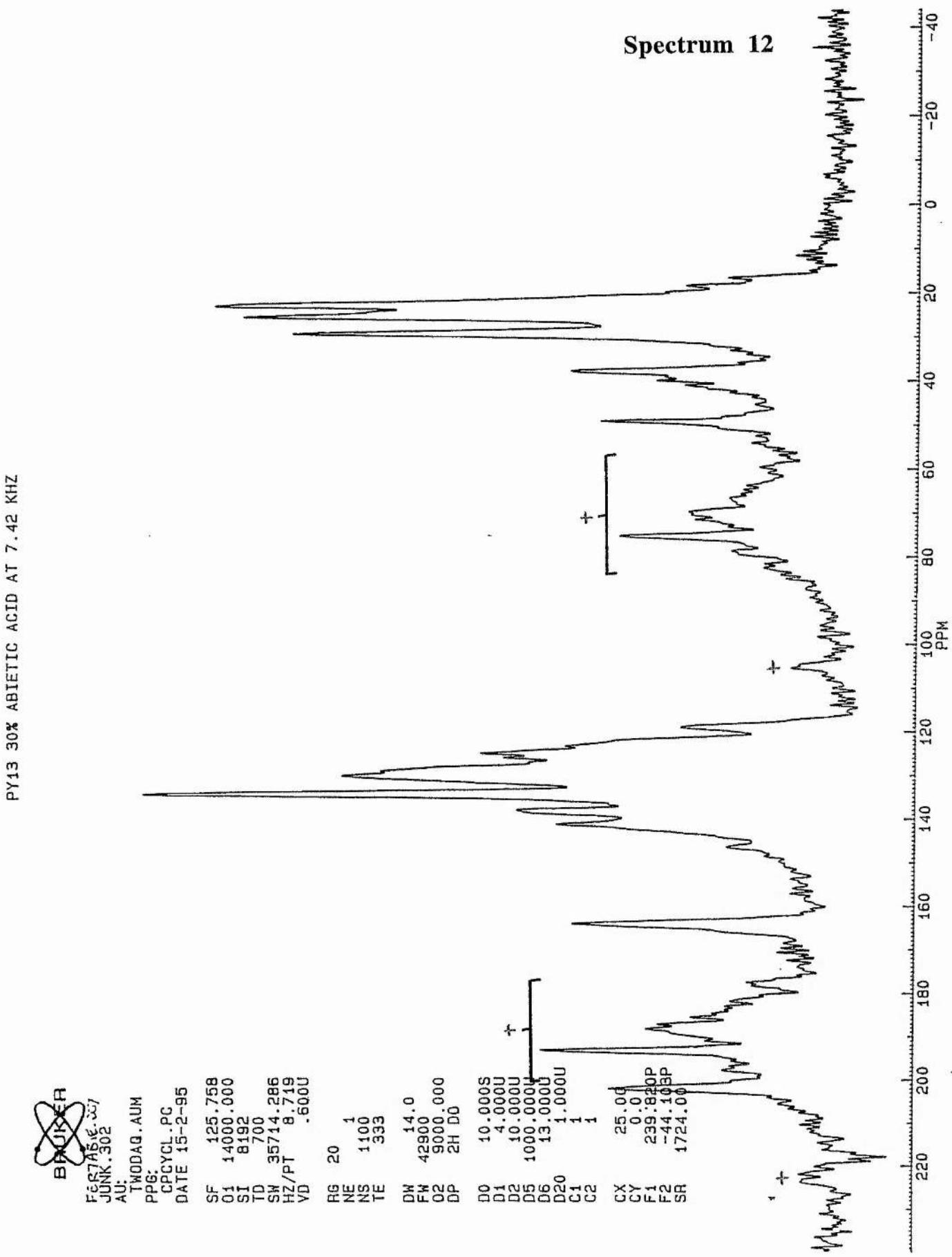
Spectrum 10


PY13 10% ABIETIC ACID AT 7.26 KHZ
BRUKER
PPM
FGR7ABIE.100
AU: TWODAQ.AUM
PPG: CPCYCL.PC
DATE 4-2-95
SF 125.758
O1 14000.000
SI 8192
TD 700
SW 35714.286
HZ/PT 8.719
VD .600U
RG 20
NE 1
NS 280
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H D0
D0 7.000S
D1 4.000U
D2 10.000U
D3 30.000U
D5 1000.000U
D6 13.000U
D7 15.000M
D8 1.000U
D20 1.000U
C1 1
C2 1
CX 25.00
CY 0.0
F1 239.826P
F2 -44.097P
SR 1723.28
131.779
26.776
22.860
20.271
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40

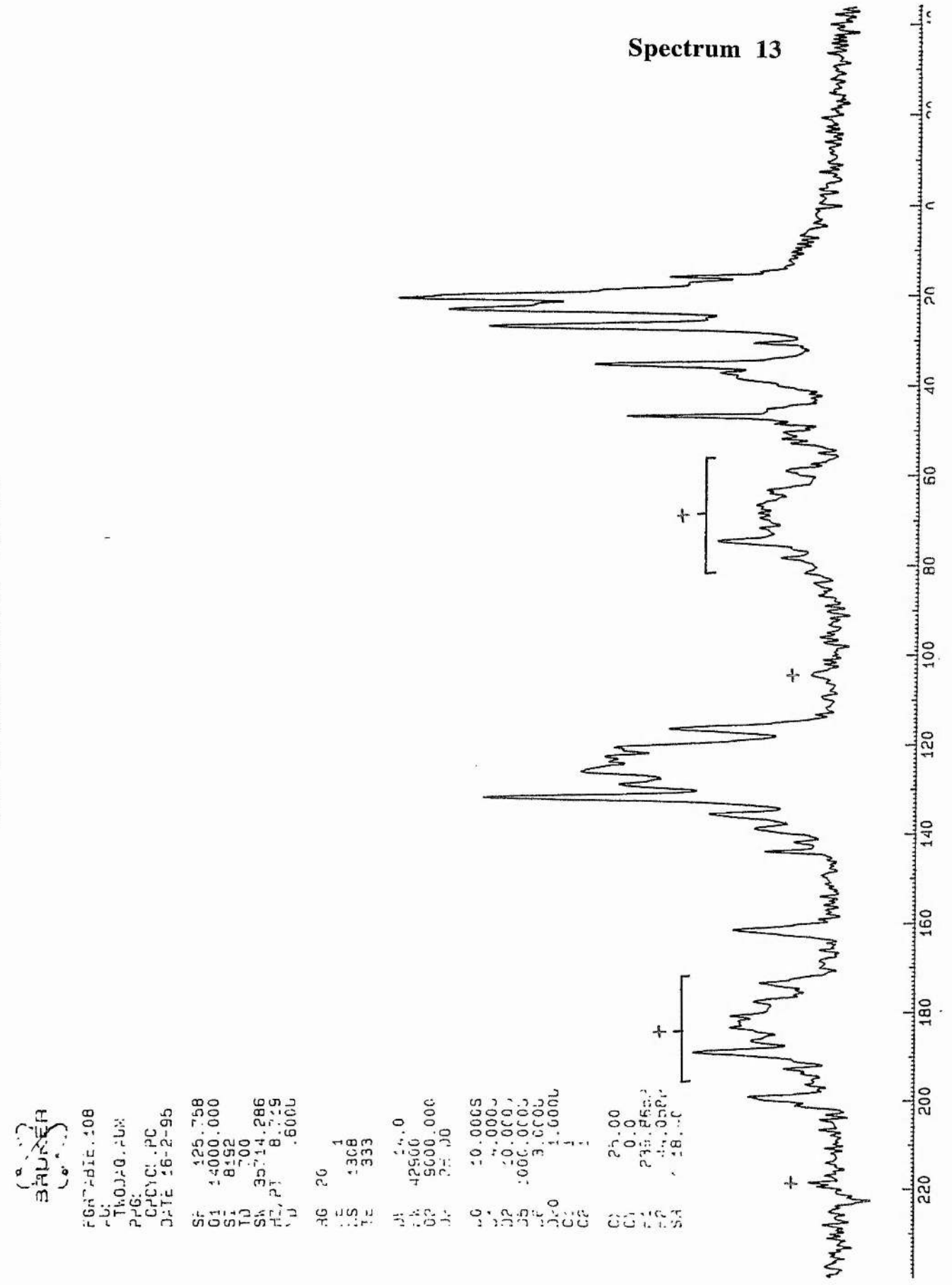
Spectrum 11

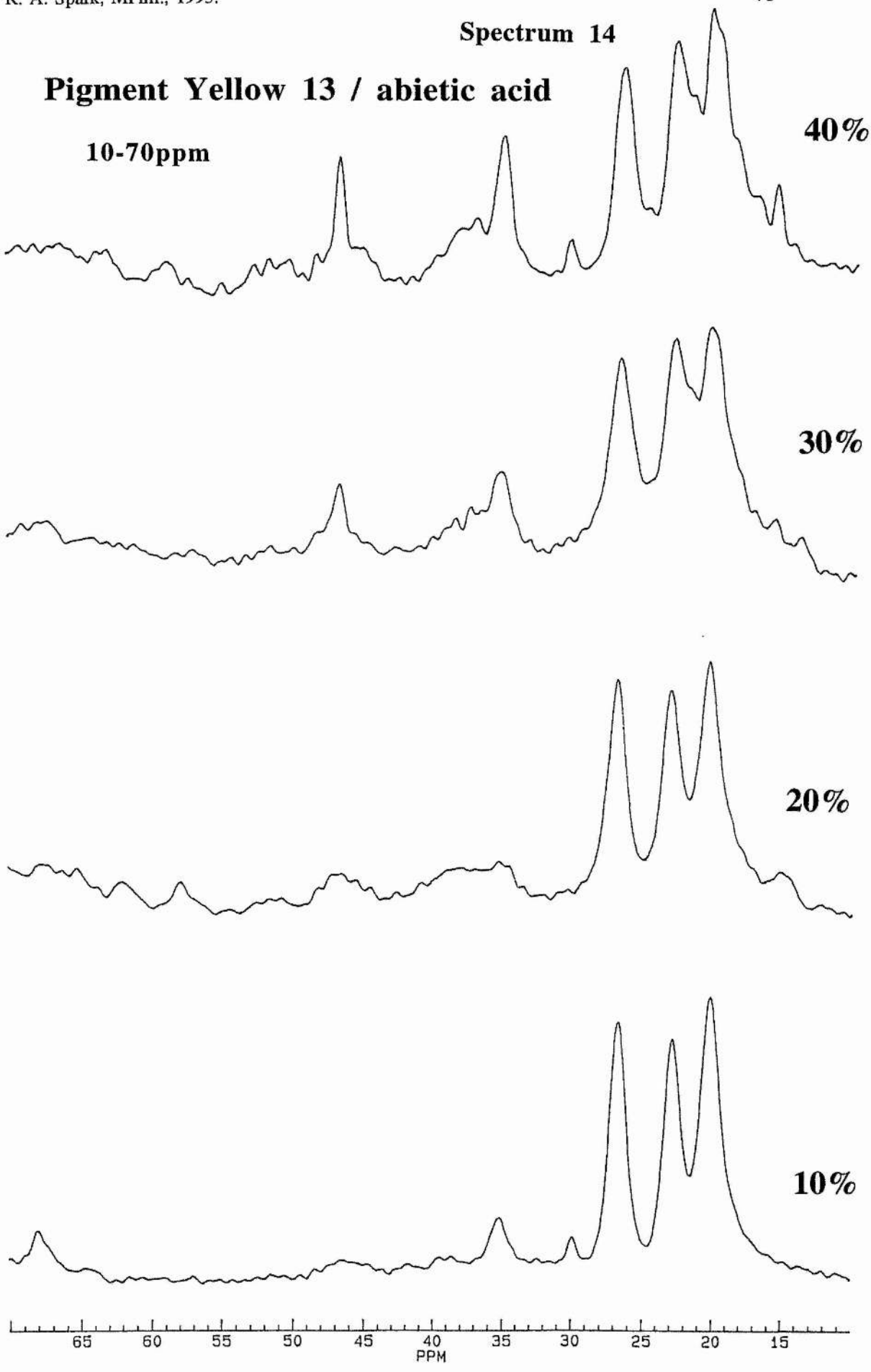

PY 13 20% ABIETIC ACID AT 7.36 KHZ
BRUKER
FGR7ABIE.103
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 5-2-95
SF 125.758
O1 14000.000
SI 8192
TD 700
SW 35714.286
HZ/PT 8.719
VD .600U
RG 20
NE 1
NS 1664
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DD
D0 10.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
CX 25.00
CY 0.0
F1 237.037P
F2 -46.608P
SR 1724.50
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
PPM

Spectrum 12


PY13 30% ABIETIC ACID AT 7.42 KHZ
BRUKER
FEGTAB
JUNK.302
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 15-2-95
SF 125.758
O1 14000.000
SI 8192
TD 700
SW 35714.286
HZ/PT 8.719
VD .600U
RG 20
NE 1
NS 1100
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DD
D0 10.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
CX 25.00
CY 0.0
F1 239.820P
F2 -44.105P
SR 1724.00
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
PPM

Spectrum 13


PY13 40% ABIETIC ACID AT 7.18 KHZ
BRUKER
220
200
180
160
140
120
100
80
60
40
20
0


Spectrum 14
Pigment Yellow 13 / abietic acid
10-70ppm
40%
30%
20%
10%
65
60
55
50
45
40
35
30
25
20
15
PPM

The presence of abietic acid, even at 10% loading, during resination of P.Y.13 would appear to enhance crystallinity of the pigment dramatically since the spectra are much better resolved. The amount of abietic acid incorporated seems to make little difference to the enhancement of crystallinity.

The emergence of peaks due to the abietic acid from 10 through to 40% loading can be observed in the region at around 40ppm. Two of the abietic acid peaks are obvious, but others are not so clear since they are emerging beneath the methyl resonances of P.Y.13 at around 25ppm, evident as shoulders of the methyl peaks. The emerging abietic acid peaks appear to be broader in the spectrum of the resinated pigment than in the spectrum of abietic acid itself.

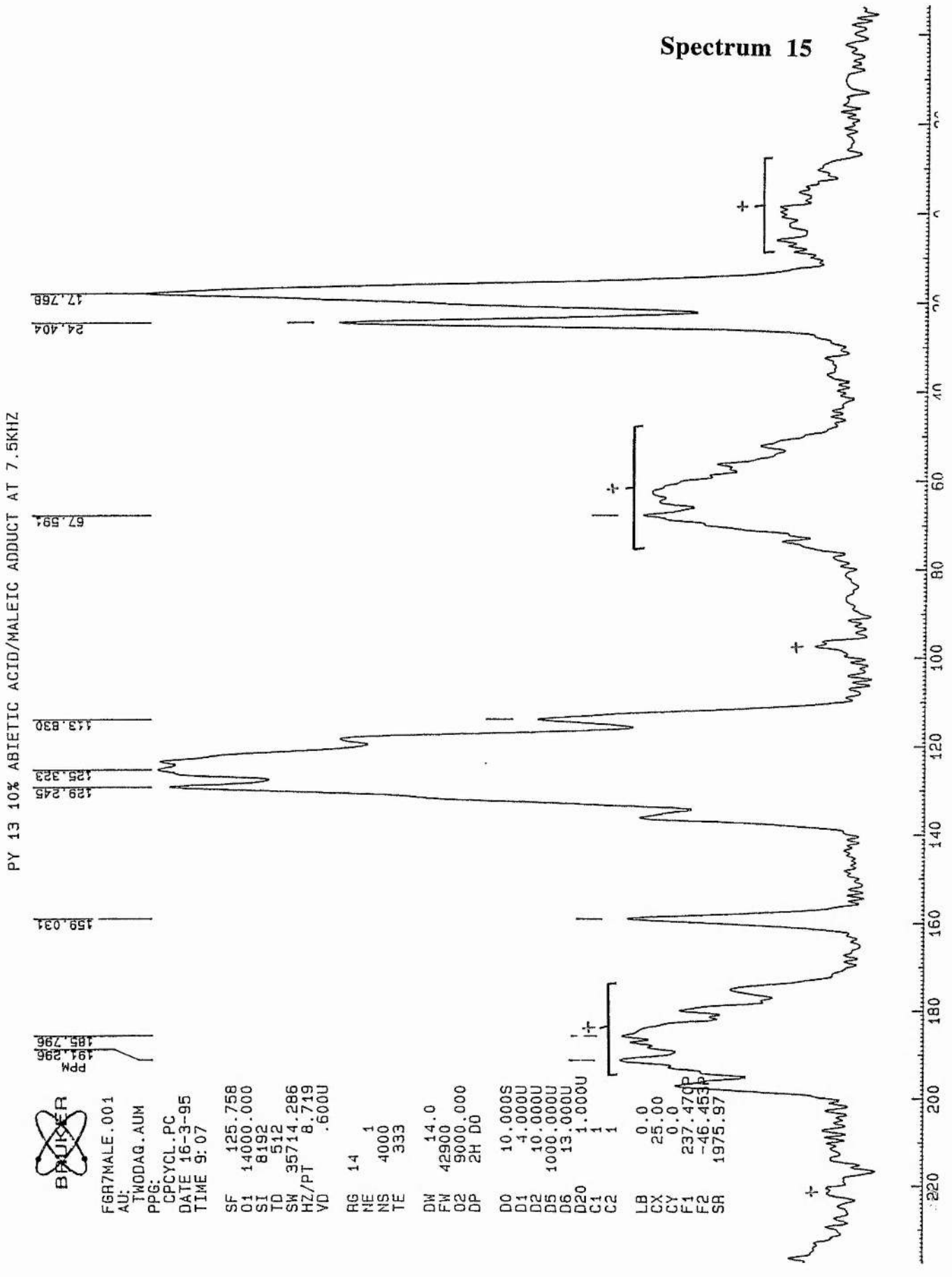
The stacked plot, Spectrum 14, is supplied to make clear the emergence of the abietic acid.

4.6 Pigment Yellow 13 / maleopimaric acid (Ennesin MU4)

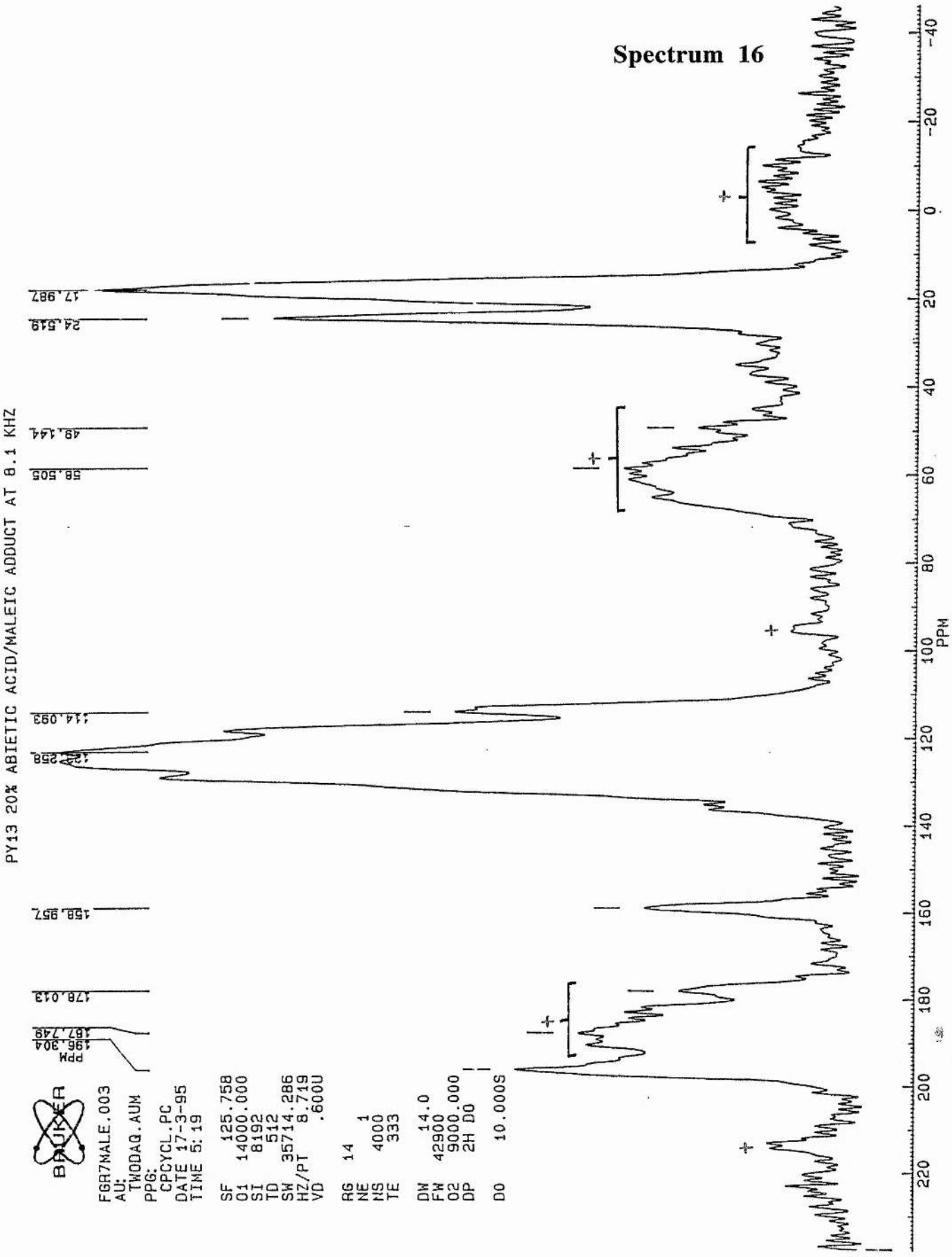
Spectra 15 to 17 relate to Pigment Yellow 13 resinated with 10-30% Ennesin MU4 resin.

As discussed previously, little of this particular resin acid is retained during the resination process. Accordingly, the pigment peaks are broad which reflects the crude nature of the starting P.Y.13, which is unchanged by this experiment. This is best seen around 20ppm, where the broad methyl resonances are merged into only two signals. Since the sample has undergone the 'heat treatment', we can confirm that this process alone does not serve to promote crystallinity in the pigment particles. Also, there is no indication of the presence of maleopimaric acid in the spectra, even at 30% loading.

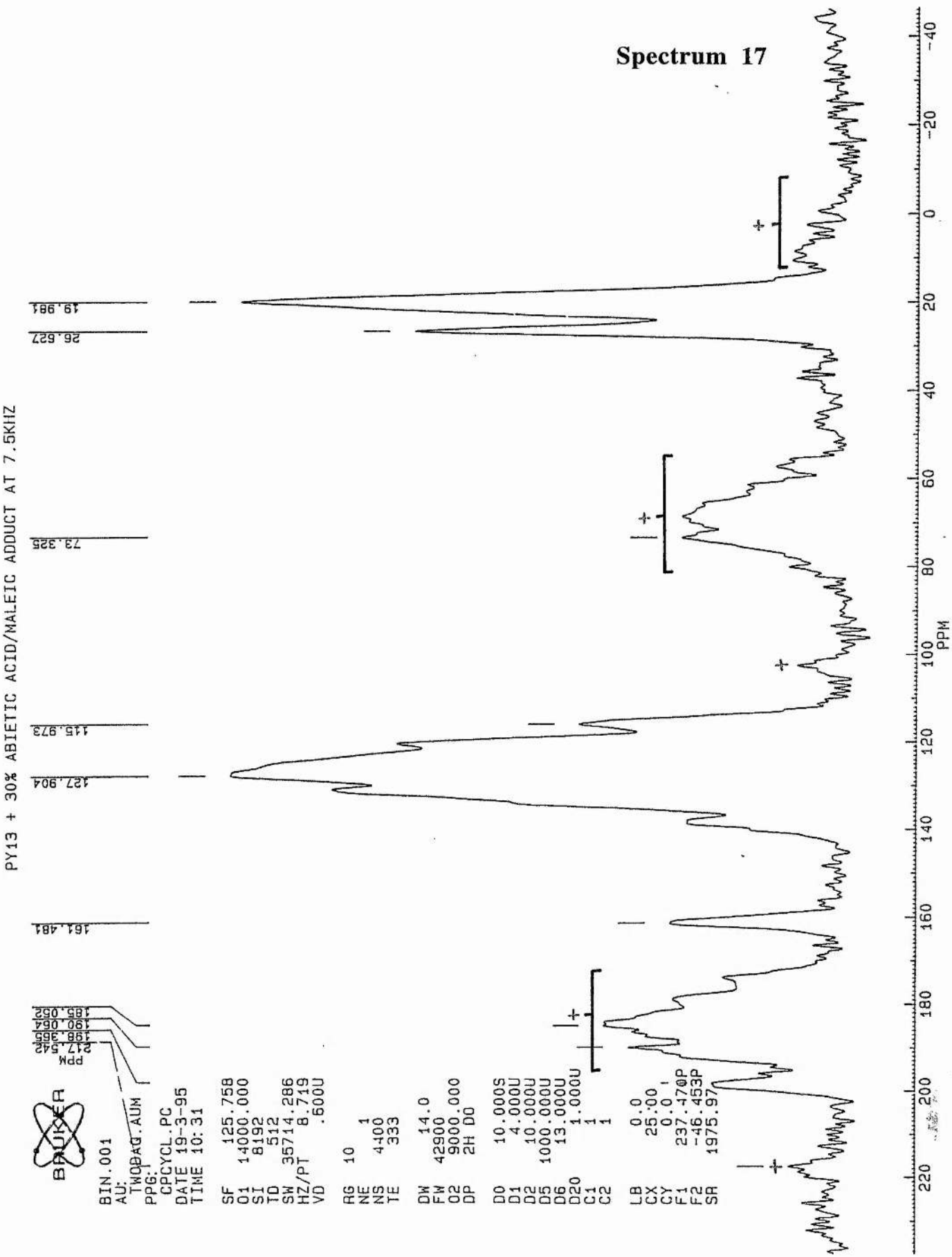
Spectrum 15


PY 13 10% ABIETIC ACID/MALEIC ADDUCT AT 7.5KHZ
BRUKER
PPM
191.296
185.796
159.031
129.245
125.323
113.830
67.594
24.404
17.768
FGR7MALE.001
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 16-3-95
TIME 9:07
SF 125.758
O1 14000.000
SI 8192
TD 512
SW 35714.286
HZ/PT 8.719
VD .600U
RG 14
NE 1
NS 4000
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DD
D0 10.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 237.470
F2 -46.453
SR 1975.97

Spectrum 16


PY13 20% ABIETIC ACID/MALEIC ADDUCT AT 8.1 KHZ
BRUKER
FGR7NALE.003
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 17-3-95
TIME 5:19
SF 125.758
O1 14000.000
SI 8192
TD 512
SW 35714.286
HZ/PT 8.719
VD .600U
RG 14
NE 1
NS 4000
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H D0
D0 10.000S
PPM
196.304
187.749
178.013
158.957
114.093
58.505
49.144
24.549
17.987
PPM

Spectrum 17


PY13 + 30% ABIETIC ACID/MALEIC ADDUCT AT 7.5KHZ
BRUKER
BIN.001
AU:
TWOBAD.AUM
PPG:1
CPCYCL.PC
DATE 19-3-95
TIME 10:31
SF 125.758
O1 14000.000
SI 8192
TD 512
SW 35714.286
HZ/PT 8.719
VD .600U
RG 10
NE 1
NS 4400
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H D0
D0 10.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 237.470P
F2 -46.453P
SR 1975.97
217.542
198.355
190.064
185.052
161.481
127.904
115.973
73.325
26.627
19.981
PPM

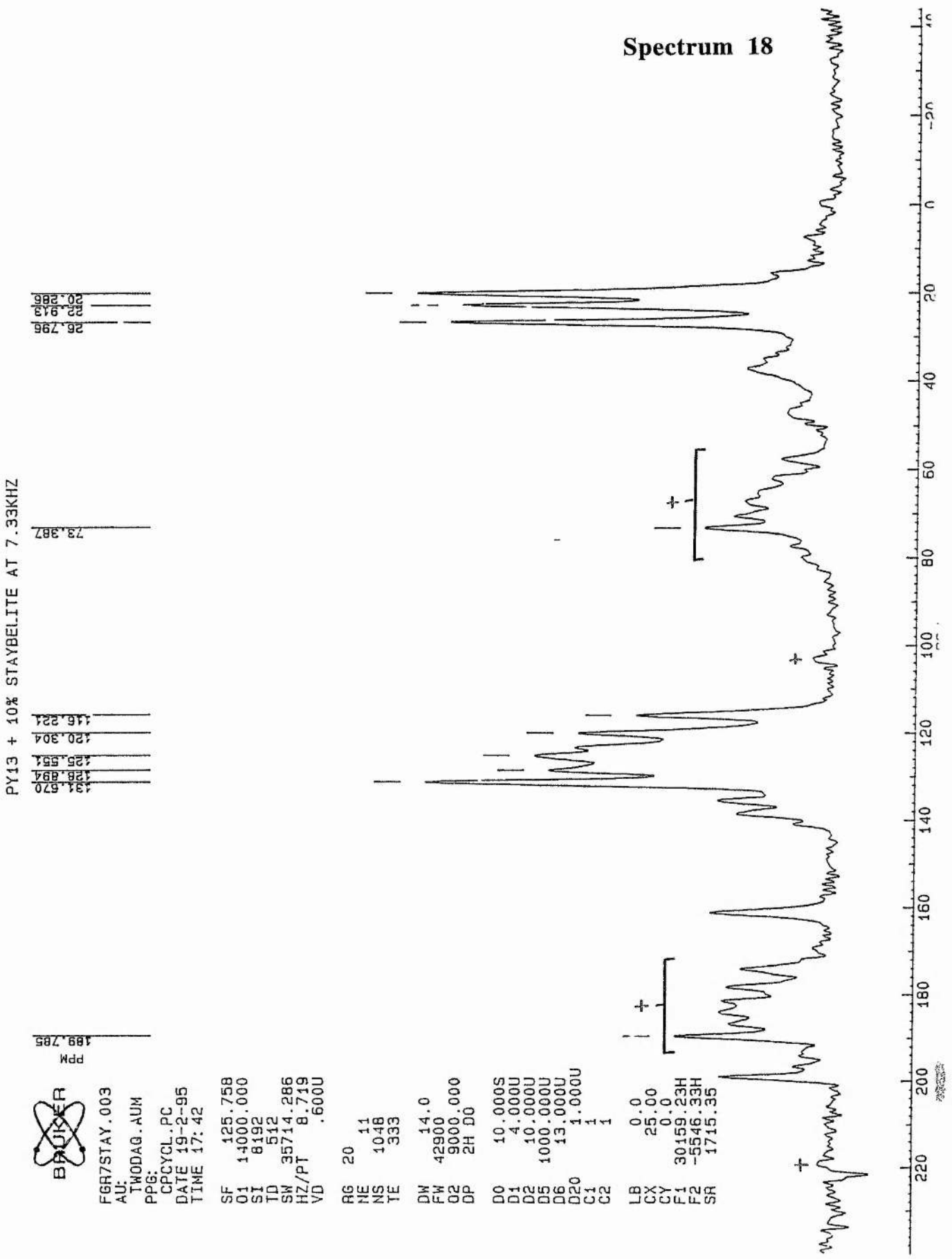
4.7 Pigment Yellow 13 / dihydroabietic acid (Staybelite)

Spectra 18 to 21 relate to Pigment Yellow 13 resinated with 10-40% Staybelite resin. Spectrum 22 is a stacked plot of these spectra, from 0 to 90ppm. Spectrum 23 is a stacked plot of the same Staybelite coated resin samples, from 150 to 220ppm, but recorded at a spinning speed of ~10kHz, in order to remove spinning sidebands from the COOH region.

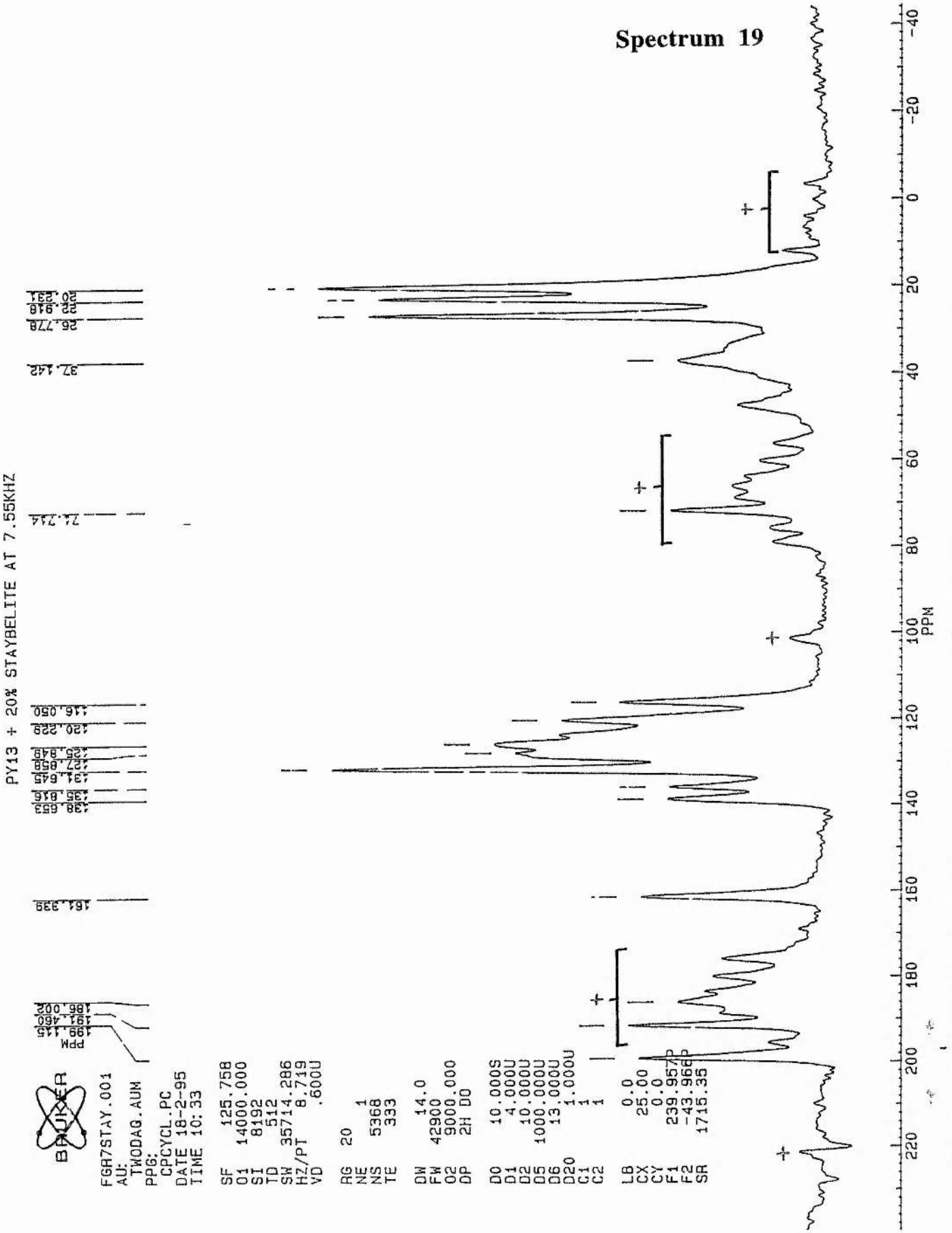
Again, as for P.Y.13 resinated with abietic acid, the pigment peaks in each case are relatively well resolved, indicating improved order in the pigment crystals. The emergence of the Staybelite resin peaks can be clearly seen, mainly at around 40ppm, with these resin peaks appearing to be broad when coated on the pigment. The stacked plot, Spectrum 22, displays the emergence of the Staybelite.

Especially important to note is the emergence of the Staybelite resonance at 187ppm in the stacked plot, Spectrum 23. These experiments were run at ~10kHz, so the spinning sidebands no longer obscure this resonance, accountable to the carboxylic acid carbon. This indicates that the carboxylic functionality of the resin acid remains untouched throughout the resination, instead of being involved in some chemical interaction with the pigment molecules.

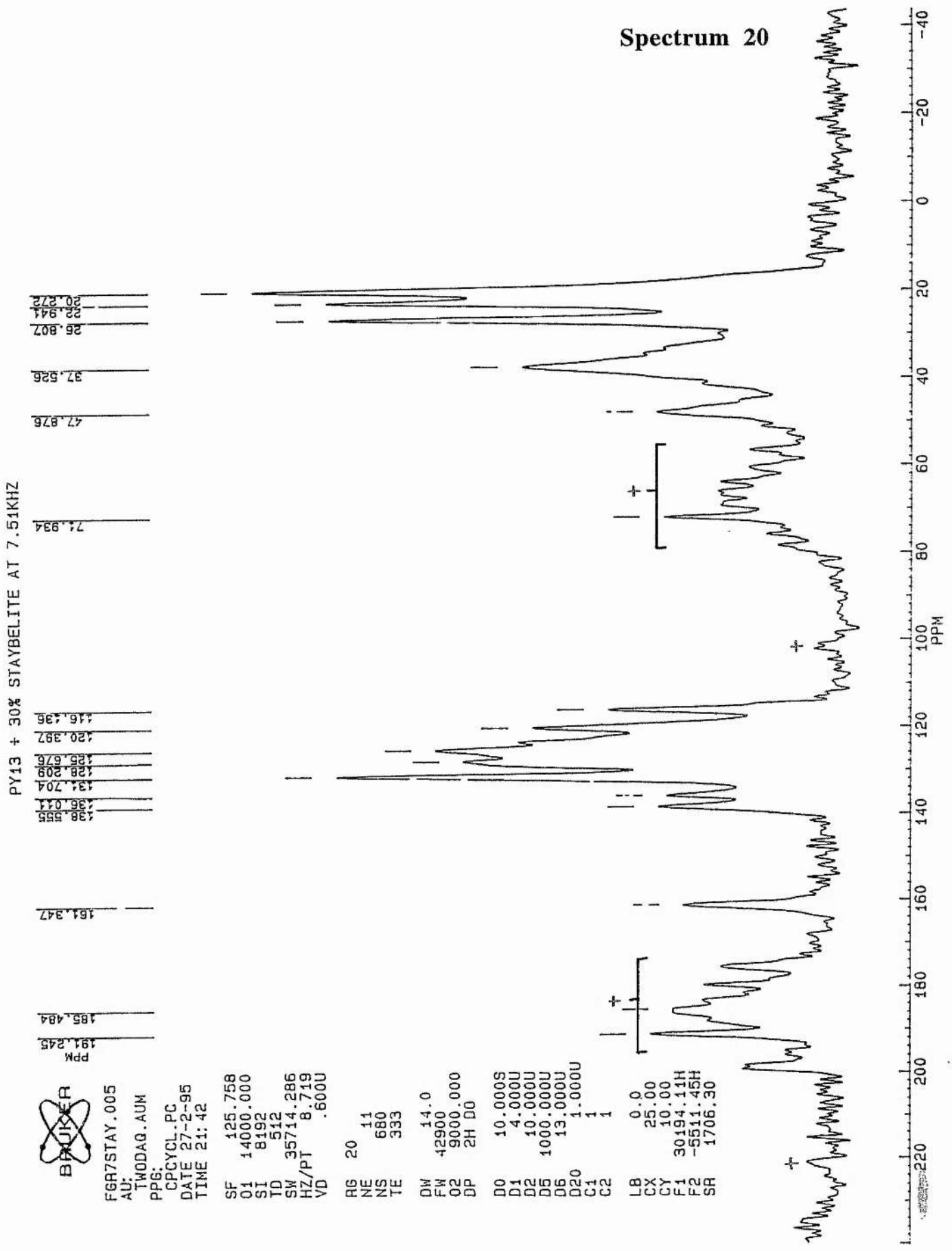
Spectrum 18


PY13 + 10% STAYBELITE AT 7.33KHZ
189.785
134.670
128.894
125.551
120.304
116.221
73.387
26.796
22.913
20.286
PPM
BRUKER
FGR7STAY.003
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 19-2-95
TIME 17:42
SF 125.758
O1 14000.000
SI 8192
TD 512
SW 35714.286
HZ/PT 8.719
VD .600U
RG 20
NE 11
NS 1048
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DO
DO 10.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 30159.23H
F2 -5546.33H
SR 1715.35

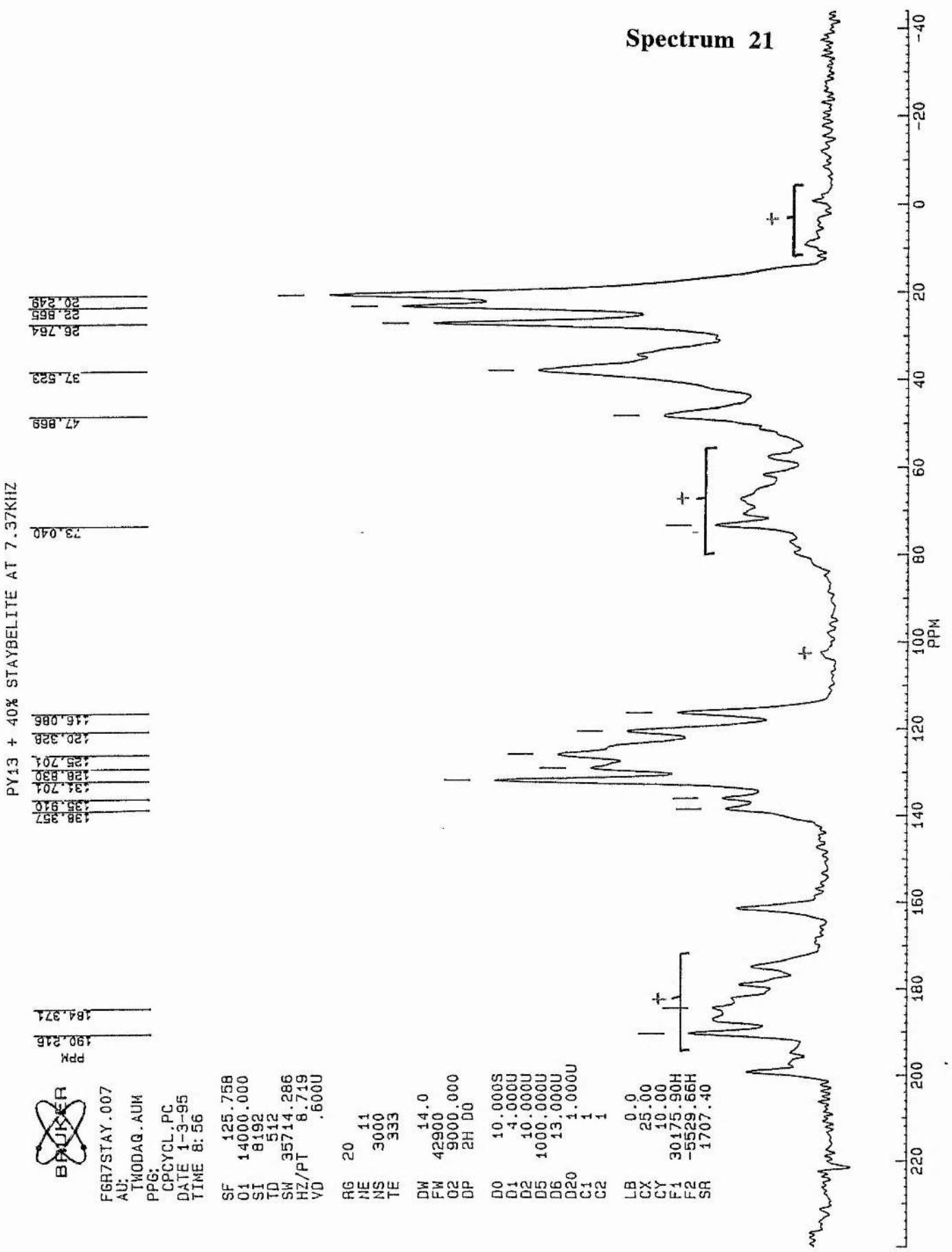
Spectrum 19

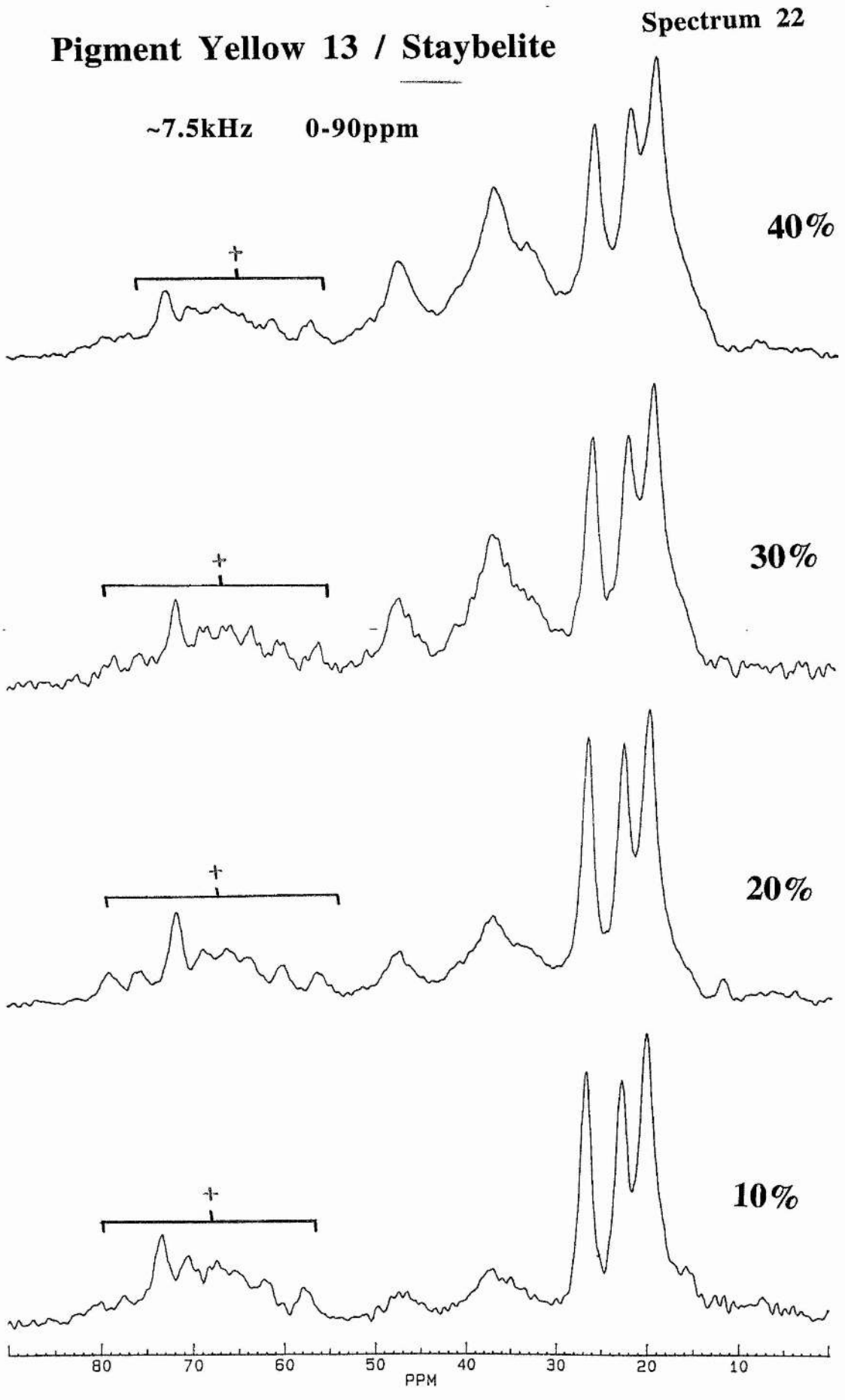

PY13 + 20% STAYBELITE AT 7.55KHZ
199.115
191.460
186.002
161.339
138.653
135.816
131.645
127.858
125.848
120.228
116.050
74.214
37.142
26.778
22.918
20.231
PPM
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
FGR7STAY.001
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 18-2-95
TIME 10:33
SF 125.758
O1 14000.000
SI 8192
TD 512
SW 35714.286
HZ/PT 8.719
VD .600U
RG 20
NE 1
NS 5368
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DO
D0 10.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 239.957P
F2 -43.966P
SR 1715.35

Spectrum 20

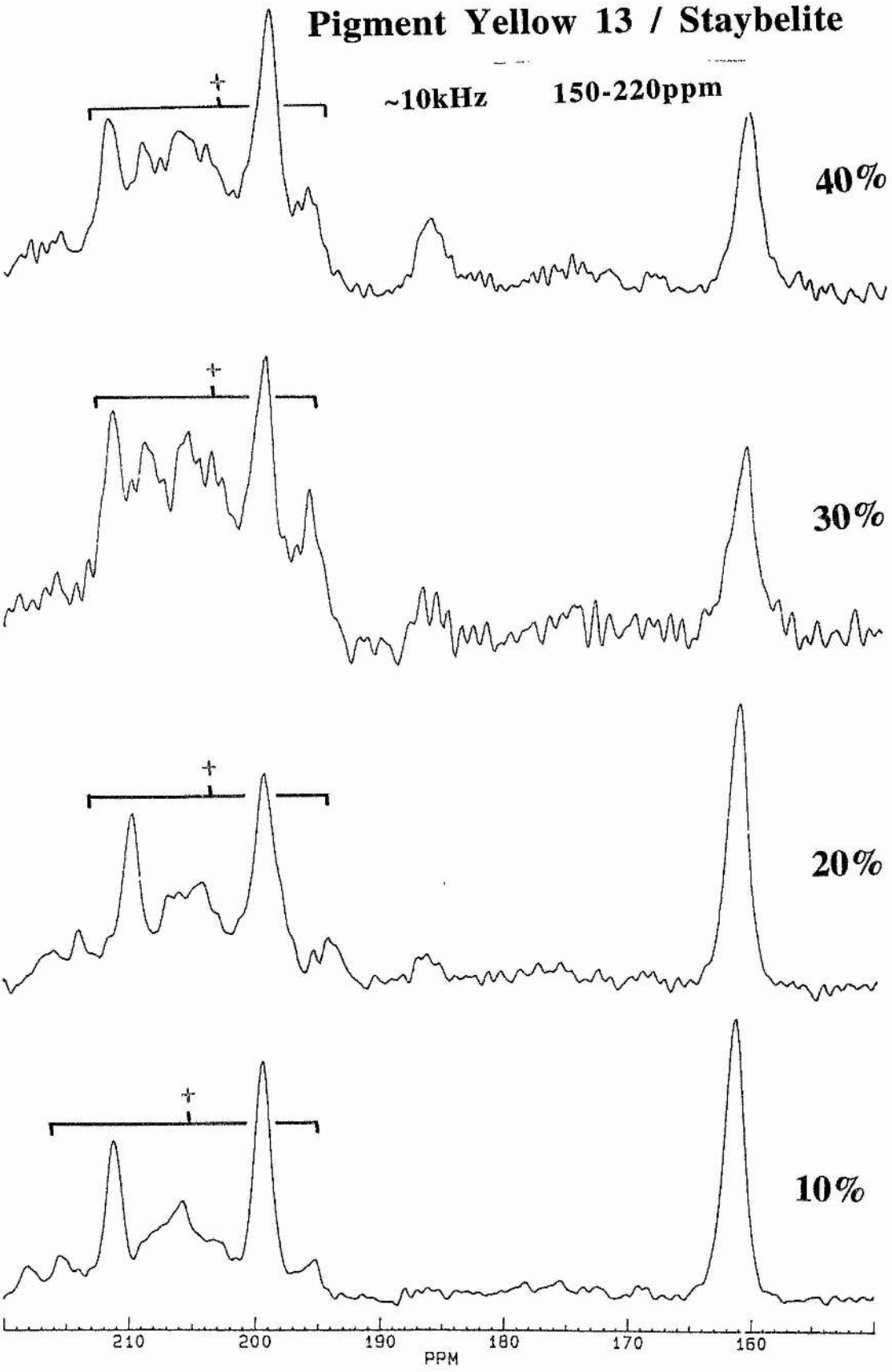

PY13 + 30% STAYBELITE AT 7.51KHZ
PPM
FGR7STAY.005
AU: TWODAQ.AUM
PPG: CPCYCL.PC
DATE 27-2-95
TIME 21:42
SF 125.758
O1 14000.000
SI 8192
TD 512
SW 35714.286
HZ/PT 8.719
VD .600U
RG 20
NE 11
NS 680
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H D0
D0 10.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 10.00
F1 30194.11H
F2 -5511.45H
SR 1706.30

Spectrum 21


PY13 + 40% STAYBELITE AT 7.37KHZ
FGR7STAY.007
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 1-3-95
TIME 8:56
SF 125.758
O1 14000.000
SI 8192
TD 512
SW 35714.286
HZ/PT 8.719
VD .600U
RG 20
NE 11
NS 3000
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DO
D0 10.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 10.00
F1 30175.90H
F2 -5529.66H
SR 1707.40
PPM
184.374
190.216
138.357
135.910
134.704
128.830
125.704
120.328
116.086
73.040
47.869
37.523
26.764
22.865
20.249
PPM


Spectrum 22
Pigment Yellow 13 / Staybelite
~7.5kHz 0-90ppm
40%
30%
20%
10%
80
70
60
50
40
30
20
10
PPM

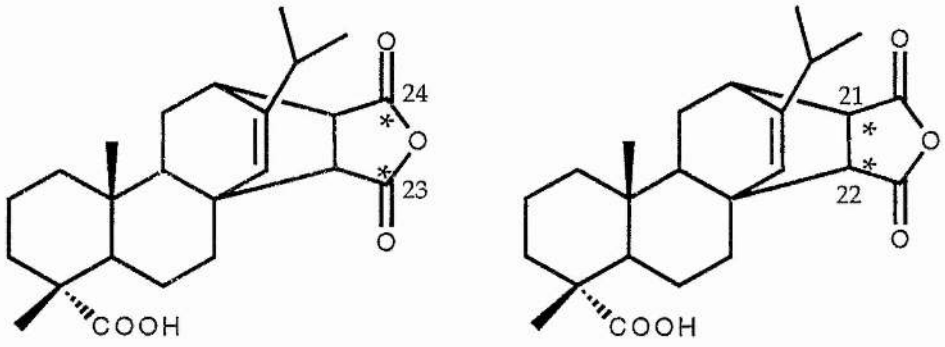
Spectrum 23


Pigment Yellow 13 / Staybelite
~10kHz
150-220ppm
40%
30%
20%
10%
210
200
190
180
170
160
PPM

Other Experiments

Apart from resinated Pigment Yellow 13 samples, there were other samples which were required to be run to complete the solid-state ^{13}C NMR study.

4.8 C-13 labelled maleopimaric acids



23,24-$^{13}C_2$ 21,22-$^{13}C_2$

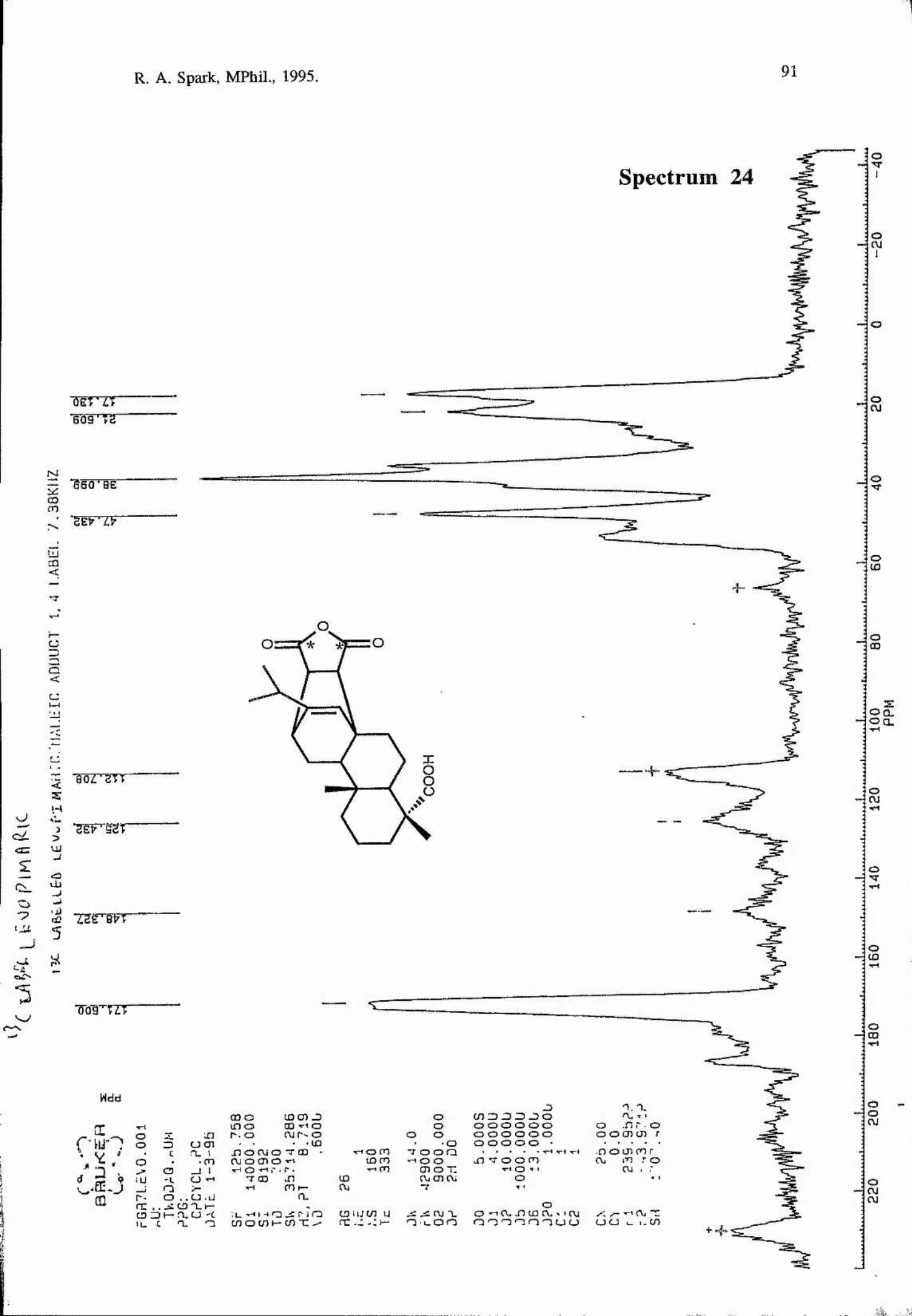
Fig. 4.5 C-13 labelled maleopimaric acids.

It is necessary to compare the spectra of the crude 23,24-$^{13}C_2$ and 21,22-$^{13}C_2$ labelled maleopimaric acid adducts with normal lab. synthesised maleopimaric acid (Spectrum 7). Both samples were prepared with 10% of the ^{13}C labelled maleic anhydride.

Spectrum 24 shows the adduct prepared from 1,4-$^{13}C_2$ maleic anhydride. The enhanced signals for C-23 and C-24 in the adduct are actually seen to merge at ~171ppm. Of course, recrystallisation of the labelled adduct would improve the resolution of the spectrum.

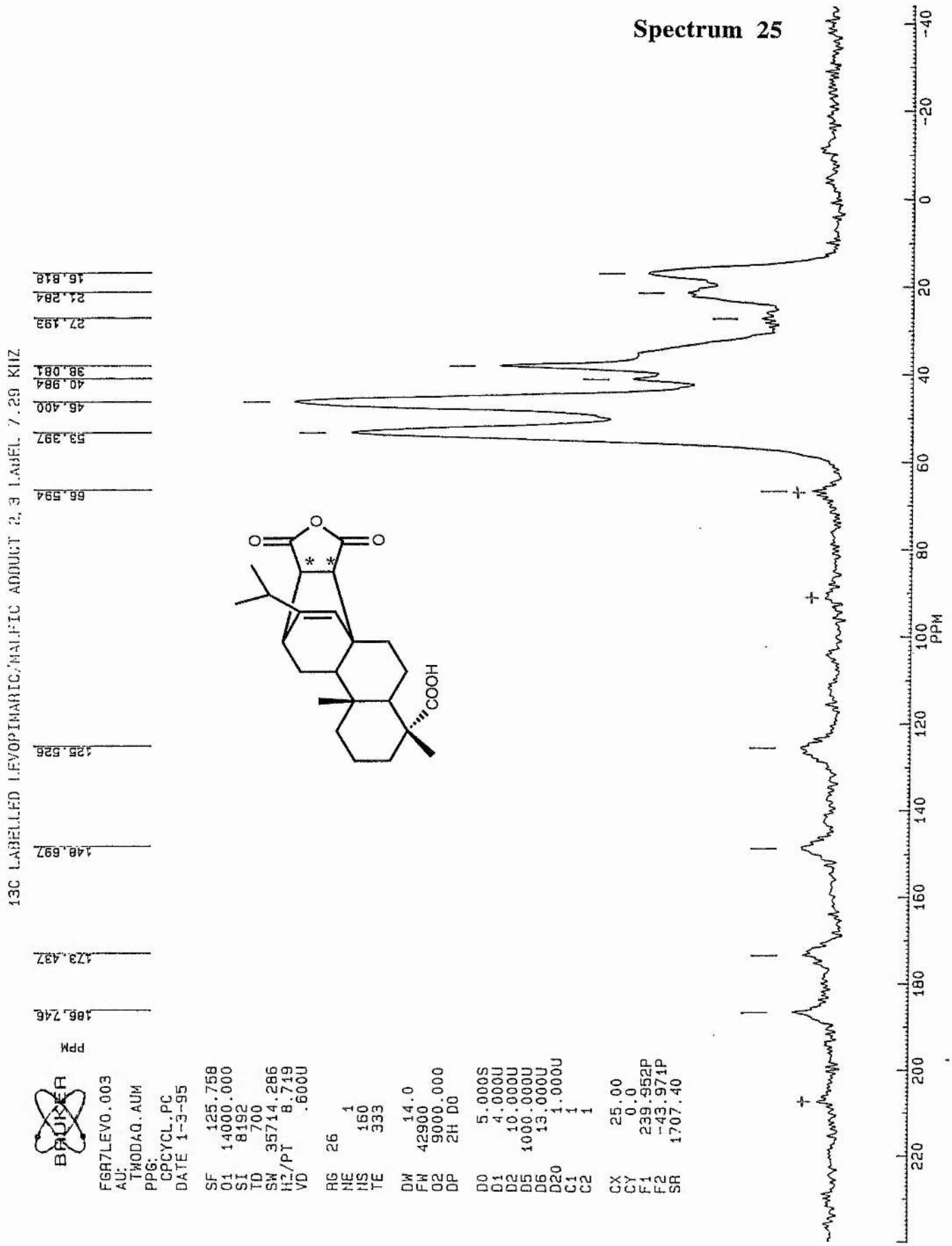
Spectrum 25 shows the adduct prepared from 2,3-$^{13}C_2$ maleic anhydride. The two enhanced signals for C-21 and C-22 in the adduct can be seen at 46.4 and 53.4ppm respectively.

Spectrum 24

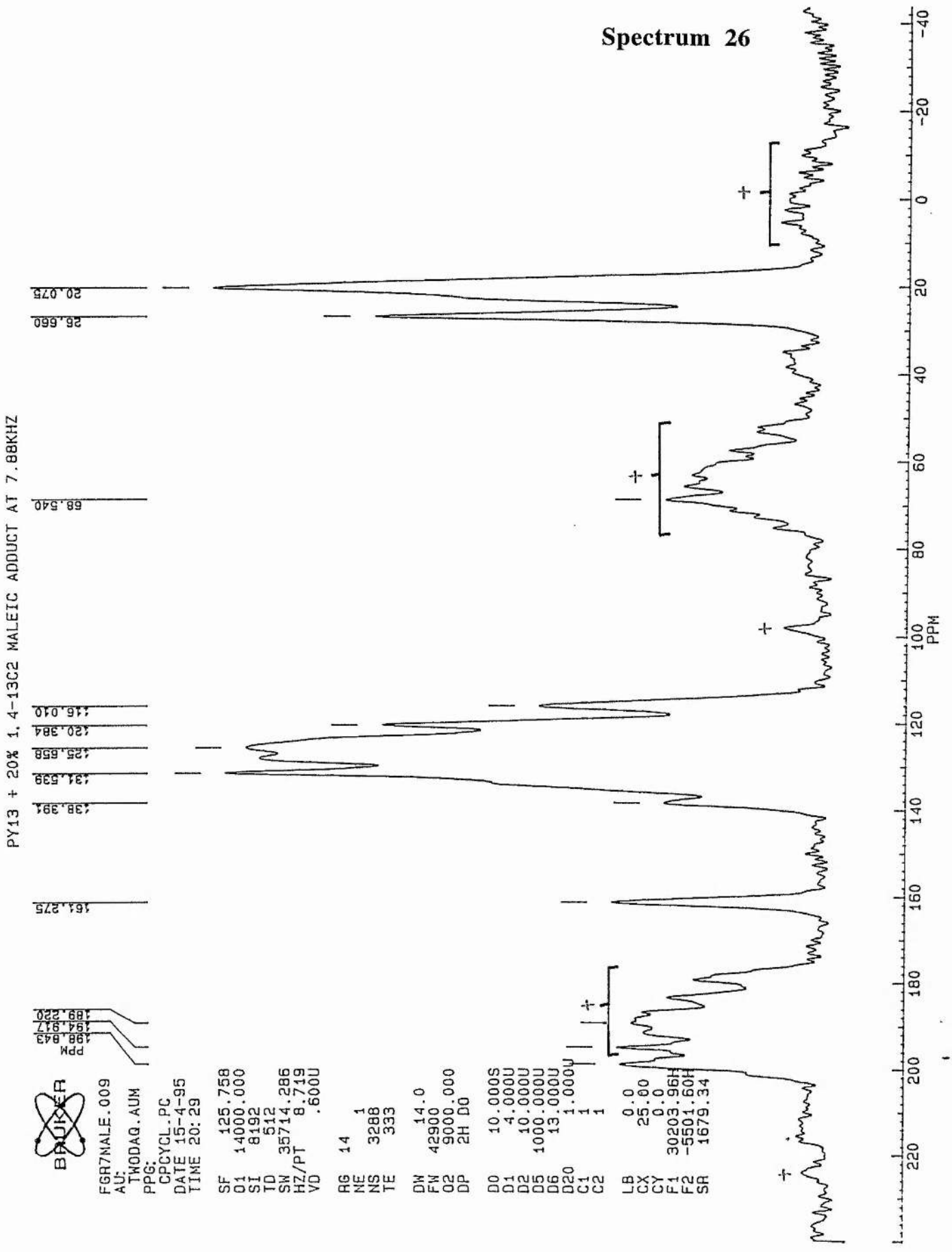


^{13}C LABEL LEVOPIMARIC

Spectrum 25


13C LABELLED LEVOPIMARIC/MALEIC ADDUCT 2,3 LABEL 7.29 KHZ
186.246
173.437
148.692
125.526
66.594
53.397
46.400
40.984
38.081
27.193
21.284
16.818
PPM
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
COOH
BRUKER
FGR7LEVO.003
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 1-3-95
SF 125.758
O1 14000.000
SI 8192
TD 700
SW 35714.286
HZ/PT 8.719
VD .600U
RG 26
NE 1
NS 160
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H D0
D0 5.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
CX 25.00
CY 0.0
F1 239.952P
F2 -43.971P
SR 1707.40

Spectrum 26


PY13 + 20% 1,4-13C2 MALEIC ADDUCT AT 7.88KHZ
PPM
198.843
194.917
189.220
164.275
138.391
131.539
125.658
120.384
116.010
68.540
26.660
20.075
FGR7NALE.009
AU: TWODAQ.AUM
PPG: CPCYCL.PC
DATE 15-4-95
TIME 20:29
SF 125.758
O1 14000.000
SI 8192
TD 512
SW 35714.286
HZ/PT 8.719
VD .600U
RG 14
NE 1
NS 3288
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DO
D0 10.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 30203.96H
F2 -5501.60H
SR 1679.34
PPM

The sample of P.Y.13 resinated with 20% of 23,24-$^{13}C_2$ labelled maleopimaric acid was run. It was already suspected that there would be no significant change noted, since the adduct is not retained during the resination. Spectrum 26 serves to confirm this belief. The pigment peaks remain broad, and there is no evidence of an enhanced signal for the labelled acid expected at ~171ppm.

4.9 P.Y.13 + 20% abietic acid added at end of heat treatment

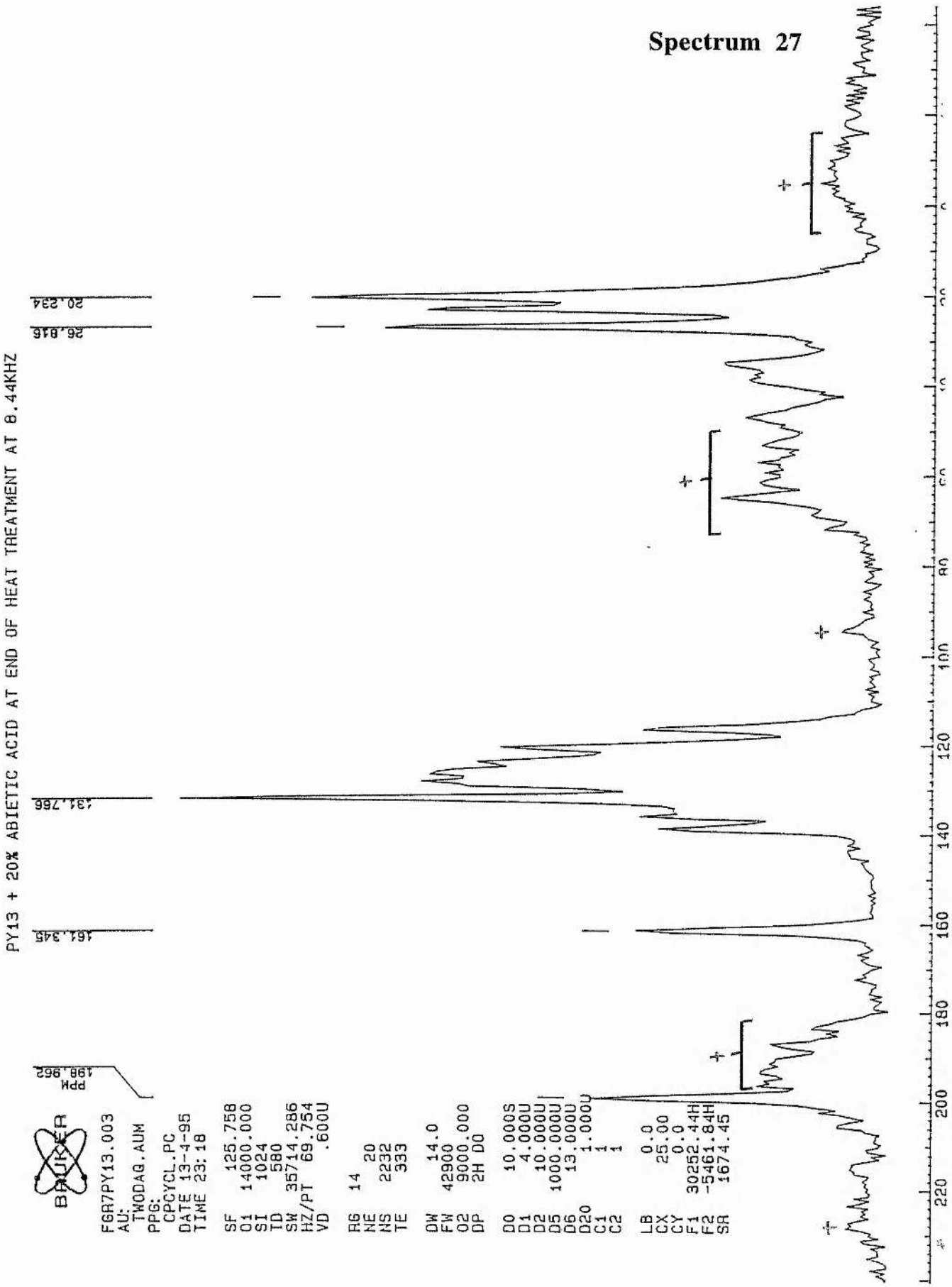
The purpose of this experiment was to assess if pigment crystallinity was enhanced, even when adding the abietic acid to the crude pigment crystals for a short time only. The heat treatment was continued as normal for 25 minutes, before adding the resin solution, reprecipitating the resin and stirring at 90-95°C for a further 5 minutes. During the 25 minutes of the heat treatment in the absence of any resin, pigment particle size was presumably increased.

Spectrum 27 shows that crystallinity has indeed been enhanced. It should be noted that the "development of colour", where the pigment slurry is normally observed to get brighter in colour, was only seen to occur after the abietic had been added and reprecipitated.

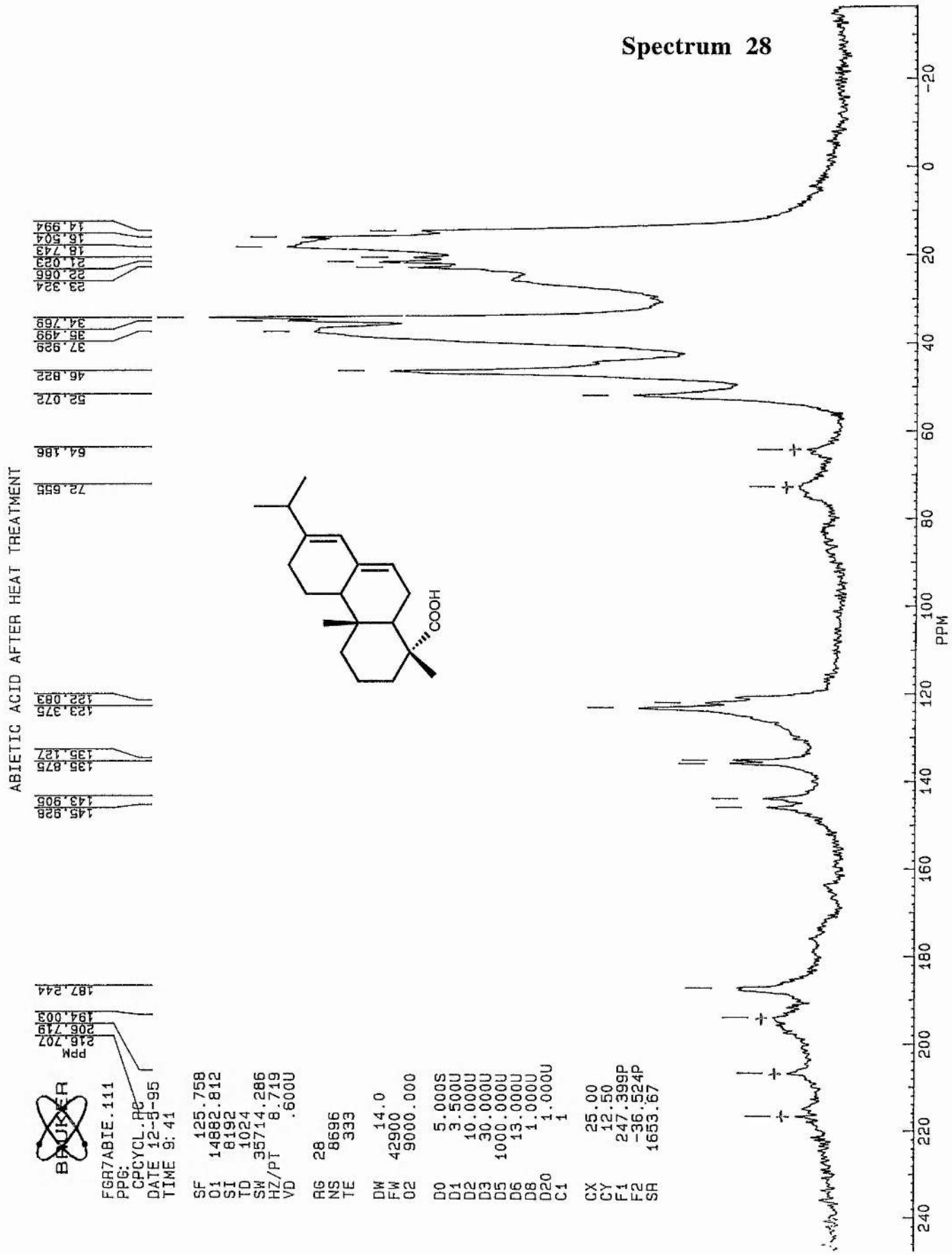
4.10 Form of resin acids after heat treatment

The physical and chemical states of the resin acids when precipitated on the pigment crystals needed to be evaluated. Solution NMR has already indicated that abietic acid and Staybelite are unchanged chemically, while Ennesin MU4 is chemically altered.

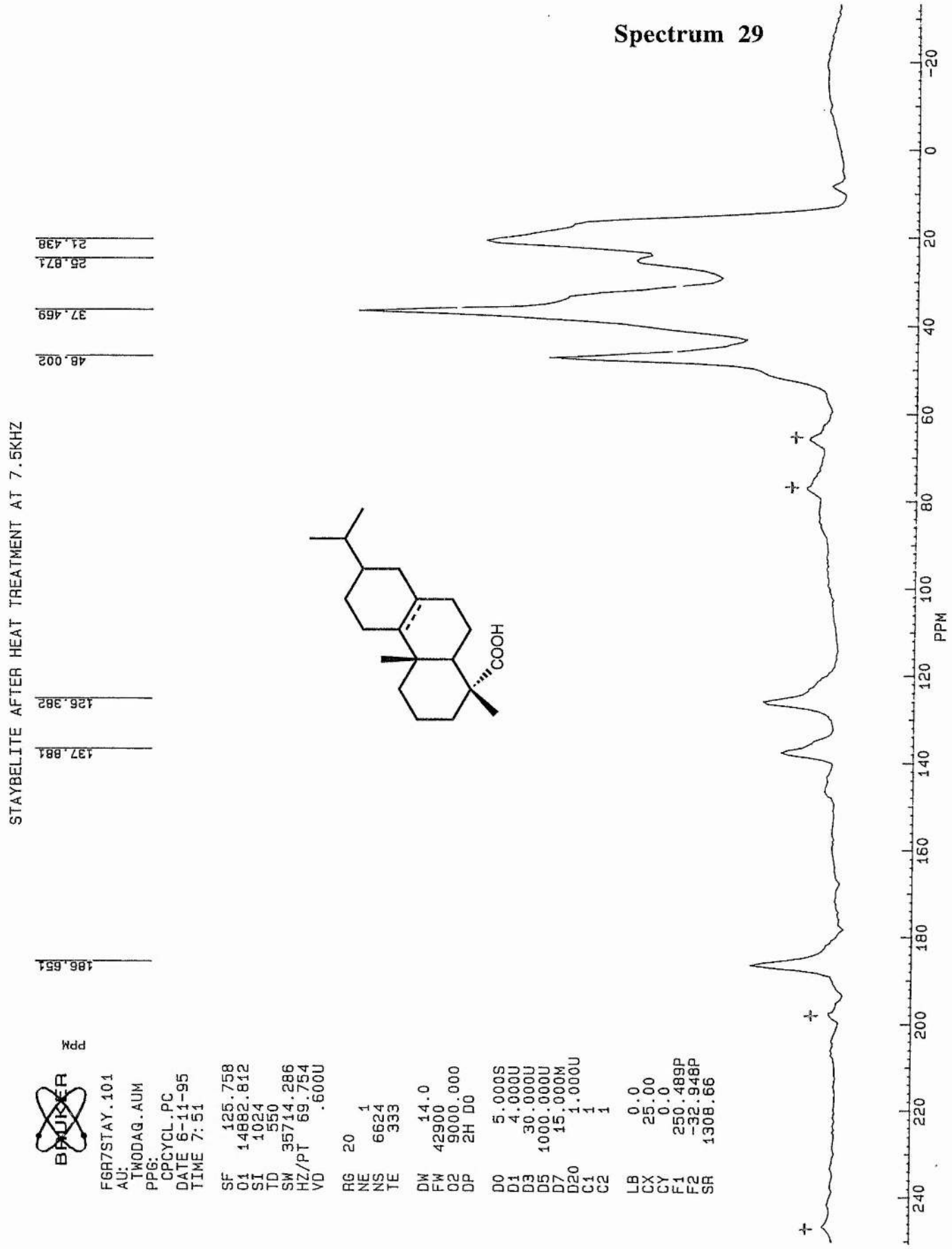
Spectrum 27


PY13 + 20% ABIETIC ACID AT END OF HEAT TREATMENT AT 8.44KHZ
198.962
161.345
131.766
26.846
20.234
BRUKER
FGR7PY13.003
AU: TWODAQ.AUM
PPG: CPCYCL.PC
DATE 13-4-95
TIME 23:18
SF 125.758
O1 14000.000
SI 1024
TD 580
SW 35714.286
HZ/PT 69.754
VD .600U
RG 14
NE 20
NS 2232
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DO
D0 10.000S
D1 4.000U
D2 10.000U
D5 1000.000U
D6 13.000U
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 30252.44H
F2 -5461.84H
SR 1674.45
PPM
220
200
180
160
140
120
100
80
60
40
20

Spectrum 28


ABIETIC ACID AFTER HEAT TREATMENT
BRUKER
FGR7ABIE.111
PPG:
CPCYCL.RE
DATE 12-5-95
TIME 9:41
SF 125.758
O1 14882.812
SI 8192
TD 1024
SW 35714.286
HZ/PT 8.719
VD .600U
RG 28
NS 8696
TE 333
DW 14.0
FW 42900
O2 9000.000
D0 5.000S
D1 3.500U
D2 10.000U
D3 30.000U
D5 1000.000U
D6 13.000U
D8 1.000U
D20 1.000U
C1 1
CX 25.00
CY 12.50
F1 247.399P
F2 -36.524P
SR 1653.67
COOH
PPM

Spectrum 29


STAYBELITE AFTER HEAT TREATMENT AT 7.5KHZ
186.651
137.881
126.382
48.002
37.469
25.871
21.438
COOH
PPM
FGR7STAY.101
AU: TWODAQ.AUM
PPG: CPCYCL.PC
DATE 6-11-95
TIME 7:51
SF 125.758
O1 14882.812
SI 1024
TD 550
SW 35714.286
HZ/PT 69.754
VD .600U
RG 20
NE 1
NS 6624
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DO
D0 5.000S
D1 4.000U
D3 30.000U
D5 1000.000U
D7 15.000M
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 250.489P
F2 -32.948P
SR 1308.66

Spectrum 28 shows a sample of abietic acid which has been subjected to the heat treatment process, in the absence of any pigment. Although the lines are broader than for the recrystallised sample (Spectrum 3), doubling of resonances in the solid-state is again observed, due to the presence of two independent molecules in the asymmetric unit cell.

When compared to the recrystallised abietic acid, the isolated acid appears to be much more amorphous because of the broad nature of all the signals. This would account for the broad abietic acid peaks noted in the spectra of the resinated pigments. We can conclude that recrystallised abietic acid is reprecipitated in a more amorphous physical form, the form which is coated on the pigment crystals.

Spectrum 29 shows a sample of Staybelite resin which has been subjected to the heat treatment. When compared to commercial Staybelite in Spectrum 9, broader and less well resolved signals again indicate a more amorphous product. There are several well resolved shoulders in Spectrum 9 which are not present for the isolated acid. The difference is not as marked as for abietic acid, but this is because the starting Staybelite is crude anyway, while the inputted abietic acid is recrystallised.

4.11 **Recrystallised P.Y.13 + 40% abietic acid**

One last experiment was carried out to complete the NMR study. What would be the effect of resinating previously recrystallised Pigment Yellow 13? It would be interesting to find out if crystallinity was enhanced further by the resination process. 1,2,4-Trichlorobenzene (b.p. 214°C) was used to recrystallise P.Y.13 (m.p. 351-353°C).

An aqueous slurry of recrystallised P.Y.13 was prepared, and adjusted to pH10. A solution of abietic acid (40% by weight of P.Y.13) in aqueous NaOH was made up with heat and stirring. The resin solution was added to the P.Y.13 aqueous slurry at pH10. The mixture was heated to 95°C, and the pH was adjusted to 7.0 to

reprecipitate the resin. The mixture was stirred for 30 minutes at 90-95°C, before allowing to cool to 70°C. The resinated sample was filtered, washed with water and dried at 70°C overnight.

The isolated product was peachy pink in colour, rather than the intense orange of the recrystallised Pigment Yellow 13. This dramatic loss of colour strength can be explained: there is a relationship between particle size and colour strength, whereby the colour strength decreases rapidly with increasing particle size. Maximum colour strength is achieved with a particle size of 0.01 to 0.1microns.

Crude pigment particles are very small and so have a huge surface area, whereas recrystallised pigment crystals are comparatively large and so have a very much smaller surface area. Therefore, crude pigment particles will have a thin layer of coated resin while the recrystallised particles will have a thick layer.

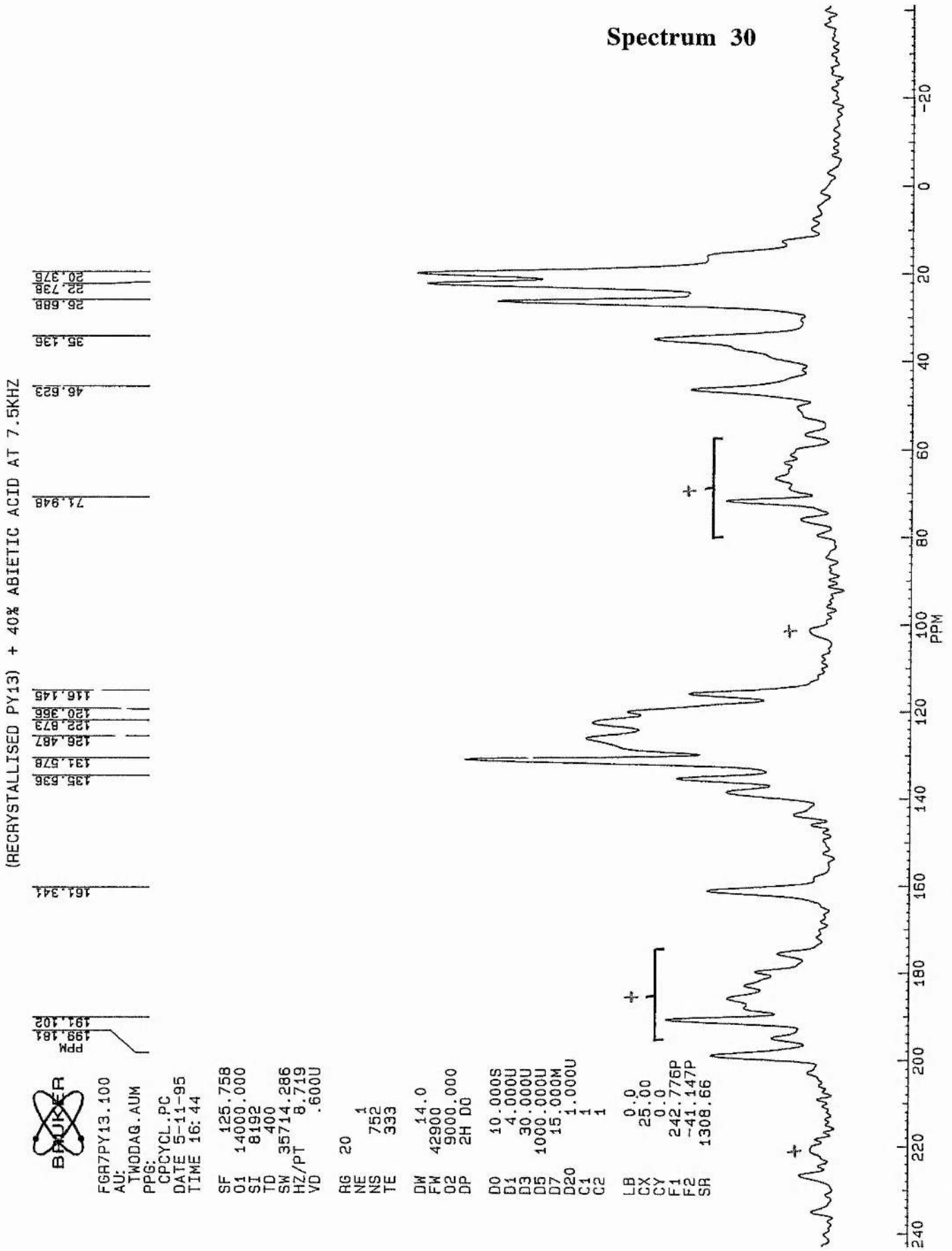
With the smaller pigmented particles, the incident light is not greatly hindered by the resin layer and almost all of the light is reflected by the pigment crystals. For the larger pigmented particles, much of the incident light is absorbed or reflected by the resin layer, diluting the colour.

It should be noted that when a portion of the recrystallised P.Y.13 was added to chloroform, the resin was dissolved and the bright orange pigment crystals reappeared.

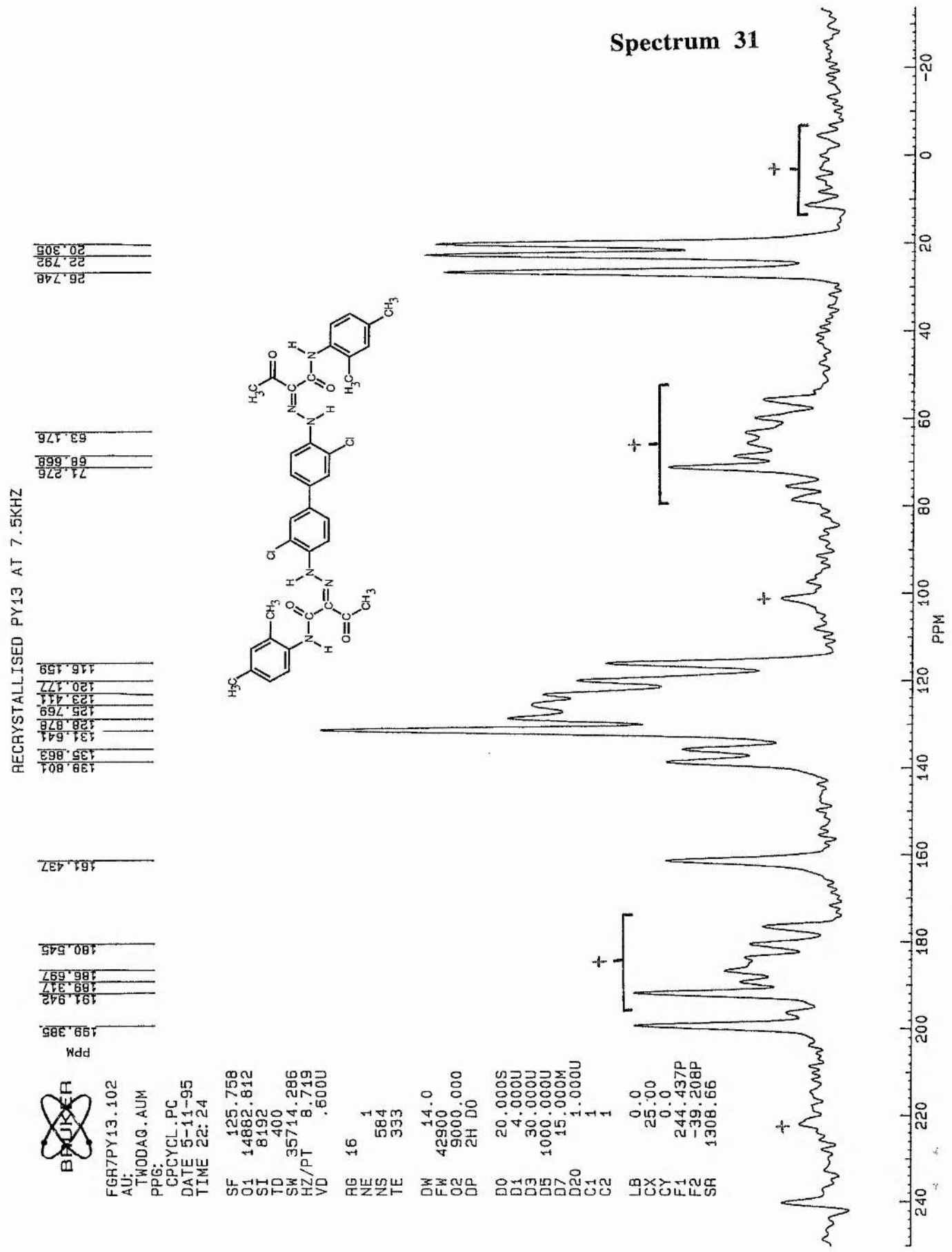
Spectrum 30 shows the recrystallised P.Y.13 coated with 40% abietic acid. The inputted recrystallised P.Y.13 used in this experiment can be seen in Spectrum 31. However, a comparison is difficult due to the abietic acid peaks which overlap the pigment peaks in Spectrum 30.

Therefore, it was necessary to carry out a powder X-ray diffraction experiment to make a conclusion, in the hope that there may be some observable difference.

Spectrum 30


(RECRYSTALLISED PY13) + 40% ABIETIC ACID AT 7.5KHZ
191.102
199.181
PPM
161.341
135.536
134.578
126.487
122.873
120.366
116.145
74.948
46.623
35.136
26.688
22.738
20.378
BRUKER
FGR7PY13.100
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 5-11-95
TIME 16:44
SF 125.758
O1 14000.000
SI 8192
TD 400
SW 35714.286
HZ/PT 8.719
VD .600U
RG 20
NE 1
NS 752
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DO
D0 10.000S
D1 4.000U
D3 30.000U
D5 1000.000U
D7 15.000M
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 242.776P
F2 -41.147P
SR 1308.66
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
PPM

Spectrum 31


RECRYSTALLISED PY13 AT 7.5KHZ
199.385
191.942
189.317
186.697
180.545
161.437
139.801
135.863
131.641
128.878
125.769
123.441
120.177
116.159
74.276
68.668
63.176
26.748
22.792
20.305
PPM
BRUKER
FGR7PY13.102
AU:
TWODAQ.AUM
PPG:
CPCYCL.PC
DATE 5-11-95
TIME 22:24
SF 125.758
O1 14882.812
SI 8192
TD 400
SW 35714.286
HZ/PT 8.719
VD .600U
RG 16
NE 1
NS 584
TE 333
DW 14.0
FW 42900
O2 9000.000
DP 2H DO
D0 20.000S
D1 4.000U
D3 30.000U
D5 1000.000U
D7 15.000M
D20 1.000U
C1 1
C2 1
LB 0.0
CX 25.00
CY 0.0
F1 244.437P
F2 -39.208P
SR 1308.66

5 POWDER X-RAY DIFFRACTION STUDIES

Powder X-ray diffraction data were collected on a STOE Stadi diffractometer. The samples were mounted in 0.5mm glass capillaries and the detector was programmed to collect data within a suitable scattering angle range in 0.5° increments. The detector range used and the length of time at each increment varied according to the sample.

5.1 Crude / recrystallised Pigment Yellow 13

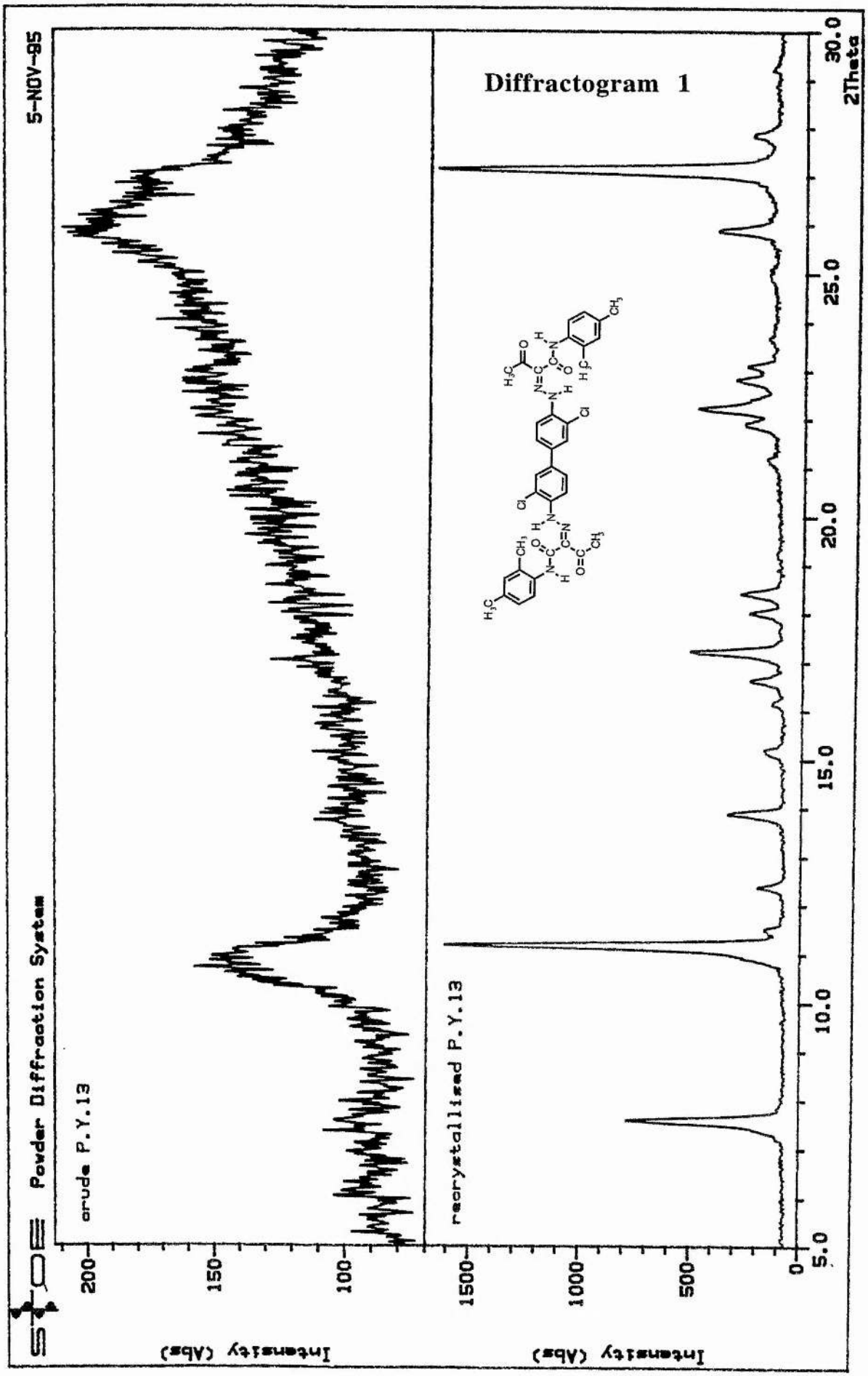
Diffractogram 1 shows the diffraction pattern obtained for crude P.Y.13 and also P.Y.13 recrystallised from 1.2.4-trichlorobenzene . Crude P.Y.13 gives a similarly crude diffraction pattern, containing two broad amorphous humps and a noisy baseline.

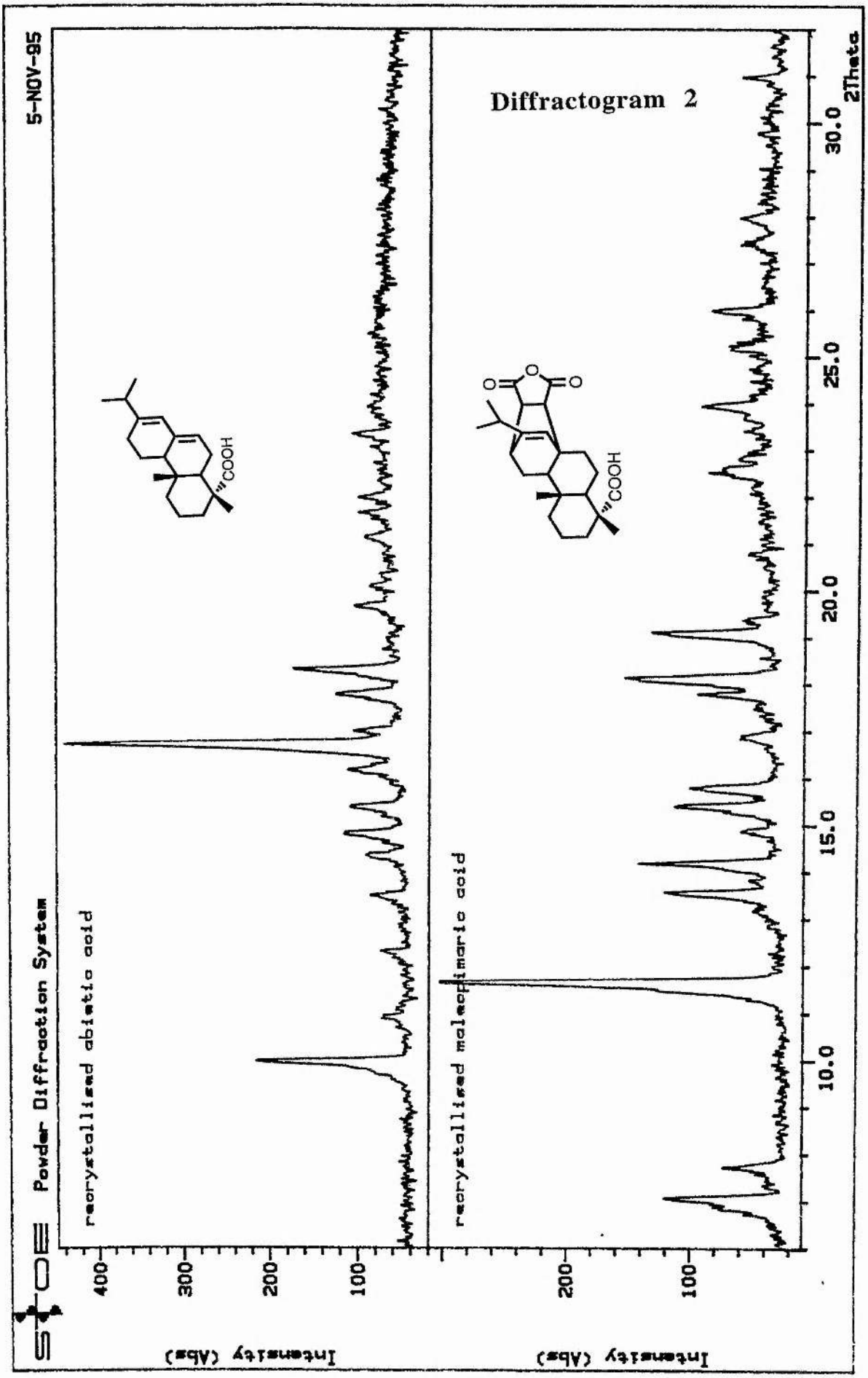
When running recrystallised P.Y.13 under the same conditions, a remarkable transformation has occurred. Three intense sharp peaks are observed, as well as several smaller peaks. The two largest peaks, with scattering angles of 11° and 27°, do not exactly correspond to the maxima of the two amorphous humps for the crude sample, although an approximate correlation is observed.

5.2 Abietic acid and maleopimaric acid

Diffractogram 2 shows the patterns obtained for abietic acid recrystallised from aqueous ethanol and maleopimaric acid recrystallised from acetic acid. These are provided for information only, and provide a useful "fingerprint" for the acids.

Abietic acid has a maximum absorbance at a scattering angle of 16.5°, while maleopimaric acid has a maximum at 11.5°.


Diffractogram 1
5-NOV-95
Powder Diffraction System
crude P.Y.13
recrystallised P.Y.13
Intensity (Abs)
Intensity (Abs)
2Theta
200
150
100
1500
1000
500
0
5.0
10.0
15.0
20.0
25.0
30.0


Diffractogram 2
STOE Powder Diffraction System
5-NOV-95
recrystallised abietic acid
recrystallised maleopimaric acid
COOH
COOH
Intensity (Abs)
Intensity (Abs)
2Theta
10.0
15.0
20.0
25.0
30.0
100
200
300
400

5.3 Resinated Pigment Yellow 13

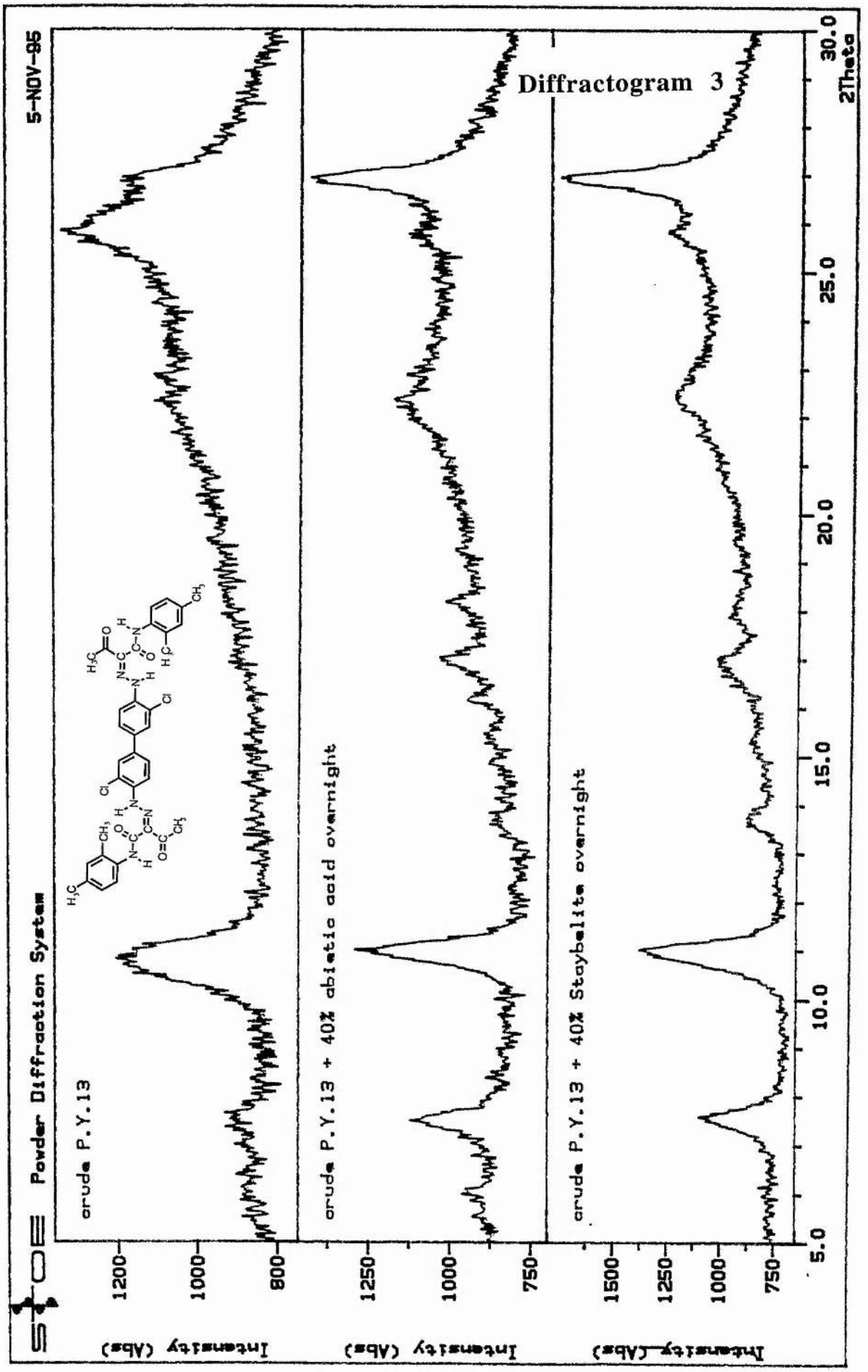
Resinated samples of P.Y.13 were then examined by powder XRD, to assess any effect on crystallinity of the pigment crystals. As we have seen already, recrystallisation of the crude pigment results in a much better defined diffraction pattern. However, when recrystallising resinated P.Y.13 the resin is lost and solely recrystallised P.Y.13 is obtained.

Therefore, samples of crude P.Y.13 resinated with 40% loadings of abietic acid and Staybelite resin were run for 15 hours and compared with crude P.Y.13 run for a similar time. The results of the experiment are seen in Diffractogram 3.

The diffraction patterns for the resinated samples are clearly better resolved and so are more crystalline in nature, or less amorphous. It is interesting to note that the amorphous hump for the crude P.Y.13, at a scattering angle of 26°, is lost after resination. But all other peaks are sharper and better defined, and small peaks are seen to appear from the baseline. Especially noticeable is the appearance of a sizeable peak at a scattering angle of 7.5°, which is where one of the larger peaks in recrystallised P.Y.13 occurs.

It should be pointed out that all the peaks present in the patterns of the resinated P.Y.13 samples correspond to P.Y.13 itself, and not the resin acids.

This result confirms those found by ^{13}C CP/MAS NMR i.e. that degree of crystallinity in the pigment crystals is enhanced in the presence of resin acids.


Diffractogram 3
STOE Powder Diffraction System
5-NOV-95
crude P.Y.13
crude P.Y.13 + 40% abietic acid overnight
crude P.Y.13 + 40% Staybelite overnight
Intensity (Abs)
2Theta
5.0
10.0
15.0
20.0
25.0
30.0

5.4 Form of resin acids after heat treatment

The purpose of this experiment was to try to determine what happens to the physical form of the resin acids, when they are processed through the heat treatment in the absence of any pigment. This should reflect the form of the resin acids when coated on the pigment crystals during resination. Solid-state NMR studies carried out previously suggest the resin acids are more amorphous when reprecipitated during the resination process.

Diffractogram 4 shows a sample of abietic acid isolated after the heat treatment, as well as a sample of recrystallised abietic acid used as starting material for the experiment. The reprecipitated abietic acid is indeed much more amorphous than the starting material, as evidenced by the lack of definition in the diffraction pattern.

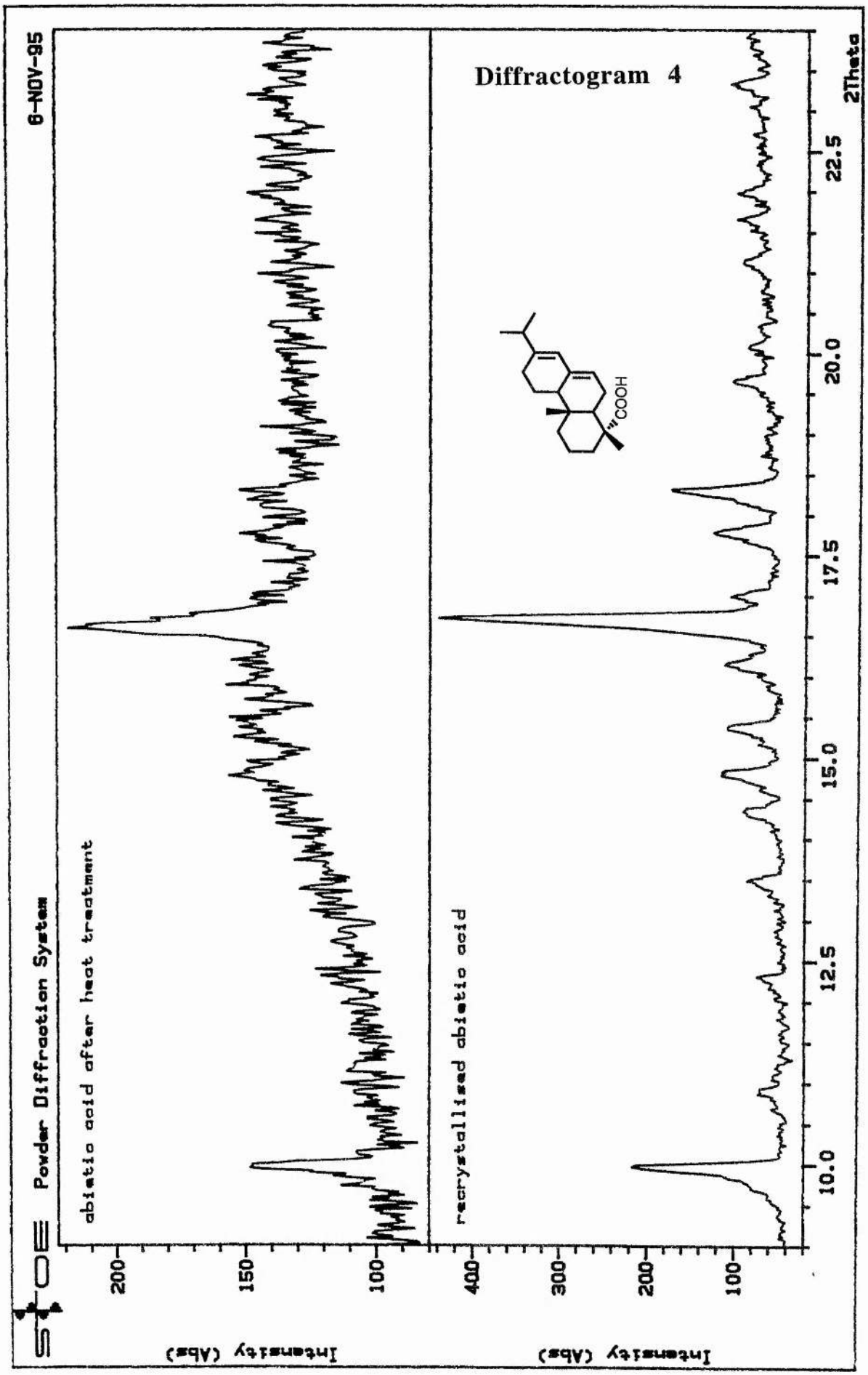
It is considered pointless to carry out this study with Staybelite resin, since commercial Staybelite is amorphous anyway, and so the diffraction patterns obtained would be difficult to compare.

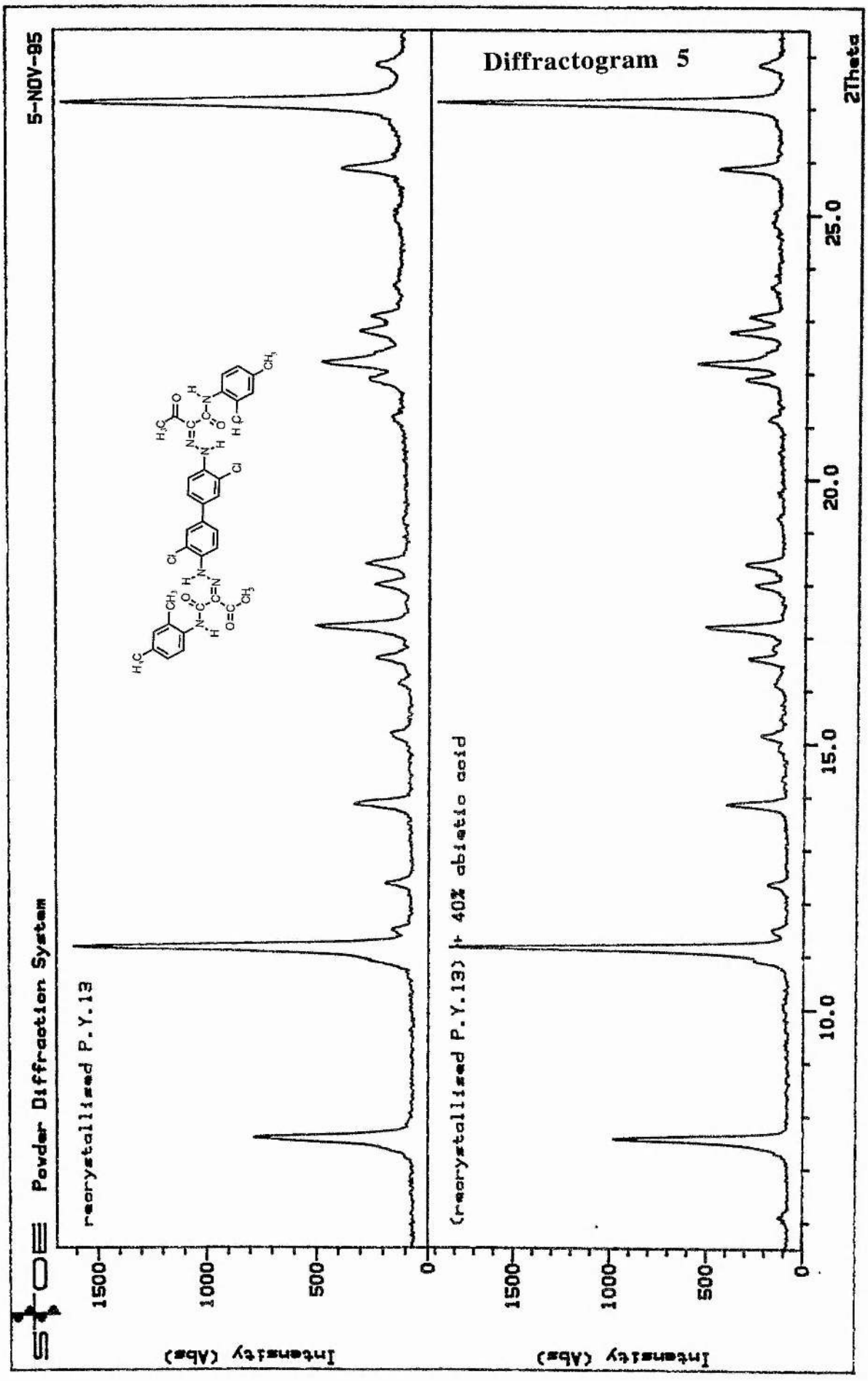
5.5 Recrystallised P.Y.13 + 40% abietic acid

No conclusion was made after the solid-state NMR study due to the abietic acid peaks overlapping the pigment peaks. It is useful then that the abietic acid peaks do not appear to obscure X-ray diffraction patterns of the resinated pigments.

The results of this study can be seen in Diffractogram 5. The resinated recrystallised P.Y.13 gives a diffraction pattern which is slightly better resolved when compared with the pattern for the pigment itself. This is clearly seen within a scattering angle range of 21.5 to 23.5°; the peaks are sharper and the wells are deeper. The improved sharpness of the shoulder on the peak at 11° also serves to make this point.

So, even when starting with crystalline Pigment Yellow 13, the crystallinity in the pigment crystals is further enhanced.


Diffractogram 4
STOE Powder Diffraction System
6-NOV-95
abietic acid after heat treatment
recrystallised abietic acid
COOH
Intensity (Abs)
2Theta
10.0
12.5
15.0
17.5
20.0
22.5
100
150
200
300
400


Diffractogram 5
STOE Powder Diffraction System
5-NOV-95
recrystallised P.Y.13
(recrystallised P.Y.13) + 40% abietic acid
Intensity (Abs)
2Theta
0
500
1000
1500
10.0
15.0
20.0
25.0

6 CONCLUSION

It appears, both from solid-state ^{13}C CP/MAS NMR and powder X-ray diffraction (XRD) studies, that the resins applied to pigments industrially to improve their characteristics have a profound effect on their crystallisation. Whereas the heat treatment enhances pigment crystal size, resination serves to improve crystallinity, or degree of order, within the pigment crystals. This knowledge is in addition to what is traditionally understood about the resination process; limitation of aggregation and agglomeration and the subsequent benefits of smaller particle size, improvement of dispersibility in liquid media and reduction in interfacial tension.

Increased sharpness and resolution seen in both solid-state ^{13}C NMR spectra and powder XRD diffraction patterns of resinated Pigment Yellow 13 samples was a good indication of improved crystallinity of the pigment crystals.

Even when a recrystallised Pigment Yellow 13 sample is resinated, a further increase in pigment crystal order is observed in the resinated sample.

The mechanism of this improved crystal order is uncertain, although a physical phenomenon could be responsible, where the resin layer applies a degree of pressure on the pigment crystals to reduce volume and so increase order.

It is a popular theory that the carboxylic acid group of the resin acids takes part in some chemical interaction with the pigment molecule. In the solid-state ^{13}C NMR spectra of Pigment Yellow 13 resinated with Staybelite resin, a peak is seen to emerge with a chemical shift which is accountable to the carboxylic acid carbon of the Staybelite resin.

Also, in the XRD diffractograms for resinated Pigment Yellow 13, there are no peaks present which can not be allocated to either P.Y.13 or the resin acid.

These observations would seem to conclusively prove that there is no chemical interaction between the carboxylic acid of the resin acids and the pigment molecule, but merely a physical coating of resin on to the pigment particles.

Lines observed for the resins in solid-state ^{13}C NMR spectra of resinated Pigment Yellow 13 samples appear to be broader than those seen in spectra for the resins themselves. This result is confirmed by powder XRD. where a sample of abietic acid subjected to the heat treatment in the absence of any pigment gave a diffraction pattern much more amorphous than that observed for the starting abietic acid.

It would appear, therefore, that the resin acids, when reprecipitated and applied to the pigment, are physically more amorphous in nature i.e. their molecules are arranged in a relatively random fashion on the pigment particles. This may be a consequence of the relatively harsh caustic conditions experienced during the resination process.

Lastly, it is unfortunate that attempts to synthesise a useful ^{13}C labelled resin acid analogue were unsuccessful.

Initial investigations, to carry out a Barton reaction to provide a ^{13}C labelled carboxylic acid group in abietic acid, proved difficult in the model compound due to steric hindrance, and so would be impossible in abietic acid itself due to further steric effects.

The two ^{13}C labelled resin acid analogues which were synthesised, ^{13}C labelled maleopimaric acids, were washed out during the resination process, so no label was retained and no information was gained. Attempts to overcome this by synthesising a more stable analogue, from *N*-methylmaleimide rather than maleic anhydride, were only partially successful. Conversion from maleic anhydride to *N*-methylmaleimide was low, but this was to no avail since the Diels-Alder reaction between isomerised abietic acid and *N*-methylmaleimide did not proceed.

Diazald esterification of various molecules, with a view to introducing a ^{13}C-Me labelled group, proved to be difficult also.

7 EXPERIMENTAL

Melting points were carried out on a Gallenkamp melting point apparatus. Infra Red spectra were recorded on a Perkin Elmer 1310IR spectrophotometer and ^{1}H and ^{13}C NMR solution spectra were recorded on a Varian Gemini 200 NMR spectrometer, operating at 200MHz and 50MHz for ^{1}H and ^{13}C respectively.

1-Methylcyclohexanol

The Grignard reagent was prepared by reacting magnesium turnings (24.30g, 1mol.) and methyl iodide (141.94g, 1mol.) in ether (60ml), under nitrogen. Freshly distilled cyclohexanone (52.36g, 0.53mol.) in ether (50ml) was added to the prepared Grignard reagent. Further ether (80ml) was necessary to mobilise the reaction. After refluxing for 1 hour, the reaction mixture was poured onto 2M H_2SO_4 in crushed ice (400g). The separated aqueous layer was washed twice with ether. The combined ether was dried over $MgSO_4$, evaporated under reduced pressure and purified by Vigreux distillation. Yield 45.94g (75.4%), b.p. 61°C/16mmHg, m.p. 24-26°C, IR νmax 2850cm^{-1} (C-H), 3340cm^{-1} (broad, O-H), NMR ($CDCl_3$) δ_H 1.5 (10H, m, cyclic aliphatics), 1.05 (3H, s, CH_3).

1-Bromo-1-methylcyclohexane

1-Methylcyclohexanol (40.0g, 0.35mol.) was stirred vigorously with 48.5% hydrobromic acid (400ml). The mixture was extracted with ether and washed with water. The ether was dried over $MgSO_4$, evaporated under reduced pressure and the product was purified by Vigreux distillation. Yield 50.52g (81.4%), b.p. 56°C/16mmHg, IR ν_{max} 2850cm^{-1} (C-H), 750cm^{-1} (C-Br), NMR ($CDCl_3$) δ_H 1.8 (3H, s, CH_3), 1.6 (10H, m, cyclic aliphatics).

1-Methyl-1-cyclohexanecarboxylic acid

Conc. formic acid (3ml) was added dropwise to conc. sulphuric acid (392g, 4mol.) with vigorous stirring at 15-20°C to generate carbon monoxide. Freshly distilled 2-methylcyclohexanol (28.5g, 0.25mol.) in formic acid (46g, 1mol.) was added over 1 hour, during which time vigorous foaming of CO occurred. The mixture was stirred for 1 hour at 15-20°C and poured onto crushed ice (1Kg) with stirring. The acid separated as a white solid and was taken up in hexane (200ml). The separated aqueous layer was washed with hexane (2x150ml). The combined hexane layers were extracted with a mixture of 1.4M KOH (175ml) and crushed ice (50g) twice. The combined alkaline aqueous layer was extracted with hexane (100ml) and acidified with conc. HCl to pH2. The liberated carboxylic acid was taken up in hexane (150ml). The aqueous layer was washed with hexane (100ml). The combined hexane layers were washed with water, dried over $MgSO_4$, evaporated under reduced pressure and purified by Vigreux distillation. Yield 27.03g (76.2%), b.p. 125°C/20mmHg, m.p. 35-37°C, IR ν_{max} 2950cm^{-1} (C-H), 3000cm^{-1} (broad, COOH), NMR ($CDCl_3$) δ_H 1.4 (10H, m, cyclic aliphatics), 1.2 (3H, s, CH_3).

Pigment Yellow 13

A solution of AAMX (62.5g, 0.305mol.) in 47% NaOH (27.5g) and water (440ml) was prepared. A solution of glacial acetic acid (23.4g) in water (83ml) was added dropwise to adjust the mixture to pH6, with vigorous stirring,to re-precipitate the AAMX. The mixture was stirred for 15 minutes before cooling with ice to 16°C. Meanwhile, a solution of DCB tetrazo (~11%; 361.1g, 0.14mol.) was cooled with ice. A little sulphamic acid was added to the DCB tetrazo to eliminate nitrite. DCB tatrazo was added to the AAMX via a peristaltic pump, maintaining the temperature at 16°C. The pH was kept at 4.8 throughout by the addition of a solution of 47% NaOH (50g) in water (150ml). Towards the end of the coupling reaction, the mixture was checked for excess DCB tetrazo with a solution of 'H'-acid (4-amino-5-hydroxy-2,7-naphthalene disulphonic acid). The coupling took one hour, after which the mixture

was allowed to stir for 90 minutes, while warming naturally to room temperature, before adjusting the pH to 6.0 with 47% NaOH. The prepared P.Y.13 was stored as an aqueous slurry at pH 6.0. A quantitative amount of P.Y.13 was produced i.e. ~97g.

Resinated Pigment Yellow 13 (general procedure)

Pigment Yellow 13 aqueous slurry (containing ~9.7g P.Y.13) was stirred, and adjusted to pH10 with dil. NaOH. Meanwhile, a solution of resin acid;

A	0.97g	(10% by weight of P.Y.13)
B	1.94g	(20%)
C	2.91g	(30%)
D	3.88g	(40%)

in water (~40ml) and 47% NaOH (few drops) was made up with heat and stirring. The hot resin solution was added to the P.Y.13 slurry at pH10, which retains the resin in solution. Steam was applied directly to the mixture until a temperature of 95°C was reached, at which point dil. HCl was added to pH7.0 to precipitate the resin. Stirring was continued at 90-95°C for 30 minutes. After allowing to cool to 70°C, the resinated product was filtered under vacuum and washed with water until salt free (conductivity < 250μs). The product was oven dried at 70°C overnight. Yields and total resin contents of the resinated products are reported in Table 3.1 and Table 3.2 respectively.

Recrystallised P.Y.13 resinated with 40% abietic acid

Pigment Yellow 13, recrystallised from 1,2,4-trichlorobenzene (3.0g), was added to water to make an aqueous slurry, which was adjusted to pH10 with dil. NaOH. Meanwhile, a solution of abietic acid (1.2g; 40% by weight of P.Y.13) in water and 47% NaOH (few drops) was made up with heat and stirring. The hot resin solution was added to the recrystallised P.Y.13 slurry at pH10, which retains the resin in solution. The mixture was heated on an electric hotplate until a temperature of 95°C

was reached. at which point dil. HCl was added to pH7.0 to precipitate the resin. Stirring was continued at 90-95°C for 30 minutes. After allowing to cool to 70°C, the resinated product was filtered under vacuum, washed with water and oven dried at 70°C overnight. Yield 3.56g, Total resin 21.2%.

Maleopimaric acid

Twice recrystallised abietic acid (5g, 16.5mmol.) and maleic anhydride (2.43g, 24.8mmol., 1.5eq.) were combined and heated until molten and reacted at 160°C for 2 hours, after which the mixture was allowed to cool. The remaining glassy residue was dissolved in ether and washed with water. The ether was dried over $MgSO_4$ and evaporated under reduced pressure. Yield 6.13g (92.6%), m.p. 146-150°C, ^{13}C NMR ($CDCl_3$) δ_C 185.8 (C-18), 173.3 (C-23), 171.5 (C-24), 148.6 (C-13), 125.6 (C-14), 53.8 (C-9), 53.5 (C-22), 49.5 (C-5), 47.3 (C-4), 46.1 (C-21), 40.9 (C-8), 38.4 (C-1), 38.0 (C-10), 37.2 (C-3), 36.1 (C-12), 35.2 (C-7), 33.3 (C-15), 27.7 (C-11), 22.2 (C-6), 21.1 (C-17), 20.4 (C-16), 17.4 (C-2), 16.9 (C-19), 16.0 (C-20).

23,24-$^{13}C_2$ Maleopimaric acid (10% label)

Twice recrystallised abietic acid (0.70g, 2.3mmol.) and maleic anhydride (250mg, 2.5mmol., 1.1eq.; 25mg 1,4-$^{13}C_2$, 225mg normal) were combined and heated until molten, and reacted at 160°C for 2.5 hours. The mixture was allowed to cool and dissolved in ether. The ether was dried over $MgSO_4$ and evaporated under reduced pressure. Yield 0.76g (81.9%), ^{13}C NMR ($CDCl_3$) as for maleopimaric acid except δ_C 173.3 (C-23, t), 171.5 (C-24, t).

21,22-$^{13}C_2$ Maleopimaric acid (10% label)

Procedure as for 23,24-$^{13}C_2$ maleopimaric acid except maleic anhydride (250mg, 2.5mmol., 1.1eq.; 25mg 2,3-$^{13}C_2$, 225mg normal). Yield 0.77g (83.0%), ^{13}C NMR ($CDCl_3$) as for maleopimaric acid except δ_C 53.5 (C-22, t), 46.1 (C-21, t).

Maleic acid monomethylamide

Methylamine (33% ethanolic solution; 37.5ml, 0.3mol.) in ether (50ml) was added to a stirred solution of maleic anhydride (19.62g, 0.2mol.) in dry ether (200ml) with cooling, over 20 minutes. An off-white precipitate formed immediately and the resultant thick mixture was diluted with ether (50ml). The precipitate was filtered under vacuum, washed with ether, collected and dried. The product was recrystallised from ethanol. Yield 7.91g (30.6%), m.p. 148-150°C, NMR (D_2O) δ_H 7.35 (1H, quart., NH), 4.75 (2H, s, olefinics), 2.8 (3H, d, CH_3).

N-Methylmaleimide

Maleic acid monomethylamide (2.0g, 15.5mmol.) was heated in a test-tube at 160°C for 2 hours. A brown residue remained in the bottom of the tube. A white crystalline product was deposited in the mouth of the tube, and identified as *N*-methylmaleimide by spectroscopy and its characteristic irritating odour. Yield 0.15g (8.7%), m.p. 82-86°C, NMR ($CDCl_3$) δ_H 7.0 (2H, s, olefinics), 2.8 (3H, s, CH_3).

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