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Reaction of Abietic Acid with Maleic Anhydride and Fumaric Acid and Attempts to Find the Fundamental Component of Fortified Rosin

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Abstract: Identification of the Diels-Alder adduct of Abietic Acid (AA) and maleic anhydride (MA) or Fumaric Acid (FA) using a Shimadzu QP 5050A Gas chromatograph Mass spectrometer revealed that AA and MA produced endo-maleopimaric acid (MPA) and endo-maleopimaric acid tricarboxylic acid. A reaction product of abietic acid and fumaric acid generated three peaks identified based on their mass spectra as fumaropimaric acid (FPA), FPA adducts and endo-MPA. To maximize the reaction between AA and MA or FA, molar ratio (AA and MA or FA), reaction time and reaction temperature were investigated. The best Diels-Alder reaction between abietic and maleic anhydride was at 125°C for 1 h with a molar ratio of AA to MA of 1: 2. The best Diels-Alder reaction between AA and FA was at 200°C for 1 h with a molar ratio of AA and FA of 1: 2.

Key words: Abietic acid, maleic anhydride, fumaric acid, maleopimaric acid, fumaropimaric acid

INTRODUCTION

In Indonesia, plantations of *Pinus merkusii* cover around 300,000 hectares. This species grows mostly in Sumatra, especially the Nangru Aceh Darussalam, North Sumatra, West Sumatra and Jambi provinces and Java. It also grows in Sulawesi and in some cases, West Kalimantan. The species is a commodity of Non Wood Forest Product (NWFP) in Indonesia, producing pine gum resin with a production capacity of more than 500,000 tons a year. This natural resin is used as a source of raw materials for distillation in the rosin and turpentine industries, mostly in Java Island. In the last ten years, the average amount of rosin produced in Indonesia has been about 40,000 tons a year and the average amount of turpentine, about 10,000 tons a year (Ministry of Forestry of Indonesia, 2003). Rosin is widely used in adhesives, paints and printing inks. It is also used in the sizing of paper to make it hydrophobic and as an emulsifying agent in the emulsifying polymerization of synthetic rubber (Gafvert, 1994).

Today, most of the rosin used in industry is modified in different ways by causing the resin to react with a suitable chemical. Certain desirable properties of rosin can be achieved through modification, such as enhancing hydrophilic properties; rosin could be reacted with maleic anhydride or fumaric acid (dienophile), which adds to levopimaric acid in a Diels-Alder addition at room temperature. At elevated temperatures, other resin acids such as palustric and neoabietic acids with a conjugated double bond in rosin are isomerized to levopimaric acid, which then reacts with the dienophile to form maleopimaric acid (MPA) or fumaropimaric acid (FPA) (Gafvert, 1994). The advantages of this product over unmodified rosin are a wider variety of uses and better quality. For paper-making purposes, fortified rosin can be used in smaller quantities than unfortified rosin. Further, MPA can serve as a substitute for trimellitic anhydride as the key chemical for the synthesis of polyester imides, polyamide imides and copolyimides (Maiti *et al*., 1989).

Previous studies indicated that the main constituents of rosin from *Pinus merkusii* in Indonesia are abietic and palustric acids (Wiyono *et al*., 2006) and these major constituents, including neoabietic acid, could be reacted with maleic anhydride (MA) or fumaric acid (FA) to form fortified rosin (Kirk-Othmer, 1972). The objective of this study is to identify the best conditions for the reaction of abietic acid with maleic anhydride (MA) or fumaric acid (FA) and identify the product, i.e., maleopimaric acid (MPA) or fumaropimaric acid (FPA).

MATERIALS AND METHODS

Sources of chemical: All the chemicals used in this experiment, including Abietic Acid (AA), maleic anhydride (MA) and Fumaric Acid (FA), were purchased from Wako Pure Chemical Company Ltd., Japan.

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Purification of AA: Abietic acid was purified by repeated recrystallization from ethanol and water, mp 172-175°C (Anonymous, 2001).

Synthesis of Maleopimaric acid (MPA) and Fumaropimaric acid (FPA): MPA was produced by the method of Karlberg *et al.* (1990) with some modifications. After drying in a vacuum oven, 0.520 g of purified abietic acid (1.7 mmol) and 380 mg of maleic anhydride (1.6 mmol) were well mixed in a mortar. The powder was transferred to a small flask (25 mL) and heated at 220°C for 8 h under nitrogen atmosphere. The brownish-red reaction products were dissolved in toluene and extracted with water to remove the excess of MA; dried with $MgSO_4$, filtered and evaporated. Further purification was performed by column chromatography on silica gel eluted with ethyl acetate with increasing amounts of acetic acid (1-10%).

FPA was synthesized by the method of Gafvert *et al.* (1995) with some modifications. Three hundred and one milligrams (0.99 mmol) of purified abietic acid and 258 mg (2.22 mmol) of fumaric acid, after being dried in a vacuum oven, were blended in a mortar. The mixture was then transferred into a small flask and heated at 220°C for 1 h under a stream of nitrogen gas. The brownish-red reaction products were dissolved in toluene and extracted with water until the water layer was neutral, dried with Na_2SO_4, filtered and evaporated. Both MPA and FPA were analyzed using GLC and GC-MS after methylation with diazomethane.

Effect of reaction temperature and time and molar ratio on the reaction of AA with MA or FA: The procedure used to react an abietic acid with MA or FA was that of Karlberg *et al.* (1990). Fifty milligrams of pure abietic acid and 35 mg of MA or FA were mixed in a mortar, then transferred to a small glass flask and heated at 125, 150, 175 or 200°C in an oil bath for one hour under a nitrogen atmosphere. The reaction products were dissolved in toluene and then washed with water. The water was removed with anhydrous sodium sulphate, the toluene solution was concentrated under a stream of nitrogen gas and the concentrate was dried in a vacuum oven. After methylation, the methylated products were analyzed using GLC and GC-MS.

The best reaction temperature was used to determine suitable reaction times. The procedure used to react an abietic acid with MA or FA was that reported by Karlberg *et al.* (1990). Fifty milligrams of abietic acid and 35 mg of MA or FA were blended in a mortar, then transferred to a small glass flask and heated in an oil bath at the best reaction temperature for 0.5, 1, 2, 3 or 4 h under a nitrogen atmosphere. The reaction products were dissolved in toluene and then washed with water. The water was removed with anhydrous sodium sulphate, the toluene solution was concentrated under a stream of nitrogen gas and the concentrate was dried in a vacuum oven. After methylation, the methylated products were analyzed using GLC and GC-MS.

Using the best reaction temperature and time and a similar procedure to that described above (Karlberg *et al.*, 1990), abietic acid and MA or FA at molar ratios of 1:1, 1:2, 1:3, 1:4 and 1:5 were mixed together in a mortar, then transferred to a small glass flask and heated in an oil bath. The reaction products were dissolved in toluene and then washed with water. The water was removed with anhydrous sodium sulphate, the toluene solution was concentrated under a stream of nitrogen gas and the concentrate was dried in a vacuum oven. After methylation, the methylated products were analyzed using GLC and GC-MS.

GLC and identification of reaction products: MPA, FPA and the products obtained under various reaction conditions were methylated into their methyl esters, then analyzed using GLC. The GLC-based analysis of reaction products was performed using a HITACHI 3000 Gas chromatograph, equipped with an electronic Chromato-integrator D-2500, a FID detector, an injector and a TC-5 capillary column (30 m×0.25 mm i.d. and film thickness 0.25 μm). The column temperature was initially 220°C, rising at 5°C min^{-1} to 290°C and remaining at 290°C for 30 min. The carrier gas was Helium delivered at a flow rate 2.3 mL min^{-1} with a split ratio of 1:20. Both the FID detector and injector port temperature were maintained at 280°C.

Identification and quantification of constituents: MPA, FPA and reaction products were identified using a Shimadzu QP 5050A Gas chromatograph-Mass spectrometer. A capillary column (TC-5, 30 m×0.25 mm i.d., film thickness 0.25 μm) was also used for the identification. The analysis was performed under the same conditions as for GC. Compounds of interest were identified by comparing mass spectra for the injected samples to mass spectra in the literature (Mayr *et al.*, 1984). Several papers were also helpful for the identification (Gafvert, 1994; Gafvert *et al.*, 1995).

The quantification of constituents was conducted with a GC-FID profile obtained on a capillary column according to the peak area percent method without response factor correction (Pteifhover, 2000).

RESULTS AND DISCUSSION

Abietic acid as a representative of resin acids: As rosin consists of many isomers of resin acids, i.e., abietic acid, palustric acid, isopimaric acid, etc., it is very hard to

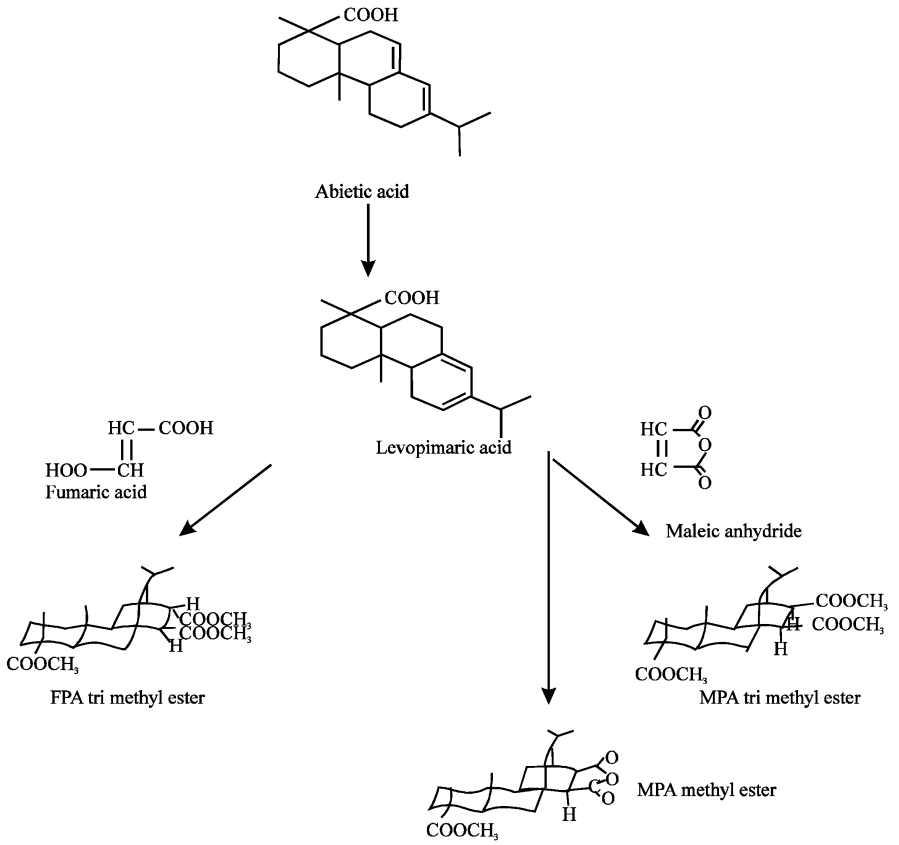

Fig. 1: Reaction of abietic acid with maleic anhydride or fumaric acid (Mayr *et al*., 1984; Sundqvist *et al*., 2001)

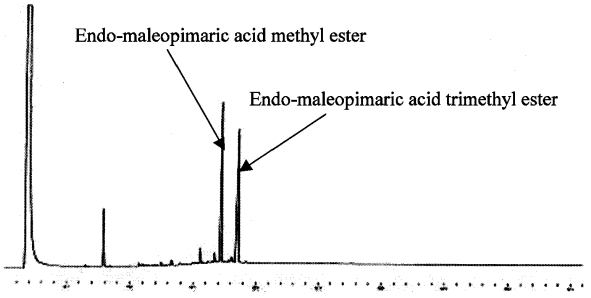

Fig. 2: A chromatographic profile of the MPA reaction product

isolate a single isomer from rosin (Lee and Hong, 2002). In this study, abietic acid was used to form both MPA and FPA through a Diels-Alder reaction with maleic anhydride or fumaric acid, as an initial attempt to find the best conditions for reacting rosin with these chemicals. Before the making of MPA or FPA, abietic acid available commercially was purified by repeated recrystallization from ethanol and water. The purified abietic acid melted at 172-175°C (Anonymous, 2001). It only showed one spot on a TLC plate with a mobile phase of hexane and ethyl acetate at a ratio of 7:5 (v/v).

Reaction products of abietic acid and maleic anhydride: The Diels-Alder adducts of abietic acid and maleic anhydride or fumaric acids have been used as a sizing agent for paper sizing process. During the reaction, abietic acid is isomerized to levopimaric acid, which reacts with maleic anhydride or fumaric acid. This isomerization occurs until all the abietic acid is converted to levopimaric acid and reacted with these dieneophiles, as shown in Fig. 1.

Maleic anhydride adducts were identified using a Shimadzu QP 5050A Gas chromatograph-Mass spectrometer by comparing mass spectra for the injected samples with mass spectra in the literature (Mayr *et al*., 1984). When a sample of the reaction product was injected into the GLC or GC-MS system, two main peaks of adduct were obtained on the chromatogram (Fig. 2). The second of these peaks had a similar profile to one in the literature (Mayr *et al*., 1984). Its base peak was at m/e = 146 with a molecular weight of 460. Apart from the base peak, in the central part of this spectrum there was one prominent ion at m/e = 187, but another small ion at m/e = 121 compared to the reference was also observed. Further, a significant peak was observed at m/e = 400 and 428, arising from the loss of methyl formate and methanol molecules from the

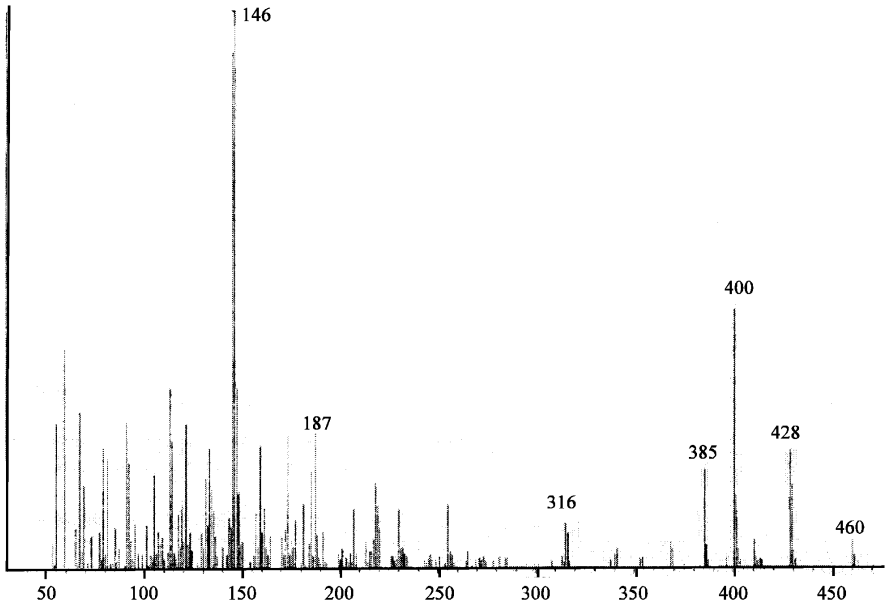

Fig. 3: An example of a mass spectrum of Endo-maleopimaric acid trimethyl ester

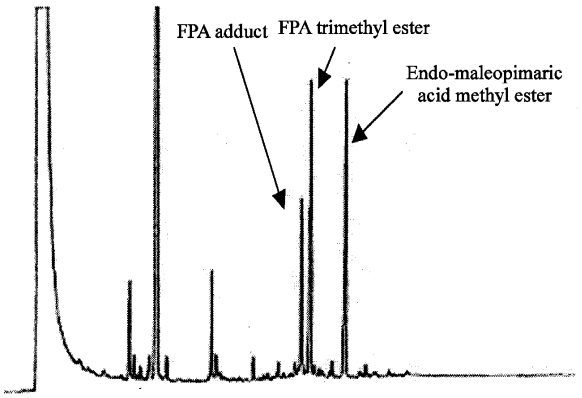

Fig. 4: A chromatographic profile of the FPA reaction product

molecular ion (Mayr *et al*., 1984). Therefore, based on this spectrum, the second peak of the adduct was identified as endo-maleic acid trimethyl ester. This second peak could not be exo-maleopimaric acid methyl ester due to the base peak at m/e = 91 and molecular weight of 414 (Mayr *et al*., 1984). Moreover, GC-MS of the first peak of the adduct, even though its mass spectrum was not as high as in the reference (ions at m/e = 121, 187, 316 and 386) (Mayr *et al*., 1984), identified it as an endo-maleopimaric acid methyl ester. An example of the mass spectrum of a major peak of the adduct is shown in Fig. 3.

Reaction products of abietic acid and fumaric acid: The fumaric acid adduct was identified using similar equipment to that used for identification of the maleic anhydride adduct. When a sample of adduct was injected into the GLC or GC-MS system, three main peaks were obtained on the chromatogram (Fig. 4). All mass spectra of these peaks had a base peak at m/e = 146 with a molecular weight of 460. In the mass spectrum of the first peak of the fumaric acid adduct, a significant peak was observed at m/e = 400, arising from the loss of methyl formate molecules from the molecular ion. Further, the pattern of its mass spectrum looks like the pattern of mass spectrum for fumaropimaric acid (Mayr *et al*., 1984). As in the mass spectrum of the first peak, in the spectrum of the second peak of the adduct, there were two significant ions at m/e = 400 and 428 coming from the loss of methyl formate and methanol molecules from the molecular ion (Mayr *et al*., 1984). Therefore, this second peak was identified as fumaropimaric acid (FPA). The third peak had a base peak at m/e =146 with a molecular weight of 414 as in the literature (Mayr *et al*., 1984). A characteristic of the mass spectrum of the adduct was the elimination of CO, resulting in an ion at m/e = 386. In the central part of the spectrum, there is one prominent ion at m/e = 187 and also an ion at m/e = 121. So, the third peak was identified as endo-MPA methyl ester (Mayr *et al*., 1984). Corresponding to findings above, these results were consistent with the data in the literature (Gafvert *et al*., 1995), which mentioned that the reaction of fumaric acid with abietic acid could produce three compounds, i.e., the first FPA isomer, the second FPA isomer (trimethyl ester)

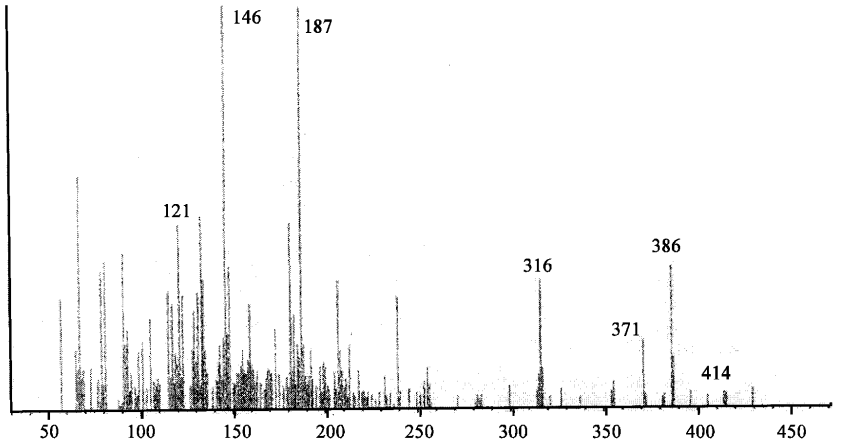

Fig. 5: An example of a mass spectrum of Endo-maleopimaric acid methyl ester (Endo-MPA)

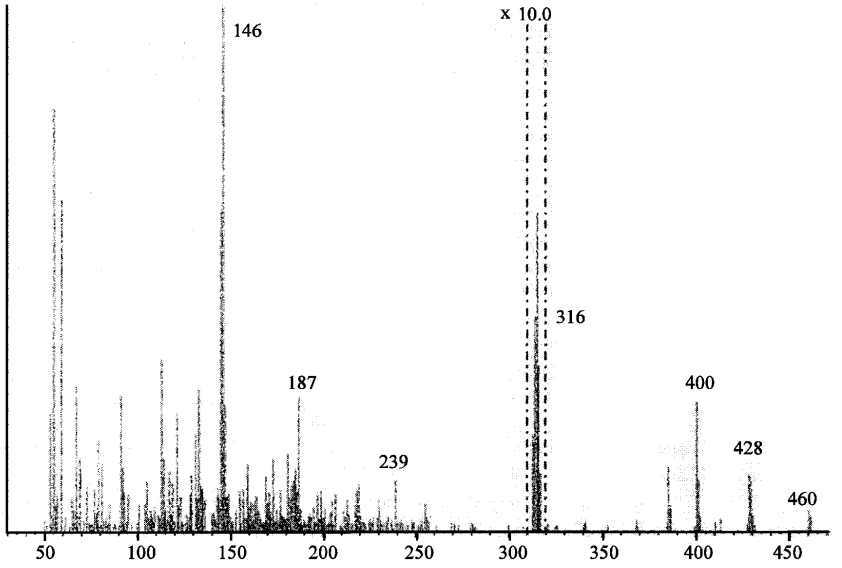

Fig. 6: An example of a mass spectrum of Fumaropimaric acid trimethyl ester (FPA)

and endo-MPA (Gafvert *et al*., 1995). Further, when the reaction of fumaric acid with abietic acid was carried out, not only FPA but also endo-MPA was formed (Halbrook and Lawrence, 1957; Gafvert, 1994). This compound was formed after prolonging the reaction, with MPA formed after FPA. This probably occurred through the epimerization of one carboxyl group of FPA followed by the spontaneous formation of an anhydride between two carboxyl groups. Another possibility is that the reactant fumaric acid would partly isomerise to maleic acid, followed by loss of water to produce maleic anhydride (Gafvert, 1994). Others have mentioned that at higher temperatures, a MPA adduct was formed during fumaric modification (Panda and Panda, 1986). An example of the mass spectrum for Endo-MPA methyl ester is shown in Fig. 5 and that for FPA trimethyl ester in Fig. 6.

Calculation of amounts of MPA and MPA tricarboxylic acid or FPA in the products of the reaction of abietic acid with maleic anhydride or fumaric acid: The above results were used to detect maleic anhydride and fumaric adducts in the reaction of abietic acid with maleic anhydride or fumaric acid at various temperatures and times and molar ratios. Before calculating the amount of MPA and FPA produced at the various reaction temperatures, times and molar ratios; calibration curves based on a regression analysis using Microsoft Excel software were developed to describe the relationship between reaction temperature, time and molar ratio and the concentration of MPA and FPA, respectively. The reaction temperatures, times and molar ratios were used as descriptor variable X in the calibration curve. The concentrations of MPA and FPA were calibrated with the regression linear model. The

Table 1: Effect of reaction temperature, time and molar ratio on formation of MPA and MPA tricarboxylic acid

Temperature (°C)	MPA methyl ester (%)	MPA trimethyl ester (%)	Time (h)	MPA methyl ester (%)	MPA trimethyl ester (%)	Molar ratio (AA: MA)	MPA methyl ester (%)	MPA trimethyl ester (%)
100	4.87	1.23	0.5	3.62	6.23	1: 1	2.45	0.83
125	23.96	51.39	1.0	23.96	51.39	1: 2	23.96	51.39
150	25.95	32.24	2.0	7.40	15.88	1: 3	7.48	2.79
175	19.33	9.41	3.0	0.43	2.46	1: 4	6.04	2.17
200	15.56	5.65	4.0	0.44	12.65	1: 5	1.27	6.46

Table 2: Effect of reaction temperature, time and molar ratio on formation of FPA

Temperature (°C)	FPA (%)	Time (h)	FPA (%)	Molar ratio (AA: FA)	FPA (%)
100	0.26	0.5	0.00	1: 1	0.26
125	0.23	1.0	0.94	1: 2	1.84
150	0.16	2.0	0.07	1: 3	0.31
175	0.33	3.0	0.00	1: 4	0.00
200	1.75	4.0	0.00	1: 5	0.00

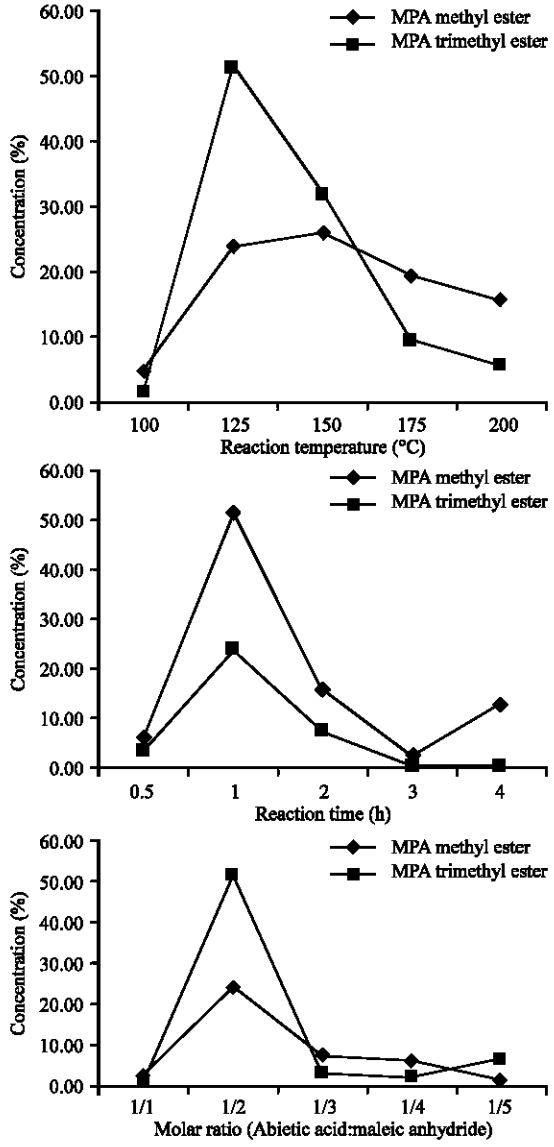

Fig. 7: Effect of formation of MPA and MPA tricarboxylic acid on reaction temperature, time and molar ratio

model of linear regression for MPA was Y = 62.264 X with a coefficient determination (R^2) of 0.9941. That of FPA was Y = 77.562 X with an R^2 of 0.992. Using these equations, the concentrations of MPA and FPA resulting from various reaction temperatures, times and molar ratios could be calculated. The results are shown in Table 1 and 2, respectively.

Effect of reaction temperature and time and molar ratio on formation of MPA and MPA tricarboxylic acid: The Diels-Alder reaction between abietic acid and maleic anhydride for 1 h at various temperatures showed that the concentration of MPA adduct (MPA 1 referring to MPA methyl ester and MPA 2 referring to MPA trimethyl ester) initially increased up to 125°C and then decreased as the reaction temperature increased further. At this temperature, the reaction between AA and MA produced the most MPA trimethyl ester, i.e., 51.39%. As the reaction temperature rose, abietic acid was initially converted into levopimaric acid; however before this compound reacted with MA, it was probably isomerized to other compounds such as pimaric-type acids that could not react with MA (Halbrook and Lawrence, 1957). As a result, the amount of MPA adduct decreased as the reaction temperature increased. The best reaction temperature for producing the MPA adduct was 125°C. An investigation was carried out to look at the MPA adduct obtained from reacting AA and MA using the best reaction temperature (125°C) at various reaction times. During the investigation, the amount of MPA adduct initially increased when the reaction was prolonged to 1 h, then decreased. The concentration of MPA at this time was 51.39%, the highest produced during the reaction. The best reaction time to produce the MPA adduct was 1 h. Furthermore, using a reaction temperature of 125°C and a reaction time of 1 h, we tried to look at the MPA adduct at various molar ratios

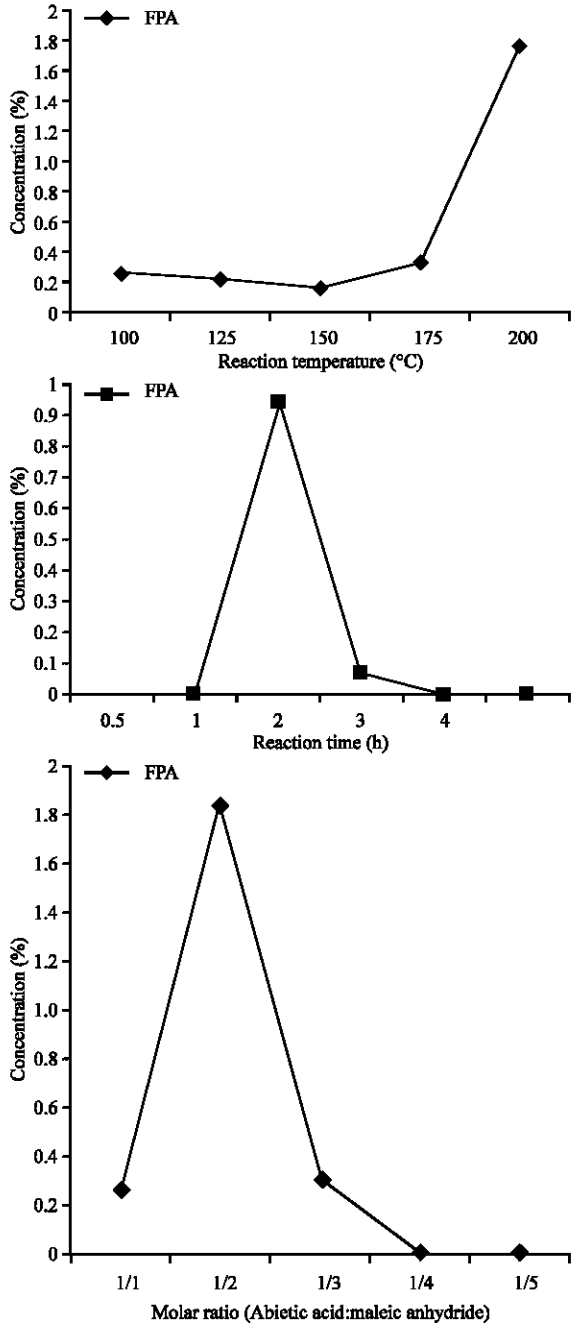

Fig. 8: Effect of formation of FPA on reaction temperature, time and molar ratio

(Table 1). A molar ratio of AA to MA of 1:2 produced the most MPA adduct. All results are shown in Fig. 7.

Effect of reaction temperature and time and molar ratio on the formation of FPA: FPA is a tricarboxylic acid prepared via a Diels-Alder reaction between abietic acid and fumaric acid. Only the abietic type takes part in the reaction, there is no reaction between fumaric acid and the pimaric type acids (Panda and Panda, 1986). The investigation of the reaction between abietic acid and fumaric acid for one hour at various temperatures showed that the concentration of FPA trimethyl ester increased when the reaction temperature increased. Of the reaction temperatures used in this research, 200°C gave the greatest concentration of FPA trimethyl ester, 1.75%. According to Panda and Panda (1986), at higher temperatures, MPA adduct was produced in a significant quantities (Panda and Panda, 1986). However, even at 200°C, this product was formed in a very small quantity that could be ignored. On further investigation of the FPA product using the best temperature (200°C) at reaction times of 0.5 to 4 h, it seemed that initially the FPA adduct increased when the reaction time was prolonged to one hour, then decreased at longer reaction times. When a reaction time of half an hour was used, no FPA product formed probably because there was not enough time to isomerize abietic acid into levopimaric acid. A reaction time of one hour produced the most FPA adduct, 0.94%. On prolonging the reaction to more than 1 h, the FPA adduct decreased. Furthermore, a reaction temperature of 200°C and reaction time of one hour were used to look at FPA adduct at various molar ratios (Table 2). A molar ratio of AA to MA of 1:2 produced the most FPA adduct, around 1.84%. All these results can be seen in Fig. 8.

Identification of the Diels-Alder adduct of abietic acid and maleic anhydride or fumaric acid using a Shimadzu QP 5050A Gas chromatograph-Mass spectrometer revealed that the reaction of abietic acid with maleic anhydride produced endo-maleopimaric acid methyl ester with endo-maleopimaric acid trimethyl ester. Both compounds possessed a base peak at m/e = 146 with a molecular weight of 460, but the values for peak ions at m/e = 187, 385, 400, 428 and 460 were higher for endo-maleopimaric acid trimethyl ester than endo-maleopimaric acid methyl ester. A product of the reaction of abietic acid with fumaric acid produced three peaks identified based on their mass spectra as FPA adduct fumaropimaric acid trimethyl ester and endo-MPA methyl ester. The mass spectra of the first two compounds covered an ion at m/e 146 as a base peak with a molecular weight of 460, with two significant ions at m/e = 400 and 428. Mass spectra of the last compound covered ion at m/e 146 as a base peak with a molecular weight of 414 and two prominent ions at m/e 187 and 121. The best Diels-Alder reaction between abietic acid a maleic anhydride was at 125°C for 1 h with a molar ratio of AA to MA of 1:2. The best Diels-Alder reaction between abietic acid and fumaric acid was at 200°C for one hour with a molar ratio of AA to FA of 1:2.

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