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Characteristics and Chemical Composition of Maleo-Pimaric and Fumaro-Pimaric Rosins Made of Indonesian *Pinus merkusii* Rosin

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Abstract: This study was directed to look at the chemical composition of maleo-pimaric and fumaro-pimaric rosins made of unmodified rosin with maleic anhydride (MA) or fumaric acid (FA). The results showed that one peak of a maleopimaric acid (MPA) adduct on the chromatogram was obtained when a sample of this reaction product was injected into a Gas liquid chromatography (GLC) or Gas chromatograph-Mass spectrometer (GC-MS) system. Identification of this adduct using a GC-MS showed that a reaction product of rosin and MA produced endo-maleopimaric acid methyl ester. This peak of the adduct had a similar profile as in a previous study with a base peak at $m/z = 146$ and prominent ions at $m/z = 386$, $m/z = 187$ and at $m/z = 121$. In the making of MPA and fumaropimaric acid (FPA) adducts, the increase in molar ratio for both reaction temperatures of 125 and 200°C and all rosin samples used in the reaction process gave a higher yield of endo maleopimaric acid. The largest amount of this product was obtained at a molar ratio of 1:10 with the reaction at 200°C. Among the origin of the rosin used in this experiment, rosin from Central Java produced the highest MPA, while the highest FPA was achieved by using rosin from North Sumatra. The relationship between the molar ratio and the concentration of MPA or FPA could be expressed as a quadratic equation. From the equation, one could predict the best molar ratio to produce the highest MPA or FPA adducts at a suitable molar ratio. Using the equation $Y = -0.8475 X^2 + 10.448X - 9.7125$, at the reaction temperature 200°C, the highest MPA (around 22.50%) could be achieved by using a molar ratio of rosin and MA of 1:6.2.

Key words: Rosin, MA, FA, maleopimaric acid, fumaropimaric acid, molar ratio

INTRODUCTION

Pinus merkusii is an important plant in the plantations of Indonesia, covering 300,000 hectares with a production capacity for pine gum resin of more than 500,000 tons a year (Ministry of Forestry of Indonesia, 2003). This pine resin is an important forest product, traditionally obtained by tapping the bark of pine trees and collecting exudates. Pine resins are complex mixtures of acidic and neutral diterpenes together with a fraction of volatile compounds (Rezzi *et al.*, 2005). In the industry, pine resin is used as a source of raw materials for distillation, mostly in Java, to produce turpentine oil (volatile compounds) and rosin (diterpenes). Both products are further processed into chemical industrial products such as food gums, adhesives, coatings, printing inks, disinfectants, cleaners, pharmaceuticals, fragrances and flavoring. Indonesia is the third biggest rosin producing country in the world after China and Portugal (Anonymous, 2003). In the last ten years, production of rosin in Indonesia has averaged about

40,000 tons a year and that of turpentine, about 10,000 tons a year (Ministry of Forestry of Indonesia, 2003).

Rosin is a thermoplastic acidic product isolated from pine resin. The major acidic of rosin is known as resin acids. The acid content depends upon the treatment used to obtain the rosin. Gum rosin from the exudate of pine trees and wood rosin from pine stumps are 90% resin acids, while tall oil, a by-product of manufacturing kraft paper from pine trees, is 95%. Gum rosin consists of the residue obtained upon distillation of oleoresin from pine and wood rosin obtained by solvent extraction of the stump is usually of a darker color. It is a translucent, brittle, friable resin used for varnish and in manufacturing many products. It is sticky when warm and has a faint pine-like odor (Luna-Moreno *et al.*, 1998). The predominant resin acid in unmodified rosin is abietic acid. This substance and palustric acid as well as neoabietic acid could be reacted with maleic anhydride or fumaric acid (dieneophiles), where abietic acid is converted into levopimaric acid in a Diels-Alder addition at a room temperature. At elevated temperatures, other resin acids

covering palustric and neoabietic acids with conjugated double bonds are isomerized to levopimaric acid, which then react with the dieneophiles to form maleo-pimaric acid or fumaro-pimaric acid (Gafvert, 1994). The advantages of this modified rosin over unmodified rosin are that this product has more uses and is better quality. For paper-making purposes, fortified rosin could be used in smaller quantities compared to unfortified rosin (Maiti *et al.*, 1989).

Previous study has indicated that main constituents of rosin from *Pinus merkusii* in Indonesia are abietic and palustric acids (Wiyono *et al.*, 2006) and these are major constituents, including neoabietic acid, that could be reacted with MA or FA to form fortified rosin (Sunqvist *et al.*, 2001). Moreover, Diels-Alder reactions of abietic acid (AA) and MA or FA have been studied and the adduct has been identified by using a Shimadzu QP 5050A GC-MS. The reaction product of abietic acid and maleic anhydride produced endo-maleopimaric acid (MPA) and endo-maleopimaric acid tricarboxylic acid; while, the reaction product of abietic acid and fumaric acid produced fumaro-pimaric acid (FPA) and endo-MPA (Wiyono *et al.*, 2007). Further study was directed to look at the chemical composition of maleo-pimaric and fumaro-pimaric rosins made of unmodified rosin with MA or FA.

MATERIALS AND METHODS

Sources of chemical: Several chemicals were used in this experiment including rosin, maleic anhydride (MA), fumaric acid (FA), toluene, methanol, potassium hydroxide, N-methyl-N-nitroso-p-toluen sulfonamide and nitrogen. Various rosin samples were collected from the rosin and turpentine industry in East, Central and West Java in Indonesia. Meanwhile, chemicals were available in the Laboratory of Chemistry and Biotechnology for Utilization of Forest Resources, Faculty of Agriculture Ehime University Japan and all of them were purchased from Wako Pure Chemical Company Ltd., Japan.

Preliminary investigation of reaction temperatures and times on MPA and FPA: This research study was conducted in 2006. The procedure to make MPA and FPA followed a previous study (Wiyono *et al.*, 2007). About 100 mg (0.33 mmol based on abietic acid) of East Java rosin and 65 mg (0.66 mmol) of MA or FA, after being dried in a vacuum oven, were blended in a mortar, then transferred to a small glass and heated at 125 and 200°C in an oil bath for one, two and four hours in a nitrogen atmosphere, respectively. The reaction products were dissolved in toluene and then washed with water. The remaining water was removed with anhydrous sodium sulphate, the toluene solution was concentrated under a

nitrogen stream and the concentrate was dried in a vacuum oven. After methylation, the methylated products were analyzed using GLC and GC-MS.

Effect of molar ratios and reaction temperatures on MPA and FPA: Using the best reaction time from a preliminary investigation, with a similar procedure (Wiyono *et al.*, 2007), rosin and MA or FA with the molar ratios 1:1, 1:2, 1:3, 1:4, 1:6, 1:8, 1:10, 1:15 and 1:20 were mixed together in a mortar, respectively, then transferred to a small glass flask and heated in an oil bath at 125 and 200°C for one hour under a nitrogen atmosphere. The brownish reaction products were dissolved in toluene and then washed with water. The remaining water was removed with anhydrous sodium sulphate, the toluene solution was concentrated under a nitrogen stream and the concentrate was dried in the vacuum oven. After methylation, the methylated products were ready to be analyzed using GLC and GC-MS.

GLC Analysis and identification of MPA and FPA: MPA and FPA were methylated into their methyl ester and then analyzed by using GLC. The GLC analysis of reacted products was performed using a HITACHI-3000 Gas chromatograph equipped with an electronic chromatointegrator 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 program was isotherm at 220°C and maintained for 30 min. The carrier gas was Helium at a flow rate of 2.3 mL min⁻¹ with a split ratio of 1:20. Both the FID detector and injector port were maintained at 280°C, respectively.

Identification and Quantification of Constituents: A Shimadzu QP 5050A Gas chromatograph-Mass spectrometer equipped with a capillary column (TC-5, 30 m × 0.25 mm i.d., film thickness 0.25 µm) containing 5% methyl siloxane was used to analyze MPA and FPA. The oven temperature was held at 100°C for 1 min and programmed to increase to 280°C at a rate of 10°C min⁻¹. The final temperature was held for another 11 min. Both the inlet and GC interface temperatures were 260°C, respectively. The carrier gas was helium at 10 psi. The mass spectrometer was operated in the electron impact ionization mode with an ionizing energy of 70 eV. Full scan data were obtained by scanning from m/z 50 to 500 at a rate of 1.0 scan sec⁻¹. The interested compounds were identified by comparing mass spectra for the injected samples to mass spectra in a library and the literature (Mayr *et al.*, 1984). Some papers were also helpful for the identification of compounds (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

Preliminary investigation of reaction temperatures, times and molar ratio: Rosin is a thermoplastic acidic product isolated from exudate of living pine trees. The major constituent of rosin is resin acids which are predominantly abietic acids (Lee and Hong, 2002). In this study, rosin obtained from East Java-Indonesia was applied to form both MPA and FPA. The main constituent of this rosin is abietic acid followed by isopimaric acid and palustric acid (Wiyono *et al.*, 2006). At room temperature, only abietic acid is reacted with maleic anhydride or fumaric acid (dienophile), which adds to levopimaric acid in a Diels-Alder addition. However, at elevated temperatures, not only this resin but also palustric and neoabietic acids with conjugated double bonds in rosin are isomerized to levopimaric acid, which then react with the dienophile to form maleopimaric acid (MPA) or fumaropimaric acid (FPA). During the reaction, these resin acids are isomerized to levopimaric acid and at the same time this compound reacted with maleic anhydride or fumaric acid (Kirk-Othmer, 1972; Gafvert, 1994; Panda and Panda, 1986). This isomerization occurred until all these acids were converted to levopimaric acid and reacted with these dieneophile, as shown in Fig. 1.

Using the reaction conditions of a previous study (Wiyono *et al.*, 2007), East Java rosin was reacted with MA at a molar ratio of 1:2 at 125 and 200°C for various reaction times. Results indicated that the Diels-Alder reaction between rosin and maleic anhydride at both 125 and 200°C tended to decrease the concentration of MPA adduct a long with the increase in reaction time from one hour to four hours. The reaction time of one hour is still the best time to make MPA for the reaction temperature of 125°C (around 5.6% of MPA adduct). However, a reaction temperature of 200°C gave higher MPA adduct (around 6.5%). Besides MPA adduct, unmodified diterpene acids (i.e., sandaracopimaric acid, isopimaric acid, dehydroabietic acid, abietic acid, merkusic acid, etc) were also observed in the sample (Fig. 2).

MPA adduct was identified by using a Shimadzu QP 5050A Gas chromatograph-Mass spectrometer by comparing mass spectra for the injected samples to mass spectra in the literature (Mayr *et al.*, 1984). When a sample of the reaction product was injected into the GLC or GC-MS, there was one peak of adduct on the chromatogram (Fig. 2). Based on the mass spectrum, this peak of adduct

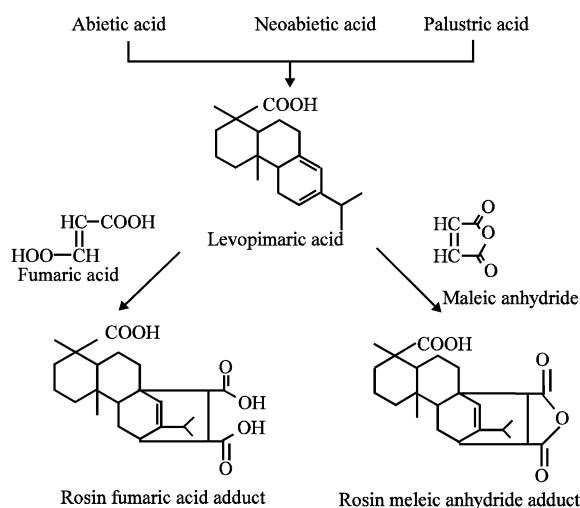


Fig. 1: Reaction process for abietic, palustric and neoabietic acids with maleic anhydride or fumaric acid (Sundqvist *et al.*, 2001)

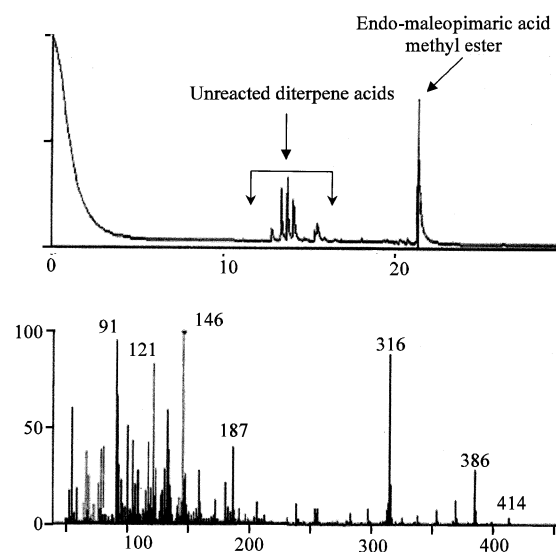


Fig. 2: An example of GC-MS chromatograms and mass spectrum profiles of endo-maleopimaric acid methyl ester (endo-MPA)

had similar profile as in the literature (Mayr *et al.*, 1984). Its base peak was at $m/z = 146$. A very characteristic fragmentation in the mass spectra of the MPA adduct is the elimination of CO, resulting in an ion at $m/z = 386$. Apart from the base peak, in the central part of this spectrum there were two prominent ions at $m/z = 187$ and at $m/z = 121$ as in the reference (Mayr *et al.*, 1984). Therefore, based on this spectrum this peak of adduct was identified as endo-maleopimaric acid methyl ester.

In a previous study, we found that the best reaction in making MPA or FPA is at a reaction temperature 125 or 200°C for one hour and at a molar ratio of 1:2 (abietic acid: MA or FA) (Wiyono *et al.*, 2007). In this study, we expand the reaction time and molar ratio of rosin and MA. These expansions are required to seek a proper reaction time and molar ratio which were used in the main experiment using rosin not only from East Java but also from Central and West Java and from North Sumatra. Experimental results showed that the reaction time for one hour was still the best time in producing MPA for both the reaction temperatures (Table 1). Further, by using a reaction time of one hour the increase in molar ratio of rosin and MA increased MPA adduct until the molar ratio of 1:10, slightly decreased at molar ratio of 1:15, it then increased again (Table 2). Nilsson *et al.* (2002) mentioned that the amount of MPA in modified rosin varied from 8-20%. Referring to this result, in this study the amount of endo maleopimaric acid in MPA adduct was achieved from a molar ratio of 1:4 (8.03%). The highest content of endo maleopimaric acid could be obtained at a molar ratio of 1:20. Considering that at a molar ratio of 1:15, the content of endo maleopimaric acid was decreased, so, even though the highest endo maleopimaric acid was attained at this molar ratio, for the main experiment we used molar ratios of 1:2, 1:6 and 1:10. Further, not all resin acids would be observed in the main experiment, only resin acids corresponded with the reaction products covering pimaric, palustric, dehydroabietic, abietic and neoabietic acids.

Reaction products of rosin and MA or FA at various molar ratio and reaction temperature:

From the results of a preliminary investigation, using rosin obtained from East Java but also from Central and West Java and from North Sumatra as raw materials we applied three molar ratios and two reaction temperatures for one hour in making MPA and FPA.

Table 3 shows the results of experiments in making MPA and FPA adducts, using rosin obtained from East and Central Java, at various molar ratios and reaction temperatures. Using rosin attained from one of enterprise

in East Java Indonesia, the increase in molar ratio for both reaction temperatures of 125 and 200°C gave a higher yield of endo maleopimaric acid. At the reaction temperature of 125°C, the endo maleopimaric acid obtained from the results of this research was in a range of 5-18%; while at 200°C varied 6-21.5% (Table 3). The highest of this product was obtained at a molar ratio of 1:10 with the reaction time of 200°C. The previous result mentioned that the amount of MPA in modified rosin varied from 8-20% (Nilsson *et al.*, 2002). Compared to this result, the results of this experiment gave a little bit higher, especially at a reaction temperature of 200°C. Furthermore, using similar conditions as in previous experiments (Wiyono *et al.*, 2007) with a molar ratio of rosin and FA of 1:10, the increase in molar ratio gave an increase in FPA adduct for the reaction temperature of 125°C, but the amount of the product was small, varying 0.45-2.0%. However, at the reaction temperature of 200°C, the increase in molar ratio tended to increase the FPA adduct, 0.60-4.0% (Table 3).

As can be seen in Table 3, using rosin from the rosin industry in Central Java-Indonesia, the increase in molar ratio of rosin and MA or FA led to an increase in MPA and FPA adducts for both the reaction temperature of 125 and 200°C. The concentrations of endo maleopimaric acid in MPA adduct varied 3-19% at 125°C and ranged 12-23% at 200°C. At all molar ratio levels, changing the reaction temperature to 200°C caused an increased in the MPA adduct (Table 3 and Fig. 3). This also happened in making FPA adduct. The concentration of fumaropimaric acid in the FPA adduct ranged 0.20-9.0%.

Table 1: MPA adduct at various reaction temperatures and times

Components	Concentration of MPA adduct (%)					
	125°C			200°C		
	1 h	2 h	4 h	1 h	2 h	4 h
Pimaric acid	0.00	0.75	1.04	0.77	0.62	0.39
Palustric acid	25.03	28.41	24.35	12.21	10.47	8.56
Dehydroabietic	27.60	25.71	20.76	37.89	33.76	36.87
Abietic acid	8.12	4.73	7.48	0.00	0.00	0.00
Neoabietic acid	5.53	5.56	6.01	2.83	2.61	1.50
MPA	5.64	4.29	3.54	6.54	5.56	0.42

Rosin from East Java was used in this experiment

Table 2: MPA adduct at various molar ratios and at a reaction temperature of 125°C for 1 h

Identified components	Rosin	Concentration of MPA adduct (%)						
		Molar ratios						
		1:2	1:4	1:6	1:8	1:10	1:15	1:20
Pimaric acid ME	0.00	4.11	20.82	24.05	32.04	29.72	25.75	19.76
Palustric acid	20.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dehydroabietic ME	11.70	29.03	21.95	25.99	25.10	27.13	29.43	48.29
Abietic acid ME	25.79	8.54	6.06	0.39	1.00	0.70	0.00	0.00
Neoabietic acid ME	2.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MPA	0.00	5.93	8.03	9.04	12.64	17.93	15.39	20.02

Rosin from East Java was used in this experiment

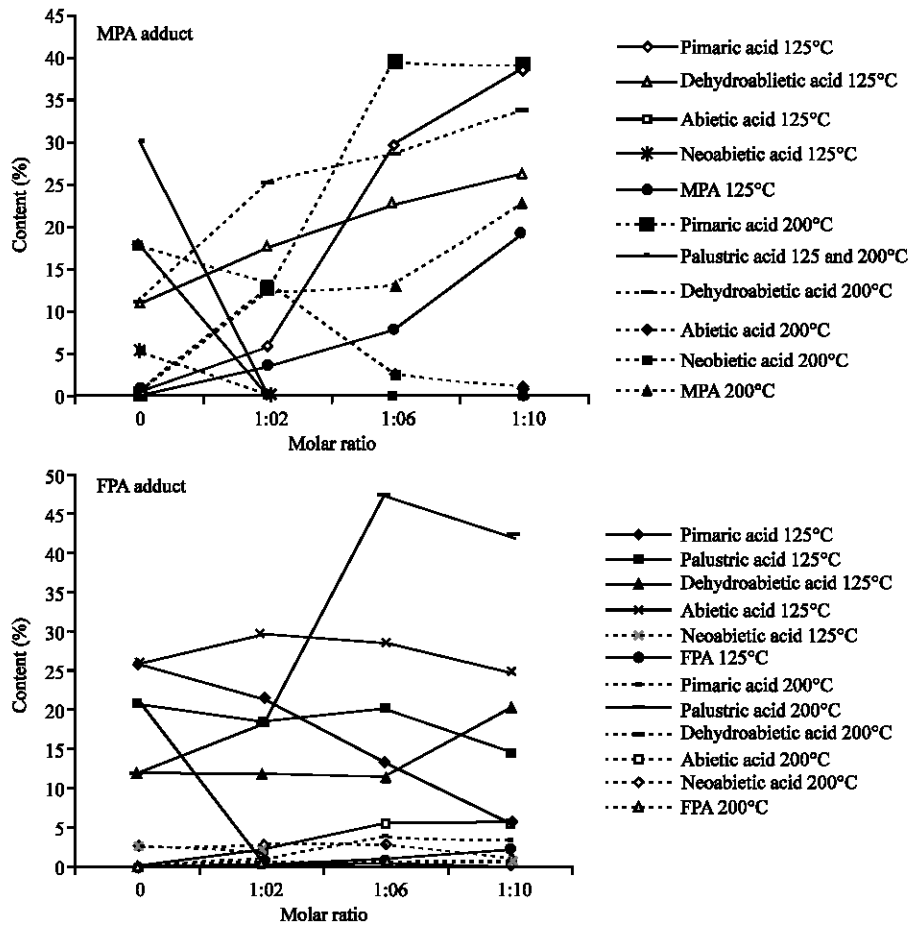


Fig. 3: MPA, FPA and unreacted resin acids of reaction products at various reaction times and molar ratios (using rosin from Central Java)

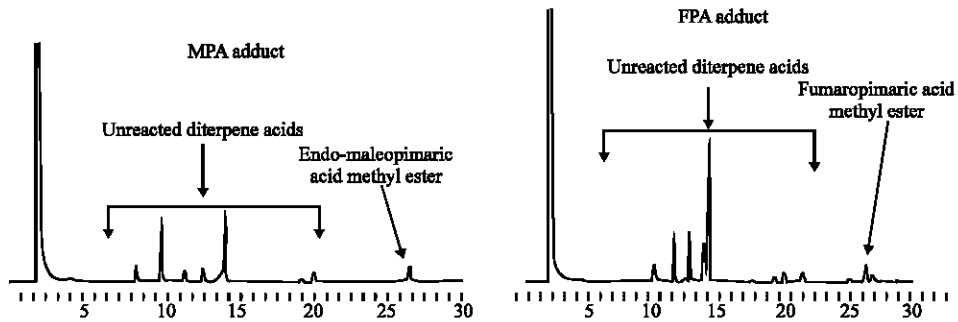


Fig. 4: An example of GC-chromatogram profiles of endo-maleopimaric acid methyl ester and fumaropimaric acid (using rosin from West Java)

During the MPA or FPA making process, no diterpene acids reacted with MA or FA. Some diterpene acids reacting with MA or FA still remained in the unreacted form (Fig. 4, Table 3 and 4). Further, It has been mentioned in a previous study that pimaric acid does not

exist in the rosin of *Pinus merkusii* (Wiyono *et al.*, 2006). However, in the making of MPA and FPA adducts at either 125 or 200°C, this compound was found in the reaction product, which can be identified by using GC-MS. This indicated that there are some resin acids

Table 3: MPA and FPA adducts at various reaction temperatures and molar ratios

Components	Rosin	Concentration of MPA adduct (%)						Concentration of FPA adduct (%)					
		125°C			200°C			125°C			200°C		
		Molar ratio			Molar ratio			Molar ratio			Molar ratio		
		1:2	1:6	1:10	1:2	1:6	1:10	1:2	1:6	1:10	1:2	1:6	1:10
Rosin from East Java													
Pimaric acid ME	0.00	4.11	24.05	29.72	14.62	23.22	34.19	0.73	0.62	0.34	2.42	5.54	5.69
Palustric acid	20.78	0.00	0.00	0.00	0.00	0.00	0.00	18.54	20.16	14.50	0.63	0.00	0.00
Dehydroabietic ME	11.70	29.03	25.99	27.13	37.89	31.64	38.33	11.75	11.42	20.13	18.17	47.20	41.98
Abietic acid ME	25.79	8.54	0.39	0.70	0.00	0.00	0.00	29.42	28.43	24.70	21.41	13.41	5.69
Neoabietic acid ME	2.58	0.00	0.00	0.00	2.83	0.00	0.00	2.90	2.86	1.16	1.73	0.00	0.00
MPA/FPA	0.00	5.93	9.04	17.93	6.54	13.53	21.42	0.45	1.06	1.99	0.62	3.91	3.53
Rosin from Central Java													
Pimaric acid ME	0.26	5.61	29.70	38.53	12.59	39.25	39.06	1.84	0.40	0.34	1.77	0.56	0.34
Palustric acid	30.03	0.00	0.00	0.00	0.00	0.00	0.00	19.25	17.74	17.17	0.56	0.00	0.00
Dehydroabietic ME	10.75	17.42	22.33	26.11	25.29	28.62	33.58	10.58	12.13	15.04	16.31	25.22	59.57
Abietic acid ME	17.75	13.34	2.38	0.88	0.00	0.00	0.00	24.36	23.84	21.32	24.71	16.21	0.00
Neoabietic acid ME	5.14	0.00	0.00	0.00	0.00	0.00	0.00	3.47	3.18	1.75	1.15	0.95	0.00
MPA/FPA	0.00	3.21	7.64	19.04	12.43	12.94	22.70	0.94	0.65	0.27	0.95	1.21	8.17

Rosin from East and Central Java was used in this experiment

Table 4: MPA and FPA adducts at various reaction temperatures and molar ratios

Components	Rosin	Concentration of MPA adduct (%)						Concentration of FPA adduct (%)					
		125°C			200°C			125°C			200°C		
		Molar ratio			Molar ratio			Molar ratio			Molar ratio		
		1:2	1:6	1:10	1:2	1:6	1:10	1:2	1:6	1:10	1:2	1:6	1:10
Rosin from West Java													
Pimaric acid ME	0.00	6.21	23.60	28.52	12.52	25.06	22.74	0.00	0.00	0.00	2.76	3.46	6.17
Palustric acid	13.10	0.00	0.00	0.00	0.00	0.00	0.00	14.93	2.75	0.37	0.00	0.00	0.00
Dehydroabietic ME	28.21	46.91	40.46	38.67	31.96	55.16	53.80	16.55	31.61	28.75	37.96	42.11	55.61
Abietic acid ME	16.00	0.00	0.00	0.00	0.00	0.00	0.00	22.70	14.95	17.30	5.44	1.31	0.90
Neoabietic acid ME	1.99	0.00	0.00	0.00	0.00	0.00	0.00	2.23	0.00	0.00	0.00	0.00	0.00
MPA/FPA	3.28	6.95	11.27	16.62	8.13	15.41	19.06	0.98	3.05	2.77	4.90	6.32	9.61
Rosin from North Sumatra													
Pimaric acid ME	0.00	3.00	12.59	36.87	7.60	24.08	28.86	0.16	0.06	0.20	3.10	5.78	27.22
Palustric acid	8.57	0.00	0.00	0.00	0.00	0.00	0.00	4.67	0.73	6.91	0.00	0.00	0.00
Dehydroabietic ME	22.27	31.01	31.07	31.95	41.13	26.74	47.24	14.79	18.83	18.67	26.92	38.16	43.89
Abietic acid ME	21.18	5.07	2.71	0.23	2.84	0.00	0.00	32.72	30.34	33.97	10.81	3.75	0.00
Neoabietic acid ME	1.29	0.00	0.00	0.00	0.00	0.00	0.00	1.64	0.76	0.95	0.00	0.00	0.00
MPA/FPA	0.00	5.14	5.86	11.10	5.36	8.39	17.96	1.95	3.15	1.48	2.91	5.24	10.18

Rosin from West Java and North Sumatra was used in this experiment

isomerized into pimaric acid during the MPA or FPA making process. Moreover, the concentration of dehydroabietic acid, which does not react with MA or FA, increased during the reaction process. It is well known that abietic type resin acids, which possess a conjugated double bond system, easily isomerize upon the action of heat or mineral acids. The thermal and acid isomerizations of resin acids are similar reactions; it has been reported that the thermal isomerization of some resin acids is actually catalyzed by the carboxyl group (Takeda *et al.*, 1969). He further stated that the action of heat levopimaric acid yielded dehydroabietic acids (DHA), besides the abietic type isomers plus. These side reactions were found to be enhanced by trace amounts of oxygen. Furthermore, levopimaric and palustric acids have been reported to yield dehydroabietic acid upon air oxidation,

while abietic and neoabietic acids do not (Enoki, 1976). This argument supported the result of the experiment that the concentration of DHA increased during the reaction process.

Using rosin obtained from the rosin industry in West Java and North Sumatra-Indonesia, the increase in molar ratio of rosin and MA or FA led to an increase in MPA and FPA adducts for both the reaction temperature of 125 and 200°C, except the making of FPA at 125°C. With rosin from West Java, the concentrations of endo maleopimaric acid in the MPA adduct varied 6-17% at 125°C and 8-20% at a reaction temperature of 200°C. Meanwhile, using rosin from North Sumatra the concentrations of endo maleopimaric acid in MPA adduct varied 5-12% at 125°C and 5-18% at 200°C. At all molar ratio levels, changing the reaction temperature to 200°C caused an increase in the

MPA adduct (Table 4). This also happened in making FPA adduct, except at 125°C. At this temperature, the concentration of fumaropimaric acid in the FPA adduct ranged 1.0-3.50% for rosin from North Sumatra; while in rosin from West Java, the concentration of fumaropimaric acid in the FPA adduct varied 0.9-3.5%. Further, among the origin of rosin used in this experiment, it seems that rosin obtained from Central Java produced the highest level of MPA. This indicated that the amount of MPA was affected by the quality of rosin that was used in the production process. Meanwhile, the highest level of FPA could be achieved by using rosin from North Sumatra. This product was not influenced by the quality of rosin in this experiment.

The previous experiment using abietic acid as a raw material showed that the best molar ratio to produce MPA or FPA was at a molar ratio of 1:2 (Wiyono *et al.*, 2007), but this recent result showed that the increase in molar ratio increased the MPA or FPA adducts. This seems to be contradiction, but it is actually not. As we mentioned before that the previous experiment used abietic acid, while in the recent experiment we used rosin as a raw material to produce MPA or FPA. As we know that this rosin not only contains abietic acid but also palustric acid and neoabietic acid (Wiyono *et al.*, 2006). During the Diels-Alder reaction, when all abietic acid in rosin has been isomerized into levopimaric acid, other resin acids (palustric acid and neoabietic acid) started to be isomerized into levopimaric acid (Sundqvist *et al.*, 2001). The more levopimaric acid formed the more MA or FA needed. This meant that the molar ratio of AA and MA or

FA needed to be increased. This is why that the molar ratio for this recent study is higher than that of previous one.

To look at the relationship between molar ratio and the concentration of MPA or FPA, we conducted a regression analysis with Microsoft Excel software. The molar ratio was used as descriptor variable X and concentration as descriptor variable Y in the curve (Fig. 5). The regression analysis showed that there was a relationship between molar ratio and the concentration of MPA or FPA expressed as quadratic equations for both adducts at all observed reaction temperatures. MPA and molar ratio at the reaction temperature of 125°C could be expressed as $Y = -0.675X^2 + 7.871X - 6.92$ with coefficient determination (R^2) = 0.98; while, at the reaction temperature of 200°C this relationship could be expressed as $Y = -0.8475 X^2 + 10.448X - 9.7125$ with coefficient determination (R^2) = 0.999. Furthermore, the relationship between molar ratio and the concentration of FPA expressed as a quadratic equation at the reaction temperature of 125°C as $Y = -0.46X^2 + 5.268X - 4.47$ with coefficient determination (R^2) = 0.97; while, at the reaction temperature of 200°C this relationship could be expressed as $Y = -0.31 X^2 + 2.448X - 2.445$ with coefficient determination (R^2) = 0.91. From these equations, there could be predicted the best molar ratio to produce the most MPA or FPA adducts. For example, using the equation $Y = -0.8475 X^2 + 10.448X - 9.7125$, at the reaction temperature of 200°C, the highest MPA (around 22.50%) could be achieved by using the molar ratio of rosin and MA at 1:6.2.

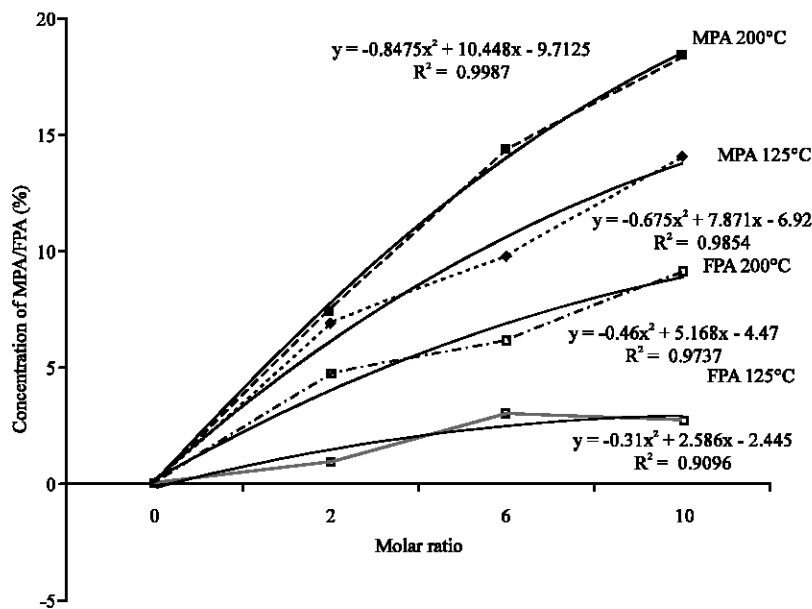


Fig. 5: An example of equations for the relationship between molar ratio (X) and concentration of MPA or FPA (using rosin from West Java)

Preliminary experiments showed that a reaction time of 1 h is still the best in making MPA. There was one peak of MPA adduct coming out on the chromatogram when a sample of this reaction product was injected into the GLC or GC-MS system. Identification of this adduct using a Shimadzu QP 5050A Gas chromatograph-Mass spectrometer showed that a reaction product of rosin and MA produced endo-maleopimaric acid methyl ester. This peak of the adduct had a similar profile as in a previous study with a base peak at $m/e = 146$ and prominent ions at $m/e = 386$, $m/e = 187$ and at $m/e = 121$. In the experiment to make MPA and FPA adducts, the increase in molar ratio for both reaction temperatures of 125 and 200°C and all rosin samples used in the reaction process gave a higher yield of endo maleopimaric acid. The highest level of this product was obtained at a molar ratio of 1: 10 with the reaction at 200°C. Among the origin of the rosin used in this experiment, rosin from Central Java produced the most MPA and the most FPA was achieved by using rosin from North Sumatra. The relationship between molar ratio and the concentration of MPA or FPA could be expressed as a quadratic equation. From the equations, there could be predicted the best molar ratio to produce the most MPA or FPA adducts at a suitable molar ratio. Using the equation $Y = -0.8475 X^2 + 10.448X - 9.7125$, at the reaction temperature of 200°C, the highest MPA (around 22.50%) could be achieved by using the molar ratio of rosin and MA of 1:6.2.

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