Study Direction to Oxidize a Local Pine Rosin with Potassium Permanganate

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ABSTRACT

Pine rosin acid or Gondorukem is a solid resin obtained from pine sap. It is yielded as residue from a high temperature distillation process. In industry, rosin acid is widely used and modified as raw material in paint, ink, adhesive, resin, thermoplastic, and thermosetting polymer. Modification process generally is undergone to generate rosin acid with specific properties and for certain purposes. This paper report, potassium permanganate oxidation reaction of pine rosin acid under acidic process at low temperature. Product identified as 13,14-*seco*-13-oxoabiet-7-ene-dioic acid (0.52%), 7,8-dihydroxy-abietic acid (6.62%), and 7-oxo-dehydroabietic acid (1.49%). The crude product was isolated as a pale to white solid. Under high temperature a yellowish product was resulted. In overall, the yield isolated in between 46.4% and 86.0%.

Key words: pine, rosin, abietic acid, oxidation, dehydroabietic acid

INTRODUCTION

Pine is a solid resin obtained from pine and several other plants. Pine rosin acid is produced by heating fresh molten resin to vaporize the volatile liquid terpene component. Pine rosin acid is semi-transparent and varies in colour from yellow to black. Pine Rosin is brittle at room temperature, but melts at high temperatures, especially abietic acid [1]. Based on the acid content, 90% of rosin or pine rosin acid is an isomer of abietic acid and 10% is dehydroabietic acid and dehydroabietic acid. The isomer of abietic acid forms two groups of abietic acid with a conjugated double bond (40-60%) and neoabietic acid with an unconjugated double bond (9-27%). Abietic acid contains isopropyl groups in C-ring, while neoabietic acid has methyl and vinyl groups [2].



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Previous study indicated that main constituents of rosin from *Pinus merkusii* in Indonesia are abietic, palustric acid and neoabietic acid [3]. Pine rosin obtained from tapping pine trees is referred to as non-modified pine rosin. This non-modified pine rosin has a weakness because it tends to crystallize, is easily oxidized by oxygen in the open air due to its unsaturated nature and easily reacts with heavy metal salts in varnish [4, 5]. The production is exported and classified based on the colour and level of clarity. They are X, WW, WG and N grades, which relate to the rosin colour from yellow to brownish [6]. Moreover, for the modified rosin, several derivatives products are conducted following the common reaction. Diels-Alder reaction between abietic acid and maleic anhydride as dienophile to produce DA adducts. This adducts is applied as starting material for industrial production of vinyl ester resins [7] and polyesters [8] polymer plastic.

The other modified rosin acid as the hydroxy-methylated derivatives is used directly [9] or further modification with triglycerides for production of polyurethane films. Isomerisation of the abietic acid into dehydroabietic acid, which transform the diene position into aromatic ring after hydride migration provide a more stable structure. This product is more stable than hydro phenanthrene ring, and easily esterified with acrylic moiety. This ester acrylic group can be polymerized form polyacrylate products of dehydroabietic acid [10]. However, still there are many opportunities to have another derivates of pine rosin acid to expand the applications and reduce the potency of weakening colour and stability. This paper reports the oxidation of pine rosin acid. The oxidation reaction can be undergone using oxidating agent using different type of catalyst such as nickel, ruthenium, palladium, and platinum-based catalyst [11,12]. Recently, our group applied potassium permanganate as a reagent to oxidize alpha-pinene [13]. The reaction take place on the double bond of alphapinene, and it is controlled by the acidity of reaction. Major products were isolated as cleavage oxidation product, however minor diol-products were detected. Double hydroxyl group (-OH) attach in both carbon double bond after converted into carbon-carbon single bond. This reaction is not like that attached hydroxyl group in the C-H activation reaction [14]. The oxidation hydroxylation converts -C-H bonds into -C-OH [15]. Meanwhile potassium permanganate coupling to the C=C double bond form complex of alpha-pinene oxo-manganate. Hydrolysis of this complex produce the diols of alpha-pinene and release the MnO₂. This strategy is applied to oxidate the rosin acid. The oxidation occurs in the diene position from abietic acid, neoabietic acid or palustric acid. The effect of reaction temperature is reported toward the yield isolated.

EXPERIMENT

Chemicals

The chemicals used were the following: Pine Rosin obtained from PT Perhutani Anugerah Kimia, potassium permanganate (Merck), sodium hydroxide (Emsure), hydrochloric acid (Smart-Lab), phenolphthalein indicator (Sigma-Aldrich), ethanol (Emsure), potassium hydroxide (Smart-Lab), sodium hydrogen sulphite (Merck), magnesium chloride (Sigma), ethyl acetate (Smart lab), n-hexane (Smart lab), and acetic acid (Merck). These reagents were used directly and without purification.

Instrumentation

Several instruments were operated for analysis includes UV-Vis spectrophotometer (Shimadzu UV-1601), Fourier Transformed Infrared (Shimadzu FTIR 8400s), Liquid Chromatography-Mass Spectrometer (UPLC Waters, QTOF-MS/MS).

Procedure

The procedure oxidation reaction was undergone following reference [16] with modification. Pine rosin (1.058 g; 3.5 mmol) in beaker glass was added with sodium hydroxide (1.0 g; 25 mmol). This mixture is added 100 mL of water until complete solution was formed. Oxidation reaction is tarted by addition of potassium permanganate to the mixture. Mole ratio applied for rosin acid/potassium permanganate was (1:0.5; 1:1; and 1:1.5). The reaction temperature studied by maintaining reaction at 5, 25, and 50 °C. Stirring of the mixture was stopped until completed reaction by consuming all potassium permanganate. Then, the solid precipitate, MnO₂, was converted into Mn(II) and dissolved in water phase by addition of aqueous hydrochloric acid 30 mL. The white product was solidified at room temperature. Separation of the mixture under filtration yield the product as white to pale solid product.

UV-Vis spectra analysis

The isolated product was analysed using UV-Vis spectrometry. Sample was dissolved in ethanol, and baseline was performed with blank sample prior to analysis. Data was scanned in between 200-800 nm.

FTIR spectra analysis

Sample was mixed with potassium bromide in 1:1 ratio (w/w) form a clear disk. The instrument was baselined, prior to analysis. Data was recorded between 500-5000 cm⁻¹ wavelength.

LCMS/MS measurement

A 10 mg of sample was dissolved in methanol. UPLC QTOF-MS/MS (Waters) with equipped with C18 RP-column (1.8 μ m, 2.1 x 150 mm) capillary column, flow rate 0.2 mL/min, and collision energy 4 Volt and 25-70 Volt was operated.

Acid value measurement

Procedure to determine acid value was conducted under titration method using potassium hydroxide. a 10 mg of sample was dissolved 10 mL solvent, and it was titrated with solution of potassium hydroxide 1.0 M. Phenolphthalein was applied as indicator to monitor the titration completion. Acid value was quantified as each mg of potassium hydroxide react to g of sample.

RESULT AND DISCUSSION

The oxidation products of pine rosin in aqueous potassium permanganate and basic conditions (pH > 8) are displayed in Figure 2. In general, the oxidation reaction gives a white to pale solid product, except for reaction undergo at 50 °C. It gives a pale-brownish powder. Furthermore, the effect of mole ratio of potassium permanganate and reaction temperature is summarized in Table 1 and Table 2. Mole ratio of pine rosin and potassium permanganate does not affect to the colour of the products. All the products are yielded as a white solid. However, increasing mole potassium permanganate accelerate the reaction [12] and improve the products yield from 61.4% to 86.0%. Products yield increase means the number of hydroxyl group in the rosin acid structure also increase. This affects the number of the acid value, since hydroxyl group can react to the base. The acid values were recorded at 193.2, 199.8, and 200 mg KOH/g product for mole ratio 1:0.5, 1:1, and 1:1.5, respectively. Meanwhile the starting material has acid value 168.3 mg KOH/g rosin acid (Table 1).

Conversely, the reaction temperature affects lower the product yield (Table 2). It was isolated in 86.0% at 0 °C and dropped to 46.4% when reaction was maintained at 50 °C. Furthermore, reaction temperature also increases the product acid values. It was recorded at 234.9 and 244.4 mg KOH/g product when reaction was conducted at 25 and 50 °C. In some rosin products, the acid value is controlled due to affect and can interact with other starting materials during industrial processing [17]. However, this addition functional groups can also open another possibility by generating the pine rosin derivatives based on hydroxylfunctionality reaction.



Figure 2. Effect reaction conditions on the product colour. (a) Starting material. Mole ratio reactant: potassium permanganate (b) 1:0.5, (c) mole ratio 1:0.5, (d) mole ratio 1:5; and reaction temperature (d) 0°C, (e) 25°C, and (f) 50°C

Table 1. The effect of mole ratio of oxidation reagent toward yield, colour, and acid value

Sample	% Yield	Color	Acid Value (mg KOH/g)		
Starting material	-	Yellow	168.3		
Product (mole ratio 1:0.5)	61.4 %	White	193.2		
Product (mole ratio 1:1)	75.6 %	White	199.8		
Product (mole ratio 1:1.5)	86.0 %	White	200.3		
Note: reaction was an language in 0 °C for 20 min					

Note: reaction was undergone in 0 °C for 30 min.

Table 2. The effect of reaction temperature toward yield, color, and acid value

Sample	% Yield	Color	Acid Value	
		X 7 11	(mg KOH/g)	
Starting Material	-	Yellow	168.3	
Product (0°C)	86.0 %	White	200.3	
Product (25°C)	68.0 %	Yellowish White	234.9	
Product (50°C)	46.4 %	Yellow	244.4	

Note: Reaction was undergone using mole ratio 1:1.5

Product analysis

Analysis using UV-Vis spectrometer give the absorption spectrum 240-250 nm (Figure 3a). This peaks absorption relates to the electronic transition for $\pi \rightarrow \pi^*$ of functional group, such as C=C from alkene and C=O from carbonyl or carboxylic acid [18].



Figure 3. UV-Vis (a) and FTIR spectra (b) of starting material and reaction products

Potassium permanganate catalysis oxidation of pine rosin produce hydroxylated of pine rosin. The reaction converts C=C diene of pine rosin become single bond (OH-C-C-OH) attached hydroxyl group. This hydroxyl group can be detected on FTIR spectra (at 3500 cm⁻¹) of products or disappearing of H-C= olefins vibration (at 3050 cm⁻¹) from the starting material (Figure 3b). This band absorption in agreement to the references [19], that -O-H stretching vibration between 3500-3400 cm⁻¹ for O-H group from alcohol or diols. Meanwhile, the -O-H vibration band of carboxylic acid group give a broad spectrum between 3500-2500 cm⁻¹. In addition to that, band absorption also detected at 1700 cm⁻¹ correlate to the C=O stretching band. This band is detected in both sample, that indicate the reaction did not undergo at carbonyl group or carboxylic acid functionality. Another band spectra are recorded in 3000-2900 cm⁻¹ which correlate to -C-H stretching band for methyl or alkyl groups [19]



Figure 4. Chromatogram LCMS/MS of starting material and oxidation products

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Further product analysis was conducted using LCMS/MS. This analysis provides chromatogram (Figure 4) and mass spectra data. Mass spectra data is synchronized and matched with mass spectra library. The summary of detected compound and type reactions are tabulated in Table 3. The chromatogram peaks indicate number of compounds can be detected based on their separation of mass molecules. Minimum 12 compounds composed the product, and minimum 9 compound was detected as the starting material. In addition, reducing compound percentage was observed. For example, occur in methyl sandaracopimarate, methyl isopimarate, dehydroabietic acid, methyl neoabietate, and methyl abietate. However, upscaling percentage found for 12-hydroxy dehydroabietic acid, methyl palustrate, and methyl abietate.

Three new compounds (Table 3) were derived in the reaction and was determined as 13,14-seco-13-oxoabiet-7-ene-14,18-dioic acid (0.52%) [20]. This compound was also reported composed in "*Pini resina*" and have cytotoxic activity [20]. Second product was identified as 7,8-dihydroxy abietic acid, which was previously reported [18], and the 7,8-oxo-dehydriabietic acid was yielded in 1.49%. This product was reported previously from plant species of *Anisochilus harmandii* [21] and showed antiplasmodial against *Plasmodium falciparum* and antimicrobial against *Mycobacterium tuberculosis* [21].

	Compounds	Molecular	Molecular Weight (g/mol)	Percentage (%)	
No				Rosin	Products
		Formula	weight (g/mor)	acid	
1	Methyl sandaracopimarate	$C_{21}H_{32}O_2$	316.49	2.57	1.37
2	12-Hydroxydehydroabietic	$C_{20}H_{28}O_3$	316.44	2.48	10.82
	acid				
3	Methyl isopimarate	$C_{21}H_{32}O_2$	316.49	7.87	1.21
4	Methyl palustrate	$C_{21}H_{32}O_2$	316.49	8.57	10.88
5	Dehydroabietic acid	$C_{20}H_{28}O_2$	300.44	13.48	6.77
6	Methyl neoabietate	$C_{21}H_{32}O_2$	316.49	9.22	3.66
7	Methyl abietate	$C_{21}H_{32}O_2$	316.49	31.31	51.37
8	Abietic acid	$C_{20}H_{30}O_2$	302.46	6.95	-
9	Neoabietic acid	$C_{20}H_{30}O_2$	302.46	2.21	-
10	13,14-seco-13-oxoabiet-7-	$C_{20}H_{30}O_5$	350.46	-	0.52
	ene-dioic acid				
11	7,8-Dihydroxy-abietic acid	$C_{20}H_{32}O_4$	336.47	-	6.62
12	7-oxo-Dehydroabietic acid	$C_{20}H_{26}O_3$	314.43	-	1.49

Table 3. Tabulation of identified con	pound from starting	material and	products
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Predicted reaction mechanism

This section focuses on prediction of the oxidation product of the two compounds i.e. 13-14-seco-13-oxoabiet-7-ene-14,18-dioic acid and 7,8-dihydroxy abietic acid. Both compounds are predicted derived from abietic acid (Figure 6), but potassium permanganate react at different position of the alkene. The 7,8-dihydroxy abietic acid was derived from C7-C8-alkene position oxidation. The formation of complex transition (**b**) occur by coupling Mn(VIII) to form Mn(VI) with C7-C8 [13, 22]. The direct hydrolysis of this complex releases the 1,2-diol oxidation product of abietic acid. The diol-1,2 product from similar alkene was resulted [23] using potassium permanganate under aqueous conditions. Meanwhile product

13-14-seco-13-oxoabiet-7-ene-14,18-dioic acid was derived from complex compound (a). Further cleavage oxidation [16,18,24] and the dioic acid compound after hydrolysis.



Figure 6. Plausible mechanism for abietic acid oxidation forms represented product.

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7,8-dihydroxy abietic acid

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CONCLUSION

Oxidation of pine rosin acid with potassium permanganate under aqueous acidic conditions forms 1,2-diol product of abietic acid (7,8-dihydroxy abietic acid). The oxidation occurs at C7-C8 position. The cleavage oxidation product at C13-C14-alkene position product 13-14-seco-13-oxoabiet-7-ene-14,18-dioic acid. The optimum condition conditions was obtained using mole ratio pine rosin acid : potassium permanganate (1:1.5) at 0 °C. It gives a higher yield, best acid value, and a stable white colour.

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REFERENCES

- [1] K. Fiebach and D. Grimm, "Resins, Natural," *in* Ullmann's Encyclopedia of Industrial Chemistry, **2012**, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.
- [2] L. McKeon, Characterisation and Determination of Rosin Compositions Using Analytical Approaches, PhD Thesis, Dublin City University, Dublin City, **2014**.
- [3] Wiyono, B., Tachibana, S. and Tinambunan, D. Pak. J. Biol. Sci., 2006, 9 (1), 7–14,
- [4] Liu, P., Liu, X., Saburi, T., Kubota, S., Huang, P. and Wada, Y., ACS Omega, 2020, 4(45), 29102-29109.
- [5] Silvestre, A. J. and Gandini, A. Rosin: Major sources, properties and applications, *in* Monomer, polymer and composite from renewable resources, Elsevier Ltd. Germany, 2008
- [6] Standar Nasional Indonesia, "Standar Nasional Indonesia 7636 : 2011," Jakarta, 2011.
- [7] A. M. Atta, S. M. El-Saeed, and R. K. Farag, *React. Funct. Polym.*, **2006**, 66 (12), 1596-1608.
- [8] F. Mustata and I. Bicu, *Eur. Polym. J.*, **2010**, 46 (6), 1316-1327.
- [9] Lewis, J.B. and Hedrick, G.W., Ind. Eng. Chem. Prod. Res. Dev., 1970, 9 (3), 304-310.
- [10] Zheng, Y., Yao, K., Lee, J., Chandler, D., Wang, J., Wang, C., Chu, F. and Tang, C., *Macromolecules*, 2010, 43, (14), 5922
- [11] Li, Y., Xu, X., Niu, M., Chen, J., Wen, J., Bian, H., Yu, C., Liang, M., Ma, L., Lai, F. and Liu, X. Energy Fuels, 2019, 33 (11), 11200–11209.
- [12] Prinz, S., Mullner, U., Heilmann, J., Winkelmann, K., Sticher, O., Haslinger, E. and Hufner, A. J. Nat. Prod., 2002, 65 (11), 1530–1534.
- [13] M. Masruri, R. W. Amini, and M. F. Rahman, Indones. J. Chem., 2018, 16 (1), 59.
- [14] Huang, X. and Groves, J. T., JBIC J. Biol. Inorg. Chem., 2014, 22 (2–3), 185-207.
- [15] Yang, P. and Yang, W., ACS Appl. Mater. Interfaces, 2014, 6 (6), 3759-3770.
- [16] Wiberg, K. B. and Saegebarth, K. A., J. Am. Chem. Soc., 1957, 79 (11), 2822-2824.
- [17] T. Silitonga, S. Sumadiwangsa, and S. Nayasapoetra, "Pengolahan dan Pengawasan Kualitas Gondorukem dan Terpentin," Direkorat Jendral Kehutanan, Bogor, **1973**.
- [18] Afifah, S. N., Masruri, M., Srihardyastutie, A. and Rahman, M. F., Jurnal Kimia Valensi, 2022, 8 (1), 92-105.
- [19] Coates, J., Interpretation of Infrared Spectra, A Practical Approach, *in* Encyclopedia of Analytical Chemistry, R. A. Meyers, Ed., **2006**, John Wiley & Sons Ltd., UK.
- [19] Koyama, H., Okawara, H., Kobayashi, S. and Ohno, M., *Tetrahedron Lett.*, 1985, 26 (22), 2685–2688.
- [20] Zaidi, S.F.H., Awale, S., Kalauni, S.K., Tezuka, Y., Esumi, H. and Kadota, S., *Planta medica*, 2006, 72 (13), 1231-1234.

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- [21] Lekphrom, R., Kanokmedhakul, S. and Kanokmedhakul, K., *Planta medica*, **2010**, 76 (7), 726-728.
- [22] Wiberg, K.B., Wang, Y.G., Sklenak, S., Deutsch, C. and Trucks, G., J. Am. Chem. Soc., 2006, 128 (35), 11537-11544.
- [23] Varma, R.S. and Naicker, K.P., Tetrahedron Let., 1998, 39 (41), 7463-7466.
- [24] Krapcho, A.P., Larson, J.R. and Eldridge, J.M., J. Org. Chem., 1977, 42 (23), 3749-3753.