Acidity-controlled selective oxidation of alpha-pinene, isolated from Indonesian pine’s turpentine oils (*pinus merkusii*)

Masruri*, Mohamad Farid Rahman, and Bagus Nurkam Ramadhan
Chemistry Department, Brawijaya University, Jl. Veteran 65145 Malang, Indonesia

*E-mail: masruri@ub.ac.id

Abstract. Alpha-pinene was isolated in high purity from turpentine oil harvested from *Pinus merkusii* plantation. The recent investigation on selective oxidation of alpha-pinene using potassium permanganate was undertaken under acidic conditions. The result taught the selective oxidation of alpha-pinene in acidic using potassium permanganate lead to the formation of 2-(3-acetyl-2,2-dimethylcyclobutyl)acetaldehyde or pinon aldehyde. The study method applied reaction in various different buffer conditions i.e. pH 3, 4, 5, and 6, respectively, and each reaction product was monitored using TLC every hour. Product determination was undertaken on spectrometry basis such as infrared, ultra violet-visible, gas chromatography- and liquid chromatography-mass spectrometry.

1. Introduction
Selective oxidation of naturally abundant substrates is an invaluable strategy in order to get industrially important starting materials for synthesis, pharmaceuticals, and or agrichemicals. Alpha-pinene, isolated as a major volatile component from turpentine oils become focused our study. Recently, it has been reported as antibacterial [1], anti-inflammation [2], and insect attractant. Oxidation of its carbon-carbon double bond was also reported, such as provided its 1,2-amino-alcohol [3] and 1,2-diol [4-5]. This paper is disclosed recent study for its selective transformation provided pinon aldehyde. Similar papers have reported using a different strategy such as using catalyst ruthenium [6-9], analysis [10-11], palladium [12], metal-oxo [13], and potassium permanganate [14-15]. However, it was found low yield and selectivity were reported.

2. Materials and methods

2.1 Chemical and instrument
Chemicals for research is used and bought from the manufacturer or as mentioned, including potassium permanganate (Merck), ethyl acetate (SAP), n-hexane (SAP), magnesium sulfate anhydrate (Merck), sodium sulfate anhydrate (Merck), silica gel (column chromatography, Merck), chloroform (Smart Lab), acetone (Smart Lab), ethanol (LIPI), methanol (Smart Lab), and pre-coated TLC silica (Merck). Alpha-pinene was isolated and purified from turpentine oils (got from PT. Perhutani Anugerah Kimia). Procedure and analysis were performed following Masruri et al. (2007) [1]. Meanwhile, instrumentation for analysis the product such as an ultra violet-visible spectrophotometer (Shimadzu UV-1601), an infrared spectrophotometer (Shimadzu FTIR-8400S), gas chromatograph-mass spectrometer (Shimadzu QP2010S). Operational condition: capillary column Restex 30 m,
programed-temperature with increasing rate 10 °C per min, initial temperature 80 °C for 5 min, end temperature 250 °C, carrier gas nitrogen), and UV lamp for TLC spot detection.

2.2 General procedure
To a mixture of alpha-pinene (5.00 mL, 31.56 mmol) and potassium permanganate (7.48 g, 47.34 mmol) was added buffer sodium acetate solution (2.5 mL, 1.0 M) at 10 °C. This reaction mixture was stirred until reaction complete. Reaction’s progress was monitored with spotting the sample on TLC plate, and the completed reaction was indicated as disappearing or consumed alpha-pinene during the reaction. Then, the reaction mixture was filtered, and the filtrate was extracted with ethyl acetate (3 x 10 mL). The combined ethyl acetate layers were dried under sodium sulfate anhydrate and concentrated by evaporation in a vacuum. Product purification was undertaken using flash column chromatography using ethyl acetate/n-hexane as eluent, and the purified product was isolated for further analysis using spectrometry methods (UV-Vis, FTIR, and GCMS).

2.3 Procedure for study pH reaction
The general procedure was followed with minor modification. The buffer sodium acetate solution was added in variation pH condition such as pH 3, 4, 5, and 6. Product separation, purification, and analysis were conducted using a similar procedure.

3. Result and discussion

3.1 alpha-Pinene from turpentine oils
Starting with the preparation of alpha-pinene from turpentine oil was the first step. Even though, the procedure already established for its purification, it was common founded that source of turpentine oil in different harvesting time and different manufacturer slightly provided different purity and composition [16].

Purification of alpha-pinene from turpentine oils produced by PT Perhutani Anugerah Kimia, as starting material was undertaken using fractional distillation under reduced pressure [1] (Masruri et al., 2007). Alpha-pinene was afforded in first fraction as clear oil with 97% of purity (Figure 1b), density 0.8406 g/mL (29 °C), index refractive 1.4648 (26 °C), and boiling point 77-79 °C (40 mmHg). The
structure is showed in scheme 1. Characterization of the alpha-pinene structure followed spectrometry data (Figure 1). Its infrared spectra significantly support the presence of functional groups contained (Figure 1a). Stretching vibration of =C-H was detected at 3070 cm$^{-1}$. This band was also correlated with the presence C=C stretching vibration at 1650 cm$^{-1}$, and its bending out of a plane in 788 cm$^{-1}$. The C=C alkene is the only functional group constructs its structure [1] (Masruri et al., 2007). Besides that, alkyl-group (CH$_3$, CH$_2$, and CH) was also detected. Symmetry and asymmetric stretching vibration found in between 2980 and 2820 cm$^{-1}$ meanwhile bending vibration around 1442 and 1371 cm$^{-1}$. In addition, the mass spectra gave ion-molecule (m/z) 136.00 that correlates to the molecular weight of alpha-pinene with molecular formula C$_{10}$H$_{16}$ (Figure 1c). The exact calculation for C$_{10}$H$_{16}$ itself gave 136.1252 mass units. Moreover, the resulted spectra confirmed and agreed to that recorded in library spectra (Wiley7) by providing similarity index (SI) value 95% similarities to alpha-pinene.

3.2 Oxidation reaction

Previously, some papers reported oxidation of alpha-pinene using ozonolysis strategy provided low yield and selectivity of pinon aldehyde, pinonic acid, and some others oxidation products [10-11]. Another strategy was applied by employing ruthenium trichloride [6-9]. This catalyst is a precious metal and not easily accessed. Another metal such as osmium [5] and palladium [12] was also reported as a catalyst. This finding applied potassium permanganate to convert alpha-pinene. It was found the acidic condition lead the reaction formed pinon aldehyde as the major product. The range of pH study was conditioned at 3, 4, 5, and 6 respectively (scheme 1). Increasing the acidity of reaction mixture significantly improved the yield of pinon aldehyde. For example, reaction under buffer pH 6 provided pinon aldehyde in 17.46 %yield. It improved to 33.70% at pH 5, 38.16% at pH 4, and 77.68% at pH 3 (table 1). A different result was recorded that increasing of acidity did not affect the formation of pinonic acid. In average, it was isolated in between 4.20 and 8.98 %yield.

![Figure 2. Oxidation reaction of alpha-pinene in acidic and basic condition using potassium permanganate](image)

| Table 1. Tabulation of oxidation of alpha-pinene in acidic condition |
|-------------------------------------------------------------|
| **Entry** | **Reaction** | **Time** | **Pinonaldehyde (yield, %)$^b$** | **Pinonic acid (yield, %)$^b$** |
| 1$^a$ | pH<6 | 6 | 77.68 | 8.98 |
| 2$^a$ | pH>6 | 6 | 38.16 | 7.25 |
| 3$^a$ | pH>6 | 5 | 33.70 | 4.20 |
| 4$^a$ | pH<6 | 6 | 17.46 | 5.61 |

$^a$Reaction using buffer acetate and conducted at 10 °C

$^b$Product yield were determined from GC chromatogram.
3.3 Product characterization

Pinonaldehyde was not a new compound. It has been reported and analyzed using gas chromatography-mass spectrometry of its deuterated compound. During the course, pinonaldehyde was characterized using infrared, ultraviolet-visible and mass spectra data (figure 3).

![Figure 3](image)

**Figure 3.** Spectra characteristic of pinonaldehyde: (a) infrared spectra, (b) ultra violet-visible spectra, and (c) mass spectra afforded from GCMS analysis.

The mass spectra provided a peak at m/z 168 for molecular ion (M⁺). Fragmentation of this ion provided daughter ions such as m/z 140, 125, 99, 71, and 43 (base peak). Peak m/z 140 was predicted as the peak for decomposed of carbon monoxide of molecule ion. This fragmentation is characteristic for an aldehyde compound [17]. Another specific fragmentation was displacement of acylium group (CH₃CO) formed m/s 125 and m/z 43 (base peak). Moreover, characterization using ultraviolet-visible spectrophotometer gave two maximum wavelengths i.e. 233 and 272 nm. It was predicted 233 nm for \(\pi\rightarrow\pi^*\) transition of C=C double bond, meanwhile 272 (low absorbance) as n→\(\pi^*\) transition on carbonyl group. In addition to this, the infrared spectra detected vibration band for C=O carbonyl of aldehyde (1743 cm⁻¹) and its C-H stretching (2727 cm⁻¹). The alkyl group was also detected their C-H stretching vibration in 1981-1885 cm⁻¹ include the bending vibration in 1444 and1371 cm⁻¹. A minor O-H vibration still was detected, in 3431 cm⁻¹. In short, all the spectra support the existence of pinonaldehyde as the reaction product oxidation of alpha-pinene catalyzed by potassium permanganate under acidic condition.
Analysis using GCMS, in fact, was also afforded chromatogram (figure 4). Pinonaldehyde was detected as it in retention time 11.25 min. alpha-Pinene, starting material was detected as well at 5.62 min, including other minor products. At the same time, the product was also sent for LCMS analysis. The result was reported for it chromatogram and mass spectra (figure 5a-b). Mass spectra for pinon aldehyde were scanned at retention time 3.10-3.51 min (peak at 3.33 min). Pinonaldehyde was detected as its [M+Na] ion found at 190.99 and [M+H] detected at 169.01 mass units. Theoretical calculation for pinon aldehyde molecular formula C\textsubscript{10}H\textsubscript{16}O\textsubscript{2} was 168.12 mass units. Its mass plus sodium (C\textsubscript{10}H\textsubscript{16}O\textsubscript{2}Na) gave 191.10 mass units while its protonated molecule (C\textsubscript{10}H\textsubscript{17}O\textsubscript{2}) gave 169.12 mass units.
4. Conclusion
In summary, oxidation of alpha-pinene using potassium permanganate in acidic condition provided major product, pinon aldehyde. It chemoselectivity is improved by increasing the acidity of reaction conditions. Other products were also detected as pinonic acid. Its quantity slightly affected by the acidic condition.

Acknowledgement
Authors thanks to the Indonesian Ministry of Research, Technology, and Higher Education through Brawijaya University for the “Penelitian Unggulan Perguruan Tinggi (PUPT) research grant year 2015 to MSR and MFR. All authors have an equal contribution to preparation the paper; BNR is collecting data, MSR analyzing and writing the manuscript, and MFR evaluating the result.

References
[1] Masruri, Rahman M F and Prasdjo T I 2007 Jurnal Ilmu-Ilmu Hayati (Life Sciences), 19 (1), 32-35.
[2] Khotimah H, Lyrawati D and Masruri 2006 Antiinflammatory effects of alpha-pinene extracted from Pinus mercury on levels of TNF-alpha signaling, iNOS, and apoptosis of neuronal cells, Asian Symposium on Medicinal Plants, Spices, and Other Natural Products (ASOMP XII), 13-18 November 2006, Padang, Indonesia.
[3] Łączkowski K Z, Kmiec iak A and Kozakiewicz A 2009 Tetrahedron: Asym., 20 (13), 1487-1492.
[4] Erdik E, K [acaron] hya D and Daşkapan T 1998 Synth. Comm., 28 (1), 1-7.
[5] Gomes M, and Antunes O A C 2001 Catal. Comm., 2 (6), 225-227.
[6] Carlsen P H J, Katsuki T Martin, V S and Sharpless K B 1981 J. Org. Chem., 46 (19), 3936-3938.
[7] Moglioni, Albertina G, Garcia-Expósito E, Aguado G P, Parella T, Branchadell V, Moltrasio G Y and Ortuno R M 2000 J. Org. Chem., 65, 13, 3934-3940.
[8] Ziyat H, Ali M A, Karim A, Meliet C, Castanet Y and Mortreux A 2004 Acta Chim. Slov., 51, 223-230.
[9] Padala, Kishor and Jeganmohan M 2012 Org. Let., 14, 4, 1134-1137.
[10] Holloway F, Anderson H J and Rodin W 1955 Ind. Eng. Chem., 47, 10, 2111-2113.
[11] Fisher G S, Goldblatt L A and Stinson J S 1956 Converting alpha-pinene to mixtures of acids. In US Patents No US2750411 A: 1956
[12] Liu, Yan-Yun, Ren-Jie S, Cui-Yan W, Lu-Bin G, Ming H, Zhi-Qiang Wa, Ye-Xiang X and Jin-Heng L 2012 Adv. Synth. Cat., 354, 2/3, 347-353.
[13] Rubinstein, Amir, Jiménez-Lozanao P, Carbó J J, Poblet J M and Neumann R 2014 J. Am. Chem. Soc., 136, 31, 10941-10948.
[14] Tercio J, Ferreira B, Cruz W O, Vieira P C and Yonashiro M 1987 J. Org. Chem., 52, (16), 3698-3699.
[15] Masruri, Amini R W and Rahman M F 2015 Antibacterial activity of alpha-pinene derivative and its coordination compounds Indonesian Journal of Chemistry (Submitted, under reviewed)
[16] Amini R W, Masruri and Rahman M F 2014 Jurnal Ilmu Kimia Universitas Brawijaya, 1 (1), 147-153.
[17] Silverstein R M, Francis X, Webster and Kiemle D J 2005 Spectrometric Identification of Organic Compound, 7th edition, John Wiley & Sons Inc., USA