

ANTHRAQUINONE FROM THALLUS OF LICHEN *Ramalina javanica* Nyl

Suyanto^{a,*}, Wahyudi Priyono Suwarso^b, Soleh Kosela^b, Hery Suwito^a, Pratiwi Pudjiastuti^a, Sri Winiati^c, and Nurdin Saidi^d

^aDepartment of Chemistry, Faculty of Sciences, Airlangga University, Surabaya, Indonesia

^bDepartment of Chemistry, Faculty of Sciences, Indonesia University, Depok, Indonesia

^cDepartment of Chemistry, Faculty of Sciences, Jakarta State University, Jakarta, Indonesia

^dDepartment of Chemistry, Faculty of Sciences, Syah Kuala University, Banda Aceh, Indonesia

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ABSTRACT

The isolation of 1,3,8- trihydroxy-2(1'-pentanol)-6-methoxy anthraquinone from acetone extract of lichen thallus of *Ramalina javanica* Nyl. was carried out. Its structure was determined based on spectroscopic evidences.

Keywords: *Ramalina javanica* Nyl., anthraquinone.

INTRODUCTION

Lichen is a unique plant because it is composed of two completely different organisms, green or blue-green algae related to free living algae, and colorless fungal threads called hypae. These two different organisms grow together in harmonious association referred to as symbiosis, or more simply living together. Lichen symbiosis, differs basically from all other kinds in that new plant body this thallus, is formed [1]. Lichens belong to the lower plant-kingdom that are rich source of secondary metabolites. All secondary substances which are so characteristic for lichen are of fungal origin. Consequently, it seems rather surprising that more than 630 secondary metabolites are found from lichen, most of them unique to this organism and only a small amount are known in other fungi or higher plants [2].

EXPERIMENTAL SECTION

General Experimental Procedures

FTIR spectrum was measured on a Jasco 5300, UV spectrum was performed on Shimadzu Pharmaspec 1700 and melting point was measured on a Fisher Johns melting point apparatus (without any correction). The NMR spectrum was recorded on FTNMR Hitachi 400 MHz, and Mass spectrum analysis was carried out on a GCMS Shimadzu QP-5000 spectrometer.

Plant Material

The thallus of lichen *R. javanica* Nyl was collected from Cibodas National Botanical Garden, West Java, Indonesia, in June 2001.

Extraction and Isolation

The air dried thallus (2000 g) was first soaked in n-hexane for 2 weeks giving n-hexane extract. The residue was then soaked in acetone for two weeks. The acetone

filtrate was concentrated to give acetone extract (40 g) which was then subjected to fractionation on silica gel column chromatography and eluted with a mixture of n-hexane-ethyl acetate giving 0.9 mg white powder of anthraquinone.

RESULT AND DISCUSSION

Structure Elucidation

The acetone extract of the thallus lichen of *Ramalina javanica* Nyl was fractionated on silica gel column chromatography. An extensive purification of the green fraction in column chromatography yielded anthraquinone. Anthraquinone was isolated as white powder has a melting point of 198 – 200^o C, and a molecular ion peak (M⁺) of 372 with molecular formula C₂₀H₂₀O₇. It showed λ_{max} (CHCl₃) at 272 nm on the UV spectrum. Analysis of IR spectrum (KBr) gives peaks at the following wave numbers, ν = 3389, 2924, 1726, 1664, 1589, 1535, 1440, 1271. cm⁻¹. The ¹H-NMR spectrum showed protons at δ (ppm): 7.24 (s,H-5); 6.69 (s, H-4); 6.18(s, H-7); 5.28 (s,-CHOH-); 3.83 (s,-OMe);2.47(t,J=18.5 Hz,-CH₂-); 1.58(s,-CH₂-); 1.23(s,-CH₂-); 0.85(s,-Me). The MS spectrum (70 eV) gave ion fragment (m/z): 372(M⁺); 368; 353; 333; 325; 305; 277; 251; 234; 199; 184; 155; 142; 127; 107; 91; 77; 51; 39.

Maximum wave length at λ = 272 nm, indicate >C=O group, and supported by wave number at ν = 1726 cm⁻¹ on IR spectrum. Wave number at ν = 1664 cm⁻¹ indicated a quinone group and wave number at ν = 2924 cm⁻¹ indicated intra molecular hydrogen bridge which formed chelate 5 ring. Wave number at ν = 1271 cm⁻¹ indicated stretching vibration of C-O-C. The profile of MS spectrum at ion fragment m/z = 77, 51 and 39 indicated aromatic compound [3,4]. Difference ion fragment from m/z = 251 to 234, Δ(m/z) = 17 indicate a hydroxyl group (-OH). This case was supported by

* Corresponding author.

chemical shift at $\delta = 5.28$ ppm on $^1\text{H-NMR}$ spectrum. Difference ion fragment from $m/z = 305$ to 277 and from $m/z=155$ to 127 , $\Delta(m/z) = 28$ indicate a two $>\text{C}=\text{O}$ groups [5]. The difference ion fragment from $m/z = 184$ to 155 , $\Delta(m/z) = 29$ indicated phenol group, because HCO group are losses [5]. Then this data was compared with data in Huneck & Yoshimura [6] as shown in Table 1.

Based on mentioned data and discussion above the structure of isolated compound can be visualized in Figure 1, and considered as a new compound.

Table 1 The comparison of physics and spectroscopic properties of isolated compound and 6-O-metilaverantin [6]

Properties	isolated compound	6-O-metilaverantin
Melting point ($^{\circ}\text{C}$)	198-200	213
UV (nm)	(CHCl_3): 272	(MeOH): 250, 292
MS (m/z)	372(M^+), 368, 333, 325, 305	386(M^+), 368, 339, 325, 311
$^1\text{H-NMR}$ (δ , ppm)	(CDCl_3 , 400 MHz): 7,24(s, H-5); 6,69(s, H-4); 6,18(s, H-7); 5,28(s, -CHOH-); 3,83(s, -OMe); 2,47(t, $J=18,5\text{Hz}$, - CH_2^-); 1,58(s, - CH_2^-); 1,23(s, - CH_2^-); 0,85(s, -Me)	(CD_3COCD_3 , 100 MHz): 7,26(d, $J=2\text{Hz}$, H-5); 7,14(s, H-4); 6,73d, $J=2\text{Hz}$, H-7); 5,46(dd, -CHOH-); 3,98(s, OMe); 2,50(m, - CH_2^-); 1,84(m, - CH_2^-); 1,40(m, 2x- CH_2^-); 0,86(t, $J=7\text{Hz}$, -Me)

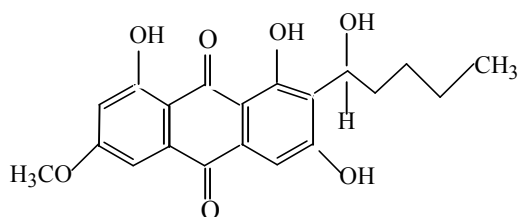


Fig 1 The interpretation structure of isolated compound.

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REFERENCES

- Hale, M.E., 1979, *How To Know The Lichens*, 2nd ed., Smithsonian Institution, The Nature Series Wm C.Brown Company Publishers Dubuque Iowa, p 1.
- Elix, J.A., 1997, *Biochemistry and Secondary Metabolites*, in Nash, T.H., Lichen Biology, Cambridge University Press, Cambridge, 155.
- Padmawinata, K. and Soediro, I., 1982, *Analisis Spektrum Senyawa Organik, Translate from Spectrum Analysis of Organic Compound, An introductory programmed text*, by Creswell, C.J., Runquist, O.A. & Campell, M.M., x+360 page, ITB Press, Bandung.
- Silverstein, R.M. and Webster, F.X., 1998, *Spectrometric Identification of Organic Compound*, 6th, Ed., John Wiley & Sons, Inc. New York,
- Sanagi, M.M., 1999, *Spektrometri JISIM*, Universiti Teknologi Malaysia, Johor Darul Ta'zim
- Huneck, S., and Yoshimura, I., *Identification of Lichen Substances*, Springer-Verlag, Berlin, 1996, p 3-5, 352.
- Dewick, P.M., 1992, *Medicinal Natural Products A Biosynthetic Approach*, John Wiley & Sons, Chichester

Appendix : Biosynthesis of the compound

