Jurnal Akta Kimia Indonesia
INDONESIA CHIMICA ACTA

PAPER

View Article Online
View Journal View Issue

Antifeedant Activity of Benzopyrans from *Melicope latifolia*

Rizdhana Juliana Putri[1], Muhammad Fajar Aldin[1], Ratih Dewi Saputri[1], Tjitjik Srie Tjahjandarie[1], and Mulyadi Tanjung[1*]

Cite this: *Indo. Chim. Acta.*, 2020, **13**, 2.

Received Date:
20th June 2020
Accepted Date:
12rd December 2020

Keywords:
Melicope latifolia;
Benzopyran;
Evodionol;
Evodion;
antifeedant

DOI:
http://dx.doi.org/10.20956/ica.v13i2.10439

Abstract. Melicope latifolia is one species that belongs to the family Rutaceae. The aim of the research is the isolation of benzopyrans from the stem bark of M. latifolia and their antifeedant activity against Plutella xylostella. Two benzopyrans, evodionol (**1**), and evodion (**2**) were isolated from the stem bark of Melicope latifolia. The structure of both compounds was identified based on 1D and 2D NMR, UV, and IR spectroscopy. Antifeedant activity of compounds **1-2**, and ethyl acetate extract, showing inhibition value of 28.9; 31.3, and 46.8%, respectively, which were categorized as moderate.

Introduction

Melicope latifolia is a plant species that belongs to the family Rutaceae. This plant is found throughout the Indonesian archipelago (Hartley *et al.,* 2001). In Indonesia, the *Melicope* plant is known by the local name 'Ki Sampang'. *Melicope* plants produce various secondary metabolites such as alkaloids (Chen *et al.,* 2001; Nakashima *et.al.,* 2012; Tanjung *et al.,* 2017; Tjahjandarie *et al.,* 2018), flavonoids (Saputri *et al.,* 2018), benzopyrans (Kamperdick *et al.,* 1997), coumarins (Kassim *et al.,* 2013), and terpenoids (Chandramu *et al.,* 2013). Alkaloid, benzopyrans, coumarins, and flavonoid *Melicope*, showing isoprenyl (C_5) or geranyl (C_{10}) (Kamperdick *et al.,* 1999; Saputri *et al.,* 20019). The purpose of the research is the isolation of benzopyrans from the stem bark of *M. latifolia* and their antifeedant activity. Two benzopyran derivatives, evodionol (**1**) and evodion (**2**), were isolated from the stem bark of *M. latifolia.* The antifeedant activity of compounds 1-2, and ethyl acetate extract against *Plutella xylostella* also reported.

Experimental

Material and Methods

The stem bark of *M. latifolia* was obtained from Werekopa Village, South Fakfak District, Fakfak Regency, Papua. Plant identification was carried out at the Bogoriensis Herbarium, Botany Garden, Cibinong, Bogor. Thin-layer chromatography (TLC) analysis using TLC silica gel 60 GF_{254} 0.25 mm. Gravity column chromatography uses silica gel 60 (Merck), radial chromatography using 60 PF_{254} silica gel (Merck). The UV spectrum was determined with a Shimadzu 1800 UV-Vis spectrophotometer The IR spectrum was determined with the Shimadzu IR spectrophotometer. The NMR spectrum was determined by the NMR JEOL ECA 400, which operates at 400 MHz (^{1}H-NMR) and 100 MHz (^{13}C-NMR). Test the antifeedant activity of the *Plutella xylostella* caterpillar by using the leaf disc method of choice.

Extraction and Isolation

The extraction of the stem bark of *M. latifolia* (2.1 kg) by maceration using methanol at room temperature. The methanol solvent is then evaporated with a rotary vacuum evaporator to produce a thick methanol extract. Separation of nonpolar compounds contained in viscous methanol extract was carried out by liquid-liquid extraction using n-hexane solvent. The methanol extract that is free of nonpolar compounds is then repartitioned with ethyl acetate to produce 20 grams of ethyl acetate extract. Separation of ethyl acetate extract (20 g) by gravity column chromatography with a mixture n-hexane : ethyl acetate (9: 1 to 4: 1) as eluent to get two fractions A and B. Separation of fraction A (6.8 g) using gravity column chromatography using Sephadex LH-20 with methanol eluent produces A_1, A_2,

[1]*Natural Product of Chemistry, Department of Chemistry, Faculty of Science and Technology, Airlangga University, Surabaya;* ***Email: mulyadi-t@fst.unair.ac.id***

This article is licensed under a Creative Commons Attribution-ShareAlike 4.0 International License.

and A_3 subfractions. Separation of A_1 subfraction by gravity chromatography column using Sephadex LH-20 produces two subfractions, A_{11} and A_{12}. Separation of A_{11} subfractions (4.4 grams) by radial chromatography using n-hexane: ethyl acetate (9: 1 and 4: 1) as eluent produced four subfractions namely, A_{111}, A_{112}, A_{113}, and A_{114}. Purification of A_{113} subfraction using radial chromatography with n-hexane: diisopropyl ether (1:38) eluent to get evodion (**2**) as a yellow oil as much as 26.6 mg.

Separation of subfraction A_2 (1.8 gram) by gravity column chromatography using Sephadex LH-20 produced three subfractions, namely A_{21}, A_{22}, and A_{23}. Separation of subfraction A_{22} (1.2 gram) using radial chromatography with a mixture n-hexane: diisopropyl ether (9: 1, 4: 1, and 7: 3) as eluent produces three subfractions, namely, subfraction A_{221}, A_{222}, and A_{223}. Purification of the subfraction A_{221} by radial chromatography using n-hexane: chloroform as eluent (1:38) to get evodionol (**1**) as a yellow solid as much as 25 mg.

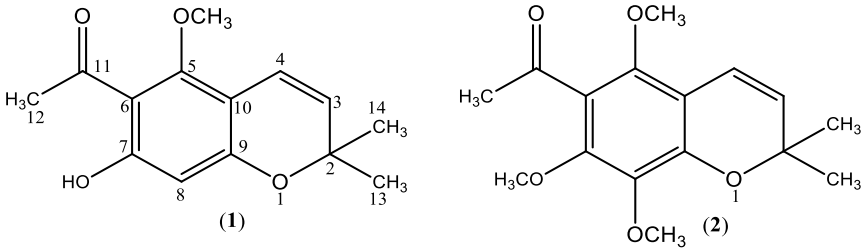

Figure 1. Benzopyrans of *M. latifolia*

Antifeedant Activity

The antifeedant activity screening of compound 1 and 2 as well as ethyl acetate extract was tested against the *P. xylostella* caterpillar by the chosen leaf disc method. Compound 1 and 2 as well as ethyl acetate extract were each made to various concentrations of 1, 5, 10, 50, 100, and 500 µg/mL in 1% acetone (each of the two applications). Cabbage leaf discs of 2 cm are divided into two parts, namely for the control section and the test compound section. Water is used as a control and is dripped on leaves with the same volume as the test compound (Chandramu *et al.,* 2003).

Results And Discussion

Evodionol (**1**) was isolated as a light yellow solid with a melting point of 66-67^{0}C. The UV spectrum (MeOH) λ_{max} (log ε): 221 (3.93), 278 (4.24), and 283 nm (4.21), which is a characteristic for benzopyran moiety (Kamperdick *et al.,* 1997). The IR spectrum showed absorption bands at 3500 cm^{-1} for a hydroxy group (-OH), 1707 cm^{-1} for conjugated carbonyl (C=O), and 1639-1491 cm^{-1} from a C=C aromatic, respectively. The ^{1}H NMR spectrum showed the resonances of 2,2-dimethyl-pyrano ring consist of a pair of a *cis* vinylic proton at δ_H 6.54 (1H, d, *J* = 10.0 Hz, H-4), δ_H 5.41 (1H, d, *J* = 10.0 Hz, H-3), a gem-dimethyl proton at δ_H 1.48 (6H, s, H-13/H-14)]. One singlet aromatic proton signal at δ_H 5.99 and the resonances of the 2,2-dimethyl-pyrano ring is a characteristic of benzopyran moiety (Kamperdick *et al.,* 1997). Other proton signals bound to the benzopyran in an aromatic nucleus are one acetyl proton singlet signal at δ_H 2.66, one methoxy proton singlet signal at δ_H 3.83, and one hydroxy proton singlet signal at δ_H 13.83. The ^{13}C-NMR spectrum of **1**, shows 13 carbon signals, representing seven quarternary carbons, three methine carbons, and four methyl carbons. The HMBC spectrum determined the placement of the methoxy, hydroxy, and acetyl substituents in compound **1**. Based on the HMBC spectrum analysis, it was concluded that compound **1** was evodionol (Table 1 and Figure 2).

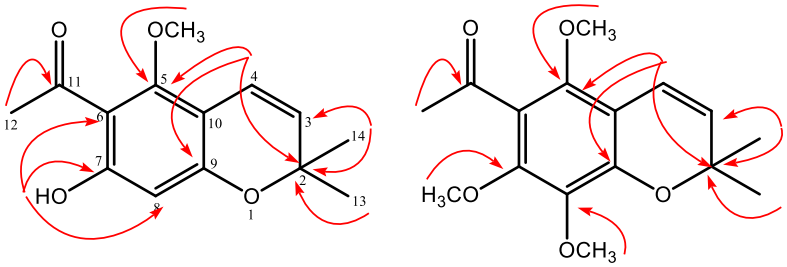

Figure 2. Selected HMBC correlations for **1-2**

This article is licensed under a Creative Commons Attribution-ShareAlike 4.0 International License.

Table 1. NMR data of compounds **1-2** in $CDCl_3$

No	Evodionol (1)			Evodion (2)		
	δ_H (mult, in Hz)	δ_C	HMBC	δ_H (mult, in Hz)	δ_C	HMBC
2	-	77.8	-	-	76.9	-
3	5.41 (*d*, 10,0)	124.6	C-2; C-10	5.60 (*d*, 10.0)	129.4	C-2; C-10
4	6.54 (*d*, 10,0)	116.6	C-2; C-9	6.48 (*d*, 10.0)	116.6	C-2; C-5; C-9
5	-	161.0	-	-	148.4	-
6	-	106.0	-	-	122.8	-
7	-	166.4	-	-	150.5	-
8	5.99 (*s*)	92.3	C-7; C-10	-	138.1	-
9	-	156.3	-	-	148.4	-
10	-	102.8	-	-	111.9	-
11	-	203.4	-	-	201.4	-
12	2.66 (*s*)	33.2	C-11	2.49 (*s*)	32.7	C-11
13	1.48 (*s*)	27.9	C-2. C-3; C-14	1.47 (*s*)	27.9	C-2. C-3; C-14
14	1.48 (*s*)	27.9	C-2. C-3; C-13	1.47 (*s*)	27.9	C-2. C-3; C-13
5-OCH_3	3.83 (*s*)	55.8	C-5	3.71 (*s*)	63.8	C-5
7-OCH_3	-	-	-	3.89 (*s*)	62.0	C-7
8-OCH_3	-	-	-	3.83 (*s*)	61.1	C-8
7-OH	13.83 (*s*)	-	C-6; C-7; C-8	-	-	

The antifeedant activity of **1-2** and ethyl acetate extract against *P. xylostella* by the selected leaf disk method. The antifeedant activity of **1-2** and ethyl acetate extract showed a percentage inhibition of 28.9, 31.3, and 46.8%, categorized as moderate.

Conclusion

Two benzopyrans, evodionol (**1**) and evodion (**2**), have been isolated from the stem bark of *M. latifolia*. The antifeedant activity of compounds 1 and 2, and ethyl acetate extract against *P. xylostella* caterpillars categorized as moderate activity.

Conflict of Interest

The authors proclaim no potential conflict of interest.

Acknowledgements

Thank you to Mr. A. Permadi for the supply of *M. latifolia.*

References

Chandramu, C., Manohar, R.D., Krupadanam, .D. G., Dashayantha, R.V. (2003), Isolation, characterization and biological activity of betulinic acid and ursolic acid from *Vitex negundo* L., *Phytoter. Res.*, 17: 129-134.

Chen, I. S., Chen, H. F., Cheng, M. J., Chang, Y. L., Teng, C.M., Tsutomu, I., Tsai, I.L. (2001), Quinoline alkaloids and other constituents of *Melicope semecarpifolia* with antiplatelet aggregation activity, *J. Nat. Prod*, 64 (9): 1143-1147.

Hartley, T.G. (2001), Taxonomy and biogeo-graphy of *Evodia* and *Melicope* (Rutaceae), *Allertonia*, 8(1): 1–328.

Kamperdick, C., Van, N.H., Sung, T., Adam, G. (1999), Bisquinolinone alkaloids from *Melicope ptelefolia*," *Phytochem*., 50(1): 177-181.

Kamperdick, C., Van, N.H., Sung, T., Adam, G., (1997), Benzopyrans from *Melicope ptelefolia* leaves," *Phytochem*., 45(5): 1049-1056.

Kassim, N.K., Rahmani, M., Ismail, A., Sukari, M.A., Ee, G.C.L., Nasir, N.M., Awang, K., (2013), Antioxidant activity-guided separation of coumarins and lignan from *Melicope glabra* (Rutaceae), *Food. Chem*., 139: 87-92.

Nakashima, K**.,** Oyama, M., Ito, T. , Witono, J.R., Darnaedi, D., Tanaka, T., Murata, T., Iinuma, M., (2011), Melicodenines A and B, novel Diels-Alder type adduct isolated from *Melicope denhamii*, *Tetrahedron Lett*, 52:4694-4696

Saputri, R.D., Tjahjandarie. T.S., Tanjung, M, (2019), Alkaloid furokuinolin dan asam sinamat ter-*O*-geranilasi dari Melicope hookeri T.G. Hartley, *J Sains & Kesehatan*, 2: 1-7.

Saputri, R.D., Tjahjandarie. T.S., Tanjung, M, (2018), Meliglabrin, a new flavonol derivative from the leaves of Melicope glabra (Blume) T.G. Hartley, *Nat Prod Sci.*, 24: 155-158.

Saputri, R.D., Tjahjandarie. T.S., Tanjung, M, (2018), Alkaloid kuinolin dari Melicope denhamii dan uji aktivitas antikankernya, *J Sains & Kesehatan*, 1: 505-509.

Tanjung, M, Saputri, R.D., Wahjoedi, R.A., Tjahjandarie, T.S., (2017), 4-Methoxy-3-(3-methylbut-2-en-1-yl)-7-((3-methylbut-2-en-1-yl)oxy) quinolin-2(1H)-one from *Melicope moluccana* T.G. Hartley, *Molbank*, 1-5,

This article is licensed under a Creative Commons Attribution-ShareAlike 4.0 International License.

https://www.mdpi.com/1422-8599/2017/2/M939.

Tjahjandarie, T.S., Tanjung, M, Saputri, R.D., (2018), Melimoluccanin, A new isoprenylated quinolone alkaloid from the leaves of *Melicope moluccana* TG Hartley, *Journal of Physics: Conference Series*, 1095(1): 012042.

This article is licensed under a Creative Commons Attribution-ShareAlike 4.0 International License.