Supplementary Materials

Constituents and Anti-Multidrug Resistance Activity of *Taiwanofungus camphoratus* **on Human Cervical Cancer Cells**

Hsin-Yi Hung ¹, Chin-Chuan Hung ², Jun-Weil Liang ³, Chin-Fu Chen ⁴, Hung-Yi Chen ², Po-Chuen Shieh ⁵, Ping-Chung Kuo ^{1,*} and Tian-Shung Wu ^{1,5,*}

- ¹ School of Pharmacy, College of Medicine, National Cheng Kung University, Tainan 701, Taiwan; z10308005@email.ncku.edu.tw
- ² Department of Pharmacy, College of Pharmacy, China Medical University, Taichung 402, Taiwan; cc0206hung@gmail.com (C.-C.H.), hungyi@mail.cmu.edu.tw (H.-Y.C.)
- ³ Department of Chemistry, National Cheng Kung University, Tainan 701, Taiwan; p77625@hotmail.com
- ⁴ Department of Life Sciences, National Cheng Kung University, Tainan 701, Taiwan; chinfu9999@gmail.com
- ⁵ Department of Pharmacy, College of Pharmacy and Health Care, Tajen University, Pingtung 907, Taiwan; pochuen@tajen.edu.tw (P.-C.S.)
- * Correspondence: tswu@mail.ncku.edu.tw (T.-S.W.); z10502016@email.ncku.edu.tw (P.-C.K.); Tel.: +886-2353535-65333 (T.-S.W.); Tel.: +886-6-2353535-6806 (P.-C.K.)

Contents

- S01. References of the known compounds.
- Fig. S01. ESI-MS spectrum of Camphoratin K (1)
- Fig. S02. HRMS spectrum of Camphoratin K (1)
- Fig. S03. IR spectrum of Camphoratin K (1).
- Fig. S04. ¹H NMR spectrum of Camphoratin K (1)
- Fig. S05. ¹³C and DEPT NMR spectrum of Camphoratin K (1)
- Fig. S06. COSY spectrum of Camphoratin K (1)
- Fig. S07. HSQC spectrum of Camphoratin K (1)
- Fig. S08. HMBC spectrum of Camphoratin K (1)
- Fig. S09. NOESY spectrum of Camphoratin K (1)
- Fig. S10. ESI-MS spectrum of Camphoratin N (2)
- Fig. S11. HRMS spectrum of Camphoratin N (2)
- Fig. S12. IR spectrum of Camphoratin N (2)
- Fig. S13. ¹H NMR spectrum of Camphoratin N (2)
- Fig. S14. ¹³C and DEPT NMR spectrum of Camphoratin N (2)
- Fig. S15. COSY spectrum of Camphoratin N (2)
- Fig. S16. HSQC spectrum of Camphoratin N (2)
- Fig. S17. HMBC spectrum of Camphoratin N (2)
- Fig. S18. NOESY spectrum of Camphoratin N (2)
- Fig. S19. ESI-MS spectrum of Benzocamphorin G (3).
- Fig. S20. HRMS spectrum of Benzocamphorin G (3)
- Fig. S21. IR spectrum of Benzocamphorin G (3).
- Fig. S22. ¹H NMR spectrum of Benzocamphorin G (3)
- Fig. S23. ¹³C and DEPT NMR spectrum of Benzocamphorin G (3)
- Fig. S24. COSY spectrum of Benzocamphorin G (3)
- Fig. S25. HSQC spectrum of Benzocamphorin G (3)
- Fig. S26. HMBC spectrum of Benzocamphorin G (3)
- Fig. S27. NOESY spectrum of Benzocamphorin G (3)
- Fig. S28. ESI-MS spectrum of Benzocamphorin I (4).
- Fig. S29. HRMS spectrum of Benzocamphorin I (4)
- Fig. S30. IR spectrum of Benzocamphorin I (4).

- Fig. S31. ¹H NMR spectrum of Benzocamphorin I (4)
- Fig. S32. ¹³C and DEPT NMR spectrum of Benzocamphorin I (4)
- Fig. S33. COSY spectrum of Benzocamphorin I (4)
- Fig. S34. HSQC spectrum of Benzocamphorin I (4)
- Fig. S35. HMBC spectrum of Benzocamphorin I (4)
- Fig. S36. NOESY spectrum of Benzocamphorin I (4)

S01. References of the known compounds.

Methyl antcinate A (5)[1],

Antcins A (6), C (12), and K (18), zhankuic acid A methyl ester (7), zhankuic acids A

(8), B (11), C (9), camphoratins E (13) and F (14), methyl antcinate H (15),

antcamphin D (17), antcamphins A (19), B (16), ergosterol (24), ergosterol peroxide

(25), camphoratin I (26), sesamin (27) and 4-hydroxysesamin (28), antrocamphins A

(30) and B (29), methyl 3,4,5-trimethoxybenzoate (33), benzocamphorins C (37), D

(44), E (43), methyl 2,5-dimethoxy-3,4-methylenedioxybenzoate (38), 4,7-

dimethoxyl-5-methyl-1,3-benzodioxole (40), 2,2,5,5-tetramethoxyl-3,4,3,4-

bimethylenedioxyl-6,6-dimethylbiphenyl (42)[2,3]

Zhankuic acid D (10)[4]

1-Hydroxy-*p*-menth-3-en-2-one (20)[5]

Coenzyme Q (22)[6]

4-Acetylantroquinonol B (23)[7]

Benzocamphorin F (31)[8]

Benzocamphorin H (32)[9]

Methyl 2,3,4,5-tetramethoxy benzoate (34), 1-methyl-2,3,4,5-trimethoxy benzene

(35)[10]

2,3,6-Trimethoxy-5-methylphenol (36), 2,3-(methylenedioxy)-4-methyl-5-

methylphenol (41)[11]

4,5-Dimethoxy-6-methyl-1,3-benzodioxole (39)[12]

Tetracanyl ferulate (45)[13]

Reference:

- Tsai, W.C.; Rao, Y.K.; Lin, S.S.; Chou, M.Y.; Shen, Y.T.; Wu, C.H.; Geethangili, M.; Yang, C.C.; Tzeng, Y.M. Methylantcinate A induces tumor specific growth inhibition in oral cancer cells via Bax-mediated mitochondrial apoptotic pathway. *Bioorg Med Chem Lett* 2010, 20, 6145-6148, doi:10.1016/j.bmcl.2010.08.006.
- 2 Shi, L.S.; Chao, C.H.; Shen, D.Y.; Chan, H.H.; Chen, C.H.; Liao, Y.R.; Wu, S.J.; Leu, Y.L.; Shen, Y.C.; Kuo, Y.H., et al. Biologically active constituents from the fruiting body of Taiwanofungus camphoratus. *Bioorg Med Chem* 2011, *19*, 677-683, doi:10.1016/j.bmc.2010.10.032.
- 3. Wu, S.J.; Leu, Y.L.; Chen, C.H.; Chao, C.H.; Shen, D.Y.; Chan, H.H.; Lee, E.J.; Wu, T.S.; Wang, Y.H.; Shen, Y.C., et al. Camphoratins A-J, potent cytotoxic and antiinflammatory triterpenoids from the fruiting body of

Taiwanofungus camphoratus. J Nat Prod 2010, 73, 1756-1762, doi:10.1021/np1002143.

- 4. Yang, S.-W.; Shen, Y.-C.; Chen, C.-H. Steroids and triterpenoids of Antodia cinnamomea—A fungus parasitic on Cinnamomum micranthum. *Phytochemistry* **1996**, *41*, 1389-1392, doi:https://doi.org/10.1016/0031-9422(95)00767-9.
- 5. Matsuura, T.; Suga, T. Oxidation of Terpene Compounds with t-Butyl Chromate. VIII.1 The Oxidation of α-Terpinene2. *The Journal of Organic Chemistry* **1965**, *30*, 518-520, doi:10.1021/jo01013a052.
- Wu, M.D.; Cheng, M.J.; Wang, W.Y.; Huang, H.C.; Yuan, G.F.; Chen, J.J.; Chen, I.S.; Wang, B.C. Antioxidant activities of extracts and metabolites isolated from the fungus Antrodia cinnamomea. *Nat Prod Res* 2011, 25, 1488-1496, doi:10.1080/14786410903132563.
- Chen, M.-C.; Cho, T.-Y.; Kuo, Y.-H.; Lee, T.-H. Meroterpenoids from a Medicinal Fungus Antrodia cinnamomea. *Journal of Natural Products* 2017, *80*, 2439-2446, doi:10.1021/acs.jnatprod.7b00223.
- Lee, C.L.; Huang, C.H.; Wang, H.C.; Chuang, D.W.; Wu, M.J.; Wang, S.Y.; Hwang, T.L.; Wu, C.C.; Chen, Y.L.; Chang, F.R., et al. First total synthesis of antrocamphin A and its analogs as anti-inflammatory and anti-platelet aggregation agents. *Org Biomol Chem* 2011, 9, 70-73, doi:10.1039/c0ob00616e.
- 9. Liao, Y.-R.; Kuo, P.-C.; Huang, S.-C.; Liang, J.-W.; Wu, T.-S. An efficient total synthesis of Benzocamphorin H and its anti-inflammatory activity. *Tetrahedron Letters* **2012**, *53*, 6202-6204, doi:https://doi.org/10.1016/j.tetlet.2012.08.138.
- Syper, L.; Kloc, K.; Mz.xl; lochowski, J. Synthesis of ubiquinone and menaquinone analogues by oxidative demethylation of alkenylhydroquinone ethers with argentic oxide or ceric ammonium nitrat. *Tetrahedron* 1980, 36, 123-129, doi:https://doi.org/10.1016/0040-4020(80)85034-4.
- 11. Chiu, H.-L.; Wu, J.-H.; Tung, Y.-T.; Lee, T.-H.; Chien, S.-C.; Kuo, Y.-H. Triterpenoids and Aromatics from Derris laxiflora. *Journal of Natural Products* **2008**, *71*, 1829-1832, doi:10.1021/np800253s.
- 12 Liu, S.Y.W., W.C.; Tsou, W.L.; Kuo, M. T. Compounds from antrodia camphorata for inhibiting the growth of cancer tumor cells. US2008/103195,2008,A1, 2008.
- Shi, Y.G.; Zhu, Y.J.; Shao, S.Y.; Zhang, R.R.; Wu, Y.; Zhu, C.M.; Liang, X.R.; Cai, W.Q. Alkyl Ferulate Esters as Multifunctional Food Additives: Antibacterial Activity and Mode of Action against Escherichia coli in Vitro. *J. Agric Food Chem* 2018, 66, 12088-12101, doi:10.1021/acs.jafc.8b04429.

Fig. S01. ESI-MS spectrum of Camphoratin K (1)



/d=/Data/yu/acfe236262/2/pdata/1 Administrator Fri Nov 11 16:15:29 2011

Fig. S02. HRMS spectrum of Camphoratin K (1)



/d=/Data/yu/acfe236262/1/pdata/1 Administrator Fri Nov 11 16:17:45 2011





Fig. S05. ¹³C and DEPT NMR spectrum of Camphoratin K (1) ACFE2 36262 CDC13 AV400 2011/07/28 13C











Fig. S10. ESI-MS spectrum of Camphoratin N (2)



/d=/Data/yu/acfe28153/2/pdata/1 Administrator Mon Apr 9 10:26:21 2012

26:21 201

Fig. S11. HRMS spectrum of Camphoratin N (2)



/d=/Data/yu/acfe28153/1/pdata/1 Administrator Mon Apr 9 10:27:57 2012





Fig. S14. ¹³C and DEPT NMR spectrum of Camphoratin N (2) ACFE2-8153 CDC13 100MHz 2011/12/12 13C & DEPT 135



.



Fig. S15. COSY spectrum of Camphoratin N (2) ACFE2-8153 CDCl3 400MHz 2011/12/12 COSY









Fig. S19. ESI-MS spectrum of Benzocamphorin G (3)



/d=/Data/yu/acfe22467/1/pdata/1 Administrator Fri Nov 11 15:42:39 2011

Fig. S20. HRMS spectrum of Benzocamphorin G (3)



/d=/Data/yu/acfe22467/2/pdata/1 Administrator Fri Nov 11 15:42:06 2011











										mantun									TLL
190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10 p	pm

Fig. S24. COSY spectrum of Benzocamphorin G (3)

ACFE2 2467 CDCl3 400MHz 2011/04/08 COSY









Fig. S28. ESI-MS spectrum of Benzocamphorin I (4)



/d=/Data/yu/acfe23332212/1/pdata/1 Administrator Wed May 30 14:15:22 2012

Fig. S29. HRMS spectrum of Benzocamphorin I (4)



/d=/Data/yu/acfe23332212/2/pdata/1 Administrator Wed May 30 14:14:52 2012







Fig. S33. COSY spectrum of Benzocamphorin I (4) ACFE2 3332212 CDC13 AV400 2011/05/21 COSY90



- -








