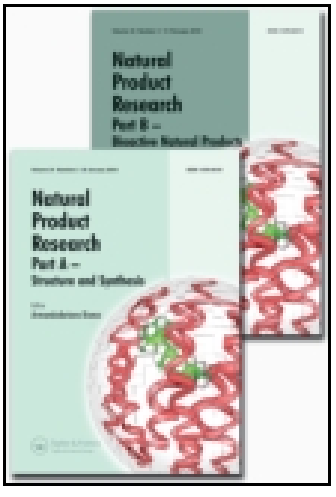

Natural Product Research: Formerly Natural Product Letters
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gnpl20

Phenolic constituents from the fruit juice of Flacourtia inermis

Lalith Jayasinghe [a], Madhubhashini Lakdusinghe [a], Noriyuki Hara [b] & Yoshinori Fujimoto [b]

[a] Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

[b] Department of Chemistry and Materials Science, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan

Published online: 10 Oct 2011.

To cite this article: Lalith Jayasinghe, Madhubhashini Lakdusinghe, Noriyuki Hara & Yoshinori Fujimoto (2012) Phenolic constituents from the fruit juice of Flacourtia inermis, Natural Product Research: Formerly Natural Product Letters, 26:3, 278-281, DOI: 10.1080/14786419.2011.586638

To link to this article: http://dx.doi.org/10.1080/14786419.2011.586638

Natural Product Research
Vol. 26, No. 3, February 2012, 278–281

SHORT COMMUNICATION

Phenolic constituents from the fruit juice of *Flacourtia inermis*

Lalith Jayasinghe[a]*, Madhubhashini Lakdusinghe[a], Noriyuki Hara[b] and Yoshinori Fujimoto[b]

[a]*Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka;* [b]*Department of Chemistry and Materials Science, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan*

(*Received 20 August 2010; final version received 12 April 2011*)

A chemical investigation of the fruit juice of *Flacourtia inermis* furnished five caffeoylquinic acid derivatives: methyl chlorogenate (**1**), methyl 5-*O*-caffeoylquinate (**2**), methyl 4-*O*-caffeoylquinate (**3**), *n*-butyl chlorogenate (**4**), *n*-butyl 5-*O*-caffeoylquinate (**5**) and a rare phenolic glucoside (*rel*)-6α-benzoyloxy-1α,2α-dihydroxy-5-oxocyclohex-3-enecarboxylic acid 2-(6-*O*-benzoyl-β-D-glucopyranosyloxy)-5-hydroxybenzyl ester (**6**), together with quinic acid (**7**) and malic acid (**8**). Compounds **1**, **2**, **4** and **5** showed strong radical scavenging properties towards the 2,2′-diphenyl-1-picrylhydrazyl radical.

Keywords: *Flacourtia inermis*; Flacourtiaceae; chlorogenic acid esters; phenolic glucoside; antioxidant activity; DPPH

1. Introduction

In a continuation of our research work on search for biologically active compounds from Sri Lankan plants, this investigation is carried out on the fruits of *Flacourtia inermis* Roxb. *F. inermis* (Sri Lankan name: Lovi) of the family Flacourtiaceae is a tree of moderate size, growing in Sri Lanka. Its red-coloured fruits are edible and very popular in Sri Lanka. Antifungal activities of the acetone extract of *F. inermis* against some human opportunistic pathogens have been reported (Shibumon & Benny, 2010). There are two *Flacourtia* species, *F. inermis* and *Flacourtia indica*, available in Sri Lanka (Ashton et al., 1997). Recently, we have reported a new glucoside ester flacourside, 4-oxo-2-cyclopentenylmethyl 6-*O*-(*E*)-*p*-coumaroyl-β-D-glucopyranoside together with known 6-*O*-(*E*)-*p*-coumaroyl-β-D-glucopyranose and its methyl glucoside from the *n*-butanol extract of the fruit juice of *F. indica* (Amarasinghe, Jayasinghe, Hara, & Fujimoto, 2007). In this article, we report the isolation and structure elucidation of five caffeoylquinic acid derivatives **1**–**5** and a rare phenolic glucoside (*rel*)-6α-benzoyloxy-1α,2α-dihydroxy-5-oxocyclohex-3-enecarboxylic acid 2-(6-*O*-benzoyl-β-D-glucopyranosyloxy)-5-hydroxybenzyl ester (**6**) together with quinic acid (**7**) and malic acid (**8**) (Figure 1) from the fruit juice of *F. inermis* and their antioxidant activities towards the 2,2′-diphenyl-1-picrylhydrazyl (DPPH) radical.

Antioxidants are compounds that can delay or inhibit the oxidation of lipids or other molecules by inhibiting the initiation or propagation of oxidative chain reactions (Velioglu, Mazza, Gao, & Oomah, 1998). Antioxidants are important in the prevention of human diseases such as Alzheimer's disease, ageing, and diabetic rheumatoid

*Corresponding author. Email: ulbj2003@yahoo.com

ISSN 1478–6419 print/ISSN 1478–6427 online

http://dx.doi.org/10.1080/14786419.2011.586638
http://www.tandfonline.com

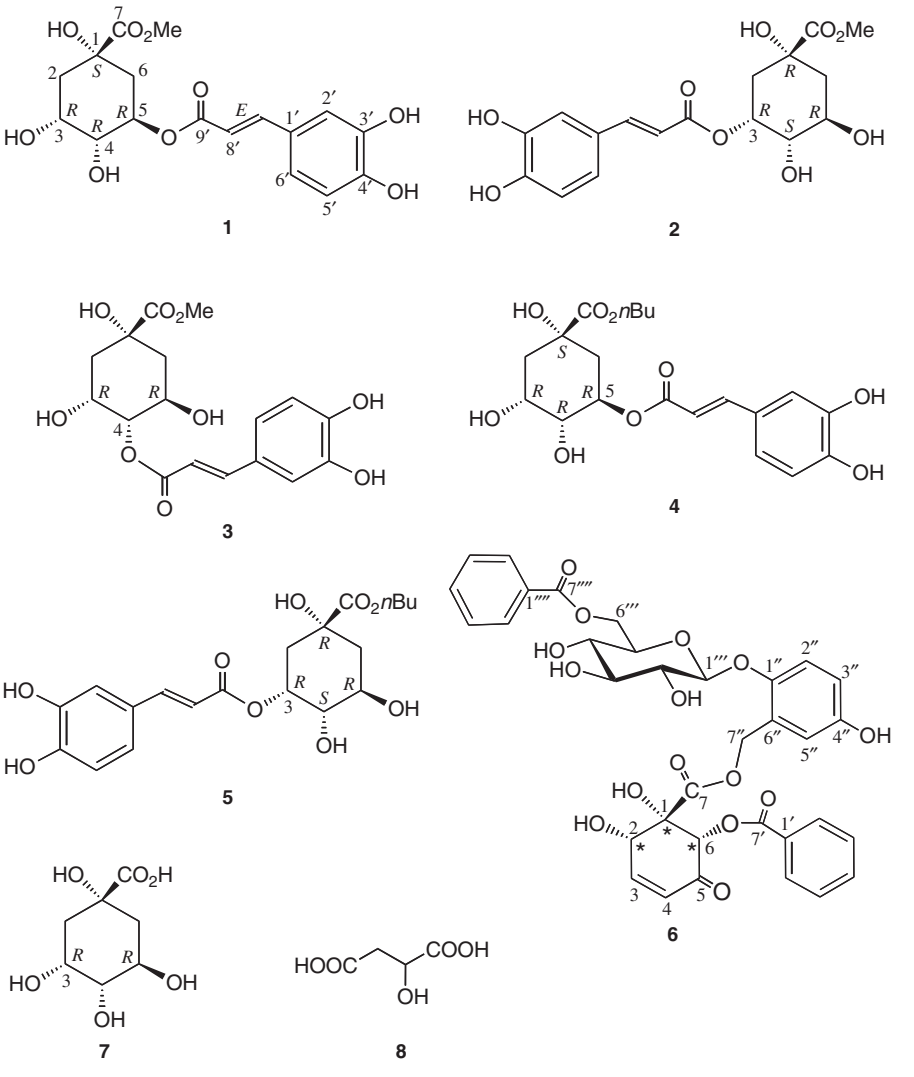

Figure 1. Structures of compounds **1**–**8**. The asterisks in compound **6** represent relative stereochemistry.

arthritis, cataracts. The harmful actions of free radicals can be reduced by antioxidants. Earlier, scientists have paid attention to the natural compounds such as vitamins C, E and carotenoids, and during the recent years, the powerful antioxidant capacity of phenolics aroused more interest. Antioxidants are also of immense interest to health professionals as they may help to protect the body against damage caused by reactive oxygen species (Shahidi, Janitha, & Wanasundara, 1992). Free radicals can result in food sourness, oil rottenness and most industrial product ageing. Butylated hydroxyltoluene (BHT), butylated hydroxylanisole (BHA) and *tert*-butylhydroquinone are extensively used as antioxidants at present, in order to reduce the harm caused by free radicals (Tepe, Eminagaoglu, Akpulat, & Aydin, 2007). Synthetic antioxidants such as BHA and BHT have restricted uses in food as they are reported to be carcinogenic (Ito, Fukushima, & Tsuda, 1985). Hence, it is very important to search for human-friendly

natural antioxidants. It is well known that the diet rich in fruits and vegetables significantly reduced the incidence and mortality rates of cardiovascular diseases and certain cancers in the human.

2. Results and discussion

A preliminary screening of antioxidant properties of EtOAc and the *n*-butanol extracts from the fruit juice of *F. inermis* using a TLC bio-autography method (Takao, Kitatani, Watanabe, Yagi, & Sakata, 1994) revealed that both the extracts are active. Chromatographic separation of the combined EtOAc and the *n*-butanol extracts furnished compounds **1**–**8** (Figure 1).

Compounds **1**–**5** were identified by spectral analysis including 2-D NMR as methyl chlorogenate (**1**) (Zhu, Dong, Wang, Ju, & Luo, 2005), methyl 5-*O*-caffeoylquinate (**2**) (Zhu et al., 2005). This compound should be named 'methyl 3-*O*-caffeoylquinate' according to the proposal by Rumbero-Sanchez and Vazquez (1991). We use 'methyl 5-*O*-caffeoylquinate' in this article, since the trivial name has been used even in the recent papers. The carbon atoms of the cyclohexane ring in Figure 1 are numbered according to the International Union of Pure and Applied Chemistry system that was adopted by Rumbero-Sanchez and Vazquez (1991); methyl 4-*O*-caffeoylquinate (**3**) (Zhu et al., 2005), *n*-butyl chlorogenate (**4**) (Corthout, Pieters, Claeys, Berghe, & Vlietinck, 1992) and *n*-butyl 5-*O*-caffeoylquinate (**5**) (Zhang et al., 2001). Compound **6** was characterised similarly as a rare phenolic glucoside (*rel*)-6α-benzoyloxy-1α,2α-dihydroxy-5-oxocyclohex-3-enecarboxylic acid 2-(6-*O*-benzoyl-β-D-glucopyranosyloxy)-5-hydroxybenzyl ester, which has been isolated from *Homalium longifolium* of the family Flacourtiaceae (Shaari & Waterman, 1995). Compounds **7** and **8** were identified as well-known quinic acid (He & Liu, 2006) and malic acid (Nilsson et al., 2004), respectively, by spectral means. The general experimental procedures and the physico-chemical, NMR and FAB-MS data of compounds **1**–**6** are listed in the supplementary material.

The antioxidant properties of **1**–**8** were evaluated against DPPH radical spectrophotometrically according to the procedure reported previously (Burtis & Bucar, 2000; Cuendet, Hostettmann, Dyatmiko, & Potterat, 1997) and expressed in terms of IC_{50} values ($\mu g\,mL^{-1}$, concentration required to inhibit the DPPH radical formation by 50%). Our results indicated that compound **1** ($5.1\,\mu g\,mL^{-1}$), **2** ($3.1\,\mu g\,mL^{-1}$), **3** ($25\,\mu g\,mL^{-1}$), **4** ($4.4\,\mu g\,mL^{-1}$), **5** ($4\,\mu g\,mL^{-1}$), **6** ($12\,\mu g\,mL^{-1}$), **7** ($>125\,\mu g\,mL^{-1}$) and **8** ($>125\,\mu g\,mL^{-1}$) have shown antioxidant activities in comparison with the antioxidant properties of positive controls, ascorbic acid ($3.1\,\mu g\,mL^{-1}$) and BHA ($3.5\,\mu g\,mL^{-1}$). Compounds **1**, **2**, **4** and **5** exhibited antioxidant activities nearly comparable to those of ascorbic acid and BHA in this assay.

3. Conclusions

The strong antioxidant activities observed for compounds **1**, **2**, **4** and **5** suggested that the fruits of *F. inermis* greatly benefit humans, as a rich source of natural antioxidants.

Supplementary material

Experimental details relating to this article are available online.

References

Amarasinghe, N.R., Jayasinghe, L., Hara, N., & Fujimoto, Y. (2007). Flacourside, a new 4-oxo-2 cyclopentenylmethyl glucoside from the fruit juice of *Flacourtia indica*. *Food Chemistry, 102*, 95–97.

Ashton, M.S., Gunatilleke, S., De Zoysa, N., Dassanayake, M.D., Gunatilleke, N., & Wijesundara, S. (1997). *A field guide to the common trees and shrubs of Sri Lanka*. Colombo, Sri Lanka: Gunaratne Press.

Burtis, M., & Bucar, F. (2000). Antioxidant activity of *Nigella sativa* essential oil. *Phytotherapy Research, 14*, 323–328.

Corthout, J., Pieters, L., Claeys, M., Berghe, V.D., & Vlietinck, A. (1992). Antiviral caffeoyl esters from *Spondias monbin*. *Phytochemistry, 31*, 1979–1981.

Cuendet, M., Hostettmann, K., Dyatmiko, W., & Potterat, O. (1997). Iridoid glucosides with free radical scavenging properties from *Fagraea blumei*. *Helvetica Chimica Acta, 80*, 1144–1152.

He, X., & Liu, R.H. (2006). Cranberry phytochemicals: Isolation, structure elucidation, and their antiproliferative and antioxidant activities. *Journal of Agricultural and Food Chemistry, 54*, 7069–7074.

Ito, N., Fukushima, S., & Tsuda, H. (1985). Carcinogenicity and modification of the carcinogenic response by BHA, BHT, and other antioxidants. *CRC Critical Reviews in Toxicology, 5*, 109–150.

Nilsson, M., Duarte, I.F., Almeida, C., Delgadillo, I., Goodfellow, B.J., Gil, A.M., & Morris, G.A. (2004). High-resolution NMR and diffusion-ordered spectroscopy of port wine. *Journal of Agricultural and Food Chemistry, 52*, 3736–3743.

Rumbero-Sanchez, A., & Vazquez, P. (1991). Quinic acid esters from *Isertia hankeana*. *Phytochemistry, 30*, 311–313.

Shaari, K., & Waterman, P.G. (1995). Glucosides of 2,5-dihydroxybenzyl alcohol from *Homalium longifolium*. *Phytochemistry, 39*, 1415–1421.

Shahidi, F., Janitha, P.K., & Wanasundara, P.D. (1992). Phenolic antioxidants. *Critical Reviews of Food Science and Nutrition, 32*, 67–103.

Shibumon, G., & Benny, P.J. (2010). Antifungal activity of acetonic extract of *Flacourtia inermis* fruits against human opportunistic pathogens. *Journal of Global Pharma Technology, 2*, 28–34.

Takao, T., Kitatani, F., Watanabe, N., Yagi, A., & Sakata, K. (1994). A simple screening method for antioxidants and isolation of several antioxidants produced by marine bacteria from fish and shellfish. *Biotechnology and Biochemistry, 58*, 1780–1783.

Tepe, B., Eminagaoglu, O., Akpulat, H.A., & Aydin, E. (2007). Antioxidant potentials and rosmarinic acid levels of the methanolic extracts of *Salvia verticillata* (L.) subsp. *verticillata* and *S. verticillata* (L.) subsp. *amasiaca* (Freyn & Bornm.) Bornm. *Food Chemistry, 100*, 985–989.

Velioglu, Y.S., Mazza, G., Gao, L., & Oomah, B.D. (1998). Antioxidant activity of total phenolics in selected fruits, vegetables and grain products. *Journal of Agricultural and Food Chemistry, 46*, 4113–4117.

Zhang, W., Ha, T.B.T., Chen, W., Kong, D., Li, H., Wang, Y., & Isabella, F. (2001). Study on the structure and activity of new phenolic acid compounds from *Erigeron breviscapus*. *Yaoxue Xuebao, 36*, 360–363.

Zhu, X., Dong, X., Wang, Y., Ju, P., & Luo, S. (2005). Phenolic compounds from *Viburnum cylindricum*. *Helvetica Chimica Acta, 88*, 339–342.