Molecules **2007**, *12*, 149-154

molecules
ISSN 1420-3049
http://www.mdpi.org

Communication

Comparative Chemical Analysis of the Essential Oil Constituents in the Bark, Heartwood and Fruits of *Cryptocarya massoy* (Oken) Kosterm. (Lauraceae) from Papua New Guinea

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Received: 8 November 2006; in revised form: 20 December 2006 /Accepted: 3 February 2007 / Published: 5 February 2007

Abstract: Exhaustive hydro-distillation of the bark, heartwood and fruits of *Cryptocarya massoy* (Lauraceae) afforded pale yellow-coloured oils in 0.7, 1.2 and 1.0 % yields, respectively. Detailed chemical evaluation of these distillates using GC/MS revealed the major components in the bark and the heartwood oils to be the C-10 (5,6-dihydro-6-pentyl-2H-pyran-2-one) and C-12 (5,6-dihydro-6-heptyl-2H-pyran-2-one) massoia lactones, while the major fruit oil constituent was benzyl benzoate (68.3 %). The heartwood also contained trace amounts of the C-14 (5,6-dihydro-6-nonyl-2H-pyran-2-one) massoia lactone (1.4 %) and the saturated C-10 derivative δ-decalactone (2.5 %).

Keywords: *Cryptocarya massoy*; Lauraceae; massoia lactones; 5,6-dihydro-6-pentyl-2H-pyran-2-one (C-10 massoia lactone); benzyl benzoate; 5,6-dihydro-6-heptyl-2H-pyran-2-one (C-12 massoia lactones); essential oil analysis; α,β-unsaturated δ-lactone; 5,6-dihydro-6-nonyl-2H-pyran-2-one (C-14 massoia lactones); δ-decalactone.

Introduction

The genus *Cryptocarya* of the family Lauraceae is comprised of more than 350 species distributed throughout the tropics, subtropics and the temperate regions of the world. Kosterman had established detailed taxonomic descriptions and classifications for this family [1], which has recently been the subject of much interest [2]. The growing wealth of phytochemical literature on the family Lauraceae further indicate their chemosystematics to be in agreement with the established classification schemes [3]. Several species from this genus have been used extensively as traditional medicines in a number of ethnobotanical practices [4,5] and detailed phytochemical and pharmacological studies have shown the chemical constituents to consist mostly of pyrones and styrylpyrones that exhibit anticancer, larvicidal and antifertility activities [6-8].

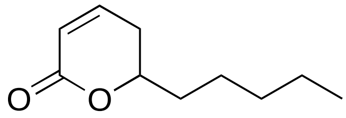
Information about the distribution of members of the family Lauraceae in Papua New Guinea (PNG) is scant, but pharmacological screenings of six species of Cryptocarya have indicated that they do exhibit biological activity [9]. No detailed phytochemical investigations were pursued, except for *C. ainikini* Kosterm. where a (+)-(5*S*)-δ-lactone previously identified in *C. caloneura* (Scheff.) Kosterm., was found to be one of the main constituents [10].

The massoia lactones (Figure 1) are 10, 12 and 14 carbon chain compounds, hereon referred to as the C-10, C-12 and C-14 massoia lactones, respectively, that possess characteristic α,β-unsaturated δ-lactone moieties They also present substitution at the C6 position of the α,β-unsaturated δ-lactone structures with chains of variable length containing five, seven or nine carbons. In nature these compounds are rare essential oil components that were first characterized by Abe in 1937 [11]. The report by Cavill and co-workers [12] on the essential oil composition in the bark oil of *C. massoia* and the formicine ants indicated that the constituents of the bark oil were the C-10 (5,6-dihydro-6-pentyl-2H-pyran-2-one) massoia lactone, with traces of the C-12 (5,6-dihydro-6-heptyl-2H-pyran-2-one) and C-14 (5,6-dihydro-6-nonyl-2H-pyran-2-one) ones. The analysis of the light petroleum extract of the whole ant, on the other hand, indicated the presence of C-10 massoia lactone as the major constituent, correlating with its presence as a mode of chemical defense. This was further confirmed by the work of Lloyd and coworkers [13] investigating the chemistry of the mandibular gland secretion of the carpenter ant, *Camponotus thoracicus fellah* emery, another member of the formicine ants. Fleisher and Fleisher [14] also noted the occurrence of C-10 massoia lactone as a minor constituent in the volatile oils of *Achillea fragrantissima*. Brophy and co-workers [15] also reported the leaf oil of *C. cunninghamii* to contain all three series of the massoia lactones, with the C-14 massoia lactone being the major component.

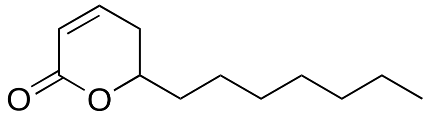
The characteristic α,β-unsaturated δ-lactone moiety found in the massoia lactones is also a common feature in a number of biologically active natural products such as (+)-goniothalamin, (-)-callystatin A, canolide A and the kava lactones, either differing in the substituents at the C6 position or having a molecular structural architecture that maintains the α,β-unsaturated δ-lactone skeleton. Such interesting biological activities of this class of compounds have made their production a synthetic challenge [16-22], and biotechnological [23] and microbe-assisted conversion of various substrates into the desired massoia lactones have been described [24-27].

As part of an ongoing research program to identify and document the chemical constituents in the essential oils from endemic flora of PNG, we report herein a complete analysis of the essential oils obtained from the bark, heartwood and fruits of *C. massoia* from in this location.

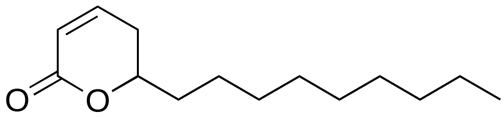
Figure 1. Structures of the massoia lactones from *C. massoia* oil.



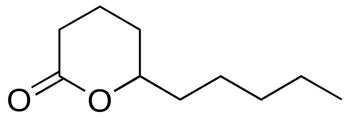
C-10 massoia lactone



C-12 massoia lactone



C-14 massoia lactone



δ-decalactone

Results and Discussion

Comparative data on the different volatile oil constituents in the bark, heartwood and fruits of *C. massoia* is presented in Table 1. The results indicate that C-10 massoia lactone is the major compound, present in similar amounts in the bark and heartwood and found in the fruit oil in trace amounts. This lactone is an important commercial oil, whose presence in the heartwood has not been reported previously. The heartwood oil also contained more C-12 massoia lactone, compared to the bark or fruit oils, and small amounts of C-14 massoia lactone, which was not found in the bark or fruit oils and is the main constituent of the leaf oil of *Cryptocarya cunninghamii* Meissner (Lauraceae) [15]. Benzyl benzoate is the main compound found in the fruit oil but it is present to a lesser extent in the bark and is absent in the heartwood oil.

Table 1. A comparative analysis of the composition of the chemical constituents (area %) in the bark, heartwood and fruit oils of *C. massoia*.

Chemical Component	RI	Bark Oil	Heartwood Oil	Fruit Oil
α-pinene	953	-	-	0.2
β-pinene	1000	-	-	0.3
limonene	1050	-	-	0.4
linalool	1110	0.9	-	-
borneol	1210	0.7	-	-
α-cubebene	1375	-	-	0.3
α-copaene	1413	-	-	2.1
β-elemene	1420	-	-	1.3
β-caryophyllene	1468	-	-	12.9
α-humulene	1505	-	-	2.2
E,*E*-α-farnesene	1516	-	-	1.3
C-10 massoia lactone	1520	64.8	68.4	1.4
ledene	1543	-	-	0.2
β-bisabolene	1555	1.4	-	-
δ-cadinene	1556	-	-	1.2
cis-calamene	1566	-	-	0.2
δ-decalactone	1615	-	2.5	-

Table 1. Cont.

Chemical Component	RI	Bark Oil	Heartwood Oil	Fruit Oil
caryophyllene oxide	1647	-	-	2.2
C-12 massoia lactone	1739	17.4	27.7	0.2
benzyl benzoate	1838	13.4	-	68.3
benzyl salicylate	1948	-	-	1.8
C-14 massoia lactone	2068	-	1.4	-

Conclusions

The tree *Cryptocarya massoia* (Oken) Kostern (Lauraceae) is a species endemic to the island of New Guinea, from which the massoia lactones [11, 12] could be obtained from either Irian Jaya [15] or PNG. A comparative study of the bark, heartwood and fruit oils indicates the heartwood and bark oils to be the main natural sources of the C-10 and the C-12 massoia lactones. The C-14 massoia lactone and δ-decalactone were found to occur as minor constituents in the heartwood oil. The fruit oil, on the other hand, was found to be composed predominantly of benzyl benzoate.

Acknowledgements

The authors are grateful to Mr. Pius Piskaut of the University of Papua New Guinea Herbarium for the plant description and identification and the University of Papua New Guinea Research Council for a research grant and scholarship (to SW). The authors also thank Dr. Joseph J. Brophy for pointing out previous research work on massoia oil by Garnero and Joulain [28]. One of us (TR) would like to thank the people of Inawabui village for permission to access their traditional land to collect fresh samples of massoia bark and heartwood.

Experimental

Materials and Methods

The bark and heartwood of *C. massoia* (Oken) Kosterm were collected from forests near Epa village, Central Province of PNG, in February 2003. The fruits were obtained from the same location during the fruiting season in August 2003. The fresh bark and heartwood were milled to a very fine homogeneous composition and the fruits were chopped into smaller pieces and ground to a fine powdery mixture. The individual plant parts were exhaustively hydrodistilled over an 8 hr period in an all-glass standard distillation set-up. The pure oils obtained were separated and dried over anhydrous magnesium sulphate to give pale yellow coloured oils in 0.70, 1.20 and 1.03 % yields from the bark, heartwood and fruits, respectively. The analyses of the oils were done using GC/MS on an Agilent 6890 Gas Chromatograph, equipped with a split/splitless injector and a 7963 Mass Selective Detector (MSD). Chromatography was performed on a BPX-5 capillary column (SGE, 50 m × 0.22 mm) terminated at the MSD operating as follows: transfer temperature: 310 °C; ionization 70 eV, source temperature: 230 °C; quadrupole temperature 150 °C and scanning a mass range 35-550 m/z. The injector temperature was 250 °C and the carrier gas was helium at 23.10 psi with an average velocity to the MSD of 28 cm/sec. The column oven was programmed as follows: initial temperature: 50 °C; initial time 1.0 min; program rate 4 °C/min; final temperature 300 °C; final time 10 min.

Identification of Oil Components

The oil samples were injected in hexane. The individual compounds in the oil were identified by their retention indices relative to known compounds and further by comparison of their mass spectra with either the known compounds or published spectral data [29-31].

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Sample Availability: Available from the authors.