



ISSN: 2321 9114
 AJEONP 2016; 4(4): 04-05
 © 2016 AkiNik Publications
 Received: 02-08-2016
 Accepted: 03-09-2016

Matthew S Garrison
 Department of Chemistry,
 University of Alabama in
 Huntsville, Huntsville, AL, USA

Anthony K Irvine
 CSIRO Tropical Forest Research
 Centre, Atherton, Queensland,
 Australia

William N Setzer
 Department of Chemistry,
 University of Alabama in
 Huntsville, Huntsville, AL, USA

Chemical composition of the resin essential oil from *Agathis atropurpurea* from North Queensland, Australia

Matthew S Garrison, Anthony K Irvine and William N Setzer

Abstract

The volatile materials from the resin of *Agathis atropurpurea* were obtained by hydrodistillation and analyzed by gas chromatography–mass spectrometry. A total of 17 compounds were identified in the distilled oils accounting for 98.1–99.6% of the compositions. The oils were dominated by limonene (89.8–97.4%) and were devoid of diterpenoids.

Keywords: Essential oil composition, *Agathis atropurpurea*, Araucariaceae, limonene

1. Introduction

The genus *Agathis* (Araucariaceae) is made up of at least 13 species found in Malesia, Australia, New Zealand and the South Pacific islands [1,2]. *Agathis atropurpurea* B. Hyland (Queensland kauri pine) is endemic to northeast Queensland, and is found in mountain rainforest ranging from around 16°25'S south to around 17°23'S, at an altitudinal range of 750–1500 m [2]. The resin from *A. atropurpurea* oozes profusely from wounds on the tree trunk and is used by Australian Aborigines to start fires. In this work, we present the composition of the volatiles obtained by hydrodistillation of the resin from *A. atropurpurea*.

2. Materials and Methods

2.1 Plant Material

Resin of *A. atropurpurea* was collected from several trees growing in the Longland's Gap/Repeater Station Road area (17°28'S, 145°29'E, 1200 m asl) of north Queensland, Australia, in June, 1999. The plant was identified by A.K. Irvine and a voucher specimen has been deposited in the CSIRO herbarium. The resin was stored in brown jars at -20 °C until analysis. Four different resin samples were crushed and hydrodistilled for 4 h using a Likens-Nickerson apparatus with continuous extraction with dichloromethane.

2.2 Gas Chromatography–Mass Spectrometry

The resin oils of *A. atropurpurea* were subjected to gas chromatographic – mass spectral analysis using an Agilent 6890 GC with Agilent 5973 mass selective detector, fused silica capillary column [HP-5ms, (5% phenyl)-methyl polysiloxane stationary phase, film thickness 0.25 µm 30 m length × 0.25 mm diameter], helium carrier gas, 1.0 mL/min flow rate; inj. temp. 200 °C, oven temperature program: 40 °C initial temperature, hold for 10 min; increased at 3°/min to 200 °C; increased 2°/min to 220 °C, and interface temperature 280 °C; EIMS, electron energy, 70 eV. The samples were dissolved in CH₂Cl₂ to give 1% w/v solutions; 1-mL injections using a splitless injection technique were used. Identification of oil components was achieved based on their retention indices (determined with reference to a homologous series of normal alkanes), and by comparison of their mass spectral fragmentation patterns with those reported in the literature [3] and stored on the MS library [NIST database (G1036A, revision D.01.00)/Chem Station data system (G1701CA, version C.00.01.08)].

3. Results and Discussion

The volatile materials from *Agathis atropurpurea* resin are summarized in Table 1. The compositions are dominated by limonene (89.8–97.4%) with much smaller amounts of other monoterpenoids. This is comparable to the hydrodistilled resin of *Agathis philippinensis*, which was also rich in limonene (72%) [4].

Correspondence
William N Setzer
 Department of Chemistry,
 University of Alabama in
 Huntsville, Huntsville, AL, USA

Only one sesquiterpene, β -bisabolene, was detected in the resin volatiles from *A. atropurpurea*. Curiously, although *Agathis* resins are known to be rich in diterpenoids [5-11], there were no diterpenoids present in the volatile mixtures from *A. atropurpurea*. In comparison, the leaf essential oil of *A. atropurpurea* was rich in diterpenoids (36.4%) and sesquiterpenoids (22.5%), with very little limonene (1.5%) [12].

Table 1: Chemical composition of *Agathis atropurpurea* resin essential oils

RI ^a	Compound	% Composition			
		#1	#2	#3	#4
926	Tricyclene	0.1	0.5	1.1	0.9
952	Camphene	tr ^b	tr	tr	0.1
994	Dehydro-1,8-cineole	tr	tr	tr	0.1
1029	Limonene	96.9	97.4	89.8	93.2
1063	γ -Terpinene	tr	tr	tr	tr
1087	Terpinolene	0.1	0.1	tr	tr
1087	<i>m</i> -Cymene	tr	tr	tr	tr
1109	1,3,8- <i>p</i> -Menthatriene	tr	tr	tr	tr
1112	1-Octen-3-yl acetate	tr	tr	tr	---
1134	1,5,8- <i>p</i> -Menthatriene	tr	tr	0.2	0.1
1144	<i>cis</i> - β -Terpineol	tr	tr	tr	tr
1188	α -Terpineol	1.9	1.4	6.2	4.3
1194	Dihydrocarveol	tr	tr	0.1	0.1
1218	Unidentified (C ₁₀ H ₁₆ O) ^c	0.3	0.3	0.9	0.5
1243	Carvone	0.2	0.1	0.4	0.2
1287	Bornyl acetate	tr	tr	tr	tr
1426	2,5-Dimethoxy- <i>p</i> -cymene	tr	tr	tr	tr
1505	β -Bisabolene	tr	tr	0.3	tr
	Total identified	99.3	99.6	98.1	99.1

^a RI = "Retention Index" based on a homologous series of *n*-alkanes on an HP-5ms column.

^b tr = "trace" (< 0.05%).

^c MS, m/e: 152(6%) M+, 134(38%), 119(60%), 109(100%), 91(100%), 84(49%), 83(33%), 79(30%), 77(42%), 69(23%), 67(23%), 65(19%), 55(32%), 53(25%).

4. Conclusions

The essential oil obtained from the resin of *Agathis atropurpurea* had a relatively simple composition, composed mostly of the monoterpene hydrocarbon limonene with no detectable diterpenoids.

5. Acknowledgments

We are grateful to the Queensland Forest Service and to the Queensland National Parks and Wildlife Service for allowing access to State Forest and National Park lands. WNS is indebted to an anonymous private donor for the purchase of the GC-MS equipment. We thank Prof. Bernhard Vogler for technical assistance with the collection of GC-MS data.

6. References

1. Mabberley DJ. Mabberley's Plant Book, 3rd Ed., Cambridge University Press, UK, 2008, 19.
2. Hyland BPM, Whiffen T. Australian Tropical Rain Forest Trees, CSIRO, Melbourne, Victoria, Australia, 1993; 2:34-35.
3. Adams RP. Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry, 4th Ed. Allured Publishing, Carol Stream, Illinois, USA, 2007.
4. Lassak EV, Brophy JJ. The steam-volatile oil of commercial Almaciga resin (*Agathis philippinensis* Warb.) from the Philippines. Journal of Essential Oil Bearing Plants. 2008; 11:634-637.
5. Carman RM, Dennis N. The diterpene acids of *Agathis robusta* oleoresin. Australian Journal of Chemistry. 1964; 17:390-392.
6. Carman RM, Marty RA. Diterpenoids IX. *Agathis microstachya* oleoresin. Australian Journal of Chemistry. 1966; 19:2403-2406.
7. Carman RM, Marty RA. Diterpenoids XVI. Agathalic acid – A new naturally occurring diterpenoid. Australian Journal of Chemistry. 1968; 21:1923-1925.
8. Carman RM, Marty RA. Diterpenoids XXIV. A survey of the *Agathis* species of north Queensland. Two new resin acids. Australian Journal of Chemistry. 1970; 23:1457-1464.
9. Smith RM, Marty RA, Peters CF. The diterpene acids in the bled resins of three Pacific kauri, *Agathis vitiensis*, *A. lanceolata* and *A. macrophylla*. Phytochemistry, 1981; 20:2205-2207.
10. Bates RB, Cai S, Cantor RS, Carducci MD, Irvine AK, Jiorle BV *et al.* Agatholic acid. Acta Crystallographica Section E, 2003; E59:097-098.
11. Cox RE, Yamamoto S, Otto A, Simoneit BRT. Oxygenated di- and tricyclic diterpenoids of southern hemisphere conifers. Biochemical Systematics and Ecology, 2007; 35:342-362.
12. Brophy JJ, Goldsack RJ, Wu MZ, Fookes CJR, Forster PI. The steam volatile oil of *Wollemia nobilis* and its comparison with other members of the Araucariaceae (*Agathis* and *Araucaria*). Biochemical Systematics and Ecology, 2000; 28:563-578.