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Florida Atlantic University

CHARLES E. SCHMIDT COLLEGE OF SCIENCE

A Method for Determining Chemotypes of *Briareum asbestinum*

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Briareum asbestinum, a soft coral, is a rich source of diterpenoid natural products, many with biological activity. The secondary metabolites of *B. asbestinum* fall into three chemotypes; asbestinins, briarellins, and briaranes. Briareolate esters, a subset of the briarane category, have been shown to possess significant biological activity and were previously only reported from Tobago. Our group recently isolated briareolate esters from a specimen collected off the coast of Boca Raton, FL. In order to determine whether location has an impact on the chemistry exhibited by the organism, a method to qualitatively discern between chemotypes was sought. Several techniques including thin layer chromatography (TLC), high performance liquid chromatography (HPLC), and nuclear magnetic resonance (NMR), were employed, with NMR being the most successful method. By utilizing both ^1H and COSY NMR experiments, it is possible to differentiate between the chemotypes of *B. asbestinum*. Application of this method allowed analysis of location and chemotype. It was shown that location is a factor in the chemistry of *Briareum asbestinum*.

A Qualitative Method for Determining Chemotypes of

Briareum asbestinum

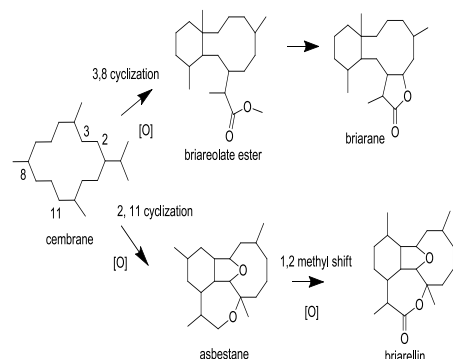
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BACKGROUND



- Briareum asbestinum* (Family Briareidae; Order Alcyonacea) is a soft coral found in tropical and subtropical marine environments
- B. asbestinum* is a rich source of cembranoid natural products, many with biological activity
- The secondary metabolites of *B. asbestinum* fall into three chemotypes; briarane, asbestane, and briarellin^{1,2}



- Briareolate esters possess significant biological activity and were previously only reported from Tobago³
- Our group recently isolated briareolate esters from a collection off the coast of southeast Florida

OBJECTIVE

Develop an analytical method to qualitatively differentiate between the chemotypes of *Briareum asbestinum* to determine whether location impacts chemistry.



METHOD DEVELOPMENT

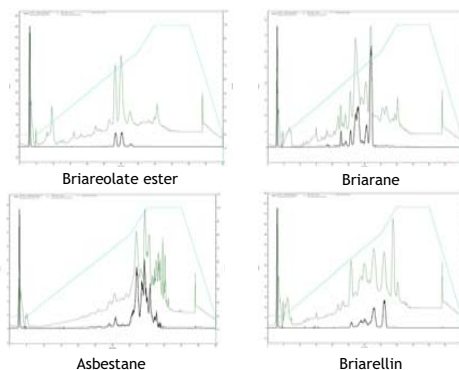
TLC

10% CH₂Cl₂/MeOH



HPLC

Column: PFP 250 x 10 mm
Injection: 5 mg in 200 µL MeOH
Flow rate: 4 mL / min
Gradient MeCN / H₂O:
5 mins 20%
35 mins 80%
40 mins 100%
50 mins 100%
60 mins 20%

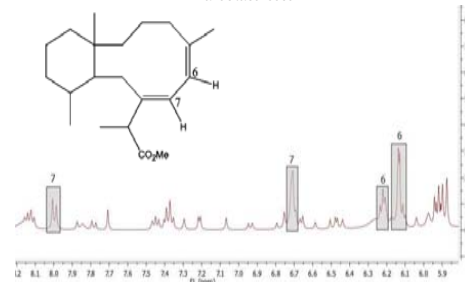


ANALYTICAL METHOD

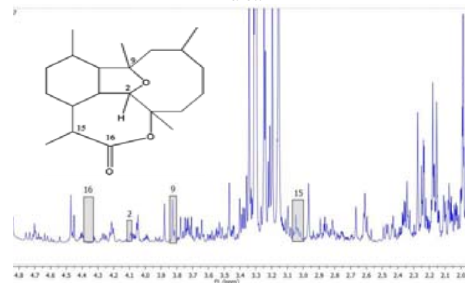
1.0 g dry weight *B. asbestinum*
↓
Crush and add 6.0 mL MeOH
Sonicate 10 mins
Filter and dry onto 3.0 g HP20
↓
Acetone/water fractionation
15.0 mL aliquots
40% 75% 100%
↓
Dry
Dissolve in 600 µL CD₃OD
↓
Perform ¹H NMR experiment
↓
Assess NMR spectrum for characteristic chemical shifts

CHARACTERISTIC CHEMICAL SHIFTS

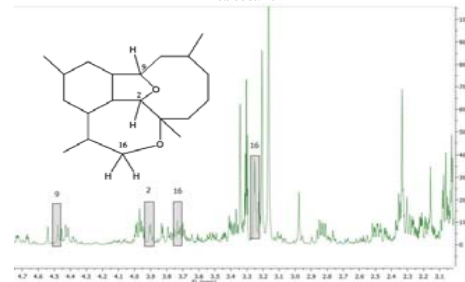
Briareolate ester



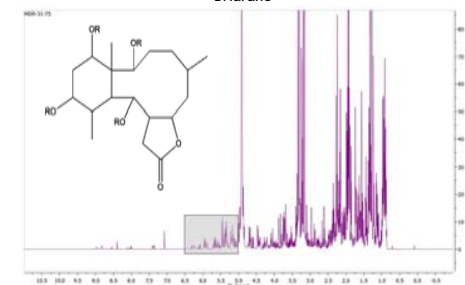
Briarellin



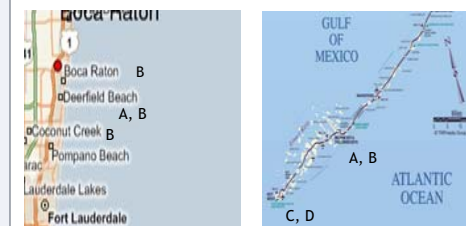
Asbestane



Briarane



LOCATION



A = Asbestin B = Briareolate ester C = Briarellin D = briarane

CONCLUSIONS

- Both TLC and HPLC were ineffective methods for discerning chemotype due to the limited range of polarity associated with the molecules, thus giving similar separations
- NMR is the most effective method for differentiating between the chemotypes due to protons giving characteristic chemical shifts unique to a chemotype
- Location does affect the chemistry of *B. asbestinum*, as indicated by the different chemistry produced by the same organism in different regions

ACKNOWLEDGEMENTS

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REFERENCES

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- Sung, P.-J., Sheu, J.-H., Xu, J.-P., *Heterocycles*, 2002, **57**, 535
- Gupta, P., et. al., *Org. Lett.*, 2011, **13**, 3920