

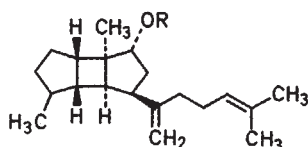
# 5(R)-Acetoxyspata-13,17-diene, A Novel Diterpenoid from the Brown Alga *Stoechospermum marginatum*

Solimabi Wahidullah<sup>1</sup>, S. Y. Kamat<sup>1</sup>, S. K. Paknikar<sup>2</sup>, and R. B. Bates<sup>3</sup>

Received: April 24, 1987

*Stoechospermum marginatum* (C. Agardh) is a brown alga which has been reported (1) to contain several metabolites with the unusual "spatane" tricyclic diterpenoid ring system. A previous report (2) from this laboratory describes the isolation from this marine alga of the diterpene alcohol stoechospermol (1) which was found to be identical with the 5(R)-hydroxyspata-13,17-diene reported by Fenical and co-workers (1). In continuation of our investigation on the isolation of active principle, we present here the isolation and structural elucidation of another minor spatane diterpenoid identified as stoechospermol acetate (2).

The non-polar fraction of the dichloromethane extract of *Stoechospermum marginatum* on extensive column chromatography over silica gel and elution



1 R = H  
2 R = Ac

with 2% EtOAc in petroleum ether yielded **2** as a crystalline solid, m.p. 65–66 °C. The IR spectra had prominent bands at 1730 and 1235 cm<sup>-1</sup> (OAc) and 1635, 890 and 3090 cm<sup>-1</sup> (=CH<sub>2</sub>) besides bands at 2900, 1440, 1365, 1175, 1100, 1025, 1010, 990, 960 and 820 cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectrum (220 MHz, CDCl<sub>3</sub>) is strongly reminiscent of that of **1** (2), the main differences being that the methine proton doublet at δ = 3.74 ppm observed in **1** is shifted downfield and appears as a doublet at δ = 4.91 ppm (*J* = 4.4 Hz) and there is an additional methyl singlet at δ = 2.03 ppm due to the acetoxy methyl. This indicated that the new compound must be an acetyl derivative of stoechospermol and was assigned structure **2**.

The <sup>13</sup>C-NMR signals of **2** further supported the assignments, the spectra of al-

cohol and acetate being distinct from one another essentially only in that there is an additional singlet at δ = 169.6 ppm assigned to the acetoxy carbonyl carbon and a quartet at δ = 20.8 ppm due to the methyl of the acyl group. Definite proof of the structure of **2** was provided by acetylation of **1** with Ac<sub>2</sub>O/pyridine to yield **2**. The acetate obtained was identical in all respects with the natural product thus establishing **2** as 5(R)-acetoxyspata-13,17-diene.

## Acknowledgements

The authors wish to thank Dr. William Fenical, Scripps Institute of Oceanography, California for establishing the identity of stoechospermol with 5(R)-hydroxyspata-13,17-diene and the late Dr. H. N. Siddiquie, Ex-Director, NIO, Dr. R. Sen Gupta, Head, Chemical Oceanography Division and the late Mr. C. V. G. Reddy for their keen interest in the work. This work was partly financed by the Indo-US Collaborative Project "Bioactive Substances from the Indian Ocean".

## References

- (1) Gerwick, W. H., Fenical, W., Sultanbawa, M. U. S. (1981) *J. Org. Chem.* 46, 2233.
- (2) Solimabi, Fernandes, L., Kamat, S. Y., Paknikar, S. K. (1980) *Tetrahedron Lett.* 2249.
- (3) Trautmann, D. (1980) *Chem. Ber.* 113, 3848.
- (4) Kropp, P. J. (1966) *J. Am. Chem. Soc.* 88, 4926.

<sup>1</sup> National Institute of Oceanography, Dona Paula, Goa 403 004, India.

<sup>2</sup> Department of Chemistry, Goa University, Bambolim, Goa 403 001, India.

<sup>3</sup> Department of Chemistry, University of Arizona, Tucson, Arizona 85721, USA.

<sup>4</sup> Address for correspondence.

## Erratum

Daily, A., Seligmann, O., Nonnenmacher, G., Fessler, B., Wong, S.-m., Wagner, H. (1988) *Planta Med.* 54, 50–52.

The structures of compounds **1**, **1a**, and **2** (p. 51) should be:

