SHORT COMMUNICATION

SESQUITERPENE LACTONES OF ARTEMISIA: ARTEMORIN AND DEHYDROARTEMORIN (ANHYDROVERLOTORIN)*

T. A. GEISSMAN and K. H. LEE

Department of Chemistry, University of California, Los Angeles, California 90024, U.S.A.

(Received 18 May 1970)

Abstract—Anhydroverlotorin (I) was assigned the structure of 1-dehydroartemorin by chemical and physical evidence. It has now been prepared by oxidation of artemorin (II) with chromic acid, thus providing confirmation of the structures assigned to II and verlotorin.

INTRODUCTION

ARTEMORIN (II) and verlotorin (III) have been described as constituents of Artemisia verlotorum Lamotte. The structures advanced for these lactones were arrived at by an interpretation of chemical and physical data and by a consideration of their relationship to other constituents of other plants of the vulgaris complex.¹

In the initial studies of the plant, the structure of anhydroverlotorin (I) was based upon the manner of its formation from verlotorin. The fact that anhydroverlotorin is also 1dehydroartemorin could not be directly substantiated at that time because of the instability of artemorin and the consequent impossibility of carrying out the necessary supporting experiments.

RESULTS AND DISCUSSION

A new specimen of artemorin has been isolated from A. verlotorum and its direct conversion into dehydroartemorin (I) by chromic acid oxidation has been accomplished. This result, coupled with the previously described observations on artemorin (II), verlotorin (III) and I. completes the structural interrelationship of the three compounds.

- * Contribution No. 2613 from the Department of Chemistry, UCLA.
- ¹ T. A. GEISSMAN, Phytochem. 9, 2377 (1970).

Anhydroartemorin (I), prepared in the manner indicated, proved to be identical (i.r., NMR, TLC) with the specimen isolated from the plant and prepared by the removal of the elements of water from verlotorin.

A specimen of artemorin p-bromobenzoate, to be used for X-ray studies, has also been prepared.

EXPERIMENTAL

Isolation of artemorin (II). Artemorin (310 mg, m.p. 115-117°) was isolated from a specimen of A. verlotorum Lamotte collected in the Tessin region of southeastern Switzerland,* substantially in the manner previously described.¹

Dehydroartemorin (I). A solution of 100 mg of artemorin in 1 ml of pyridine was treated with 75 mg of CrO₃ at room temp. After 30 min the solution was poured into water and extracted with CHCl₃. The syrupy residue remaining after removal of the solvent was chromatographed over silica gel. Elution with benzene–EtOAc (3:1) yielded a crystalline mixture of artemorin and dehydroartemorin. This was separated by trituration with ether into insoluble (artemorin) and soluble (dehydroartemorin) components. The latter formed colorless needles, m.p. 124–125°, the identity of which with the material isolated earlier¹ was established by comparison of the i.r. and NMR spectra, and by direct comparison on TLC.

Artemorin p-Bromobenzoate. A solution of 100 mg of artemorin and 180 mg of p-bromobenzoyl chloride in 1 ml of pyridine was allowed to stand overnight. The reaction mixture was diluted with water and extracted with CHCl₃, and the CHCl₃ extracts washed with aq. NaHCO₃ and water, dried, and evaporated. The residue crystallized when rubbed with ether. Recrystallized from MeOH-CH₂Cl₂, the compound formed colorless needles, m.p. $168-70^{\circ}$. Its i.r. and NMR spectra were in complete accord with its structure as the 1-p-bromobenzoyl ester of II, and its mass spectrum showed the isotopic molecular ions at m/e 430 and 432 and prominent peaks at m/e 247 and 249 (M-(BrC₆H₄CO)) and 230 and 232 (M-(BrC₆H₄COOH)). Anal. Calc. for C₂₂H₂₃O₄Br: C, 61·24; H, 5·37; Found, C, 60·78; H, 5·33%.

Acknowledgement.—This study was supported by a research grant GM14240-04, provided by the U.S. Public Health Service. Analyses are by Miss Heather King.

* We are grateful to Professor T. Reichstein for providing the plant material used in this study and for authenticating its identity.