□ -ASARONE AND ASARONALDEHYDE IN PIPER SARMENTOSUM*

KITTISAK LIKHITWITAYAWUID, a NIJSIRI RUANGRUNGSI, a GORDON L. LANGE, b,c AND CARL P. DECICCO. b

- ^a Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Chulalongkorn University, Bangkok 10500, Thailand.
- ^b Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada.
- ^c Address for correspondence.
- * Part VIII in the series of "Studies on Thai Medicinal Plants". For Part VII see ref. (1).

(Received 11 February 1988)

Abstract

Examination of a non-polar fraction from the fruit of Piper sarmentosum Roxb. (Piperaceae) revealed the presence of α -asarone and asaronaldehyde.

In a previous report² we described the isolation and structural elucidation of six components obtained from the fruit of *Piper sarmentosum*. The ubiquitous β -sitosterol and the known unsaturated amide, pellitorine, were found along with four new natural products: an aromatic alkene, a novel pyrrole amide, and two unsaturated pyrrolidine amides which were named sarmentine and sarmentosine. Herein we report the structure determination of two components isolated from a non-polar chromatographic fraction obtained from the fruit of *P. sarmentosum*.

The less polar component,1, was a low-melting solid which exhibited an intense parent peak in its electron impact mass spectrum (MS EI) at m/z 208, consistent with the molecular formula $\rm C_{12}H_{16}O_3$. The ¹H NMR spectrum indicated the presence of a 2, 4, 5-trimethoxybenzene ring with a *trans*-1-propenyl side chain ($\rm J_{H_1-H_2}=15.0~Hz$). Both the ¹H and ¹³C NMR spectra were in excellent agreement with the previously reported data³ for (E)-1-(2, 4, 5-trimethoxyphenyl)-1-propene, 1 (α -asarone).⁴

The MS EI of the second component had a parent ion (m/z 196) consistent with the molecular formula $C_{10}H_{12}O_4$. Its IR absorption bands at 1676 and 2740 cm⁻¹ indicated the presence of an aromatic aldehyde. Comparison of the ¹H and ¹³C NMR spectra of the two components revealed similarities in the aromatic ring and thus 2 was assigned the structure 2, 4, 5-trimethoxybenzaldehyde or asaronaldehyde.⁵ The NMR spectra were in excellent agreement with those reported previously for 2.6,7

A number of *Piper* species are noted for their ethnomedical properties⁸⁻¹⁰ and *P. sarmentosum* has been reported to exhibit *in vitro* activities in the reduction of blood sugar in alloxan diabetic rabbits. ¹⁰ Other medicinal uses of this and related species were mentioned in our previous report.²

 α -Asarone, 1, and asaronaldehyde, 2, have not been isolated previously from any *Piper* species. The former was shown to be the hypnotic potentiating principle in the essential oil of *Acorus calamus* L.⁴ and more recently has been shown to possess tranquilizing, sedative, antiulcer, spasmolytic and antisclerosis activities in various animal species. ¹¹ Calamus root oil, which contains both 1 and 2, has been shown to exhibit insecticidal properties. ⁷

Instrumentation and Plant Material: For details see reference (2).

Isolation of 1 - 2: The material that eluted before (E)-1-(3,4-methylenedioxyphenyl)-1-tetradecene upon chromatography of residue A $(1.5 \text{ g})^2$ was examined further. Rechromatography of this less polar material on silica gel with 5% acetone/benzene gave 100 mg of 1 and 20 mg of 2.

(E)-1-(2,4,5-trimethoxyphenyl)-1-propene (α -asarone), 1. M.p. 59-63°C [lit.⁴ 62-63°C]; MS EI m/z (rel. int.) 208 (M⁺, 100), 193(42), 165(18), 91(9); IR, see ref. (4); ¹H and ¹³C NMR, see ref. (3).

2,4,5-trimethoxybenzaldehyde (asaronaldehyde), 2. M.p. 110-114°C [lit.⁵ 114°C]; MS EI m/z (rel. int.) 196 (M⁺, 100), 181(53),150(19); IR and 1 H NMR, see ref. (7); 13 C NMR, see ref. (6).

Acknowledgements

K.L. acknowledges Chulalongkorn University for financial support in the form of a Rachadapiseksompoch Research Fund, G.L.L. acknowledges the Natural Sciences and Engineering Research Council of Canada (N.S.E.R.C.) for support in the form of an operating grant and C.P.D. acknowledges N.S.E.R.C. for support in the form of a post-graduate scholarship.

References

- 1. Likhitwitayawuid, K., Ruangrungsi, N., Boriboon, M., Lange, G.L. and Deciceo, C.P., accompanying article.
- 2. Likhitwitayawuid, K., Ruangrungsi, N., Lange, G.L. and Decicco, C.P. (1987) Tetrahedron 43, 3689.
- 3. Patra, A. and Mitra, A.K. (1981) J. Nat. Prod. 44, 668.
- 4. Baxter, R.M., Dandiya, P.C., Kandel, S.I., Okany, A. and Walker, G.C. (1960) Nature 185, 466.
- 5. Starkovsky, N.A. (1962) J. Org. Chem. 27, 3733.
- 6. Patra, A., Mukhopadhyay, P.K. (1983) J. Ind. Chem. Soc. 60, 265.
- 7. Jacobson, M., Keiser, I., Miyashita, D.H. and Harris, E.J. (1976) Lloydia 39, 412.
- 8. Pongboonrod, S. (1976) The Medicinal Plants in Thailand, Kasembanakit Press, Bangkok, pp. 180.
- 9. Perry, L.M. (1981) *Medicinal Plants of East and Southeast Asia*, MIT Press, Cambridge, Mass., pp. 314-315.
- 10. Pongmarutai, M. (1980) M.Sc. Thesis, Mahidol University, Bangkok.
- 11. Belova, L.F., Alibekov, S.D., Baginskaya, A.I., Sokolov, S. Ya., Pokrovskaya, G.V., Stikhin, V.A., Trumpe, T. and Gorodnyuk, T.I. (1985) Farmakol Toksikol 48, 17; (1986) Chem. Abst. 104, 28405a.

บทคัดย่อ

จากการตรวจสอบส่วนที่ non-polar ของสิ่งสกัดของถูกชะพลู (Piper sarmentosum) พบสารประกอบเพิ่มอีก 2 ชนิดคือ a -asarone และ asaronaldehyde

Supplementary material: Spectrocopic data of compounds described in this article are available upon request.