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SHORT COMMUNICATION

THE STRUCTURE OF IPOMEAMARONOL: A NEW TOXIC FURANOSESQUITERPENE FROM MOLDY SWEET POTATOES

D. T. C. YANG, B. J. WILSON and T. M. HARRIS
Biochemistry Department, Vanderbilt University, Nashville, Tennessee, U.S.A.

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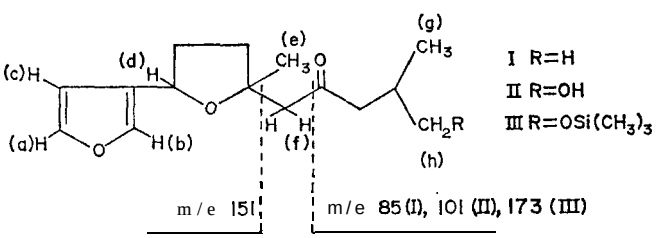
Abstract-The isolation and structure of a new hepatotoxic metabolite, ipomeamaronol, from mold damaged sweet potatoes (*Ipomoea batatas*) is described.

INTRODUCTION

THE TOXICITY of mold damaged sweet potatoes, *Ipomoea batatas*, has been recognized for many decades both in the United States' and Japan.[2] A prominent toxic metabolite produced by sweet potatoes in response to black rot mold infection,[2] insect injury,[3] or chemical insult[4] is ipomeamarone (I). Other well characterized furanoterpenoids[2] are ipomeanine, batatic acid and furan β-carboxylic acid. We have found that although ipomeamarone is hepatotoxic, it is not the principal factor responsible for a fatal pulmonary edema of animals consuming molded sweet potatoes.[5] The hepatotoxicity of ipomeamarone was not surprising since its enantiomer, ngaione,[6] from leaves of the Ngaio tree (*Myoporum laetum*) is also a liver poison. The latter compound, however, is apparently a normal plant metabolite as opposed to ipomeamarone which is only produced in response to various exogenous stimuli.

We have isolated a new hepatotoxic metabolite from naturally and artificially mold-contaminated sweet potatoes for which we propose the name ipomeamaronol and structure (II).



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RESULTS

Ether extracts of moldy potatoes were column chromatographed on silica gel to provide a toxin enriched eluate. This was treated with bis(trimethylsilyl)trifluoroacetamide to form the trimethylsilyl ether (III). Final purification of the derivative (III) was effected by preparative TLC. Hydrolysis of the ether (III) provided a colorless oil with the molecular formula $C_{15}H_{22}O_4$. The extra oxygen in ipomeamaronol as compared to ipomeamarone, $C_{15}H_{22}O_3$, was assigned to a hydroxyl group as shown by ν_{max} 3400 cm-' and *m/e* 248, $C_{15}H_{20}O_3$ (parent peak—H_2O). The spectral features of compound (II) clearly indicate the presence of a β-substituted furan; λ_{max} (CH_3OH) 212 (ϵ 9100), ν_{max} ($CHCl_3$) 1500, 875 cm-' and τ 2·63 (2H, d) and 3·63 (1H, t). This was also supported by a purple color in the Ehrlich test. Both I and II show an i.r. absorption peak at 1710 cm-' due to C = 0 stretching.

Analysis of the mass spectra revealed that the hydroxyl group of II is located on the isobutyl chain since: (a) *m/e* 151, $C_9H_{11}O_2$, was observed in compounds I, II and TIT, (b) u-cleavage of the ketone afforded *m/e* 85, 101 and 173 for I, II, and III, respectively. In a basic medium a total of five deuterium exchangeable protons in II was observed by the shift in parent peak from *m/e* 266 to 271. This fact further restricted the hydroxyl group to the terminal isopropyl portion of the chain. The close structural similarity of ipomeamarone and ipomeamaronol was evident from their NMR data summarized in Table 1.

TABLE 1

Protons	I	III
a And b	2.63 (2H, d)	2.63 (2H, d)
c	3.63 (1H, t)	3.63 (1H, t)
d	5·09 (1H, m)	5·09 (1H, m)
e	8.67 (3H, s)	8.67 (3H, s)
f	7.32 (2H, s)	7.29 (2H, s)
-CH($\underline{CH_3}$)$_2$	9.12 (6H, d)	
g		9.14 (3H, d)
h		6.61 (2H, d)
-Si(CH_3)$_3$		9.92 (9H, s)

Finally, compound III was hydrolyzed at room temperature to afford ipomeamaronol whose NMR data were in total agreement with proposed structure (II). As expected the doublet at τ 6·61 in III was transformed to a doublet of doublets at τ 6·58 in II (h). Detailed bioproduction and toxicity studies will be published elsewhere.

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