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THE STRUCTURE OF EPILUBIMIN, A STRESS METABOLITE FROM DISEASED POTATO TUBERS[1)]

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The structure of epilubimin, a stress metabolite isolated from diseased potato tubers, was determined as shown in formula 1 on the basis of the chemical and spectral data.

In a continuing study on phytoalexins produced by tuber tissues of white potatoes (Solanum tuberlosum and S. demissum) infected by an incompatible race of Phytophthora infestans,[2)] we isolated a new sesquiterpene, designated as epilubimin, in a 2×10^{-5}% yield. The present paper describes the isolation and structure elucidation of the stress metabolite.

Neutral ether extracts (51 g), obtained from the diseased potato tubers (300 kg), were separated by column chromatography (CC) over silica gel (Merck Kieselgel 70-230 mesh) to give a "lubimin and epilubimin fraction"[3)] (1.7 g) as eluates with benzene and ether (5:1 and 3:1), which was further purified by repeated CC followed by preparative TLC[4)] over silica gel (Merck GF-254) to yield lubimin[2a)] (2, 360 mg) (more polar) and epilubimin (1, 59 mg) (less polar) in pure state.

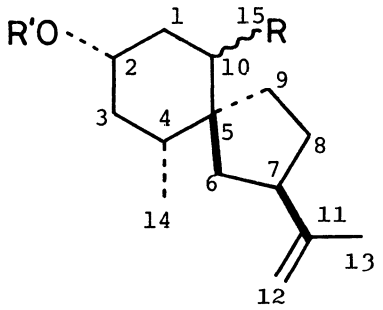
Epilubimin (1), colorless oil, $[\alpha]_D$ 0°,[5)] $C_{15}H_{24}O_2$, gave its monoacetate (1a), oil, and a glycol (3), mp 135-136°C, on hydride reduction ($NaBH_4$), which also formed its diacetate (3a), oil. The MS, IR and NMR spectra[5)] indicated that 1 contains the following structural units: $CH_3\dot{C}H$- [1, δ 0.94 (3H, d J = 6.5 Hz); 3, δ 0.85 (3H, d J = 7 Hz]: CH_2=C(CH_3)- [1, ν_{max} 1652 and 888 cm^{-1}, δ 1.72 (3H, s) and 4.68 (2H, s); 3, ν_{max} 1640 and 891 cm^{-1}, δ 1.68 (3H, s) and 4.64 (2H, s)]: -CHO [1, ν_{max} 1715 cm^{-1}, δ 9.81 (1H, s); 3a, no absorption near 3400 cm^{-1} and near δ 9]: -CH(OH)- [1, ν_{max} 3300 cm^{-1}, δ 3.69 (1H, br W_H = 25 Hz); 1a, ν_{max} 1740 cm^{-1}, δ 4.64 (1H, br W_H = 25 Hz)]. The ^{13}C NMR spectra (Table 1) of 3 and 3a revealed the presence of a quaternary carbon atom (■) of spiro type (3, δ 46.2; 3a, δ 46.2) in 1.[6)] Addition of 0.25 mol equiv of the shift reagent Eu(dpm)$_3$ to the chloroform-d solution of 1 effected down-field shift of the NMR signals, leading to separation of most of the protons (Fig. 1), and spin-decoupling studies on the spectrum elucidated the existence of a structural moiety: (■?)-(CH_3)CH-CH_2-CH(OH)-CH_2-CH(CHO?)-(■). All the results suggested that epilubimin (1) would be an epimer (with an axial formyl group) of lubimin (2) (with an equatorial), though only a sharp singlet due to the formyl proton was observed in each of the NMR spectra of 1 and 1a irrespective of the presence of the shift reagent. Compound 1 was then treated with base (4% KOH in

CH_3OH, room temp, 1 h) to give a mixture, from which lubimin, oil, $[\alpha]_D$ +31°, identical with natural lubimin (2), oil, $[\alpha]_D$ +36°, in the MS, IR and NMR spectra, was isolated in a 60% yield. Hence epilubimin must be represented correctly by formula 1.

Table 1. The ^{13}C NMR spectra of 3 and 3a (25.2 MHz, $CDCl_3$, TMS)

Compd	3	3a
Carbon	Chemical shift (δ)	a)
1	48.9	41.3
2	66.0	69.1
3	42.1	36.0
4	35.2	35.2 or 44.0
5	46.2	46.2
6	31.1	31.1
7	47.8	47.5
8	40.0	31.5
9	31.1	30.4
10	35.2	44.0 or 35.2
11	147.9	147.3
12	107.8	108.0
13	21.3	20.9
14	17.1	16.8
15	61.2	63.9

a) Cf., ref. 6.



1 R=β-CHO, R'=H
1a R=β-CHO, R'=Ac
2 R=α-CHO, R'=H
3 R=β-CH_2OH, R'=H
3a R=β-CH_2OAc, R'=Ac

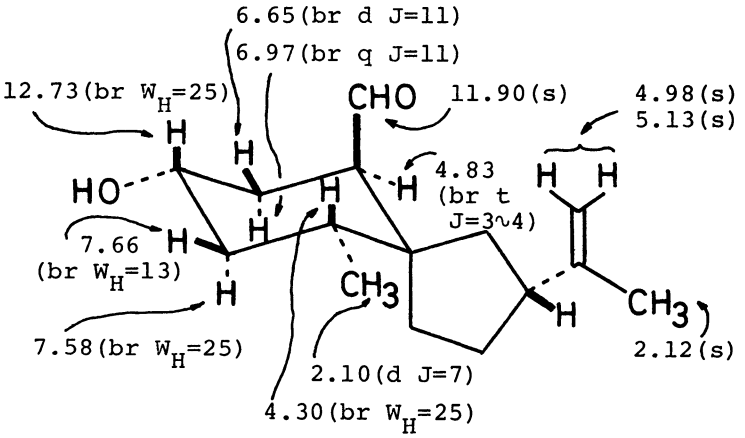


Fig. 1. The NMR spectrum (100 MHz, $CDCl_3$) of 1 in the presence of the shift reagent Eu(dpm)$_3$.

REFERENCES and FOOTNOTES

1) Part XVI of "Studies on the Phytoalexins;" Part XV, A. Murai, H. Taketsuru, F. Yagihashi, N. Katsui, and T. Masamune, Chem. Lett. (in press).

2) a) N. Katsui, A. Matsunaga, H. Kitahara, F. Yagihashi, A. Murai, T. Masamune, and N. Sato, Bull. Chem. Soc. Jpn., 50, 1217 (1977), and their previous papers. b) For a recent review, see, A. Stoessl, J. B. Stothers, and E. W. B. Ward, Phytochemistry, 15, 855 (1976).

3) The fraction corresponds to "fraction E" in "Isolation of Rishitin;" T. Masamune, A. Murai, M. Takasugi, A. Matsunaga, N. Katsui, N. Sato, and K. Tomiyama, Bull. Chem. Soc. Jpn., 50, 1201 (1977).

4) Cf., ref. 2a, "Isolation of Lubimin, Oxylubimin, and Lubiminol" (p. 1222).

5) All the compounds described herein gave MS, IR and NMR spectra in good accord with the assigned structures. The optical rotations, IR and NMR spectra were measured in ethanol, in liquid (oil) or chloroform (3), and in chloroform-d, respectively.

6) Cf., ref. 2a, Table 1 (p. 1218).

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