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STRUCTURE OF A NEW SESQUITERPENOID, IPOMEAMARONOL, IN DISEASED SWEET POTATO ROOT TISSUE

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When infected by Ceratocystis fimbriata, black rot pathogen, sweet potato root tissue accumulates in the infected region various kinds of terpenoid including ipomeamarone (I),[1,2] ipomeanine[2] and component B[3]. Since comp. B was produced almost at the same time as I and ^{14}C-acetate was efficiently incorporated into comp. B as well as I, it was predicted that comp. B may be a substance biosynthetically related to I, a main constituent of the terpenoid accumulated in the tissue after infection. This paper reports the chemical structure of comp. B, a new sesquiterpenoid related structurally to I.

Comp. B was separated as a viscous liquid by repeated fractional column chromatography over silica gel, and its TLC showed one spot when developed with the Ehrlich's reagent. IR spectrum of the liquid was very similar to that of I except a strong OH absorption at 3390 cm^{-1}(neat film). Comp. B, named ipomeamaronol (II, R=H), showed equivocally several signals on the NMR spectrum ($CDCl_3$, 60 MHz)[4] : δ 0.87 (3H, br.d, J=6.1 Hz), 1.26 (3H, s), 2.61 (2H, s), 2.65 (1H, m) and 7.27 (2H, m).

Esterification of the liquid with 3,5-dinitrobenzoyl chloride in pyridine for 3 hrs at room temperature gave a needle crystal of ipomeamaronol 3,5-dinitrobenzoate (III, R=3,5-$(NO_2)_2C_6H_3CO$-) : mp 81°; ν_{max}^{KBr} 1733, 1710, 1548, 872 cm^{-1}; M^+ 460. Anal. Calcd for $C_{22}H_{24}N_2O_9$: C, 57.39; H, 5.25; N, 6.08. Found: C, 57.42; H, 5.26; N, 5.96.

In order to determine the structure of II, we examined NMR spectrum of I. The result is as follows ($CDCl_3$, 100 MHz): the C_1 and C_4 protons on the furan ring are observed as a doublet (J=1.8 Hz) at δ 7.29 and as a singlet at δ 7.30, respectively. The C_1 proton is coupled with the neighboring C_2 proton of a doublet (J=1.8 Hz) at δ 6.29. The multiplet at δ 4.84 (eight lines, J=6.0, 4.2, 1.8 Hz) may be due to the C_5 proton and is revealed as an X part of an ABMX pattern, which is coupled with the C_6 protons and one of the C_7 protons (δ 1.85).

A signal of the C_{10} protons may be assigned to an AB-quartet signal ($J \leqq 15.8$ Hz) at δ 2.62, whose chemical-shift difference between A and B parts of an AB pattern is close to 0 ppm. A doublet ($J = 6.2$ Hz) at δ 2.29 is due to the C_{12} methylene-protons coupled with the C_{13} methine proton. The C_9 methyl protons appear as a singlet signal at δ 1.29. Furthermore, the highest field signal (6H, d, $J = 6.0$ Hz) at δ 0.87 is due to the gem-dimethyl of the C_{14} and C_{15}.

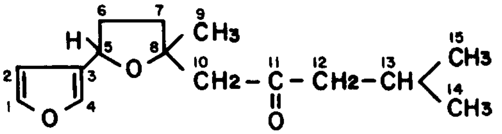
These assignments were applied to the analysis of NMR spectrum of III taken in $CDCl_3$(100 MHz). Three aromatic protons appear as a multiplet of an AB_2 pattern at δ 9.10 Signals at δ7.23 (1H, d, $J = 1.6$ Hz), 7.19 (1H, s), 6.24 (1H, d, $J = 1.6$ Hz), 4.80 (1H, eight lines, $J = 6.0$, 4.2, 1.8 Hz) and 1.26 (3H, s) may correspond to protons C_1, C_4, C_2, C_5 and C_9, respectively.

The C_{10} protons appear at δ 2.61 and 2.67 as an AB-quartet signal with a 14-Hz coupling. Furthermore, the spectrum shows a methyl signal (d, $J = 6.7$ Hz) at δ 0.98 and an octet signal (2H, $J = 6.0$ and 10.4 Hz) centering at δ 4.25 (Part a of Fig. 1). By irradiation of a multiplet at δ 2.52, the signals vary to a sharp singlet and a remarkable AB-quartet ($J = 10.4$ Hz), as shown in Part b of Fig. 1. These signal shapes do not show a significant alteration by a temperature change from 24 to 80°C. From these results, the somewhat strange shapes of the signals in Part a may be explained in terms of the virtual spin-coupling between the methyl protons or the C_{14} protons and the C_{13} methine proton which is situated at about the same chemical-shift as that of the C_{12} protons[5]. In a pyridine-d_5 solution, the methyl and C_{14} protons are shown as the doublet signals ($J = 6.5$ and 5.6 Hz) with a slight virtual-spin-coupling at δ 1.00 and 4.38, respectively. Disappearance of the AB pattern of the latter signal may be attributed to the same chemical-shifts of the two C_{14}-protons.

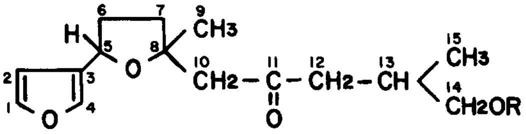
Fig. 1

An enol acetate (IV) of III was then prepared. To a solution of III (400 mg) in 10 ml of isopropenyl acetate was added p-toluenesulfonic acid (40 mg) and 2 drops of DMSO[7]. The solution was refluxed for 120 hrs at 110°C, then concentrated. The residue was chromatographed over silica gel to give a mixture[8] (160 mg) as a viscous liquid: $\nu_{max}^{neat\ film}$ 1755, 1736, 1685, 872 cm^{-1} ; NMR ($CDCl_3$, 100 MHz): multiplets at δ 9.17 (aromatic protons), 7.35 and 6.35 (furan ring protons) and 4.86 (C_5-H), and singlets at δ 1.23 (C_8-Me) and 2.07 (AcO-). In addition, the signal of the C_{10} protons shifts to a higher field at δ 1.96 (2H, s), and a doublet (J = 5.0 Hz) of one proton (C_{12}-H) appears at δ 4.95 instead of the multiplet at δ 2.55 of III[9] The signals of the geminal methyl and carbinol methylene-protons show sharp doublets (J = 6.9 and 7.5 Hz) at δ 1.07 and 4.27, respectively. The observations indicate that the enol double-bond of IV forms between carbon atoms C_{11} and C_{12}

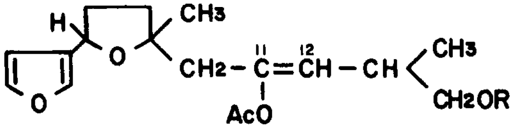
Ozonolysis[10] of the mixture (45 mg) containing IV afforded an aldehyde (13 mg) as a crystal: mp 125-125.5° ;$[\alpha]_D^{21}$ - 6.97°(C, 1.22, $CHCl_3$); ν_{max}^{KBr} 1740, 1729, 1630 cm^{-1}; M^+ 282. Anal. Calcd for $C_{11}H_{10}N_2O_7 \cdot 1/3H_2O$: C, 45.83; H, 3.73; N, 9.72. Found: C, 45.76; H, 3.44; N, 9.65.



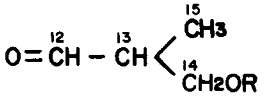
I



II, R = H
III, R = 3,5-$(NO_2)_2C_6H_3CO$-



IV, R = 3,5-$(NO_2)_2C_6H_3CO$-



$$O{=}\overset{12}{C}H-\overset{13}{C}H\left\langle\begin{array}{l}\overset{15}{C}H_3\\ {}_{14}CH_2OR\end{array}\right.$$

V, R = 3,5-$(NO_2)_2C_6H_3CO$-

The NMR spectrum of the aldehyde in $CDCl_3$(100 MHz) showed absorption of five kinds of proton, and these are assigned as follows: (a) a multiplet at δ 9.18 to the three protons of the substituted phenyl group; (b) a singlet at δ 9.80 to a proton of aldehyde group, (c) a doublet (J = 7.6 Hz) at δ 1.55 to the C_{15} methyl-protons, (d) a multiplet at δ 3.20 to a C_{13}

methine proton, and (e) sharp eight lines centered at δ 4.89 to the substituted carbinol methylene protons. When irradiated at δ 3.20, the sharp multiplet signal shows a typical AB pattern with splitting (J_{AB}= 11.3 Hz) at δ_A= 4.84 ppm and δ_B= 4.94 ppm. The principal coupling of the methylene protons with the C_{13} methine-proton as an X part of the ABX pattern affords J_{AX}= 5.1 Hz for the A part and J_{BX}= 6.6 Hz for the B part. Similarly, the doublet signal at δ 1.55 appears as a singlet with irradiating at the methine proton. The results confirmed the aldehyde as V.

Ipomeamaronol, then, can be represented by structure II$^{11)}$.

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(4) The liquid contained 60 % of II whose composition was estimated from the area under the NMR peak at δ 0.87. Further purification by column, thin layer or gas chromatography was found to be almost impossible.

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(8) The mixture was composed of III, IV and other compounds, and it was difficult to separate IV by column or thin layer chromatography. It contained 40 % of IV whose composition was estimated from the area under the NMR peaks at δ 1.98 and 4.95.

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(11) Dr. D. T. C. Yang recently communicated privately his independent arrival at this same structure for ipomeamaronol.