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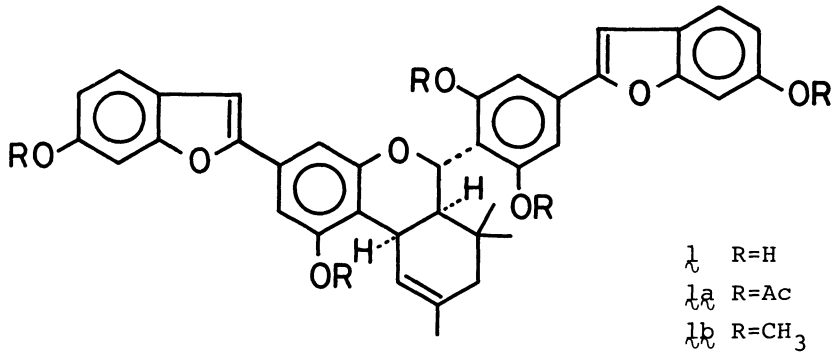
STRUCTURE OF DIMORACIN, A NEW NATURAL DIELS-ALDER ADDUCT FROM DISEASED MULBERRY[1)]

Mitsuo TAKASUGI, Shigemitsu NAGAO, and Tadashi MASAMUNE*
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

The structure of a new phytoalexin, isolated from diseased mulberry shoots and designated as dimoracin, is described. The compound is regarded biogenetically as a Diels-Alder adduct of moracin C, a 2-phenylbenzofuran phytoalexin isolated from the same tissues, and its dehydro derivative.

In previous papers we reported the structures of eight 2-phenylbenzofuran type of phytoalexins,[2)] moracins A ∿ H, and a Diels-Alder adduct type of phytoalexin,[3)] chalcomoracin, which were isolated from cortex and phloem tissues of decorticated mulberry shoots (Morus alba Linné) infected with Fusarium solani f. sp. mori. Further fractionation of acetone extracts of the tissues by repeated chromatography over silica gel (CH_2Cl_2-MeOH and CH_2Cl_2-EtOAc) led to isolation of a new Diels-Alder adduct type of phytoalexin, designated as dimoracin, in 0.0028% yield. We report herein the structure elucidation of the compound, based on comparison with the spectral data of the known moracins.

Dimoracin (1), mp 238-240 °C and $[\alpha]_D$ -5° (EtOH), exhibited the following spectra: FD-MS, m/e 616 (M^+, 67%), 374 (100), and 362 (87); EI-MS, m/e 374 (16%), 359 (25), and 242 (100); UV_{max} (EtOH), 334 nm (ε 67200), 320 (76000), 296 (sh 34000), 285 (sh 29000), 261 (17600), 254 (21200), 247 (sh 25400), 241 (sh 31800), and 220 (64200); IR (KBr), 3450 and 1620 cm^{-1}. Acetylation (Ac_2O and Py, room temp, 16 h) and methylation (Me_2SO_4 and K_2CO_3 in acetone, reflux, 3 h) afforded its pentaacetate (1a), amorphous and $[\alpha]_D$ 0° ($CHCl_3$), and pentamethyl ether (1b), mp 229-230 °C and $[\alpha]_D$ 0° ($CHCl_3$), in 75 and 90% yields, respectively.: 1a, EI-MS, m/e 826 (M^+, 6%) and 242 (100); UV_{max} (EtOH), 326 nm (ε 64800) and 311 (73900); IR ($CHCl_3$), 1765 and 1630 cm^{-1}: 1b, EI-MS, m/e 686 (M^+, 10%) and 351 (100); UV_{max} (EtOH), 337 nm (ε 85400) and 323 (99300); IR ($CHCl_3$), 1610, 1115, 1125, and 1150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δ 0.59 and 1.09 (each 3H, s), 1.44 and 1.98 (each 1H, ABq, J = 18 Hz), 1.69 (3H, br s), 2.70 (1H, dd, J = 10 and 4 Hz), 3.80 and 3.83 (each 3H, s), 3.84 (6H, s), 3.95 (3H, s), 3.84 (1H, br s), 5.41 (1H, br s), 5.58 (1H, d, J = 10 Hz), 6.7-7.1 (10H, m), and 7.32 and 7.38 (each 1H, d, J = 8 Hz). The molecular formula of dimoracin (1) was determined to be $C_{38}H_{32}O_8$ by the high-resolution (HR) mass spectra of 1 (HR-FDMS, m/e 616.1958; calcd, 616.2095) and 1b (HR-EIMS, m/e 686.2850; calcd, 686.2878).



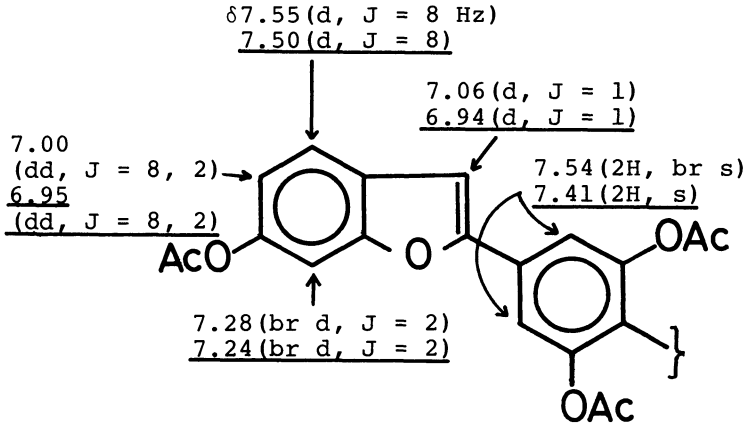
1 R=H
1a R=Ac
1b R=CH_3

The ^1H NMR spectrum (400 MHz, $CDCl_3$) of 1a revealed well-separated signals due to twelve aromatic protons (δ 6.9-7.6). The chemical shifts and splitting patterns of these protons, coupled with the spin-decoupling experiments and compared with those of the aromatic protons of moracin C triacetate[4] (2a) and moracin D diacetate[4] (3a), indicated the presence of two partial structures with moracins C and D type of chromophores as shown in Figures 1 and 2[5] in dimoracin. These partial structures were supported by comparison of the UV spectrum of 1 with that of moracin C[4] (2)..

The ^1H NMR spectrum (400 MHz, CD_3COCD_3) of 1 displayed signals due to nine methyl protons (three singlets) at δ 0.76, 1.12, and 1.69 (CH_3-C=C), one olefinic proton at δ 5.57, and five aliphatic protons at δ 1.50, 2.33, 2.79, 3.91 (Ar-CH-C=C), and 5.64 (Ar-CH-O-), besides the twelve aromatic protons (δ 6.7-7.5) and five hydroxy protons (δ 8.4-8.7). Detailed analysis of these protons using sequential decoupling indicated the presence of a cyclohexene type of partial structure shown in Figure 3, to which the chemical shifts (δ) and coupling constants (Hz) of the relevant protons were assigned unambiguously. This partial structure was consistent with appearance of signals at δ 23.31, 28.12, and 29.47 (each q), 31.29 (d), 32.17 (s), 39.80 (d), 69.63 (d), and 122.40 (d) in the ^{13}C NMR spectrum (25.2 MHz, CD_3SOCD_3).[6]

Combination of these three partial structures shown in Figures 1 ∿ 3 led to assignment of structure 1 with the indicated (relative) configuration to dimoracin. This assignment was substantiated by examination of the mass spectrum of 1b; that is, the methyl ether (1b) exhibited fragmentation species corresponding to $C_{22}H_{23}O_4$, $C_{22}H_{22}O_4$, $C_{21}H_{20}O_4$, and $C_{20}H_{17}O_4$ at m/e 351 (100%) (EI-MS, m/e 351.1575; calcd, 351.1595), 350 (8) (m/e 350.1507; calcd, 350.1517), 336 (5) (m/e 336.1364; calcd, 336.1362), and 321 (26) (m/e 321.1140; calcd, 321.1127), respectively. This fragmentation is interpreted reasonably by assuming that the reaction is initiated by retro-Diels-Alder reaction followed by cleavage of the benzyl-carbon and oxygen bond. Hence dimoracin is represented favorably by formula 1.

Dimoracin (1) is optically active and is considered to be formed by enzymatic Diels-Alder reaction of moracin C, coexisting in the same tissues, and its dehydro derivative and subsequent cyclodehydrogenation.



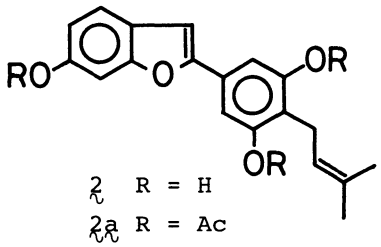
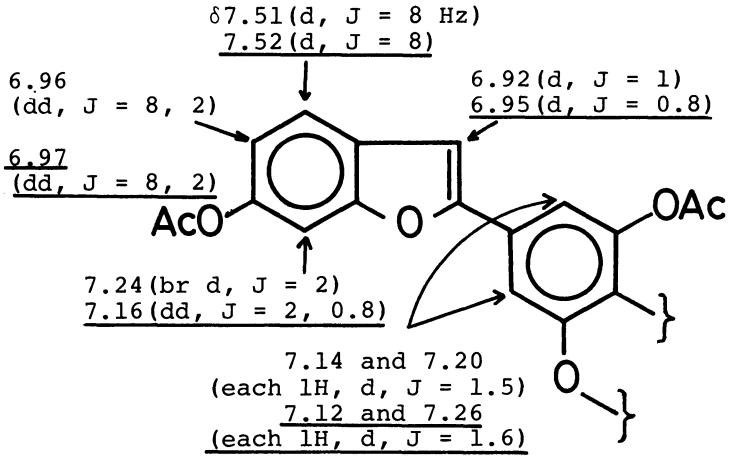


Fig. 1



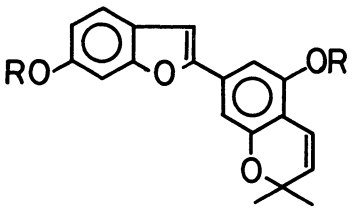


Fig. 2

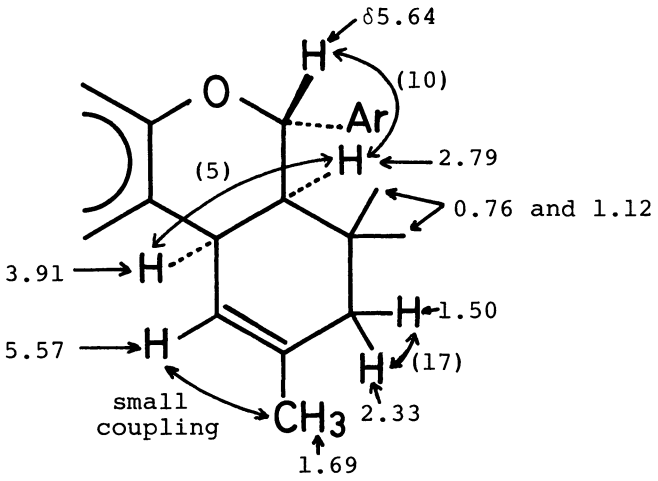
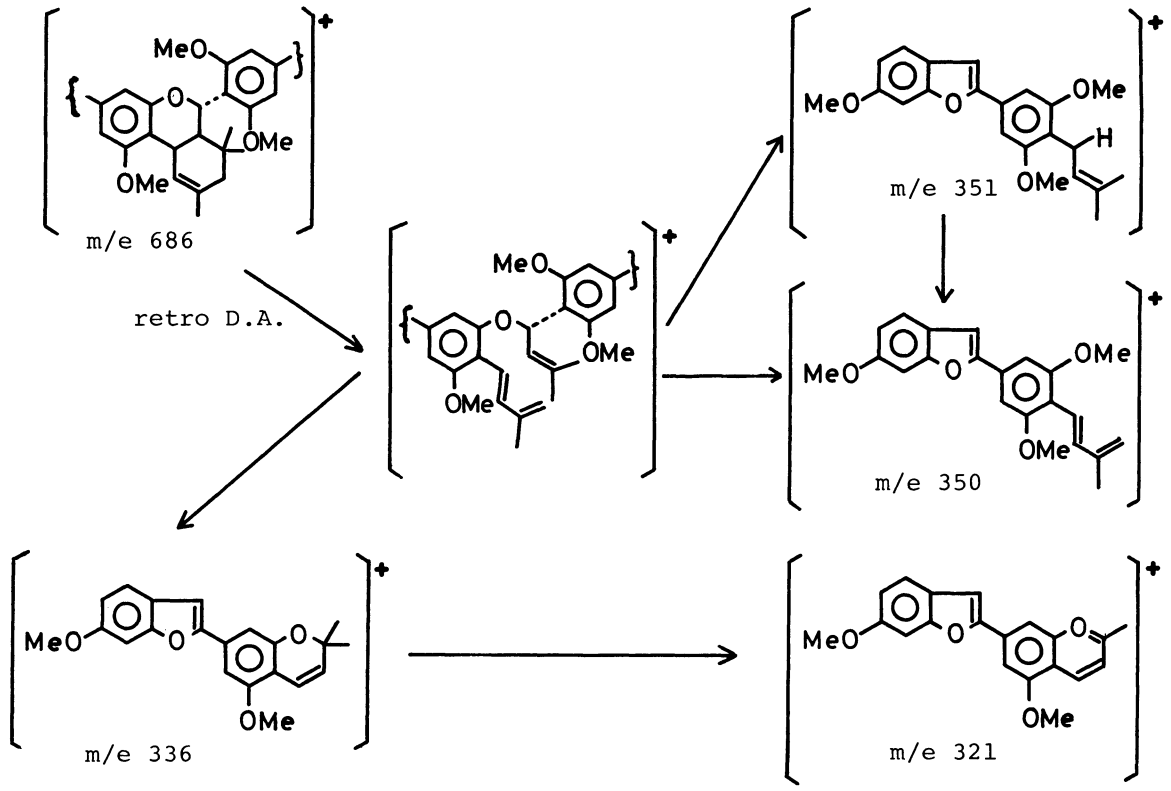


Fig. 3



References

1) Part 10 in the series "Studies on Phytoalexins of the Moraceae." The reference "T. Nomura, T. Fukai, T. Narita, S. Terada, J. Uzawa, Y. Iitaka, M. Takasugi, S. Ishikawa, S. Nagao, and T. Masamune, Tetrahedron Lett., 22, 2195 (1981)" is regarded as Part 9 in this series.

2) M. Takasugi, S. Nagao, T. Masamune, A. Shirata, and K. Takahashi, Tetrahedron Lett., 4675 (1979), and their previous papers.

3) M. Takasugi, S. Nagao, T. Masamune, A. Shirata, and K. Takahashi, Chem. Lett., 1573 (1980).

4) M. Takasugi, S. Nagao, T. Masamune, A. Shirata, and K. Takahashi, Chem. Lett., 1239 (1978).

5) The underlined figures in Figures 1 and 2 denote the chemical shifts and coupling constants of the corresponding protons of 2a and 3a.

6) The signal due to the methylene carbon atom was hidden beneath that (δ ∿39) due to the undeuterated solvent.

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