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ALBAFURAN C, A NATURAL DIELS-ALDER ADDUCT OF A DEHYDROPRENYL-2-PHENYLBENZOFURAN WITH A CHALCONE FROM MULBERRY[1)]

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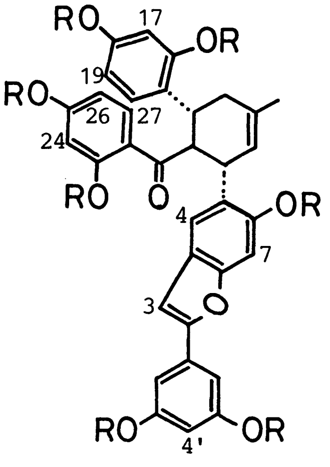
The structure elucidation of a minor antifungal compound, isolated from "intact" epidermis of mulberry shoots and named albafuran C, is described.

In the preceding paper[2)] we reported the structure of two minor antifungal compounds, albafurans A and B, isolated from shoot epidermis of mulberry (*Morus alba* Linné). Further extensive fractionation of acetone extracts of the shoot epidermis led to isolation of a new antifungal compound, named albafuran C, in 0.004% yield. We report herein the structure elucidation of this compound.

Albafuran C (**1**), $C_{34}H_{28}O_9$ (FD-MS, m/e 580, M^+), amorphous and $[\alpha]_D$ -302° (EtOH), gave its heptamethyl ether (**1a**), $C_{41}H_{42}O_9$ (HR EI-MS, m/e 678.2847, M^+), amorphous and $[\alpha]_D$ -267° ($CHCl_3$), on methylation (Me_2SO_4, K_2CO_3, and crown ether in acetone, reflux, 15 h). The IR spectra of **1** and **1a** [**1**, IR (KBr) 3420, 1630, and 1620 cm^{-1}; **1a**, IR ($CHCl_3$) no absorption near 3400 cm^{-1}, 1670 and 1610 cm^{-1}] indicated the presence of a carbonyl group in **1** and the absence of a hydroxyl group in **1a**. The UV spectrum [UV_{max} (EtOH) 336 nm (ε 25700), 322 (31700), 294 (19600), 284 (22300), and 216 (47000)] of **1** closely resembled that [UV_{max} (EtOH) 335 nm (ε 20900), 321 (24400), 295 (sh 9600), 285 (sh 7700), and 218 (24000)] of moracin N[3)] (**2**), suggesting that **1** would involve a 5-substituted 6,3',5'-trihydroxy-2-phenylbenzofuran chromophore. This was supported by the ^1H NMR spectrum (CD_3COCD_3) [δ 6.76 (1H, br s, 7-H), 6.99 (1H, br s, 3-H), 7.42 (1H, s, 4-H), 6.35 (1H, t, J = 2 Hz, 4'-H), and 6.82 (2H, d, J = 2, 2'- and 6'-H)]. The spectrum also revealed the presence of seven phenolic hydroxy protons [δ 7.89, 8.15, 8.29, 9.07, and 13.11 (each 1H, s), and 8.42 (2H, s)] and six aromatic protons due to two 2,4-dihydroxyphenyl groups [δ 6.13 (1H, dd, J = 8 and 2 Hz, 19-H), 6.23 (1H, d, J = 2, 17-H), and 6.93 (1H, d, J = 8, 20-H); δ 5.92 (1H, dd, J = 9 and 2 Hz, 26-H), 5.97 (1H, d, J = 2, 24-H), and 7.46 (1H, d, J = 9, 27-H)] besides nine protons due to a methylcyclohexenyl group described below (*cf.*, Fig. 1).

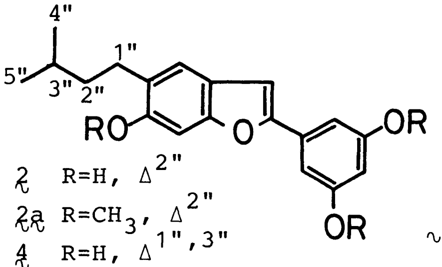
Pyrolysis of the methyl ether (**1a**) in toluene in the presence of 2,6-di-*t*-butyl-*p*-cresol at 280 °C for 3 h in a sealed tube afforded two fragmentation products (**3a**) and (**4a**) in 28 and 31% yields, respectively. The latter (**4a**) was unstable and immediately hydrogenated (Pd-$CaCO_3$, 2 h) to form its tetrahydro derivative (**4b**), $C_{22}H_{26}O_4$ (HR EI-MS, m/e 354.1831, M^+), amorphous, which was identified as dihydromoracin N trimethyl ether by direct comparison with an authentic sample prepared by hydrogenation of moracin N trimethyl ether[3] (2a). The former (3a) was found to be identical with trans-2,2',4,4'-tetramethoxychalcone[4] in all respects. The formation of 3a and 4a by pyrolysis of 1a strongly suggested that albafuran C would probably be formulated as a Diels-Alder adduct of the respective demethylated compounds (3) and (4). Detailed analysis of the ^1H NMR spectrum (CD_3COCD_3) of 1a using sequential decoupling experiments elucidated the presence of an expected cyclohexene moiety with signal patterns (δ and Hz) shown in Fig. 1. The result, coupled with the chemical shift and coupling constant assigned to the protons on the corresponding cyclohexene rings of albanins F and G,[4] chalcomoracin,[5] and mulberrofuran C,[6] indicates that albafuran C is represented by formula 1 with the indicated (relative) configuration.

Albafuran C completely inhibits spore germination of Bipolaris leersiae at $10^{-4} \sim 10^{-5}$ M. As described in the preceding paper,[2] it is to be noted that the compound (1), regarded as a Diels-Alder adduct of a chalcone and a dehydromoracin N with a 2-phenylbenzofuran skeleton characteristic for stress compounds in mulberry tissues, has been isolated from "intact" epidermis of mulberry.



1 R=H

1a $R=CH_3$



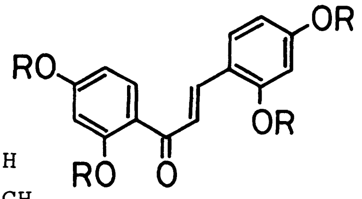
2 R=H, $\Delta^{2''}$

2a $R=CH_3$, $\Delta^{2''}$

4 R=H, $\Delta^{1'',3''}$

4a $R=CH_3$, $\Delta^{1'',3''}$

4b $R=CH_3$, without Δ



3 R=H

3a $R=CH_3$

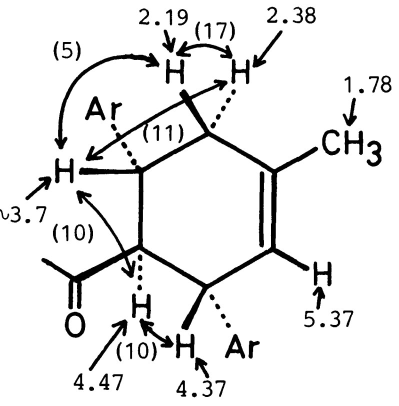


Fig. 1

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