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TWO PHENOLIC CONSTITUENTS FROM *ALPINIA GALANGA* RHIZOMES

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Key Word Index—*Alpinia galanga*; Zingiberaceae; *p*-hydroxycinnamaldehyde and [di-(*p*-hydroxy-*cis*-styryl)] methane.

Abstract—Chemical investigation of the chloroform extract of the rhizomes of *Alpinia galanga* yielded *p*-hydroxycinnamaldehyde and [di-(*p*-hydroxy-*cis*-styryl)] methane. The former is isolated for the first time in nature and the latter is a new chemical component. These compounds were characterized from spectral studies and chemical reactions.

INTRODUCTION

Alpinia galanga Willd is used in the treatment of bronchitis and heart disease [1]. Reports of several biogenetically important chemical constituents in *A. galanga* [2–4] led us to further analyse this plant. Two new compounds *p*-hydroxycinnamaldehyde (**1**) and [di-(*p*-hydroxy-*cis*-styryl)] methane (**3**), which was characterized as its diacetate (**4**), were identified.

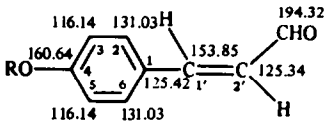
RESULTS AND DISCUSSION

Compound **1** is known synthetically but has not previously been found as a natural product. It was characterized from detailed analysis of its physical and spectral data and also the equivalent data of its methyl ether (**2**) (see Experimental).

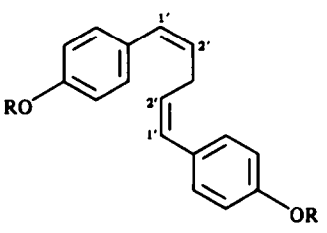
Chromatography of a concentrated chloroform rhizome extract of *A. galanga* over a Tswett column yielded a coloured residue from methanolic chloroform eluates. The residue could not, however, be purified by the usual chromatographic methods or by crystallization but its IR spectrum indicated the presence of a phenolic hydroxyl group. It was purified by extraction with 2% sodium hydroxide solution and subsequent acetylation of the resulting product. The crude acetate was chromatographed over silica gel to afford [di-(*p*-acetoxy-*cis*-styryl)] methane (**4**).

Compound (**4**), $C_{21}H_{20}O_4$ ([M]$^+$ 336), mp 140–142°, λ_{max}^{EtOH} 263, 207 nm (log ε 3.53, 3.51); + NaOH 294, 229 nm (log ε 3.56, 3.85) lacked the hydroxyl band in the IR spectrum (KBr) and showed the presence of acetate (1745 and 1220 cm^{-1}). The 80 MHz ^{1}H NMR spectrum (in $CDCl_3$) of the acetate revealed all the structural features of the molecule. The ^{1}H NMR spectrum displayed a six proton singlet at δ2.20 assignable to two acetate methyl protons and two doublets (one proton each) merged into a triplet (J = 5 Hz) appeared at δ3.03 for methylene protons. A complex multiplet of two protons at δ6.25 was assigned to the C-2′ protons due to its coupling with C-1′ protons and protons of the methylene group. The signal at δ7.23 for two C-1′ protons appeared as a doublet (J = 8 Hz) which clearly indicated that C-1′ and C-2′ protons are oriented *cis*. Two doublets (J = 8 Hz) for four protons each at δ6.94 and 7.29 were ascribed to the protons in the aromatic ring which formed a part of A_2B_2 system. These data agree with structure (**4**) for the diacetate which was further supported by mass spectral data.

Based on the structure of diacetate (**4**) the structure of the natural product has been formulated as [di-(*p*-hydroxy-*cis*-styryl)] methane (**3**).



1 R = H
2 R = Me



3 R = H
4 R = Ac

EXPERIMENTAL

Plant material was procured from the local market and identified by Dr. S. R. Das, Survey Officer, Regional Research Institute (Ay.), Calcutta 700009. A voucher specimen has been deposited at the Department of Chemistry, Calcutta University. Mps were determined on a Köfler block and are uncorr. ^{1}H NMR (80 and 90 MHz) and ^{13}C NMR (20 MHz) spectra were recorded with TMS as an internal standard. MS was operated at 70 eV. Silica gel (BDH, 60-120 mesh) and silica gel G (Merck) were used for CC and TLC, respectively. The analytical samples were dried *in vacuo* over P_2O_5 for 24 hr.

Isolation of p-*hydroxycinnamaldehyde.* The dried rhizomes (2 kg) of *A. galanga* were crushed and extracted successively with hot petrol and $CHCl_3$. After removal of solvent the crude extract was chromatographed over silica gel. Elution with $CHCl_3$ yielded a solid residue which was purified by crystallization from $CHCl_3$ to afford *p*-hydroxycinnamaldehyde (**1**) yield: 0.01%; $C_9H_8O_2$ ([M]$^+$ 148); mp 136–138°; R_f 0.16 [$CHCl_3$–MeOH (1:1)], 0.42 [EtOAc–$CHCl_3$ (3:7)], 0.73 (EtOAc: λ_{max}^{EtOH} 325, 236, nm (log ε 4.55 and 4.13), + NaOH 399, 313, 303, 254, 211 nm (log ε 4.77, 3.72, 3.65, 4.04, 4.33); ν_{max}^{KBr} 3120 (phenolic OH), 1645 (conjugated carbonyl), 1600, 1570, 1500 cm^{-1} (olefinic double bond and aromatic nucleus); ^{1}H NMR (80 MHz, in d_6-DMSO): δ10.11 (1H, broad, phenolic O<u>H</u>, D_2O-exchangeable), 9.50 (–C<u>H</u>O), 6.63 and 7.55 (two olefinic and four aromatic protons); MS: *m/z* 148 ([M]$^+$, 100%), 147 (76.8), 131 (21.6), 120 (39.2), 119 (36.8), 94 (24.8), 91 (41.6), 65 (28.0).

Methylation of p-*hydroxycinnamaldehyde* (**1**). *p*-Hydroxycinnamaldehyde (**1**, 75 mg) in Me_2CO (20 ml) was methylated with MeI (0.3 ml) in the cold. The reaction mixture after the usual work-up was chromatographed over silica gel using C_6H_6–EtOAc (9:1) as eluent. The product was crystallized from petrol–Me_2CO to furnish *p*-methoxycinnamaldehyde (**2**, yield 70 mg); $C_{10}H_{10}O_2$, mp. 56–57° (lit mp 58° [5]); R_f 0.62 [C_6H_6–EtOAc (7:3)]; ν_{max}^{KBr} 1660 cm^{-1} (formyl group); ^{1}H NMR (90 MHz; in $CDCl_3$): δ 9.6 (1H, *d*, J = 7.5 Hz,–C<u>H</u>O); 6.52 (1H, *dd*, J_1 = 15 and J_2 = 7.5 Hz, C_2–<u>H</u>), 7.39 (1H, *d*, J = 15 Hz, C_1'–<u>H</u>). 7.46 (2H, *d*, J = 9 Hz, C_2– and C_6–<u>H</u>), 6.82 (2H, *d*, J = 9 Hz, C_3– and C_5–<u>H</u>), 3.75 (3H, *s*, Ar–OC<u>H</u>$_3$).

Isolation of [*di*-p-*acetoxy*-cis-*styryl*] *methane* (**4**). Elution of a $CHCl_3$ rhizome extract of *A. galanga* on a Tswett column with 15–20% methanolic $CHCl_3$ gave a residue [R_f 0.15, EtOAc–$CHCl_3$ (3:7)] which was separated from its acidic part by extraction with 2% NaOH. The alkali soluble portion after acidification with 10% HCl was extracted into Et_2O, washed with H_2O, dried and conc. The conc. extract was acetylated with Ac_2O–pyridine at room temp. After the usual work-up the acetylated product was chromatographed over silica gel. Petrol–C_6H_6 (1:1 and 1:3) eluates furnished a residue which was rechromatographed over silica gel. Elution with C_6H_6 yielded a solid which crystallized from petrol–C_6H_6 to give **4** (yield: 0.0005%) (found: C, 77.52, H, 5.81; $C_{21}H_{20}O_4$ requires: C, 77.38, H, 5.95); R_f 0.29 (C_6H_6 on a $AgNO_3$–treated silica gel plate).

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