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TWO CINNAMOYL DERIVATIVES FROM *CINNAMOMUM TRIPLINERVIS*

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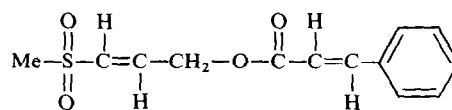
(Revised received 13 October 1980)

Key Word Index—*Cinnamomum triplinervis*; Lauraceae; cinnamoyl derivatives; *trans*-3-methylsulphonylallyl *trans*-cinnamate; 3-[2-(*trans*-cinnamoylamino)-ethyl]-3-hydroxyindolin-2-one.

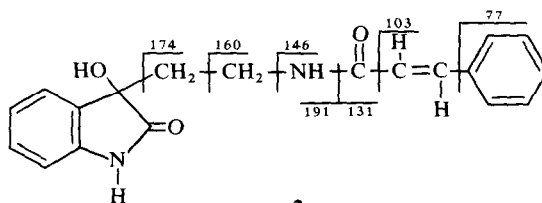
Abstract—Two new compounds have been isolated from leaves of *Cinnamomum triplinervis*, the spectroscopic properties of which are in accordance with the structures of *trans*-3-methylsulphonylallyl *trans*-cinnamate and 3-[2-(*trans*-cinnamoylamino)-ethyl]-3-hydroxyindolin-2-one.

High resolution MS revealed the elemental composition $C_{13}H_{14}O_4S$ for compound 1. In addition to signals for the *trans*-cinnamoyl residue the 1H NMR spectrum shows absorption due to $MeSO_2$ and the *trans*-allyl moiety. Other possible structures are excluded by chemical shift considerations (see refs. [1] and [2]). High resolution electron impact MS (EI), electron addition MS, the UV and IR spectrum are in accordance with structure 1 (see Experimental).

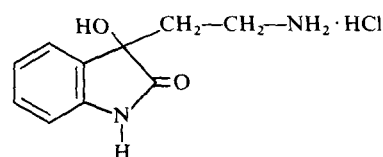
High resolution MS proved the elemental composition to be $C_{19}H_{18}N_2O_3$ for compound 2. Acid hydrolysis gave the 3-hydroxyindolin-2-one derivative 3 and *trans*-cinnamic acid. The spectroscopic properties of 2 and 3 have been compared with a model compound, 3-hydroxy-3-methylindolin-2-one [3, 4]. This substance and 3 show similar IR and UV spectra (see Experimental). In dilute solution ($CHCl_3$) 2 possesses IR bands at 3586 (OH) and 3434 cm^{-1} (NHCO). Compound 2 and 3-hydroxy-3-methylindolin-2-one show corresponding MS fragments (elimination of O, H_2O , CO, side-chain). Further important fragmentation is indicated schematically in formula 2. The position, intensity and appearance of the 1H NMR signals for the indolinone part of 2 are in total agreement with those of the aromatic protons of 3-



1



2



3

hydroxy-3-methylindolin-2-one. As expected, the ^{13}C NMR spectrum contains 17 signals and is in accordance with structure **2** (see Experimental). Surprisingly, **2** is optically inactive according to ORD measurements, perhaps because of easy racemization of the benzylic carbon atom.

Compounds **1** and **2**, as well as similar cinnamoyl derivatives, have not been described before in the literature.

EXPERIMENTAL

Cinnamomum triplinervis (R. & P.) Kosterm. was collected in March in Sierra del Rosario, Pinar del Rio, Cuba, and determined by Lic. Pedro Herrera. A voucher specimen is retained in the Herbarium of the Institute of Botany, Academy of Sciences of Cuba, Havana.

trans-3-Methylsulfonylallyl *trans*-cinnamate (**1**). Dried (40°) and ground leaves of *C. triplinervis* were extracted with EtOH at room temp. Evaporation of the major part of the solvent *in vacuo* gave crystals; from EtOH plates, yield 0.29%, mp 97–100°, $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1708 (C=O), 1637 (C=C), 1577 (C_6H_5), 1497 (C_6H_5), 1300 (SO_2 [5]), 1126 (SO_2 [5]), 770 (C_6H_5). $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 279 (4.34), 223 (4.13), 217 (4.20). ^1H NMR (100 MHz, CDCl_3 , TMS): δ 2.98 (s, 3H, MeSO_2), 4.95 (dd, $J = 3$ and 1 Hz, 2H, CH_2), 6.46 (d, $J = 16$ Hz, 1H, $\text{C}_6\text{H}_5\text{CH}$), 6.65 (dt, $J = 16$ and 1 Hz, 1H, 3-H of allyl), 7.02 (dt, $J = 16$ and 3 Hz, 1H, 2-H of allyl), 7.42 (m, 5H, C_6H_5), 7.76 (d, $J = 16$ Hz, 1H, $\text{C}_6\text{H}_5\text{CH}=\text{CH}$). On irradiation at 4.95 ppm the two doublets of triplets at 6.65 and 7.02 ppm are converted into an AB quartet. MS EI, 70 eV m/z (rel. int.): 266.0618 (calc. for $\text{C}_{13}\text{H}_{14}\text{O}_4\text{S}$: 266.0613, $\text{M}^+ - 5$), 187 ($\text{M}^+ - \text{MeSO}_2$; 8), 186.0682 (calc. for $\text{C}_{12}\text{H}_{10}\text{O}_2$: 186.0681; 12), 147.0450 (calc. for $\text{C}_9\text{H}_7\text{O}_2$: 147.0446, cinnamoyloxy; 3), 131.0496 (calc. for $\text{C}_9\text{H}_7\text{O}$: 131.0497, cinnamoyl; 100), 119.0165 (calc. for $\text{C}_4\text{H}_7\text{O}_2\text{S}$: 119.0167, $\text{MeSO}_2\text{CH}=\text{CH}-\text{CH}_2$; 5), 103.0545 (calc. for C_8H_7 : 103.0548, styryl; 45), 62.9909 (calc. for CH_3OS : 62.9905, MeSO [6]; 6). MS, electron addition, 2–4 eV m/z (rel. int.): 266 ($\text{M}^+ - 31$), 147 (100).

3-[2-(*trans*-Cinnamoylamino)-ethyl]-3-hydroxyindolin-2-one (**2**). Evaporation of the EtOH extract (see above) *in vacuo* gave a residue which was partitioned between 0.5M HCl and C_6H_6 -Et $_2\text{O}$ (1:1). After addition of NaHCO_3 to the aq. layer, the latter was extracted with CHCl_3 -EtOH (2:1). Evaporation of the organic solvents gave raw material, which was chromatographed over Si gel with C_6H_6 -MeOH (23:2). Crystallization from MeOH- C_6H_6 afforded **2**, yield 0.082%, mp 162–4°, $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1750 (γ -lactam), 1685 (amide), 1649, 758. $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 269 (4.38). ^1H NMR (100 MHz, CD_3OD , TMS): δ 2.19 (ca t, $J = 7$ Hz, $\text{C}-\text{CH}_2-\text{C}$), 3.34 (ca t, $J = 7$ Hz, CH_2N), 6.48 (d, $J = 16$ Hz, $\text{C}_6\text{H}_5\text{CH}$), 6.86–7.24 (m, indolinone), 7.38 (m, C_6H_5), 7.46 (d, $J = 16$ Hz, $\text{C}_6\text{H}_5\text{CH}=\text{CH}$). ^{13}C NMR (50 MHz, CD_3OD , TMS): δ 35.7 (t), 38.1 (t) (2CH_2), 76.5 (s, carbinol C-atom), 111.4 (d), 121.8 (d), 123.8 (d), 125.2 (d), 128.8 (d), 129.9 (d), 130.6 (d), 130.7 (d), 132.5 (s), 136.3 (s), 141.6 (d), 142.6 (s) (aromatic and olefinic C-atoms), 168.4 (s), 181.7 (s) ($2\text{C}=\text{O}$).

MS EI, 70 eV m/z (rel. int.): 322.1315 (calc. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3$: 322.1317, M^+ ; 3), 306.1367 (calc. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$: 306.1368, $\text{M}^+ - \text{O}$; 6), 304 ($\text{M}^+ - \text{H}_2\text{O}$; 2), 294.1360 (calc. for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$: 294.1368, $\text{M}^+ - \text{CO}$; 5), 276.1259 (calc. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}$: 276.1263; 2), 191 (1), 174.0917 (calc. for $\text{C}_{11}\text{H}_{12}\text{NO}$: 174.0919; 39), 163.0874 (calc. for $\text{C}_9\text{H}_{11}\text{N}_2\text{O}$: 163.0871, 191 – CO; 10), 160.0761 (calc. for $\text{C}_{10}\text{H}_{10}\text{NO}$: 160.0762; 16), 147 (McLafferty rearrangement starting from cinnamoyl carbonyl; 16), 146.0612 (calc. for $\text{C}_9\text{H}_8\text{NO}$: 146.0606; 26), 131.0499 (calc. for $\text{C}_9\text{H}_7\text{O}$: 131.0497; 100), 120.0449 (calc. for $\text{C}_7\text{H}_6\text{NO}$: 120.0449, $\text{M}^+ - \text{CO}$ – side-chain; 22), 103.0545 (calc. for C_8H_7 : 103.0548; 56), 77.0392 (calc. for C_6H_5 : 77.0391; 35); regarding the interpretation cf. formula **2**. MS, electron addition, 2–4 eV m/z (rel. int.): 322 ($\text{M}^+ - 62$), 304 ($\text{M}^+ - \text{H}_2\text{O}$; 67), 159 (100).

3-(2-Aminoethyl)-3-hydroxyindolin-2-one hydrochloride (**3**). A soln of 57 mg **2** in 9 ml conc HCl and 12.5 ml EtOH was refluxed 48 hr under N_2 . Evaporation gave a residue, from which *trans*-cinnamic acid was extracted with Et $_2\text{O}$ (mp, IR). The remaining hydrochloride was crystallized from EtOH. Needles: mp 267–72° (decomp.). $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1719 (γ -lactam), 1621, 1471, 1198, 759. $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 289 (3.19), 251 (3.80). ^1H NMR (80 MHz, D_2O , TMS): δ 2.18 (ca t, $J = 8$ Hz, 2H, $\text{C}-\text{CH}_2-\text{C}$), 3.06 (ca t, $J = 8$ Hz, 2H, CH_2N), 6.93–7.42 (m, 4H, indolinone).

3-Hydroxy-3-methylindolin-2-one. Prepared according to refs. [3, 4] and chromatographed over Si gel with CHCl_3 -MeOH (97:3); mp 166–8°, $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1710 (γ -lactam), 1626, 1476, 1197, 764. $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 287 (3.09), 253 (3.89). ^1H NMR (100 MHz, CD_3OD , TMS): δ 1.50 (s, 3H, Me), 6.84–7.36 (m, 4H, indolinone). MS EI, 6–16 eV m/z (rel. int.): 163 ($\text{M}^+ - 100$), 148 ($\text{M}^+ - \text{Me}$; 60), 147 ($\text{M}^+ - \text{O}$; 40), 145 ($\text{M}^+ - \text{H}_2\text{O}$; 30), 135 ($\text{M}^+ - \text{CO}$; 100), 120 ($\text{M}^+ - \text{CO} - \text{Me}$; 100). MS, electron addition, 2–4 eV m/z (rel. int.): 163 ($\text{M}^+ - 74$), 162 (90), 161 (95), 145 ($\text{M}^+ - \text{H}_2\text{O}$; 100).

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