EXPERIMENTAL

Plant material. Fronds of *Asplenium adiantum-nigrum* L. were collected on Mount Etna, Sicily.

Isolation procedure. Fresh fronds of *Asplenium adiantum-nigrum* were homogenized and extrd 3 × with hot EtOH. The combined extracts were filtered, concd to small vol. *in vacuo* and re-filtered. The xanthone was isolated by successive prep. PC in BAW, 5% HOAc and BEW. R_f data are: BAW 0.45, 5% HOAc 0.25, BEW 0.17. Total acid hydrolysis was carried out with 2 N HCl (1 hr at 100° under N_2); controlled acid hydrolysis was carried out with 10% aq. HOAc (2.5 hr under reflux). Treatment with β-glucosidase was carried out in citrate–phosphate buffer, pH 4.5, at 37° for 20 hr. 1,3,7,8-Tetrahydroxyxanthone was identified by UV spectral analysis with shift reagents [2,4], MS and comparison with an authentic sample (TLC on Si gel: 3 solvents); D-glucose and laminaribiose were identified by Co-PC (4 solvents), TLC on Si gel (*n*-BuOH–HOAc–Et_2O–H_2O, 9:6:3:1) and GLC of their trimethylsilyl derivatives [13].

Methylation of xanthone. The xanthone was methylated (Me_2SO_4–K_2CO_3–Me_2CO) and hydrolysed with 0.3 N HCl (4 hr under reflux). The partially methylated aglycone was identified as 1-hydroxy-3,7,8-trimethoxyxanthone by UV spectral analysis with shift reagents [2,4], MS and comparison with an authentic sample (TLC on Si gel; 3 solvents); methylated sugars were identified by PC according to ref. [14] and TLC on Si gel (EtOAc–$CHCl_3$, 1:1).

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AN UNSYMMETRICAL DIARYLHEPTANOID FROM *CURCUMA LONGA*

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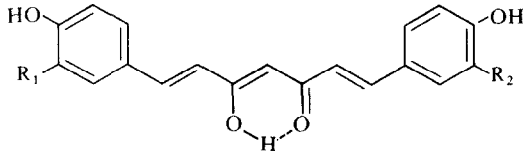
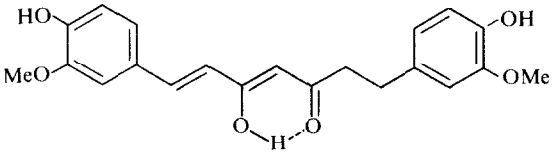
Key Word Index—*Curcuma longa*; Zingiberaceae; turmeric; diarylheptanoid; dihydrocurcumin; 1,7-bis-(4-hydroxy-3-methoxyphenyl)-hept-1-en-3,5-dione.

Earlier work on the pigments of turmeric (*Curcuma longa* L.) revealed the presence of three major phenolic diarylheptanoids, namely curcumin (**1**), feruloyl-(4-hydroxycinnamoyl)methane (**2**) and bis-(4-hydroxycinnamoyl)methane (**3**) [1,2]. Biosynthesis and metabolism of diarylheptanoids have recently attracted attention [2,3]. In the course of our work on the metabolism of curcumin [4], we have isolated a new diarylheptanoid from the benzene extract of *Curcuma longa* rhizomes.

This compound, $C_{21}H_{22}O_6$ (M^+ 370), had a UV maximum at 375 nm and its IR specrum showed bands at 3400 (OH), 1630 ($COCH_2CO$), 1600 and 1510 cm^{-1} (C=C and aromatic). It gave the rubrocurcumin reaction [5] with boric acid and oxalic acid (with visible max shifting to 420 nm), a characteristic reaction of β-diketones. The 270 MHz ^1H NMR spectrum in DMSO-d_6 showed signals for two phenolic hydroxyl protons at δ 9.65 and 8.76 (disappearing on exchange with D_2O), two singlets at 3.74 (3 H) and 3.83 (3 H) (OMe), two doublets at 7.48 and 6.64 (J = 14 Hz) for two *trans*-related olefinic protons, clusters of aromatic proton signals centred around 6.65,



1 $R_1 = R_2 = OMe$
2 $R_1 = H$; $R_2 = OMe$
3 $R_1 = R_2 = H$



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6.80 and 7.11 for 3, 2 and 1 protons, respectively, and a one-proton singlet at 5.88 attributable to the proton on the central carbon of the β-diketone in its enol form. In addition, it showed two triplets at δ 2.70 and 2.90 for two protons each ($J = 6$ Hz) indicating the presence of two methylene groups, possibly attached to each other. These data indicate the compound to be dihydrocurcumin (**4**). This was supported by the mass spectral fragmentation which showed the base peak at *m/e* 137 for hydroxy-(methoxy)benzyl ion and peaks at 233 for feruloylacetylmethyl, 219 for feruloylacetyl, 191 for feruloylmethyl and 177 for feruloyl ions.

Structure **4** for this compound was confirmed by the oxidation of the compound with dichlorodicyanobenzoquinone in tetrahydrofuran, which yielded curcumin (**1**). The isolation of an unsymmetrical diarylheptanoid from *Curcuma longa* may be of biogenetic significance [2].

EXPERIMENTAL

Mps are uncorr. UV spectra were measured in EtOH and IR as KBr discs. ^{1}H NMR spectra were recorded in DMSO-d_6 at 270 MHz using TMS as int. standard. MS were recorded at 70 eV.

Isolation. Dry turmeric powder (7 kg, Allepey variety) was extracted in cold with hexane for 48 hr followed by C_6H_6 (48 hr). The C_6H_6 extract was concd and the mixture of the three major pigments (**1**, **2** and **3**) which separated was filtered off. The mother liquor was transferred to a Si gel column and eluted with hexane followed by hexane–C_6H_6 (1:1). The latter fraction was then chromatographed on a column of Sephadex LH-20 in hexane–$CHCl_3$–MeOH (2:1:1). Repeated chromatography over Sephadex LH-20 in the above solvent mixture gave **4** as yellow crystals, mp 178° ($CHCl_3$) (0.4 g). (Found: C, 66.38; H, 5.9. $C_{21}H_{22}O_6 \cdot 0.5\,H_2O$ requires: C, 66.4; H, 6.0%). UV λ_{max}^{EtOH} nm (log ε): 375 (4.39), 305 (3.73), 280 (3.84), 260 sh, 250 (4.10). ^{1}H NMR: δ 2.69 (2H, *t*, $J = 6$ Hz), 2.78 (2H, *t*, $J = 6$ Hz), 3.74 (3H, *s*), 3.82 (3H, *s*), 5.88 (1H, *s*), 6.65 (3H, *m* and 1H, *d*, $J = 14$ Hz), 6.80 (2H, *m*), 7.11 (1H, *dd*, $J = 7$, 1 Hz), 7.30 (1H, *s*), 7.48 (1H, *d*, $J = 14$ Hz), 8.76 (1H, *s*), 9.65 (1H, *s*). MS *m/e* (rel. int.): 370 (14.4), 233 (6), 219 (28), 191 (28), 177 (88), 150 (32), 137 (100).

Oxidation of dihydrocurcumin. The compound (10 mg) was stirred with recrystallized DDQ (6 mg) in THF at room temp. for 30 min. The product was purified by column chromatography over Sephadex LH-20 in hexane–$CHCl_3$–MeOH (2:1:1) yielding curcumin, mp and mmp 181–182° (IR superimposable with that of authentic sample).

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