3. Thomson, R. H. (1951) *J. Chem. Soc.* 1237.
4. Tezuka, M., Takahashi, C., Kuroyanagi, M., Satake, M., Yoshihira, K. and Natori, S. (1973) *Phytochemistry* **12**, 175.
5. Platzer, N., Basselier, J. and Demerseman, P. (1974) *Bull. Soc. Chim. Fr.* 905.
6. Erichsen Jones, J. R. (1964) *Fish and River Pollution.* Butterworths, London.
7. Devavaram, P. J. T. (1977) M.Sc. Thesis, University of Sierra Leone.

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# PHENYLBUTANOIDS FROM *ZINGIBER CASSUMUNAR*

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**Key Word Index**—*Zingiber cassumunar*; Zingiberaceae; structure elucidation and syntheses; 1-arylbut-1,3-dienes; 1-arylbut-1-enes; (*E*)-4-(3′,4′-dimethoxy)but-3-en-1-yl palmitate; aryl aldehydes.

**Abstract**—Five novel phenylbutanoids have been isolated from the rhizomes of *Zingiber cassumunar*. 3,4-Dimethoxybenzaldehyde and 2,4,5-trimethoxy-benzaldehyde are also reported from the same source.

## INTRODUCTION

Recent work from our laboratories has led to the isolation, structure elucidation [1] and syntheses [2] of six novel aromatic compounds. We have further investigated the hexane extract of the rhizomes of the title plant and the details are now reported.

## RESULTS AND DISCUSSION

The milled rhizomes of the *Zingiber cassumunar* were extracted exhaustively with hexane in a Soxhlet apparatus. The hexane-soluble fraction [1] was chromatographed on a column of silica gel using hexane–ether as eluant to give four major fractions I–IV. Fraction I was analysed by GC–MS to give two components which were assigned as 4-(3′,4′-dimethoxyphenyl)but-1,3-diene **1** [1] and 4-(3′,4′-dimethoxyphenyl)but-3-ene **2**. Fraction II was further separated by prep. TLC to give a pale yellow oil and a colourless solid. GC–MS analysis of the oil led to the identification of 4-(2′,4′,5′-trimethoxyphenyl)but-1,3-diene **3** [2] and 4-(2′,4′,5′-trimethoxyphenyl)but-3-ene **4**. The colourless solid has been identified as (*E*)-4-(3′,4′-dimethoxyphenyl)but-3-en-1-yl palmitate **5**. Purification of fraction III and IV by prep. TLC yielded 3,4-dimethoxybenzaldehyde **6** and 2,4,5-trimethoxybenzaldehyde **7**, respectively.

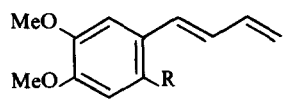
The identities of compounds **1**–**5** were further confirmed by comparing their spectral data with those of the synthetic materials [1, 2] (for details, see Experimental). Compounds **6** and **7** were identical with the authentic samples.

The five phenylbutanoids have not been reported before from plant sources. The two benzaldehydes **6** and **7** are known substances, but have not been reported before from this species of *Zingiber*.

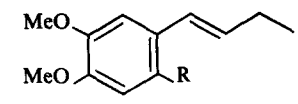
## EXPERIMENTAL

$^1$H NMR (60 MHz) spectra were recorded in $CDCl_3$ with TMS as an internal standard. Analytical GC was carried out with a stainless steel column (2 m × 3 mm) packed with silicone OV-17 on chromosorb under two different conditions: temp. programmed 120–200°, 5°/min (condition A) and temp. programmed 150–200° at 5° min (condition B). $N_2$ flow rate at 50 ml/min and FID were employed for both conditions.

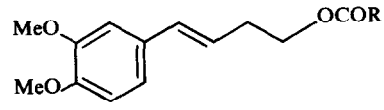
Extraction of the milled rhizomes of *Z. cassumunar* and separation of the concd extract into hexane-soluble and less-soluble fractions have been described previously [1]. The hexane-soluble fraction (30.0 g) was chromatographed on a column of silica gel (1.3 kg) using hexane–$Et_2O$ as the eluting solvent to give four major fractions (I–IV, 5.8, 2.4, 1.0 and 8.5 g respectively, all fractions appearing as yellow viscous oil).



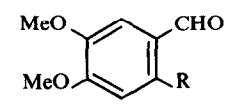
**1** R = H
**3** R = OMe



**2** R = H
**4** R = OMe



**5** R = $C_{15}H_{31}$



**6** R = H
**7** R = OMe

*4-(3′,4′-Dimethoxyphenyl)but-1,3-diene* **1** *and* 4-(3′,4′-*dimethoxyphenyl)but-3-ene*, **2**. Fraction I was analysed by GC–MS to yield two compounds: 4-(3′,4′-dimethoxyphenyl)but-1,3-diene **1** [1] ($R_t$ 10.5 min, condition A), MS *m/e* (rel. int.): 190 (85), 175 (21), 159 (90), 144 (48), 115 (100); 4-(3′,4′-dimethoxyphenyl)but-3-ene **2** ($R_t$ 11.8 min, condition A), MS: *m/e* (rel. int.): 192 (100), 177 (81), 161 (45), 149 (14), 146 (38). Attempts to separate compounds **1** and **2** by prep. TLC hexane–$CHCl_3$ (4:1) were unsuccessful.

*Synthesis of* 4-(3′,4′-*dimethoxyphenyl)but-3-ene* **2**. Propyltriphenylphosphonium bromide [3] (9.6 g) was stirred with THF (220.0 ml) under $N_2$ at room temp. while 1.1 N ethereal PhLi (22.0 ml) was added dropwise. After 1 hr, a solution of 3,4-dimethoxybenzaldehyde (3.3 g) in THF (10.0 ml) was slowly added and stirring was continued for 2 hr. The reaction mixture was then refluxed for 3 hr, cooled at room temp. and treated with $H_2O$ (3.0 ml). After the removal of THF, the residue was extracted with $CHCl_3$. The $CHCl_3$ layer was dried and evapd to give a residue which was chromatographed on a column of silica gel. Evaporation of the hexane–$CHCl_3$ (3:2) eluate gave compound **2** (2.8 g) as a slightly yellow liquid. (Found: C, 75.1; H, 8.2. $C_{12}H_{16}O_2$ requires: C, 75.0; H, 8.4%). $\nu_{max}^{neat}$ $cm^{-1}$: 1590, 1500. $\lambda_{max}^{EtOH}$ nm (log ε): 215 (4.32), 260 (4.16), 295 sh (3.63). $^1H$ NMR: δ 6.89–6.80 (3H, *m*, 3 × ArH), 6.50–5.32 (2H, *m*, C<u>H</u>=C<u>H</u>), 3.83, 3.80 (6H, both *s*, 2 × $OCH_3$), 2.22 (2H, quintet, $J$ = 7.0 Hz, CH=CHC<u>H</u>$_2$$CH_3$), 1.07 (3H, *t*, $J$ = 7.0 Hz, 1 × $CH_3$). MS *m/e* (rel. int): 192 (100%), 177 (81), 161 (46), 149 (19), 146 (38). The MS, $R_t$ and the behaviour on TLC hexane–$CHCl_3$ (4:1) of the synthetic and natural products **2** were identical.

*4-(2′,4′,5′-Trimethoxyphenyl)but-1,3-diene* **3**, 4-(2′,4′,5′-*trimethoxyphenyl)but-3-ene* **4**, *and* (E)-4-(3′,4′-*dimethoxyphenyl)but-3-en-1-yl palmitate* **5**. Fraction II (0.4 g) was purified by prep. TLC with hexane–$CHCl_3$ (4:1) as the mobile phase to give a pale yellow oil (70 mg) and a colourless solid (80 mg). GC–MS analysis of the oil yielded two compounds: 4-(2′,4′,5′-trimethoxyphenyl)but-1,3-diene **3** [2] ($R_t$ 8.8 min, condition B), MS *m/e* (rel. int.): 220 (85), 205 (19), 189 (100), 173 (33), 158 (15); and 4-(2′,4′,5′-trimethoxyphenyl)but-3-ene **4** ($R_t$ 10.6 min, condition B), MS *m/e* (rel. int.): 222 (100), 217 (47), 191 (20), 179 (39), 176 (26). Attempts to separate compounds **3** and **4** by prep. TLC were unsuccessful.

The colourless solid was further purified by prep. TLC in hexane–$CHCl_3$ (7:2) to give 50 mg of a colourless precipitate of the palmitate **5**.

*Synthesis of* 4-(2′,4′,5′-*trimethoxyphenyl)but-3-ene* **4**. Compound **4** was prepared by the procedure used for **2** except 2,4,5-trimethoxybenzaldehyde (3.9 g) was used instead of 3,4-dimethoxybenzaldehyde. After the work up, the residue obtained was chromatographed on a column of silica gel. Evapn of the hexane–$CHCl_3$ (3:2) eluate afforded compound **4** (2.5 g) as a slightly yellow oil (Found: C, 70.2; H, 8.0. $C_{13}H_{18}O_3$ requires: C, 70.2; H, 8.2%). $\nu_{max}^{neat}$ $cm^{-1}$: 1605, 1505. $\lambda_{max}^{EtOH}$ nm (log ε): 213 (4.30), 257 (4.11), 310 (3.79). $^1H$ NMR: δ 7.01–5.53 (4H, *m*, 2 × ArH, C<u>H</u>=C<u>H</u>), 3.83 (6H, *s*, 2 × $OCH_3$), 3.77 (3H, *s*, 1 × $OCH_3$), 2.25 (2H, *quintet*, $J$ = 7.0 Hz, C<u>H</u>$_2$$CH_3$), 1.08 (3H, *t*, $J$ = 7.0 Hz, 1 × $CH_3$). MS *m/e* (rel. int.): 222 (100), 217 (59), 191 (30), 179 (32), 176 (38). The MS, $R_t$ and behaviour on TLC of the synthetic and natural products **4** were identical.

*Synthesis of* (E)-4-(3′,4′-*dimethoxyphenyl)but-3-en-1-yl palmitate* **5**. NaH (0.4 g) was added into a cold soln of (*E*)-4-(3′,4′-dimethoxyphenyl)but-3-ene-1-ol [1] (0.2 g) in dry DME (10.0 ml) under $N_2$. After stirring for a few min, palmitoyl chloride (0.5 ml) was added dropwise and the reaction mixture was stirred at room temp. for 10 hr. The brown mixture was poured over ice and then the aq. mixture was extracted with $CHCl_3$. The extract was dried and evapd to give a brown residue which was purified by prep. TLC hexane–$CHCl_3$ (7:3). The palmitate **5** (160 mg) was obtained as a colourless solid, mp 55–6° (Found: C, 75.3; H, 10.1. $C_{28}H_{46}O_4$ requires: C, 75.3; H, 10.3%). $\nu_{max}^{nujol}$ $cm^{-1}$: 1725, 1590, 1510. $^1H$ NMR: δ 6.87 (3H, *m*, 3 × ArH), 6.43 (1H, *d*, $J$ = 16 Hz, ArC<u>H</u>=CH), 6.11, 5.85 (1H, *dt*, $J$ = 16.0 and 6.5 Hz, ArCH=C<u>H</u>), 4.18 (2H, *t*, $J$ = 6.5 Hz, C<u>H</u>$_2$O), 3.86, 3.84 (6H, both *s*, 2 × $OCH_3$), 2.51 (2H, *q*, $J$ = 6.5 Hz, CH=CH-C<u>H</u>$_2$), 2.30 (2H, *t*, $J$ = 6.5 Hz, COC<u>H</u>$_2$), 1.25 (26 H, *m*, 13 × $CH_2$), 0.88 (3H, *t*, $J$ = 6.5 Hz, 1 × $CH_3$). The IR, $^1H$ NMR, MS spectra of the synthetic and natural products **5** and their behaviour on TLC were identical.

*3,4-Dimethoxybenzaldehyde* **6** *and* 2,4,5-*trimethoxybenzaldehyde* **7**. Fraction III (1.0 g) was purified by repeated prep. TLC with hexane–$CHCl_3$ (1:4) as the mobile phase; 3,4-dimethoxybenzaldehyde **6** was obtained as a pale yellow solid (40 mg). Purification of fraction IV (2.0 g) by repeated prep. TLC with hexane–$CHCl_3$ (1:4) as the mobile phase gave 2,4,5-trimethoxybenzaldehyde **7** as a pale yellow solid (10 mg). The IR and MS spectra and the behaviour on TLC of the natural products **6** and **7** and those of authentic samples were identical.

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## REFERENCES

1. Amatayakul, T., Cannon, J. R., Dampawan, P., Dechatiwongse, T., Giles, R. G. F., Huntrakul, C., Kusamran, K., Mokkhasamit, M., Raston, C. L., Reutrakul, V. and White, A. H. (1979) *Aust. J. Chem.* **32**, 71.
2. Tuntiwachwuittikul, P., Limchawfar, B., Reutrakul, V., Pancharoen, O., Kusamran, K. and Byrne, L. T. (1980) *Aust. J. Chem.* **33**, 913.
3. Friedrich, K. and Henning, H. G. (1959) *Chem. Ber.* **92**, 2756.