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TERPENOIDS FROM *CURCUMA HEYNEANA**

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Key Word Index—*Curcuma heyneana*; Zingiberaceae; oxycurcumenol; guaiane; labdane; X-ray crystallography; chemotaxonomy.

Abstract—A new guaiane sesquiterpene named oxycurcumenol was isolated from the steam-distilled essential oil fraction of *Curcuma heyneana* in addition to known sesquiterpenes germacrone, dehydrocurdione, isocurcumenol, curcumenol, curcumanolide A, B and zerumbone. Its structure was elucidated on the basis of spectroscopic and chemical studies, and finally confirmed by X-ray crystallography. (*E*)-Labda-8(17),12-diene-15,16-dial was isolated from the benzene extract of the same plant together with dehydrocurdione, curcumenol, curcumanolide A and B. The taxonomic status of *C. heyneana* is briefly discussed based on the chemotaxonomic significance of these findings.

INTRODUCTION

Curcuma heyneana Val. & V. Zijp is one of the zingiberaceous plants indigenous to Java Island, Indonesia. The rhizome of this plant, which is called 'temu giring' in Javanese, is of wide medicinal value in Indonesia, and is considered to be useful for the treatment of skin diseases, abrasions and injuries. It is not only found commonly as one of the main ingredients in traditional Indonesian mixed herbal medicines (jamu), but is also widely used in the form of a juice prepared from fresh rhizome as an anthelminthic against intestinal worms. In fact, the preliminary experiment revealed potent anthelminthic activity of the juice against swine ascaris (*Ascaris lumbricoides* var. *suis*), and the main part of the activity was found to occur in its essential oil fraction (K. Firman, unpublished work). However, there is no available chemical information on this plant. We were thus encouraged to investigate the rhizome and we now report on the isolation and structure elucidation of a new guaiane sesquiterpene, and also the isolation of compounds of chemotaxonomic significance with regard to the taxonomical status of *C. heyneana* among the genus *Curcuma*.

RESULTS AND DISCUSSION

The essential oil fraction obtained from the commercially available rhizome of *C. heyneana* was repeatedly chromatographed on silica gel to give compounds **1**–**8**. Compounds **1**–**4** were readily elucidated as germacrone [1], dehydrocurdione [2], isocurcumenol [3] and curcumenol [4] respectively by spectroscopic methods, and finally identified by direct comparison with authentic samples. Compounds **5** and **6** were found to be identical to curcumanolide A and B respectively by comparison with spectroscopic data reported in the literature [5]. Compound **7** was elucidated as zerumbone [6], whose detailed spectral data are not currently available, based on the ^1H and ^{13}C NMR data (Tables 1 and 2), and its structure was further substantiated by long range ^1H–^{13}C shift correlated 2D NMR (data not shown).

Compound **8**, for which the name of oxycurcumenol is proposed, had no UV absorption and no IR absorption band in the carbonyl region. The ^{13}C NMR spectrum was similar to that of the known guaiane sesquiterpene curcumenol (**4**); the difference being the presence of two sp^3 carbons in place of two sp^2 carbons (Table 2). The molecular formula, $C_{15}H_{22}O_3$, was confirmed by mass spectrometry and elementary analysis, and indicated that **8** contained one more oxygen atom than **4**. The additional oxygen was shown to be a 7,11-epoxide from the chemical shifts of C-7 and C-11 (δ 61.8, 75.6). The configuration of the epoxide was established on the basis of the following evidence. Irradiation of Me-13 at δ 1.26 ppm resulted in an 8.5% NOE on H-9 (δ 5.67), and a 4% NOE on OH-8 (δ 3.79), which strongly suggested the proximity of H-9, OH-8 and Me-13 in the molecular structure of oxycurcumenol (**8**) and thus unequivocally assigned the configuration of the epoxide as β. The above results suggested the presence of steric hindrance around the epoxide ring, making its structure distinguishable from those of ordinary guaiane hemiketals. This led us to investigate the molecular structure by X-ray crystallography. Recrystallization of **8** from *n*-hexane furnished colourless prisms of mp 75–76° suitable for X-ray analysis. The computer generated perspective drawing (Fig. 1) indicated that the isopropyl residue is bent over toward the 9,10-double bond, and implied the presence of hydrogen bonding between OH-8 and the epoxy oxygen, which confirmed the results of NOE experiments.

In order to determine the absolute stereochemistry of oxycurcumenol (**8**), the direct transformation into **8** of curcumenol (**4**), whose absolute structure has been established by the X-ray analysis [7], was attempted using *m*-chloroperbenzoic acid (MCPBA). The reaction proceeded stereoselectively to give the β-epoxide, which is identical to natural oxycurcumenol (**8**) in every respect including

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Table 1. ^{1}H NMR data of compounds **7**, **8** and **12** (400 MHz, TMS as internal standard)

H	**7** ($CDCl_3$)	**8** (C_6D_6)	**8** ($CDCl_3$)	**12** ($CDCl_3$)
1	—			2.49 *m*
2	—	1.5–1.8 *m*	1.85–1.95 *m*	1.57 *m* (2H)
3	6.02 *d* (*br*), $J=5.5$	(6H)	(4H)	2.08 *m* (2H)
4	2.23 *m*		1.55–1.70 *m*	1.90 *m*
	2.45 *m*		(2H)	
5	0.87 *m*	—	—	—
	1.26 *m*			
6	—	1.73 *d*, $J=14.3$	1.99 *d*, $J=14.2$	1.77 *d*, $J=11$
		1.97 *d*, $J=14.3$	2.04 *d*, $J=14.2$	2.34 *d*, $J=11$
7	5.25 *d* (*br*), $J=5.5$	—	—	—
8	1.90 *d* (*br*), $J=5.5$	3.79 *s* (*br*)	3.60 *s* (*br*)	—
	2.35 *dd* (*br*), $J=5.5$, 5.5			
9	—	5.67 *s* (*br*)	5.56 *s* (*br*)	5.86 *s* (*br*)
10	5.98 *d*, $J=8.5$	—	—	—
11	5.86 *d*, $J=8.5$	—	—	—
12	1.80 *s* (*br*)	1.08 *s*	*1.37 *s*	1.21 *s*
13	1.54 *s* (*br*)	1.26 *s*	*1.33 *s*	1.33 *s*
14	*1.20 *s*	1.10 *d*, $J=6.6$	1.03 *d*, $J=6.4$	1.07 *d*, $J=6.5$
15	*1.07 *s*	1.49 *s* (*br*)	1.71 *s* (*br*)	1.71 *s* (*br*)

*Figures in the same column may be interchangeable. Assignments were confirmed by ^{1}H–^{1}H shift correlated 2D NMR.

Table 2. ^{13}C NMR data of compounds **3**, **4**, **7**, **8** and **12** (25 MHz, $CDCl_3$, δppm, TMS as the internal standard)

C	**3**	**4**	**7**	**8**	**12**
1	52.7 *d*	52.1 *d*	204.1 *s*	51.7 *d*	51.1 *d*
2	28.3 *t*	28.4 *t*	137.9 *s*	27.4 *t*	23.2 *t*
3	30.8 *t*	32.3 *t*	148.7 *d*	31.0 *t*	29.8 *t*
4	41.7 *d*	41.3 *d*	24.5 *t*	40.1 *d*	38.3 *d*
5	86.9 *s*	86.2 *s*	39.5 *t*	84.7 *s*	91.8 *s*
6	38.9 *t*	38.1 *t*	136.2 *s*	36.2 *t*	36.9 *t*
7	133.0 *s*	138.2 *s*	124.9 *d*	75.6 *s*	70.5 *s*
8	103.8 *s*	102.4 *s*	42.5 *t*	97.8 *s*	178.3 *s*
9	36.2 *t*	128.0 *d*	38.0 *s*	122.6 *d*	121.4 *d*
10	144.8 *s*	137.9 *s*	127.1 *d*	141.0 *s*	139.1 *s*
11	126.5 *s*	121.7 *s*	160.6 *d*	61.8 *s*	56.6 *s*
12	22.4 *q*	22.9 *q*	11.9 *q*	23.3 *q*	26.0 *q*
13	18.9 *q*	19.7 *q*	15.4 *q*	19.0 *q*	20.4 *q*
14	12.4 *q*	12.8 *q*	*29.6 *q*	11.5 *q*	12.3 *q*
15	111.9 *t*	21.4 *q*	*24.4 *q*	20.9 *q*	24.8 *q*

Letters *s*, *d*, *t* and *q* indicate multiplicity of each signal in off-resonance spectrum.

*Figures may be interchangeable.

Assignments were confirmed by ^{1}H–^{13}C and long-range ^{1}H–^{13}C shift correlated 2D NMR.

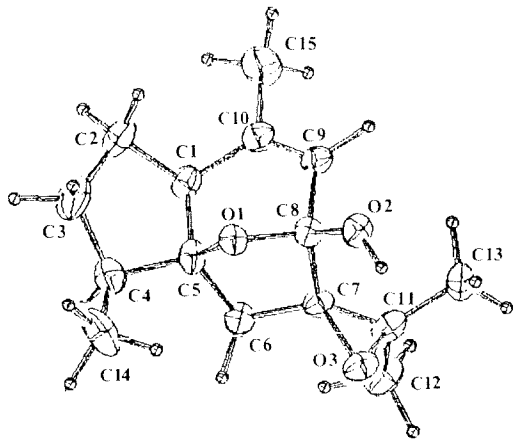
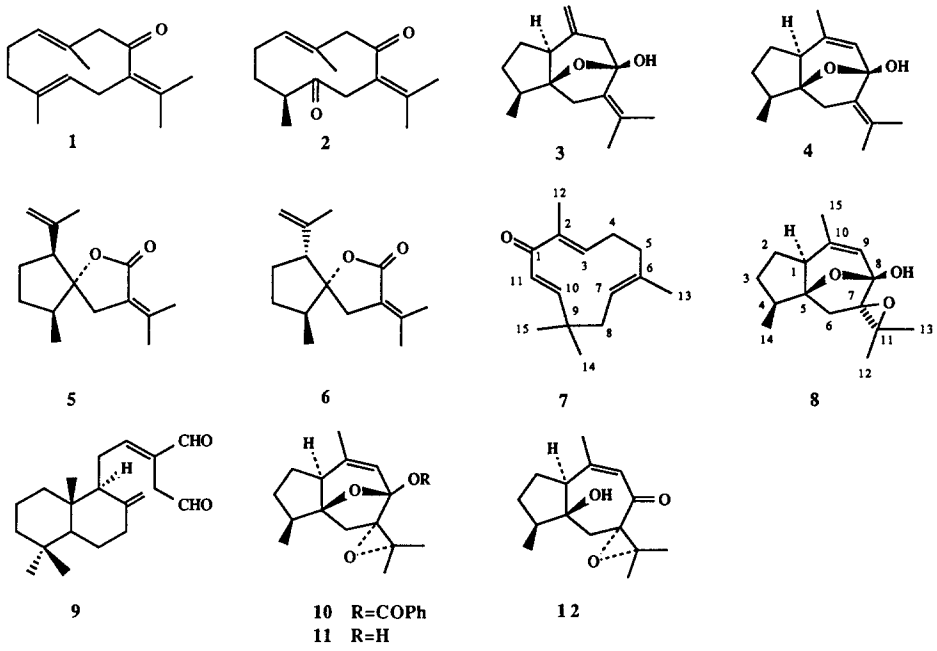


Fig. 1. Computer generated perspective drawing of **8** from X-ray coordinates showing the relative stereochemistry.

optical rotation. Thus the absolute stereochemistry of **8** was determined as that shown by the structure **8**. In general the oxidation by the peracid of the olefin possessing a free hydroxyl at the allylic position is considered to be affected by the hydrogen bonding between the hydroxyl and the attacking peracid; the epoxidation occurring in the same direction as the orientation of the hydroxyl. Therefore it is quite reasonable that the β-epoxide is the sole product in the above reaction. An epimeric isomer (α-epoxide) was also prepared. The epoxidation of curcumenol benzoate by MCPBA produced a mixture of epimeric epoxides ($\alpha:\beta = 3:1$), but recrystallization from methanol afforded a single product (**10**), which upon alkaline hydrolysis furnished a pure α-epoxide (**12**). However, its IR and ^{13}C NMR spectra suggested the presence of α,β-unsaturated ketone (1735 cm^{-1} and δ178.3), which led to the assignment of the structure **12** rather than **11**. It is presumed that the hemiketal of oxycurcumenol (**8**), though sterically hindered, is substantially stabilized by the hydrogen bonding between HO-8 and the epoxy oxygen. This is supported by the results of X-ray analysis, while that of the corresponding epimer (**11**) undergoes cleavage to generate the keto-form due to lack of the hydrogen bonding needed to stabilize the hemiketal ring.

Dehydrocurdione (**2**) has a unique germacrene-dione structure which, as expected, is prone to chemical cycliz-



1 2 3 4 5 6 7 8 9 10 R=COPh 11 R=H 12

ation under relatively mild condition, and in fact has been reported to give rise to curcumenol (**4**) on treatment with base, isocurcumenol (**3**) on pyrolysis, and curcumanolide A (**5**) and B (**6**) on acid-treatment [7]. Since compounds **1**–**8** were isolated from the essential oil fraction obtained under the drastic conditions of steam distillation, a chemical investigation was also carried out on the benzene extract made at room temperature in order to minimize the formation of artefacts. Compounds **2**, **4**–**6** and **9** [8] were isolated from the benzene extract, and compounds **2** and **4**–**6** were identified with those obtained from the essential oil. The isolation of **5** and **6** from the benzene extract indicates that conversion of **2** into spirolactones takes place even under mild condition. It appears, however, that isocurcumenol (**3**) was an artefact derived from pyrolytic conversion of **2** during steam distillation since it was not found in the benzene extract.

All compounds obtained from the rhizome of *C. heyneana* except for compounds **7**–**9** have also been isolated from that of *C. zedoaria* [5], which arouses chemotaxonomic interest in view of the taxonomical relation of *C. heyneana* to other *Curcuma* species. The isolation of curcumenol (**4**) and its biogenetic precursor dehydrocurdione (**2**) from this plant may indicate a close taxonomical relationship between *C. zedoaria* and *C. heyneana* since the occurrence of these characteristic sesquiterpenes is currently restricted to the above two species among the genus *Curcuma*. Zerumbone (**7**) was isolated as a main constituent of the rhizomes of *Zingiber zerumbet* [9] and *Z. amaricans* (Zingiberaceae) [10], but there have been no reports of its isolation from the genus *Curcuma*. A characteristic diterpene, (*E*)-labda-8(17),12-diene-15,16-dial (**9**), which occurred only in the benzene extract, was found to be identical to the one isolated from *Hedychium coronarium* (Zingiberaceae) [8]. Interestingly, its optical isomer has been obtained from *Alpinia speciosa* [11]. The labdane is the only type of diterpene which is known to occur in the zingiberaceous plants, and recently a number of related compounds have been isolated from genera *Hedychium* [8, 12, 13], *Afromomum* [14] and *Alpinia* [11, 15, 16]. Since there have been only a few reports on the isolation of diterpenes from zingiberaceous plants, the isolation of a diterpene from *Curcuma* species, which has not been reported, is of interest from a chemotaxonomic point of view.

As stated above, this work was initiated as a result of our deep interest in the characteristic use of the rhizome of *C. heyneana* as an anthelminthic in Indonesian traditional medicine. Investigation on the anthelminthic activity of compounds isolated in this study is currently under way.

EXPERIMENTAL

General procedure. Mps: uncorr; IR: $CHCl_3$ or KBr; UV: 95% EtOH; $[\alpha]_D$: $CHCl_3$ or MeOH; ^1H NMR (400 or 100 MHz) and ^{13}C NMR (100 or 25 MHz): $CDCl_3$ or C_6D_6, with TMS as int. standard; CC: silica gel (Wakogel C-200 or Kieselgel 60); HPLC: JAIGEL 1H + 2H (2 × 50 cm) on LC-09 (Japan Anal. Ind. Co., Ltd, Tokyo), $CHCl_3$ as solvents; TLC: 0.25 mm precoated silica gel ($60F_{254}$, Merck), *n*-hexane–Me_2CO or C_6H_6–Me_2CO; Spots were detected by UV light (254 nm) or heating after spraying with 10% H_2SO_4.

Plant materials. The fresh rhizome of *C. heyneana*, which is widely cultivated in Java, was purchased in Bandung, Indonesia and plant specimens were deposited in the Department of Pharmacy, Bandung Institute of Technology, Bandung, Indonesia.

Isolation of constituents from the essential oil fraction. The essential oil fraction (40 g) obtained from the dried rhizome (about 10 kg) of *C. heyneana* by use of a Karlsruhe apparatus was subjected to CC on silica gel (2 kg) and gave, on elution with a gradient solvent system of C_6H_6, $CHCl_3$ and Me_2CO increasing the amount of $CHCl_3$ and Me_2CO stepwise: (i) with C_6H_6, **1** (0.3 g); (ii) with C_6H_6–$CHCl_3$ (3:1), **3** (0.5 g); (iii) with C_6H_6–$CHCl_3$–Me_2CO (4:2:1), a mixture which was separated by CC on silica gel (200 g) using a C_6H_6–Me_2CO gradient (1–5%) to give **2** (0.6 g), **8** (0.2 g) and **4** (2.5 g). Fractions eluted with

C_6H_6–$CHCl_3$ (49:1) were rechromatographed on silica gel (250 g) with a C_6H_6–$CHCl_3$ gradient system. Fractions eluted with C_6H_6–$CHCl_3$ (99:1) were further subjected to CC on silica gel (250 g; *n*-hexane–Me_2CO gradient) yielding a mixture of **5** and **6** (2.0 g), which was separated by recycling HPLC to give **5** (15 mg) and **6** (70 mg) in pure forms (recycled 95 times). Fractions eluted with C_6H_6–$CHCl_3$ (49:1) were rechromatographed on silica gel (120 g; C_6H_6–$CHCl_3$ gradient) to give **7** (40 mg).

Isolation of constituents from the C_6H_6 extract. The fresh rhizome (1 kg) was sliced, air-dried and extracted with C_6H_6 (3 l) at room temp. for 2 days. The C_6H_6 soln was concd *in vacuo* below 35° to give a dark brown oil (22.2 g). The whole extract was chromatographed over silica gel (160 g) using a C_6H_6–Me_2CO gradient. The elute was collected as 200 ml fractions. Fractions 1–10 eluted with C_6H_6 were subjected to CC on silica gel (100 g) to give **5**, **6** and **9** (600 mg) as colourless oils on elution with C_6H_6. **5** and **6** were obtained as a mixture (10 mg) which was identical to that isolated from the essential oil, and was not further separated. Fractions 19–25 eluted with C_6H_6 were rechromatographed on silica gel (160 g; C_6H_6–Me_2CO, 19:1) to give **2** (300 mg) as a colourless oil. The residue of fractions 48–61 eluted with C_6H_6–Me_2CO (49:1) was subjected to CC on silica gel (50 g). On elution with C_6H_6–Me_2CO (14:1) **4** (500 mg) was obtained as crystals. The presence of oxycurcumenol (**8**) was observed on TLC (Merck Kieselgel F_{254}, R_f, 0.60, *n*-hexane–Me_2CO, 9:1; pale red on heating after spraying with 10% H_2SO_4) during separation procedure, but could not be isolated in a substantial amount.

Germacrone (**1**). Colourless needles, mp 55–56° (MeOH); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2920, 1710 (C=O), 1680 (C=O), 1453, 1375; (100 MHz, $CDCl_3$): δ 1.44 (3H, *s*), 1.62 (3H, *s*), 1.71 (3H, *s*), 1.77 (3H, *s*), 2.0–2.5 (4H, *m*), 2.90 (3H, *m*), 3.40 (1H, *br d*, J = 10 Hz), 4.70 (1H, *m*), 4.95 (1H, *br d*, J = 10 Hz); ^{13}C NMR (25 MHz $CDCl_3$): δ 15.6 (*q*), 16.7 (*q*), 19.9 (*q*), 22.3 (*q*), 24.1 (*t*), 29.2 (*t*), 38.1 (*t*), 55.8 (*t*), 125.2 (*d*), 126.5 (*s*), 129.1 (*s*), 132.4 (*d*), 134.7 (*s*), 137.1 (*s*), 207.3 (*s*); EIMS *m/z* (rel. int.): 218 $[M]^+$ (9), 176 $[M-CO]^+$ (10), 175 (24), 136 (66), 135 (86), 107 (100).

Dehydrocurdione (**2**). Viscous oil, $[\alpha]_D^{20}$ + 280° ($CHCl_3$; *c* 0.3); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2920, 1710 (C=O), 1680 (C=O), 1453, 1375; ^1H NMR (100 MHz, $CDCl_3$): δ 1.03 (3H, *d*, J = 7 Hz), 1.66, 1.74, 1.77 (3H each, *s*), 1.9–2.6 (4H, *m*), 3.0–3.3 (4H, *m*), 5.17 (1H, *t*, J = 7 Hz); ^{13}C NMR (25 MHz, $CDCl_3$): δ 16.2 (*q*), 18.3 (*q*), 20.9 (*q*), 22.0 (*q*), 26.2 (*t*), 34.1 (*t*), 43.3 (*t*), 46.3 (*d*), 56.7 (*t*), 129.1 (*s*), 129.8 (*s*), 132.5 (*d*), 136.6 (*s*), 206.0 (*s*), 210.2 (*s*); EIMS *m/z* (rel. int.): 234 $[M]^+$ (44), 191 (27), 178 (51), 165 (87), 164 (86), 152 (81), 121 (44), 96 (60), 68 (100).

Isocurcumenol (**3**). Colourless needles, mp 144–146° (*n*-hexane); $[\alpha]_D^{20}$ + 36.5° ($CHCl_3$; *c* 0.21); IR ν_{max}^{KBr} cm^{-1}: 3400, 2920, 1660 (C=C), 1310, 1100, 980, 880; ^1H NMR (400 MHz, $CDCl_3$): δ 1.01 (3H, *d*, J = 6.4 Hz), 1.5–1.6 (2H, *m*), 1.62 (3H, *s*), 1.65–1.8 (2H, *m*), 1.80 (3H, *s*), 1.9–2.0 (3H, *m*), 2.22 (1H, *t*, J = 14 Hz), 2.5–2.6 (2H, *m*), 2.67 (1H, *d*, J = 14 Hz), 2.83 (1H, *br s*), 4.73 (1H, *t*, J = 2.1 Hz), 4.78 (1H, *t*, J = 2.1 Hz); EIMS *m/z* (rel. int.): 234 $[M]^+$ (12), 219 (10), 216 (14), 201 (11), 191 (84), 173 (22), 147 (37), 133 (28), 121 (100), 105 (87).

Curcumenol (**4**). Colourless needles, mp 114–116° (AcOEt); $[\alpha]_D^{20}$ + 362° ($CHCl_3$; *c* 0.2); IR ν_{max}^{KBr} cm^{-1}: 3420, 2900, 1655 (C=C), 1375, 1300, 1270, 1150, 805; ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (3H, *d*, J = 6.2 Hz), 1.59, 1.66, 1.81 (3H each, *s*), 1.5–2.0 (6H, *m*), 2.11 (1H, *d*, J = 15.5 Hz), 2.65 (1H, *d*, J = 15.5 Hz), 3.05 (1H, *br s*), 5.75 (1H, *br s*); EIMS *m/z* (rel. int.): 234 $[M]^+$ (33), 191 (31), 189 (64), 165 (34), 147 (53), 133 (59), 105 (100).

Curcumanolide A (**5**). Colourless oil; $[\alpha]_D^{18}$ −63° ($CHCl_3$; *c* 0.30); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2960, 1733, 1662, 1445, 1378, 1270; UV λ_{max}^{MeOH} nm (ε): 233 (10600); ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, *d*, J = 7 Hz), 1.6–2.35 (5H, *m*), 1.72 (3H, *br s*), 1.85 (3H, *br s*), 2.23 (3H, *br s*), 2.46 (1H, *br s*), 2.80 (1H, *dd*, J = 12, 9 Hz), 4.74 (1H, *br s*), 4.93 (1H, *br s*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.9 (*q*), 19.7 (*q*), 23.0 (*t*), 23.6 (*q*), 24.2 (*q*), 26.2 (*t*), 27.3 (*t*), 42.5 (*d*), 52.0 (*d*), 89.7 (*s*), 112.6 (*t*), 120.6 (*s*), 143.4 (*s*), 149.4 (*s*), 169.9 (*s*); EIMS *m/z* (rel. int.): 234 $[M]^+$ (38), 178 (59), 165 (97), 164 (100), 152 (93).

Curcumanolide B (**6**). Colourless needles, mp 32–34° (MeOH); $[\alpha]_D^{19}$ + 33° ($CHCl_3$, *c* 1.18); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2960, 1730, 1663, 1450, 1375, 1268; UV λ_{max}^{MeOH} nm (ε): 233 (7300); ^1H NMR (400 MHz, $CDCl_3$): δ 0.97 (3H, *d*, J = 6.5 Hz), 1.5–2.5 (5H, *m*), 1.67 (3H, *br s*), 1.84 (3H, *br s*), 2.24 (3H, *br t*, J = 2.5 Hz), 2.49 (1H, *dt*, J = 1.5, 17 Hz), 2.84 (1H, *t*, J = 8.0 Hz), 2.86 (1H, *dt*, J = 2.5, 17 Hz), 4.75 (1H, *br s*), 4.88 (1H, *br s*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.9 (*q*), 19.6 (*q*), 21.7 (*q*), 24.1 (*q*), 27.2 (*t*), 30.6 (*t*), 33.7 (*t*), 45.0 (*d*), 55.8 (*d*), 91.4 (*s*), 113.8 (*t*), 120.6 (*s*), 145.1 (*s*), 148.6 (*s*), 169.5 (*s*); EIMS *m/z* (rel. int.): 234 $[M]^+$ (42), 178 (63), 165 (99), 164 (100), 152 (94).

Zerumbone (**7**). Viscous oil solidified as refrigerated. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3350, 2900, 1655 (C=O), 1450, 1255, 964. EIMS *m/z* (rel. int.): 218 $[M]^+$ (26), 160 (20), 150 (22), 135 (96), 109 (30), 108 (43), 107 (100).

Oxycurcumenol (**8**). Colourless prisms, mp 114–116° (MeOH); 75–76° (*n*-hexane); $[\alpha]_D^{20}$ − 133° ($CHCl_3$; *c* 0.1); IR ν_{max}^{KBr} cm^{-1}: 3460, 2950, 1670 (C=C), 1300, 1280, 1240, 905, 755; EIMS *m/z* (rel. int.): 250 $[M]^+$ (1), 232 $[M-H_2O]^+$ (9), 191 (22), 165 (100), 147 (88), 121 (31); Anal.: Calc. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.98; H, 8.86.

(E)-*Labda*-8(17),12-*diene*-15,16-*dial* (**9**). Colourless oil, $[\alpha]_D^{20}$ + 16° (MeOH; *c* 0.23); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2950, 1730 (CHO), 1680 (C=C), 1640; UV λ_{max}^{MeOH} nm (ε): 234 (11380); ^1H NMR (400 MHz, $CDCl_3$): δ 0.64, 0.74, 0.80 (3H each, *s*), 2.1–2.45 (5H, *m*), 3.29 (1H, *br d*, J = 17 Hz), 3.37 (1H, *br d*, J = 17 Hz), 4.29 (1H, *d*, J = 1.5 Hz), 4.78 (1H, *d*, J = 1.5 Hz), 6.67 (1H, *t*, J = 7 Hz), 9.31 (1H, *s*), 9.54 (1H, *t*, J = 1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3 (*q*), 19.2 (*t*), 21.6 (*q*), 24.0 (*t*), 24.6 (*t*), 33.5 (*s* and *q*), 37.7 (*t*), 39.1 (*t*), 39.2 (*t*), 39.5 (*s*), 41.9 (*t*), 55.3 (*d*), 56.5 (*d*), 107.8 (*t*), 134.8 (*s*), 147.9 (*s*), 159.7 (*d*), 193.4 (*d*), 197.1 (*d*); EIMS *m/z* (rel. int.): 302 $[M]^+$ (25), 137 (100), 123 (46), 121 (24), 109 (31), 107 (27).

Epoxidation of **4**. To a mixture of **4** (1.2 g) in CH_2Cl_2 (6 ml) was added a soln of MCPBA (1.1 g) in CH_2Cl_2 (10 ml). After stirring for 2 hr at room temp., the ppt. was filtered off. The filtrate was washed successively with 10% Na_2SO_3, satd $NaHCO_3$ and H_2O, dried over Na_2SO_4, and evapd under reduced pressure. The residue was chromatographed on silica gel (eluted with C_6H_6–Me_2CO, 9:1) to give the epoxide **8** (950 mg) along with the starting material (**4**) (200 mg). The oxide **8** was recrystallized from MeOH, mp 114–116°. Mp 75–76° (*n*-hexane). $[\alpha]_D^{22}$ − 130° ($CHCl_3$; *c* 0.2).

Preparation of **12**. A mixture of **4** (300 mg) and NaH (60 mg) in C_6H_6 (10 ml) was heated at 70–80° for 90 min. To this mixture benzoyl chloride (560 mg) was added dropwise, and the reaction mixture was kept at room temp. overnight. The mixture was diluted with H_2O and extracted with C_6H_6. The C_6H_6 layer was washed with H_2O, dried over Na_2SO_4, and evapd to dryness under red. pres. The residue was purified by CC on silica gel to give the benzoate of **4** (282 mg). Epoxidation of the benzoate was carried out, and worked-up according to the procedure described above. The reaction mixture was chromatographed on silica gel to give a mixture of two epimeric epoxides (220 mg). Recrystallization of the mixture from MeOH gave only one epimer **10** (60 mg), mp 188–190°. Hydrolysis of **10** in MeOH–NaOH gave 20 mg of the epoxide **12**, mp 95–96° (*n*-hexane). IR ν_{max}^{KBr} cm^{-1}: 3460, 2960, 1735, 1665, 1450, 1380, 1300.

X-ray diffraction analysis of oxycurcumenol (**8**). Suitable crystals of **8**, which were obtained from *n*-hexane soln, were used for the X-ray crystal analysis. The crystal belongs to an orthorhom-

bic space group $P2_12_12_1$, with four molecules in a unit cell of $a = 12.935(3)$ Å, $b = 10.457(3)$ Å, $c = 21.607(5)$ Å. A total of 2612, non-zero, independent reflections were measured in a Philips PW1100 four-circle diffractometer, using Cu-Kα radiation monochromated by a graphite plate. The structure was solved by the direct method using the KANTAN program. An E-map yielded the whole locations of non-hydrogen atoms. The structure was refined by the block-diagonal least-squares calculations, and the hydrogen atoms were on a difference Fourier synthesis map. The function $w\ (|F_o|-|F_c|)^2$ with $w = 1$ for all reflections was minimized to give the final R-factor of 0.080, assuming the anisotropic temperature factors for the non-hydrogen atoms (hydrogen atoms not refined). The structure factors used for carbon and oxygen were taken from the International Tables for X-ray Crystallography, and for hydrogen were taken from those of Stewart, Davidson and Simpson. Tables I–IV containing the final fractional coordinates, temperature parameters, bond distances and bond angles have been deposited at the Cambridge Crystallographic Data Centre, Cambridge, England.

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