

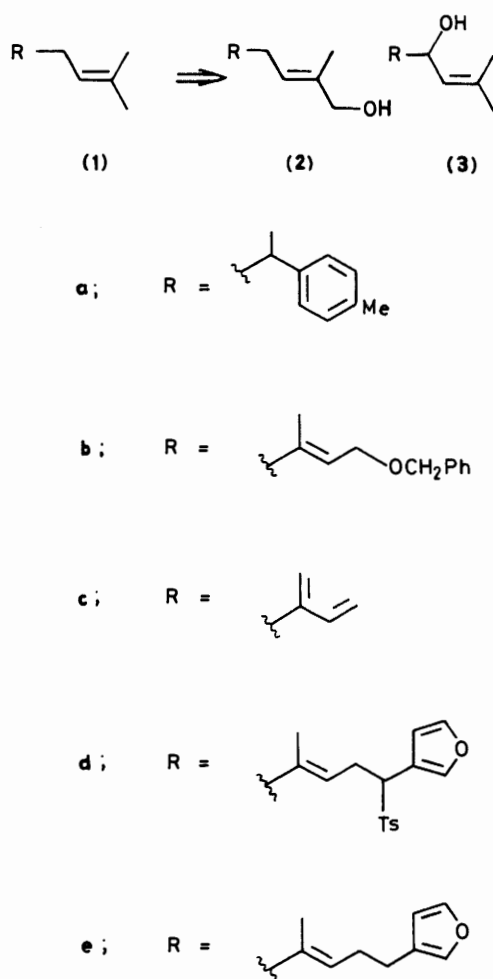
## Facile Regio- and Stereo-specific Allylic Oxidation of *gem*-Dimethyl Olefins via Addition of Benzenesulphenyl Chloride. Synthesis of Allylic Oxygenated Terpenes

Yukio Masaki,\* Kinji Hashimoto, Kazuhiko Sakuma, and Kenji Kaji  
Gifu College of Pharmacy, 5-6-1 Mitahora Higashi, Gifu 502 Japan

Novel and facile terminal *trans*-allylic and internal allylic oxidations of the *gem*-dimethyl olefin terminus of the terpenoids (**1**) are described which take place site-, regio-, and stereo-specifically via the same intermediate adduct between benzenesulphenyl chloride and (**1**). By this method, the allylic oxygenated terpenes ( $\pm$ )-nuciferal (**11**), ( $\pm$ )-*ar*-turmerone (**12**), ( $\pm$ )-ipsdienol (**3c**), neotorreyol (**2e**), ( $\pm$ )-6-hydroxydendrolasin (**3e**), and 6-oxodendrolasin (**14**) were synthesized.

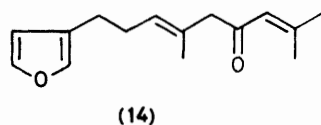
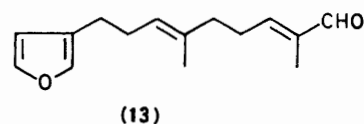
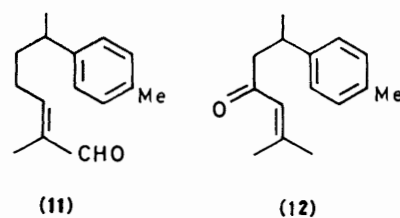
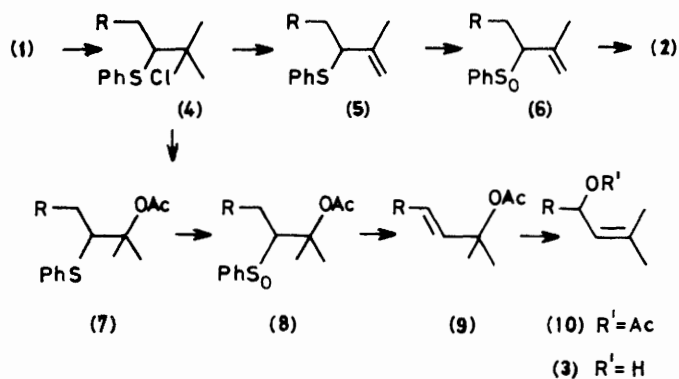
Highly chemo-, site-, regio-, and stereo-selective methods for the modification and functionalization of easily accessible isoprenoids are extremely important for the synthesis of complicated and physiologically significant terpenoids because the whole carbon framework of the starting isoprenoid, including the geometry and the stereochemistry, is effectively incorporated into the target molecule.<sup>1</sup> Of the possible functionalizations of acyclic isoprenoids, terminal [to give (**2**)] and internal [to give (**3**)] allylic oxidation of the isopropylidene terminus of the isoprenoids (**1**) with regio- and stereo-chemical control are potential methods for the synthesis of various types of compound: these include biologically important oxygenated terpenes such as ipsdienol (**3c**) (an active component of the pheromone of *Ips confusus*),<sup>2</sup> dehydrojuvabione (a compound with juvenile hormone activity),<sup>3</sup> and sirenin (a sex attractant pheromone of the water mould *Allomyces*);<sup>4</sup> perfume materials such as nuciferal (**11**),<sup>5</sup> *ar*-turmerone (**12**),<sup>6</sup> neotorreyol (**2e**),<sup>5a</sup> and torreyol (**13**);<sup>5a</sup> miscellaneous naturally occurring oxygenated sesquiterpenes such as 6-hydroxydendrolasin (**3e**),<sup>7</sup> 6-oxodendrolasin (**14**),<sup>7</sup> and 9-oxygenated farnesols (metabolites from HgCl<sub>2</sub>-treated sweet potatoes);<sup>7</sup> and the linear diterpenes isolated from marine sponge<sup>8</sup> and the polyisoprenols<sup>9</sup> which are important building blocks for various physiologically active polyisoprenoid-quinones.<sup>10</sup> Although the direct stereo- and regio-specific oxygenation of the isopropylidene terminus of the isoprenoids (**1**), giving the terminal *trans*-allylic alcohols (**2**), has been carried out with SeO<sub>2</sub> stoichiometrically or catalytically on a laboratory scale,<sup>1c</sup> to our knowledge no generally applicable and large-scale direct or sequential method for the regioselective oxygenation of the internal allylic position [to give (**3**)] of *gem*-dimethyl olefins has been reported.†

We have investigated a novel method of terminal functionalization of isoprenoids utilizing benzenesulphenyl chloride addition.<sup>11</sup> Here we report facile, regio-, and stereo-specific, terminal *trans*-allylic and internal allylic oxidations, which proceed via the same intermediate adduct between benzenesulphenyl chloride and the terpenoids (**1**) containing the isopropylidene terminus. By this method, the allylic oxygenated terpenes ( $\pm$ )-nuciferal (**11**), ( $\pm$ )-*ar*-turmerone (**12**), ( $\pm$ )-ipsdienol (**3c**), and the oxygenated dendrolasins neotorreyol (**2e**), ( $\pm$ )-(**3e**), and (**14**) were synthesized from the readily available isoprenoid starting materials ( $\pm$ )- $\alpha$ -curcumene (**1a**), myrcene (**1c**), and 1-*p*-tosylidendrolasin (**1d**). The overall



sequence displayed in the Scheme involves (i) quantitative and site-specific addition of benzenesulphenyl chloride to the isopropylidene terminus of the terpenoids (**1**); (ii) stereospecific formation of the terminal *trans*-allylic alcohols (**2**) via the terminal methallylic sulphides (**5**), prepared by regioselective dehydrochlorination of the adducts (**4**), followed by oxidation of sulphur and rearrangement; (iii) internal allylic oxygenation affording (**3**) via regioselective acetoxylation of the adducts (**4**) leading to (**7**) followed by oxidation of sulphur, thermal double bond formation to give (**9**), and finally allylic rearrangement providing the internal allylic acetates (**10**).

† In the racemic synthesis of ipsdienol (**3c**), Mori oxidized the internal allylic position of myrcene (**1c**) by a method utilizing consecutive reactions. His synthesis, however, suffered from serious limitations on the large-scale owing to the use of stoichiometric quantities of expensive and poisonous organoselenium compounds, and also because of the poor regioselectivity in the allylic oxygen transposition step (ref. 2c).



## Results and Discussion

The regio- and stereo-specific transformation of ( $\pm$ )- $\alpha$ -curcumene (**1a**) into the terminal *trans*-allylic alcohol (**2a**) and the internal allylic alcohol (**3a**) is representative of the method. The starting material, ( $\pm$ )- $\alpha$ -curcumene (**1a**), was prepared from *p*-bromotoluene and 2-methylhept-2-en-6-one according to the literature.<sup>12a</sup> Dropwise addition of benzenesulphenyl chloride (1 equiv.) into a solution of compound (**1a**) in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$  gave, instantaneously and quantitatively with discharge of the orange colour of the benzenesulphenyl chloride, a regioisomeric mixture of the adducts (**4a**);<sup>11</sup> this, without purification, was warmed at  $60^\circ\text{C}$  for 20 h in dimethylformamide (DMF) with excess of triethylamine ( $\text{Et}_3\text{N}$ ) to give the terminal methallylic sulphide (**5a**) in 76% overall yield from (**1a**). In the  $^1\text{H}$  n.m.r. spectrum the characteristic signal of the allylic methyne proton attached to the carbon bearing sulphur, as a broad triplet at  $\delta$  3.43, and two broad singlets at  $\delta$  4.50 and 4.62, assignable to terminal methylene protons, confirmed the structure (**5a**). The terminal *trans*-allylic alcohol (**2a**) was obtained in 80% overall yield from (**5a**) by the method of Evans:<sup>13</sup> oxidation of (**5a**) with 30%  $\text{H}_2\text{O}_2$  (1.2 equiv.) in acetic acid (AcOH) at  $20^\circ\text{C}$  for 20 h and then rearrangement of the resultant sulfoxide (**6a**) with trimethyl phosphite in MeOH at  $20^\circ\text{C}$  for 2 days. The structure of the alcohol (**2a**) was verified by spectral analysis: i.r.,  $\nu_{\text{max}}$  3 560  $\text{cm}^{-1}$  (OH), and  $^1\text{H}$  n.m.r.,  $\delta$  3.82 (2 H, s, allylic protons adjacent to OH) and 5.26 (1 H, br t, olefinic proton). The *trans*-stereochemistry of the alcohol (**2a**) was confirmed by the agreement of its  $^1\text{H}$  n.m.r. data with those of the authentic compound, ( $\pm$ )-(*E*)-nuciferol,<sup>14</sup> and by its derivatization to ( $\pm$ )-nuciferal (**11**) in 76% yield by oxidation with active  $\text{MnO}_2$ .<sup>\*</sup> The spectral properties of the racemic nuciferal (**11**) obtained were identical with those reported;<sup>5</sup> there was no signal assignable to the *cis*- $\alpha,\beta$ -unsaturated  $\alpha$ -methyl aldehyde (which would appear at  $\delta$  9.95–10.20 $\dagger$ ) and instead a sharp one-proton singlet at  $\delta$  9.27 was observed in the  $^1\text{H}$  n.m.r. spectrum.

Alternatively, treatment of the adduct (**4a**) with NaOAc in AcOH at  $20^\circ\text{C}$  for 1 h led to the regiospecific formation of the tertiary acetoxy sulphide (**7a**) in excellent (94%) overall yield from the starting olefin (**1a**). The  $^1\text{H}$  n.m.r. spectrum of the acetoxy sulphide (**7a**) showed it to be a diastereoisomeric mixture: it showed two doublets due to a methyl group attached to the benzylic carbon ( $\delta$  1.14 and 1.20, intensity *ca.* 1:1) and

two acetoxy singlets ( $\delta$  1.61 and 1.66, *ca.* 1:1) as well as two signals due to a diastereoisotopic methyl adjacent to the acetoxy group ( $\delta$  1.33 and 1.43). Compound (**7a**) was converted into the *trans*-allylic acetate (**9a**) in 84% yield by oxidation with 30%  $\text{H}_2\text{O}_2$  in AcOH followed by thermal elimination of sulphenic acid<sup>15</sup> from the intermediary sulphoxide (**8a**) in toluene under reflux in the presence of  $\text{NaHCO}_3$ . The acetate (**9a**) showed a clear homogeneous  $^1\text{H}$  n.m.r. spectrum confirming the proposed structure: a doublet at  $\delta$  1.19 assignable to the benzylic methyl, a six-proton singlet at  $\delta$  1.40, a three-proton singlet at  $\delta$  1.86 due to the  $\text{Me}_2\text{C}(\text{OAc})$  system, and one-proton triplets at  $\delta$  5.34 (*J* 15.5, 6.0 Hz), and a one-proton doublet at  $\delta$  5.69 (*J* 15.5 Hz) due to the *trans*-olefinic protons.

Allylic rearrangement<sup>16</sup> of compound (**9a**) to the internal allylic acetate (**10a**) was achieved in excellent yield (85%); the starting allylic acetate (**9a**) was completely removed by treatment with a catalytic amount of toluene-*p*-sulphonic acid in  $\text{AcOH-Et}_2\text{O}$  (1:1) at  $0^\circ\text{C}$  for 1 h. Although the rearranged acetate (**10a**) showed two acetoxy singlets at  $\delta$  1.35 and 1.41 because it is a diastereoisomeric mixture, an olefinic proton doublet at  $\delta$  4.80–5.10 and a one-proton multiplet at  $\delta$  5.10–5.40, assignable to the system  $\text{CH}_2\text{CH}(\text{OAc})\text{CH}=\text{C}$ , indicated structure (**10a**). Alkaline hydrolysis of compound (**10a**) gave the internal allylic alcohol (**3a**) in 83% yield. Racemic *ar*-turmeron ( $\pm$ )-(**12**) was obtained in 88% yield by the oxidation of (**10a**) with active  $\text{MnO}_2$ , and was spectroscopically identical with the authentic compound.<sup>6b</sup>

The versatility of the method was demonstrated with other terpenoids containing additional unsaturated system(s), *e.g.* the trisubstituted double bond in benzyl geranyl ether (**1b**), the 1,3-conjugated diene system in myrcene (**1c**), and the furan skeleton in the dendrolasin derivatives (**1d**) as well as the isopropylidene terminus. The results are summarized in Table 1. Thus, myrcene (**1c**) was converted in 47% overall yield into the terminal *trans*-allylic alcohol (**2c**), which is the key intermediate for the synthesis of  $\beta$ -sinensal,<sup>17</sup> a fragrant compound from Chinese orange oil which has juvenile hormone activities, and also into ( $\pm$ )-ipsdienol (**3c**)<sup>2b</sup> in 25% overall yield from (**1c**).

It should be noted that instead of dendrolasin (**1e**) itself, a synthetic intermediate (**1d**), prepared by C–C coupling<sup>18</sup> between *p*-tolyl 3-furfuryl sulphone and geranyl bromide, was used for the allylic oxidation leading to the oxygenated dendrolasin derivatives (**2e**) and (**3e**) because the bulky

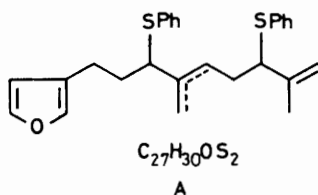
\* It is well known that the oxidation of allylic alcohols with active  $\text{MnO}_2$  generally gives  $\alpha,\beta$ -unsaturated aldehydes or ketones without *cis-trans* isomerization of the double bond (A. J. Fatiadi, *Synthesis*, 1976, 65).

$\dagger$  For the  $^1\text{H}$  n.m.r. spectra of various  $\beta$ -substituted  $\alpha$ -methyl acroleins see: ref. 5b and refs. cited therein; A. F. Thomas, *Chem. Commun.*, 1968, 1657; K. C. Chan, R. A. Jewell, W. H. Nutting, and H. Rapoport, *J. Org. Chem.*, 1968, 33, 3382 and refs. cited therein; D. J. Faulkner, *Synthesis*, 1971, 175.

**Table 1.** Transformation of the terpenoids (1) into the terminal *trans*-allylic and internal allylic alcohols (2) and (3)

Terpenoid	Product (% Yield)					
	(5a) (76)	(2a) (80)	(7a) (94)	(9a) (84)	(10a) (85)	(3a) (83)
(1a)	(5a) (76)	(2a) (80)	(7a) (94)	(9a) (84)	(10a) (85)	(3a) (83)
(1b)	(5b) (88)	(2b) (87)	(7b) (75)	(9b) (89)	(10b) (80)	(3b) (77)
(1c)	(5c) (68)	(2c) (69)	(7c) (65)	(9c) (68)	(10c) (68)	(3c) (83)
(1d)	(5d) (89)	(2d) (75)	(7d) (78)	(9d) (77)	(10d) (78)	(3d) (95)

sulphonyl group was expected to block the internal trisubstituted olefinic site in (1d) against electrophilic attack by benzenesulphenyl chloride and to thus enhance the terminal olefinic site-selectivity of the addition reaction, as observed in the preliminary experiment.<sup>11b</sup> Thus, the olefin (1d) reacted with benzenesulphenyl chloride (1 equiv.) exclusively at the isopropylidene terminus and provided the allylic sulphide (5d) (89%) and the acetoxy sulphide (7d) (78%). The results contrast markedly with those from the sulphenylation of dendrolasin (1e) via the addition of an equimolar amount of benzenesulphenyl chloride, which gave a poor yield (32%) of the desired allylic sulphide (5e) and a greater amount (27%) of the undesirable bis(allylic) sulphide (structure A) (which arises



from the bis-adduct with benzenesulphenyl chloride). Reductive desulphonylation of the terminal *trans*-allylic alcohol (2d) with Na and EtOH in THF according to the method of Tsuchihashi,<sup>19</sup> and of the internal allylic alcohol (3d) with Li in liquid NH<sub>3</sub> at -78 °C afforded the oxygenated dendrolasins neotorreyol (2e) (66%) and (±)-6-hydroxydendrolasin (3e) (70%), respectively. Oxidation of the alcohol (2e) with active MnO<sub>2</sub> was reported by Kondo *et al.*<sup>1a</sup> to give torreyol (13). The alcohol (3e) was oxidized with pyridinium chlorochromate<sup>20</sup> to give 6-oxodendrolasin (14) (67%). The oxygenated dendrolasins [(2e), (3e), (14)] obtained were found to be identical with the natural products<sup>5,7</sup> on comparison of the spectra (i.r. and <sup>1</sup>H n.m.r.).

We believe that the novel method for allylic oxidations described here can be generally applied to a variety of *gem*-dimethyl olefins. Although several reaction steps are necessary for the requisite transformation, specific oxidation of a terminal or of an internal allylic position can be carried out *via* adducts between *gem*-dimethyl olefins and benzenesulphenyl chloride. The method is suitable for large-scale production of oxygenated terpenes because benzenesulphenyl chloride is readily available and the organosulphur compounds used are not as poisonous as the organoselenium compounds hitherto widely employed.

## Experimental

**General.**—I.r. spectra were recorded on a Jasco IRA-1 spectrometer, usually as CHCl<sub>3</sub> solutions. <sup>1</sup>H N.m.r. spectra were obtained in CCl<sub>4</sub> solutions with a Hitachi R-20B (60 MHz) spectrometer. Chemical shifts are reported in δ (p.p.m.)

relative to SiMe<sub>4</sub> and coupling constants (*J*) in Hz. Mass spectra were obtained on a JMS-D300 instrument at an ionizing potential of 70 eV. Column chromatography was accomplished on Wakogel C-200 (100–200 mesh) silica gel and was eluted with hexane–Et<sub>2</sub>O. Thin layer chromatography was performed on Wakogel B-5F silica gel by developing with hexane–Et<sub>2</sub>O. The solvents were distilled before use, as follows: dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) over P<sub>2</sub>O<sub>5</sub>; dimethylformamide (DMF), hexamethylphosphoric triamide (HMPA), and toluene over calcium hydride; diethyl ether (Et<sub>2</sub>O) over lithium aluminium hydride; tetrahydrofuran (THF) over sodium diphenylketyl; and methanol (MeOH) and ethanol (EtOH) with Na. The usual reaction work-up was as follows unless otherwise noted: extraction with Et<sub>2</sub>O, washing with 5% NaHCO<sub>3</sub>, if necessary, and with water or brine, drying (MgSO<sub>4</sub>), evaporation of the solvent under reduced pressure, and then purification of the product by column chromatography on silica gel. Satisfactory elemental analytical data were obtained for all new compounds (within ±0.3% of the theoretical values). The <sup>1</sup>H n.m.r. spectra of the compounds obtained are summarized in Table 2.

Benzenesulphenyl chloride (PhSCl) was prepared according to the literature,<sup>21</sup> and obtained as an orange oil, b.p. 55 °C (5 mmHg).

**Synthesis of (±)- $\alpha$ -Curcumene (1a).**—Compound (±)-(1a) was synthesized according to the literature<sup>12a</sup> except that lithium was used in place of magnesium for the C–C bond formation step between *p*-bromotoluene and 2-methylhept-2-en-6-one; it was obtained in 81% overall yield (b.p. 111–113 °C, 5 mmHg). The spectral properties (Table 2) were identical with those reported.<sup>12b</sup>

**Synthesis of 1-(3-Furyl)-4,8-dimethyl-1-*p*-tosylnona-3(E),7-diene (1-*p*-Tosyl)dendrolasin (1d).**—To a mixture of 3-furfuryl-*p*-tolyl sulphone (720 mg, 3.03 mmol), HMPA (0.6 ml), and THF (6 ml) was added dropwise Bu<sup>n</sup>Li–hexane (1.5 mol/l) (2.2 ml, 3.3 mmol) at -78 °C under argon. After being stirred for 20 min at this temperature, a solution of geranyl bromide (600 mg, 2.76 mmol) in THF (1.0 ml) was added, and the mixture was stirred for 2 h whilst gradually warming up to room temperature. The usual work-up and product isolation gave compound (1d) (740 mg, 72%) as an oil (Found: C, 70.8; H, 7.7. C<sub>22</sub>H<sub>28</sub>O<sub>3</sub>S requires C, 70.93; H, 7.58%).

**Synthesis of Dendrolasin (1e).**—To a mixture of 1-*p*-tosyl-dendrolasin (1d) (372 mg, 1.0 mmol) and EtOH (0.5 ml) in THF (7 ml) were added pieces of Na (200 mg, 8.7 mmol) at -20 °C and the mixture was stirred for 1.5 h at that temperature.<sup>19</sup> The usual work-up and product isolation gave dendrolasin (1e) (183 mg, 84%) as an oil. The spectral properties (Table 2) were identical with those reported.<sup>22</sup>

**Synthesis of 2-Methyl-3-phenylthio-6-*p*-tolylhept-1-ene (5a) from (±)- $\alpha$ -Curcumene (1a).** **General Procedure for the Transformation of *gem*-Dimethyl Olefins (1a–d) into the Terminal Methylallylic Sulphides (5a–d) via PhSCl Addition.**—

Table 2. Data for the compounds obtained

Compound	Formula ( $M^+$ )	I.r. $\nu_{\max.}(\text{cm}^{-1})$	$^1\text{H}$ N.m.r. $\delta$ (p.p.m.) ( $J$ in Hz)	Ref.
(1a)	$\text{C}_{15}\text{H}_{22}$ (202)	1 520	1.19 (3 H, d, $J$ 7.5, MeCH), 1.50, 1.65 (each 3 H, br s, $\text{Me}_2\text{C}=\text{}$ ), 2.29 (3 H, s, arom Me), 2.40—2.83 (1 H, m, arom MeCH), 5.02 (1 H, br t, $J$ 6.5, $\text{CH}=\text{}$ ), 6.96 (4 H, s, arom H)	12b
(1d)	$\text{C}_{22}\text{H}_{28}\text{O}_3\text{S}$ (372)	1 595	1.52 (3 H, s, $\text{MeC}=\text{}$ ), 1.58 (6 H, s, $\text{Me}_2\text{C}=\text{}$ ), 2.39 (3 H, s, arom Me), 3.81 (1 H, dd, $J$ 11.5, 4.0, CHTs), 4.92 (2 H, br t, $J$ 7.0, 2 $\text{CH}=\text{}$ ), 6.31, 7.00 (each 1 H, br s, 4-H and 2-H of furan), 7.28 (1 H, t, $J$ 2.0, 5-H of furan), 7.08—7.53 (4 H, $\text{A}_2\text{B}_2\text{q}$ , $J$ 8.5, $\text{SO}_2\text{C}_6\text{H}_4\text{Me}$ ).	
(1e)	$\text{C}_{15}\text{H}_{22}\text{O}$ (218)	1 560	1.58 (6 H, s, 2 $\text{MeC}=\text{}$ ), 1.67 (3 H, s, $\text{MeC}=\text{}$ ), 4.85—5.23 (2 H, br, 2 $\text{CH}=\text{}$ ), 6.17, 7.11 (each 1 H, br s, 4-H and 2-H of furan), 7.21 (1 H, t, $J$ 2.0, 5-H of furan)	22
(5a)	$\text{C}_{21}\text{H}_{26}\text{S}$ (310)	1 630 1 590 1 510	1.20 (3 H, d, $J$ 7.0, MeCH), 1.65 (3 H, br s, $\text{MeC}=\text{}$ ), 2.30 (3 H, s, arom Me), 3.43 (1 H, bt, $J$ 6.5, CHSPh), 4.50, 4.62 (each 1 H, br s, $\text{H}_2\text{C}=\text{}$ ), 6.96 (4 H, s, arom H), 7.06—7.30 (5 H, m, arom H)	
(5b)	$\text{C}_{23}\text{H}_{28}\text{OS}$ (352)	1 630 1 595	1.77, 1.59 (each 3 H, br s, 2 $\text{MeC}=\text{}$ ), 3.47 (1 H, t, $J$ 7.0, CHSPh), 3.88 (2 H, d, $J$ 7.0, $=\text{CHCH}_2\text{OCH}_2\text{Ph}$ ), 4.35 (2 H, s, $\text{OCH}_2\text{Ph}$ ), 4.50, 4.60 (each 1 H, br s, $\text{H}_2\text{C}=\text{}$ ), 5.30 (1 H, br t, $J$ 7.0, $\text{CH}=\text{}$ ), 6.97—7.28 (10 H, br, arom H)	
(5c)	$\text{C}_{16}\text{H}_{20}\text{S}$ (244)	1 635 1 595	1.79 (3 H, br s, $\text{MeC}=\text{}$ ), 3.53 (1 H, t, $J$ 7.0, CHSPh), 4.57, 4.67 (each 1 H, br s, $\text{H}_2\text{C}=\text{}$ ), 4.96 (2 H, br s, $\text{H}_2\text{C}=\text{}$ ), 4.90—5.30 (2 H, m, $\text{CH}=\text{CH}_2$ ), 6.06—6.35 (1 H, dd, $J$ 18.0, 11.0, $\text{CH}=\text{CH}_2$ ), 7.05—7.33 (5 H, br, arom H)	
(5d)	$\text{C}_{28}\text{H}_{32}\text{O}_3\text{S}_2$ (480)	1 635 1 595	1.53, 1.68 (each 3 H, s, 2 $\text{MeC}=\text{}$ ), 2.33 (3 H, s, arom Me), 3.38 (1 H, t, $J$ 8.0, CHSPh), 3.85 (1 H, dd, $J$ 11.0, 4.0, CHTs), 4.42, 4.59 (each 1 H, br s, $\text{H}_2\text{C}=\text{}$ ), 4.95 (1 H, br t, $J$ 7.0, $\text{CH}=\text{}$ ), 6.30 (1 H, br s, 4-H of furan), 6.92—7.53 (11 H, m, arom H)	
(5e)	$\text{C}_{21}\text{H}_{26}\text{OS}$ (326)	1 630 1 590	1.58, 1.77 (each 3 H, s, 2 $\text{MeC}=\text{}$ ), 3.47 (1 H, t, $J$ 6.5, CHSPh), 4.48, 4.62 (each 1 H, br s, $\text{H}_2\text{C}=\text{}$ ), 5.10 (1 H, br t, $J$ 7.0, $\text{CH}=\text{}$ ), 6.10 (1 H, br s, 4-H of furan), 7.00—7.30 (7 H, m, arom H)	
(2a)	$\text{C}_{15}\text{H}_{22}\text{O}$ (218)	3 560 1 510	1.19 (3 H, d, $J$ 7.0, MeCH), 1.51 (3 H, br s, $\text{MeC}=\text{}$ ), 2.30 (3 H, s, arom Me), 3.82 (2 H, br s, $\text{HOCH}_2\text{C}=\text{}$ ), 5.26 (1 H, br t, $J$ 7.0, $\text{CH}=\text{}$ ), 6.98 (4 H, s, arom H)	14
(2b)	$\text{C}_{17}\text{H}_{24}\text{O}_2$ (260)	3 580 1 660 1 500	1.63 (6 H, br s, 2 $\text{MeC}=\text{}$ ), 3.84 (2 H, br s, $\text{HOCH}_2\text{C}=\text{}$ ), 3.90 (2 H, d, $J$ 7.5, $=\text{CHCH}_2\text{OCH}_2\text{Ph}$ ), 4.40 (2 H, s, $\text{OCH}_2\text{Ph}$ ), 5.30 (2 H, br t, $J$ 7.5, 2 $\text{CH}=\text{}$ ), 7.23 (5 H, s, arom H)	9a
(2c)	$\text{C}_{10}\text{H}_{16}\text{O}$ (152)	3 580 1 595	1.63 (3 H, s, $\text{MeC}=\text{}$ ), 2.15—2.28 (4 H, br d, $J$ 3.5, $\text{CH}_2\text{CH}_2$ ), 3.87 (2 H, br s, $\text{HOCH}_2\text{C}=\text{}$ ), 4.94 (2 H, br s, $\text{H}_2\text{C}=\text{}$ ), 4.90—5.35 (2 H, m, $\text{CH}=\text{CH}_2$ ), 6.07—6.56 (1 H, dd, $J$ 18.0, 11.0, $\text{CH}=\text{CH}_2$ )	a
(2d)	$\text{C}_{22}\text{H}_{28}\text{O}_4\text{S}$ (388)	3 560 1 600	1.55 (6 H, s, 2 $\text{MeC}=\text{}$ ), 2.38 (3 H, s, arom Me), 3.79 (2 H, br s, $\text{HOCH}_2\text{C}=\text{}$ ), 3.80—4.00 (1 H, m, CHTs), 4.95 (1 H, br t, $J$ 8.0, $\text{CH}=\text{}$ ), 5.00—5.22 (1 H, br, $\text{CH}=\text{}$ ), 6.31, 7.03, 7.27 (each 1 H, br s, 4-H, 2-H, 5-H of furan), 7.08—7.53 (4 H, $\text{A}_2\text{B}_2\text{q}$ , $J$ 8.0, $\text{SO}_2\text{C}_6\text{H}_4\text{Me}$ )	
(2e)	$\text{C}_{15}\text{H}_{22}\text{O}_2$ (234)	3 560 1 660 1 570	1.60, 1.63 (each 3 H, s, 2 $\text{MeC}=\text{}$ ), 1.95—2.45 (8 H, m, 2 $\text{CH}_2\text{CH}_2$ ), 3.88 (2 H, s, $\text{HOCH}_2\text{C}=\text{}$ ), 5.00—5.40 (2 H, br, 2 $\text{CH}=\text{}$ ), 6.19, 7.14 (each 1 H, br s, 4-H, 2-H of furan), 7.26 (1 H, t, $J$ 2.0, 5-H of furan)	5a
(11)	$\text{C}_{15}\text{H}_{20}\text{O}$ (216)	1 675 1 635 1 510	1.25 (3 H, d, $J$ 7.0, MeCH), 1.60 (3 H, s, $\text{MeC}=\text{}$ ), 2.30 (3 H, s, arom Me), 6.30 (1 H, br t, $J$ 6.0, $\text{CH}=\text{CHO}$ ), 7.00 (4 H, s, arom H), 9.27 (1 H, s, CHO)	5
(7a)	$\text{C}_{23}\text{H}_{30}\text{O}_2\text{S}$ (370)	1 715 1 580 1 510	1.14, 1.20 (each 3 H/2, d, $J$ 7.0, MeCH), 1.33, 1.43 (each 3 H, s, $\text{Me}_2\text{COAc}$ ), 1.61, 1.66 (each 3 H/2, s, $\text{MeCO}_2$ ), 2.29 (3 H, s, arom Me), 3.60—4.00 (1 H, m, CHSPh), 6.95, 6.98 (each 4 H/2, s, arom H), 7.05—7.46 (5 H, m, arom H)	
(7b)	$\text{C}_{25}\text{H}_{32}\text{O}_3\text{S}$ (412)	1 710 1 580	1.46, 1.50 (each 3 H, s, $\text{Me}_2\text{COAc}$ ), 1.60 (3 H, br s, $\text{MeC}=\text{}$ ), 1.73 (3 H, s, $\text{MeCO}_2$ ), 3.66—3.90 (1 H, dd, $J$ 10.5, 3.0, CHSPh), 3.93 (2 H, d, $J$ 6.5, $=\text{CHCH}_2\text{OCH}_2\text{Ph}$ ), 4.41 (2 H, s, $\text{OCH}_2\text{Ph}$ ), 5.32 (1 H, t, $J$ 6.5, $=\text{CHCH}_2$ ), 7.03—7.50 (10 H, m, arom H)	
(7c)	$\text{C}_{18}\text{H}_{24}\text{O}_2\text{S}$ (304)	1 730 1 595 1 585	1.44, 1.51 (each 3 H, s, $\text{Me}_2\text{COAc}$ ), 1.76 (3 H, s, $\text{MeCO}_2$ ), 3.75—4.00 (1 H, dd, $J$ 11.0, 3.0, CHSPh), 4.96 (2 H, br s, $\text{H}_2\text{C}=\text{}$ ), 4.90—5.36 (2 H, m, $\text{CH}=\text{CH}_2$ ), 6.10—6.58 (1 H, dd, $J$ 17.5, 11.0, $\text{CH}=\text{CH}_2$ ), 7.10—7.56 (5 H, m, arom H)	
(7d)	$\text{C}_{30}\text{H}_{36}\text{O}_5\text{S}_2$ (540)	1 720 1 600 1 585	1.40, 1.45, 1.56 (each 3 H, s, $\text{Me}_2\text{COAc}$ , $\text{MeC}=\text{}$ ), 1.73, 1.80 (each 3 H/2, s, $\text{MeCO}_2$ ), 2.39 (3 H, s, arom Me), 3.20—4.00 (2 H, m, CHSPh, CHTs), 4.70—5.00 (1 H, br, $\text{CH}=\text{}$ ), 6.33 (1 H, br s, 4-H of furan), 6.95—7.55 (11 H, m, arom H)	
(9a)	$\text{C}_{17}\text{H}_{24}\text{O}_2$ (260)	1 720 1 510	1.20 (3 H, d, $J$ 7.0, MeCH), 1.40 (6 H, s, $\text{Me}_2\text{COAc}$ ), 1.85 (3 H, s, $\text{MeCO}_2$ ), 2.29 (3 H, s, arom Me), 5.28 (1 H, dt, $J$ 15.0, 6.0, $=\text{CHCH}_2$ ), 5.68 (1 H, d, $J$ 15.0, $\text{CH}=\text{CHCH}_2$ ), 6.98 (4 H, s, arom H)	

Table 2. (cont.)

Compound	Formula ( $M^+$ )	I.r. $\nu_{\max}$ (cm $^{-1}$ )	$^1\text{H}$ N.m.r. $\delta$ (p.p.m.) ( $J$ in Hz)	Ref.
(9b)	$\text{C}_{15}\text{H}_{26}\text{O}_3$ (302)	1 720	1.48 (6 H, s, $\text{Me}_2\text{COAc}$ ), 1.59 (3 H, br s, $\text{MeC}=\text{}$ ), 1.90 (3 H, s, $\text{MeCO}_2$ ), 2.70 (2 H, d, $J$ 6.0, $=\text{CHCH}_2\text{C}=\text{}$ ), 3.94 (2 H, d, $J$ 6.5, $=\text{CHCH}_2\text{OCH}_2\text{Ph}$ ), 4.40 (2 H, s, $\text{OCH}_2\text{Ph}$ ), 5.32 (1 H, br t, $J$ 6.5, $=\text{CHCH}_2\text{O}$ ), 5.43 (1 H, dt, $J$ 15.0, 6.0, $\text{CH}=\text{CHCH}_2$ ), 5.76 (1 H, d, $J$ 15.0, $\text{CH}=\text{CHCH}_2$ ), 7.23 (5 H, s, arom H)	
(9c)	$\text{C}_{12}\text{H}_{18}\text{O}_2$ (194)	1 720 1 590	1.49 (6 H, s, $\text{Me}_2\text{COAc}$ ), 1.90 (3 H, s, $\text{MeCO}_2$ ), 2.88 (2 H, d, $J$ 5.0, $=\text{CHCH}_2\text{C}=\text{}$ ), 4.98 (2 H, br s, $\text{H}_2\text{C}=\text{}$ ), 4.87—5.32 (2 H, m, $\text{CH}=\text{CH}_2$ ), 5.50 (1 H, dt, $J$ 14.5, 5.0, $\text{CH}=\text{CHCH}_2$ ), 5.80 (1 H, d, $J$ 14.5, $\text{CH}=\text{CHCH}_2$ ), 6.10—6.57 (1 H, dd, $J$ 17.0, 11.0, $\text{CH}=\text{CH}_2$ )	
(9d)	$\text{C}_{24}\text{H}_{30}\text{O}_5\text{S}$ (430)	1 720 1 600	1.38 (6 H, s, $\text{Me}_2\text{COAc}$ ), 1.53 (3 H, br s, $\text{MeC}=\text{}$ ), 1.85 (3 H, s, $\text{MeCO}_2$ ), 2.38 (3 H, s, arom Me), 2.55 (2 H, d, $J$ 6.0, $=\text{CHCH}_2\text{C}=\text{}$ ), 3.85 (1 H, dd, $J$ 11.5, 4.0, CHTs), 4.95 (1 H, br t, $J$ 7.0, $\text{CH}=\text{}$ ), 5.23 (1 H, dt, $J$ 15.5, 6.0, $\text{CH}=\text{CHCH}_2\text{C}=\text{}$ ), 5.64 (1 H, d, $J$ 15.5, $\text{CH}=\text{CHCH}_2$ ), 6.32, 7.05 (each 1 H, br s, 4-H, 2-H of furan), 7.28 (1 H, t, $J$ 2.0, 5-H of furan), 7.00—7.57 (4 H, $\text{A}_2\text{B}_2\text{q}$ , $J$ 8.0, arom H)	
(10a)	$\text{C}_{17}\text{H}_{24}\text{O}_2$ (260)	1 720 1 510	1.22 (3 H, d, $J$ 7.0, $\text{MeCH}$ ), 1.55, 1.70 (each 3 H, br s, $\text{Me}_2\text{C}=\text{}$ ), 1.85, 1.91 (each 3 H/2, s, $\text{MeCO}_2$ ), 2.30 (3 H, s, arom Me), 4.93 (1 H, br, d, $J$ 10.5, $=\text{CHCHOAc}$ ), 5.10—5.40 [1 H, m, $=\text{CHCH}(\text{OAc})\text{CH}_2$ ], 6.99 (4 H, s, arom H)	
(10b)	$\text{C}_{15}\text{H}_{26}\text{O}_3$ (302)	1 720	1.66 (3 H, br s, $\text{MeC}=\text{}$ ), 1.70, 1.73 (each 3 H, s, 2 $\text{MeC}=\text{}$ ), 1.91 (3 H, s, $\text{MeCO}_2$ ), 3.92 (2 H, d, $J$ 6.5, $=\text{CHCH}_2\text{OCH}_2\text{Ph}$ ), 4.40 (2 H, s, $\text{OCH}_2\text{Ph}$ ), 4.95—5.80 (3 H, m, 2 $\text{CH}=\text{}$ , $\text{CHOAc}$ ), 7.24 (5 H, s, arom H)	
(10c)	$\text{C}_{12}\text{H}_{18}\text{O}_2$ (194)	1 720 1 590	1.68, 1.72 (each 3 H, br s, $\text{Me}_2\text{C}=\text{}$ ), 1.95 (3 H, s, $\text{MeCO}_2$ ), 2.05—2.77 [2 H, m, $\text{CH}(\text{OAc})\text{CH}_2\text{C}=\text{}$ ], 4.99 (2 H, br s, $\text{H}_2\text{C}=\text{}$ ), 4.90—5.77 (4 H, m, $\text{CH}=\text{CH}_2$ , $=\text{CHCHOAc}$ ), 6.08—6.56 (1 H, dd, $J$ 17.5, 10.5, $\text{CH}=\text{CH}_2$ )	2c
(10d)	$\text{C}_{24}\text{H}_{30}\text{O}_5\text{S}$ (430)	1 720 1 600	1.63 (9 H, br s, $\text{Me}_2\text{C}=\text{}$ , $\text{MeC}=\text{}$ ), 1.80, 1.82 (each 3 H/2, s, $\text{MeCO}_2$ ), 2.39 (3 H, s, arom Me), 3.81 (1 H, dd, $J$ 11.5, 4.0, CHTs), 4.70—4.95 (1 H, br, $\text{CH}=\text{}$ ), 4.98 (1 H, br t, $J$ 6.0, $\text{CH}=\text{}$ ), 5.15—5.66 (1 H, m, $\text{CHOAc}$ ), 6.32, 7.00 (each 1 H, br s, 4-H, 2-H of furan), 7.28 (1 H, t, $J$ 2.0, 5-H of furan), 7.08—7.53 (4 H, $\text{A}_2\text{B}_2\text{q}$ , $J$ 8.0, arom H)	
(3a)	$\text{C}_{15}\text{H}_{22}\text{O}$ (218)	3 560 1 515	1.20 (3 H, d, $J$ 7.0, $\text{MeCH}$ ), 1.45, 1.50, 1.63, 1.69 (each 3 H/2, br s, $\text{Me}_2\text{C}=\text{}$ ), 2.30 (3 H, s, arom Me), 3.75—4.35 (1 H, m, $\text{CHOAc}$ ), 5.07 (1 H, br d, $J$ 8.5, $=\text{CHCHOAc}$ ), 6.97, 7.00 (each 4 H/2, s, arom H)	
(3b)	$\text{C}_{17}\text{H}_{24}\text{O}_2$ (260)	3 560	1.66 (9 H, br s, $\text{Me}_2\text{C}=\text{}$ , $\text{MeC}=\text{}$ ), 3.93 (2 H, d, $J$ 6.0, $=\text{CHCH}_2\text{OCH}_2\text{Ph}$ ), 4.42 (2 H, s, $\text{OCH}_2\text{Ph}$ ), 4.10—4.65 (1 H, m, $=\text{CHCHOH}$ ), 5.10 (1 H, br d, $J$ 8.5, $=\text{CHCHOH}$ ), 5.38 (2 H, br t, $J$ 6.5, 2 $\text{CH}=\text{}$ ), 7.24 (5 H, s, arom H)	
(3c)	$\text{C}_{10}\text{H}_{16}\text{O}$ (152)	3 560 1 600	1.66, 1.71 (each 3 H, br s, $\text{Me}_2\text{C}=\text{}$ ), 2.31 (2 H, d, $J$ 6.5, $=\text{CCH}_2\text{CHOH}$ ), 4.34 [1 H, dt, $J$ 8.5, 6.5, $=\text{CHCH}(\text{OH})\text{CH}_2\text{C}=\text{}$ ], 5.03 (2 H, br s, $\text{H}_2\text{C}=\text{}$ ), 4.90—5.37 (3 H, m, $\text{CH}=\text{CH}_2$ , $=\text{CHCHOH}$ ), 6.08—6.57 (1 H, dd, $J$ 18.0, 10.0, $\text{CH}=\text{CH}_2$ )	2c
(3d)	$\text{C}_{22}\text{H}_{28}\text{O}_4\text{S}$ (388)	3 470 1 600	1.65 (9 H, br s, $\text{Me}_2\text{C}=\text{}$ ), 2.00 (2 H, d, $J$ 6.0, $=\text{CCH}_2\text{CHOH}$ ), 2.39 (3 H, s, arom Me), 2.50—3.20 (2 H, m, $=\text{CHCH}_2\text{CHT}$ s), 3.70—4.50 (2 H, m, $\text{CHOH}$ , CHTs), 5.02 [1 H, br d, $J$ 7.0, $\text{CH}(\text{OH})\text{CH}=\text{}$ ], 4.90—5.20 (1 H, br, $=\text{CHCH}_2$ ), 6.33, 7.03, 7.28 (each 1 H, br s, 4-H, 2-H, 5-H of furan), 7.07—7.54 (4 H, $\text{A}_2\text{B}_2\text{q}$ , $J$ 8.5, arom H)	
(3e) <sup>b</sup>	$\text{C}_{15}\text{H}_{22}\text{O}_2$ (234)	3 450 1 500	1.65, 1.69, 1.71 (each 3 H, $\text{Me}_2\text{C}=\text{}$ , $\text{MeC}=\text{}$ ), 2.15 (2 H, d, $J$ 6.5, $=\text{CCH}_2\text{CHOH}$ ), 2.20—2.60 (4 H, br, furyl- $\text{CH}_2\text{CH}_2$ ), 4.40 [1 H, dt, $J$ 8.5, 6.5, $\text{CH}_2\text{CH}(\text{OH})\text{CH}=\text{}$ ], 5.15 [1 H, br d, $J$ 8.5, $\text{CH}(\text{OH})\text{CH}=\text{}$ ], 5.25 (1 H, br t, $J$ 7.5, $\text{CH}_2\text{CH}=\text{}$ ), 6.28, 7.21 (each 1 H, br s, 4-H, 2-H of furan), 7.33 (1 H, t, $J$ 2.0, 5-H of furan)	7
(12)	$\text{C}_{15}\text{H}_{20}\text{O}$ (216)	1 680 1 620 1 510	1.20 (3 H, d, $J$ 7.0, $\text{MeCH}$ ), 1.81, 2.07 (each 3 H, d, $J$ 1.5, $\text{Me}_2\text{C}=\text{}$ ), 2.29 (3 H, s, arom Me), 2.43—2.59 [2 H, m, $\text{C}(\text{O})\text{CH}_2\text{CH}$ ], 3.05—3.40 [1 H, m, $\text{CH}_2\text{CH}(\text{Me})\text{ToI}$ ], 5.90 (1 H, br s, $=\text{CHCO}$ ), 7.00 (4 H, s, arom H)	6b
(14) <sup>b</sup>	$\text{C}_{15}\text{H}_{20}\text{O}_2$ (232)	1 680 1 620	1.62, 1.88, 2.17 (each 3 H, br s, $\text{Me}_2\text{C}=\text{}$ , $\text{MeC}=\text{}$ ), 2.20—2.55 (4 H, br, furyl- $\text{CH}_2\text{CH}_2$ ), 3.04 (2 H, br s, $=\text{CCH}_2\text{CO}$ ), 5.18—5.45 (1 H, br, $\text{CH}_2\text{CH}=\text{}$ ), 6.10 [1 H, br s, $\text{C}(\text{O})\text{CH}=\text{}$ ], 6.30, 7.25 (each 1 H, br s, 4-H, 2-H of furan), 7.35 (1 H, t, $J$ 2.0, 5-H of furan)	7

<sup>a</sup>G. Büchi and H. Wüest, *Helv. Chim. Acta*, 1967, **50**, 2440. <sup>b</sup> $^1\text{H}$  N.m.r. spectrum obtained in  $\text{CDCl}_3$  solution.

To a solution of ( $\pm$ )- $\alpha$ -curcumene (**1a**) (202 mg, 1.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (2.0 ml) was added dropwise a solution of  $\text{PhSCl}$  (145 mg, 1.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 ml) during 5 min at  $0^\circ\text{C}$ . After being stirred for 10 min the mixture was concentrated under reduced pressure to give the crude adduct (**4a**) (340 mg) as an

oil, which was warmed directly in DMF (5 ml) with triethylamine (1.0 ml) at  $60^\circ\text{C}$  for 20 h. The usual work-up and product isolation gave the allylic sulphide (**5a**) (236 mg, 76%) as an oil (Found: C, 81.4; H, 8.3.  $\text{C}_{21}\text{H}_{26}\text{S}$  requires C, 81.25; H, 8.44%). For spectral properties, see Table 2.

**Synthesis of 9-(3-Furyl)-2,6-dimethyl-3-phenylthionona-1,6(E)-diene (5e).**—Dendrolasin (**1e**) (218 mg, 1.0 mmol) was treated with PhSCl (145 mg, 1.0 mmol) in the same way and the crude adduct was warmed in DMF with triethylamine at 60 °C for 20 h. The product was chromatographed to give three fractions: fraction 1 was recovered starting material (**1e**) (41 mg, 19%); fraction 2 gave the desired sulphide (**5e**) (104 mg, 32%) as an oil (Found: C, 77.35; H, 8.2. C<sub>21</sub>H<sub>26</sub>OS requires C, 77.27; H, 8.03%); the spectral properties are listed in Table 2; fraction 3 (117 mg, 27%), the mass, *M*<sup>+</sup> 434, the <sup>1</sup>H n.m.r. spectrum, δ 1.60–1.80 (m, CH<sub>3</sub>C=), 3.20–3.70 [m, CH(SPh)C=], 4.37–5.20 (m, CH=, =CH<sub>2</sub>), 6.10 (br s, 4-H of furan), 7.00–7.30 (br, aromatic H), suggested the structure A (regioisomeric olefinic mixture) (see Discussion section).

**Synthesis of (E)-2-Methyl-6-p-tolylhept-2-en-1-ol [(±)-Nuciferol] (2a).** *General Procedure for the Preparation of the Terminal trans-Allylic Alcohols (2a–d) from the Terminal Methylallylic Sulphides (5a–d).*—To a solution of the allylic sulphide (**5a**) (310 mg, 1.0 mmol) in AcOH (4 ml) was added 30% H<sub>2</sub>O<sub>2</sub> (130 μl) at 20 °C and the mixture was stirred for 20 h at 20 °C. Work-up gave the crude sulphoxide (**6a**) (314 mg), which was stirred with trimethyl phosphite (200 mg, 1.6 mmol) in MeOH (9 ml) at 20 °C for 2 days. Concentration of the mixture under reduced pressure, followed by work-up of the residue and isolation of the product gave the terminal *trans*-allylic alcohol (**2a**) (174 mg, 80%) as an oil. The <sup>1</sup>H n.m.r. spectrum (Table 2) was in good agreement with that reported for an authentic compound.<sup>14</sup>

**Synthesis of Neotorreyol (2e).**—9-*p*-Tosylneotorreyol (**2d**) was obtained in 67% overall yield from 1-*p*-tosylidendrolasin (**1d**) by the general procedure described above. Compound (**2d**) (195 mg, 0.5 mmol) was treated with Na (120 mg, 5.2 mmol) and EtOH (0.3 ml) in THF (3.0 ml) as in the preparation of (**1e**) by the method of Tsuchihashi to give neotorreyol (**2e**) (77 mg, 66%) as an oil. The spectral properties (Table 2) were identical with those reported for the authentic compound.<sup>5a</sup>

**Synthesis of (±)-Nuciferol (11).**—(±)-(*E*)-Nuciferol (**2a**) (220 mg, 1.0 mmol) was oxidized with active MnO<sub>2</sub> (2.0 g) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) at 20 °C for 20 h to give (±)-nuciferol (**11**) (165 mg, 76%) as an oil, whose spectral properties (Table 2) were identical with those reported for the authentic compound.<sup>5</sup>

**Synthesis of 2-Acetoxy-2-methyl-3-phenylthio-6-p-tolylheptane (7a) from (±)-α-Curcumene (1a).** *General Procedure for the Transformation of the gem-Dimethyl Olefins (1a–d) into the Tertiary β-Acetoxy Sulphides (7a–d) via PhSCl Addition.*—The PhSCl-adduct (**4a**), prepared as above from (±)-α-curcumene (**1a**) (202 mg, 1.0 mmol), was stirred with AcONa (246 mg, 3.0 mmol) in AcOH (5.0 ml) at 20 °C for 1 h. The usual work-up and product isolation gave the β-acetoxy sulphide (**7a**) (348 mg, 94%) as an oil (Found: C, 74.5; H, 8.0. C<sub>23</sub>H<sub>30</sub>O<sub>2</sub>S requires C, 74.56; H, 8.16%). The spectral properties are listed in Table 2.

**Synthesis of (E)-2-Acetoxy-2-methyl-6-p-tolylhept-3-ene (9a).** *General Procedure for the Transformation of the β-Acetoxy Sulphides (7a–d) into the Tertiary Allylic Acetates (9a–d).*—The β-acetoxy sulphide (**7a**) (370 mg, 1.0 mmol) was oxidized with 30% H<sub>2</sub>O<sub>2</sub> (150 μl) in AcOH (5.0 ml) at 20 °C for 20 h, and work-up afforded the sulphoxide (**8a**) (350 mg) as an oily diastereoisomeric mixture, which was heated in toluene (10 ml) with NaHCO<sub>3</sub> (350 mg) under reflux for 1.5 h. Work-up and product isolation gave the tertiary allylic acetate (**9a**) (218 mg, 84%) as an oil (Found: C, 78.65; H, 9.2. C<sub>17</sub>H<sub>24</sub>O<sub>2</sub> requires C, 78.42; H, 9.29%). The spectral properties are listed in Table 2.

**Synthesis of 4-Acetoxy-2-methyl-6-p-tolylhept-2-ene (10a).** *General Procedure for the Allylic Rearrangement of the Tertiary Allylic Acetates (9a–d) to give the Internal Allylic Acetates (10a–d).*—The tertiary allylic acetate (**9a**) (260 mg, 1.0 mmol) was stirred in Et<sub>2</sub>O–AcOH (1:1) (12 ml) with aqueous toluene-*p*-sulphonic acid (40 mg, 0.2 mmol) at 0 °C for 1 h. The reaction mixture was worked up as usual and product isolation gave the internal allylic acetate (**10a**) (220 mg, 85%) as an oil (Found: C, 78.65; H, 9.25. C<sub>17</sub>H<sub>24</sub>O<sub>2</sub> requires C, 78.42; H, 9.29%). The spectral properties are listed in Table 2.

**Synthesis of 4-Hydroxy-2-methyl-6-p-tolylhept-2-ene (3a).** *General Procedure for the Alkaline Hydrolysis of the Internal Allylic Acetates (10–d) to give the Internal Allylic Alcohols (3a–d).*—The internal allylic acetate (**10a**) (260 mg, 1.0 mmol) was stirred in EtOH–10% aqueous KOH (2:1) (16 ml) at 20 °C for 3 h. Work-up of the mixture and product isolation gave the internal allylic alcohol (**3a**) (180 mg, 83%) as an oil (Found: C, 82.7; H, 10.1. C<sub>15</sub>H<sub>22</sub>O requires C, 82.51; H, 10.16%). The spectral properties are listed in Table 2.

**Synthesis of (±)-Ipsdienol (3c).**—(±)-Ipsdienol (**3c**) was synthesized in 25% overall yield from myrcene (**1c**) by the above sequence of reactions. It was obtained as an oil, b.p. 73–77 °C (5 mmHg). The spectral properties of the alcohol (**3c**) (Table 2) were identical with those of the authentic compound.<sup>2</sup>

**Synthesis of 6-Hydroxydendrolasin (3e).**—6-Hydroxy-1-*p*-tosylidendrolasin (**3d**) was prepared in 45% overall yield from 1-*p*-tosylidendrolasin (**1d**) by the above sequence of reactions. To a blue solution of Li (90 mg, 13 mmol) in liquid NH<sub>3</sub> (ca. 10 ml) was added dropwise a solution of (**3d**) (195 mg, 0.5 mmol) in THF (1.0 ml) at –78 °C under N<sub>2</sub>. After being stirred for 45 min at that temperature, the excess of Li was removed by introducing buta-1,3-diene into the reaction mixture at –78 °C. The evaporation of NH<sub>3</sub> and work-up of the residue followed by product isolation by chromatography gave 6-hydroxydendrolasin (**3e**) (82 mg, 70%) as an oil, whose spectral properties were identical with those reported for the authentic compound.<sup>7</sup>

**Synthesis of (±)-ar-Turmerone (12).**—The internal allylic alcohol (**3a**) (218 mg, 1.0 mmol) was stirred with active MnO<sub>2</sub> (2.5 g) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) at 20 °C for 15 h. The mixture was filtered and evaporation of the solvent gave pure (±)-ar-turmerone (**12**) (190 mg, 88%) as an oil, whose spectral properties were identical with those reported for the authentic compound.<sup>6</sup>

**Synthesis of 6-Oxodendrolasin (14).**—To a stirred solution of 6-hydroxydendrolasin (**3e**) (120 mg, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added a solution of pyridinium chlorochromate<sup>20</sup> (250 mg, 1.16 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (7.5 ml) at 20 °C and the mixture was stirred for 1.5 h at 20 °C. To the mixture, Et<sub>2</sub>O (50 ml) was added and the insoluble material was filtered off. Evaporation and chromatography of the filtrate gave 6-oxodendrolasin (**14**) (80 mg, 67%) as an oil, whose spectral properties were identical with those reported for the authentic compound.<sup>7</sup>

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