

## Turmerones: Isolation from Turmeric and their Structure Determination

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The presence of two turmerones in turmeric is demonstrated and their structures are defined as 2-methyl-6-(4-methylcyclohexa-2,4-dien-1-yl)hept-2-en-4-one (**5**, ' $\alpha$ -turmerone') and 2-methyl-6-(4-methylenecyclohex-2-en-1-yl)hept-2-en-4-one (**2**, ' $\beta$ -turmerone').

Turmeric, from the Rhizomes of *Curcuma longa* has been known for its colouring, flavouring, and digestive properties since at least the second millenium B.C.<sup>1</sup> It is a constituent of curry powders and contributes to their characteristic colour and odour. Nearly fifty years ago,<sup>2</sup> the major constituents of the essential oil of turmeric were recognised to be ketonic sesquiterpenes  $C_{15}H_{20}O$  and  $C_{15}H_{22}O$ . The structure of the former was shown<sup>3</sup> to be (**1**) and it was called ar-turmerone. The latter, known as turmerone, was considered to have the enone and carbon skeleton of (**1**) but the aromatic ring was partially reduced. However, it was not possible to isolate it in pure form, to locate its double bonds, or even to be sure that it was a single isomer. Later, it was reported that turmerone could be isolated *via* an inclusion compound with thiourea, and from the evidence of u.v. and i.r. spectra the structure was assigned as either (**2**) or (**3**).<sup>4</sup> Structure (**4**) has also been proposed<sup>5</sup> and is the basis for the current Chemical Abstracts name (Reg. Number 56485-42-8).

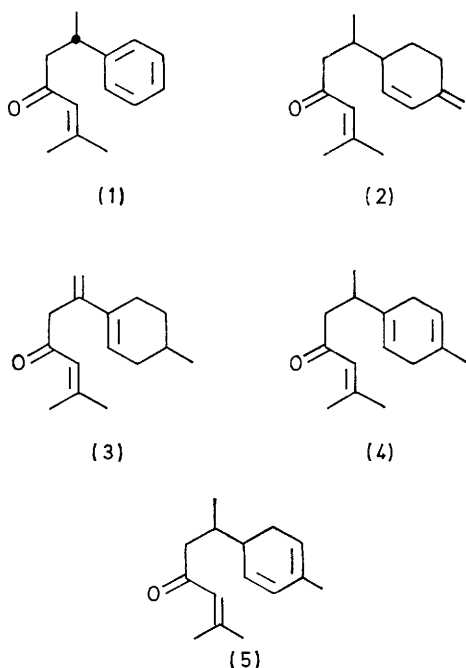
We report here the isolation and spectroscopic characterisation of two isomeric turmerones to which we assign the structures 2-methyl-6-(4-methylcyclohexa-2,4-dien-1-yl)hept-2-en-4-one (**5**) and 2-methyl-6-(4-methylenecyclohex-2-en-1-yl)

hept-2-en-4-one (**2**). We give these compounds the trivial names  $\alpha$ - and  $\beta$ -turmerone, respectively, by analogy with their lower prenylogues, the phellandrenes.

Flash chromatography<sup>6</sup> [silica gel 60, 1% triethylamine† and 5% ether in light petroleum (b.p. 40–60 °C)] of turmeric oil gave a fraction of turmerone free from ar-turmerone, which was further fractionated by h.p.l.c. (Hichrom S5W-500SP, 1% triethylamine† in hexanes). The low value for the relative retention times of the major turmerones ( $\alpha = 1.11$ ) and the presence of minor components (see below) made separation of the turmerones very difficult and recycling (8–10 times) was necessary to obtain pure  $\alpha$ - and  $\beta$ -turmerone, albeit in only milligram amounts.

The faster eluting component was shown by high resolution mass spectrometry to have the formula  $C_{15}H_{22}O$ . Bands at 1681 and 1627  $cm^{-1}$  in the i.r. spectrum and a coupled spin system in the  $^1H$  n.m.r. spectrum [ $\delta(CDCl_3)$  6.05 (1 H, septet,  $J$  1.3 Hz), 2.14 (3 H, d,  $J$  1.3 Hz), and 1.89 (3 H, d,  $J$  1.3 Hz)]

† In the absence of triethylamine, silica gel caused isomerisation and degradation of the turmerones.



show the presence of the  $\text{Me}_2\text{C}=\text{CHCOX}$  fragment where X is a saturated carbon atom. The other signals at low field [ $\delta$  5.79 (1 H, dt,  $J$  10, 2 Hz), 5.63 (1 H, dd,  $J$  10, 3 Hz), and 5.42 (1 H, broad s,  $\Sigma J$  16 Hz)] and the 3 H multiplet at  $\delta$  1.72 are very similar in their chemical shift and multiplicity to four resonances in the spectrum of  $\alpha$ -phellandrene,<sup>7</sup> and show that  $\alpha$ -turmerone has a 4-methylcyclohexa-2,4-dien-1-yl fragment. Interpretation of the remaining high field regions of the  $^1\text{H}$  n.m.r. spectrum secures structure (5). The u.v. spectrum of (5) before and after the addition of sodium borohydride and the difference spectrum gave  $\lambda_{\text{max}}$  (enone) 238 nm and  $\lambda_{\text{max}}$  (diene) 261 nm, which compare well with data for mesityl oxide ( $\lambda_{\text{max}}$  237 nm) and  $\alpha$ -phellandrene ( $\lambda_{\text{max}}$  263 nm).

For the slower eluting component, mass spectrometry con-

firmed the molecular formula  $\text{C}_{15}\text{H}_{22}\text{O}$ , and the fragment  $\text{Me}_2\text{C}=\text{CHCOX}$  was indicated by i.r. bands at 1681 and  $1626\text{ cm}^{-1}$  and the coupled  $^1\text{H}$  spin system [ $\delta(\text{C}_6\text{D}_6)$  5.83 (1 H, septet,  $J$  1.2 Hz), 2.16 (3 H, d,  $J$  1.2 Hz), and 1.51 (3 H, d,  $J$  1.2 Hz)]. The remaining four low field signals [ $\delta$  6.24 (1 H, dd,  $J$  10, 2 Hz), 5.61 (1 H, d,  $J$  10 Hz), 4.87 (1 H, s), and 4.82 (1 H, s)] define the nature of the 6-membered ring as in (2). A similar u.v. study to that described for (5) gave  $\lambda_{\text{max}}$  (enone) 237 nm and  $\lambda_{\text{max}}$  (diene) 232 nm [*cf.* mesityl oxide ( $\lambda_{\text{max}}$  237) and  $\beta$ -phellandrene ( $\lambda_{\text{max}}$  232 nm)] and an i.r. band at  $881\text{ cm}^{-1}$  confirmed the exo-methylene group of (2). The question of the configurations at the chiral centres in (2) and (5) is currently under study.

Careful comparison of the low field regions of the  $^1\text{H}$  n.m.r. spectra of crude turmeric oil, the turmerone fraction from flash chromatography, and the isolated  $\alpha$ -,  $\alpha$ -, and  $\beta$ -turmerones showed that these three compounds are not artefacts, but are, indeed, the major components of the crude oil, and that other minor components are present in the turmerone fraction from flash chromatography. G.l.c.-mass spectroscopic analysis of that fraction showed a single peak in the mass chromatogram for  $m/z$  216 ( $\alpha$ -turmerone), whereas for  $m/z$  218 there were two major, one minor, and other trace peaks.

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