

## Synthesis of 2,3-Dimethoxy-*p*-cymene

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A simple and straightforward synthesis of the title compound (1) is described starting from menthone (2). The synthetic 2,3-dimethoxy-*p*-cymene (1) is not identical with the natural product reported by Zutshi and Bokadia [*Indian J Chem*, 14B (1976) 711].

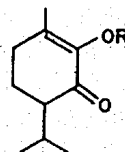
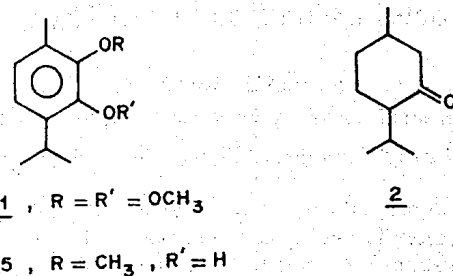
Although the natural occurrence of 2,5-dihydroxy-*p*-cymene and the corresponding mono and dimethyl ethers in several essential oils is well known<sup>1-5</sup>, there is a solitary reference on the isolation of 2,3-dimethoxy-*p*-cymene (1) from the essential oil of *Lagdera aurita*<sup>6</sup> (Schultz). Because of its rare occurrence it was thought desirable to confirm structure (1) by synthesis. We report herein the synthesis of title compound starting from menthone (2).

The diosphenol (3) obtained upon refluxing menthone (2) with hydrated ferric chloride in acetic acid was methylated to the corresponding methyl ether (4) with dimethyl sulphate in acetone under anhydrous conditions. Selenium dehydrogenation of (4) at 300°C for 2 hr afforded 2-methoxythymol (5) which without purification was subjected to methylation to yield 1.

Compound (1) analysed for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub> and displayed characteristic IR bands at 1570, 1600 and 810 cm<sup>-1</sup> (1,2,3,4-tetrasubstituted aromatic ring); and 1020, 1270 cm<sup>-1</sup> (aromatic-OCH<sub>3</sub>). Its PMR spectrum in CDCl<sub>3</sub> exhibited signals at δ 1.12 [*d*, 6H, *J* = 6.6 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>], 2.09 (*s*, 3H, Ar-CH<sub>3</sub>), 3.03 (*m*, 1H, Ar-CH(CH<sub>3</sub>)<sub>2</sub>), 3.57 and 3.6 (*s* each, 3H, Ar-OCH<sub>3</sub>) and 6.45 (*s*, 2H, Ar-H). The PMR data broadly tallied with those reported for 2,3-dihydroxy-*p*-cymene<sup>7</sup>, except for the signals at δ 3.57 and 3.60 for the two -OCH<sub>3</sub> groups instead of a singlet at δ 5.28 which was assigned to -OH protons. The chemical shifts of synthetic 2,3-dimethoxy-*p*-cymene did not agree with those reported for the natural product<sup>6</sup> and hence assignment of 2,3-dimethoxy-*p*-cymene structure by Zutshi and Bokadia<sup>6</sup> calls for a fresh look.

### Diosphenol (3)

Menthone (2) (10 g) was refluxed with hydrated



3, R = H  
4, R = CH<sub>3</sub>

FeCl<sub>3</sub> for 1.5 hr in 50% CH<sub>3</sub>COOH (100 ml), extracted with ether, the ether extract washed with H<sub>2</sub>O, aq NaHCO<sub>3</sub>, water, dried and concentrated. On cooling it, crystals of 3 separated out which were washed with cold petroleum ether and finally purified by sublimation, m.p. 81-82°, yield 0.75 g; IR: ν 3460 (-OH), 1675, 1640 and 940 (enolized 1,2-diketone), 1390 and 1368 cm<sup>-1</sup> [-CH(CH<sub>3</sub>)<sub>2</sub>].

### Diosphenol methyl ether (4)

A solution of 3 (0.75 g) in dry acetone (25 ml) containing anhydrous K<sub>2</sub>CO<sub>3</sub> (4 g) and (CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub> was refluxed for 24 hr, filtered, the filtrate taken in ether, washed with H<sub>2</sub>O, dried and concentrated. The crude product (4) was purified by using petroleum ether for chromatography, yield (0.516 g), b.p. 231°; IR: 1020, 1200 cm<sup>-1</sup> (-OCH<sub>3</sub>) and 1665 cm<sup>-1</sup> (conjugated)C=O.

### 2,3-Dimethoxy-*p*-cymene (1)

Methyl ether (4, 2.3 g) was dehydrogenated with selenium (4 g) at 300°C for 2 hr. The reaction product was extracted with ether and concentrated. The crude product (1.896 g) containing the unreacted methyl ether was methylated with (CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub> under anhydrous conditions to yield crude 1 (0.108 g) which was purified by chromatography over silica gel and elution with petroleum ether; IR: 1570, 1600, 810, 1020 and 1270 cm<sup>-1</sup>; PMR: δ 1.12 (*d*, 6H, *J* = 6.6 Hz), 2.09 (*s*, 3H); 3.03 (*m*, 1H); 3.57 (*s*, 3H); 3.6 (*s*, 3H) and 6.45 (*s*, 2H).

## NOTES

We thank Dr Aravind Geda for the spectral data of natural compound.

### References

- 1 Rechler, *Bull Soc chim Fr*, 7 (1892) 35.
- 2 Malavya B K & Dutt S, *Proc Indian Acad Sci*, 16A (1942) 157; *Chem Abstr*, 37 (1943) 1010.
- 3 Park R J & Sutherland M D, *Aust J Chem*, 22 (1969) 495.
- 4 Lasswell (Jr) W L & Hufford C D, *Phytochemistry*, 16 (1977) 1439.
- 5 Bohlman F, Fritz U, King M R & Robinson H, *Phytochemistry*, 20 (1981) 743.
- 6 Zutshi S K & Bokadia M M, *Indian J Chem*, 14B (1976) 711.
- 7 Gray R T & Smith H E, *Tetrahedron*, 23 (1967) 4229.