

Anisoxide: an Artefact from Star Anise Oil formed by Claisen Rearrangement

By H. M. OKELY and M. F. GRUNDON*

(School of Physical Sciences, The New University of Ulster, Coleraine, Northern Ireland)

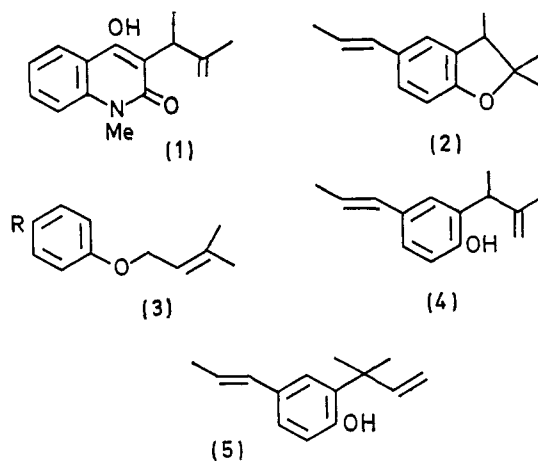
Summary The 1,2-dimethylallyl derivative, anisoxide, is not present in star anise oil or in the seeds of *Illicium verum*; its synthesis from a 3,3-dimethylallyl ether present in the oil suggests that it was obtained earlier as a result of the isolation procedure.

As a result of an interest in 1,1- and 1,2-dimethylallyl compounds and our demonstration¹ that the biosynthesis of the alkaloid ravenoline (1) involves an abnormal Claisen rearrangement of an *O*-3,3-dimethylallyl ether, we have re-investigated the occurrence of anisoxide (2) in star anise oil (obtained from the seeds of *Illicium verum*).

Anisoxide was first isolated by Jackson and Short² and its structure was established by Barton and his co-workers³ by means of degradative work and of synthesis. The compound is reported to be optically inactive and it may, therefore, be an artefact of the isolation procedure. Alternatively, the drastic conditions employed in purification (distillation from sodium-potassium alloy) may have resulted in racemisation. We sought to resolve this question.

After removal of anethole from the commercial oil, the ether fraction was examined by chromatography on silica

and by preparative gas chromatography. The major constituent was the *O*-3,3-dimethylallyl ether (3; R =



-CH=CHMe) and a small yield of the isomer (3; R =

$-\text{CH}_2\cdot\text{CH}=\text{CH}_2$) was also obtained. Mixed injection of fractions with authentic anisoxide showed that the cyclic ether was not present. Similar results were obtained with the oil derived from the seeds of *Illicium verum* by extraction with light petroleum.

We then investigated the rearrangement of the *O*-3,3-dimethylallyl derivative (3; R = $-\text{CH}=\text{CHMe}$). The ether, prepared from anethole,⁴ was heated at 185° in dimethylformamide and gave a mixture of the 'abnormal' Claisen compound (4) and its cyclisation product, anisoxide (2). Rearrangement at 153° in the same solvent furnished the Claisen rearrangement product (5) which was slowly

converted into the 'abnormal' phenol (4). These observations accord with the accepted mechanism of the abnormal reaction⁵ and correspond to our experience of rearrangement in the quinoline series.⁶ Heating star anise oil enriched with the ether (3; R = $-\text{CH}=\text{CHMe}$) at 180° also gave anisoxide. We conclude that the isolation of anisoxide by Jackson and Short² was due to the prolonged distillation procedure employed, resulting in rearrangement of the dimethylallyl ether present in star anise oil.

(Received, July 27th, 1971; Com. 1306.)

¹ T. R. Chamberlain, J. F. Collins, and M. F. Grundon, *Chem. Comm.*, 1969, 1269.

² R. W. Jackson and W. F. Short, *J. Chem. Soc.*, 1937, 513.

³ D. H. R. Barton, A. Bhati, P. de Mayo, and G. A. Morrison, *J. Chem. Soc.*, 1958, 4393.

⁴ Cf. E. Spath and J. Bruck, *Ber.*, 1938, 71, 2711; E. Spath, *Monatsh.*, 1914, 35, 326.

⁵ E. N. Marvell, D. R. Anderson, and J. Ong, *J. Org. Chem.*, 1962, 27, 1109; A. von Habich, R. Barner, R. M. Roberts, and H. Schmid, *Helv. Chem. Acta*, 1962, 45, 1943.

⁶ T. R. Chamberlain and M. F. Grundon, *J. Chem. Soc. (C)*, 1971, 910.