Identification of Azulene Compounds in the Dehydrogenation Products of the Sesquiterpene Hydrocarbon Fraction of Camphor Oil

Shûichi HAYASHI, Shinji KUROKAWA and Tamon MATSUURA

Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima

(Received December 28, 1967)

In a previous investigation[1] of the colored matter in blue camphor oil,[*1] in which S- and Se-guaiazulene (85 : 5 ratio) were identified, the authors pointed out that a mixture of azulene compounds obtained on the sulfur dehydrogenation of the sesquiterpene hydrocarbon fraction of the blue camphor oil behaved differently on thin-layer chromatography from a mixture extracted directly from the blue oil.

The present experiment was undertaken to clarify the structure of azulenes obtained from the sulfur dehydrogenation of the sesquiterpene hydrocarbon fraction of the blue camphor oil; the sesquiterpene hydrocarbon fraction was dehydrogenated with sulfur, and then a mixture of azulene compounds extracted from the reaction mixture was separated, by the use of silica gel - *n*-hexane chromatography, to yield S-guaiazulene (85%), vetivazulene (8%), and 3,5,8-trimethylazuleno[6,5-*b*]thiophene (7%).

This composition is remarkably different from the azulene composition in the blue camphor oil. The detection of vetivazulene was the first such case in the dehydrogenation products of camphor oil, and presented interesting information for the study of the constituents of camphor oil, because no constituent which may be considered to be a precursor has not been detected. 3,5,8-Trimethylazuleno[6,5-*b*]-thiophene may be a secondary reaction product of the S-guaiazulene produced in the dehydrogenation of camphor oil, for the azulenothiophene had also been produced in a similar yield in the high-temperature reaction of S-guaiazulene and sulfur.[2]

Experimental

Dehydrogenation of the Sesquiterpene Hydrocarbon Fraction. A high-boiling fraction of camphor oil,

---

[*1] The high-boiling fraction of camphor oil containing sesquiterpene hydrocarbons and alcohols and other high-boiling constituents is called blue camphor oil, because of its color.

[1] S. Hayashi, T. Matsuura, O. Yamamoto and M. Okano, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **81**, 1186 (1960).

[2] S. Hayashi, S. Kurokawa, M. Okano and T. Matsuura, *Tetrahedron Letters*, **1967**, 3443; *J. Sci. Hiroshima Univ., Ser. A-II*, **31**, 79 (1967).

obtained by distilling out a monoterpene fraction, bp above 215°C, d_4^{25} 0.9625, n_D^{25} 0.5057, $[\alpha]_D^{25}$ +40.0°, was fractionated through a Dixon-packed distillation column, and then the whole sesquiterpene hydrocarbon fraction, bp 104—120°C/9 mmHg, d_4^{25} 0.9289, n_D^{25} 1.5060, $[\alpha]_D^{25}$ +11.54°, was collected.

The fraction was dehydrogenated by heating it together with powdered sulfur at 180—240°C for 4 hr. The dehydrogenation products separated by distillation were then treated in the usual manner, phosphoric acid extraction and silica gel - benzene chromatography; a mixture of azulene compounds free from non-azulene products was thus obtained. This azulene mixture was then separated by chromatography on a silica-gel column using *n*-hexane. The results are shown in Table. 1

TABLE 1. SEPARATION OF AZULENE COMPOUNDS PRODUCED IN THE DEHYDROGENATION OF THE SESQUITERPENE HYDROCARBON FRACTION

Eluting order	Appearance	Yield, g (%)
1	Blue, solidifiable	6.470 (84.9)
2	Violet, liquid	0.647 (8.3)
3	Dark violet, solid	0.517 (6.8)

Identification of the Azulene Compound. *S-Guaiazulene.* The blue azulene which was first eluted out from the column, solidified when stored. Its gas chromatogram (Chromosorb-W impregnated with 10% Silicone SE-30, Diasolid-L with 10% neopentyl glycol succinate, each column 1 m in length), IR,3) UV,4) visible4) and NMR5) spectra are in good agreement with those of S-guaiazulene. It gave the trinitrobenzoate,6) mp 149—150°C, and the picrate,6) mp 121—122°C, of S-guaiazulene (admixing).

Vetivazulene. The violet oil obtained from the second eluate was then purified by repeated phosphoric acid extraction and silica gel - *n*-hexane chromatography. The azulene oil thus obtained showed only one peak in gas chromatography, and its IR,7) UV8) and visible4,8) absorption spectra agreed well with those of vetivazulene. The NMR and mass spectra of the oil can reasonably be explained by the structure of vetivazulene.

3,5,8-*Trimethylazuleno*[6,5-*b*]*thiophene.* From the third eluate, a dark violet crystalline mass, mp 95—107°C, was obtained after the solvent had been evaporated. It was further purified by repeated silica gel - *n*-hexane chromatography, and by subsequent recrystallization from methanol, to give dark violet needles melting at 116.0—116.5°C. A mixed-melting-point determination with 3,5,8-trimethylazuleno[6,5-*b*]thiophene2) showed no depression. The NMR spectra of the compounds measured in chloroform and in trifluoroacetic acid both coincided with those of the azulenothiophene.2) These findings were also supported by the IR and mass spectra.

---

3) Hs. H. Günthard and Pl. A. Plattner, *Helv. Chim. Acta*, **32**, 284 (1948).

4) Pl. A. Plattner, *ibid.*, **24**, 283E (1941).

5) D. Meuche, B. B. Molloy, D. H. Reid and E. Heilbronner, *ibid.*, **46**, 2483 (1963).

6) Pl. A. Plattner, A. Fürst and L. Marti, *ibid.*, **32**, 2452 (1949).

7) J. Pliva, H. Horak, V. Herout and F. Šorm, "Terpenspektren," Akademie-Verlag, Berlin (1960), p. 161.

8) B. Susz, A. St. Pfau and Pl. A. Plattner, *Helv. Chim. Acta*, **20**, 469 (1937).