Phytochemistry, 1970, Vol. 9, pp. 1157 to 1158. Pergamon Press. Printed in England.

SHORT COMMUNICATION

1,2-DIHYDRO-1,1,6-TRIMETHYLNAPHTHALENE FROM STRAWBERRY OIL

L. P. STOLTZ, T. R. KEMP, WILLIAM O. SMITH, JR., W. T. SMITH, JR. and C. E. CHAPLIN

Department of Horticulture and Department of Chemistry, University of Kentucky,
Lexington, Kentucky, U.S.A.

(*Received* 26 *September* 1969)

Abstract—1,2-Dihydro-1,1,6-trimethylnaphthalene (3,4-dehydroionene) has been identified in the essential oil of strawberry fruit and foliage.

INTRODUCTION

IN OUR previous work[1] with the essential oil of strawberry foliage we encountered a component which was believed to be a dihydrotrimethylnaphthalene. We now wish to report a structure determination of the compound and, in addition, its isolation from strawberry fruit volatiles obtained by steam distillation. To our knowledge this compound has not been reported previously as a constituent of plant or fruit oils. McFadden *et al.*[2] obtained mass spectral data which indicated the presence of three other naphthalenes in strawberry volatiles —naphthalene, 1-methylnaphthalene and 2-methylnaphthalene.

RESULTS AND DISCUSSION

The mass spectrum (Fig. 1) showed the molecular weight of the compound to be 172. Also, two metastable peaks were observed, one at m/e 143·5 implying the loss of a methyl group from the parent compound to give an ion with mass 157. This ion in turn lost a methyl group, as indicated by a metastable peak at m/e 128·5, to give an ion with mass 142. The fragment with mass 142 had a spectrum corresponding to methylnaphthalene.[3] There were several doubly charged fragments in the spectrum, the major one occurring at m/e 77·5. In addition, the u.v. spectrum was consistent with a 1,2-dihydronaphthalene.[4] Hence, these data indicated the compound was a dihydrotrimethylnaphthalene. The i.r. spectrum showed a strong band at 3030 cm^{-1} which implied an aromatic ring and/or a *cis*, 1,2-disubstituted double bond. The moderate bands at 1360 cm^{-1} and 1380 cm^{-1} were consistent with geminal dimethyl substitution. A moderate peak at 885 cm^{-1} suggested a 1,2,4-trisubstituted benzene

---

[1] T. R. KEMP, L. P. STOLTZ, W. T. SMITH, JR., and C. E. CHAPLIN, *Am. Soc. Hort. Sci.* **93**, 334 (1968).

[2] W. H. MCFADDEN, R. TERANISHI, J. CORSE, D. R. BLACK and T. R. MON, *J. Chromatog.* **18**, 10 (1965).

[3] *Am. Petroleum Inst. Catalog of Mass Spectral Data*, 1966, 894. Research Project 44, Chemical Thermodynamics Properties Center, Agr. and Mech. Coll. of Texas, College Station Texas.

[4] P. KARRER and P. OCHSNER, *Helv. Chim. Acta* **31**, 2093 (1948).

while the strong band at 700 cm^{-1} indicated a *cis* 1,2-disubstituted double bond. Hence, this analysis led to 1,2-dihydro-1,1,6-trimethylnaphthalene (3,4-dehydroionene) as a possible structure.

1,2-Dihydro-1,1,6-trimethylnaphthalene, a hydrocarbon with a piney odor, was synthesized from α-ionone by the method of Karrer and Oschner.[4] Comparison of mass spectra, i.r., u.v. and GLC retention data of the synthetic material with that of the plant compound confirmed identification.

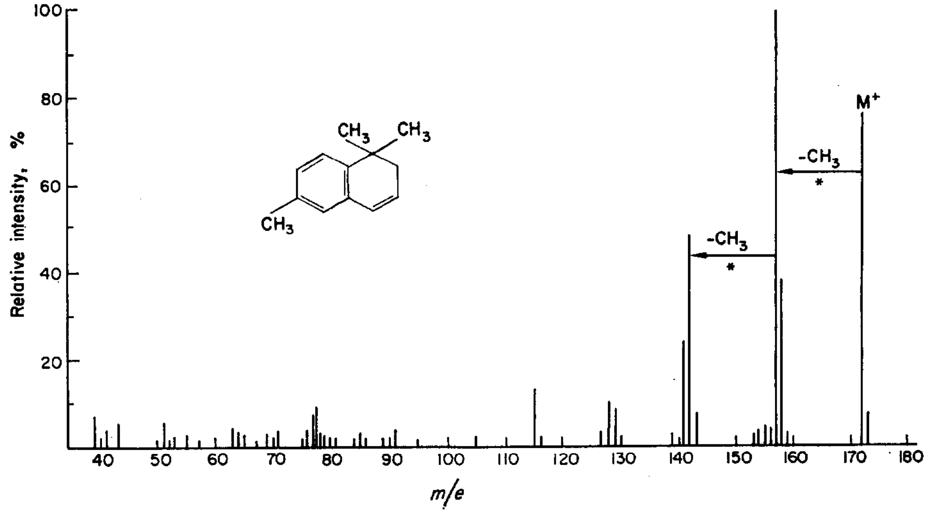

FIG. 1. MASS SPECTRUM OF 1,2-DIHYDRO-1,1,6-TRIMETHYLNAPHTHALENE.

EXPERIMENTAL

Isolation of the Oil Constituent

Foliage and fruit from the *Fragaria* × *ananassa* (Rosaceae) cultivar "Citation" were harvested in 1968 at Lexington, Kentucky, and steam distilled by the method previously described.[1] The component of interest was obtained from the oil by gas chromatography on a Beckman GC 2A gas chromatograph equipped with a thermal conductivity detector using the following scheme. First, the oil was fractionated at 130° and 100 ml/min He flow rate on a 6 ft long $\frac{1}{4}$ in. OD stainless-steel column packed with 20% (w/w) Apiezon L on silanized chromosorb W. The component was further purified at 130° and 150 ml/min He flow rate on a 6 ft long, $\frac{1}{4}$ in. OD stainless-steel column packed with 20% Carbowax 20 M (w/w) on silanized Chromosorb W.

Spectroscopy

Mass spectra were run with source and oven temperatures at 200°. The u.v. spectra were recorded in cyclohexane. The i.r. spectra were run in CCl_4.

Synthesis

1,2-Dihydro-1,1,6-trimethylnaphthalene was prepared by treatment of α-ionone with *N*-bromosuccinimide followed by dehydrobromination with *N,N*-diethylaniline after the method of Karrer and Oschner.[4] The major product was purified by gas chromatography on Carbowax 20 M using the same conditions reported above for the purification of the plant oil sample.

Acknowledgements—Research supported in part by USDA ARS Grant 12-14-9130 (33). The investigation reported in this paper (69-10-117) is in connection with a project of the Kentucky Agricultural Experiment Station and the paper is published with the approval of the Director.