

Isolation and Identification of Benzyl Ether in a Sample of Basil Oil

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A gas chromatographic fraction of a sample of basil oil was found to contain benzyl ether, a compound heretofore not reported to be present in this oil. Identification was established by comparison of various spectra of known samples of the ether. It was further observed that the published mass spectral data for benzyl ether was in error.

IN THE COURSE of an investigation dealing in part with the analysis of an essential oil obtained from basil, it became necessary to establish the reproducibility of the method of assay. For this purpose a commercial¹ sample of oil of basil was purchased and subsequently analyzed by gas chromatographic and spectroscopic methods. It was observed that among other known components (1, 2) an ether (benzyl ether) could be isolated from this particular sample of oil.

EXPERIMENTAL

The oil of basil was subjected to gas chromatographic separation and the fractions were examined spectroscopically.

Gas Chromatography—Instrument: Aerograph Autoprep, model A-700, gas chromatograph equipped with a thermal conductivity detector. Conditions: a 20 ft. \times $\frac{3}{8}$ in. o.d. aluminum column packed with 30% SE-30 on Chromosorb W (mesh 45/60) was used. The flow rate of the carrier gas, helium, was 200 ml./min. The oven temperature was programmed (nonlinear) between 100 and 250°. Sample: an 0.5-ml. portion of the oil was injected for each of five consecutive runs.

Nuclear Magnetic Resonance Spectroscopy—Instrument: Varian model A-60. Conditions: an approximately 50% solution of the fraction and a known sample of benzyl ether were prepared using $\text{CDCl}_3 + 1\%$ TMS² and the spectrum was taken in a glass microcell at probe temperature.

Mass Spectroscopy—Instrument: Hitachi-Perkin-Elmer model RMU-6D. Conditions: the sample was introduced through the reservoir and a heated glass inlet kept at a temperature of 200° and at a sample pressure of 2×10^{-7} mm. The ionizing electron beam was set at 75 ev.

Infrared Spectroscopy—Instrument: Perkin-Elmer grating infrared spectrophotometer model 337. Conditions: the sample was introduced as a film between two sodium chloride plates.

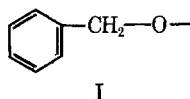
RESULTS AND DISCUSSION

Fractions of oil of basil isolated by preparative gas chromatography were examined by mass spectroscopy and the m/e values obtained were those expected for terpenoids or sesquiterpenoids. Some of the compounds identified so far include the following: 1,8-cineole, linalool, anethole, methyl chavicol, *o*- or *p*-methoxy cinnamaldehyde, and methyl eugenol. The sesquiterpene fractions, all

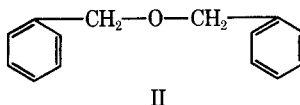
with an m/e of 204, have not as yet been completely identified.

Upon examination of the last fraction of the oil which eluted approximately 1.5 hr. after injection in the gas chromatograph, it was found that its apparent parent ion in the mass spectrum was at m/e 107. This was unexpected for two reasons. First, the time of elution in the nonpolar liquid phase in general followed the order of increasing molecular weight, and second, this odd-numbered molecular weight indicated the presence of an odd number of nitrogens (3) in the molecule. Since the chemical analysis of this particular fraction did not show the presence of nitrogen, it was assumed that the apparent molecular ion, 107, was actually a fragment of a larger parent ion. Further examination of this fraction by nuclear magnetic resonance showed a very simple spectrum with only two sharp absorption signals, one at 4.54 δ and one at 7.33 δ downfield from the tetramethylsilane signal. Their integrated areas were in the ratio of 2:5, respectively. The signal at 7.33 δ indicated an unconjugated phenyl group resonance. The position of the less intensive signal at 4.54 δ is at a somewhat lower field than expected for a simple R—CH₂—O— group. This indicates that the methylene group is adjacent not only to an oxygen but also to another deshielding group.

From these data it was assumed that the compound has the structural element shown in I.



The absence of any other signal in the NMR spectrum and the lack of exchangeable protons as well as the mass spectral data lead to the postulation that the molecule is a symmetrical ether with the formula shown in II.



An infrared spectrum of the fraction was taken and compared with that of benzyl ether reported in the Sadtler standard spectra. These spectra were found to be identical (4). It was concluded, therefore, that the fraction as isolated was indeed benzyl ether.

As further verification, benzyl ether was not only prepared in our laboratory (5) but also purchased from the Eastman Kodak Co. Both samples were purified by gas chromatography and examined spectroscopically. The mass, infrared, and NMR

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¹ This sample was characterized by the supplier, Magnus Mabee and Reynard, Inc., to have been "received directly from Comores Islands."

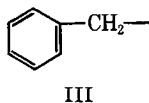
² Marketed as Silanar C by Merck Sharp & Dohme of Canada.

TABLE I—SIX MOST ABUNDANT PEAKS IN THE SPECTRA OF BENZYL ETHER IN DECREASING ORDER OF ABUNDANCE

Peak No.	Present Findings		Published Findings (6)	
	<i>m/e</i>	% Rel. Abundance	<i>m/e</i>	% Rel. Abundance
1	92	100	77	100
2	91	83	105	75
3	79	20	106	74
4	65	18	51	57
5	77	17	50	33
6	107	15	78	22

spectra were found to be identical with those of the fraction obtained from the oil.

Six major peaks are shown in the mass spectrum of benzyl ether as published in a compilation of mass spectral data (6). In the comparison of our observations with these published data the great discrepancy shown in Table I was found. The spectrum as reported (6) is obviously in error since compounds having a moiety (III) will invariably give rise to a *m/e* 91 fragment (tropylium ion) in substantial abundance. It has been reported that benzyl ether slowly decomposes to benzaldehyde (7). A comparison of the six major peaks for benzaldehyde with those in the spectrum published for benzyl ether showed that they were coincidental and almost identical in relative abundances.



The correct mass spectrum of benzyl ether is shown in Fig. 1. The lack of the parent ion (*m/e* 198) is not entirely unexpected since it is a common occurrence with higher molecular weight ethers (8). In this case the parent ion is apparently much less stable than either the benzyloxy or the tropylium ions.

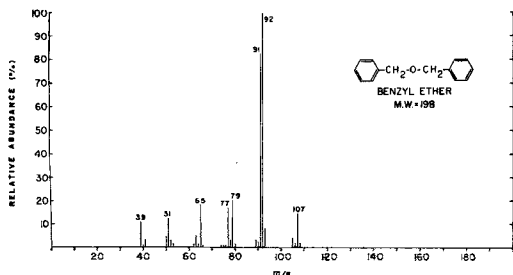
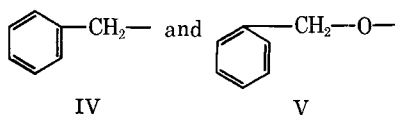
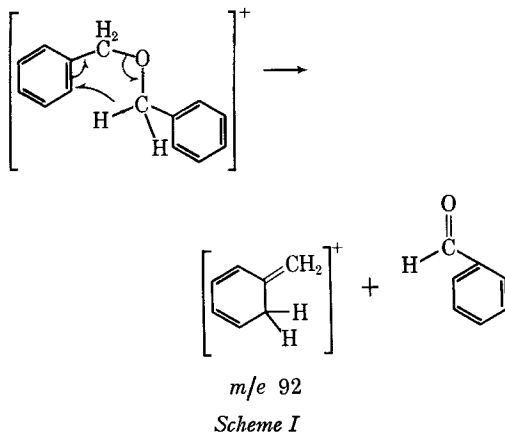


Fig. 1—Mass spectrum of benzyl ether.

The cleavage of the carbon-oxygen bond occurs readily, giving rise to IV and V with the positive charge being carried by either fragment (*m/e* 91 and *m/e* 107); however, the very stable tropylium ion (*m/e* 91) is favored and has the greater abundance.



The *m/e* 92 fragment is the base peak and somewhat unexpected; however, this occurrence has been reported for compounds with the general structure of AR—CH₂—O—RH (9). This can occur by the postulated rearrangement (10) shown in Scheme I.



Based on the comparison of the spectral data of the fraction isolated from oil of basil with those of the known samples of benzyl ether, the presence of the latter has been definitely established in a sample of oil of basil, in a concentration of about 4%. Another sample of oil of basil was obtained in this laboratory by steam distillation of *Ocimum basilicum* L., var. *glabratum* Bentham, sub-var. *vulgare* Alefeld, forme *thyrsiflorum* L.³ The benzyl ether could not be detected in this particular oil. Studies reported on the chemical composition of *O. basilicum* as reviewed by the authors have not indicated the presence of this ether in the oil.

Benzyl ether was detected by MacLeod *et al.* as a component not natural to lemon in a commercial sample purported to be cold-pressed lemon oil (11). These investigations suggest that the ether had been added to the sample of lemon oil.

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