

-2.2. The effect of refractive index on the position and size of the light spot was measured directly by photographing the spot near the face of the phototube. A 30% decrease in area of the spot was observed when a 10-cm. cell filled with water was introduced into the beam. Further successive decreases in area of the order of 5% were observed when the water (R.I. = 1.33) was replaced first by dioxane (1.42) and then by benzene (1.50) and small changes in the positions of the spots were also noticed.

Although for the 5 and 10 cm. cells the differences in matching factors may be large and quite variable with refractive index, good agreement can be obtained using both phototubes as long as the matching factors at a given wave length are obtained separately for each phototube and each liquid used. In this way discontinuities in absorption curves, which are sometimes obtained at the point where the tubes are interchanged, can be eliminated. The source of error discussed is particularly important when solutions varying widely in refractive index are matched against one solvent.

The effect was also determined for 1-cm. cells which are used by the majority of investigators. The difference in the matching factors for several of these cells changed by 0.1-0.3% (in terms of transmission) when benzene in the cells was replaced by water. These amounts become appreciable in terms of optical density only when very low absorptions are being measured.

For work of the highest accuracy, matching factors should be rechecked with any change of operating conditions whatsoever. Due to the zonal variations in spectral sensitivity of phototubes, differences in matching factors may be expected whenever the effective area of the phototube illuminated is altered in any way. In addition to the effect of refractive index, such changes may be brought about by slight localized variations in transmission of the absorption cells due to striae, scratches, etc., and when cells are shifted in orientation with respect to the phototubes.

The authors wish to acknowledge the assistance of Mr. J. C. Hyde.

DEFENCE RESEARCH CHEMICAL LABORATORIES
OTTAWA, ONTARIO RECEIVED SEPTEMBER 11, 1948

Phenoxyacetaldehyde

BY ROBERT J. SPEER AND HENRY R. MAHLER

Hatch and Nesbitt¹ have reported the synthesis of phenoxyacetaldehyde in 45% yield by the lead tetraacetate oxidation of glycerol α -phenyl ether. In connection with the radiochemical program of this Laboratory, the aldehyde in question has been prepared as an intermediate for certain labeled amino acids. It has been found that a modification of the above preparative technique results in an improved yield.

(1) L. F. Hatch and S. S. Nesbitt, *This Journal*, **67**, 39 (1945).

In order to avoid even a temporary excess of oxidant, the order of addition of reagents has been reversed. That is, a slurry of lead tetraacetate (1.0 mole) in benzene was added slowly to a stirred benzene solution of glycerol α -phenyl ether² (1.0 mole). This addition was accomplished during *ca.* two hours while the reaction mixture was stirred vigorously at a temperature of 20-25°. After isolation as previously described,¹ the product was fractionated through a 24-in. Widmer column, b. p. 82-83°(4-5 mm.). The aldehyde thus obtained represented a yield of 60% of theory; n_{D}^{20} 1.5360, d_{4}^{20} 1.1308 (*cf.* Huntress and Mulliken³ n_{D}^{21} 1.5380, d_{4}^{21} 1.1310). Molecular refraction, 37.54 (found), 37.20 (calcd.).

The value of this simple modification has been confirmed by one of us⁴ in the case of other sensitive aldehydes.

(2) Supplied through courtesy of the Miner Laboratories, Chicago, Ill.

(3) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds—Order I," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 66.

(4) Henry R. Mahler, Thesis, University of California, 1948.

INDUSTRIAL RESEARCH DIVISION

TEXAS RESEARCH FOUNDATION

RENNER, TEXAS

RECEIVED NOVEMBER 15, 1948

Ascaridole in Oil of *Chenopodium*. III.¹ The Characterization of Ascaridole

BY H. HARRY SZMANT AND ALFRED HALPERN

In connection with the investigation of the chemistry of ascaridole in progress in our Laboratories^{1,2} it was desirable to reexamine the physical properties of ascaridole in view of the discrepancies noted in the literature.³ The physical properties of ascaridole are of particular importance since no solid derivative of ascaridole is known.

Oil of *chenopodium*⁴ was fractionated using an all-glass system equipped with a Vigreux column. The physical properties and yields of the various fractions are summarized in Table I.

The fractions obtained from the preliminary distillation above, were analyzed for ascaridole content according to the method of Cocking and Hymas⁵ and the results are included in Table I. A portion of fraction "C," which analyzed iodometrically for pure ascaridole, was subjected to a careful fractionation in a two-foot glass-helices-packed column. The physical properties of the fractions obtained during this refractionation are reported in Table II.

(1) For paper II in this series see Halpern, *J. Am. Pharm. Assoc.*, **37**, 465 (1948).

(2) Halpern, *ibid.*, **37**, 161-165 (1948).

(3) Henry and Paget, *J. Chem. Soc.*, **119**, 1714 (1921); Paget, *ibid.*, 829-833 (1938); Paget, *Analyst*, **51**, 180-186 (1930); Khavin, *Ukrain. Gosudarst. Inst. Ekspl. Farm. (Kharkov), Konsultatsionnye Materialy* **1939**, No. 6, 165, *cf. C. A.*, **36**, 2997 (1942); Janot and Chaigneau, *Compt. rend.*, **214**, 746-747 (1942); Thoms and Dobke, *Arch. Pharm.*, **268**, 128-137 (1930).

(4) Oil of *chenopodium* meeting all of the N. F. VIII requirements was obtained from Magnus, Mabee and Reynard, Inc., New York.

(5) Cocking and Hymas, *Analyst*, **55**, 183 (1930).

TABLE I
FRACTIONATION OF OIL OF CHENOPODIUM^a

Fraction	B. p., ° at 0.5-1 mm.	Weight, g.	n_{20}^D	d_{20}^{25}	Apparent ascaridole content, % ^b
A	34-36	25.0	1.4755	0.8733	22.1
B	57-58	5.1	1.4740	0.9513	87.6
C	58.5-60	61.5	1.4720	1.0012	102.7 ^c
D	61-63	5.0	1.4715	1.0216	79.0
E	64-68	5.4	1.4715	1.0467	63.8

^a The original oil of chenopodium had the following constants: d_{20}^{25} 0.9782, n_{20}^D 1.4740; weight of oil sample fractionated 110 g., containing 68% ascaridole. ^b Based on the assumption that ascaridole is the only reactant of oil of chenopodium in the determination. ^c Freezing point 3.5°.

TABLE II
THE FRACTIONATION OF ASCARIDOLE

Fraction	B. p., °C., 1 mm.	Weight, g.	n_{20}^D	d_{20}^{25}	F. p., °C.
1	32-65	2.0	1.4732
2	64-70	1.0	1.4720
3	74-75 ^a	8.2	1.4722	1.0047	5
4	74 ^c	8.3	1.4724	1.0051	5
5	75 ^c	16.3	1.4718	1.0061	5 ^b
6	76-77	7.9	1.4720
Residue

^a B. p. at 1.5 mm. ^b M_D calcd. 46.80; found 46.79. The peroxide linkage assumed to be equivalent to two ether values.

Fraction "5" was analyzed⁶ and was found to contain 71.00% carbon, and 9.45% hydrogen in agreement with the calculated analysis of ascaridole (calcd. for $C_{10}H_{16}O_2$: C, 71.38; H, 9.58). The ultraviolet absorption spectrum in absolute methanol determined by means of the Beckman quartz spectrophotometer, and the infrared absorption spectrum,⁷ of fraction "5" are reproduced in Figs. 1 and 2, respectively.

It is of interest to note that the ultraviolet absorption spectrum indicates the presence of only one major absorbing group, namely, that of the

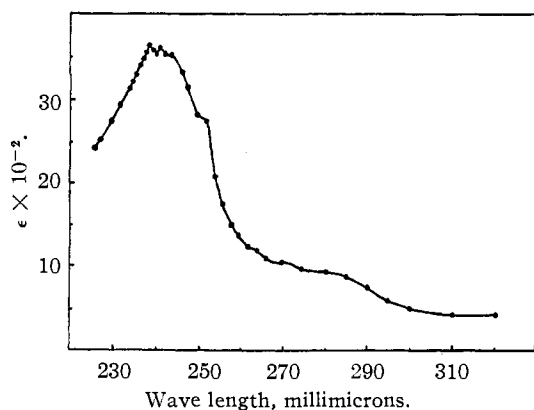


Fig. 1.—The ultraviolet absorption spectrum of ascaridole.

(6) Microanalyses by Samuel P. Sadtler & Son, Philadelphia, Pa.

(7) We gratefully acknowledge the cooperation of Dr. Philip Sadtler of Samuel P. Sadtler & Son, Philadelphia, Pa., in determining the absorption spectrum.

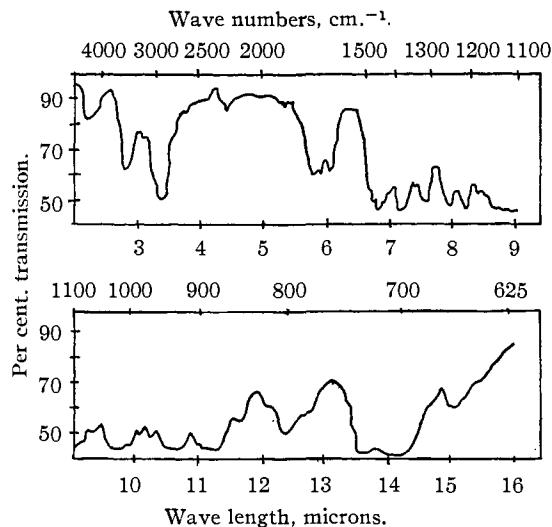


Fig. 2.—The infrared absorption spectrum of ascaridole.

simple carbon-carbon double bond. This is of significance since the oil of chenopodium contains an appreciable quantity of compounds possessing conjugated double bond systems.

In view of the correct analysis, the relative simplicity of the ultraviolet absorption spectrum, and the higher freezing point of our product, we believe to have obtained ascaridole of a higher purity than has hitherto been reported. The physical properties of ascaridole were found to be as follows: b. p. 75° (1.5 mm.); n_{20}^D 1.4718; d_{20}^{25} 1.0061; f. p. 5°.

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RECEIVED SEPTEMBER 8, 1948

The Preparation of 3,4-bis-(3'-Methyl-4'-hydroxy-5'-allylphenyl)-2,4-hexadiene

BY PHILIP WEISS¹ AND JOSEPH B. NIEDERL

Subsequent to studies in tetra alkyl substituted analogs of dienestrol and hexestrol,² an investigation was undertaken to study the estrogenic effects produced by the introduction of an allyl group in the 5'-position of the synthetic estrogen 3,4-bis-(3'-methyl-4'-hydroxyphenyl)-2,4-hexadiene.³

The synthesis of 3,4-bis-(3'-methyl-4'-hydroxy-5'-allylphenyl)-2,4-hexadiene was accomplished in the following manner. The diallyl ether of 3,4-bis-(3'-methyl-4'-hydroxyphenyl)-2,4-hexadiene was prepared by refluxing the substituted dienestrol with allyl bromide in the presence of anhydrous potassium carbonate, using dry acetone as the solvent. The Claisen rearrangement⁴ was effected by refluxing with diethylaniline thus

(1) Present address: Wallace and Tiernan Products Inc., Belleville 9, New Jersey.

(2) J. B. Niederl and P. Weiss, *THIS JOURNAL*, **70**, 2894 (1948).

(3) V. Niederl and co-workers, *ibid.*, **70**, 508 (1948).

(4) E. Kaiser and J. J. Svarz, *ibid.*, **68**, 636 (1946).