TABLE I

FRACTIONATION OF OIL OF CHENOPODIUM[a]

Fraction	B. p.° at 0.5–1 mm.	Weight, g.	$n^{25}\text{D}$	d^{25}_{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^{25}_{25} 0.9782, $n^{25}\text{D}$ 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.	$n^{25}\text{D}$	d^{25}_{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[a]	8.3	1.4724	1.0051	5
5	75[a]	16.3	1.4718	1.0061	5[b]
6	76–77	7.9	1.4720	....	..
Residue	...	..	....	....	..

[a] B. p. at 1.5 mm. [b] $M\text{D}$ calcd. 46.80; found 46.79. The peroxide linkage assumed to be equivalent to two ether values.

Fraction "5" was analyzed[6] 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 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.

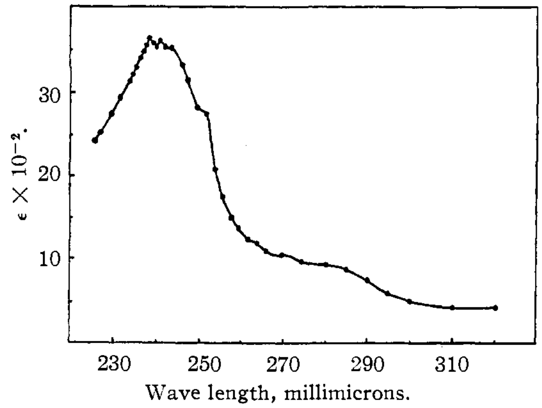

Fig. 1.—The ultraviolet absorption spectrum of ascaridole.

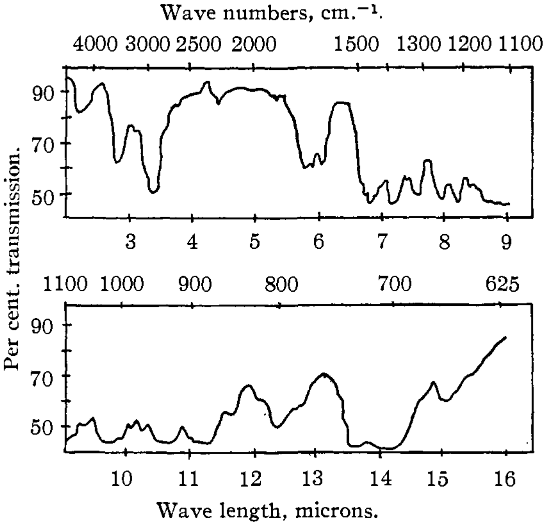

Fig. 2.—The infrared absorption spectrum of ascaridole.

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.); $n^{25}\text{D}$ 1.4718; d^{25}_{25} 1.0061; f. p. 5°.

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[6] Microanalyses by Samuel P. Sadtler & Son, Philadelphia, Pa.

[7] We gratefully acknowledge the coöperation of Dr. Philip Sadtler of Samuel P. Sadtler & Son, Philadelphia, Pa., in determining the absorption spectrum.

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

BY PHILIP WEISS[1] 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 rearrangement[4] was effected by refluxing with diethylaniline thus

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[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).

yielding the desired 3,4-bis-(3′-methyl-4′-hydroxy-5′-allylphenyl)-2,4-hexadiene, as a red gum. This tetraalkyl substituted analog of dienestrol was characterized by the preparation of the corresponding diacetate and dipropionate.

The estrogenic assays on these compounds were carried out by administering orally the test sample to ovariectomized female rats. Vaginal smears were examined and only full cornification was regarded as a positive oestrus response. The results of preliminary measurements of gross estrogenic activity indicate that at the 100 microgram dose level; the 3,4-bis-(3′-methyl-4′-propionoxy-5′-allylphenyl)-2,4-hexadiene shows a 20% oestrus response; the 3,4-bis-(3′-methyl-4′-acetoxy-5′-allylphenyl)-2,4-hexadiene gives a 25% response, and the 3,4-bis-(3′-methyl-4′-hydroxy-5′-allylphenyl)-2,4-hexadiene shows a 35% oestrus response. Control rats injected with 0.65 microgram of U.S.P. Reference Estrone produced a 40% oestrus response.

Acknowledgment.—The authors desire to express their appreciation to Dr. C. T. Van Meter of Reed and Carnrick, Jersey City, N. J., for the estrogenic assays.

Experimental[5]

3,4-bis(3′-Methyl-4′-allyloxyphenyl)-2,4-hexadiene.—A mixture of 15 g. (0.05 mole) of 3,4-bis-(3′-methyl-4′-hydroxyphenyl)-2,4-hexadiene,[3] 15 g. (0.11 mole) of allyl bromide, 15 g. (0.1 mole) of anhydrous potassium carbonate, and 200 ml. of dry acetone were refluxed for six hours, and then set aside at room temperature for twenty-four hours. Water was added to the reaction mixture, it was extracted with ether, and the ether layer was extracted with ice cold 10% aqueous sodium hydroxide solution to remove any unreacted dihydroxy compound. The excess alkali was removed by washing with water, the neutral ether solution was dried over anhydrous potassium carbonate, filtered, and the solvent removed by distillation. Crystallization and re-crystallization from dilute ethanol yielded 11.2 g. (59%) of a white crystalline solid; m. p. 67.5–68°.

Anal. Calcd. for $C_{26}H_{30}O_2$: C, 83.42; H, 8.02. Found: C, 83.57; H, 8.31.

3,4-bis-(3′-Methyl-4′-hydroxy-5′-allylphenyl)-2,4-hexadiene.—The procedure used by Kaiser and Svarz[4] for the preparation of 3,4-bis-(3′-allyl-4′-hydroxyphenyl)-hexene-3 was employed. A solution of 6.8 g. of 3,4-bis-(3′-methyl-4′-allyloxyphenyl)-2,4-hexadiene in 40 ml. of diethylaniline was refluxed for five hours in a nitrogen atmosphere. The desired product was isolated as a red gum (2.2 g. or 32%) which could not be crystallized, but gave proper analytical results.

Anal. Calcd. for $C_{26}H_{30}O_2$: C, 83.42; H, 8.02. Found: C, 83.20; H, 8.26.

The diacetate, prepared in 68% yield by refluxing in acetic anhydride for four hours, formed white crystals from dilute ethanol, m. p. 125–126°.

Anal. Calcd. for $C_{30}H_{34}O_4$: C, 78.60; H, 7.42. Found: C, 78.31; H, 7.29.

The dipropionate was prepared in 61% yield in a similar manner, m. p. 114–115°.

Anal. Calcd. for $C_{32}H_{38}O_4$: C, 79.01; H, 7.81. Found: C, 78.83; H, 7.71.

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Closed-Circuit Seals in Glassblowing

By Roger K. Taylor

In fabricating glass apparatus in which one part is multiply connected to the rest, the customary procedure is to make the seals after the first by using a thin rod to pull together or bridge over the edges of the open-ended immobilized tubes that are to be joined. Difficulties occasionally arise, especially when the seal is not readily accessible from all directions, in manipulating the rod and obtaining a completely tight seal.

The writer for some years has on occasion used an alternative method which avoids these troubles. Although it is difficult to believe that the same idea has not occurred to others, neither the method nor a description of it has been seen elsewhere; and it is in the hope that the scheme may be of some general assistance that the following exposition is offered.

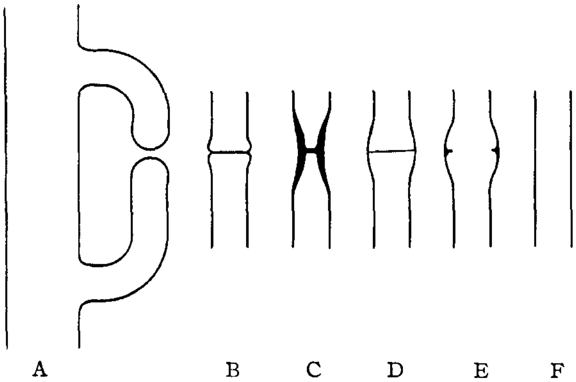

Fig. 1.—Closed-circuit seals in glassblowing.

The innovation consists in closing the ends of the tubes where the joint is to be made (a). Then, when both ends are hot, blowing brings together the bulbs formed, producing a septum (b). When the enlarged portion is permitted to shrink (c), a portion of the glass of the septum is picked up by the wall; alternate blowing and shrinking (d, c) ultimately reduces the thickness of the septum to the point that it breaks (e), after which the joint is readily smoothed out (f). Glass can of course be added or removed with a thin rod as necessary, if the wall thickness at the seal does not match that of the rest of the tubing.

An advantage is that the annoyance of air leakage is avoided in the blowing, during making the seal; and this is particularly important when several connections have to be made between immobilized parts. It is also unnecessary to fit the parts so precisely, to give the small clearances required for easy working when the tubes are open. Furthermore there is no chance of leaving pinholes in the seals. The chief disadvantage is that prolonged working of the glass may lead to devitrification.

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[5] All melting points given are uncorrected.