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THE ODOR OF ORANGES PROTECTED BY BIPHENYL-IMPREGNATED  
WRAPS AND STORED IN WOODEN BOXES

By

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I N T R O D U C T I O N

Biphenyl-impregnated packing materials constitute, at present, the best means of protection of citrus fruit against the development of decay during transportation and storage. The use of biphenyl has great advantages, both for the citrus industry as well as for the consumer (11). Biphenyl is very useful in the control of citrus fruit decay, and meets the requirements for food additives. However, the packing materials have the characteristic odor of biphenyl, which can be imparted to the fruits. According to many research workers, the odor is faint and detectable only on fruit just removed from packing materials which still contain a certain amount of biphenyl; this odor disappears from the fruit rapidly, generally within a day or two after removal of the packing materials (1, 2, 3, 4, 5, 6, 7, 8, 12, 13, 14, 15). However, according to some consumers, the biphenyl odor is persistent and detectable on all biphenyl-protected fruit, and this opinion has brought about opposition to the use of biphenyl-impregnated materials.

The various attempts made to suppress the perceptibility of biphenyl odor on fruit, through the addition of odoriferous substances to the packing materials or by coating the fruit with wax containing biphenyl have, as yet, not produced satisfactory results. Moreover, even with the very considerable amount of research work carried out for several years on many thousands of substances, no substitute for biphenyl has yet been found.

The objections against the use of biphenyl-impregnated packing materials are based on an organoleptic, and thus subjective, evaluation of the odor. In view of



the importance of the use of biphenyl to the citrus industry, it is necessary to verify, by objective chemical methods, to what degree these objections are valid.

A priori, the odor of biphenyl is due to the biphenyl volatilizing from the fruit with an intensity strong enough to be distinguished. Consequently, it should be possible to study the problem in an objective manner by determining the amount of biphenyl volatilizing from fruit. With this principle in mind, it was found necessary to check the following:

- (a) If, after the removal of packing materials, measurable amounts of biphenyl volatilize from the fruit; and, if so, to study the progress of biphenyl volatilization.
- (b) If a relationship exists between biphenyl volatilization and odor perceptibility; and, if so, to proceed with an objective study of the fruit odor.

On the other hand, in order to determine whether it is possible to protect the citrus fruit during transportation with biphenyl and to market fruit on which the odor of biphenyl is not perceptible, it was found necessary to examine if and to what extent the odor of the fruit is dependent on certain factors such as mode of packing, amount of biphenyl in the packing material, or amount of biphenyl residue in the fruit.

#### MATERIALS AND METHODS

The experiments were conducted on Shamouti oranges picked on 22.XII.1963 and 29.I.1964, and on Valencia oranges picked on 6.IV.1964. The fruit which was destined for one experiment came from the same grove, was of uniform size, and underwent the same washing and waxing treatments in the packing house. The oranges were divided into two lots, and each lot into several groups of fruit. The oranges were packed into crates, each of which contained four layers of fruit, totaling approximately 140 pieces.



The fruit was protected with biphenyl-impregnated wraps in use for the individual wrapping of oranges. One lot of fruit was protected with wraps containing 34 or 38 mg. of biphenyl, and the other lot with 17 or 18 mg. per wrap. In order that all the fruits belonging to the same lot of fruit, independent of the mode of packing, would be protected with the same amount of biphenyl, the number of wraps used in any one crate of fruit was the same as the number of fruits placed therein.

Each group of fruit, belonging to the same lot, was packed according to a different mode of packing, namely:

- (a) each fruit was wrapped in an individual wrap (individual packing);
- (b) strips of paper, 1-cm wide, were laid uniformly between the fruits;
- (c) two layers of paper, formed by an equivalent number of wraps, were placed, one at the bottom of the crate, and the other on the surface of the fruit;
- (d) five layers of paper, formed by an equivalent number of wraps, were placed, one at the bottom of the crate, one on the surface of the fruit, and the remaining three between the layers of fruit in such a manner that each layer of fruit rested between two layers of paper; and
- (e) oranges wrapped in individual wraps and unwrapped oranges were placed alternately in the crate (alternate packing).

The fruit was stored at 17°C. In order to avoid the eventual influence of biphenyl dispersed in the store-rooms on the experimental results, each lot of oranges was placed in a separate store-room.

At predetermined dates, a sample consisting of three or four oranges, together with the corresponding number of biphenyl wraps, was taken from each group of fruit. The amount of biphenyl remaining in the wraps was determined colorimetrically (9).

Immediately after the removal of the wraps, the odor of the oranges was evaluated and the fruit submitted to the determination of biphenyl volatilizing from the fruit. The remaining fruit from groups in which the odor of biphenyl was detectable was unwrapped and placed in wooden boxes as control. This fruit was, after one or two



days, submitted to evaluation of the odor and to determination of the amount of volatilizing biphenyl.

The organoleptic odor evaluation was effected by a panel of 8-10 members selected for their ability to detect the odor of biphenyl on the fruit. Since this odor is usually difficult to detect, and is perceptible sometimes only on certain parts of the surface of the fruit, the odor was tracked over the entire fruit surface. In all cases where at least one examiner detected the odor of biphenyl, the fruit was classified as fruit with odor of biphenyl.

In order to determine biphenyl volatilizing from fruit, the oranges were placed in air-tight containers, just large enough to contain the fruit, and through which passed a very slow flow of air of 1.2 to 1.5 liters per hour. Biphenyl volatilizing from the fruit was drawn by air, extracted from air by passing through acetic acid containing traces of formaldehyde, and determined in the acetic extract by a colorimetric micro-method \*, based on principles described previously (9, 10).

The amounts of volatilized biphenyl were determined twice every 24 hours, after six and eighteen hours of aeration, and, in those cases where the amounts of volatilizing biphenyl were extremely small, once every 24 hours. These data served for determining the average volatilization intensity of biphenyl during a given period. The amounts of volatilized biphenyl were calculated in  $\mu\text{g}$  per fruit and in ppm of whole fruit, and the average volatilization intensities in  $\mu\text{g}$  of biphenyl per fruit and per hour.

After the aeration, the biphenyl residues in the fruit were determined colorimetrically (10). The amount of biphenyl absorbed by the fruit during storage, expressed in ppm of whole fruit, was calculated by adding the amount of volatilized biphenyl to the amount of biphenyl found in the aerated fruit.

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\* Rajzman, Anna. In preparation.



## RESULTS AND DISCUSSION

### Biphenyl volatilization from the fruit

It can be seen from Tables 1 and 2 that, after removal of the wraps, measurable amounts of biphenyl volatilize from the oranges. The period during which biphenyl volatilization takes place varies from one fruit to another, and, in general, does not exceed a few days.

The intensity of biphenyl volatilization decreased rapidly with time (Fig. 1), especially during the first day following removal of the wraps. E.g. during the first six hours of aeration, the average volatilization intensities corresponded according to fruit, (Fig. 1) to 6, 10, 13 and 17  $\mu\text{g}$ . of biphenyl/fruit/hour and during the next 18 hours, to 2.2, 3.0, 5.0 and 9.0  $\mu\text{g}$ , respectively. During the second day, 1.0, 1.5, 2.0 and 3.5  $\mu\text{g}$ , respectively, were volatilized from the same fruit and during the third day 0.3, 0.5 0.8 and 1.6  $\mu\text{g}$  of biphenyl/fruit/ hour, The average biphenyl volatilization intensities during the fifth and sixth days are very small, generally between 0.04 and 0.1  $\mu\text{g}$  of biphenyl/fruit/hour, so that biphenyl volatilization practically ceases.

In all cases (Tables 1 and 2) the amounts of biphenyl volatilized per 24 hours from the fruit, decreased rapidly during aeration, so that, during the first day, these amounts oscillated between 1 and 470  $\mu\text{g}$ , and during the sixth day they did not exceed 3  $\mu\text{g}$  of biphenyl per fruit. The amounts of biphenyl volatilized from the various fruits during the entire aeration period varied between 2 and 630  $\mu\text{g}$  of biphenyl per per fruit. The major part was volatilized during the first day following removal of the wraps, and approximately 80 to 100% during the first two days (Tables 1 and 2). On the whole (Table 3), the number of fruits from which were volatilized smaller and smaller amounts of biphenyl increased rapidly with duration of aeration, and, starting from the third day, very small quantities, not exceeding 5  $\mu\text{g}$  of biphenyl /fruit/ 24 hours, were volatilized from most of the fruits.



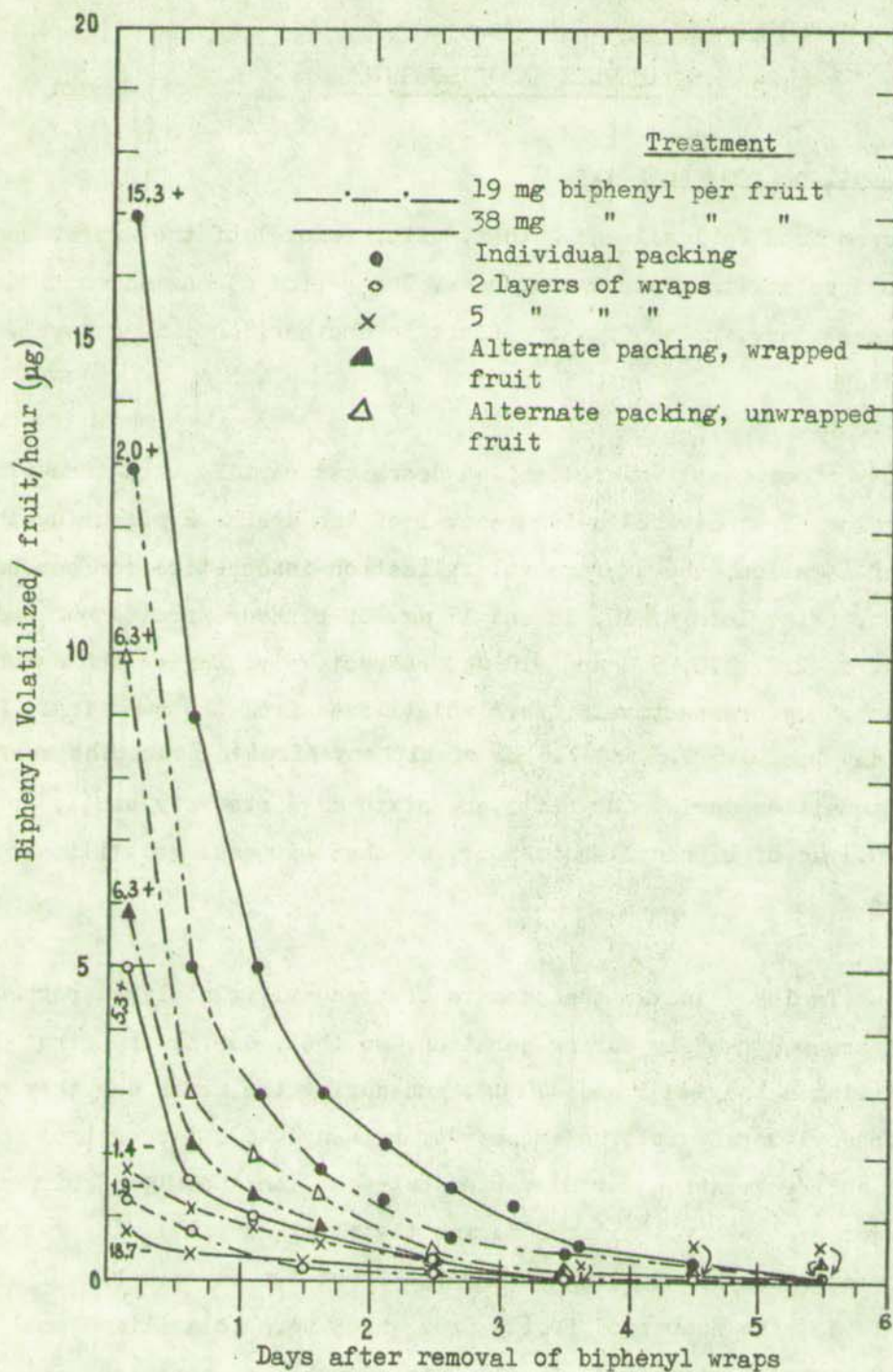


Fig. 1.

Biphenyl volatilized from oranges after removal of biphenyl- impregnated wraps. Figures indicate residual biphenyl in the wraps, in mg per fruit. + indicates detectable biphenyl odor on fruit after removal of wraps; - indicates not detectable.



Biphenyl volatilized more rapidly from fruit placed in wooden boxes than from fruit placed in the air-tight containers; for example, during the second day following removal of the wraps, 8, 24 and 60  $\mu\text{g}$  of biphenyl were volatilized from fruit from three groups submitted to experimental aeration, vs. only 1, 5 and 15  $\mu\text{g}$  of biphenyl from the fruits in wooden boxes, respectively.

The amounts of biphenyl (in ppm of whole fruit) volatilized during aeration varied between 0.01 and 1.92 ppm (Tables 4, 5 and 6). The volatilized biphenyl constituted a variable, but very small portion of the biphenyl absorbed by the fruit during storage, and oscillated between 0.05 and 6.2% of the biphenyl absorbed (Tables 4 and 5). The amounts of biphenyl volatilized from the fruit, after removal of the wraps, decreased when the storage time of fruit in the presence of biphenyl increased. Fruits taken successively from the same group at various periods of their storage, eliminated decreasing quantities of biphenyl, corresponding, for example, after 6, 13, 19 and 27 days of storage, to 1.09, 0.29, 0.17 and 0.03 ppm, respectively (Table 4).

#### Biphenyl volatilization and fruit odor

It seems possible, according to the amounts of biphenyl volatilized, to determine objectively the odor of the fruit. After the removal of biphenyl wraps, biphenyl odor was not detectable on all the biphenyl-protected fruit, even when measurable amounts of biphenyl (Tables 1 and 2) were volatilized from the fruit.

During the present study, the odor was generally perceptible on fruit from which at least 41  $\mu\text{g}$  of biphenyl were volatilized during the first day of aeration (Tables 1 and 2) and when average volatilization intensity at the beginning of aeration corresponded to at least 5  $\mu\text{g}$  of biphenyl/fruit/hour (Fig. 1). It is probable that, in all cases where measurable amounts of biphenyl were volatilized from fruit without odor of biphenyl, the amounts were not sufficiently high to be sensed, or the odor of biphenyl was concealed by odoriferous products emitted by the fruit.



Table 1  
Volatilization of biphenyl from Shamouti oranges  
after removal of biphenyl wraps

Mode of packing	Residual biphenyl in wraps (mg/fruit)	Odor of fruit <sup>a</sup>	Biphenyl volatilized during aeration (µg of biphenyl per fruit)							Biphenyl volatilized (% of total)	
			1st day	2nd day	2rd day	4th day	5th day	6th day	Total	1st day	1st and 2nd days
Individual	12.0	±	470	80	40	27	10	3	630	74.6	87.3
Individual	3.5	±	360	60	38	29	10	3	500	72.0	84.0
Individual	30.0	±	314	77	15	25	0	0	431	72.8	90.7
Individual	15.3	±	267	85	40	17	5	2	416	64.2	84.6
Individual	2.0	±	163	60	25	14	8	2	277	60.6	82.3
Individual	10.0	±	209	34	31	9	5	2	290	72.1	83.8
Individual	17.5	±	150	38	24	22	0	0	234	64.1	80.3
Alternate	6.3	±	116	37	12	3	1	1	170	68.2	90.0
Alternate	6.3	±	77	24	8	3	1	0	113	68.1	89.4
2 layers of wraps	5.3	±	59	20	1	0	-	-	80	73.7	98.7
Strips of wraps	present	±	74	0.7	0.7	0.7	0	-	76	97.3	98.2
5 layers of wraps	11.4	±	41	32	0	0	-	-	73	56.1	100.0
Individual	4.5	±	44	8	7	5	3	2	69	63.7	75.3
2 layers of wraps	7.5	-	54	7	4	2	0.5	0.5	68	79.4	89.7
5 layers of wraps	0.4	-	32	17	10	1	1	1	62	51.6	79.0
Alternate	1.8	±	41	12	5	1	1	0	60	68.3	88.3
Individual	traces	±	53	4	1	-	-	-	58	91.3	98.2
Strips of wraps	present	±	48	10	0	0	-	-	58	82.7	100.0
5 layers of wraps	4.7	±	52	---traces---			-	-	52	100.0	100.0
Alternate	2.5	±	41	8	0	0	-	-	49	83.6	100.0
Individual	0	-	25	20	0	0	-	-	45	55.5	100.0

(cont'd)



Table 1 (cont.)

Mode of packing	Residual biphenyl in wraps (mg/fruit)	Odor of fruit <sup>a</sup>	Biphenyl volatilized during aeration							Biphenyl volatilized (% of total)	
			mg of biphenyl per fruit							1st day	1st and 2nd days
5 layers of wraps	1.9	-	30	5	4	3	0.5	0.5	43	69.7	81.4
Individual	2.7	-	23	8	4	2.5	1	1	39	58.9	79.5
Alternate	2.5	-	31	4	1	0	-	-	36	86.1	97.2
2 layers of wraps	1.9	-	21	5	4	2	1	1	34	62.0	76.4
Alternate	1.2	-	17	5	4	3	0.5	0.5	30	56.6	73.3
5 layers of wraps	18.7	-	12	8	4	3	2	1	30	40.0	66.6
Strips of wraps	0	-	17	7	2	0.5	0.5	-	27	63.0	88.8
Alternate	0	-	13	6	5	2	2	-	28	46.4	68.0
5 layers of wraps	10.0	-	16	8	0.7	0	-	-	25	64.0	96.0
Individual	0	-	13	9	1.5	0.25	0.25	0	24	54.1	91.7
Alternate	2.2	-	16	6	1	0	-	-	23	69.6	95.6
5 layers of wraps	0	-	14	3	3	0.5	0.5	0	21	66.6	80.9
Individual	0	-	21	0	0	-	-	-	21	100.0	100.0
2 layers of wraps	26.7	-	18	1	0.7	0.7	0.7	-	21	85.7	90.5
Individual	0	-	10	7	2	1	-	-	20	50.0	85.0
Strips of wraps	0	-	10	6	4	traces	0	-	20	50.0	80.0
Alternate	0	-	10	6	3	0	-	-	19	55.5	84.2
5 layers of wraps	4.2	-	10	7	0	0	-	-	17	58.8	100.0
Alternate	2.2	-	15	1	1	0	-	-	17	88.2	94.1
Individual	0	-	16	0	0	-	-	-	16	100.0	100.0
Alternate	1.2	-	7	4	2	1	1	1	16	43.7	68.8
Strips of wraps	present	-	13	2	0	-	-	-	15	86.6	100.0

(Cont'd)



Table 1 (Cont.)

Mode of packing	Residual biphenyl in wraps (mg/fruit)	Odor of fruit <sup>a</sup>	Biphenyl volatilized during aeration							Biphenyl volatilized (% of total)	
			µg of biphenyl per fruit							1st day	1st and 2nd days
			1st day	2nd day	3rd day	4th day	5th day	6th day	Total		
2 layers of wraps	20.8	-	13	2	0	-	-	-	15	86.6	100.0
Alternate	0	-	12	3	0	0	-	-	15	80.0	100.0
5 layers of wraps	0	-	12	2	1	0	-	-	15	80.0	93.3
Alternate	0	-	12	2	0	0	-	-	14	85.7	100.0
Alternate	0	-	7	6	1	0	0	-	14	50.0	87.1
2 layers of wraps	14.6	-	6	4	2	0.5	0.5	0	13	46.1	77.0
Individual	0	-	11	2	0	0	-	-	13	84.6	100.0
Individual	0	-	11	1	0	-	-	-	12	91.7	100.0
Alternate	0	-	8	2	2	0	-	-	12	66.6	83.3
2 layers of wraps	5.2	-	6	3	1	0	0	-	11	54.5	82.0
Strips of wraps	0	-	5	3	1	1	0	-	10	50.0	80.0
5 layers of wraps	0	-	5	3	2	0	0	-	10	50.0	80.0
2 layers of wraps	3.5	-	8	1	0	-	-	-	9	88.8	100.0
Strips of wraps	0	-	7	2	0	-	-	-	9	77.8	100.0
Strips of wraps	0	-	5	3	1	0	-	-	9	55.5	89.0
Alternate	0	-	5	4	0	-	-	-	9	55.5	100.0
Alternate	0	-	6	2	1	0	0	-	9	66.6	89.0
Individual	0	-	7	-traces-	-	-	-	-	7	100.0	100.0
2 layers of wraps	2.3	-	3	4	0	-	-	-	7	42.8	100.0
Alternate	0	-	4	3	0	-	-	-	7	57.1	100.0
5 layers of wraps	0	-	4	2	0	0	-	-	6	66.6	100.0

(Cont'd)



Table 1 (Cont.)

Mode of packing	Residual biphenyl in wraps (mg/fruit)	Odor of fruit <sup>a</sup>	Biphenyl volatilized during aeration							Biphenyl volatilized (% of total)	
			μg of biphenyl per fruit							1st day	1st and 2nd days
			1st day	2nd day	3rd day	4th day	5th day	6th day	Total		
Alternate	0	-	3	2	1	0	-	-	6	50.0	84.0
Alternate	0	-	2	2	0.5	0.5	0	-	5	40.0	80.0
Alternate	0	-	3	0	0	-	-	-	3	100.0	100.0
Alternate	0	-	1	1	0	-	-	-	2	50.0	100.0

a Biphenyl, + detectable, - not detectable.

Table 2

Volatilization of biphenyl from Valencia oranges  
after removal of biphenyl wraps

Mode of packing	Residual biphenyl in wraps (mg/fruit)	Odor of fruit <sup>a</sup>	Biphenyl volatilized during aeration							Biphenyl volatilized (% of total)	
			μg of biphenyl per fruit							1st day	1st and 2nd days
			1st day	2nd day	3rd day	4th day	5th day	6th day	Total		
Individual	14	+	93	25	12	0	0	-	130	71.5	90.7
5 layers of wraps	5.8	+	75	21	16	1	0	-	113	66.4	84.8
Individual	1.3	+	57	25	2	2	0	-	86	66.3	95.3
Individual	4	+	50	23	6	1	0	-	80	62.5	91.2
Individual	8	+	52	21	2	0	0	-	75	69.3	97.3
Alternate	1	+	45	17	4	2	2	0	70	64.3	88.6
Individual	7	+	50	10	2	0	0	-	62	80.6	96.8
Strips of wraps	1.2	-	40	7	9	0	-	-	56	71.4	83.9
Individual	4	-	36	13	0	-	-	-	49	73.4	100.0
Strips of wraps	0	-	30	11	3	3	2	0	49	61.2	83.6
Individual	0	-	38	3	2	2	0	0	45	84.4	91.1
Alternate	1	-	18	10	6	2	0	0	36	50.0	77.7
2 layers of wraps	2	-	17	6	4	3	1	0	31	54.8	74.2

(Cont'd)



Table 2 (Cont.)

Mode of packing	Residual biphenyl in wraps (mg/fruit)	Odor of fruit <sup>a</sup>	Biphenyl volatilized during aeration							Biphenyl volatilized	
			(µg of biphenyl per fruit)							(% of total)	
			1st day	2nd day	3rd day	4th day	5th day	6th day	Total	1st day	1st and 2nd days
Alternate	1	-	17	8	4	2	0	-	31	54.3	80.6
5 layers of wraps	traces	-	14	6	4	0	0	-	24	58.3	83.3
Individual	0	-	12	5	3	2	0	-	22	54.5	77.2
Individual	0	-	13	6	1	1	0	-	21	61.9	90.5
Alternate	1	-	9	3	0	-	-	-	12	75.0	100.0
2 layers of wraps	0.4	-	8	2	0	-	-	-	10	80.0	100.0
Individual	0	-	6	4	0	-	-	-	10	60.0	100.0
Individual	0	-	4	2	2	0	-	-	8	50.0	75.0

a Biphenyl, + detectable, - not detectable.

Table 3

Grouping of oranges according to amounts of biphenyl volatilized from fruit during six consecutive days of aeration (data from 89 samples)

Aeration period	µg of biphenyl volatilized/fruit/day						
	0- $\leq$ 1	1-5	6-10	11-20	21-40	41-100	100-470
	<u>Number of samples</u>						
1st day	0	12	16	24	11	18	8
2nd day	6	39	22	6	11	5	0
3rd day	31	42	6	4	6	0	0
4th day	55	27	1	2	4	0	0
5th day	61	25	3	0	0	0	0
6th day	74	15	0	0	0	0	0



A certain parallelism was noted between the amounts of volatilized biphenyl and the intensity of odor of biphenyl. During the first day of aeration, relatively high amounts of biphenyl, reaching a few hundred micrograms of biphenyl per fruit, were volatilized from oranges having an easily detectable odor of biphenyl whereas no more than a few tens of micrograms of biphenyl per fruit were volatilized from oranges having a weak or barely detectable odor. The amounts of biphenyl volatilized during the first 24 or 48 hours could, to a certain degree, serve as an indicator of intensity of biphenyl odor on the fruit at the moment of removal of biphenyl wraps.

Biphenyl odor is not persistent. Odor intensities follow the volatilization intensities, and clearly decrease during aeration of the fruit, especially during the first few hours of aeration. The odor of biphenyl disappears within a day or two after removal of the wraps, and before biphenyl volatilization ceases. If, during the first day of aeration up to  $470\mu\text{g}$  of biphenyl were volatilized from oranges which had the odor of biphenyl after removal of the wraps, then, after one or two days of aeration (just like the fruit without biphenyl odor), amounts of biphenyl less than  $41\mu\text{g}$  per day (Tables 1 and 2) are volatilized. The average volatilization intensities were less than  $5\mu\text{g}$  of biphenyl/fruit/hour (Fig. 1).

These observations, resulting from the objective study of fruit odor, agree with the findings (mentioned in the introduction) based on organoleptic evaluation of the odor, according to which odor of biphenyl is not perceptible on all the fruits, is not persistent, and disappears after a day or two of aeration of the fruit.

#### Effect of packing materials and biphenyl quantities on fruit odor

##### Mode of packing

There is a clear relationship between the mode of packing and fruit odor. Larger amounts of biphenyl were volatilized from fruit which was in direct contact with the wraps (individual packing and alternate packing) and the fruit more often



had the odor of biphenyl than did fruit protected by two layers of paper (Tables 4 and 5). It is possible that proximity of the biphenyl source to the fruit plays a role in the amount of biphenyl existing on the fruit at the moment of removal of the wraps, and, consequently, in the quantities of volatilized biphenyl and in odor perceptibility.

It is worthwhile noting that, of the various modes of packing studied, individual wrapping is generally the most effective, whereas packing with two layers of paper is the least effective for the protection of fruit stored in wooden boxes. Proximity of biphenyl source to fruit, although undesirable insofar as odor of fruit is concerned, is nevertheless necessary in order to ensure a sufficiently rich atmosphere of biphenyl around all the fruit, thus protecting it from rot development.

#### Initial and residual amounts of biphenyl in the wraps

The initial amount of biphenyl in the wraps does not play a decisive role in the odor of the fruit. Fruit both with and without biphenyl odor was found to exist according to mode of packing or length of storage, in crates protected by 17 and 19 mg of biphenyl per fruit, and 34 and 38 mg per fruit (Tables 4 and 5).

The biphenyl that remains in the wraps at the time of their removal is the essential cause of the odor of biphenyl detectable in the fruit (Tables 4, 5 and 7). With individual wraps, the odor of biphenyl was detectable on almost all the fruit even when the wraps still contained only very small amounts of biphenyl, of the magnitude of a few mg. With this mode of packing, there seems to be a relationship between odor intensity and the amount of biphenyl that remains in the wraps. This is so since, generally, the amounts of biphenyl volatilized from the fruits, taken at successive periods of storage, and, accordingly, the odor intensities, decrease as do the residual amounts of biphenyl in the corresponding wraps (Table 4). With the other modes of packing, the fruit sometimes smelled of biphenyl and sometimes did not, even when the wraps still contained relatively high amounts of biphenyl (such as 27 mg of biphenyl per fruit).



Table 4

Effect of mode of packing and of biphenyl absorbed by fruit, on the odor of Shamouti oranges (picked 22.XII.63) and on the amounts of biphenyl volatilized after removal of the wraps

Mode of packing	Storage duration (days)	Residual biphenyl in wraps (mg/fruit)	Odor of fruit <sup>a</sup>	Average weight of fruit (g)	B i p h e n y l		
					Absorbed	volatilized during 5-6 days of aeration	
					ppm whole fruit	ppm whole fruit	% of biphenyl absorbed
ORANGES PROTECTED WITH 38 MG OF BIPHENYL PER FRUIT							
Individual packing <sup>b)</sup>	6	17.5	±	221	17.41	1.09	6.20
	13	4.5	±	238	35.22	0.29	0.82
	19	2.7	-	221	39.83	0.17	0.40
	27	0.0	-	207	62.42	0.03	0.05
Strips of wraps <sup>b)</sup>	13	present	±	219	43.46	0.34	0.78
	19	present	±	221	48.88	0.07	0.15
	27	0	-	199	47.61	0.07	0.15
Two layers of wraps	6 <sup>c</sup>	20.8	-	208	9.96	0.06	0.63
	6 <sup>f</sup>	20.8	-	179	3.81	traces	-
	13 <sup>h</sup>	26.7	-	213	16.15	0.09	0.58
	19 <sup>g</sup>	7.5	-	187	23.68	0.37	1.56
	27 <sup>g</sup>	14.6	-	216	26.21	0.05	0.19
Five layers of wraps	6 <sup>e</sup>	11.4	±	198	22.77	0.37	1.62
	13 <sup>d</sup>	10.0	-	205	21.36	0.12	0.56
	19 <sup>d</sup>	1.9	-	189	38.97	0.22	0.52
	27 <sup>d</sup>	0.0	-	182	55.40	0.11	0.20

(Cont'd)



Table 4 (Cont.)

Mode of packing	Storage duration (days)	Residual biphenyl in wraps (mg/fruit)	Odor of fruit <sup>a</sup>	Average weight of fruit (g)	B i p h e n y l		
					Absorbed ppm whole fruit	volatilized during 5-6 days of aeration	
						ppm whole fruit	% of biphenyl absorbed
ORANGES PROTECTED WITH 19 MG OF BIPHENYL PER FRUIT							
Individual packing <sup>b)</sup>	13	0	-	223	23.74	0.10	0.42
	19	traces	±	191	40.60	0.29	0.75
	27	0	-	208	29.76	0.06	0.20
Strips of wraps <sup>b)</sup>	6	present	±	210	20.17	0.27	1.83
	13	0	-	243	25.13	0.11	0.44
	19	0	-	214	42.19	0.04	0.09
	27	0	-	226	23.47	0.04	0.17
Two layers of wraps	6 <sup>c</sup>	5.2	-	215	7.25	0.05	0.68
	6 <sup>f</sup>	5.2	-	212	3.55	traces	-
	13 <sup>f</sup>	11.7	-	221	10.13	0.05	0.49
	19 <sup>f</sup>	3.5	-	216	17.87	0.04	0.22
	27 <sup>d</sup>	2.3	-	228	5.03	0.03	0.59
Five layers of wraps	6 <sup>c</sup>	4.7	±	228	20.73	0.23	1.19
	6 <sup>d</sup>	4.0	-	214	16.43	0.03	0.18
	13 <sup>e</sup>	4.2	-	217	31.25	0.07	0.22
	19 <sup>d</sup>	0	-	211	31.30	0.07	0.23
	27 <sup>d</sup>	0	-	215	34.99	0.04	0.13
<u>Alternate packing</u>							
One wrapped and unwarppd fruit							
Wrapped fruits	13	0	-	222	19.14	0.04	0.21
	19	0	-	200	31.71	0.03	0.09
	27	0	-	217	33.58	0.03	0.09

(Cont'd)



Table 4 (Cont.)

Mode of packing	Storage duration (days)	Residual biphenyl in wraps (mg/fruit)	Odor of fruit <sup>a</sup>	Average weight of fruit (g)	B i p h e n y l		
					Absorbed	volatilized during 5-6 days of aeration	
					ppm whole fruit	ppm whole fruit	% of biphenyl absorbed
Unwrapped fruits	13	0	-	221	19.21	0.01	0.07
	19	0	-	199	28.38	0.09	0.32
	27	0	-	203	24.38	0.03	0.12
One layer of wrapped fruit and one of unwrapped fruit							
Wrapped fruits	6	1.8	±	199	16.60	0.30	1.80
	13	2.2	-	229	18.61	0.10	0.56
	19	0	-	250	15.96	0.06	0.37
	27	0	-	216	32.04	0.04	0.12
Unwrapped fruits	6	1.8	-	207	23.62	traces	-
	13	2.2	-	188	19.74	0.09	0.45
	19	0	-	228	12.35	0.12	0.97
	27	0	-	228	36.46	0.06	0.15
One row of wrapped fruit and one of unwrapped fruit							
Wrapped fruits	13	2.5	-	197	20.61	0.18	0.87
	19	1.2	-	203	30.19	0.15	0.49
	27	0	-	198	31.37	0.07	0.24
Unwrapped fruits	13	2.5	±	213	20.23	0.23	1.13
	19	1.2	-	229	24.35	0.07	0.29
	27	0	-	216	21.79	0.09	0.41

a - Biphenyl, ± detectable, - not detectable.

Fruits and wraps were taken from: b - various places in the box, c - beneath the lid, d - the middle of the box, e - the bottom of the box, f - the fruit was taken from the middle of the box and the wraps beneath the lid, g - the fruit was taken from the middle and the wraps from the bottom of the box.



Table 5

Effect of mode of packing and of biphenyl absorbed by oranges  
on the odor of the fruit and on the amounts of biphenyl vola-  
tilized after removal of the wraps

Mode of packing	Residual biphenyl in wraps (mg/ fruit)	Odor of fruit <sup>a</sup>	Average weight of fruit (g/ fruit)	B i p h e n y l		
				absorbed	volatilized during	
				ppm whole fruit	5-6 days of aeration	% of biphenyl absorbed
SHAMOUTI ORANGES <sup>b</sup>						
<u>Oranges protected with 38 mg of biphenyl per fruit</u>						
Individual packing	15.3	±	217	45.22	1.92	4.24
Two layers of wraps	5.3	±	214	14.17	0.37	2.62
Five layers of wraps	18.7	-	218	28.24	0.14	0.60
<u>Oranges protected with 19 mg of biphenyl per fruit</u>						
Individual packing	2.0	±	218	29.80	1.20	4.60
Two layers of wraps	1.9	-	191	12.68	0.18	1.41
Five layers of wraps	0.4	-	188	36.80	0.34	0.93
Alternate packing						
Wrapped fruits	6.3	±	183	51.12	0.62	1.21
Unwrapped fruits	6.3	±	189	27.11	0.91	3.31

(Cont'd)



Table 5 (Cont.)

Mode of packing	Residual biphenyl in wraps (mg/fruit)	Odor of fruit <sup>a</sup>	Average weight of fruit (g/fruit)	B i p h e n y l		
				absorbed	volatilized during 5-6 days of aeration	
				ppm whole fruit	ppm whole fruit	% of biphenyl absorbed
VALENCIA ORANGES <sup>c</sup>						
<u>Oranges protected with 34 mg of biphenyl per fruit</u>						
Individual packing	1.3	±	153	45.55	0.56	1.2
Strips of wraps	present	-	182	21.73	0.31	1.4
Two layers of wraps	2.0	-	150	15.70	0.20	1.3
Five layers of wraps	5.8	±	150	27.11	0.75	2.7
Alternate packing						
Wrapped fruits	1.0	±	147	39.17	0.47	1.2
Unwrapped fruits	1.0	-	160	22.81	0.21	0.9
<u>Oranges protected with 17 mg of biphenyl per fruit</u>						
Individual packing	0	-	149	17.31	0.13	0.8
Strips of wraps	0	-	174	18.87	0.27	1.4
Two layers of wraps	0.4	-	175	17.65	0.05	0.3
Five layers of wraps	traces	-	145	27.66	0.16	0.6
Alternate packing						
Wrapped fruits	1.0	-	155	22.49	0.19	0.8
Unwrapped fruits	1.0	-	178	14.73	0.06	0.4

a Biphenyl ± detectable, - not detectable.

b Oranges picked on 27.I.1964, wraps removed after 11 days of storage.

c Oranges picked on 6.IV.1964, wraps removed after 10 days of storage.



Table 6

Effect of mode of packing on the odor of fruit and on the amounts  
of biphenyl volatilized after removal of the wraps

Mode of Packing	Number of samples examined	<u>Samples with odor of biphenyl</u>		<u>Samples without odor of biphenyl</u>	
		Number of samples	Biphenyl volatilized from fruit (ppm whole fruit)	Number of samples	Biphenyl volatilized from fruit (ppm whole fruit)
Individual packing	11	6	0.24 - 1.92	5	0.03 - 0.17
Strips of wraps	9	2	0.27 - 0.34	7	0.04 - 0.31
Two layers of wraps	14	1	0.37	13	0.03 - 0.37
Five layers of wraps	13	3	0.23 - 0.75	10	0.03 - 0.34
Alternate packing	26	5	0.23 - 0.91	21	0.01 - 0.21

Table 7

Effect of the presence of biphenyl in the wraps at time of their removal,  
on the odor of oranges

Mode of Packing	Number of samples examined	<u>Samples with wraps which still contained biphenyl</u>				<u>Samples with wraps which no longer contained biphenyl</u>		
		Number of samples	Residual biphenyl in wraps (mg/fruit)	Number of samples with odor of biphenyl	Number of samples without odor of biphenyl	Number of samples	Number of samples with odor of biphenyl	Number of samples without odor of biphenyl
Individual packing	11	7	1.2-17.5	6	1	4	0	4
Strips of wraps	9	4	present	2	2	5	0	5
Two layers of wraps	14	14	2.4-26.7	1	13	0	0	0
Five layers of wraps	13	10	traces-18.7	3	7	3	0	3
Alternate packing	26	14	1.0 - 6.3	5	9	12	0	12



On the other hand, in all cases where the wraps, regardless of the mode of packing, no longer contained biphenyl, the odor was not detectable on the fruit (Tables 4, 5 and 7). Thus, in order to avoid marketing fruit with the odor of biphenyl, all traces of biphenyl have to disappear from the wraps before distribution of the fruit.

The choice of initial amount of biphenyl in the wraps, therefore, is most important; such amount must be as small as possible, and must correspond, according to mode of packing, condition and period of transportation and storage, to the minimum amount of biphenyl necessary to protect the fruit against rot. In cases where, at the time of distribution of the fruit, a small amount of biphenyl still remains in the wraps, the eventual resultant light odor should disappear very rapidly after removal of the wraps.

In spite of the fact that, apparently, odor of biphenyl is more often perceptible on fruit that is wrapped individually, this mode of packing, with papers impregnated with a well-fixed amount of biphenyl, appears to be the best. This is so since, because of the weaker concentration of biphenyl per  $\text{cm}^2$  of packing material, the biphenyl disappears more rapidly, and more evenly, from the individual packing than from the other modes of packing, where two or five sheets of papers are used.

#### Effect of biphenyl absorbed by fruit during storage on the odor of the fruit

No relationship exists between the amount of biphenyl absorbed by the fruit and the odor of the fruit (Tables 4 and 5). The amounts of biphenyl absorbed by the fruit on which odor was detectable oscillated, in the three experiments, between 14.17 and 45.55 ppm; and in the fruit without odor, between 3.81 and 62.42 ppm. The amounts of biphenyl absorbed by the fruit generally increase with storage time, whereas the quantities of biphenyl volatilized from the fruit, after removal of the wraps, decrease respectively, so that intensities of biphenyl odor on the fruit become weaker and weaker, or the odor ceases to be detectable. A significant example is that of four samples of fruit taken from the same group of fruit, successively, after 6, 13, 19 and 27 days of storage (Table 4). The fruit absorbed



increasing amounts of biphenyl, of 17.41, 35.33, 39.83 and 62.42 ppm, whereas decreasing amounts of 1.09, 0.29, 0.17 and 0.03 ppm of biphenyl, respectively, were volatilized, and the odor of biphenyl was detectable only on the fruit removed after 6 and 13 days of storage.

In the cases studied in this work relating to oranges protected with biphenyl wraps and stored in wooden boxes, the amounts of biphenyl volatilized from the fruit after removal of the wraps constitute a very small part of biphenyl absorbed, so that the aeration and disappearance of the odor have a very slight influence on the amounts of biphenyl residue in the fruit, and have, from that viewpoint, very little importance.

### C O N C L U S I O N S

The following conclusions can be drawn from the objective study of the odor on biphenyl-protected oranges, based on determination of biphenyl volatilized from the fruit. The fruit was protected by biphenyl wraps and stored in wooden boxes.

1. During the first day following removal of the biphenyl wraps, there volatilize from the oranges very different amounts of biphenyl, ranging from one to a few hundred micrograms of biphenyl per fruit. Volatilization intensity decreases very rapidly, and, after a maximum of a few days, biphenyl volatilization ceases. The major part of the volatilized biphenyl is volatilized during the first 24 or 48 hours.
2. The odor of biphenyl is not detectable on all biphenyl-protected/fruit, even on all the fruit from which measurable amounts of biphenyl are volatilized. The odor was detectable only on fruit from which, during 24 hours, at least some tens of micrograms of biphenyl were volatilized per fruit.
3. The odor of biphenyl is not persistent, its intensity decreases rapidly, and one or two days after removal of the wraps relatively small amounts of biphenyl are volatilized from the fruit, so that the odor of biphenyl is no longer detectable on the fruit.



4. No relationship exists between the amount of biphenyl absorbed by the oranges during storage and the odor of the fruit. The amount of biphenyl absorbed is very slightly affected by the volatilization of biphenyl from the fruit after removal of the wraps and the disappearance of the odor.
5. The essential cause of the odor of biphenyl which is detectable on some fruits at the time of removal of the wraps is the biphenyl which has remained in the wraps. In order to avoid marketing fruits which might have an odor of biphenyl, the wraps used must contain a minimum amount of biphenyl, just sufficient to protect the fruit during transportation and storage, so that the biphenyl may disappear from the wraps prior to distribution of the fruit.

The conclusions from the objective study of the odor of fruit protected by biphenyl wraps are in accordance with the observations made by various research workers based on organoleptic evaluation of the odor, but contradict the observations of some consumers regarding the persistence of the odor of biphenyl on fruit.

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## ריח תפוזים הארוזים בנייר-דיפניל ומאוחסנים בארגזי ברז

מאת

אנה רייזמן

### ת ק צ י ר

בעונת ההדרים תשכ"ד (1963/64) נערך מחקר לבחינת ריח התפוזים לאחר הסרת נייר הדיפניל מהפרי. הבחינה נעשתה בשיטה אובייקטיבית המתבססת על בדיקת כמות הדיפניל הנפלטת מהפרי. המחקר נערך בתפוזי שאמוטי וואלנסיה אשר נארוזו בצורות שונות בנייר דיפניל, ואוחסנו בארגזי ברז במשך 7-27 ימים.

מהמחקר התברר, שלאחר הסרת ניירות הדיפניל נפלטו מהתפוזים, במשך 24 שעות, כמויות שונות מאוד של דיפניל, והן נעו ממקורגראם אחד ועד לכמה מאות מיקרוגראם לפרי.

עוצמת הפליטה יורדת מהר מאוד עם הזמן, ואחרי כמה ימי איורור היא מסתיימת, למעשה

לאחר הסרת ניירות דיפניל לא הורגש ריח הדיפניל בכל הפירות אשר אוחסנו כשהם ארוזים בניירות אלה, אלא רק באלה, אשר מהם נפלטו במשך 24 שעות לפחות כמה עשרות מיקרוגראמים דיפניל לפרי.

ריח הדיפניל אינו קבוע (persistent), עומצתו יורדת במהירות, ויום או יומיים לאחר הסרת הניירות אין הריח מורגש יותר. הסיבה העיקרית לריח הדיפניל המורגש בפירות נובעת מן הדיפניל שנותר עוד בניירות בעת ההסרה.

על-מנת למנוע שיווקם של תפוזים בעלי ריח של דיפניל, צריכים ניירות הדיפניל להכיל את החומר בכמויות המינימאליות ההכרחיות למניעת רקבונות. כמויות אלה יש להתאים לתנאי האחסון והמשלוח, וחשוב שכל הדיפניל יעלם מהניירות עוד לפני הסרתם.



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המכון הלאומי והאוניברסיטאי לחקלאות  
מכון וולקני לחקר החקלאות  
האגף לאיחסון וטכנולוגיה של מזון  
המחלקה לאיחסון פירות וירקות

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מאת

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