Biphenyl Absorption of Citrus Fruits: The Effect of Variety, Color Class, and Injury by Freezing, Peeling, and Lack of Oxygen

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Biphenyl Absorption Of Citrus Fruits: The Effect Of Variety, Color Class, and Injury By Freezing, Peeling, and Lack Of Oxygen

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SUMMARY

Some biological and environmental factors affecting biphenyl absorption were investigated to determine to what extent biphenyl residues in citrus could be controlled during storage and shipping.

Valencia and navel oranges held 14 days in a near-saturated biphenyl atmosphere at room temperature (76° to 84° F.) absorbed comparable amounts of biphenyl. Valencia oranges held 6 weeks in a near-saturated biphenyl atmosphere at room temperature absorbed nearly 375 parts per million (p.p.m.) biphenyl. Eureka lemons held under the same conditions absorbed less than 70 p.p.m. biphenyl.

Green oranges and lemons absorbed more biphenyl than the fully colored fruit of comparable size.

Oranges absorbed 3 times as much biphenyl as lemons when held 3 or 4 days in a biphenyl atmosphere. Injury by freezing increased biphenyl absorption by oranges 2 to 4 times and by lemons 6 to 12 times compared with uninjured fruit. Different kinds of citrus absorbed similar amounts of biphenyl when injured by freezing.

When held in nitrogen with biphenyl, Valencia oranges absorbed more than twice as much biphenyl and lemons absorbed nearly 6 times as much biphenyl as comparable fruit held in air.

Injury by peeling increased biphenyl absorption. On a whole fruit basis, separated orange peel absorbed 4 times more biphenyl and separated pulp segments absorbed slightly more biphenyl than the whole intact fruit.

Increasing the respiration rate of oranges and lemons by treating with Ethrel did not increase biphenyl absorption.

INTRODUCTION

Biphenyl has been used as a fungistatic agent in the control of citrus fruit decay since Tomkins first reported its effectiveness in 1935 *(11, pp. 129–131)*.[1] In commercial practice, pads of kraft paper treated with biphenyl are placed inside cartons of citrus fruit during packaging. The biphenyl volatilizes from the pads into the atmosphere of the carton. The biphenyl vapor controls decay in citrus fruit through inhibition of fungal vegetative growth and normal spore formation (*7*). At the same time, however, biphenyl is absorbed by the citrus fruit in the carton. The accumulation of biphenyl in the fruit must be kept below the legal tolerance of 110 p.p.m. for the United States and 70 p.p.m. for the European Economic Community (EEC). Previous research (*9*) has indicated that oranges might exceed the EEC's tolerance because of the prolonged storage required for overseas shipments.

[1] Italic numbers in parentheses refer to Literature Cited, p. 6.

The amount of biphenyl absorbed by the fruit varies with storage conditions and kind of citrus. Rygg and others (*10*) reported that oranges absorb 2 to 5 times as much biphenyl as lemons and twice as much as grapefruit under the same storage conditions. Hayward and Edwards (*3*) compared biphenyl absorption by 14 different varieties and kinds of citrus during 2 weeks' storage at 70° F. Kumquats, tangerines, and possibly tangelos absorbed biphenyl in excess of 110 p.p.m. Valencia oranges absorbed about 70 p.p.m., while Hamlin oranges, Duncan and Marsh grapefruit, and Temple oranges absorbed 40 to 60 p.p.m. biphenyl. Pineapple oranges and limes absorbed 30 to 40 p.p.m. and lemons absorbed less than 20 p.p.m. biphenyl. Hayward and Edwards (*4*) reported that tangerines absorbed twice as much biphenyl as oranges and 4 times as much as grapefruit under the same conditions.

Some biological and environmental factors affecting biphenyl absorption were investigated to determine to what extent biphenyl residues could be controlled during storage and shipping. Tests were undertaken to determine the effect of (1) color class, (2) 2-chloroethane phosphonic acid (Ethrel), (3) oxygen-free atmospheres, and (4) mechanical and freezing injury on biphenyl absorption by citrus fruits. In addition, the daily and weekly accumulation of biphenyl by oranges and lemons was followed in a near-saturated atmosphere of biphenyl to determine how much biphenyl would be absorbed by citrus fruits.

EXPERIMENTAL METHODS

Biphenyl Chamber

The biphenyl chamber consisted of a large enclosed metal cabinet. Biphenyl crystals were spread evenly on the bottom of the chamber. An open container of biphenyl crystals was placed inside at the top of the chamber. Because of the restricted ventilation of the chamber, the biphenyl vapor in the atmosphere inside the chamber was probably near saturation. The maximum concentration of biphenyl vapor possible at room temperature is approximately 73 to 79 micrograms per liter (*1*). Wire baskets containing the citrus fruit were placed on shelves inside the chamber. The fruit did not come in contact with the biphenyl crystals.

Aeration Jars

Anaero-Jars, size No. 3, 5-gal. capacity were used in place of the chamber when an atmosphere other than air was desired. Humidified air or nitrogen was flushed through the jars at a rate of 200 milliliters (ml.) per minute.

Temperature

Since it was desirable for the fruit to absorb a maximum amount of biphenyl in the chamber and to have a maximum amount of biphenyl vapor available in the jars, room temperature (76° to 84° F.) was chosen for all tests except one. Green and fully colored oranges were held at 50°.

Biphenyl Pads

Biphenyl pads, each containing 2.38 ± 0.07 grams of biphenyl, were used as a source of biphenyl vapor in the jars. Four pads were placed inside each jar.

Citrus Fruit

Unwaxed fruit, washed by standard packinghouse procedures, were used except for the green and fully colored fruit which were hand picked in the orchard and washed in the laboratory. Green and fully colored fruits were of comparable size.

Biphenyl Analyses

Biphenyl residues were determined by thin-layer chromatography and spectrophotometric measurements according to Norman and others (*5*). Duplicate samples of 300 grams of fruit were analyzed. Biphenyl content represents parts per million of biphenyl on the basis of fresh fruit weight.

Ethrel Treatment

The citrus fruits were submerged in a water solution containing 5,000 p.p.m. 2-choloroethane phosphonic acid (Ethrel) for 2 minutes and then air dried.

Treatments

The absorption of biphenyl in a near-saturated biphenyl atmosphere was determined for the following treatments:

(1) Valencia and navel oranges and Eureka lemons were held in the biphenyl chamber 6 weeks and analyzed daily or weekly;

(2) Green and fully colored Valencia oranges and Eureka lemons were compared after 7 days in the biphenyl chamber;

(3) Valencia and navel oranges, Lisbon and Eureka lemons, and Satsuma tangerines were frozen at —10° F., thawed overnight, and then held 3 days in the biphenyl chamber along with uninjured control fruit;

(4) Valencia and navel oranges and Eureka lemons were held 4 and 7 days in jars flushed with humidified air or nitrogen;

(5) Valencia orange peel and pulp, separated carefully by hand, were compared with whole fruit after storage for 3 days in the biphenyl chamber;

(6) Valencia and navel oranges and Eureka lemons, untreated and treated with Ethrel, were held 4 and 7 days in jars flushed with humidified air.

RESULTS AND DISCUSSION

The absorption of biphenyl by Valencia and navel oranges on a daily basis for a period of 14 days at room temperature is shown in figure 1. The rate of absorption was somewhat higher at the beginning than after the fruit had been in the biphenyl atmosphere for a few days. Very little difference in absorption was noted between Valencia and navel oranges. These oranges absorbed about 75 p.p.m. biphenyl by the 7th day and 106 to 134 p.p.m. by the 14th day in the biphenyl atmosphere.

The absorption of biphenyl by Valencia oranges and Eureka lemons on a weekly basis for a period of 6 weeks is shown in figure 2. The oranges lost 10 percent moisture in the 6-week period and the lemons, 16 percent. The biphenyl data are corrected to the initial weight basis. Room temperature was somewhat higher during this test than that shown in figure 1. The oranges absorbed nearly 120 p.p.m. biphenyl in 1 week and nearly 375 p.p.m. biphenyl by the end of the 6-week period. The lemons approached 70 p.p.m. biphenyl after 5 weeks but never exceeded this amount. The oranges absorbed 4½ times as much biphenyl as the lemons during the first 2 weeks, 5½ times as much the third week, and 6 times as much during the last 3 weeks of storage.

The absorption of biphenyl by different color classes of Valencia oranges and Eureka lemons was compared after storage for 7 days in a biphenyl atmosphere at room temperature. One lot of green lemons absorbed 150 p.p.m. biphenyl or twice the amount of biphenyl ab-

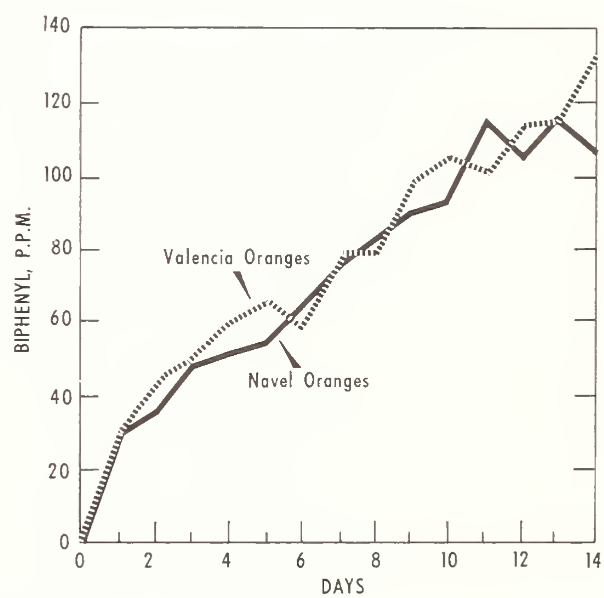

FIGURE 1.—The absorption of biphenyl by Valencia and navel oranges held in a near-saturated biphenyl atmosphere 14 days at 78° ±2° F.

TABLE 1.—*Absorption of biphenyl by citrus fruits injured by freezing and uninjured control fruit after storage in a near-saturated atmosphere of biphenyl at 78° ± 2° F.*

Kind of citrus	Days in biphenyl atmosphere	Biphenyl content of—	
		Fruit injured by freezing	Uninjured control fruit
		P.p.m.	*P.p.m.*
Valencia oranges	2	94	44
Valencia oranges	5	236	59
Navel oranges	4	140	53
Navel oranges	4	190	59
Lisbon lemons	3	164	28
Eureka lemons	3	240	20
Eureka lemons	4	179	15
Eureka lemons	4	235	20
Satsuma tangerines	4	154	54

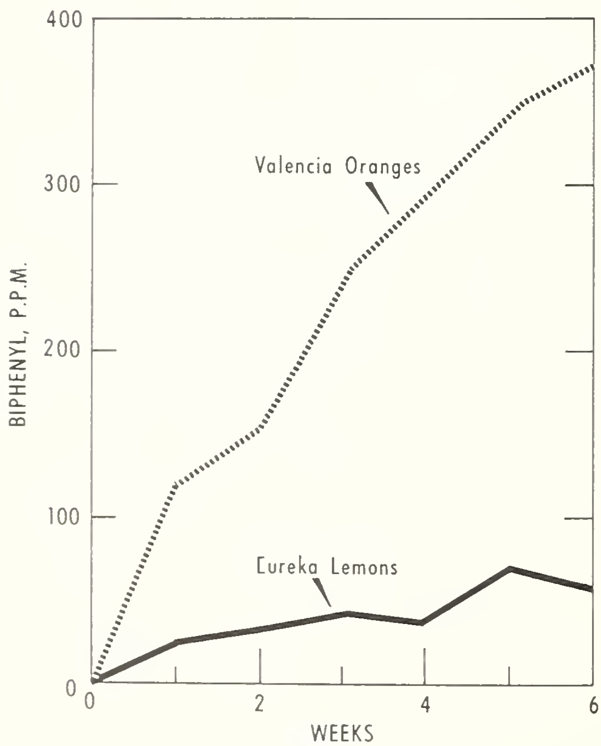

FIGURE 2.—The absorption of biphenyl by Valencia oranges and Eureka lemons held in a near-saturated biphenyl atmosphere 6 weeks at 82°± 2° F.

sorbed by fully colored lemons (70 p.p.m.). Another lot of green lemons absorbed 81 p.p.m. biphenyl or 5 times as much as that absorbed by fully colored lemons (16 p.p.m.). The difference in absorption between green and fully colored oranges was not as great as it was with lemons. Green oranges absorbed 55 p.p.m. or 1.4 times as much biphenyl as that absorbed by fully colored oranges (39 p.p.m.) after 2 weeks' storage at 50° F. The absorption of more biphenyl by green lemons and oranges than by fully colored fruit agrees with data reported by Rajzman (*6*).

Biphenyl absorption by fruit injured by freezing and uninjured control fruit after storage in a biphenyl atmosphere at room temperature is shown in table 1. Valencia oranges, injured by freezing, absorbed 2 to 4 times as much biphenyl as the control fruit. Tangerines and navel oranges injured by freezing absorbed 3 times as much biphenyl as comparable control fruit. Lisbon lemons injured by freezing absorbed 6 times as much and injured Eureka lemons absorbed 12 times as much biphenyl as the control fruit. Injury by freezing reduced the effectiveness of the physiological barrier limiting biphenyl absorption by the fruit. The difference in the amount of biphenyl absorbed by different kinds of citrus was no longer apparent when injured by freezing; injured lemons absorbed as much biphenyl as injured oranges.

Biphenyl absorption of oranges and lemons at room temperature in air and in nitrogen was measured. Valencia oranges held 7 days absorbed 87 p.p.m. biphenyl in air compared with 209 p.p.m. in nitrogen. Navel oranges held 4 days absorbed 48 p.p.m. biphenyl in air compared with 97 p.p.m. in nitrogen. Eureka lemons held 4 days absorbed 14 p.p.m. in air and 82 p.p.m. biphenyl in nitrogen. Injury of oranges and lemons caused by the lack of oxygen indicated that the effectiveness of the physiological barrier limiting absorption was reduced. In comparison to oranges injured by freezing, which absorbed 2 to 4 times as much biphenyl as uninjured oranges, Valencias held in nitrogen absorbed 2½ times and navels twice as much biphenyl as comparable oranges held in air. Eureka lemons injured by freezing absorbed 12 times as much biphenyl as uninjured fruit compared with lemons held in nitrogen which absorbed nearly 6 times as much biphenyl as comparable lemons held in air.

Absorption of biphenyl by the peel and pulp as separate fractions compared with the whole fruit when held in a biphenyl atmosphere 3 days at room temperature was measured. Two lots of whole Valencia oranges absorbed an average of 63 p.p.m. biphenyl. The peel absorbed an average of 243 p.p.m. and the pulp, 73 p.p.m. biphenyl on a whole fruit basis. Again, injury increased biphenyl absorption. The pulp, which normally contains only minute quantities of biphenyl in the whole fruit, absorbed more biphenyl as a separate fraction than the whole fruit.

Ethylene has been shown to increase the respiration rate of citrus (*2*). Ethrel has been shown to have physiological effects similar to gaseous ethylene (*8*). Ethrel was convenient to use in place of gaseous ethylene to increase the respiration rate of oranges and lemons while in the presence of biphenyl vapor. Biphenyl absorption by navel and Valencia oranges treated with Ethrel and held 4 and 7 days, respectively, at room temperature in a biphenyl atmosphere was measured. Ethrel-treated Valencias absorbed 56 p.p.m. biphenyl compared with 87 p.p.m. by untreated fruit after 7 days. Ethrel-treated navel oranges held 4 days in a biphenyl atmosphere absorbed 41 p.p.m. biphenyl compared with 48 p.p.m. by untreated fruit. Lemons treated with Ethrel and held 4 days in a biphenyl atmosphere absorbed 14 p.p.m. biphenyl and untreated lemons absorbed the same amount. Biphenyl absorption by citrus is apparently not affected by the rate of respiration.

These experiments indicate that (1) oranges may absorb as much as 375 p.p.m. biphenyl in 6 weeks at room temperature and possibly more with additional storage time, (2) lemons absorb considerably less biphenyl than oranges, (3) green oranges and lemons absorb more biphenyl than fully colored fruits, (4) biphenyl absorption by citrus fruit is increased by mechanical injury, injury by freezing, and injury from lack of oxygen, and (5) increasing the respiration rate of oranges and lemons with Ethrel treatment does not increase biphenyl absorption.

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