APPLE SCALD
Production and Control in the Laboratory

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This investigation was undertaken to determine the nature of the volatiles responsible for storage scald of apples. Crude ether extracts of activated carbon used for a storage season in a unit located in a commercial apple-storage warehouse were shown to have high activity in producing scaldlike injury to apples. This injury was initially indistinguishable from apple scald as it occurs in commercial refrigerated storage. Scald tests using fractions of the crude ether-free extract revealed that esters were most active in producing scaldlike injury; both alcohols and acids were much less active. Tests with synthetic compounds confirmed these observations. An apparatus was devised for testing various chemical solutions as scrubbing agents to remove injury-producing volatiles from the air. Of the solutions tested, aqueous alkaline permanganate proved to be the most effective.

Apple scald is physiological storage disorder that annually results in a major economic loss to the apple growers of the world. Because marketing of fall and winter varieties of apples directly from the tree is limited to about 3 months of the year, storage of a large portion of the crop is essential if apples are to be available to the consumer throughout the year at reasonable prices.

Characteristics of storage scald include a superficial browning of the apple surface, which affects only a few layers of cells directly below the cuticle. The unsightly appearance of the scalded apples lowers their market value, and the damage to the skin increases susceptibility to invasion by fungi. While scald affects most varieties of apples customarily held in refrigerated storage, some varieties are noticeably more susceptible than others. Rhode Island Greening, Northwestern Greening, Cortland, Stayman, Rome, and Grimes are among the varieties highly susceptible to scald. McIntosh, Delicious, and Wealthy are fairly resistant. Apple scald is almost entirely prevented in some varieties by delaying picking until the fruit is well matured. However, for long-term storage it is desirable to pick apples while in the firm or firm-ripe stage, thus necessitating the use of improved methods of scald prevention.

Brooks, Cooley, and Fisher (*1*) demonstrated that scald is a physiological disorder, which could be partially controlled by packing or wrapping apples in paper impregnated with mineral oil. Kidd and West (*5*) and Elmer (*2*) observed that apples in storage emitted volatile products which could affect storage behavior. Power and Chestnut (*6*, *7*) found that essential oils from McIntosh and other varieties of apples contained substantial amounts of isoamyl formate, isoamyl acetate, and isoamyl *n*-caproate, smaller amounts of isoamyl *n*-caprylate, geranyl formate, and geranyl acetate, and traces of geraniol and acetaldehyde. Recently, Henze *et al.* (*3*) analyzed apple storage volatiles collected on activated carbon, and reported methods for the separation of more than 30 constituents. Esters comprised the bulk of the volatiles, but alcohols, acids, and carbonyl compounds were also found. The free alcohols, methyl to octyl, were present, and the ester fraction upon hydrolysis and subsequent chromatographic separation of the ester components on silicic acid columns yielded methyl, ethyl, isopropyl, *n*-butyl, *n*-amyl, and *n*-hexyl alcohols. Propionic, *n*-butyric, *n*-caproic, and *n*-caprylic acids were identified, and formic, acetic, and *n*-valeric acids were indicated present. Acetaldehyde, acetone, propionaldehyde, and at least 15 additional and as yet unidentified carbonyl compounds also were present. Thompson (*14*, *15*) analyzed apple storage volatiles collected in dry ice traps. She reported formic, acetic, *n*-butric, and *n*-caproic acids present in the esterified form, and showed that formic and acetic acids occur in both the free and esterified form. The alcohols obtained upon saponification of the esters were found to be predominately methanol, ethanol, 1-propanol, and an unidentified six-carbon alcohol. Recently Huelin (*4*) reported acetaldehyde, propionaldehyde, and acetone as the predominant carbonyl compounds in volatiles produced by Granny Smith apples. Apple "essence" was analyzed by White (*16*), who found 92% of the volatile fraction to be alcohols. Those identified were methanol, ethanol, 2-propanol, 1-butanol, 2-butanol, *d*-2-methylbutanol, and 1-hexanol.

In attempts to remove volatiles from the storage atmosphere, Smock and Southwick (*11–13*) used activated carbon and activated carbon treated with bromine with some success. Schomer and Marth (*9*) showed that surface treatment of apples with a lanolin emulsion containing 100 p.p.m. of 1-napthaleneacetic acid minimized the incidence and severity of scald.

Table I. Surface Damage to Rome or Stayman Apples by Various Fractions of Apple Storage Volatiles

(Moving air test)

Treatment	Time (Hours) and Degree of Damage 8	12	24	30	36
(a) Crude ether-free extract	++	+++			
(b) Neutral fraction from (a)	++	+++			
(c) Saponified (b)	–	–	–[a]	++	+++
(d) Alcohols from (c)	–	–	–	++	+++
(e) Acids from (c)	–	–	–	–	–[b]
(f) Carbonyl-free (b)	++	+++			
(g) Alcohol-free (b)	++	+++			
(h) Satd. hydrocarbons from (b)	–	–	–	–	–

[a] Slight damage observed at 26 hours.
[b] Severe damage after 1 week.
– No damage.
\+ Slight damage, less than 1/5 apple surface damaged.
++ Medium damage, 1/5–3/5 apple surface damaged.
+++ Severe damage, more than 3/5 apple surface damaged.

Though activated carbon and oiled paper find wide use today in apple storage warehouses, more efficient control measures need to be developed.

Materials and Methods

Apple storage volatiles were collected by passing air through activated carbon in a commercial unit (W. B. Connor Engineering Corp., Danbury, Conn.). The unit was situated in a commercial warehouse of 10,000-bushel capacity which contained chiefly Grimes, Romes, McIntosh, Delicious, and Stayman apples. Material collected on the carbon, therefore, represented a mixture of the volatile products from the various apple varieties as well as volatile materials from the boxes in which the apples were stored. At the end of the storage period the carbon was removed from the unit and 1180-gram portions were extracted with 2.5 liters of ethyl ether in a Soxhlet extractor for 24 hours. Ether was removed with the aid of a fractionating column at 35–36° C. and the yield of crude ether-free extract was approximately 14% of the total carbon weight extracted. This oily product had a pH of approximately 6 and an average saponification number of 161.0, and showed green fluorescence under ultraviolet radiation. All tests for nitrogen, sulfur, and halogens were negative. Tests for alcohols, esters, carbonyl compounds, and organic acids were positive.

The crude ether-free extract was separated into water-soluble, acidic, basic, and neutral fractions according to the procedures described by Shriner and Fuson (*10*). An alcohol-free fraction was prepared by warming for 15 minutes 75 grams of the crude ether-free extract in a solution containing 70 grams of potassium dichromate in 300 ml. of 2.5% sulfuric acid. A carbonyl-free fraction was prepared by removing carbonyl compounds from a portion of the neutral fraction with Girard's reagent T (*8*). Saturated hydrocarbons were separated by treating the neutral fraction with concentrated sulfuric acid. A free-alcohol fraction was separated from the crude ether-free extract by forming the phthalic acid half-esters and subsequently saponifying them to liberate the free alcohols (*3*). An ester-free fraction was prepared by saponifying 151 grams of the neutral fraction with 200 ml. of 40% potassium hydroxide for 24 hours. The above nine fractions were then tested for their ability to produce injury according to three different testing procedures.

Painting Directly on Apple Surface. Rome apples were used. A circle was drawn on the surface of the apple with a wax pencil, and the volatile material was painted uniformly over the circled area with an artist's paint brush. Circled areas covered approximately half the surface of each apple. The apples were held at room temperatures (26–28° C.) and observed at varying time intervals for the appearance of injury.

Storage in a Static Atmosphere Containing Volatiles. Three apples each, either Rome or Stayman, were placed on wire screen near the bottom of a desiccator 25 cm. in diameter, 10 ml. of the volatile fraction was placed on the bottom, and the desiccator was covered and held at room temperature (25–26° C.). Observations were made at varying time intervals to note the appearance of injury. Not only fractions from the crude ether-free extract were used in these tests, but pure chemical compounds were also tested.

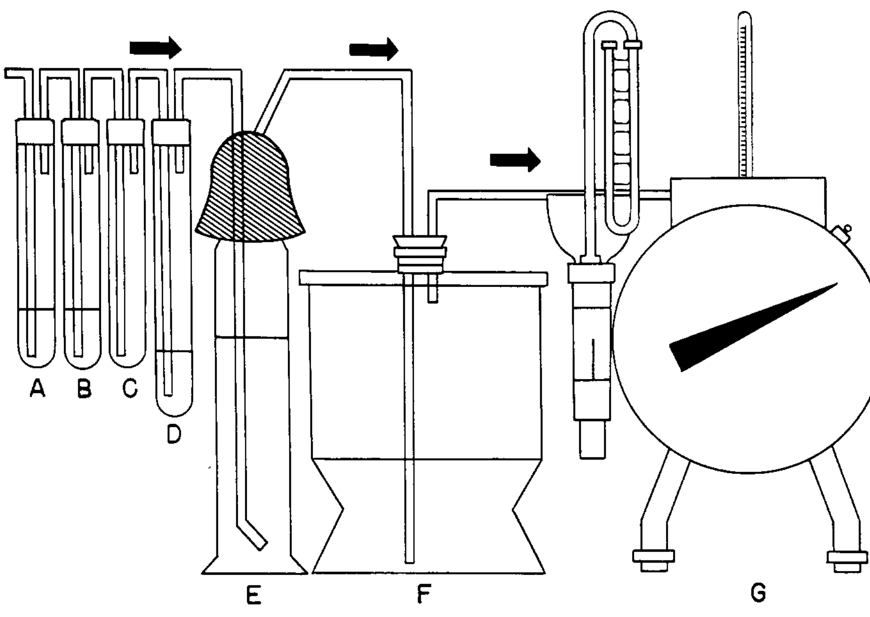
Storage in Moving Air Stream Containing Volatiles (Moving Air Test). Various fractions from the crude ether-free extract were passed over Stayman and Grimes apples in a desiccator. Air was drawn through the apparatus (Figure 1) with an aspirator at a rate of 0.8 to 1.0 cu. foot per hour. The desiccator was held at room temperature for laboratory tests (26–28° C.) and at 0° to 2° C. for cold room tests.

Effects of Crude Ether-Free Extract and Its Fractions

Differences in injury-producing ability of the different fractions were observed with all three methods of treatment.

Figure 1. Apparatus employed in moving air test

A + B. Test tubes (20 × 175 mm. borosilicate glass) containing 30 ml. of 10% KOH
C. Test tube (20 × 175 mm. borosilicate glass) to remove any entrained KOH
D. Test tube (20 × 300 mm. borosilicate glass) containing 30.0 ml. of volatile fraction
E. Air scrubber (500-ml.) containing glass wool in upper end to collect any entrained droplets
F. Desiccator (25 cm., 8-liter)
G. Air flow meter



In both the "painting" and "static" procedures the neutral apple volatiles free of alcohols and carbonyl compounds produced damage at a rate and severity equal to the crude ether-free extract containing all the apple volatile components. The acids, bases, alcohols, and carbonyl compounds required much longer periods to produce damage. The moving air test, however, seemed to duplicate most nearly the conditions which prevail in commercial apple storage and produced injury which was initially indistinguishable from the well-known storage scald. Accordingly, the results reported in detail for the different fractions are those obtained with the moving air test (Table I).

The crude ether-free extract and the neutral fraction both caused severe damage to apples in approximately 12 hours. The neutral fraction constituted over 90% of the total volatiles collected. Saponification materially reduced the toxicity of the neutral fraction; however, the neutral-saponified material was still capable of producing scaldlike injury at a rate and severity comparable to the alcohols obtained therefrom. The acids were much less active. Removal of carbonyl compounds and alcohols did not measurably reduce the toxicity of the neutral fraction. The saturated hydrocarbons which were obtained from the neutral fraction produced no injury. It was evident, therefore, that esters were the most active groups of compounds for the production of scald injury.

Effects of Individual Chemical Compounds

The differences in ability of various fractions obtained from the crude ether-free extract to produce apple injury were confirmed in studies with synthetic alcohols, acids, and esters (synthetic reagents purchased from Eastman Kodak Co., Rochester, N. Y., and Eastern Chemical Corp., Newark, N. J.). The synthetic products were purified by fractional distillation prior to use. In these tests the second or "static" procedure described earlier was used with Stayman apples.

The following esters were tested: methyl acetate, ethyl acetate, propyl acetate, *n*-butyl acetate, *n*-amyl acetate, *n*-hexyl acetate, *n*-butyl propionate, *n*-propyl butyrate, ethyl *n*-valerate, *n*-hexyl formate, ethyl *n*-caproate, ethyl propionate, ethyl *n*-butyrate. Despite their differences in volatility (boiling point range 57° to 169° C.), all these esters produced severe injury in 2 hours. The different alcohol and acid groups seemed to have little or no influence on the rate or severity with which injury was produced under these conditions.

The aliphatic organic acids from acetic to caproic produced injury at rates which decreased with chain length (Figure 2). Caprylic acid produced no injury in 24 hours.

The normal alcohols propyl to heptyl produced injury at rates which increased with chain length. Further increases were not observed with higher homologs, and indeed, lauryl alcohol produced no injury at the end of 24 hours. Ethyl alcohol also failed to produce injury after 24 hours.

These results indicated that ability of a compound to produce injury to the apple fruit was not a simple function of its volatility or functional chemical groups, but was also apparently concerned with a penetration factor relative to the apple, perhaps involving permeability of the waxy cuticle and the cells of the subepidermal region.

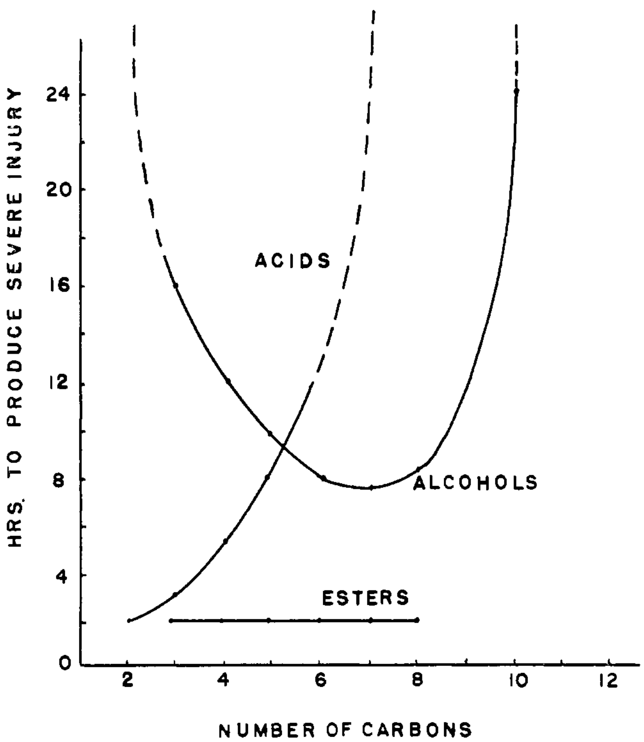


Figure 2. Production of chemical injury on apples by vapors of pure synthetic acids, alcohols, and esters of different carbon number

Chemical Solutions for Removal of Scald-Producing Volatiles

Solutions of various chemicals were tested for their effectiveness in removing scald-producing compounds from the complete apple volatiles in the moving air test (Table II). Strong alkalies, acids, or oxidizing agents were individually ineffective. The most satisfactory control was obtained with a 10% sodium or potassium hydroxide solution to which was added 10 grams of potassium permanganate per 100 ml. of solution. This combination probably converted the scald-producing esters, alcohols, acids, and carbonyl compounds to nonvolatile organic salts.

The efficiency of ester saponification under similar conditions at room temperature was determined with a weighed amount of pure ester in the moving air test. The ester vapors were passed through a standard alkali solution in the air scrubber, and after 24 hours the degree of neutralization of the standard alkali was measured. Efficiency of ester saponification increased with increased water solubility. Typical values obtained were 95% saponification for *n*-butyl formate, 75% for *n*-amyl acetate, and 51% for ethyl *n*-caproate. The use of a surface active agent would undoubtedly have increased the efficiency of saponification of water-insoluble materials.

The results of these studies suggested the possible use of alkaline permanganate as an air-scrubbing solution for control of scald in commercial apple storage warehouses. With this in view, some tests were also initiated at lower temperatures (0° to 2° C.) commonly used in apple storage (Table II). Moving air tests at room temperature had shown that a 5 p.p.m. concentration of the crude ether-free extract was sufficient to produce severe injury in 12 hours. However, at 0° to 2° C. the concentration fell far below this level and so delayed the reaction that 6 days were required for severe injury. Apples removed after exposure for 3 days at 0° to 2° C. exhibited no visible injury, but did develop severe injury upon standing at room temperature for 24 to 48 hours. This condition is commonly encountered in warehouse operations. Apples are often removed from the warehouse in apparently perfect condition only to develop severe scald on the way to market. The question whether alkaline permanganate can serve usefully in low temperature large scale storage remains for future work.

Table II. Effectiveness of Scrubbing Solutions in Removing Scald-Producing Compounds from Moving Air Stream Containing Apple Storage Volatiles

Scrubbing Solution	Time (Hours) and Degree of Damage								
	8	12	24	30	36	96	120	144	168
	Room Temperature (26° to 28° C.)								
(*a*) Distilled H_2O	++	+++							
(*b*) 1% KOH	−	−	+	+++					
(*c*) 10% KOH	−	−	−	+	+++				
(*d*) $KMnO_4$[a] + (*c*)	−	−	−	−	−	+	+++		
(*e*) $KMnO_4$[b] + (*c*)	−	−	−	−	−	−	−	+	+++
(*f*) $KMnO_4$[b]	++	+++							
(*g*) 10% H_2SO_4 + (*f*)	+	++	+++						
(*h*) 10% NaOCl + (*c*)	−	−	−	+	+++				
(*i*) 5% Alc. soln. chlorophyll	−	+	+++						
(*j*) 5% aq. soln. chlorophyll	−	+	+++						
	Cold Storage (0° to 2° C.)								
(*k*) Distilled H_2O	−	−	−	−	−	+	++	+++	
(*l*) 10% KOH or NaOH + (*f*)	−	−	−	−	−	−	−	−	−[c]

[a] 5 grams of $KMnO_4$ per 100 ml. of solution.
[b] 10 grams of $KMnO_4$ per 100 ml. of solution.
[c] Slight damage after 21 days, severe after 30 days.
− No damage.
+ Slight damage.
++ Medium damage.
+++ Severe damage.

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APPLE SCALD

Use of Alkaline Permanganate for Control in Refrigerated Storage

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Preliminary studies on the use of alkaline permanganate air scrubbing for control of apple scald in refrigerated storage rooms showed considerable promise. An experimental air-scrubbing apparatus is described and the approximate cost of operation is given.

Removal from the air of certain volatile compounds produced by apples in storage is highly desirable, as it would help delay ripening, prevent storage scald, and retain apple quality. A brief review of the chemical composition of apple volatiles and the characteristics of apple storage scald has been given (*1*).

Kuc *et al.* (*1*) showed that esters, which constitute the major fraction of apple storage volatiles, were the most active scald-producing agents under laboratory conditions. Air scrubbing with an alkaline permanganate solution was effective in trapping esters and other volatiles and suggested a possible control measure for scald in commercial apple storages. Smock (*2*) reported in a series of trials with 2-bushel lots of McIntosh apples in controlled storage that alkaline perman-