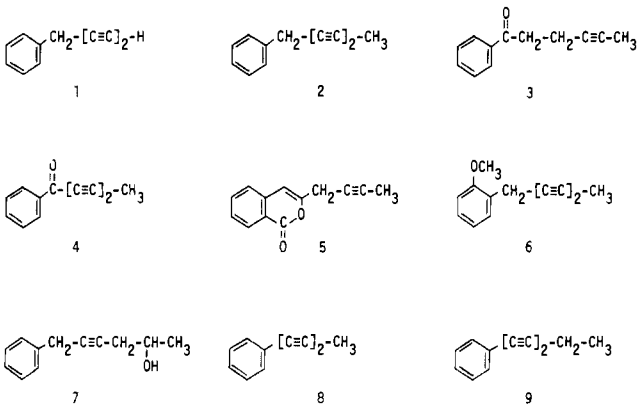

Figure 1. Phenylacetylenes: 1, 1-phenyl-2,4-pentadiyne; 2, capillen; 3, capillon; 4, capillin; 5, capillarin; 6, *o*-methoxycapillen; 7, capillanol; 8, norcapillen; 9, neocapillen.

Table I. Antifeeding Leaf Disk Test[a]

1-phenyl-2,4-pentadiyne (1)			capillen (2)		
larva of butterfly	% of eaten weight		larva of butterfly	% of eaten weight	
	sample disk[b]	control		sample disk[c]	control
A[d]	3	17	K[d]	0	49
B	0	19	L	0	41
C	0	21	M	11	58
D	0	34	N	0	85
E	0	45	O	0	35
F	0	29	P	0	39
G	0	20	Q	0	55
H	0	9	R	0	39
I	0	12	S	0	55
J	0	6	T	0	44

[a] Temperature was kept at 23-24 °C. [b] Cabbage leaf disk coated with 1-phenyl-2,4-pentadiyne (1, 0.3 mg). [c] Coated with capillen (2, 0.3 mg). [d] Average weight of 10 larvae is 0.2062 (A-J) and 0.2021 g (K-T).

139 [$(M-1)^+$, 78], 140 [M^+, 100], 141 [$(M+1)^+$, 14]; $\nu_{\equiv C-H}$ (liquid film) 3300 cm^{-1}; ν_{ArC-H} 3090, 3070, 3035 cm^{-1}; $\nu_{C\equiv C}$ 2295, 2230 cm^{-1}; $\nu_{ArC=C}$ 1600, 1495 cm^{-1}. The IR spectrum was identical with that of 1 reported by Bohlmann et al. (1962). Capillen (2, 74% of the essential oil) was isolated from the second eluate of the same fraction: ^1H NMR δ 1.88 (3 H, t, J = 1 Hz, $C\equiv C-CH_3$) 3.66 (2 H, m, Ph-CH_2-$C\equiv C$), 7.35 (5 H, s, Ar*H*); MS (rel intensity) m/z 152 [$(M-2)^+$, 43], 153 [$(M-1)^+$, 100], 154 [M^+, 97], 155 [$(M+1)^+$, 14]; ν_{ArC-H} 3090, 3070, 3035 cm^{-1}; $\nu_{C\equiv C}$ 2265, 2200, 2150 cm^{-1}; $\nu_{ArC=C}$ 1605, 1495 cm^{-1}; δ_{ArC-H} 730, 697 cm^{-1}. The IR spectrum was identical with that of 2 reported by Harada (1957).

Biological Activity. The leaf disk method, which was reported by Hosozawa et al. (1974), was used as a feeding test to the insect. A leaf disk (d = 2 cm) of cabbage, *Brassica oleracea* var. *capitata*, was punched out with a cork borer. A leaf disk coated with a sample (0.3 mg), a control disk, and a larva in the 5th instar of butterfly, *Pieris rapae crucivora*, were placed in a same dish (7.5 cm × 1.5 cm), and the temperature was kept at 23-24 °C. After 2 h, two leaf disks were removed and weighed. The test of the sample leaf disk coated with the crude essential oil revealed an antifeeding activity to the larva; it did not eat the sample disk but ate about 17% of the control. Then, 1 and 2 isolated from this essential oil were tested in the same manner. These results are listed in Table I. Only 1 larva (Table I, A) among the 10 larvae (A-J) ate a trace (3% weight) of a sample disk coated with 1, but the 9 larvae (B-J) never ate the sample disks. On the other hand, an average that the 10 larvae ate the 10 control disks was 21%. In the case of 2, the 9 larvae (K-L, N-T) among the 10 larvae (K-T) never ate the sample disks and only 1 larva (M) ate a little (11%) of a sample disk. An average of the 10 control disks eaten by the 10 larvae was 50%. It is therefore concluded that 1-phenyl-2,4-pentadiyne (1) and capillen (2) from the growing buds have an antifeeding activity to the larva of butterfly.

Registry No. 1, 41268-41-1; 2, 520-74-1.

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Received for review November 19, 1982. Accepted February 14, 1983.

Lack of Effect of pH and Titratable Hydrogen Ion Concentration on the Corrosion Rate of Low-Carbon Steel in Apples

A nail-apple model food system was used to study the effect of pH and titratable acidity on the rate of corrosion of iron into apples under largely aerobic conditions. Low-carbon steel nails were inserted into apples with varying pH (3.30-4.59) and titratable acidity (1.32-7.61 mequiv of H^+/100 g) for 4 h at room temperature, and iron uptake was measured. No correlation was found between rate of corrosion and pH or titratable acidity. These results agree with a number of studies on heated, largely anaerobic canned food systems.

Iron is an important nutrient that has been found to be deficient in the peoples of both developed and developing countries. Its deficiency in the diet causes a microcytic anemia that is common both in the United States (USHEW, 1972) and worldwide (W.H.O., 1968).

One important source of dietary iron is that leached from iron cookware during food preparation (Moore, 1965; Burroughs and Chan, 1972; Walker and Arvidsson, 1953).

0021-8561/83/1431-0668$01.50/0

Although the possible role of iron cookware in iron nutrition has been debated (Sharon, 1972; Monson et al., 1967; MacKay et al., 1945), some studies have demonstrated that intake of food exposed to iron cookware can produce a significant rise in hemoglobin values in humans (Devadas et al., 1973). The use of "apples and iron nails" as a folk remedy to correct iron deficiency anemia (Rakowska, 1978) has led us to investigate the corrosion of iron nails in apples as a model food system to study the parameters affecting corrosion rates and bioavailability of iron. Recently, we showed that the relative biological value of iron corroded from iron nails inserted into apples was from 93 to 153 when compared with $FeSO_4$ = 100 (Rosanoff and Kennedy, 1982).

The rate of corrosion of iron in foods is evidently affected by several parameters. We demonstrated that in the nail–apple model food system, iron uptakes were dependent on metallic surface area exposed and the duration of nail–apple contact (Rosanoff and Kennedy, 1982). It has been assumed that the amount of iron leached from foods is proportional to hydrogen ion concentration (Burroughs and Chan, 1972). However, a direct, controlled test of this assumption has not been made in open, aerobic systems such as those in cooking and food preparation. Apples, which have shown a particularly high iron leaching effect (Moore, 1965) and are commonly available in varieties that differ in pH, provide a model food system to study the effects of pH and titratable hydrogen ion concentration on corrosion rates of iron nails inserted in them. We, therefore, investigated the corrosion rates of iron nails in several varieties of apples with varying pH and titratable acidities.

MATERIALS AND METHODS

Apples. Nine varities of apples were studied. Except for two varieties where one sample each was used, three apples represented each variety.

Titratable Hydrogen Ion and pH. The apple halves to be measured for pH and titratable hydrogen ion were peeled, cored, and weighed, and then blended with measured amounts of distilled water in a Waring blender. The resulting slurry was divided into two weighed portions that were boiled with one or two Hengar granules for 3 min on a hot plate. Boiled apple slurry samples were cooled to room temperature, covered with parafilm, and stored at 3 °C. Taken at random, samples were allowed to equilibrate to room temperature before the pH was determined on a calibrated Corning pH meter, 125. Each sample was titrated to an end point of pH 8.2 with a freshly prepared solution of 0.1 NaoH that was standardized with a standard HCl solution. Results were expressed as milliequivalents of H^+ per 100 g fresh weight of apple. The weight of the apple titrated for each sample was calculated from the weight of the sample titrated and the percentage of apple–water slurry that was apple.

Experimental Nail Treatment. Sixteen-penny nails of low-carbon steel (SAE 1008) (99% iron) were washed in soapy water, rinsed in distilled water, and air-dried, and each was marked 5.0 cm from the tip with a file. Three nails were inserted up to the file mark in each apple to be tested for corrosion rate. Preliminary work showed the iron uptake rate in apples inserted with nails to be linearly time dependent from 0–8 h. Nails were left inserted 4.0 h at room temperature. After nail treatment, the apples were cut in half, the nail-treated halves labeled and frozen for later iron analysis, and the untreated halves used to determine pH and titratable hydrogen ion.

Total Iron. Frozen halves to be analyzed for iron were lyophilized to dryness, preashed under an infrared lamp, and ashed 24 h in a muffle furnace at 550 °C. Ash residues were dissolved in 6 mL of 1:1 HCl while heating; the solutions were filtered and brought to volume with deionized water. Iron determinations of the resulting solutions were made in duplicate by using 2,2′-bipyridine (Schaefer, 1969). Iron was reduced to the ferrous state with hydroquinone and the pH of the solutions adjusted to 4.5 with acetate buffer. The solutions were allowed to stand for 30 min for complete color development and then read on a spectrophotometer at 520 nm. Standard solutions were prepared by using analytical grade $FeSO_4 \cdot 7H_2O$.

Iron Uptake. Two untreated apple halves of each variety were frozen, lyophilized, preashed, ashed, and analyzed for iron as above. Mean values of these blanks for each variety were subtracted from that variety's total iron value to yield iron uptake.

Statistical Analysis. Analysis of variance and correlation coefficients were calculated by using the STATISTICAL PACKAGE FOR THE SOCIAL SCIENCES program on an IBM 4341 computer.

Table I. pH and Titratable Acidity of Different Varieties of Apple Used in These Studies

apple variety	pH	mequiv of H^+/100 g[a]
Washington Golden Delicious	3.88	3.54
	3.86	3.56
	3.78	3.68
California Golden Delicious	4.43	1.78
	4.59	1.32
	4.40	2.27
California Red Delicious	4.12	2.48[b]
	4.26	2.02
	4.30	1.66
Grannysmith	3.46	6.82
	3.46	4.40
	3.57	5.20
Rome Beauty	3.62	3.70
	3.64	4.55
	3.54	4.18
McIntosh	4.04	3.18
	3.65	5.66
	3.65	5.75
Winesap	3.63	7.61
	3.56	6.20
	3.58	5.64
Washington Red Delicious	3.92	3.56
Green Pippin	3.30	7.30

[a] All values are averages of duplicate determinations with a difference of 6.8% or less except as noted. [b] With a difference of 29.6%.

RESULTS AND DISCUSSION

Table I shows the varieties of apples used in these studies and their corresponding pH and titratable hydrogen ion concentrations. The pH range was 3.30 (Green Pippin) to 4.59 (California Golden Delicious), and the titratable acidity values were a low of 1.32 mequiv of H^+/100 g (California Golden Delicious, pH 4.59) and a high of 7.61 mequiv of H^+/100 g (Winesap, pH 3.63). Generally, low pH corresponded with high titratable acidity and vice versa. Analysis of variance showed that the different varieties differed significantly in pH and titratable hydrogen ion concentration. It should be pointed out that the range of pH observed in the apples represented a span of approximately 1 pH unit, corresponding to a 10-fold difference in hydrogen ion concentration. On the other hand, the low and high values for titratable acidity represented a 5-fold range.

pH and titratable hydrogen ion concentration are plotted against iron uptake in Figures 1 and 2, respectively. The wide scattering of points showed no observable pattern

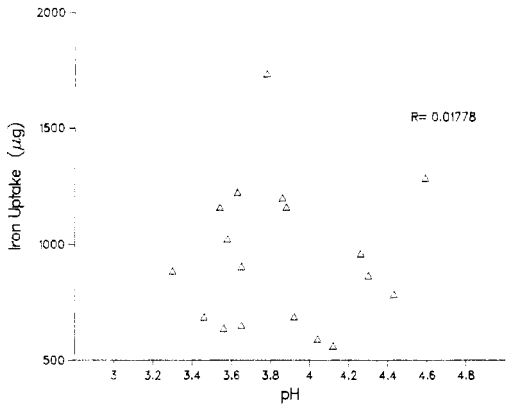

Figure 1. Effect of pH on corrosion rate of low-carbon steel nails into apples measured by iron uptake.

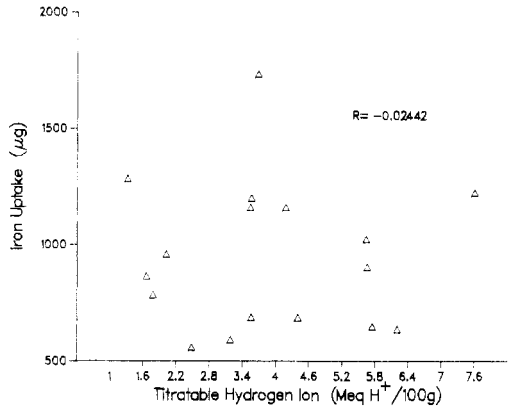

Figure 2. Effect of titratable hydrogen ion concentration on the corrosion rate of low-carbon steel nails into apples measured by iron uptake.

and the correlation coefficients were not significantly different from zero. Thus, in these samples, differences in pH and titratable acidity did not affect the corrosion of iron into the apples.

The important role of pH and acidity on metal corrosion is often assumed but unsubstantiated by experimental data. Mahadeviah (1974), summarizing the data from a number of workers (Hirst and Adam, 1937; Morris and Bryan, 1936; Adam and Dickinson, 1944), concluded that corrosion of tin and iron in canned foods was not proportional to acidity as some of the less acid fruits were more corrosive. Experiments using different organic acids demonstrated that acids alone were less corrosive than the fruit, pointing to the role of other constituents in the canned food corrosion. Constituent organic acids in foods may be a major factor in determining chelation effects of foods (Stoewsand et al., 1979). In canned applesauce, Lopez (1965) showed that the corrosion of iron was not proportional to pH by indirect measures of corrosion such as swells, perforations, and springers. More generally, Massini (1975) reported that in canned fruits, the amount of corrosion of tin plate was not necessarily proportional to pH. All of these studies, which were done on closed, largely anaerobic systems, point to the lack of correlation between iron corrosion and pH or total acidity.

Very little work has been done on the corrosion–acidity question using open, largely aerobic systems such as carried out in the present study. Burroughs and Chan (1972) studied the effects of iron, aluminum, and glass cooking utensils on the iron content of different Mexican–American foods. They concluded that with increasing amounts of tomato sauce in Spanish rice, the food had decreasing pH and increasing amounts of iron when cooked in an iron skillet. However, the surface area of the iron skillet exposed to the food during cooking would be difficult to control in this situation, unless the volume of the food was very closely monitored. The authors conducted their work on the assumption that acid contents of foods determine the amount of iron released from the container based on several studies (Moore, 1965; MacKay et al., 1945; Walker and Arvidsson, 1953; Monson et al., 1967). However, we think that these studies do not substantiate the assumption.

Thus, our present data derived from the apple–nail food model system, which is aerobic and nonheated, showed no correlation between pH or total acidity and iron corrosion. This is in agreement with the large number of studies on heated, largely anaerobic canned food systems and in contrast to one study using a heated, open, aerobic food system.

Registry No. Iron, 7439-89-6; steel, 12597-69-2.

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Received for review October 8, 1982. Accepted February 22, 1983.