On the basis of the above-mentioned virus growth, the extensive production of progeny virus took place after a 10 h infection. Addition of the polymer 10 h postinoculation followed by incubation continuously for 18 h showed that a decrease in infectivity occurred substantially at relatively high concentrations (Table III). Therefore, TMV multiplication was directly inhibited during treatment in proportion to the different concentrations tested.

The light microscopic observation showed that the morphology in treated protoplasts was similar to that in nontreated ones at the end of the experiment, regardless of the concentrations applied and timing of treatment.

Poly(vinylpyridine N-oxide) has been demonstrated to counteract the pathogenic effects of mineral dust for animal cells, and it was suggested that the protective action may be attributed to stabilization of cell membrane (Gabor et al., 1975; Schulz and Beck, 1976; Hahon, 1976). From observation of the mode of action in animal cell systems, the polymer used in this experiment may have some effect on TMV incorporation by protoplasts, which is associated with endocytosis of plasma membrane (Takebe, 1977). The early process of infection including endocytotic uptake of virus particles would be affected by addition of the polymer to the medium 30 min postinoculation, resulting in the unsuccessful infection established in most of the protoplasts (Table II). In addition to inhibition of virus infection in this early stage, the polymer blocked virus multiplication during the rapid growth stage (Table III). Preliminary experiments showed that, in protoplasts treated with PVNO at 1000 μ g/mL for 24 h, the uptake of [14C]uridine and [14C]leucine into RNA and protein was 48% and 43% less than that in nontreated protoplasts. TMV multiplication, therefore, is possibly inhibited due to the disturbance of RNA and protein synthesis in host protoplasts by the polymer.

Registry No. PVNO, 27555-41-5.

LITERATURE CITED

- Gabor, S.; Frits, T.; Anca, Z. Int. Arch. Occup. Environ. Health 1975, 36, 47.
- Hahon, N. Infect. Immun. 1976, 13, 1334.
- Hirai, T. Plant Dis. 1977, 1, 285.
- Holt, P. E. Br. J. Ind. Med. 1971, 28, 72.
- Holt, P. E.; Lindsay, H.; Nasrallah, E. T. Nature (London) 1967, 216, 611.
- Otsuki, Y.; Shimomura, T.; Takebe, I. Virology 1972, 50, 45.
- Parry, D. W. Ann. Bot. (London) 1975, 39, 815.
- Schulz, H.; Beck, E. C. Beitr. Silikose-Forsch., Pneumokoniose 1976, 28, H.1.
- Sugimura, Y.; Ushiyama, R. J. Gen. Virol. 1975, 29, 93.
- Takebe, I. Compr. Virol. 1977, 11, 237.
- Takebe, I.; Otsuki, Y. Proc. Natl. Acad. Sci. U.S.A. 1969, 64, 843.

Yukio Sugimura¹ Takeshi Hamana Tatsuo Kojima Michio Yoshida Jiro Kato*

667

College of Integrated Arts and Sciences University of Osaka Prefecture Mozu-Umemachi, Sakai Osaka 591, Japan ¹Present address: Tochigi Research Laboratories Kao Soap Co., Ltd. 2606 Akabane, Ichikaimachi, Haga Tochigi 321-34, Japan

Received for review March 23, 1982. Accepted January 24, 1983.

Insect Antifeeding Phenylacetylenes from Growing Buds of Artemisia capillaris

Two phenylacetylenes, 1-phenyl-2,4-pentadiyne and capillen, were isolated from the growing buds of *Artemisia capillaris*. These acetylenes revealed an antifeeding activity to the larva of the cabbage butterfly.

Many phenylacetylenes (Figure 1), capillon [3 (Harada, 1956)], capillin [4 (Imai, 1956)], capillen [2 (Harada, 1957)], capillarin [5 (Harada et al., 1960)], o-methoxycapillen [6 (Miyazawa and Kameoka, 1975)], capillanol [7 (Miyazawa and Kameoka, 1975)], norcapillen [8 (Miyazawa and Kameoka, 1976)], and neocapillen [9 (Miyazawa and Kameoka, 1976)], have been isolated from the essential oil of Artemisia capillaris. However, the viscous substance of the growing buds of the plant in June has not been investigated. It is supposed that the substance is effective in protecting the plant from dryness, because it has many long lateral roots to suck up water and the fine thread leaves to prevent an evaporation of water. But in Japan, June is a rainy season and it is the time of most growing for the plant. From this point, it is deduced that the antifeeding compounds to the insect may be contained in this viscous substance. In this report, 1-phenyl-2,4-pentadiyne (1) and capillen (2) given in Figure 1 were isolated as the main component from the growing buds. On phenylacetylenes, the strong antifungal activity of 4 was re-

ported by Imai (1956), but very little has been known about the biological activity of the natural acetylenes. The activities of 1 and 2 to the insect were examined, and consequently two compounds revealed an antifeeding activity to the larva of cabbage butterfly.

Isolation of Phenylacetylenes. The growing buds 634 g of A. capillaris were collected in June on the bank of the Onga River in Fukuoka Prefecture. By the steam distillation and the extraction of the distillate with ether, the essential oil was obtained (1.48 g, 0.23% yield). The essential oil was chromatographed on a silica gel column (100-200 mesh, 55 g l = 55 cm, d = 1.8 cm). Hexane eluted terpene hydrocarbons (3% of the essential oil), hexane-ethyl acetate (4:1) eluted phenylacetylenes (83%), and hexane-ethyl acetate (1:1) eluted polar components (14%). 1-Phenyl-2,4-pentadiyne (1, 9% of the essential oil) was isolated from the first eluate of the phenylacetylene fraction: ¹H NMR (CDCl₃, Me₄Si internal standard) δ 2.00 (1 H, t, J = 1 Hz, C=C-H), 3.69, (2 H, d, J = 1 Hz, Ph-CH₂-C=C), 7.34 (5 H, s, ArH); MS (rel intensity) m/z

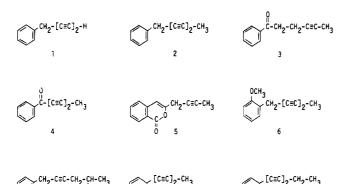


Figure 1. Phenylacetylenes: 1, 1-phenyl-2,4-pentadiyne; 2, ca-

pillen; 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 butter- fly | % of eaten weight | | larva of | % of eaten weight | |
| | sample disk ^b | control | butter- fly | sample disk ^c | control |
| \mathbf{A}^d | 3 | 17 | K^d | 0 | 49 |
| в | 0 | 19 | \mathbf{L} | 0 | 41 |
| С | 0 | 21 | Μ | 11 | 58 |
| D | 0 | 34 | N | 0 | 85 |
| E | 0 | 45 | 0 | 0 | 35 |
| F | 0 | 29 | Р | 0 | 39 |
| G | 0 | 20 | Q | 0 | 55 |
| Н | 0 | 9 | Ŕ | 0 | 39 |
| I | 0 | 12 | s | 0 | 55 |
| J | 0 | 6 | Т | 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=C-CH₃) 3.66 (2 H, m, Ph-CH₂-C=C), 7.35 (5 H, s, ArH); 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; $\nu_{C=C}$ 2265, 2200, 2150 cm⁻¹; ν_{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 \times 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.

LITERATURE CITED

Bohlmann, F.; Kleine, K.-M. Chem. Ber. 1962, 95, 39.

- Harada, R. J. Chem. Soc. Jpn., Pure Chem. Sect. 1956, 77, 990.
- Harada, R. J. Chem. Soc. Jpn., Pure Chem. Sect. 1957, 78, 415.
- Harada R.; Noguchi, S.; Sugiyama, N. J. Chem. Soc. Jpn., Pure Chem. Sect. 1960, 81, 654.
- Hosozawa, S.; Kato, N.; Munakata, K. Agric. Biol. Chem. 1974, 38, 823.
- Imai, K. J. Pharm. Soc. Jpn. 1956, 76, 400, 405.
- Miyazawa, M.; Kameoka, H. Phytochemistry 1975, 14, 1126, 1874.
- Miyazawa, M.; Kameoka, H. Phytochemistry 1976, 15, 223, 1987.

Katsumi Yano

Department of Chemistry Fukuoka University of Education Munakata, Fukuoka 811-41, Japan

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 $(1.32-7.61 \text{ mequiv of H}^+/100 \text{ g})$ 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 (USH- EW, 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).