cretion by prodding gently with a needle, and placed ten of them on each of two branches of clones R and Y. After 7 and 10 days we counted the survivors, some of which had pupated. For surviving larvae we recorded whether or not they produced salicylaldehyde droplets when prodded gently with a needle. The results (Fig. 2) indicate that by day 10 more *C. aenicollis* larvae had produced the defensive secretion (100 percent versus 0 percent, $P = 0.0011$, Fisher's exact test), more had pupated (12 versus 0, $P = 0.0069$), and more had survived (90 percent versus 30 percent, $P = 0.0001$) when feeding on willows high in salicin (Y1 and Y2) than on those low in salicin (R1 and R2).

These results demonstrate the direct effects of salicin, a plant-produced secondary chemical, on the plant and herbivore trophic levels. The observed effect of salicin on salicylaldehyde production also suggests a strong effect on the predator trophic level. Salicin enhanced survivorship of the herbivores while having a negative effect on the plants and, presumably, the predators. This illustrates that, as predicted, chemical defenses can become a problem for plants that produce them.

It is not surprising that the negative effects of salicin were seen only at certain elevations. We predict such a situation to be evolutionarily unstable, favoring plants that have deleted the chemical from their defensive repertoire.The reson why some clones of *Salix* maintain high concentrations of salicin is not known. Our results suggest that one of the costs of salicin production is increased herbivory by *C. aenicollis*, and that these localized selective agents may be responsible for some of the observed variability in salicin content. Clones with low salicin occurred largely where beetle numbers are not restricted by cold environmental conditions, suggesting that these phenotypes may have been selected by prior bouts of intense herbivory. Willow clones live for very long periods but are nonetheless variable and can undergo intraclonal selection (*22*). Interclonal variation in salicin content was not observed at high elevations with reduced numbers of *C. aenicollis*. Salicin may defend plants against generalist herbivores (*9*), including deer (*23*), or may act as an antibiotic (*24*). The variability of the herbivore response to salicin concentrations at different elevations and the variability among willow clones in salicin content suggest a means for evaluating the evolution and ecology of certain plant-herbivore-predator interactions.

References and Notes

1. D. Seigler and P. Price, *Am. Nat.* **110**, 101 (1976).
2. G. Rosenthal and D. Janzen, Eds., *Herbivores: Their Interaction with Secondary Plant Metabolites* (Academic Press, New York, 1979).
3. A. Tempel, *Oecologia* **51**, 97 (1981); S. Louda, *Biochem. Syst. Ecol.* **11**, 199 (1983); K. Sturgeon, *Evolution* **33**, 803 (1979).
4. M. Rothschild, *Symp. R. Entomol. Soc. London* **6**, 59 (1973); T. Eisner, in *Chemical Ecology*, E. Sondheimer and J. Simeone, Eds. (Academic Press, New York, 1970).
5. J. Pasteels, J. Gregoire, M. Rowell-Rahier, *Annu. Rev. Entomol.* **28**, 263 (1983).
6. K. Brown, *Nature* (*London*) **309**, 707 (1984).
7. P. Ehrlich and P. Raven, *Evolution* **18**, 586 (1964); M. Berenbaum, *ibid.* **37**, 163 (1983).
8. P. Feeny, in *Coevolution of Animals and Plants*, L. Gilbert and P. Raven, Eds. (Univ. of Texas Press, Austin, 1975).
9. M. Rowell-Rahier, *Oecologia* **62**, 26 (1983).
10. J. Pasteels, M. Rowell-Rahier, J. Braekman, A. Dupont, *Physiol. Entomol.* **8**, 307 (1983).
11. M. Rowell-Rahier, in *Insect-Plant Relationships*, J. H. Visser and A. K. Minks, Eds. (PUDOC, Wageningen, Netherlands, 1982); *Oecologia* **64**, 369 (1984); *ibid.*, p. 375.
12. J. Pasteels, M. Rowell-Rahier, J. Braekman, D. Daloze, *Ecol. Entomol.*, in press.
13. J. Wallace and M. Blum, *Ann. Entomol. Soc. Am.* **62**, 503 (1969); K. Matsuda and F. Sugawara, *Appl. Entomol. Zool.* **15**, 316 (1980).
14. Field sites were located along the north fork of Big Pine Creek, west of the town of Big Pine, Inyo County (37°7′N, 118°29′W), between 2200 and 3400 m above sea level.
15. There was great variation in twig coloration, stipule size, and bud size and coloration.
16. We measured salicin concentration in four clones of *S. orestera* and one clone of *S. Lasiolepis*, totaling 35 individual branches. Analysis of variance indicated that most of the variation present was between clones ($P < 0.0001$). Within clones, the standard deviation in salicin content averaged 36 percent of the mean.
17. Portions (200 mg) of dried leaves were extracted in 2 ml of distilled water for 24 hours. Serial 1:2 dilutions of extract were applied to silica gel TLC plates with microcapillary tubes. Plates were run in a solvent of methylene chloride and methanol (80:20), sprayed with potassium dichromate (3 mg/ml) in dilute sulfuric acid, and baked for 5 minutes at 120°C. Salicin was found at 0.32 relative to the solvent front (Rf). Quantitative estimates were obtained by comparing serial dilutions of extract and salicin standards (Sigma).
18. M. Rowell-Rahier analyzed two samples of *S. orestera* using HPLC and salicin standards. The quantities of salicin found (0.36 percent and 0.08 percent of dry weight in clones Y and R, respectively) were in agreement with our TLC estimates (0.32 percent and <0.24 percent, respectively).
19. The quantities of compound PG2 were similar to those of salicin, and PG2 migrated farther (Rf, 0.49) than salicin on our TLC plates. We estimated PG2 concentrations by comparison with the salicin standards.
20. This was determined by the gelatin precipitation and ferric chloride test. Proanthocyanidin contents were not correlated with salicin contents or with herbivory by *C. aenicollis*.
21. Leaf damage was regressed against concentrations of salicin and PG2, scored on a logarithmic scale: 0 (<0.63 percent), 1 (1.25 percent), 2 (2.5 percent), 3 (5 percent), and 4 (10 percent).
22. T. Whitham and C. Slobodchikoff, *Oecologia* **49**, 287 (1981).
23. A repellent effect of salicin on opossums was shown by W. Edwards, *N. Z. J. Science* **21**, 103 (1978).
24. M. Vickery and B. Vickery, *Secondary Plant Metabolism* (Macmillan, New York, 1981); R. Robinson, *Plant Pathosystems* (Springer-Verlag, Berlin, 1976).
25. We thank M. Rowell-Rahier for HPLC analysis, enthusiastic interest, and sharing of information about willow beetles; C. Wisdom, K. Miller, and J. Ihara for work in past summers; and M. Kingston, C. Schell, J. Evans, G. Schakaraschwili, W. Goldstein, D. Bershauer, T. Smiley, and A. Smiley for field assistance. Comments by P. Atsatt improved the manuscript. Funded by the White Mountain Research Laboratory, University of California.

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Discovery of Sodium in the Atmosphere of Mercury

Abstract. *The spectrum of Mercury at the Fraunhofer sodium D lines shows strong emission features that are attributed to resonant scattering of sunlight from sodium vapor in the atmosphere of the planet. The total column abundance of sodium was estimated to be* 8.1×10^{11} *atoms per square centimeter, which corresponds to a surface density at the subsolar point of about* 1.5×10^{5} *atoms per cubic centimeter. The most abundant atmospheric species found by the Mariner 10 mission to Mercury was helium, with a surface density of* 4.5×10^{3} *atoms per cubic centimeter. It now appears that sodium vapor is a major constituent of Mercury's atmosphere.*

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Before the Mariner 10 mission to Venus and Mercury, it was expected that Mercury might have a thin but appreciable atmosphere. Argon, derived from potassium decay, and carbon oxides were favored species (*1, 2*). However, these expectations were not realized when Mariner 10 flew by Mercury. Broadfoot and colleagues (*3*) measured the Mercury atmosphere using the ultraviolet airglow spectrometer on Mariner 10. The only definite line emissions they found were from helium and atomic hydrogen. No other constituents were observed, with the possible exception of atomic oxygen, for which a signal at the limit of detection was found. Upper limits were derived for the densities of neon, argon, and carbon, which would have been detected had they been present in sufficient amounts. Final analysis of the spectrometer data yielded a value of 2×10^{-10} millibars (*4*) as the upper limit for the surface pressure of any atmospheric constituent.

We now report the discovery of sodium vapor in the atmosphere of Mercury. This element does not have strong resonance lines in the range of the Mariner 10 ultraviolet spectrometer, and consequently it was not detected by that in-

Table 1. Sodium resonance radiation from Mercury. Data are reported as means ± standard deviations derived from noise in the continuum spectrum.

Date (1985)	Equivalent width (mÅ)		Ratio*	Column density (atom/cm^2 × 10^{11})
	D_1	D_2		
3 January	66 ± 2	83 ± 3	1.48 ± 0.09	7.0 ± 2.0
4 January	50 ± 2	60 ± 2	1.41 ± 0.08	8.8 ± 2.2
6 January	48 ± 2	58 ± 2	1.42 ± 0.08	8.5 ± 2.2

*Ratio of D_2 to D_1, corrected to equal intensities of solar illumination at the sodium lines.

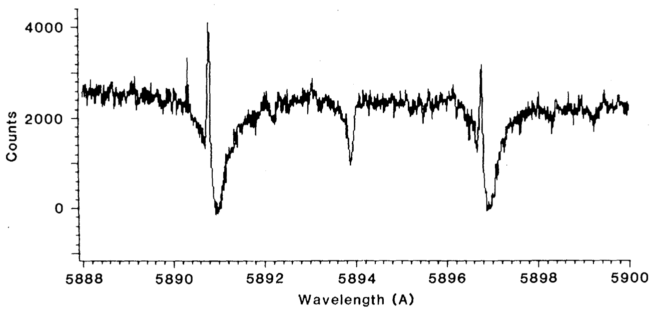

Fig. 1. Spectrum of Mercury in the sodium D line region taken at 2020 UT (3 January 1985).

strument. We detected sodium from emission lines corresponding to the sodium D lines in Mercury spectra measured with a ground-based telescope and spectrometer.

The echelle spectrometer at the Coudé focus of the University of Texas 2.7-m telescope at the McDonald Observatory was used for the measurements. In a resolution test of the instrument, the full-width at half-power (FWHP) of a spectral line from a standard Fe-Ne lamp was measured to be 55 mÅ. The slit length was set to match the apparent diameter of Mercury at the Coudé focus, and an automatic image rotator was used to maintain constant geometry. The observations were done during daytime, so that sky background had to be subtracted from the spectra. This was done by observing the planet with its associated sky background for 90 seconds and then moving the field of view four to five planet diameters away to observe the sky background alone for another 90 seconds. The sky spectrum was automatically subtracted from the planet-plus-sky spectrum at the end of each 180-second cycle by the data acquisition software. The difference spectrum (which was the spectrum of Mercury alone) was accumulated in a buffer. This cycle was repeated over a total observing period of about 90 minutes. Because the signal from Mercury was only about 30 percent of the sky signal, steady sky conditions were essential to the success of this technique. During our observations sky conditions were exceptionally good, with excellent transparency and daytime seeing in the range of 2 to 4 arc seconds.

The sodium D line region in the spectrum of Mercury is shown in Fig. 1 for an observation performed at 2020 universal time (UT) on 3 January 1985. The sodium Fraunhofer absorption lines in sunlight reflected from Mercury were Doppler-shifted redward by 0.86 Å because of the net effect of the sun-Mercury relative velocity of 9.4 km/sec and the Mercury-Earth relative velocity of 34.6 km/sec at the time of the observation. Sharp emission lines were seen on the blue side of the two sodium D absorption lines. The width of these lines (FWHP) was about 55 mÅ, which is approximately the same as that observed for lines from the calibration lamp. The emission lines were attributed to resonance scattering of sunlight by sodium vapor at rest with respect to Mercury. The Doppler shift of the emission lines relative to the solar absorption lines (0.19 Å) was consistent with this interpretation. The measurements were repeated on 4 January, and again on 6 January, with similar results. A search was made for sodium emission outside the illuminated region, but none was found.

The spectral data were analyzed to estimate the abundance of sodium vapor on Mercury (Table 1). The equivalent widths of the lines were calculated by measuring the area bounded by the emission line profile, and this area was used to determine the equivalent width relative to the solar continuum outside the sodium Fraunhofer lines. The ratios of D_2 to D_1 (Table 1) were corrected for unequal solar intensity at the location of the two lines and represent the ratios that would have been observed if the solar intensity had been the same for both lines.

If the sodium vapor were optically thin, the ratio of D_2 to D_1 for equal source strengths would be 2.0 (the ratio of oscillator strengths), subject to a correction for nonisotropic scattering by D_2, which would change the ratio by less than 10 percent. The observed ratio was approximately 1.5 (Table 1), which indicates that the sodium on Mercury is not optically thin. For determination of the sodium column density for this case, a detailed radiation transfer calculation is required. Brown and Yung (*5*) give plots of the D_2:D_1 ratio against the sodium column density for two different temperatures (500 K and 5000 K) on the basis of a radiation transfer calculation (*6*). We used their results to estimate the sodium column densities given in Table 1. For this calculation, the mean temperature was assumed to be 500 K, which corresponds to the surface temperature about 45° away from the subsolar point. This temperature is not inconsistent with the observed sodium line FWHP of about 55 mÅ, since the theoretical FWHP of the sodium D_2 line at 500 K is 50 mÅ (*5*). However, because of instrumental broadening, the true line width is probably less than this value, corresponding to a lower kinetic temperature. In that case, the calculated abundance would be smaller. On this account, the sodium column densities given in Table 1 may be too large by as much as a factor of 2, but an improved estimate is not possible without better temperature information.

The average column density from the three measurements was 8.1×10^{11} atom/cm^2. Assuming a subsolar temperature of 575 K (*3*), this corresponds to a surface density at the subsolar point of 1.5×10^5 atom/cm^3 and a pressure of 1.2×10^{-11} millibars. These values establish sodium vapor as a major constituent of the Mercury atmosphere, because Broadfoot and co-workers (*3*) found the density of helium to be 4.5×10^3 atom/cm^3 and the density of hydrogen to be 8 atom/cm^3. The upper limit for surface pressure of any atmospheric constituent was 2×10^{-10} millibars, which is consistent with our results for sodium vapor.

The similarity between the sodium emission we report and the sodium emission from Io discovered by Brown (*7*) is obvious. The same mechanisms invoked to explain the Io sodium apply also to Mercury. These include sputtering and meteoric bombardment. In the case of Io, sputtering by energetic particles in the Jovian magnetosphere appears to be favored (*8*). In the case of Mercury, the solar wind impacts the surface directly (*4*) and therefore could sputter sodium from minerals on the surface. Meteoric dust may provide a continuing source of sodium. The flux of meteoric material increases as the sun is approached and is about eight times more intense at the orbit of Mercury than at Earth (*9*). Sodium also appears in the atmosphere of Earth, and its origin has been ascribed to meteoric material (*10*).

The atomic weight of sodium is high enough that the thermal escape of sodium from Mercury should be negligible. However, it has been suggested that the solar wind can sweep away ions produced by photoionization of Mercury's atmosphere (*11, 12*), and this may be a major loss process for atmospheric gases that otherwise would not escape. Mercury's original atmosphere may have been removed by this means. The observed composition of Mercury's atmosphere and the appearance of sodium as a major constituent may then result from a steady-state balance among loss of atoms by ionization and trapping in the solar wind; supply from the surface by outgassing, sputtering, and volatilization; and neutralization of solar wind ions. Mercury's atmosphere may thus resemble a cometary coma rather than an Earth-like planetary atmosphere.

More information is needed before the sources and sinks of sodium in Mercury's atmosphere are understood. By measuring the variation of sodium emission with phase, time, and distance of Mercury from the sun, it may be possible to determine what processes control it.

References and Notes

1. U. Fink, H. P. Larson, R. F. Poppen, *Astrophys. J.* **187**, 407 (1974).
2. M. J. S. Belton, D. M. Hunten, M. B. McElroy, *ibid.* **150**, 1111 (1967).
3. A. L. Broadfoot, D. E. Shemansky, S. Kumar, *Geophys. Res. Lett.* **3**, 577 (1976).
4. S. Kumar, *Icarus* **28**, 579 (1976).
5. R. A. Brown and Y. L. Lung, in *Jupiter*, T. Gehrels, Ed. (Univ. of Arizona Press, Tucson, 1976), pp. 1102–1145.
6. M. B. McElroy and Y. L. Yung, *Astrophys. J.* **196**, 227 (1975).
7. R. A. Brown, in *Exploration of the Planetary System*, A. Woszczyk and C. Iwaniszewska, Eds. (Reidel, Boston, 1974), pp. 527–531.
8. W. Macy and L. Trafton, *Astrophys. J.* **200**, 510 (1975).
9. C. Leinert *et al.*, *Astron. Astrophys.* **103**, 177 (1981).
10. D. M. Hunten and L. Wallace, *J. Geophys. Res.* **72**, 69 (1967).
11. P. M. Banks *et al.*, *Comments Astrophys. Space Phys.* **2**, 214 (1970).
12. R. E. Hartle, S. A. Curtis, G. E. Thomas, *J. Geophys. Res.* **80**, 3689 (1975).

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Molybdenum Availability, Nitrogen Limitation, and Phytoplankton Growth in Natural Waters

Abstract. *Sulfate inhibits molybdate assimilation by phytoplankton, making molybdate less available in seawater than it is in freshwater. As a result, nitrogen fixation and nitrate assimilation, both processes that require molybdenum, may require a greater expenditure of energy in seawater than in freshwater. This may explain in part why coastal marine ecosystems are usually nitrogen limited whereas lakes usually are not. Experimentally increasing the ratio of sulfate to molybdate (i) inhibits molybdate uptake, (ii) slows nitrogen fixation rates, and (iii) slows the growth of organisms that use nitrate as their nitrogen source.*

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In most lakes, the supply of phosphorus controls primary productivity (*1*), yet phytoplankton productivity in most estuaries and coastal seas is controlled by nitrogen supply (*2*). These facts are commonly used in managing water quality, but no explanation for this major difference between the functioning of lakes and marine ecosystems has been widely accepted. The difference in nutrient limitation between most lakes and oceans is general enough to suggest that there may be a geochemical explanation related to the chemistry of seawater. A related phenomenon is that although nitrogen is limiting in coastal waters, rates of biological nitrogen fixation tend to be quite low (*3*). We propose that rates of nitrogen fixation are low in coastal waters and that phytoplankton growth in these systems is nitrogen limited because molybdenum availability is low. Molybdenum is required for nitrogen fixation (*4*), and although concentrations of dissolved molybdenum in seawater are high for a trace constituent, we found that concentrations of sulfate equal to and below those found in seawater can inhibit molybdenum assimilation by phytoplankton. The resulting molybdenum deficiency leads to low rates of nitrogen fixation, which in turn make coastal seas nitrogen limited.

Coastal waters are nitrogen limited because they are more depleted in nitrogen than in phosphorus. This condition exists in part because available nitrogen is lost from the sediments by denitrification while phosphorus is more efficiently recycled from sediments to the water column (*5*). However, denitrification is also a major process in lakes (*6*) and yet does not appear to lead to nitrogen-limiting conditions there except for brief periods of time. In most lakes, the nitrogen deficit created by denitrification (or by imbalances in loading of nitrogen relative to phosphorus from external sources) is made up through nitrogen fixation (*7*). The ratio of available phosphorus to nitrogen controls the rate of nitrogen fixation in lakes, so that phosphorus and not nitrogen controls phytoplankton productivity in most freshwaters (*7*). In coastal waters, nitrogen fixation rates tend to be much lower than in lakes (*3*), even when phosphorus concentrations are reasonably high (*8*). The nitrogen deficit and nitrogen-limiting character of seawater systems persist. A few lakes also are nitrogen limited, and it has been suggested that nitrogen limitation of one of these, Castle Lake in California, is caused by unusually low molybdenum concentrations (*9*).

Data on the relative partitioning of molybdenum between dissolved and particulate phases in natural waters suggest that molybdenum may be less available to phytoplankton in marine ecosystems than in most freshwaters. Molybdenum in rivers and lakes tends to be evenly partitioned between dissolved and particulate phases (*10, 11*), but in seawater there is usually 10,000 times more dissolved molybdenum than particulate molybdenum (*12*). Also, concentrations of dissolved molybdenum in some lakes can change seasonally by a factor of 10 or more (*11*), but dissolved molybdenum is usually a conservative constituent of seawater (*10*). The conservative behavior of molybdenum in seawater and the high ratio of dissolved to particulate molybdenum in seawater are both unusual characteristics in a metal (*13*) and indicate that biological reactivity is low. Moreover, Sugawara *et al.* (*14*) found that concentrations of marine phytoplankton in open seawater have only 2 nmol of molybdenum per gram (dry weight), a value typical of molybdenum-deficient terrestrial plants (*10*). The concentration of molybdenum in lake phytoplankton also is often low (*14*) but can