effect of a much less active component or an inert impurity on the total response of the more active (+) enantiomer. However, the presence of 1.3 percent of the (+) enantiomer in the (-) enantiomer makes it impossible to determine whether or not the (-)enantiomer has some activity of its own (12).

## ROBERT G. RILEY

**ROBERT M. SILVERSTEIN** State University of New York, College of Environmental Science and Forestry, Syracuse 13210

JOHN C. MOSER Southern Forest Experimental Station, U.S. Department of Agriculture, Alexandria, Louisiana 71360

## **References and Notes**

- 1. J. C. Moser, R. G. Brownlee, R. M. Silverstein,
- J. Insect Physiol. 14, 529 (1968).
   J. E. Amoore, G. Palmieri, E. Wanke, M. S. Blum, Science 165, 1266 (1969). 3.
- W. L. Roelofs and A. Comeau. J. Insect Physiol. 17, 435 (1971). A. G. Ogston, Nature (Lond.) 162, 936 (1948).
- L. Friedman and J. G. Miller, *Science* 172, 1044 (1972).
- 6. The synthesis of S-(+)-methylallylacetic acid was similar to that employed by S. Stallberg-Stenhagen [Ark. Kemi Mineral. Geol. 23A, 1
- 7. Resolution similar to that employed by P. A. Levene and R. E. Marker [J. Biol. Chem. 98, 1 (1932)].
- S. Stallberg-Stenhagen and E. Stenhagen, Ark. Kemi Mineral. Geol. 24B, 1 (1947).
- Each synthetic enantiomer of the ketone was 9. isolated in pure form from the reaction mix-ture on the following gas liquid chromatogra-phy (GLC) column: 4 percent TCEP [1,2,3 tris(2-cyanoethoxy)propane] on Chromosorb G 60/80 mesh, 7.3 m by 3 mm (outside diameter); He flow rate, 20 cm<sup>3</sup>/min; column temperature, 88°C. Purity was further checked on a Carbowax 20M capillary column, 30.5 m by 0.5 mm, with a He flow rate of 3 cm<sup>3</sup>/min; the column
- temperature was  $80^{\circ}$ C. The optically active synthetic precursor acids were purified from the reaction mixture on the following GLC column: FFAP (free fatty acid phase), 14 percent, was placed on Chromosorb W, 80/100 mesh; the column was 1 m by 3 mm (outside diameter); the He flow rate was 30
- (outside diameter); the re now rate was so cm<sup>3</sup>/min; the column temperature was 108°C.
   11. The natural ketone from A. texana and A. cephalotes was isolated and the purity was confirmed by GLC on the following columns. confirmed by GLC on the following columns. (i) Five percent high efficiency DEGS (diethyl-ene glycol succinate) on Chromosorb G, 60/80mesh, 3 m by 6.3 mm; He flow rate, 30 cm<sup>3</sup>/ min; column, 95°C. (ii) Four percent Carbo-wax 20M on Chromosorb G, 60/80 mesh, 7.3 m by 3 mm; He flow rate, 30 cm<sup>3</sup>/min; col-umn, 95°C. (iii) Four percent TCEP on Chromosorb G, 60/80 mesh, 7.3 m by 3 mm; He flow rate, 20 cm<sup>3</sup>/min; column, 90°C. (iv) Carbowar 20M canillary column,  $90^\circ$ C. (iv) He flow rate, 20 cm<sup>3</sup>/min; column, 90°C. (iv) Carbowax 20M capillary column, 30.5 m by 0.5 mm; He flow rate, 3 cm<sup>3</sup>/min; column, 80°C. (v) DEGS capillary column, 30.5 m by 0.5 mm; He flow rate, 3 cm<sup>3</sup>/min; column, 70°C. (vi) Apiezon L capillary column, 15.2 m by 0.5 mm; He flow rate, 3 cm<sup>3</sup>/min; column, 87°C.
  12. Details will be forthcoming on the isolation and identification of S(+)+4-methyl-3-benta-
- and identification of S-(+)-4-methyl-3-hepta-G. Riley, Tetrahedron, in press). If we accept G. Riley, Tetrahedron, in press). If we accept the optical rotation of the enantiomer produced by two species of ants as representing 100 percent optical purity, the optical purity of the synthetic enantiomers can be calculated to be 95.0 ( $\pm$  1.9) percent [97.5 parts (+), 2.5 parts (-)] for the (+) enantiomer and 97.3 ( $\pm$  1.9) percent [98.7 parts (-), 1.3 parts (+)] for the (-) enantiomer. The limit of error on the measurement of optical rotation was de-termined by comparing the optical rotations of termined by comparing the optical rotations of three individually prepared standards of a 0.05

percent aqueous solution of (+)-10-camphorsulfonic acid at 292 nm. Each standard was within 2 percent of the known value of rotation; thus all measurements of optical rotation are within 2 percent of their measured or calculated values. A temperature difference of 2°C has a negligible effect on optical rotation. C. Djerassi, Optical Rotatory Disperson (McGraw-Hill, New York, 1960), p. 27; M. K. Hargreaves, J. Chem. Soc. (1953), p. 2953.

 One milliliter of head space vapor of each sample, whose concentration had been de-termined (1), was drawn into a 10-ml syringe and serially diluted in the syringe in tenfold increments until the threshold concentration of response for each sample was achieved. Each sample was injected into a slow air

stream leading to the test chamber. The minimum concentration at which 50 percent of the ants (workers of all sizes) present in the chamber at any given time responded by character-istic antennae raising was designated as the threshold response. Each enantiomer was bio-assayed ten times, and each time its response value was compared with that of a sample of 2-heptanone, another less active component of the mandibular gland (1) (Tables 1 and 2).

We thank Dr. J. E. Amoore for pointing out the need to interpret the biological response data in terms of geometrical averages, Sup-ported by the Environmental Protection Agency and the Rockefeller Foundation.

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## **Temporal Pattern Shifts to Avoid Acoustic Interference** in Singing Birds

Abstract. Two species of forest birds, the least flycatcher and the red-eyed vireo, when breeding in the same season in the same habitat, adjust their temporal pattern of singing to avoid the overlapping of songs. The avoidance of acoustic interference is more marked in the flycatcher, which has a briefer song than the vireo.

The acoustic signals of different species communicating in the same habitat may suffer mutual interference and masking (1, 2). We report here evidence that bird species adjust the temporal patterning of their singing with respect to the singing of another species in such a way as to avoid temporal overlap between the two kinds of songs.

(Vireo olivaceus) and the least flycatcher (Empidonax minimus) breed in similar habitats at similar times. Neither species is brightly colored, and each communicates extensively with acoustic signals, particularly short advertising songs given repeatedly throughout the day while foraging. There is considerable overlap of frequency (pitch) in the songs of the two species. Five vireo-flycatcher pairs were

In North America the red-eyed vireo

Table 1. Timing of least flycatcher songs relative to singing and silent periods of a red-eyed vireo in the same area.

Fly- catcher number	Total songs (f)	Number of songs begun during vireo song		Number of songs begun during vireo silence		$\chi^2$	Probability of chance
		${(F_r)}$	Actual (f <sub>p</sub> )	$\frac{\text{Predicted}}{(F_{\bar{r}})}$	Actual $(f_{\vec{r}})$	<i>n</i>	difference
. 1	275	66.7	23	208.3	252	37.796	<.001*
2	519	130.1	23	388.9	496	117.729	< .001*
3	226	49.0	18	177.0	208	25.035	< .001*
4	43	11.3	1	31.7	42	12.690	<.001*
5	146	35.5	11	110.5	135	22.336	< .001*

\* Highly significant ( $\alpha = .001$ , where  $\alpha$  represents the level of significance chosen by the experimenter).

Table 2. Timing of red-eyed vireo songs relative to singing and silent periods of a least flycatcher in the same area.

Vireo number	Total songs (v)	Number of songs begun during flycatcher song		Number of songs begun during flycatcher silence		χ <sup>a</sup>	Probability of chance
		$\frac{1}{(V_f)}$	Actual (v <sub>1</sub> )	Predicted $(V_{\overline{I}})$	Actual (v7)	r	difference
1	195	26.4	22	168.6	173	0.854	>.3
2	512	56.9	36	455.1	476	8.617	<.01*
3	173	19.0	10	154.0	163	4.753	<.05*
4	59	4.6	6	54.4	53	0.483	>.3
5	135	14.6	3	120.4	132	10.283	<.01*

\* Significant ( $\alpha = .05$ , where  $\alpha$  represents the level of significant consensities by the experimenter).

selected for study at Lake Itasca, Minnesota. A total of 2283 songs were recorded with a tape recorder (Nagra III) and omnidirectional microphone (Sennheiser 104) at 7.5 inches per second (19 cm per second) during the period from 20 June to 5 July 1970. We analyzed the tapes, using a sonagraph (Kay 6061B) with wide band setting. The lengths of all songs and intervals were measured from the end of one song to the beginning of the next. The data were coded for computer analysis in such a way that the entire temporal patterning of acoustic signals could be represented; we plan a later extensive analysis of these temporal patterns for both species, using additional data when each species is singing in the absence of the other. Our purpose in the analysis presented here was to determine if either species was influencing the timing of song by the other.

Let v be the total amount of time during which the vireo is producing sound, and let  $\overline{v}$  be the vireo's total quiet time in the recorded sample. Then the probability of a vireo's singing is

$$p(v) = v/(v + \bar{v}) \tag{1}$$

and its probability of being silent is

$$p(\bar{v}) \equiv \bar{v}/(v + \bar{v})$$

Suppose during the same total time  $(v + \bar{v})$  the least flycatcher sings f total songs. If these songs are begun regardless of whether the vireo is singing or not, then the predicted number of flycatcher  $(F_r)$  songs begun during vireo song should be

$$F_{\rm r} = p(v) \cdot f \tag{2}$$

and, analogously, the predicted number of flycatcher songs begun during vireo silences should be

$$F_{\bar{v}} \equiv p(\bar{v}) \cdot f$$

These predicted values were calculated and compared with the actual values  $(f_r, \text{ and } f_{\bar{r}})$  by means of the  $\chi^2$  test:

$$\chi^{2} = \frac{(F_{v} - f_{v})^{2}}{F_{v}} + \frac{(F_{\bar{v}} - f_{\bar{v}})^{2}}{F_{\bar{v}}} \quad (3)$$

with one degree of freedom. A parallel analysis was made of the beginning of vireo songs relative to the periods of singing and silence of the flycatcher.

The results of the analysis of the timing of flycatcher songs are shown in Table 1, and the parallel analysis of vireo songs is given in Table 2. Table 1 shows that all the flycatchers avoid beginning a song while a vireo is singing to a degree highly significantly different

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from chance. On the other other hand, Table 2 shows a somewhat smaller unwillingness of the vireo to begin a song when a flycatcher is already singing. Despite the large sample sizes, only three of the five vireos can be shown to avoid beginning a song while a flycatcher sings, and the differences are not as pronounced as those in Table 1. In fact, vireo 4 actually began singing during flycatcher songs more often than predicted by chance, although the departure from prediction is not significant.

The two species are matched by individual numbers in Tables 1 and 2 for comparison. The total number of songs uttered during the recorded period is strikingly similar in each pair. The difference in duration between the relatively long vireo song (9 to 83 csec, usually 20 to 40 csec) and the short flycatcher song (10 to 14 csec, usually 11 csec) is accounted for in the analysis by Eq. 1; however, this difference may be of value in the interpretation of the results. Although there is some mutual avoidance of acoustic interference, the flycatcher tends more strongly to insert its short songs in between the longer songs of the vireo, rather than vice versa. Indeed, most of the overlap recorded ( $f_{c}$  of Table 1) occurred when the flycatcher began singing just after the vireo had begun, suggesting that the flycatcher had not heard the vireo begin singing. In some cases, with the recording microphone nearer the vireo, the onset of vireo sound may not even have reached the flycatcher's ears by the time the flycatcher commenced singing. In terms of selective advantage, it seems less important for the vireo to avoid interference, since a portion of its longer song will be transmitted without interference regardless of when during the vireo song the flycatcher sings. However, the song of the flycatcher can suffer total interference by the long vireo song, so that the burden of avoiding interference falls more heavily upon the flycatcher.

There are, of course, many ways in which two species can avoid acoustic interference, for example, by singing on different daily rhythms (1), in different frequency bands (2), at different heights (2), and so on. The results presented here clearly demonstrate avoidance by adjustment in the temporal patterning of singing. We have no evidence that the vireo and flycatcher discussed here are in any sort of direct ecological competition or are communicating with one another in any sense other than avoiding mutual acoustic interference. The results demonstrate the importance of assessing influences of unrelated species when attempting to study the temporal structure of acoustic communication in a given species.

**ROBERT W. FICKEN** MILLICENT S. FICKEN Department of Zoology,

University of Wisconsin-Milwaukee. Milwaukee 53211

JACK P. HAILMAN Department of Zoology, University of Wisconsin, Madison 53706

## **References and Notes**

- 1. M. L. Cody and J. H. Brown, Nature (Lond.)
- M. L. Cody and J. H. Brown, Nature (Lond.) 222, 779 (1969).
   M. J. Littlejohn and M. M. Martin, Anim. Behav. 17, 785 (1969).
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Martian Climate: An Empirical Test of Possible Gross Variations

In the wake of the discovery of sinuous channels on Mars, a number of authors have speculated about the possibility that the average climate on Mars may once have been more clement by terrestrial standards than it is at present (1). Indeed, there appears to be evidence for cyclic behavior in which the surface pressure periodically reaches values compatible with the flow of water in equatorial regions on the planet (2, 3). It is the purpose of this note to call attention to a relatively simple test of such hypotheses-a test that may be carried out as early as February 1974.

The premise on which cyclic models

are based is that a substantial reservoir of volatiles exists in frozen form at one or both poles. Warming of the polar regions by one or more processes leads to the release of the trapped volatiles and a subsequent increase in surface pressure, an enhanced greenhouse effect, and so forth. Estimates of the amount of material in these reservoirs varies; for this discussion I adopt the estimate of CO<sub>2</sub> equivalent to  $\sim 1$  bar favored by Sagan et al. (2). This estimate is based on the well-grounded assumption that the atmospheres of both Venus and Mars have developed through outgassing processes similar to those