Reports

Fossils of Uncertain Affinity from the Upper Devonian of Iowa

Abstract. *Thousands of specimens of the enigmatic fossil* Gluteus minimus *(new genus, new species) occur in a 5-centimeter-thick interval within the Maple Mill Shale and in equivalent deposits of the Devonian of eastern Iowa. They are roughly lenticular, bilobed fossils up to 11 millimeters in diameter and 8 millimeters thick. These objects, consistently asymmetrical in the same direction, defy placement in any known higher taxon when their morphology, histology, and apatitic composition are considered.*

In 1902 Stuart Weller, as part of his long-term study of the Carboniferous of the North American Midwest, visited rock exposures along the English River in Washington County, Iowa, near the Maple Mill (Fig. 1A, locality *B*) (*1*). Within what he called the English River Gritstone he found some peculiar bilobed fossils, each about 1 cm across. Apparently Weller did not know exactly what he had found, for his specimens are labeled, in the handwriting of his sister, "Fish remains?" Also about the turn of the century C. R. Eastman collected similar fossils in what he called Kinderhook Beds at Burlington, Iowa (locality *F*) (*1*). Again the identification of the fossils was uncertain: "Cone scales?" reads the sister's label. About 30 years later C. H. Belanski, at one time the geology curator at the University of Iowa, recovered more of these strange fossils from the Cerro Gordo Member of the Lime Creek Formation in Floyd County, Iowa (locality *A*). He, too, suspected fish affinities, calling the fossils "apparently dermal ossifications of some fish" in unpublished notes (*2*).

In the years following, thousands of these fossils have been collected from the Maple Mill Shale at Weller's locality (the type section of the formation) and at two additional sites nearby in Washington County, Iowa. In addition, two specimens were discovered (*3*) in cuttings of the same unit from a well at Columbus City, Louisa County, Iowa (locality *E*). However, the zoologic affinities of these fossils are still uncertain, and the noncommittal but descriptive phrase "horse collars" has been used colloquially at the University of Iowa for these fossils.

More than 3200 "horse collars" have been closely studied; of these, 1200 are nearly complete. In addition, several thousands of smaller fragments have been examined cursorily. Specimens cited with SUI numbers have been deposited in the Department of Geology, University of Iowa. Individuals identified by UCGM numbers are preserved in the University of Cincinnati Geology Museum.

Gluteus, new genus

Type: *Gluteus minimus*, new species. Because the genus is monotypic at present, the diagnosis for the species can serve for the genus.

Gluteus minimus, new species

Type material: The holotype is SUI 34978-91 (Fig. 2); paratypes are SUI 34976, 34978-1 through 34978-90, 34978-92 through 34978-100, and 34979, and UCGM 40609, 40611 through 40631, and 42685.

Diagnosis: The currently known remains of this creature are roughly lenticular, phosphatic fossils up to 11 mm in diameter and 8 mm thick. The greatest thickness is in an area between the center and the margin; the periphery opposite this thickest part is marked by a reentrant (*A* in Fig. 1B), so that each specimen is bilobed. One surface of each individual displays growth lines concentric about the area

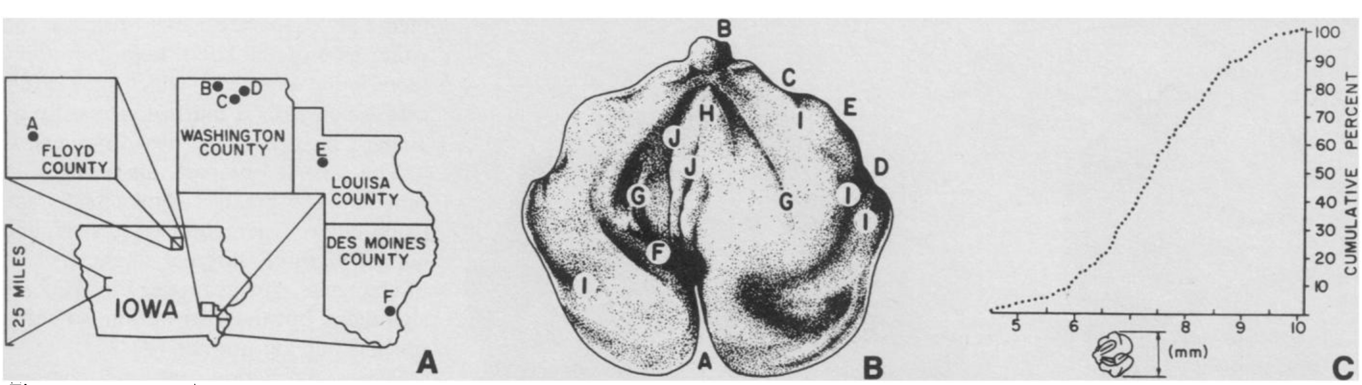

Fig. 1. (A) Locality map: *A*, SW 1/4, NW 1/4, Sec. 19, T95N, R18W, Floyd Co., Iowa (Belanski Station 19); *B*, S. bank, E. of bridge over English R. in Sec. 8, T77N, R8W, Washington Co., Iowa (type section of Maple Mill Shale); *C*, Kalona Clay Pit, excavation in gully E. of Iowa Route 1 about 1½ km S. of Kalona, NW 1/4, NW 1/4, Sec. 19, T77N, R7W, Washington Co., Iowa; *D*, High Bridge Locality, road cut on county road, S. of bridge over English R., SE 1/4, SW 1/4, Sec. 17, T77N, R7W, Washington Co., Iowa; *E*, Well in base of quarry, near Columbus City, NE 1/4, NW 1/4, Sec. 3, T77N, R5W, Louisa Co., Iowa (Iowa Geological Survey core C-179); *F*, Burlington, Iowa. (B) Diagram of smooth surface of *Gluteus minimus*. See text for explanation of letters. (C) Cumulative percentage size distribution curve of 100-specimen random sample (SUI 34978) drawn from over 400 specimens (including UCGM 40609 through 40617) from locality *D*. The maximum dimension is 9.95 mm, the minimum 4.50 mm, and the median 7.40 mm.

of greatest thickness. The reverse surface is smooth (lacks the growth lines) and virtually always bears one or (rarely) two furrows (*F* in Fig. 1B). Individual specimens appear almost bilaterally symmetrical in overall shape. However, in detail virtually all individuals are asymmetrical and, moreover, are asymmetrical in the same direction in that the single (or larger) furrow lies on the same side of the trend of the reentrant. The internal structure consists of layers concentric within the smooth surface. Each layer appears to consist of polygonal plates resting edge to edge (Fig. 3E). The positions of the plates of one layer commonly coincide with those of the adjacent layers (Fig. 3F), forming stacks of plates which, in some instances, narrow and pinch out.

Discussion: Each specimen is bilobed because of the presence of the reentrant (*A* in Fig. 1B). In about 2 percent of 1200 nearly complete specimens examined, convergent growth of the two lobes has pinched the reentrant down to almost nothing (UCGM 40611 and 40612; for example, Fig. 3A). A small knob (*B* in Fig. 1B) is commonly found on the periphery nearest the thickest part (and, hence, away from the reentrant); in other specimens this structure, although easily traceable in the growth lines, projects little, if at all, from the margin.

When looking at either the smooth or the growth-lined surface, one sees that the overall outline varies from roughly circular to nearly square to trilateral. On the outside margin of each lobe usually there are two indentations in the periphery (*C* and *D* in Fig. 1B) separated by a salient (*E* in Fig. 1B).

The fact that the single (or larger) furrow (*F* in Fig. 1B) lies on the same side of the trend of the reentrant causes virtually all specimens to be slightly but consistently asymmetrical. However, in about 3 percent of the specimens the furrow is absent, indistinct, or lies on the midline (UCGM 40614 and 40615). In only two of the nearly complete specimens examined is the furrow on the opposite side from usual (Fig. 3B), but one of these two individuals falls into that small minority of specimens with indistinct furrows (Fig. 3C).

In addition to the furrow or furrows, particularly in larger specimens, the smooth surface may bear one or two channels (*G* in Fig. 1B), each paralleling the trend of one of the lobes. Commonly the furrow is continuous with one of these channels. In some specimens (less than 4 percent) the area between these two channels (*H* in Fig. 1B) is inflated (UCGM 40616 and 40617; Fig. 3D).

Many "horse collars" bear a number of short grooves running perpendicular to the periphery of each lobe (*I* in Fig. 1B). Commonly, these grooves run inward from each indentation (*C* and *D* in Fig. 1B).

In addition to the various grooves and furrows enumerated above, the smooth surface of most specimens bears two or more striae (*J* in Fig. 1B), which run from the reentrant to the vicinity of the knob. These striae may or may not coincide with the furrow, with one or both of the channels which parallel the trends of the lobes, or with both the furrow and the one or two channels. In the vicinity of the knob the two striae usually merge, then immediately separate, one passing on either side of the knob. Less commonly there is but one stria, which may bifurcate. Each stria is marked internally by a sharp flexure of the growth layers.

The largest observed diameter is 11 mm and the greatest thickness 8 mm. Cumulative percentage distribution curves of three different diameters and of thickness (for example, Fig. 1C) are sigmoidal, but the distribution is neither normal nor log normal (*4*).

X-ray diffraction patterns obtained by the powder method indicate that specimens from four different localities (*B*, *C*, *D*, and *E* in Fig. 1A) are all apatite (*5*). Chemical analysis of specimens from one locality (*C*) yielded the following percentage composition: CaO, 55.69; P_2O_5, 38.99; F^-, 3.51; and or-

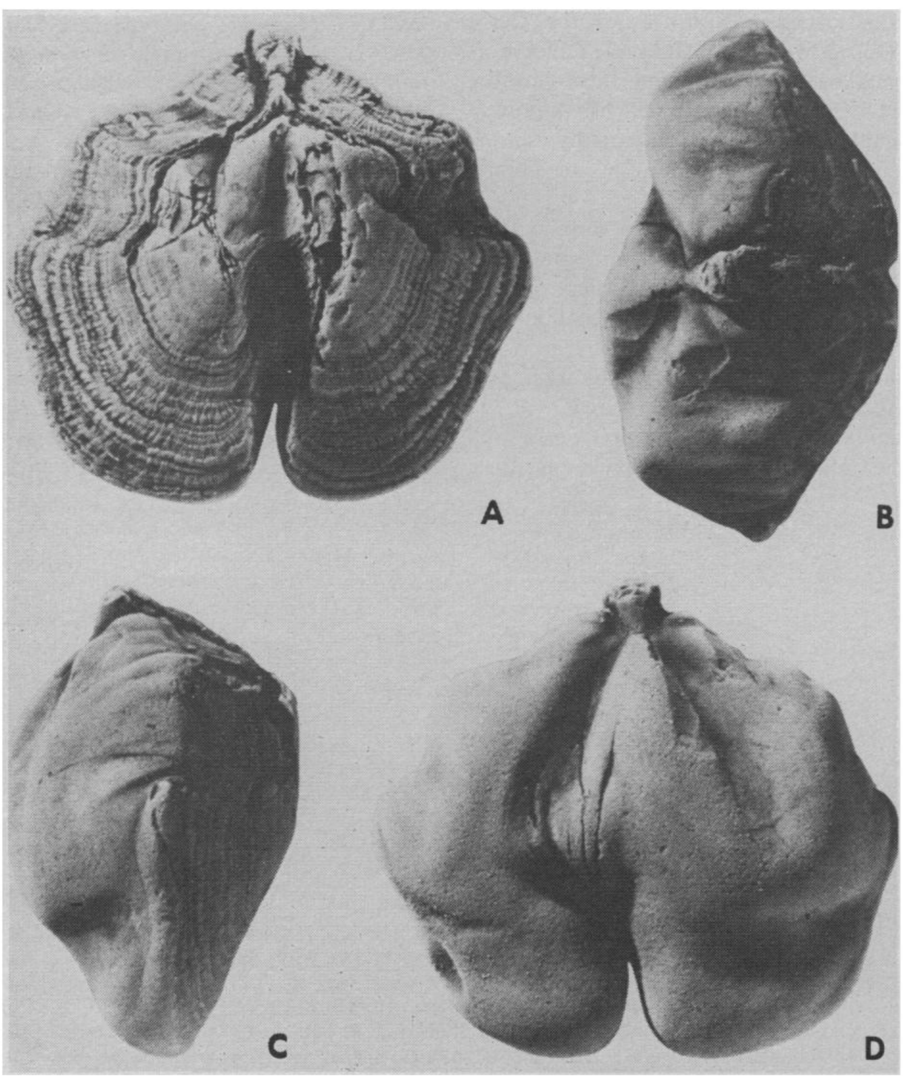

Fig. 2. Holotype of *Gluteus minimus*, new genus, new species; specimen SUI 34978-91 from locality *D* (Fig. 1A). The actual width of A and D is 9.55 mm.

ganic C, 1.45 (*6*). Specimens from locality *C* were analyzed for amino acids (*7*); none were found, even though associated fish bone material did yield amino acids.

We are uncertain that the original composition of the "horse collars" was apatitic. X-ray diffraction patterns of an associated *Bellerophon*-like snail shell (SUI 34972) at locality *E* indicate that the shell material is replaced by quartz and apatite (*5*).

Occurrence and associated fossils: Although "horse collars" have been found at six localities, they are well known only from sites *B*, *C*, and *D* (Fig. 1A) in Washington County, Iowa. At each locality the fossils occur in a single layer no more than 5 cm thick within the Maple Mill Shale. The situation appears to be similar in the Columbus City well section (locality *E*).

Associated with the "horse collars" are conodonts (*8*), inarticulate brachiopods, scolecodonts, *Tasmanites*, fish teeth and spines, bone fragments, and phosphate chunks, some apparently fecal (SUI 38196 through 38201). The layer is burrowed, with individual fillings up to 1 cm across (SUI 38202). Several pyritized articulate brachiopods have been found, plus a phosphate "blob" with the impression of part of the internal mold of an articulate brachiopod (SUI 38203 and 35301, respectively). A few minute, *Bellerophon*-like snails have been recovered from the layer, along with a similar specimen (SUI 34972) approaching 1 cm in diameter. A single tiny, high-spired snail (SUI 34974) has also been found.

The fossils are patchy in distribution and may have been sorted into depressions. Beinert (*8*), in concluding that reworking had occurred, noted the eroded condition of the conodonts and the association in the one stratum of specimens representative of six conodont zones (*Palmatolepis triangularis* up into *Polygnathus styriacus*). Klapper (*9*), however, believed that any reworking is less than a conodont zone in magnitude and would locate the Maple Mill Shale in the upper half of the *Scaphignathus velifer* conodont zone (*10*).

Affinities: The general appearance of "horse collars," with a growth-lined and a smooth surface, is not dissimilar to that of parts of a number of animal groups, for example, fish teeth and plates, snail opercula, gastropod gastric plates, vertebrate otoliths, worm tube opercula, chiton plates, and aptychi (cephalopod opercula). One worker has concluded that "horse collars" are, in fact, fish teeth (*11*). However, most animals have bilaterally symmetrical parts—chiton plates, for example—or structures which occur in mirror-image pairs—aptychi, fish teeth and plates, and vertebrate otoliths, even in the flat fish (Heterosomata). Other animals, for example, the brachiopod *Streptis grayii* (*12*), are individually asymmetric, but with both left-handed and right-handed individuals occurring in the same population in fair abundance. On the other hand, consistent asymmetry such as is present in "horse collars" does occur in certain annelid worms (*13*) and, of course, in gastropods.

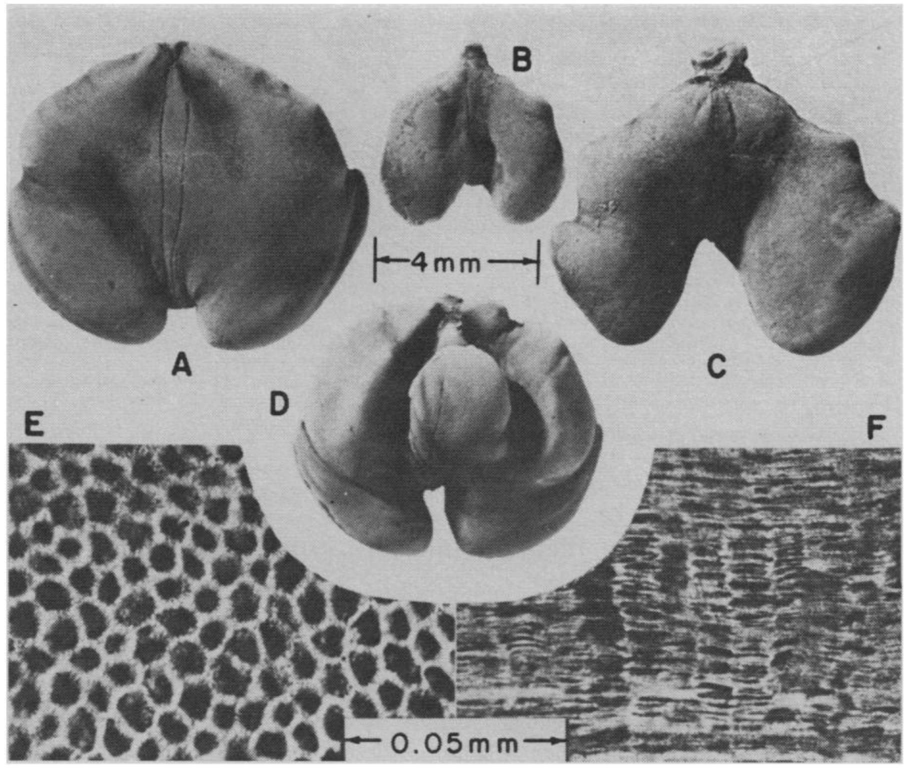

Fig. 3. Internal structure and aberrant specimens of *Gluteus minimus*. (A) UCGM 40611A, from locality *C* (Fig. 1A). (B) UCGM 40613, from locality *C*. (C) UCGM 40614A, from locality *C*. (D) UCGM 40616A, from locality *C*. (E) SUI 34976, from locality *D*; plane of section parallel to smooth and growth-lined surfaces. (F) UCGM 42685, from locality *C*; plane of section perpendicular to that of (E), down one lobe of the specimen, with the lined surface toward the top of the picture.

The internal structure of "horse collars" precludes their being internal molds of, for example, brachiopods. It does not resemble that of vertebrate bone or cartilage (*14*), nor is it closely similar to that of vertebrate otoliths (*15*). Of the various invertebrates we have examined, the closest similarity to the internal structure of "horse collars" is shown by prismatic shell material such as that of certain mollusks. However, the crystals of molluscan prismatic shell are characteristically larger and longer than the platelike entities within "horse collars" (*16*). Moreover, the latter do not seem to be vacuities such as form similar patterns in the shell of rudistid pelecypods (*17*). The internal structure of "horse collars" does not, in fact, match that of any invertebrate hard parts which we have studied (*18*).

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References and Notes

1. Weller's specimens (UC 10621) and Eastman's specimens (UF 569) are at the Field Museum of Natural History, Chicago, Illinois. M. Nitecki and E. S. Richardson, Jr., of the museum provided information on the history of their labels and cataloging.
2. Card index to Belanski's collection, Department of Geology, University of Iowa.
3. D. Koch discovered these specimens.
4. T. A. Jones, *J. Sediment. Petrol.* **39**, 1622 (1969); level of significance = 0.05.
5. J. B. Hayes, Marathon Oil Co., Littleton,

Colorado, gave advice on interpretation of x-ray patterns (including those for SUI 34972, 34973, and 35303 and UCGM 40606 through 40608 and 40610).
6. T. W. Bloxam, Department of Geology, University College of Swansea, Wales, chemically analyzed specimens for this study.
7. P. Sandberg, Department of Geology, University of Illinois, made possible amino acid analyses of our material.
8. R. J. Beinert, thesis, University of Iowa (1968).
9. G. Klapper, Department of Geology, University of Iowa, suggested one interpretation of the reworking.
10. G. Klapper *et al.*, *Geol. Soc. Am. Mem. 127* (1971), p. 306.
11. G. R. Case, *Fossil Shark and Fish Remains of North America* (Grafco, New York, 1967), p. 5.
12. M. G. Bassett, *Palaeontogr. Soc. Monogr. (Lond.)* **126** (No. 532), 74 (1972).
13. Z. Kielan-Jaworowski, *Palaeontol. Polon. No. 16* (1966).
14. R. Denison, Field Museum of Natural History; the late W. Gross, Geologisch-Paläontologisches Institut, Universität Tübingen; D. Dunkle, Cleveland Museum of Natural History; and H.-P. Schultze, Georg-August-Universität, Göttingen, offered information on vertebrate histology.
15. R. W. Morris and L. R. Kittleman, *Science* **158**, 368 (1967).
16. O. H. Schindewolf, *Palaeontogr. Abt. A Palaeozool. Stratigr.* **111**, 1 (1958).
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18. H. Mutvei, Naturhistoriska Riksmuseet, Stockholm; R. Batten, American Museum of Natural History, New York; and H. Lowenstam, California Institute of Technology, Pasadena, provided information on invertebrate shell histology.
19. Contribution No. 131 of the Department of Geology, University of Cincinnati.

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Cyclopentyl Ketones: Identification and Function in Azteca Ants

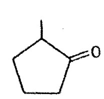
Abstract. *The anal gland secretions of dolichoderine ants in the genus* Azteca *are fortified with cyclopentyl ketones. Since these compounds, 2-methylcyclopentanone,* cis-*1-acetyl-2-methylcyclopentane, and 2-acetyl-3-methylcyclopentene, release sustained alarm behavior in ant workers, they constitute a new chemical class of insect pheromones. The ketones probably also function as defensive compounds and thus are part of the ants' alarm-defense system.*

Ants in the subfamily Dolichoderinae have yielded several novel natural products (*1*) related to nepetalactone, a characteristic compound of the catnip plant (*2*). Five of these exocrine products have been identified from ant workers in a variety of dolichoderine genera (*1*). Also, several acyclic ketones, of both terpenoid (*3*) and nonterpenoid (*4*) origin, are produced by these ants. Whereas these ketones function as both defense materials (*4*) and releasers of alarm behavior (*5*), the cyclopentanoid monoterpenes are reported to be utilized either for defense (*6*) or as fixatives for the more volatile ketones (*7*). All of these exocrine products are synthesized in the anal glands (*8*), structures which are limited to species in the subfamily Dolichoderinae and appear to have arisen de novo to function as social organs.

The dolichoderine genus *Azteca* constitutes one of the most conspicuous ant taxa in the American tropics. Many species have an obligatory relationship with myrmecophytes in the moraceous genus *Cecropia*, whereas others construct large carton nests in a variety of trees and shrubs (*9*). When disturbed, workers in the populous colonies swarm all over the intruder. Although they lack a functional sting, an emphatic deterrent message is conveyed through painful bites administered by the aggressive workers.

Disturbed workers of many species of *Azteca* are characterized by a pungent sweet-sour odor which, to our noses, differed clearly from that of any other dolichoderine genus with which we were familiar. Consistent with their distinctive organoleptic properties, three cyclopentyl ketones which have not been previously detected in ants or any other biological source and possess this odor have been identified as anal gland products (*10*). Furthermore, since these compounds function as alarm pheromones, they constitute a new chemical class of releasers of social behavior (*11*) and may also be utilized as defensive compounds.

m/e (relative intensity):



98(50), 83(10), 70(10), 69(30), 56(10), 55(60), 42(100), 41(50)

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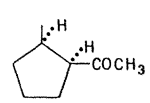
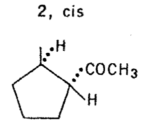


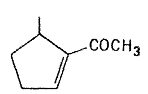
126(20), 111(9), 83(57), 71(83), 55(88), 43(100)

2, cis



126(22), 111(34), 83(60), 71(42), 55(88), 43(100)

3, trans



124(38), 109(42), 81(100), 79(24), 53(19), 43(85)

4

Fig. 1. Mass spectra of cyclopentyl ketones.

Methylene chloride extracts of two species of *Azteca* which had constructed carton nests in a spiny palm (*Astrocaryum standleyanum*) and a cashew tree (*Anacardium occidentale*) were prepared for chemical analyses. The palm species was determined as *Azteca* nr. *velox* and the cashew population as *Azteca* nr. *nigriventris* (*12*). Combined gas chromatography–mass spectroscopy (*13*) of the extracts indicated three previously unreported major volatile components with molecular weights of 98 (**1**), 126 (**2**), and 124 (**4**) (see Fig. 1) in *A.* nr. *nigriventris*, whereas the 124 component was not detected in *A.* nr. *velox*. A computer search of numerous mass spectra (*14*) indicated similarities of **1** to 2-methylcyclopentanone, and examination of authentic samples of positional isomers (*15*) confirmed the presence of the 2-isomer (**1**) in both species of *Azteca*.

The other two volatiles both appeared to be related methyl ketones from their mass spectra (base peak *m/e* 43). Comparison of **2** with acetylcyclohexane (*16*) and of **4** with acetylcyclohexene (*15*) suggested that the two unknowns might be methylcyclopentyl (or pentenyl) methyl ketones. A mixture of *cis*- and *trans*-1-acetyl-2-methylcyclopentane was synthesized by the method of Hopff (*17, 18*), and *cis*-1-acetyl-2-methylcyclopentane was prepared by catalytic hydrogenation of 1-acetyl-2-methylcyclopentene (*19, 20*). The retention time and mass spectrum of the ant volatile of *m/e* 126 (**2**) were identical to those of *cis*-1-acetyl-2-methylcyclopentane. Although synthetic *cis* and *trans* (**2** and **3**) are separable on the column used, *trans* (**3**) was not detected in either *Azteca* species. The mass spectra of the isomeric 1-acetyl-1-methylcyclopentane (*21*) and 1-acetyl-3-methylcyclopentane (*22*) were sufficiently different to distinguish them from **2**.

The mass spectral fragmentation pattern of **4** was similar to those of 1-acetyl-2-methylcyclopentene (*23*) and 3-acetyl-2-methylcyclopentene (*23*), but the relative intensities differed significantly. Ozonolysis of 2,4-dimethyl-