DEFENSIVE SECRETIONS OF TIGER BEETLES:
CYANOGENETIC BASIS

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Abstract—1. The defensive secretion of the tiger beetle Megacephala virginica contains benzaldehyde,
HCN, and mandelonitrile.
2. The significance of convergent biochemical evolution in the Arthropoda for the production of
benzaldehyde and HCN by cyanogenesis is discussed.

INTRODUCTION

Among the insects, carabid beetles have proven to be
an especially rich source of natural products that are
utilized in defensive contexts. The pygidial glands of
the Carabidae synthesize a wide variety of defensive
allomones that include aliphatic acids, hydrocarbons,
esters, ketones, cresols, and quinones (Moore & wall-
bank, 1968; Schildknecht et al., 1968; Moore, 1980).
The tiger beetles, members of the subfamily Cicindeli-
nae, are particularly distinctive in producing benzal-
dehyde (Moore & Brown, 1971; Moore, 1980), a com-
ound that has not been detected as a glandular product
of species in any of the other subfamilies analy-
ized. In the present paper we report that in tiger
beetles benzaldehyde is derived from the same apar-
ent cyanogenic precursor that has been independently
evolved by arthropods in a variety of disparate taxa.

MATERIALS AND METHODS

Adult beetles, Megacephala virginica and M. carolina,
were collected in Athens, GA and after freezing, the pygi-
dial gland reservoirs were dissected and placed directly in
methylen chloride. Extracts were analyzed by gas chromato-
ography-mass spectrometry on a LKB 2091 instrument
utilizing a 2.0 m column of 3% OV-1 programmed from
60–220°C. The presence of HCN was qualitatively deter-
mined by holding beetles over moist filter papers impreg-
nated with copper acetate-benzidine acetate (Feigl, 1966).

RESULT

The pygidial gland reservoirs of both species are
well developed and rather typical of these structures
as described for other carabid species (Forsyth, 1972).
Two compounds were detected by gas chromato-
graphic analysis of glandular extracts of M. virgini-
cica, the earlier eluting of which accounted for more
than 90% of the observed volatiles. A molecular ion at
m/z 106 and characteristic fragments at m/z 105, 77,
and 51 established the identity of this compound as
benzaldehyde. In GC analyses of glandular extracts of
M. carolina this was the only compound detected.

The minor constituent present in M. virginica
extracts possessed a molecular ion at m/z 133 and a
base peak at m/z 77. Strong fragments were also
present at m/z 106 and 105, and good signals were
detected at m/z 132, 78, 51 and 50. The mass spectrum
of this compound was completely congruent with that
of mandelonitrile. This compound, which is very un-
stable, could only be detected in initial analyses of the
extracts of M. virginica.

The presence of HCN in the secretions of both spe-
cies was demonstrated by the immediate appearance
of a strong blue color in copper acetate-benzidine
acetate treated papers placed under beetles that were
actively discharging their pygidial gland products.

DISCUSSION

Benzaldehyde appears to be a characteristic defen-
sive product of carabid beetles in the genus Megace-
phala, having been previously identified in three Aus-
tralian species (Moore & Brown, 1971; Moore, 1980),
in addition to the two reported here. Significantly,
this aromatic aldehyde has only been identified in the
secretions of species in the subfamily Cicindelinae,
notwithstanding the fact that over 200 species rep-
resenting 60% of the carabid subfamilies have been
examined (Moore, 1980). The rarity of benzaldehyde
as a carabal defensive compound is probably corre-
lated with the lack of a cyanogenetic pathway for
producing this compound in members of other sub-
families.

Benzaldehyde has a haphazard distribution in the
defensive secretions of arthropods and in every case in
which these exudates have been carefully analyzed, it
is accompanied by HCN. In arthropods, the defensive
duet of benzaldehyde and HCN has been demon-
strated to have its ultimate origin from cyanogenetic
precursors, principally mandelonitrile. In polyes-
dmoid millipedes this cyanogen is derived from aro-
matic amino acids (Duffey et al., 1974), and it will not
prove surprising if this is the case for arthropods in
other taxa as well. Cyanogenesis, resulting in the se-
cretion of benzaldehyde-HCN, has been detected in
geophilid centipedes (Jones et al., 1976), larvae of
chrysomelid beetles (Moore, 1967), and a large variety of polydesmoid millipedes (Conner et al., 1977; Duffey et al., 1977). In the cases of the centipedes, millipedes, and the carabid beetles described in the present paper, the presence of mandelonitrile in the defensive exudates is consistent with the conclusion that the arthropods in these three orders have independently evolved a common cyanogen from which their major defensive products are derived. This does not necessarily imply that the absolute configurations of the mandelonitrile produced by the species in these three arthropod taxa are identical.

The spotty distribution of benzaldehyde in the defensive secretions of arthropods may indicate that this compound is not easily produced by these invertebrates. Since cyanogenesis constitutes its only known means of derivation in the defensive secretions of arthropods, in the absence of other demonstrable biosynthetic evidence, it may well be that benzaldehyde cannot be readily produced by arthropods unless they have evolved a pathway for generating a precursory cyanogen. The instability of mandelonitrile militates against its ready detection and, since HCN can also be easily overlooked utilizing gas chromatographic detection methods, the presence of benzaldehyde in a defensive exudate in the apparent absence of these compounds may not necessarily indicate that they were not present. If benzaldehyde is subsequently detected as a glandular product of arthropods in other taxa, it would seem highly desirable to check for the presence of HCN and a cyanogen in order to further establish the distributional limits of cyanogenesis.

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REFERENCES


