

CHEMICAL ECOLOGY OF ARTHROPODS, VI<sup>(1)</sup>,

Adaline, a novel alkaloid from Adalia bipunctata L. (Coleoptera, Coccinellidae).

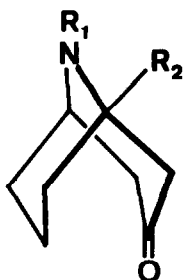
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During a survey<sup>(1a-1c,1e)</sup> of chemical defenses of Coccinellidae we have examined the European ladybug *Adalia bipunctata* L. 800 specimens, collected around Brussels, were extracted with methanol. Fractionation of the extract on alumina column afforded 35 mg of a novel, amorphous alkaloid, adaline (1) C<sub>13</sub>H<sub>23</sub>NO (M: 209 by MS), (α)<sub>D</sub><sup>-13°</sup> in CHCl<sub>3</sub>. The same compound was isolated from the varieties *quadrimaculata* Scopoli and *pantherina* L.

(1) contains a carbonyl function as indicated by an IR band at 1710 cm<sup>-1</sup> and a N-H group as suggested by a band at 3330 cm<sup>-1</sup> and confirmed by the formation of a N-monoacetyl derivative (2) (M: 251 by MS; IR: ν<sub>C=O</sub> 1700 and 1660 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>/TMS): 3H singlet at 132 Hz). Prominent features of the NMR spectrum of (1) are a poorly resolved 3H triplet at 53 Hz (J=4Hz) and a broad 1H multiplet at 222 Hz (shifted by 46 Hz downfield in the spectrum of (2)). These can be attributed to one primary C-CH<sub>3</sub> group and one proton α to the nitrogen atom respectively.



	R <sub>1</sub>	R <sub>2</sub>
1	H	n-C <sub>5</sub> H <sub>11</sub>
2	COCH <sub>3</sub>	n-C <sub>5</sub> H <sub>11</sub>
3	CH <sub>2</sub> CH <sub>3</sub>	n-C <sub>5</sub> H <sub>11</sub>
4	CH <sub>3</sub>	H
5	H	CH <sub>3</sub>

LAH reduction of N-acetyl adaline (2) yields a mixture of amino alcohols (M: 237 by MS) which is converted to N-ethyl adaline (3) by oxidation with CrO<sub>3</sub>-pyridine complex. Adaline (1) must thus be a bicyclic aminoketone possessing a skeleton different from the alkaloids previously isolated from other ladybugs<sup>(1a-1c,1e)</sup>, since the presence of a methyl triplet implies the existence of a terminal chain of at least two carbon atoms.

The complete structure (fig. 1) of adaline (1) was established by single crystal X-ray diffraction of adaline hydrochloride (m.p, 204-205°).

Crystal data : small transparent plates, space group  $P2_1$ ,  $a = 11.20(0)$  Å,  $b = 8.90(5)$  Å,  $c = 7.60(2)$  Å,  $\gamma = 109.9(8)^\circ$ . Cell parameters were refined on a Hilger-Watts four-circle diffractometer controlled by a PDP-8 computer, using  $\text{Cu-K}_\alpha$  radiation.

The data, collected on the diffractometer, were reduced to 1321 independent reflexions and corrected for  $L_p$ -factor but not for absorption. The structure was solved by direct methods using the MULTAN system of programs <sup>(2)</sup>. All light atoms were first considered as identical. After three cycles of full-matrix refinement, letting the chlorine ion vary anisotropically, an R-value of 15% was obtained and the positions of the nitrogen and oxygen atoms unequivocally determined. Further refinement is carried on at the present moment.

Other basic compounds deriving from the same bicyclic system have been isolated from natural sources : pseudopelletierine (4) <sup>(3)</sup> from *Punica granata* and 9-aza-1-methylbicyclo-(3,3,1)-nonan-3-one (5) <sup>(4)</sup> from *Euphorbia atoto*. The fragmentation pattern observed in the MS of adaline (1) is in good agreement with those observed for (5) <sup>(4)</sup> and tropinone (5).

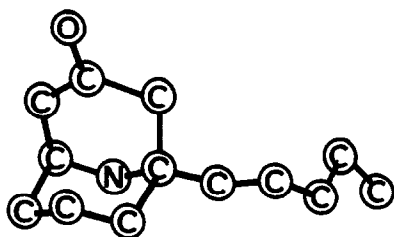


fig.1

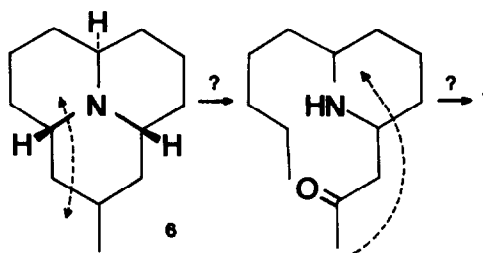


fig.2

It is tempting to speculate on a possible biogenetic interrelationship between (1) and the coccinelline type alkaloids. Obtention of (1) could be conceived for instance from precoccinelline (6) according to the scheme hereabove (fig.2).

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