

Note

Reversed-phase high-performance liquid chromatographic separation of human phenolic metabolites of propoxur (Baygon), carbofuran and carbaryl

JEFFREY E. KEISER**, KENNETH W. KIRBY** and FRED TREMMEL***

Institute of Agricultural Medicine and Environmental Health, Department of Preventive Medicine and Environmental Health, University of Iowa, Oakdale, IA 52319 (U.S.A.)

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The U.S. Environmental Protection Agency uses an electron-capture gas chromatographic procedure for the determination of human phenolic metabolites of the carbamate insecticides propoxur (Baygon), carbofuran, and carbaryl. This procedure is a modification of the one originally proposed by Kawahara¹ and involves derivatizing the phenols with pentafluorobenzyl bromide. The structures for the phenols are shown in Fig. 1. They are 3-ketocarbofuran phenol (2,3-dihydro-2,2-dimethyl-3-keto-7-hydroxybenzofuran, I) and carbofuran phenol (2,3-dihydro-2,2-dimethyl-7-hydroxybenzofuran, II) from carbofuran, 2-isopropoxyphenol (III) from propoxur (Baygon) and 1-naphthol (IV) from carbaryl.

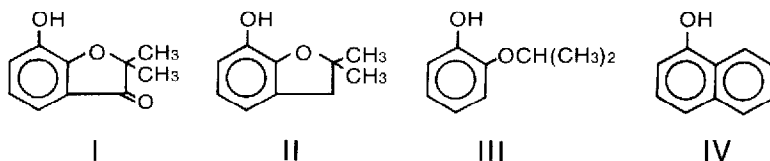


Fig. 1. Phenolic metabolites of carbofuran, propoxur (Baygon), and carbaryl in human urine. I = 3-ketocarbofuranphenol, II = carbofuranphenol, III = 2-isopropoxyphenol, IV = 1-naphthol.

As part of our continuing efforts to develop improved methods of measuring human exposure to pesticides, we have examined the high-performance liquid chromatographic separation on a reversed-phase C_{18} column of the above four compounds which are known human urinary metabolites of the parent carbamates. Since current resources and time schedules do not permit our extending this analytical procedure to urine samples, we are reporting our data in this note.

* Present address: Department of Chemistry, Coe College, Cedar Rapids, IA 52402, U.S.A.

** Present address: Penick and Ford Limited, Cedar Rapids, IA 52404, U.S.A.

*** Present address: Argonne National Laboratory, Argonne, IL 60439, U.S.A.

EXPERIMENTAL

Apparatus

The Waters liquid chromatography apparatus consisted of two 6000A pumps controlled by a Model 660 solvent programmer, a U6K injector and a Model 440 detector operated at 254 nm.

Reagents

Organic solvents were Burdick and Jackson (Muskegon, MI, USA) chromatographic grade. Chromatographic grade water was obtained from a Milli-Q-Reagent grade (Millipore, Bedford, MA, USA) water system. Solvents were suction filtered through a 0.45 μm membrane filter before use. 1-Naphthol was obtained from Eastman Kodak. 3-Ketocarbofuran phenol (I) and carbofuran phenol (II) were gifts of FMC (Middleport, NY, USA). 2-Isopropoxyphenol (III) was a gift of Mobay Chemical (Kansas City, MO, USA).

RESULTS AND DISCUSSION

Several solvent mixtures were capable of separating the four phenolic metabolites on the reversed-phase C_{18} column including acetonitrile-water (35:65),

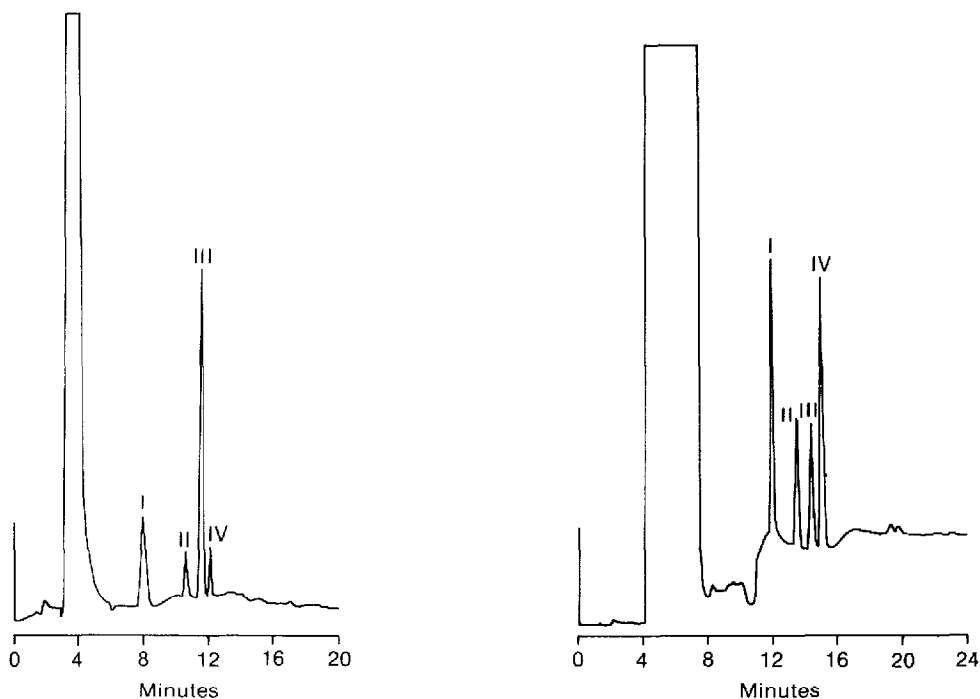


Fig. 2. Chromatogram of four phenols on $\mu\text{Bondapak C}_{18}$. Solvent: 30-60% acetonitrile-acetone in 10 min (flow of 1 ml/min). Quantities of phenols vary. 0.05 a.u.f.s.

Fig. 3. Chromatogram of four phenols on $\mu\text{Bondapak C}_{18}$. Solvent: 0-60% acetonitrile-water in 10 min (flow of 1 ml/min). 200 ng of each standard dissolved in 20 μl of acetonitrile-acetone (50:50). 0.05 a.u.f.s.

methanol-water (55:45) and tetrahydrofuran-water (35:65). Because of our interest in trace enrichment strategies such as the one developed for carbofuran and its metabolites in water, by Cramer *et al.*², we were particularly interested to find that methanol-water and acetonitrile-water gradient elutions effected separations of the four compounds.

Figs. 2 and 3 compare with two different gradient elutions using acetonitrile-water. Peak I in the 0-60% (10 min) gradient (Fig. 2) is clearly more efficient than the 30-60% (10 min) gradient (Fig. 3). Furthermore, the latter gradient would be much better for collection, since the peaks elute in less than four min as compared to a five min period in the 0-60% gradient. Under isocratic conditions (acetonitrile-water (30:40), 1 ml/min), the k' values were 3, 6, 7.5, 10.5.

Thus, we have developed separation procedures for human urinary metabolites of three commonly used carbamate insecticides under both isocratic and gradient elution conditions. These procedures have potential application in the determination of human exposure to propoxur (Baygon), carbaryl and carbofuran.

REFERENCES

- 1 F. K. Kawahara, *Anal. Chem.*, 40 (1968) 1009.
- 2 P. H. Cramer, A. D. Drinkwine, J. E. Going and A. E. Carey, *J. Chromatogr.*, 235 (1982) 489.