Identification of Metabolites Formed During Degradation of β- and δ-Hexachlorocyclohexane (HCH) by Sphingobium indicum B90A

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ABSTRACT

HCH (hexachlorocyclohexane) was once widely used as an insecticide until its environmental persistence was recognized and its use was discontinued or banned in many countries. Nevertheless, environmental problems surface now from former production and dump sites, in particular with the more stable β-HCH and δ-HCH endangering ground and surface waters. In the present study, several polar hydroxy metabolites formed during degradation of β- and δ-HCH by the soil microorganism Sphingobium indicum B90A (formerly Sphingomonas paucimobilis B90A(1,2,3)), were identified and characterized. The two metabolites from β-HCH were identified as a tetrachlorocyclohexanol and a tetrachlorocyclohexanediol. Four additional hydroxy metabolites were observed from δ-HCH and identified also as a pentachlorocyclohexanol and a tetrachlorocyclohexanediol. Four additional hydroxy metabolites were observed from δ-HCH and identified also as a pentachlorocyclohexanol and a tetrachlorocyclohexanediol. The latter cyclohexanol and cyclohexanediol are likely formed via δ-PCHC, initially formed from δ-HCH, rather than by dehydrochlorination of initially hydroxylated compounds. Such data will aid in future investigations on the degradation of HCH in environmental studies. The data suggests that hydroxylation proceeded via an S,2-type reaction with substitution of equatorial Cls and formation of axial–OH substituted compounds. The study also revealed that equatorial-Cl in β- and δ-HCH are more reactive toward hydroxylation with the enzymes of S. indicum B90A, which is in contrast to the general dehydrochlorination of HCHs where axial-Cl are far more reactive.

RESULTS AND DISCUSSION

CHLORIDE-HCH MASS BALANCE

S. indicum B90A aerobically degrades α-, β-, γ- and δ-HCH within 24h (γ > α > δ > β). However, mass balance analysis showed that α- and γ-HCH are completely mineralized (5-6 chlorines released per HCH molecule degraded), but for β- and δ-HCH only 2-3 chlorines were released per HCH molecule degraded, indicating incomplete mineralization.

FORMATION OF HYDROXYLATED METABOLITES

Two additional metabolites of δ-HCH were identified as tetrachlorocyclohexanol and trichlorocyclohexanediol which could be only formed by initial HCl elimination of δ-HCH to δ-PCHC by a simple anti-periplanar trans HCl elimination involving the axial Cl followed by hydroxylation of the equatorial Cl in allylic position which would yield the delta-3 and delta-4.

TETRACHLOROCYCLOHEXENOL

Two isomeric tetrachlorocyclohexanol and trichlorocyclohexanediol were identified from δ-HCH via δ-PCHC by simple anti-periplanar trans HCl elimination involving the axial Cl followed by hydroxylation of the equatorial Cl in allylic position which would yield the delta-3 and delta-4.

CONCLUSIONS

1. Equatorial chlorides in β- and δ-HCHs are more susceptible towards hydroxylation than the general dehydrochlorination of axial chlorides in α- and γ-HCH.
2. delta-1 and delta-2 are not precursors for delta-3 and delta-4 respectively.
3. delta-3 and delta-4 can result from the formation of δ-PCHC from δ-HCH via elimination of (trans dialcyl HCl elimination) axial Cl and followed by subsequent hydroxylation of equatorial Cl by substitution of –OH

REFERENCES:


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