Effect of Carrier on Isomalathion Formation in Malathion Powders*

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Solid pesticide carriers have been found to influence isomalathion formation in malathion powders. Of the carriers tested, formulations with only hydrated calcium silicate and silica gel-H complied with the AID/WHO requirement for isomalathion content. No relationship between isomalathion formation and physico-chemical characteristics of the carriers or period after incubation could be observed.

INTRODUCTION

Sequent to the 1976 epidemic malathion poisoning in Pakistan,1-12 few published reports explaining the possible cause of this toxicity are now available.1-4 It has been shown in these reports that S-methyl isomer of malathion, commonly known as isomalathion (O, S-dimethyl-S-(1,2-dicarboethoxy) ethyl phosphorodithioate) which is either present or formed during storage in technical malathion5,6 and malathion formulations,1-3 correlated best with the mammalian toxicity of the formulations. The presence of small amounts of isomalathion in malathion formulations, besides being toxic, potentiate the mammalian toxicity of malathion.5 It has also been reported that the auxiliaries employed in malathion formulations altered isomalathion content.5,6 However, systematic information on this subject is lacking. As a first step in this direction, effect of the commonly employed pesticide carriers on isomalathion formation in malathion powders is reported here.

MATERIALS AND METHODS

Attapulgite, bentonite, celite, Fuller’s earth, hydrated calcium silicate, kaolinite and silica gel-H were the carriers investigated. The quality of the commercial grade attapulgite, bentonite, Fuller’s earth and kaolinite used was adjudged through specific surface area measurements (respective values in m²/g being: 112 (lit. 1406), 566 (lit. 580-750), 500 and 28.7 (lit. 37-45) and differential thermal analysis (DTA, apparatus, Leeds and Northrup, USA, type G with Pt, Pt 10% Rh as thermocouples and calcined alumina as the reference material; attapulgite: endothermic peaks at 620°C and 150°C and absence of a peak around 800°C indicated montmorillonite impurity which was not substantiated by specific surface area value; bentonite: small endothermic peaks around 125°C and 780-800°C; Fuller’s earth: small endothermic peak below 150°C, medium endothermic peak below 600°C, small exothermic peak around 900°C; kaolinite: endothermic peak around 575°C, small exothermic peak around 1000°C) of the calcium saturated clay size fractions.8-10 The other carriers were pure grade.

Malathion (active ingredient, a.i., 96.96%; isomalathion content, 0.394%) was impregnated on carriers and the powder formulations sieved through BSS-100 mesh sieve. The toxicant strengths of each mixture were as follows: 20% for attapulgite, celite and kaolin-
ite; 25% for bentonite and Fuller’s earth; 40% for silica gel-H and 50% for hydrated calcium silicate. One hundred grams of each along with technical malathion control was incubated in glass containers at 55±1°C for 15 days. Samples providing 1 g equivalent of malathion were withdrawn at the start of the studies, after 1, 2, and 3 days and subsequently at 3 days interval. These were taken in stoppered test tubes, to which 15–20 ml chloroform were added, and shaken thoroughly and left for 24 hr. The extracts were filtered through cotton, the cotton was thoroughly rinsed and the collected filtrates were made up to 25 ml. Samples drawn during the first two days were concentrated to 10 ml using a Buchi type vacuum evaporator. Suitable quantity of the aliquot was taken, chloroform removed under vacuum and the residue, in isopropanol, was analysed by high performance liquid chromatography (HPLC, Waters Associates, Inc. U.S.A., Model ALC/GPC-244 equipped with Micro-porasil (10 μm) column, 3.9 mm IDx 30 cm, and solvent delivery system M 6000A, U6K injector and wavelength detector set at 254 nm). Details of estimation by

Fig. 1 Isomalathion formation on different carriers (Isomalathion content based on nominal malathion content of each formulation. That shown on right side is the permitted isomalathion content cited in literature.3,4)

○—○: Hydrated calcium silicate (50% a.i.), ●—●: Tech. malathion (96.96% a.i.), △—△: Silica gel-H (40% a.i.), □—□: Kaolinite (20% a.i.), ×—×: Attapulgite (20% a.i.), ▲—▲: Fuller’s earth (25% a.i.), Δ—Δ: Celite (20% a.i.), □—□: Bentonite (25% a.i.)
RESULTS AND DISCUSSION

The recovery studies with different carriers impregnated with known concentrations of isomalathion showed inconsistent recoveries. These studies indicated its transformation into 4–5 products (thin layer chromatography, TLC) during the period of solvent expulsion at room temperature after impregnation. No effort was made to identify these products. Similar observations have been earlier reported.\(^1\)\(^,\)\(^2\) Thus, the isomalathion content recorded in this study is, the net balance of that formed from malathion and that transformed into various products.

Isomalathion formation with different carriers is shown in Fig. 1. The permitted isomalathion content as per AID/WHO specifications,\(^3\)\(^,\)\(^4\) i.e., 1.8% of the nominal malathion content after 6 days storage at 55°C, is also indicated in the Figure. Except hydrated calcium silicate and silica gel-H, all the malathion-carrier combinations revealed a content higher than the permitted isomalathion. No correlation between any of the physicochemical properties of the carriers such as pH, pKa, bulk and particle density, cation exchange capacity, sorptivity and specific surface area, and isomalathion formation was found to exist. Isomalathion content of technical malathion increased with time but remained below the permitted level (1.8%). Throughout the exposure period, hydrated calcium silicate revealed a lower than 0.394% isomalathion content which was initially added through technical malathion. This suggested relatively quicker transformation of isomalathion to other products on this carrier. Initially faster transformation of isomalathion to other products is apparent with Fuller’s earth, attapulgite, kaolinite and silica gel as well, though the isomalathion content increased with time. Similar observations have been made in another study on a semi-quantitative appraisal of isomalathion formed in malathion powders stored under ambient and 100±1°C incubation conditions.\(^5\)\(^,\)\(^6\) Except for the case with bentonite, Fuller’s earth, hydrated calcium silicate and kaolinite where maximum isomalathion was observed around 3 days, its content with other carriers generally increased with time. This observation suggests that the prescribed 6 day period for examining the isomalathion content of malathion powders needs reconsideration. An isomalathion content at a particular time seems to be governed by the dynamic transformation of a fraction of malathion into isomalathion and the subsequent conversion of isomalathion into other products. This, in turn, is dependent upon the carrier used, temperature and period of storage, and other related factors. Knowledge of those isomalathion transformation products which differ from malathion products and their toxicological effects along with this information on the malathion transformation products thus seems to be a prerequisite to a logical appraisal of the usefulness or otherwise of the malathion formulations.

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要約
マラチオン粉剤中のイソマラチオン生成における担体の影響

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種々の異なるキャリヤーを用いて調製したマラチオン粉剤中でのイソマラチオンの生成について検討した。イソマラチオンはマラチオンの哺乳動物に対する毒性を著しく増強する作用を有することが知られている。試験に供した7種のキャリヤーのうち、ケイ酸カルシウム、およびシリカゲル-Hを用いた粉剤中のみでイソマラチオンの生成量が、各種マラチオン粉剤中のイソマラチオン含有量に関するAID/WHO規制値以下であった。アタプルジャイト、カオリナイト、ケイソウ土など5種のキャリヤーを用いた粉剤中では規制値以上のイソマラチオンの生成が認められた。なおキャリヤーの物理化学的性質あるいは粉剤の飼育時間とイソマラチオン生成量とに相関関係は認められなかった。