ISOMERS OF MCPA

By L. J. MATTHEWS, Department of Agriculture, Wellington

For several years after MCPA was introduced in England after the conclusion of the Second World War this product remained unchallenged for selective weed control. However, Swedish workers were not satisfied with the results of field trials when they used commercial lines of MCPA herbicides of varying purity. In 1950 detailed work was commenced to isolate the various materials that were sold under the comprehensive term MCPA. They isolated a range of phenols and phenoxyacetic acids and tested these for herbicidal activity.

By late 1951 their conclusions were these: 2-methyl phenol; 6-chloro, 2-methylphenol, and 2-methylphenoxyacetic acid worked as antagonists and thus decreased the herbicide effect of pure MCPA. The second group, 6-chloro, 2-methylphenoxyacetic acid assisted the effect of pure MCPA. The third group, 4-chloro 2-methylphenol; 4, 6, dichloro, 2-methylphenol, and its corresponding acid did not alter the effects of pure MCPA.¹

Later work in England at Jealott's Hill and at the A.R.C. Unit at Oxford showed that only the 2,4 isomer or 2 methyl, 4 chloro-phenoxyacetic acid had marked herbicidal properties and that 2-methyl, 6-chlorophenoxyacetic acid had insignificant herbicidal properties. In fact, work with legumes showed that some of the impurities in MCPA decreased the selectivity of the preparation. All American workers now agree that only the 2,4 isomer has marked herbicidal properties, but their research with MCPA is many years behind that of English research.

Work in New Zealand with MCPA materials started in 1946. To date there have been nearly 300 trials put down on nearly 100 weed species and over 60 trials on crops such as potatoes, peas, lucerne, all cereals, clover seed crops, linseed, *Phormium tenax*, and small seed crops. The preparations of MCPA employed included various proprietary lines of 1 and 5 per cent. dusts of the sodium salt of MCPA, liquids containing 1.0 and 3.0lb. of the sodium salt of MCPA per gallon, the potassium salt, the alkanolamines unspecified (usually a mixture of the diethanolamine and triethanolamine MCPA), the polyethylene glycol ester, and the butyl ester of MCPA. In many trials the MCPA products were compared with 2,4-D and 2,4,5-T materials and in the more recent trials a range of formulations of MCPA was employed.

When comparisons have been made of MCPA formulations and various proprietary lines of the one formulation, particularly for weeds specific in reaction to MCPA such as *Ranunculus acris* (acris), large differences were apparent in the control obtained. When proprietary lines of MCPA were compared in trials with preparations of guaranteed 2,4 isomer content, in all cases the control obtained with the materials with the known 2,4 isomer content yielded the best results. In these trials the application rates were at equivalent MCPA acid equivalents as calculated from manufacturers' statements. The effect of this on impure products would be to give a lower rate of 2,4 isomer per acre in such products.

The results of a typical trial conducted with MCPA compounds on *Ranunculus acris* are as follows:—

Preparation:—

A	90 per cent. control	Clover damage slight
B	80 per cent. control	Clover damage fairly severe
C	70 per cent. control	Clover damage severe
* D based on 2,4 isomer content	Practically complete kill	Clover damage slight

* Clover damage refers to white clover.

Preparations of MCPA have been analysed in New Zealand for 2,4 isomer content. The method of analysis employed was that laid down by the British Voluntary Approval Scheme.²

If an allowance is made for a + or - 5 per cent. variation in the analysis, the results of analysis of products carried out by Mr. K. Hoy at Rukuhia Soil Research Station are as follows: Three proprietary lines were employed and compared with a preparation of known 2,4 isomer content. All proprietary products were labelled as having 3.0lb. acid equivalent per gallon.

Total acid equivalent	2 methyl, 4 chlorophenoxyacetic acid equivalent
4.10	3.35
3.06	1.97
3.06	2.22

It will be seen that a difference between the preparations containing the lowest and highest amount of 2,4 isomer content was 1.4lb. Analysis of MCPA products made in England after the 2,4 isomer content was realised to be of importance varied widely also. More analyses are required on commercially available products in New Zealand, for field observations strongly suggest that different batches of the same proprietary material vary widely in efficiency.

There are several methods of manufacturing MCPA products. One method that has proved satisfactory is to condense o-cresol with chloroacetic acid to give 2 methyl-phenoxyacetic acid. This is then chlorinated and by careful control of chlorination it is possible to obtain 4-chloro, 2-methyl phenoxyacetic acid in a reasonably pure form. MCPA made in this way can reach a purity of 95.50 per cent. of the 2,4 isomer together with: 0.62 per cent. methyl phenoxyacetic acid, 1.49 per cent. 6 chloro 2-methyl phenoxyacetic acid, and 2.05 per cent. 4,6 dichloro, 2-methyl phenoxyacetic acid.

Another method is to chlorinate o-cresol and then condense the resulting mixture of isomers with chloroacetic acid. Yet another method, which is possible with the recent availability of 4-chloro-o-cresol, is to condense this material with chloroacetic acid. This last method gives reasonably pure MCPA, but chromatographic analysis² is probably necessary to check the purity of every batch manufactured.

The physical properties of the 2,4 isomer vary considerably from those preparations containing impurities. The impurities, largely chlorocresols, impart a strong odour to materials containing a low percentage of the 2,4 isomer. Most MCPA preparations are buffered against excess alkalinity, the cause of rapid rusting of containers in the past.

English workers agree on the whole that there is little or no difference in toxicity of organo-metallic salt preparations, such as the sodium or potassium salt of MCPA and the amine salts. The advantage of amine salts over the organo-metallic salts is that the amines are not as alkaline as the organo-metallic salts and are more soluble and hence less likely to crystallise out of solution or on the foliage of plants. In the field this has meant that under conditions which maintain the leaf surface of the plant in a moist condition for 2 to 3 days we find little or no difference in toxic effect. These conditions usually prevail in New Zealand.

With the introduction of products containing higher proportions of the 2,4 isomer, MCPA appears more favourably in comparison with 2,4-D. The organo-metallic salts of amine preparations of MCPA on the whole penetrate the leaves of the plants more quickly than the less soluble sodium salts of 2,4-D and to a less extent the amines of 2,4-D. With increased activity and with reliable standards to work to MCPA products have shown in some cases equal toxicity to 2,4-D preparations. In some

cases weeds are controlled with MCPA and not 2,4-D. Examples of these are *Ranunculus acer* and to a less extent, *Bellis perennis*. MCPA shows a greater selectivity for weed control in crops. At no stage of growth of red clover can 2,4-D be used for control of weeds in red clover stands or in pastures containing a large proportion of red clover, but MCPA can be used for this purpose. In the case of white clover areas or pastures, 2,4-D is more selective than MCPA materials on seedling white clover and for the first few months after sowing, though this difference becomes less apparent once the clover is established.

SUMMARY

1. Overseas research shows that only the 2,4 isomer has strong herbicidal properties.
2. This is supported by work conducted in New Zealand to date, where the 2,4 isomer preparations have been compared with MCPA compounds containing less than 90 to 95 per cent. of the 2,4 isomer.
3. Analyses of MCPA products available in New Zealand show that the acid equivalent content is not based only on the 2,4 isomer content.
4. MCPA products have been shown to be more selective than 2,4-D for most crop weed control work and in some cases to be as equally toxic or more toxic than 2,4-D for specific weeds.
5. In my opinion MCPA products, particularly when based only on the 2,4 isomer content, will be used more widely in New Zealand than at present.

References

1. Berit Hansen. *Physiologia Plantarum*. Vol. 4, 1951.
2. *Analyst*. Vol. 77, 1952; vol. 78, 1953.

DISCUSSION

Q.—Does the discovery that MCP is a mixture of isomers, only one of which is of marked herbicidal value, alter the recommendations on the effectiveness of MCP relative to 2,4-D?

A.—It will take some time to revise all our recommendations about MCP, basing them on the 2,4 isomer content. There are several weeds that are controlled better with MCP than 2,4-D.

Q.—With 2,4-D you can rank sodium salts, amine salts, and esters in a rising scale of toxicity. Does that ranking hold for MCP?

A.—Under optimum conditions there is no difference between the toxicity of the sodium and the amine salts of 2,4-D. The sodium salt is not very soluble, and if it is applied to dry foliage, it will crystallise out and then rain may wash it off. If fine weather follows for 3 or 4 days after application, it is as effective as the amine salt.

Q.—Is it not generally recognised that per unit and under practical conditions of spraying esters are more toxic than sodium and amine salts?

A.—Esters have much better penetration than the other two compounds, but show much less movement in the plant. If you can get penetration with a water-based material, use it.

Q.—What future uses do you visualise for MCP?

A.—I think MCP will be used more extensively for weeds in crops and young pasture, and also for some weeds not very susceptible to 2,4-D. Such weeds are giant buttercup, *Bellis perennis*, *Cerastium glomeratum*, and *Stellaria media*. *Spergula arvensis* and *Sagina* are more susceptible to MCP than 2,4-D, but in the case of the last four weeds I do not think even MCP will be the best material for these weeds. 4-C may be better.