

Synthetic Plant Hormones

I. Sulphur Analogues of Some Phenoxy Acetic Acids (Preliminary note)

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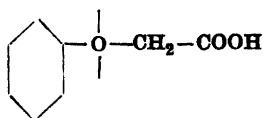
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Derivatives of phenoxy acetic acid (I) *e. g.* 2-methyl-4-chlorophenoxy acetic acid and 2,4-dichlorophenoxy acetic acid possess great practical importance as 'selective weed killers'. It has been generally assumed that the herbicidal properties of this group of compounds is related to the physiological activity of β -indolyl acetic acid ('heteroauxin') (II).

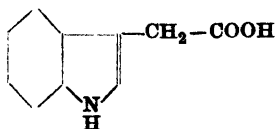
A common feature of these compounds is the occurrence of an unsaturation (double bond or lone pairs of electrons) at the atom adjacent to the α -carbon atom of the acetic acid residue. Another requirement appears to be the presence of an aromatic nucleus. A somewhat similar relation appears to exist between N-dimethylamino acet-*o*-toluidide (III) and α -N-dimethylamino methyl indole (IV) the local anesthetic properties of which were accidentally observed by the senior author^{1, 2}. The similarity of IV (a C = C-double bond in the indole nucleus) and its precursor in the synthesis (III) which contains a C = O double bond led to the rediscovery of the local anesthetic activity of anilides of type III² originally observed by Einhorn and Oppenheimer³ and ultimately to the important anesthetic 'xylocain'⁴.

Experiments were initiated to prepare the sulphur analogues of 2-methyl-4-chlorophenoxy acetic acid and 2,4-dichlorophenoxy acetic acid. (Compounds V and VI.) If physiologically active, these compounds offer an opportunity to study the physiological effect of the transformation into the corresponding sulfoxides and sulphones, reactions in which the lone pairs of electrons of the sulphur atom are involved.

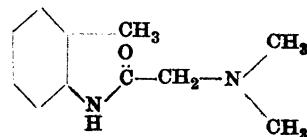
Compounds V and VI were prepared according to the general procedure outlined by Kalle and Co⁵. V melted at 127—128° and VI at 122—123°.



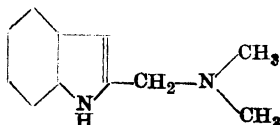
I



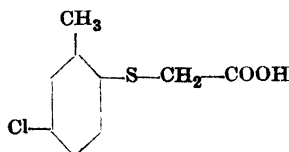
II



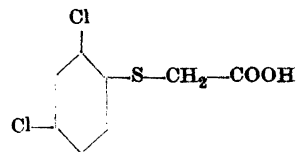
III



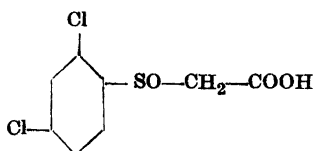
IV



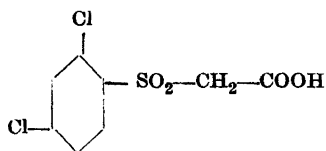
V



VI



VII



VIII

V was oxidised with potassium permanganate in the presence of sodium carbonate when the corresponding sulphone acid was formed (m. p. 147—148°). In the same manner VI was oxidised to the sulphone acid VIII m. p. 149.5—150.5°. The 2,4-dichloro phenyl sulfoxide acid VII was obtained from VI by oxidation with hydrogen peroxide in glacial acetic acid at room temperature. M. p. 145—146° (with decomposition).

Preliminary biological tests carried out in the laboratories of Professor H. Burström, Lund, by various methods indicate that the sulphur analogues of the phenoxy acetic acids show a diminished activity and that oxidation of the sulphur atom to give sulfoxides or sulphones results in complete disappearance of the activity.

SUMMARY

Some sulphur analogues of herbicidal phenoxy acetic acids have been prepared and found to possess herbicidal properties. Oxidation to the corresponding sulfoxides and sulphones apparently destroys the activity.

REFERENCES

1. v. Euler, H., and Erdtman, H. *Ann.* 520 (1935) 7.
2. Erdtman, H., and Löfgren, N. *Svensk Kem. Tid.* 49 (1937) 163.
3. Einhorn, A., and Oppenheimer, M. *Ann.* 311 (1900) 155.
4. Löfgren, N. *Arkiv Kemi, Mineral. Geol.* A 22 (1946) no. 18.
5. Kalle and Co. D. R. P. 245631 and 241839.

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