

H, 6.9. $C_{25}H_{32}O_7$ requires C, 67.6; H, 7.2%). The tetralin ester was reduced with lithium aluminium hydride in tetrahydrofuran to 3-hydroxymethyl-2-methyl-4-(3', 4', 5'-trimethoxyphenyl)-6, 7-dimethoxy-1, 2, 3, 4-tetrahydronaphthalene, m.p. 176° (Found: C, 68.3; H, 7.4. $C_{23}H_{30}O_6$ requires C, 68.6; H, 7.4%). Its tosylate was reduced with lithium aluminium hydride in tetrahydrofuran, the reaction product was chromatographed over alumina and 2, 3-dimethyl-4-(3', 4', 5'-trimethoxyphenyl)-6, 7-dimethoxy-1, 2, 3, 4-tetrahydronaphthalene (C) was isolated, m.p. 124° (Found: C, 71.2; H, 7.9. $C_{23}H_{30}O_5$ requires C, 71.5; H, 7.7%).

Similarly the isomeric methyltetralone (B) on Clemmensen reduction and chromatography over alumina gave 3-carbethoxy-2-methyl-4-(3', 4', 5'-trimethoxyphenyl)-6, 7-dimethoxy-1, 2, 3, 4-tetrahydronaphthalene, m.p. 125° (Found: C, 67.4; H, 7.1. $C_{25}H_{32}O_7$ requires C, 67.6; H, 7.2%). The reduction of the tetralin ester with lithium aluminium hydride in tetrahydrofuran yielded 3-hydroxymethyl-2-methyl-4-(3', 4', 5'-trimethoxyphenyl)-6, 7-dimethoxy-1, 2, 3, 4-tetrahydronaphthalene, m.p. 159° (Found: C, 68.6; H, 7.5. $C_{23}H_{30}O_6$ requires C, 68.6; H, 7.4%). The crude tosylate of the carbinol was reduced with lithium aluminium hydride. The oily product was chromatographed over alumina, to yield 2, 3-dimethyl-4-(3', 4', 5'-trimethoxyphenyl)-6, 7-dimethoxy-1, 2, 3, 4-tetrahydronaphthalene (D), m.p. 93° (Found: C, 71.5; H, 7.7. $C_{23}H_{30}O_5$ requires C, 71.5; H, 7.7%).

The above series of reactions constitutes the synthesis of two isomeric lignans analogous to galbulin (Ia). Detailed investigations including the stereochemistry will be reported elsewhere.

Department of Chemistry, H. D. SHROFF,
Institute of Science, A. B. KULKARNI,
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A NEW TYPE OF INSOLUBLE OXALATE IN THE LEAVES OF BATHUA (*CHENOPODIUM ALBUM* L.)

EVIDENCE for the presence of a new type of insoluble oxalate other than calcium oxalate in the leaves of *Chenopodium album* L. was demonstrated by Singh and Sur.¹ It was reported that the entire calcium content of the leaf could account for only 45% of the total

insoluble oxalate and the major part constituting a substantial portion of the leaf (at least 5% of dry leaf) existed in some unknown form not identical with calcium oxalate. This insoluble oxalate may differ from calcium oxalate in its role on the utilisation of dietary calcium. The present work was, therefore, undertaken to establish the nature of this unknown insoluble oxalate in the green leaves.

Chenopodium album L. was grown in experimental plots. Its leaves were collected and used as fresh as possible.

Soluble and Insoluble Portion of the Leaves.—Fresh leaves (100 gm.) were thoroughly washed and homogenised in a blender with about 200 ml. water. The homogenate was quantitatively transferred to a beaker and two drops of decanol were added to it. The contents were boiled for 15 min., left overnight at room temperature and then filtered through a weighed Whatman No. 1 filter-paper. The residue was washed well with water. The washings and the filtrate were mixed and diluted to 500 ml. Soluble oxalate, calcium and magnesium were estimated in this portion. The residue left on the filter-paper was dried at 100° C. and weighed after cooling in a desiccator. This residue was termed as the *insoluble portion of the leaves*. From a known quantity of the insoluble portion, green colouring matter (chlorophylls, etc.) was removed by ethanolic extraction in Soxhlet apparatus. A weighed portion (about 2 gm.) of Ifc. (Insoluble portion of leaf free of green colouring matter) was boiled with 200 ml. N-HCl for 15 min., cooled and filtered through a Whatman No. 40 filter-paper. The residue was washed well with water. The washings and filtrate were diluted to 250 ml. and total insoluble calcium, magnesium and oxalate were estimated in this portion.

Determination of Calcium, Magnesium and Oxalate.—Calcium in almost neutral solutions (neutralised with dilute ammonia) was estimated in presence of magnesium by EDTA method² modified by Knight.³ Magnesium was also estimated by using titrimetric EDTA method⁴ using eriochrome black T as an indicator. The titre value in this case was for both calcium and magnesium together. The amount of magnesium was calculated by difference.

Insoluble and soluble oxalates were determined in 10 ml. aliquots using Baker's method.⁴

Effect of pH on the Solubilities of Magnesium Oxalate, Magnesium Phosphate and Unknown Oxalate in Leaves.—Saturated solutions of magnesium oxalate, magnesium phosphate and

Ifc. (used for its unknown oxalate) were prepared by mixing sufficient quantities of these substances in 20 ml. universal buffer⁵ of varying pH values at 37° C. Magnesium was estimated in aliquots after tenfold dilution and amounts (gm./litre) were plotted against pH.

RESULTS AND DISCUSSION

The results† of the analysis of the fresh leaves of the mature Bathua plant were as follows: moisture, 85%; soluble magnesium, 0.074; soluble oxalate (C₂O₄), 8.25; insoluble residue, 55.23; insoluble calcium, 1.44; insoluble magnesium, 0.654 and insoluble oxalate (C₂O₄), 5.54.

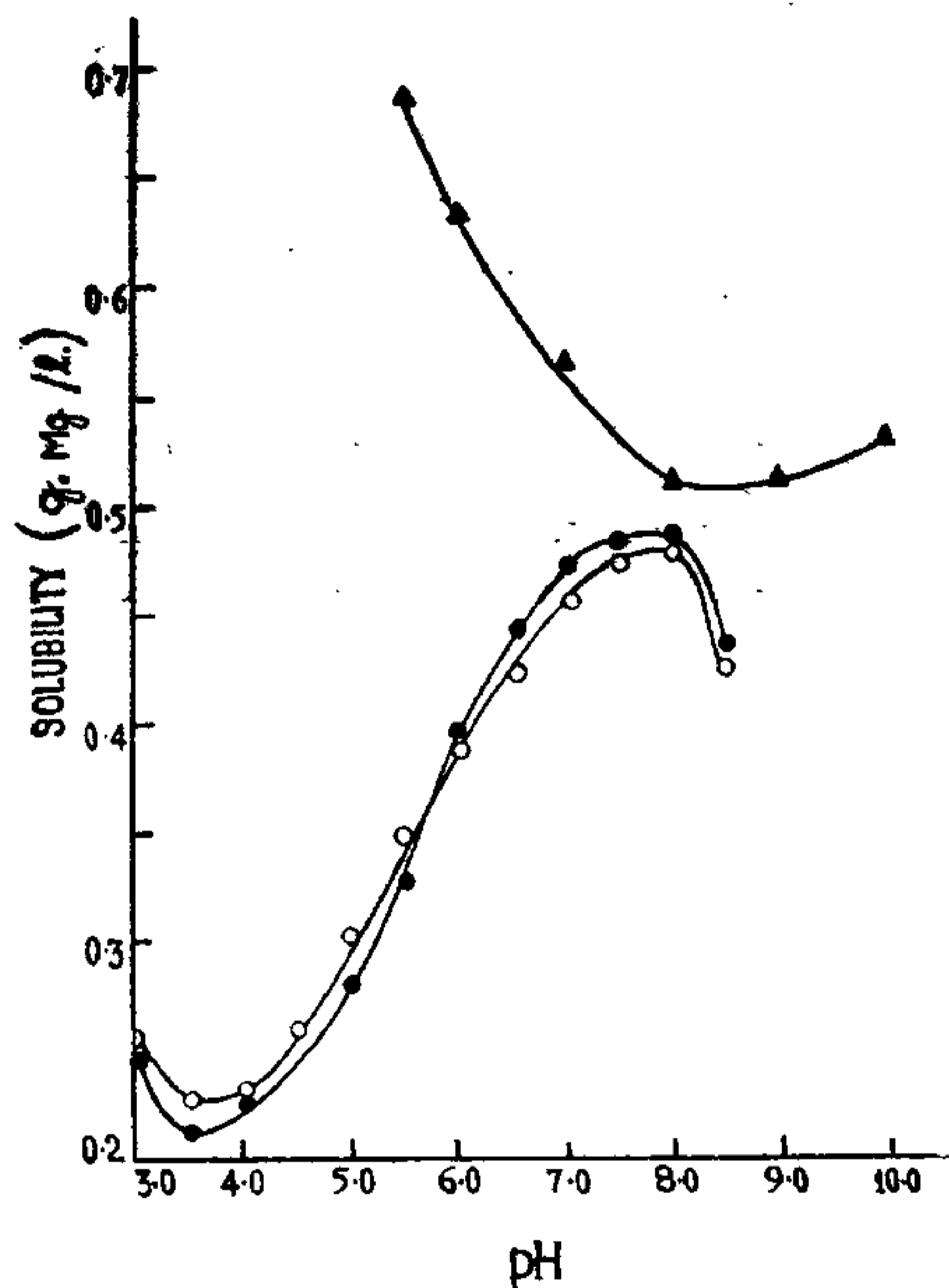


FIG. 1. A comparison of the solubilities at 37° of magnesium oxalate (O-O-O-O) and magnesium phosphate (▲-▲-▲-▲) with the substance present in the insoluble portion free of green colouring matter of *Chenopodium album* L. (●-●-●-●) in universal buffer of varying pH values.

It would be seen that 42.6% of the total insoluble oxalate could not be accounted for as calcium oxalate. The leaves of the plant, therefore, contained a large amount of a new type of insoluble oxalate. Comparison of the observed values (5.54) for total insoluble oxalate with that calculated for chemical combination with existing calcium (3.18) and magnesium (2.37) shows very close stoichiometry and, therefore, total insoluble oxalate

could be accounted for as calcium and magnesium oxalates.

Identical solubilities of magnesium oxalate and of the substance in Ifc. at varying pH values (Fig. 1) leave little doubt about their similarity in character. This type of similarity in their solubilities was also observed when acetic acid and sodium acetate buffer of varying pH values was used. These observations may, therefore, be taken as evidences demonstrating the presence of magnesium entirely as magnesium oxalate in the insoluble portion (Ifc.) of *Chenopodium album* L.

Magnesium oxalate which we have shown to occur in the insoluble portion of *Chenopodium album* L. may not be harmful as soluble oxalate or as harmless as insoluble calcium oxalate as far as calcium utilisation is concerned. Further work on the role of magnesium oxalate in calcium utilisation and its isolation from leaves is under progress.

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Dept. of Physiology, NIYAM CHARAN SHARMA.
G.S.V.M. Med. College, BIMAL KUMAR SUR.
Kanpur, October 15, 1965.

* Details of the method will appear elsewhere.

† Results expressed as gm. per cent. of dry leaf.

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A FOSSIL FRUIT FROM THE DECCAN INTERTRAPPEAN BEDS OF MOHGAONKALAN, MADHYA PRADESH

THE fossil fruit described in the present communication was found embedded in a piece of chert collected by the authors from the Deccan Intertrappean beds of Mohgaonkalan (21° 1' N; 79° 11' E.), district Chhindwara, Madhya Pradesh.

The specimen was fragile and dark grey or almost black in colour. It was broadly ovoidate, measuring about 1.1 cm. in height and 1.2 cm. in width (Fig. 1). Its internal structure could not be studied as the specimen crumbled down while sectioning. The epicarp was not