# CHEMICAL NATURE OF SALTS FROM BONES AND TEETH AND OF TRICALCIUM PHOSPHATE PRECIPITATES

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A CCORDING to recent papers<sup>1</sup>, it seems that much confusion still prevails concerning the physical and chemical properties of tricalcium phosphates. Experimental researches, performed during the War, enabled us, however, to elucidate many difficulties in this field and to demonstrate our misinterpretation of many previous experimental results. Our researches originally dealt particularly with the molecular nature of salts from bone and teeth, but were later extended to the nature of tricalcium phosphate precipitates.

(1) It is generally believed that bone salts are constituted either of hydroxylapatite which has adsorbed calcium carbonate or of carbonato-apatite, because bone salts give the same powder diffraction photograph as apatites. We have shown that in fact bone salts diffract X-rays similarly to the apatites because they are mainly made of a salt 'isomorphous' to apatites, namely,  $\alpha$  tricalcium phosphate, in a merely physical association with carbonate. The main arguments in favour of our views are as follow :

(a) If we submit bone to the fractional solubility method, we observe that small quantities of acid in contact with bone salts first dissolve only calcium carbonate, but no phosphorus. It is thus possible, with accurate quantities of citric acid, to separate chemically the carbonate of bone from the phosphate without destroying the latter. Hence, bone salts are a simple physical complex of phosphate and carbonate. If we were dealing with carbonato-apatite, the two constituents of the compound could not possibly be separated by using the same chemical method.

(b) Our X-ray diffraction studies show that ignition will transform the purified osseous  $\alpha$  phosphate into tricalcium phosphate, while it has no action upon apatite. The raw bone salts are transformed into carbonato-apatite after ignition at 900° C. by combination of the tricalcium phosphate with carbonate; in fact, this operation does not essentially modify the X-ray pattern obtained from bone salts. The main constituent of the non-ignited complex is thus 'isomorphous' with the ignited compound in spite of the alteration of the chemical properties. After ignition, however, the lines of the pattern are sharper than before because the individual crystals of carbonato-apatite are bigger than those of  $\alpha$  tricalcium phosphate.

(c) The refractive index of bone salts is equal to that of a mixture of 90 per cent pure  $\alpha$  tricalcium phosphate precipitate with 10 per cent calcium carbonate, namely, 1.590; after ignition, on account of the chemical change produced, the value of the refractive index becomes equal to that of natural apatites, namely, 1.649<sup>s</sup>.

(2) Similar observations were made with complexes of tricalcium phosphate and lime such as are obtained after partial hydrolysis of precipitated tricalcium phosphate. Indeed, it is well known that precipitated tricalcium phosphate often contains

more calcium than required by its theoretical composition; in fact, its Ca/P ratio, theoretically equal to 1.94, often reaches 2.15 (characteristic value of apatite) and may even be greater. A partially hydrolysed tricalcium phosphate with a Ca/P ratio of 2.15resulting from production of lime and adsorption during hydrolysis is not an apatite, though it shows an X-ray diffraction pattern similar to that of apatite; its main constituent is, as in bone salts, a compound 'isomorphous' with apatite, namely,  $\alpha$  tricalcium phosphate. The merely physical complex of tertiary and lime becomes an apatite when ignited at 900° C. This can be demonstrated in the same way as we did for bone<sup>3,4</sup>. We cannot admit, therefore, that the tertiary, with a Ca/P ratio of 1.94, is hydroxylapatite with adsorbed PO<sub>4</sub> ions<sup>6</sup>. That its powder diffraction pattern is the same as that of apatites is not a conclusive argument, because the tricalcium phosphate itself is 'isomorphous' with those compounds.

(3) Finally, we have shown, using up to now optical methods only, that the mineral fraction of ivory and cement from tooth is the same as that of bone. Enamel, however, has a more complex composition, its prisms being formed of real carbonato-apatite, while its interprismatic substance is organic matter impregnated mostly with  $\alpha$  tricalcium phosphate<sup>7</sup>.

- <sup>1</sup> MacIntire, W. H., Palmer, G., and Marshall, H. L., Ind. and Eng. Chem., 37, 164 (1945).
- <sup>2</sup> Dallemagne, M. J., Acta Biol. Belg., 2, 298 (1942).
- <sup>3</sup> Dallemagne, M. J., thèse d'agrégation de l'enseignement supérieur, Gordinne (Liège, 1943).
- <sup>4</sup> Dallemagne, M. J., and Brasseur, H., Bull. Soc. Sci. Liège, **11**, 451, 488 (1942).
- <sup>6</sup> Dallemagne, M. J., and Melon, J., C.R. Soc. Biol., 138, 1028 (1945).
  <sup>6</sup> Bale, W. F., Bonner, J. F., Hodge, H. C., Adler, H., Wreath, A. R., and Bell, R., Ind. and Eng. Chem. (Anal. Ed.), 17, 491 (1945).
- and Bell, R., Ind. and Eng. Chem. (Anal. Ed.), 17, 491 (1945). <sup>2</sup> Dallemagne, M. J., and Melon, J., Bull. Soc. Chim. Biol., 27, 85 (1945).

## BRITISH EMPIRE CANCER CAMPAIGN

### **REPORT FOR 1945**

A S the twenty-second annual report of the British Empire Cancer Campaign\* is the first to be published since the end of the War, it is appropriate that reference should be made to the steady progress in cancer research which has been maintained during the war years. In particular, the first practical chemotherapeutical advance—the treatment of cancer of the prostate with œstrogens—has been made. War research has developed new methods, tools and substances, and some of these should be of help in cancer research in peace-time. The present report summarizes the recent progress.

Interesting results are being obtained in experiments on animals with 2-acetylaminofluorene. Workers in Leeds and Sheffield using this compound have induced tumours of many organs, including bladder, pancreas, liver, lung, breast and ductus acusticus. By dosing mice with 2-acetylaminofluorene a number of bladder tumours have been obtained, and some of these resemble papillomata of the human bladder. In these experiments the carcinogenic agent

\* British Empire Cancer Campaign. Twenty-second Annual Report, 1945. Edited by J. P. Lockhart-Mummery. Pp. 102. (London : British Empire Cancer Campaign, 1945.)