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C.—The Occurrence of Alizarin in Rhubarb

By Hugo Müller.

During the course of an investigation of rhubarb root carried out many years ago (Jahresber., 1857, 517), Warren de la Rue and the author succeeded in isolating from this root emodin and chrysophanic acid. At a later date the author acquired a quantity of the residue which accumulates during the preparation of the

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officinal aqueous extract of rhubarb, and this was extracted in a large copper extraction apparatus with benzene, and the extract fractionally crystallised from the same solvent. During this process it was noticed that a substance was present which dissolved in alkalis with a blue colour, and was much less soluble in benzene than either emodin or chrysophanic acid. Careful investigation has now shown that this substance is alizarin. The dark orange, crystalline mass remaining after the removal of the emodin and chrysophanic acid by benzene was crystallised from tetrachloroethane,\* in which it was sparingly soluble in the cold, and from which it separated as a beautiful microcrystalline mass of orange needles:

0.1200 gave 0.3006  $CO_2$  and 0.0364  $H_2O$ . C=70.3; H=3.4.  $C_{14}H_8O_4$  requires C=70.0; H=3.3 per cent.

That this substance is alizarin was evident from its behaviour on sublimation, and from the fact that, on treatment with lime water and barium hydroxide, it gave precipitates which were exactly similar to those yielded by alizarin under the same conditions. Comparative dyeings carried out with this substance and pure alizarin gave also identical results. In order that there could be no doubt that the substance from rhubarb was alizarin, it was converted, by digesting with sodium acetate and acetic anhydride, into the diacetyl derivative, which, after repeated crystallisation from acetic acid, melted at 186-187°, which is somewhat higher than the melting point of diacetylalizarin previously observed (179-183°: Perkin, Trans., 1899, 75, 448). When, however, a very pure specimen of sublimed alizarin was acetylated under the same conditions, and the product repeatedly recrystallised from acetic acid, the diacetylalizarin obtained was also found to melt at 186-187°, and it was furthermore observed that there was no alteration in melting point when the latter preparation was mixed with the diacetylalizarin obtained from rhubarb.

Alizarin appears to be contained in rhubarb only in very small quantity, and this is no doubt the reason why its presence has, so far, been overlooked.

My thanks are due to Mr. Robert Robinson, of Manchester University, for assistance in connexion with these experiments.

\* Tetrachloroethane, which is now manufactured on the large scale, appears to be an excellent solvent for the purification, not only of alizarin, but also of other hydroxyanthraquinones and allied substances.