OBSERVATIONS ON MONARDIN,
A PECULIAR CRYS\lALINE SUBSTANCE, DERIVED FROM THE VOLATILE OIL OF MONARD\lA PUNCTATA.

By William Proctor, Jr.

The volatile oil of horsemint (Monard\l\l\l a punctata) is extensively employed in this country as a rubefacient, either by itself, or in conjunction with other substances, in the form of liniments, and from its great pungency is considered a valuable remedial agent. Several of our druggists have observed in some specimens of this oil, a crystalline deposit, analogous in appearance to camphor, and possessed of the taste and odor of the oil. As no notice has been taken of this fact in any of the works to which I have had access, the subject is possessed of sufficient interest to present, in the form of an essay, a history of its sensible properties, and some of its chemical characteristics. It evidently belongs to the camphor class, and may be the result of the absorption of oxygen. It is presented in two forms; one in amorphous translucent masses with some slight evidences of lamination in the fracture; the other in rhombic crystals closely aggregated together. The amorphous variety is white, has a conchoidal fracture, is very friable, and is reduced to powder with extreme readiness. Its amorphous condition appears to be due more to the manner in which it is deposited, than to any difference in its chemical character, as when fused, and gradually cooled, it assumes the crystalline form, and comports itself in the same manner with chemical reagents. This substance, which, for the purpose of facilitating its description, may be called monardin, possesses the burning, pungent taste, and peculiar odor of the oil of horsemint, and doubtless possesses the same medical properties. Monardin is very soluble in alcohol and ether, and is dissolved by the fixed and volatile oils, particularly oil of turpentine; hence the change of the oil of horsemint to the solid state, does not preclude its use in pharmaceutical preparations. It is very slightly soluble in water, communicating to that fluid its odor and pungent taste. Monardin fuses at 118° Fahr. into a limpid oil, and when the heat is continued it commences boiling in a glass vessel at 418° Fahr., and at 438° its point of ebullition is stationary. It boils readily and without discoloration, and may be distilled per se without change, the vapor condensing in a crystalline form if the receiver be kept cool. Fused monardin may be cooled down below 70° without solidifying, but if the smallest crystal of the substance be dropped in it, crystallization commences, and is propagated throughout in a few minutes. The usual crystalline form of monardin is the rhombohedron, or some form derivable from it. By cooling a portion of fused monardin until crystallization is partially effected, and then pouring off the superstratum, it is obtained in very regular crystals. The sp. grav. of the amorphous variety is 1.03. When in crystals the enclosed air renders them lighter than water. It is neutral to test paper.

Monardin is soluble in a solution of caustic potassa, and by saturating the alkali with acetic acid it separates in the form of an oil, which, by standing, assumes the same crystalline form, and possesses the same odor as before subjection to the alkaline menstruum.
When crystals of monardin are placed in a solution of ammonia they gradually assume the form of oily globules, without dissolving in the ammoniacal liquid, and remain at the bottom. Whilst undergoing this change they have the appearance of fusing. The globules of monardin, after treating with ammonia, solidify when subjected to a temperature as low as 180° Fahr. By exposure to the air these globules gradually assume a purple color, and when heated with caustic potassa no ammonia is evolved.

When crystallized monardin is introduced into a jar of ammoniacal gas over mercury, the ammonia is rapidly absorbed, and the crystals are liquefied. When suffered to remain until saturated, they absorb nearly one hundred times their bulk of the gas, and are increased in bulk more than 50 per cent. When the liquefied monardin is exposed to the air, it gradually assumes the crystalline form apparently unchanged. Oil of horsemint also absorbs ammonia, but not by any means in so great a quantity, or with any marked phenomena.

Monardin dissolves in cold concentrated sulphuric acid, to which it communicates a red tinge. The solution may be diluted and saturated with an alkali without the separation of any oily or crystalline matter, evidently proving that the monardin is changed.

Concentrated hydrochloric acid appears to have little, if any, action on this substance, either cold or hot; when it is treated with cold, strong nitric acid, it is rapidly decomposed with the evolution of much deutoxide of nitrogen and the production of heat—after the action ceases, a thick yellowish-brown mass remains, without any appearance of crystallization.

Having obtained a bottle of ol. monardæ, in which the monardin was in process of being deposited in crystals, the latter were separated from the superstratum of oil, and were found to possess the same properties as the other specimens previously examined. When this oil was subjected for some time to a temperature of 180° Fahr., a considerable quantity of similar crystals of monardin were deposited. The oil thus rid of most of the monardin was placed in an atmosphere of oxygen with the view of ascertaining if this principle was the result of the action of atmospheric oxygen upon it; but after forty-eight hours' exposure, no evidence was obtained of the formation of that substance, although the experiment was not continued sufficiently long to settle the question.

The particular circumstances favorable to the formation of monardin, and its separation from oil of horsemint, are as yet quite obscure. I have known this volatile oil to be kept for many years without any evidence of a deposit, while in another and a recent instance, about a quart of the oil was taken from a large bottle in which no change had occurred, and in a few hours after, a crystalline deposition had taken place in the portion removed, weighing several ounces. In all the instances where this deposit has taken place, the source of the oil was undoubted, having been obtained from the distillers in New Jersey. A careful, ultimate analysis of the oil, and of the deposit, would do much to throw light on this subject.—American Journal of Pharmacy.