

XVIII.—*Note on Gardenin.*

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GARDENIN was discovered by one of us (*Stenhouse, Phil. Trans.*, 1856, cxlvi, 155, and *Ann Chem. Pharm.*, xcvi, 316) some 20 years ago in "dekamali gum," a resinous exudation from the *Gardenia lucida*, but the amount of gardenin obtained at that time was insufficient to make a satisfactory analysis, the quantity of resin operated on being but limited. About three years ago, however, we had a larger sample of the resin, enabling us to obtain a few grams of the gardenin in the pure state. The resin from the *Gardenia lucida* has been fully described both by Dymock (*Pharm. Journ.* [3], vii, 491), and by Flückiger (*ibid.*, p. 589), the latter of whom, moreover, extracted the gardenin and analysed it.

We found that the best method of obtaining the crude gardenin was to boil the resin with alcohol, filter the solution to separate the insoluble residue, consisting chiefly of small fragments of bark and wood, and allow it to cool. It then deposited almost the whole of the gardenin in slender, pale-yellow needles, which were collected and washed with cold spirit, to free them from the amorphous greenish-yellow resin, which forms by far the larger portion of dekamali gum. These needles, however, even after several crystallisations from alcohol, were found to be still impure, being contaminated with a colourless substance of low melting point, somewhat resembling a fat in appear-

ance. After repeated trials in various ways, it was found that this impurity might be removed by means of light petroleum. A boiling saturated solution of the gardenin in alcohol was allowed to cool, and the almost pasty mass of crystals was agitated with light petroleum at a temperature of about 30°, the clear liquid poured off, and the residue again agitated with petroleum, repeating the operation several times. The gardenin was finally purified by alternate crystallisation from hot benzene, in which it is readily soluble, and from alcohol.

When pure, gardenin forms brilliant deep yellow crystals, which melt at 163—164°. Dried at 100°, and burnt in a current of oxygen it gave the following results.

I. .249 gram of substance gave .567 gram carbonic anhydride, and .119 gram of water.

II. .202 gram of substance gave .457 gram carbonic anhydride, and .102 gram of water.

		Theory.	I.	II.	Mean.	Flückiger.
C ₈	60	61·86	62·12	61·70	61·91	59·47
H ₈	5	5·16	5·31	5·60	5·45	6·71
O ₂	32	32·98	—	—	—	—
		<hr/>				
	97	100·00				

Flückiger's numbers do not agree with these, but as the specimen he analysed had merely been purified by repeated crystallisation from spirit, it is not impossible that it was contaminated with traces of the colourless fatty substance mentioned above. This is rendered very probable by the much lower melting point (155°) which he obtained.

It was stated in the earlier paper (Stenhouse, *loc. cit.*) that when gardenin is digested with concentrated nitric acid, it is rapidly decomposed, picric acid, but no oxalic acid being produced. On repeating the experiment, however, we found this to be incorrect: gardenin, when boiled with nitric acid, dissolves with evolution of nitrous fumes, forming a yellow solution, which, on evaporation, leaves a yellowish residue; this, however, on careful examination, proved to be quite free from trinitrophenol. It was noticed, in making this experiment, that at the moment the gardenin came in contact with the nitric acid, it assumed a brilliant crimson colour before dissolving. The attempts made to isolate the red substance thus formed were ultimately successful: 1 part of gardenin was dissolved in about thirty times its weight of boiling glacial acetic acid, and after being rapidly cooled two parts of nitric acid of sp. gr. 1·45 were added to the clear solution. In a few seconds hair-like crimson needles began to form, very different in appearance from gardenin. At the expiration of 5 minutes, the mixture, which was kept cold, had solidified to a pulp of needles.

It was then mixed with about 150 parts of cold water, and the gelatinous precipitate collected after it had stood a few minutes. The pasty red mass, after being well washed, was pressed into a cake and removed from the filter before drying, for it was found that if allowed to dry on the filter it adhered so firmly to the paper that it was very difficult to remove it. Gardenin yields nearly 90 per cent. of its weight of this substance, which is insoluble in water and dilute acids, but readily soluble in alkaline solutions, and reprecipitated, on the addition of an acid. We have provisionally named it *gardenic acid*. It is free from nitrogen, and after being purified by boiling with spirit, in which it is but very slightly soluble, and crystallisation from glacial acetic acid, it was found to melt at about 236° . If the nitric acid is allowed to act on the glacial acetic acid solution of gardenin for a considerable time, or on the gardenic acid itself, it becomes changed to an orange-coloured substance much more soluble in alcohol than gardenic acid.

At present the amount of gardenin at our disposal is too small to permit a thorough examination of these new compounds, and other derivatives of gardenin. As they appear, however, to be of some interest, we have made arrangements to obtain a considerable quantity of dekamali gum from India, and hope ere long to be able to continue the investigation.

Note on Ginger.

As the nature of the resinous substance contained in ginger, and to which its pungent character is due, has not as yet been investigated, it seemed possible that a careful examination of it might lead to interesting results. The few preliminary experiments we made, however, did not appear very promising.

The ground ginger, *Zingiber officinale*, from Cochin China, was extracted by boiling with alcohol, and the solution evaporated after filtration. The viscid residue had a strong odour of ginger, and when heated in a current of steam yielded a small quantity of essential oil lighter than water. A portion of the extract was fused with three times its weight of soda, and the product neutralised with sulphuric acid, and extracted with ether in the usual way. The ethereal solution, on evaporation, left a mass of crystals impregnated with a dark coloured liquid; these, after purification by pressure and two or three recrystallisations from water, were examined and proved to be protocathechuic acid. They gave the ordinary well-known reactions of protocathechuic acid, and fused at the same temperature. On heating them with excess of bromine in a sealed tube, carbonic anhydride and tetrabromopyrocatechin were formed.