DETECTION OF SALICYLIC ACID IN FOOD.[1]

BY K. P. MC ELROY.

SALICYLIC acid has been known for more than half a century, having been discovered in 1838 by Piria[1] in oxidizing the oil of meadow sweet (*Spiraea ulmaria*). But its commercial importance dates back only to 1874 when Kolbe[2] succeeded in making a synthesis of it from sodium phenolate and carbonic acid. In 1860, in conjunction with Lautemann, he devised another synthetic process[3], but as this method involved the use of metallic sodium the product was expensive.

After securing the entire success of his second process in 1874, Kolbe turned his attention to finding uses for his product. In that and the succeeding year he published a number of papers on[4] its use as a food preservative, as did several of his pupils and assistants, etc.[5] Public attention became attracted to the acid and its use as a preservative spread with great rapidity. In 1877 the French Government[6] found itself obliged to take official action regarding the use in wine of salicylic acid.

Analytical chemists of course were not slow to recognize the new demand on their skill involved by the use of this substance as an addition to food, and methods for its detection were soon elaborated. The number of these methods has yearly increased and at present a fair sized bibliography of analytical literature relative to salicylic acid might be compiled.

The most useful properties of salicylic acid, analytically speaking are that it is volatile with steam, that it is extracted from acid liquids by ether, chloroform, carbon bisulphide or benzol, that it gives a bright purple color with ferric chloride, a green color with copper acetate, and a rose color when boiled with Millon's solution and that when converted into the methyl ester it gives rise to a characteristic odor of wintergreen. The iron test is the one which is universally used for the final recognition of this substance, the previous separation from the food being made either with one of the solvents above named or by distillation. It is extremely delicate, giving a good reaction with a tenth

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[1] Read at the Baltimore Meeting, December 27, 1893.

milligram in twenty-five cc. of liquid. The copper test is not particularly delicate, nor is the methyl ester test, at least as far as I am concerned. This latter test has been brought forward particularly by Dr. Curtman, of St. Louis.[7] The test with Millon's solution is given by other substances extractable from foods by ether. The iron test is not given by any substance occurring in foods and extracted by ether to my knowledge. Carbolic acid gives the reaction nearest approaching it in color of the common substances, but this substance does not occur in food. Tannic acid, a little of which is sometimes taken up by ether from wines, gives a blackish or greenish color which has a tendency to hide the salicylic color.

In the laboratory of the Department of Agriculture the method which has been most commonly used involves the separation of the salicylic acid by distillation with water vapor. The use of distillation for this purpose, separating salicylic acid from food, I believe was first proposed in an unsigned article[8] appearing in the *Chemiker Zeitung*, in *1882*, presumably from the pen of the editor, G. Krause. It was there stated that the method had been elaborated in the laboratory of that paper. Kolbe used distillation for the analytical separation of salicylic acid in 1880.[9] In using it in this laboratory on the samples of canned vegetables, the analyses of which are recorded in *Bulletin* 13, part 8, of the Division of Chemistry, United States Department of Agriculture, the contents of the can were pulped in a mortar, water added, together with a little phosphoric acid, the mixture strained through a bag, and the liquid subjected to distillation. The distillate was then collected in small portions and each portion separately tested with iron chloride. Mr. W. D. Bigelow who was associated with me in the analyses of these goods, and who made the greater portion of the tests, found the best strength of ferric chloride to be about five mgms. to the cc. The salicylic acid has a tendency to accumulate in the later portions of the distillate, and where the amount present is small, there will be hardly any test given by the first fractions. In illustration of this the following experiment may be adduced. Twenty-five milligrams of salicylic acid were dissolved in 250 cc. of water containing a little phosphoric acid and the mixture subjected to distillation, the distillate being collected in twenty-five cc. portions and the salicylic acid estimated colorimetrically. The results may be tabulated as follows:

No.	cc.	Reaction.	Quantity found.
1	25	Distinct but pale	
2	25	Somewhat stronger	
3	25	Still stronger	0.3 mgm.
4	25	“ “	0.4 “
5	25	Bright	0.5 “
6	25	“	0.8 “
7	25	“	0.9 “
8	25	“	2.2 mgms.
9	15	“	3.0 “
	Total		8.1 mgms.

I will quote in further illustration of this tendency the method for the determination of salicylic acid in wine described by M. Ince. In this method 210 cc. of wine are mixed with ten cc. of dilute sulphuric acid and the mixture subjected to distillation, the distillate being collected in fifty cc. portions. The first portion is thrown away and the acid estimated in the next two colorimetrically. The quantity found is multiplied by eight, it being assumed that one-eighth of the total salicylic acid will come over in those two fractions when using the amounts of liquid specified.

All the samples of canned vegetables were examined in this way using the fresh contents of the cans. Afterwards, for various reasons, I had the whole series gone over again and the extraction done in a different fashion. The residual contents of the cans had in the meantime been dried and ground to a powder capable of going through a hundred mesh sieve. Portions of this powder were made into a paste, or rather a very stiff dough, with dilute sulphuric acid, and the product placed in an ordinary ether extraction apparatus where it was extracted with ether for several hours. When the ether extract was evaporated to dryness and the residue taken up with water and distilled, the distillate gave the salicylic acid reaction with much greater brilliancy than had the original test, and many samples were found to contain the acid which had before given only doubtful tests or none at all in some cases. The cause of this difference was no doubt the imperfect extraction in the first method of separation, which practically gave only the salicylic acid present in the juice, while the later method gave that existing in the solid portions as well. Many reactions were quite faint, so much so as to raise the question of the purpose of the addition of such minute quantities of salicylic acid. The smallness of these quantities was probably due, however, to a cause first pointed out by Kolbe[9] in 1880. Kolbe found that salicylic acid completely disappeared from wine and from water preserved in casks, while in similar samples preserved in glass this disappearance did not take place. Four months' standing, in some cases, were sufficient to cause this disappearance. As an experiment, he placed thoroughly washed cubes of different woods in glass flasks in contact with different solutions of salicylic acid and found that they caused a complete disappearance of the acid after various periods of time, while control samples in which no wood was placed retained their full content of salicylic acid. From the results of this work he drew the inference that woody tissue not only removed the salicylic acid from solution but caused its total destruction in some way, since he could not recover it from the cubes of woods used in the experiments just cited. The woody tissue of the canned vegetables may have caused an action similar to this.

We also use the ordinary "shaking out" method in the Department laboratory to some extent for such goods as beers and wines. The beer or wine is extracted with about half its volume of ether and the extract evaporated to dryness, and the residue taken up with warm water. The resultant solution is tested in the usual way with iron chloride. Between the two processes of separating the salicylic acid, distillation or shaking out with ether, I do not believe there is much choice, though the former is cheaper and more expeditious. The increased purity and sharpness of the reaction given by the distillate as compared with that given by the residue from the ether extract about counterbalance the fact that only a fraction of the salicylic acid appears in the distillate. Objections against the distillation process were raised in 1889 by certain Dutch chemists,[10] on the ground that in the process of fermentation certain "phenol-like bodies" were sometimes formed which interfered with the reaction. "Phenol-like bodies" would interfere not only with the distillation separation but with any other with which I am acquainted, since phenol is taken up by immiscible solvents from acid solutions precisely as is salicylic acid.

This year three chemists,[11] writing for different German brewing papers, have claimed that in what is called "color" or "caramel" malt a substance exists which gives all the ordinary salicylic acid reactions. The substance is said to exist in many malt extracts rich in isomaltose. J. Brand isolated the substance from color malt and describes all its reactions as being analogous to those of salicylic acid with the single exception of that with Millon's reagent, with which the new substance gave no reaction. I procured a set of color and caramel malts from the World's Fair and tried to obtain a salicylic acid reaction from them, but could not do so. At my request Mr. Bigelow, who not long ago examined a large number of the beers exhibited at the World's Fair, tried a large number of them with Millon's reagent, using it side by side with the iron solution. He reported to me that the Millon's reagent gave salicylic acid in all the samples, irrespective of the reaction upon the ferric chloride. The latter gave salicylic acid in comparatively few. It is only just to say, however, that where ferric chloride indicated the presence of salicylic acid, the reaction given by Millon's reagent was much brighter than where this was not the case.

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[1] Piria. Recherches sur la sálicine et les produits qui en dérivent. *Ann. de chim. et de phys.*, *1838*, 69, 281.

[2] Kolbe, H. Vorläufige Mittheilung. *J. prakt. Chem.*, *1873-4*, 8, 41. Synthese der Paraoxybenzoësäure, ibid, 336. Ueber eine neue Darstellungsmethode und einige bemerkenswerthe Eigenschaften der Salicylsäure, ibid, *1874*, 10, 89.

[3] Kolbe, H. and E. Lautemann. Ueber die Constitution und Basicität der Salicylsäure. *Liebig's Annalen*, *1860*, 115, 201.

[4] Kolbe, H. Weitere Mittheilungen über die Wirkungen der Salicylsäure. *J. prakt. Chem.*, *1875*, 11, 9; Darstellung chemisch reiner Paraoxybenzoësäure durch Umwandlung der Salicylsäure, ibid, 24; Weitere Mittheilung über die Wirkung der Salicylsäure, ibid, 213; Ueber die chemische Natur der Salicylsäure, ibid, *1875*, 12, 151; Abweisung nicht begründeter Urtheile von Halbchemikern über die antiseptischen Eigenschaften der Salicylsäure, ibid, 161; Die chemische Natur der Salicylsäure, ibid, 151; Chemische Winke für praktische Verwendungen der Salicylsäure, ibid, *1876*, 13, 106.

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Wirkung der Salicylsäure und anderer aromatischer Säuren. *J. prakt. Chem.*, *1875*, **12**, 133; Ueber die antiseptischen Wirkungen der Salicylsäure und Benzoësäure in Bierwürze und Harn, ibid, 178.

[5] Fontheimer, Karl. Ueber die Wirkung der Salicylsäure als Arzneimittel. *J. prakt. Chem.*, *1875*, **11**, 211.

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[6] Fauvel, Bergeron and Bussy (reporter). Emploi de l'acide salicylique comme agent de conservation des vins. Repport sur une demande d'avis addresse par la chambre de commerce de Paris. Recueil des travaux du comité consultatif d'hygiene *1877*, **7**, 346.

[7] Curtman, C. O. Nachweis der Salicylsäure durch Synthese des Gaultheriaöls. *Pharm. Rundschau*, *1885*, **3**, 155; abs. *Chem. Ztg.*, *1885*, **9**, 1504.

[8] Anonymous (G. Krause?). Nachweis von der Salicylsäure in Nahrungsmitteln. *Chemiker Ztg.*, *1882*, **6**, 619.

[9] Kolbe, H. Zerstörende Wirkung des Holzsubstanz auf Salicylsäure. *J. prakt. Chem.*, *1880*, **21**, 443 and **22**, 112.

[10] Horn, G. A. [Detection of Salicylic Acid in Beer.] *Pharm. Weekblaad* (*1888?*), Nos. 7 and 8; *Apoth. Ztg.*, No. 56; *Ztschr. Nahr. Hyg.*, **2**, 150; *Chem. Centrbl.*, *1888*, 1425.

[11] Erich, E. Ueber die Salicylsäurereaction der Caramelfarbmalze. *Bierbrauer*, *1893*, **24**, 465; abs. *Chem. Ztg. Rep.*, *1893*, **17**, 211.

Munsche. Ueber die scheinbare Salicylsäurereaction des isomaltosereichen Malzauszüges, der Caramelmalze und gewohnlichen Farbmalze, etc. *Wochenschr Brauerei*, *1893*, **10**, 739; abs. *Chem. Ztg. Rep.*, *1893*, **17**, 242.

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