The Chemistry of Flavoring Matters—II*

The Relationship Between the Constitution of a Body and Its Taste

By Francois Barral, of the University of Paris, and Albert Ranc, Laureate of the Institute

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III. FLAVOR IN THE ALCOHOLS.

The alcohols are of great importance from the point of view of the chemistry of the sweet flavors. It is in this class of substances that all natural sweetening agents are found. The taste of an alcohol depends entirely upon the number of hydroxyl groups (OH) present in the molecule. The compounds which contain only one such group are but faintly sweet.

When, on the contrary, we study the molecules containing four, five, or even more hydroxyl groups we observe that the sweet taste is very intense, and also that it is independent of the coexistence of the aldehyde ketone carboxyl and amido groups, which in all other circumstances profoundly modify the taste of the molecule when grafted upon it. Sometimes, however, when the sweet tasting molecule has attached to itself a heavy group, especially if the latter is aromatic, a modification of the taste may be observed. The same phenomenon may be observed when one or more hydroxyl groups are saturated by condensation with acids or with bases. The cyclic form exerts no effect upon the taste of the molecule; quinine, dambonite, and quercite are all sweet.

A. Monoatomic Alcohols.—The taste of the monoatomic alcohols is not constant. The influence of a single hydroxyl group is insufficient to furnish a predominant flavor. The halogen alcohols are sweet, the nitro-alcohols are bitter. The first members of the series of the aliphatic mono-alcohols are insipid or almost imperceptibly sweet; in the aromatic series, on the contrary, the sweet taste is found.

B. Glycols, Glycerines, Tetra-atomic Alcohols.—The sweet taste of the simple glycols diminishes in proportion as the molecule grows more complex. The glycols having many carbon atoms are bitter. A few rare members of the aromatic series are sweet. The glycerines are nearly all sweet. The presence of a heavy group in their molecule produces a bitter taste, as in the case of phenyl glycerine, for example. The existence of an aldehyde group, on the contrary, as in erythrose, for example, increases the sweetness of taste. The tetrols are all very sweet. Exceptions are octylerythritol and rhamnolose, which are bitter.

C. Penta-atomic Alcohols.—These are all sweet, and the formation in a pentol of ketone or aldehyde groups augments this property; it is only necessary to cut out the keystone radicle or the aldehyde radicle of a body in this series, by forming an oxime, for example, to cause the intensity of the sweet taste to diminish very markedly.

D. Poly-atomic Alcohols; Saccharides and Their Derivatives.—The accumulation of hydroxyl groups in the molecule of a substance, starting with the pentavalent alcohols, results in a decrease of sweetness in the taste of the various compounds obtained. Sorbite, dextro-talite, *alpha* galaheptite, and scyllite are decreasingly sweet and galactite is almost insipid. In the series of the polysaccharides (saccharose, lactose, etc.) we again find the sweet taste, but in the case of the molecules which are much less complex, like glycogen and cellulose, for example, a total absence of taste is the rule.

To sum the matter up, in the series of the alcohols and of their derivatives having aldehyde or ketone groups the sweet taste arrives at a maximum which corresponds to the presence of five hydroxyl groups in the molecule. The intimate constitution of the sugars, which is thoroughly well known from several points of view, does not solve the question of the degree of sweetening power of the various isomers. If we examine the poly-alcohol acids we find the same sweet taste as in the corresponding alcohols. The internal anhydridization, so frequent in that class of substances, generally changes their taste. Insipid lactones and bitter lactones are both well known. The amido derivatives of the sugars retain their original flavor. The basic nature of the molecule exhibits itself by the caustic action upon the tactile organs of the tongue; this causticity is banished by combination with a hydracid, being transformed into a salty taste which is comparatively rare among organic compounds.

The glucosides, whose bitter taste has so frequently been found a striking feature by men engaged in research that they have given them characteristic names, such as "bitter principle of lycopod, convallamarine," etc., have some sweet substances among their constit-

uents. Some of them, however, the methyl and ethyl glucosides, are sweet. We may mention as a remarkable exception populine which is sweet although derived from salicine, which is bitter, by the operation of etherification, which generally develops bitterness.

IV. TASTE OF THE PHENOLS.

In the class of the phenols both solubility and sweetness depend upon the number of hydroxyl groups contained in a molecule. The mono-phenols are rarely sweet, their action upon the tongue consisting chiefly of a tactile sensation. However, the sweet taste is developed in this class of bodies with the introduction into their molecule of the methoxy and azo-imido group, and this independently of their position.

The same fact has been noted previously in the case of nitro-benzene.

The di-phenols and tri-phenols of the meta series all possess a sweet taste (Resorcline, orcline, dioxy-pyridine). The same thing is true of the para series (Hydroquinone, chlorohydroquinone, dihydroquinone). The simple ortho, di, or tri-phenols are bitter (pyrocatechine, pyrogallol). Among the more or less complex substances we find sweet substances such as luteoline, brasiline, hematoxylene.

In short, whatever the position of the hydroxyl group may be the taste of the phenols tends to increase in bitterness in proportion as the molecular weight increases. An analogous phenomenon has already been pointed out in the case of the glycols and the glycerines. The introduction into the molecule of a nitro group injures the sweet taste. Thus, nitro-resorcline and nitro-hydroquinone are scarcely sweet at all and nitro-phloroglucine is distinctly bitter. The halogens also destroy the sweet taste of the phenols, and chloro-resorcline is not sweet, while iodo-resorcline is bitter. The aldehyde group has the same property, the 1-2, 1-3, 1-4, oxy-benzaldehydes not being sweet.

V. THE TASTE OF THE ORGANIC ACIDS.

The organic acids have an acid taste whenever they are soluble in water, and the smaller the molecule the more acid the taste. This fact, which is connected with the presence of the carboxyl group, and which is independent of the constitution of the molecule, obliges experimenters to taste these substances in the state of salts of sodium, which have not the acid taste nor the flavor peculiar to the sodium ion. This acid taste is also made to disappear by anhydridization. Furthermore, very few anhydrides of acids have any taste, and the sweet taste of the pyro-tartaric, pyro-cinchonic, and methyl-ethyl-maleic anhydrides forms a remarkable exception.¹⁸ The acetic-oxime-acids are extremely sweet.¹⁹ This taste is a specific characteristic of the introduction of the acid group; the insipid oximes²⁰ such as that of para-methoxy-aceto-phenol furnish a very sweet derivative upon the introduction into their molecule of the group—CH²—COOH.

Acetic isobenzaldoxime is the only isomeric compound of this class which has been tested. It is quite as sweet as the normal benzaldoxime. However, there is an essential difference of constitution between these two substances, the acetic residue being attached to nitrogen in the isomeric derivative and to oxygen in the normal derivative.

The influence of the sulfonic group upon an organic molecule is not very definite. Pseudo-cumene, methyl-iso-propyl-benzene and camphor are the sweet sulfonic compounds, while those yielded by phenanthrene and anthraquinone are bitter. In some cases sulfonation causes the sweet taste of a substance to disappear; thus the ducine sulfonate of soda no longer has a sweet taste. Finally, we must mention the curious peculiarity of the barium salt of the sulfonic methyl-iso-propyl-benzene acids, one of which is sweet while the other is bitter.

VI. TASTE OF THE ETHERS.

In the category of the ether-oxides the etherification generally interferes with the sweet taste if the latter be due to the presence of an etherifiable hydroxyl group. Thus, methyloxy-glycol is not sweet, as glycol itself is.

¹⁸Guayacol, a methyl derivative of pyrocatechine, is sweet as being a methyl ether oxide of monophenol.

¹⁹Observe that these bodies, which contain neither hydroxyl nor replaceable hydrogen, are not acids; their analogy with the imides, and hence with saccharine, should be noted.

²⁰G. Cohn (loc. cit.).

²¹Most of the oximes are sweet; we have already pointed out the influence of stereo-chemical structure on these bodies.

If the sweet taste, on the contrary, is not due to the presence of a hydroxyl group, but to that of groups such as —NO², = N—OH then the taste of the substance is not changed by etherification. Ortho-nitranisol, para-anisaldoxime are sweet. There are some exceptions to this rule, however, since diethyldioxyacetone, for example, is sweet, although this taste belongs to the etherified hydroxyls of dioxyacetone.

Among the simple ethers, which still contain hydroxyls, we find many sweet compounds (dimethyl-acetal glucose, etc.) the halogen ethers are nearly all sweet. Anethol and estragol are sweet phenolic ethers.

The ether salts often have a taste with a tendency towards bitterness, different from that of the corresponding alcohol and acid. Only three sweet ethers derived from bitter alcohols are known, namely, the acetate of 2 bromo-ethyl, carbonate of pyrogallol and populine.

VII. TASTE OF THE AMIDO ACIDS.

Glycocol, or sugar of gelatine, owes its name to its sweet taste, which has long been known. It is the prototype of the amido acids. Among these bodies the alpha amido acids are sweet in a very general and pronounced manner, to such a point that the attaching of their molecule to an aromatic nitro residue, which nearly always interferes with the sweet taste, in no way modifies these compounds. Thus phenylamine and its chloro, bromo, nitro and amido derivatives are all sweet. The alpha-amido-hydroxyacids are also sweet.²¹ The three alpha-amido acids are somewhat less sweet than those of the amido series in the alpha position. In the class of the amido acids connected with the group of sugars the position of the amido group seems to have no influence on the sweet taste of the molecule.

The fatty di-amido-acids are not sweet. The acids with nitro nuclei, pyrazols, pyridine, quinolin, are bitter with the exception, however, of the iso-cinchomeronic acid and the 1 amido —3 bromo —2 pyridone carbonic acid.

The peptids, inversely to the alpha amido acids, are insipid or bitter. In the tryptophane series some sweet peptids are found. It should be noted that among all these bodies it has been frequently found that a relationship exists between the taste and the molecular special structure. Among the amido-sulfonic acids the triazine is of particular interest because it contains glucine which is a commercial sweetening agent in the form of a mixture of a sodium salt of the di- and tri-sulfonic acids of the base obtained by the action of the benzaldihyde upon the diamido-nitric derivative.

VIII. TASTE OF THE AMIDORS AND OF THEIR DERIVATIVES.

The amidons are bitter, especially those of the aromatic series. Some of them, however, have a sweet taste due to their halogen or to their hydroxyl group or to the amido-acid complex contained in their molecule (dextro-asparagine, diacetamide erythrose, perchloro-cyano-propion-amide). In the group of the ureas several interesting sweet compounds are found, the principal one being para-ethoxyphenylurea, otherwise sucrol or dulcine, which has been employed as an artificial sweetening agent. The study of the changes of taste corresponding to changes of constitution in this substance has engaged many investigators, who have shown that nearly all the modifications to which the molecule of dulcine is subjected destroy the sweet taste; only the introduction of the amido-group is without influence.

Only a few sulfamides have been studied with respect to taste. Among those which have been tasted the only sweet one is dimethyl-sulfamide. The group of the sulfamides is very small but one of its members, saccharine or benzoic sulfimide, gives it considerable importance.²²

It is unnecessary to lay stress upon the well known sweetening power of this compound except to note that slight molecular changes cause it to disappear. The replacing of the imidic hydrogen of saccharine by an organic residue (methyl, ethyl, CH² OH, C⁶H⁵) produces insipid bodies.

The same thing is true of the introduction of any group whatever into the benzenic nucleus or of the

²²The organic bases are all bitter (amines, hydragines, cyclic bases, pyridine, quinine, alkaloids). This fact is remarkable, for the amido group has no effect on the taste of saccharine and dulcine, and when associated with the carboxyl group it usually gives sweet bodies.

²³French industry has successfully produced saccharine for a twelvemonth.

*From *Revue Scientifique*.

opening of the closed lateral chain. An exception is that the attaching of the amido group to saccharine does not alter the taste. Chlorination on the contrary produces a bitter taste.

IX. CONCLUSIONS.

If we examine in their totality all the facts which we have just set forth certain observations are inevitable concerning the influence of variations in molecular constitution upon taste. It seems to be well established, for example, that the introduction into a sweet molecule of any radicle whatever, but especially of an aromatic one, results in the destruction of the sweet taste and the obtaining of a body with a bitter taste. The heavier the radicle introduced the more clearly marked will be this modification. Nitration causes the disappearance of the sweet taste. The same thing is true for the formation of the halogen derivatives, except, however, in the class of the hydrocarbons, in which the introduction of the halogens, and especially of chlorine, causes the sweet taste to appear.

The influence of an alcoholic radicle is more complex. The alcoholization of an amido group causes the appearance of the sweet taste. But it makes it disappear when it concerns an imido group or a hydroxyl group.

The amido group does not affect the sweet taste. The sulfonation of a compound seems to have a tendency to cause the appearance of the bitter taste. Acting differently, the methoxy group introduced into an aromatic molecule produces the sweet taste and changes the bitter taste to sweet. The ethoxy group does not exhibit the same property. Finally, it is interesting to note that in the same family of substances, other things being equal, the taste tends to become increasingly bitter in proportion to an increase in the weight of the molecule.

Upon the whole our knowledge as to the tastes inherent in organic compounds is confined to a series of comparisons of more or less general character. We know almost certainly that the poly-hydroxyl bodies and the alpha amido acids are sweet and that the polynitro bodies are bitter, but in each of these classes there are cases which escape the general rule. These anomalies, which are especially frequent in those classes of substances with very complex molecules, appear to depend upon the proximity of the groups and the unknown relationships which are established between them. Sternberg²³ attributes very hypothetically to the "harmonic" arrangement of certain groups (hydroxyl and nitro) in a molecule the power of causing a definite sweet or bitter taste. However this may be there are groups (hydroxyl, nitro) which are incapable of imparting any taste by their presence singly; but they assist in the development of a case, or even create one by their multiplication or by their proximity with other groups; they might be called "sapophores" (taste bearers). And certain groups are in themselves "dulcigenes" or "acidogenes" or "amarogenes" (sweetness, acid, or bitterness bearers).

It is impossible to be more definite than this. At present we possess along this line only an accumulation of facts which lack a directing principle to bring order out of them. For further information we refer the reader to the bibliographic and personal researches of G. Cohn.²⁴

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While as we have seen we have been able to extract a few laws from the mass of information whose methodical exposition we have here attempted, we are still far from the establishment of a general law which would enable us to deduce the elementary taste of a body from a knowledge of its molecular structure.

However, a similar problem has existed with regard to all the properties of bodies, and when its solution has been found possible it has always yielded interesting results. There have been observed, especially in the case of the physical constants, certain cases of an "additivity" of properties which permit us to consider the expression of a characteristic property of any compound as being the sum total of the properties of its elements united in a simple mixture. This fact has been observed, for example, in the case of volume and molecular refraction. These are only special cases, for the contact of the atoms combined in a body does not consist of a simple proximity as in a mixture. There are physical properties such as the absorption of light, optical activity, the point of fusion, in which the mutual influence of the atoms upon each other is very evident. Other physical phenomena depend upon the relations between molecules and even, at times, between molecular weights.

The study of the functioning of the sense of sight has been greatly advanced by the knowledge of the relationship which exists between the constitution of

bodies and their selective absorption of light. The color of a substance depends upon this absorption, or, to speak more precisely, the property which a body possesses of causing a certain sensation of color is a function of its absorbent power with respect to certain luminous radiations, and this power bears a definite relation to its constitution. This precision of language is made necessary by the confusion which exists between the property which belongs to the body and the sensation which belongs to the individual. For in the course of a long and slow series of adaptations the sensations projected outwards have come to be considered as properties of the body itself.²⁵ In the case of sight the dissociation between these two elements, the internal and the external, is very clearly marked. The property belonging to the body, which is the result of its molecular structure, makes a selection, so to speak, among the vibrations of light thus choosing the photochemical agent which will act upon the retina to cause the sensation in the brain.

In the case of the sense of taste the affair is not so simple. There is an immediate contact between the substance and the sensory apparatus, and this interferes with the analysis of the mechanism of the action of bodies possessing flavor. Continuing the analogy with the sense of light we may say that the vibration which issues from the substance, and impresses the papillae concerned in taste, is not known to us, for it is impossible to follow its path and to arrest it and study it during its passage.

The study of luminous vibrations has been facilitated by photometry, by optics, by the spectrograph and by the use of the sensitive plate which, so to speak, makes a permanent record of the results of the optical properties of bodies.

But the agent which excites the action of a sense of taste cannot be arrested externally nor simplified nor selected, for it has its birth at the time of contact of the stimulating substance and the sensory cell, and its action occurs simultaneously with its formation. It is the result of a reaction between the flavor bearing body and the specially organized substance concerned in the sense of taste. This body has the property of flavor, we may say, because its chemical constitution and that of the papillae of the tongue permits of a chemical combination whose result excites the gustatory nerves. Hence it is obvious that the quality of flavor is not a measurable property easily expressed by a figure, as is a physical property, for in the present state of our knowledge we do not possess any perfectly lucid and evident method of representing the phenomenon of chemical combination, and it is this ignorance which prevents us from forming an exact theory with regard to the conditions governing flavors. To these theoretic impossibilities, which are doubtless only temporary, we must add the numerous technical difficulties with respect to experiments concerning taste.

The functions of the mouth are various, and the diverse impressions received in its different areas form a totality which is sometimes inextricably confused. The taste of a body varies with its degree of dilution in water or in saliva, and is disturbed even by mere traces of impurity; the sensation of taste which its flavor produces may also be influenced by the state in which the gustatory cells have been left by previous stimuli. Moreover, whatever the nature of the sensations experienced, it is only a notation of the mind, whose nature is unknown to us. It is the sign of an object, a sign which may be recorded objectively by the science of physics, by whose apparatus our senses are extended and improved. This is true of sensations of color, for example, but there exists nothing similar for the sensation of taste, whose determination by reason of this very fact is subject to all the errors of subjective illusion. Does this mean that we shall never be capable of comprehending the relations existing between a savory body and the taste which it excites. Not so, but it is probable that the problem has been prematurely stated. Doubtless the progress of general chemistry and of physico-physiological experimentation will one day permit us to comprehend the nature of the phenomena which cause a given taste to correspond to a given molecular structure. The poverty of the sense of taste, which has only four categories of flavors by which to classify the multitude of bodies which excite the sense of taste, is only too apparent. The elementary flavors, sweet, bitter, acid and salt, may be considered as collections of delicate gradations of perception bearing a relationship to the infinitely minute modification of the molecular structure of substances possessing flavor. Thus we may conceive of tastes as representing an ensemble of physical and chemical properties which are partially unknown to us, in analogy with the conceptions we have of sounds and sights.

²⁵Flavor and taste are usually employed as if having the same meaning.

When we have obtained a more exact knowledge of physico-chemical phenomena, the anomalies we have mentioned will doubtless disappear and some new law which will differ, perhaps, from the one which we now accept will give entire coherence to the relationships between molecular constitution and taste. Even today every effort to solve these problems will have the practical result of guiding the researches made with regard to artificial sweetening agents, and will assist in solving a problem which involves at one and the same time chemistry, physiology and psychology.

Electrochemical Behavior of Nickel

In recent years it has been shown in the Amsterdam Laboratory that one of the most characteristic properties of a metal is the velocity with which it assumes electromotive equilibrium at a definite temperature and pressure. At the ordinary temperature and pressure this velocity is very small for the metal in the dry condition; in contact with an electrolyte, however, the velocity is quite different, although complications are then caused by the appearance of catalytic actions, both positive and negative. These catalytic actions make the comparison of the behavior of different metals a difficult matter, as has already been shown in the case of iron immersed in different electrolytes.

Some metals, however, assume internal equilibrium very slowly in contact with an electrolyte, and nickel is one of these. With this metal, not only oxygen, but also hydrogen, acts as a negative catalyst, and the catalytic effect is very pronounced. For example, when hydrogen at a pressure of 1 atm. is led through a solution of nickel sulphate in which Ni electrodes are immersed, the equilibrium is disturbed either in the base or noble direction until the electron concentration of the metal equilibrium becomes equal to that of the hydrogen equilibrium in the electrolyte. It can be shown that in this case the p.d. of the Ni with respect to the electrolyte, not taking into account the volta-effect, must become equal to the p.d. of the hydrogen electrode; experimentally it was found that practical equality of these two p.d.'s exists.

It is shown by theoretical considerations that the unary equilibrium potential for Ni is only to be expected in an atmosphere free from oxygen or hydrogen, or in a vacuum, and when a solution of a nickel salt is used in which the hydrogen concentration is less than 10^{-3} for a nickel ion concentration of 1. Experiments made in accordance with these theoretical considerations gave -0.480 volt, with respect to the normal calomel electrode, as the equilibrium potential, which value agrees entirely with that calculated by Wilmore and also with that found by Schoch in an experiment in a vacuum. It is pointed out that in the many potential measurements of Ni which have been carried out in the air or in a hydrogen atmosphere, the equilibrium potential of the unary Ni has not been measured, but rather the potential of a state of this metal which has been disturbed in a base or noble direction.—*Note in Sci. Abts. on a paper by A. Smits and C. A. L. de Bruyn in K. Akad. Amsterdam.*

Pigment for Printing Inks

PRINTING inks may be divided into two classes, *viz.*, "litho" and "letterpress." The pigments used for the former class must be completely free from acidity, quite insoluble in water, possess good "solidity," moderate transparency, and not too high a specific gravity. Those for use in the manufacture of letterpress inks must be brilliant and opaque and when for use in process of three-color work have low specific gravity. Printing ink pigments are preferably composed of dyes fixed on alumina, either alone or co-precipitated with *blanc fixe*, the lake and mineral pigments being simultaneously precipitated. Barytes or other abrasive material is quite useless as a base for either class of ink. The desiderata of a good printing ink pigment are principally brightness and strength, the latter property ensuring that sufficient printed impression will be obtained by the use of a very attenuated film, thus guarding against liability to "set-off" on the adjacent superposed sheet. Other properties of the pigment are required for special purposes, *e. g.*, transparency and resistance to heat for tin-printing pigments, insolubility in alcohol for labels which are subsequently spirit varnished, resistance to alkali for use on soap wrappers. A classification into degrees of fastness to light and the adaptation to different purposes of pigments of varying stability to light, alkali, etc., is given, *e. g.*, the special suitability of a fugitive, water- and spirit-soluble pigment, non-resistant to acid and alkali, for printing on cheques, etc.—*Note in J. Soc. Chem. Ind., a paper by T. M. Tyson before the Oil and Color Chem. Assn.*

²³Arch. für Physiol. 1898 and after.

²⁴G. Cohn (loc. cit.).