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Articulo de Revisión

John Stenhouse: Contribution to the study of active charcoal, lichens, and alkaloids

John Stenhouse: Contribución al estudio del carbón activo, líquenes y alcaloides

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Abstract: John Stenhouse (1809-1880) carried a large number of experiments comparing the adsorbing power of wood and animal charcoal for the gases ammonia, hydrogen sulfide, sulfur dioxide, and carbon dioxide, as well as their decolorizing and oxidation ability. The results led him to suggest that charcoal could be used to absorb the small amount of infectious matter floating in the atmosphere of unhealthy locations (as was the belief in those days). Consequently, he designed a charcoal air filter consisting of a thin layer of charcoal powder enclosed between two sheets of wire gauze, as well as personal respirators to be used over the mouth or nostrils and mouth. Stenhouse also studied the dyes present in lichens, particularly in the varieties of Orchella weed Rocella tinctoria, Rocella Montagnei, Gyrophora pustulata, and Lecanora tartarea. He described the extraction, purification and analytical procedures of the different dyes and discovered a series of intermediate compounds, among them, alpha and beta orsellic acids, roccellinin acid, erythreselic and usnic acid, pico-erythricin, pseudo-orcin (erythromannitol), erythromannitol pentanitrate (an explosive), betorcinol (a homolog of orcinol). Stenhouse proved that it was possible to obtain, artificial alkaloids using as starting materials the highly nitrogenated compound principles (i.e. albumen, fibrin, legumin, etc.) found in all plants, known to be as rich in nitrogen as the corresponding animal compounds. He also developed an analytical procedure for detecting quinic acid, discovered the presence of sparteine in a variety of vegetables and the active principle connesine (wrightine) in the seeds of the tree Wrightia antidysenterica.

Keywords: alkaloids, astringents, conessine, gas mask, lichen, orcin.

Resumen: John Stenhouse (1809-1880) ejecutó numerosos experimentos comparando el poder adsorbente de la turba y el carbón animal por los gases amoníaco, ácido sulfhídrico, dióxido de azufre y dióxido de carbón; así como su poder oxidante y de blanqueo. Sus resultados lo llevaron a sugerir que el carbón animal podía ser usado para absorber la pequeña cantidad de material infeccioso que flotaba en lugares insalubres (como se creía en aquella época). Esto lo llevó a diseñar un filtro de aire compuesto de una capa delgada de polvo de carbón encerrada entre dos hojas de malla metálica, así como respiradores personales para ser usados sobre la boca, o la boca y la nariz. Stenhouse también estudió las tinturas presentes en los líquenes, en particular en las variedades de las algas Rocella tinctoria, Rocella Montagnei, Gyrophora pustulata y Lecanora tartarea. Describió los procedimientos de extracción, purificación y análisis de las diferentes tinturas, lo que lo llevó a descubrir una serie de nuevos compuestos intermedios, entre ellos los ácidos alfa y beta orséllico, roccellínico, erythrisélico y úsnico, la picoerythricina, la pseudo-orcina (erythromannitol), el pentanitrato de erythromannitol (un explosivo) y el betorcinol (un homólogo del orcinol. Stenhouse demostró que era posible obtener alcaloides sintéticos usando como materia prima los principios altamente nitrogenados (albumen, fibrina, legumina, etc.) presentes en todas las plantas y ricos en nitrógeno como los principios animales correspondientes. Asimismo, desarrolló un método analítico para detectar el ácido químico, y descubrió la presencia de asparteina en una variedad de vegetales y el principio activo conessina (wrightina) en las semillas del árbol Wrightia antidysenterica.

Palabras clave: alcaloides, astringentes, conessina, liquen, máscara de gases, orcina.

Life and career (Anonymous, 1881; Stronach, 1885-1890)

John Stenhouse (Figure 1) was born on October 21, 1809, in Glasgow, the eldest son of William Stenhouse, calico-printer, and Elizabeth Currie, and the only one of their children to survive beyond infancy. He took his basic education at Glasgow Grammar School and then enrolled at Glasgow University were he studied literature from 1824 to 1828. Afterwards his interests switched to chemistry (probably because of his father's business) and from 1837 to 1839 followed the courses given by Thomas Graham (1805-1869) at Glasgow University, Thomas Thomson (1773-1852) at Anderson's University, and Justus von Liebig (1803-1883) at the University of Giessen in Germany. While in Giessen he published his first scientific paper on the subject of hippuric acid esters (Stenhouse, 1839). The failure of the Glasgow Commercial Exchange (1850) led to the loss of his economical independence and his forced return to Glasgow. After failing to obtain a teaching position at Owens College he moved to London where he was appointed chemistry lecturer at the Medical School at St. Bartholomew's Hospital (1851). In 1857 he suffered a stroke which left him partially paralyzed and compelled him to abandon his teaching position. He then stayed with mother in Nice until her death in 1860. He returned to London and opened a chemical laboratory offering chemical assistance to industry. The success in this activity led to his appointment as non-resident assayer to the Royal Mint (1865), a position he kept until 1870 when the Mint was abolished. In 1871 the Royal Society awarded him a Royal Medal for his successful chemical researches (Anonymous, 1881; Stronach, 1885-1890).

Stenhouse played an active role in professional activities: co-founder of the Chemical Society of London (1841); fellow of the Royal Society of London (1848), awarded an LL.D. degree from the University of Aberdeen (1850), fellow of the Institute of Chemistry (1877), honorary member of the Berlin Chemical Society, the Philosophical Society of Manchester, and the Pharmaceutical Society of Great Britain (Anonymous, 1881; Stronach, 1885-1890).

Stenhouse passed away on December 31, 1880, in London and was buried in the High Church new cemetery, Glasgow.

Scientific contribution

Stenhouse wrote more than 100 papers on the subject of alkaloids, biochemistry, botany, lichens, organic chemistry, physiology, active principles in plants, and public hygiene. In addition to the subjects described below he also studied the preparation of artificial ultramarine (Stenhouse, 1841b); the preparation of pyrogallic acid (Stenhouse, 1843a); astringent substances (Stenhouse, 1843bc); theine and its preparation (Stenhouse, 1843d); the presence of mannitol in algae (Stenhouse, 1844); the use or urine for agricultural purposes (Stenhouse, 1845b); aloin (Stenhouse, 1850b);. the action of sulfuric acid on vegetables (Stenhouse, 1850c); Japanese pepper (Stenhouse, 1858); the varieties of tannin (Stenhouse, 1860a); larixinic acid (Stenhouse, 1860b); the adulteration of coffee (Graham et al., 1857); etc. Stenhouse was also a practical researcher who transformed many of his findings into industrial patents in the areas of dyeing, waterproofing, sugar manufacture, manufacture of glue, tanning, use of activated wood charcoal in filters and masks for disinfecting, deodorizing, and protection purposes, etc.

Active charcoals

According to Nicolas Théodore de Saussure (1767–1845), it was well known that charcoal had the remarkable property of absorbing gases (Saussure, 1812). In 1782 Felice Fontana (1730-1805) had reported that red-hot charcoal, cooled by plunging it under mercury or any other substance that isolated it from contact with air, was able to absorb more than its own volume of various gases (Fontana, 1782). Hendrik Willem Rouppe (1765-1816), Van Noorden, and Carlo Lodovico Morozzo (1743-1804) had also reported similar results with red hot charcoal cooled under water, and that this property varied with the nature of the gas and the charcoal (Rouppe, 1799; Morozzo, 1804). Saussure himself carried on an extensive inquiry about the amount of gas absorbed by a large number of solids and liquids (Saussure, 1812). His experimental procedure consisted in submerging the incandescent coal under mercury and, after it became cool, introducing the gas to be absorbed, without ever coming into contact with atmospheric air, He used as solid materials box-wood charcoal, Spanish Meerschaum from Valecas, adhesive slate of Melimontant (rock wood), asbestos from Tyrol, Saxon hydrophane, rock cork, quartz, calcium sulfate, calcium carbonate, several woods (hazel, mulberry, fir), linen thread, silk, and wool, and up to twelve different gases (NH., HCl, SO., H.S, NO., CO, CO., C.H., O., N., and H.). The results, reported as volumes of gas absorbed per volume of the solid, indicated clearly that box-wood had the highest absorption capability: it absorbed 90 volumes of ammonia, compared to 64 for hydrophane, 15 for Meerschaum, and 10 for quartz. The respective amounts of CO. were 35, 2, 1, and 0.6. The absorption capacity and rate of absorption of dry coal were substantially different from those of moistened charcoal. For example, in a dry state it absorbed 35 volumes of CO. in 24 hours while when wet it took it 14 days to absorb 15 volumes. The absorption process was sufficiently exothermic to cause a clear increase in temperature (Saussure, 1812).

Stenhouse also carried a large number of experiments comparing the absorbent power of wood, peat, and animal charcoal, for the four gases NH., H.S, SO., and CO., and in 1855 presented his results to the Royal Institution (Stenhouse, 1854-1858). From these it appeared, on the one hand, that the gas absorption capacity of wood charcoal was slightly larger that of peat charcoal, and that the capacity of both vegetable charcoals was substantially higher that of animal charcoal; on the other hand, the decolorizing power of animal charcoal was significantly higher to that of the vegetable varieties. One additional set of experiments was particularly interesting: Bodies of dogs and cats were buried and covered with wood charcoal and seen not to smell of fumes, although the decomposition was greatly accelerated. According to Stenhouse the charcoal absorbed and oxidized the secretions before they were released to the atmosphere. The effluvia reacted with the oxygen condensed in the pores and suffered a slow oxidation into water and CO. (Stenhouse, 1854- 1858). This was in opposition to the common idea that charcoal was an antiseptic.

This result led Stenhouse to suggest that charcoal could be used to absorb the small amounts of infectious matter floating in the atmosphere of unhealthy locations (as was the belief those days). Consequently, he built, for this purpose, a charcoal air filter consisting of a thin layer of charcoal powder enclosed between two sheets of wire gauze. One of this apparatus was installed in the justice room, at the Mansion-house (serving as housing for the Lord Mayors) and promptly showed its advantages. As a result, similar apparatus was installed at other public buildings, water closets, close wards of hospitals, ships, etc. These results led to the development of personal respirators to be used over the mouth or nostrils and mouth (Figure 2), which not only were seen to purify the air by filtration but also to warm it, as well as not condensing the moisture of the breath. The frame of the mask was copper, but the edges were of soft lead and were lined with velvet to allow the mask to be molded tightly to the face. These accessories proved to be particularly useful at hospitals to diminish or stop the progress of infectious diseases. Stenhouse also suggested their possible use for soldiers and sailors placed in unhealthy situations, without guessing what would happen during the First World War (Stenhouse, 1854-1858).

Stenhouse commented that the large amount of oxygen contained in the pores of the lighter kinds of charcoal explained their ability to oxidize most of the easily alterable gases and vapors. This absorbent power was substantially larger than their capacity for, chemical reactions. These characteristics were the opposite of those of platinum sponge, which had a much lower capacity for absorbing certain gases (e.g. 30 volumes of ammonia against 90 for charcoal) and a much larger power as oxidizer and promoter of chemical reactions. This led him to examine the possibility of enhancing the oxidizing ability of charcoal by combining it with finely divided platinum (Stenhouse, 1856). This platinized charcoal would have the good properties of both of its components. He suggested a very simple process for achieving this goal: Charcoal, as coarse powder or large pieces, was boiled in a solution of platinum dichloride for about 10 to 25 minutes and the thoroughly impregnated material was then heated to redness in a closed platinum crucible. The resulting charcoal did not show changes in its external appearance, although its properties were substantially changed.

Stenhouse described a series of phenomena illustrating this change. For example, contacting a few grains of platinized charcoal with a mixture of dry oxygen and hydrogen in the proportion to form water resulted in the prompt formation of water, much the same as when employing a clay ball of platinum sponge. Using instead a fragment of charcoal containing a considerably larger amount of platinum resulted in an explosive combination. Cold pieces of platinized charcoal held in a jet of hydrogen became quickly incandescent and inflamed the gas. The same pieces, held in contact with vapors of ethanol or methanol, became red hot and continue to do so until the supply of vapor was finished. Charcoal containing 1% of platinum caused a mixture of oxygen and hydrogen to combine in about two hours. Stenhouse went even further. He speculated that platinized charcoal could be used very effectively for treating malignant ulcers: its powerful oxidizing properties would make it a mild but effective caustic (Stenhouse, 1856).

Decolorizing charcoals and their power of absorbing some of the gases were described in a third publication (Stenhouse, 1857). According to Stenhouse, two varieties of bleaching charcoals were available for industrial uses: (a) bone or ivory black, prepared by pyrolysis in closed vessels until all the organic matter had become carbonized. This was the most common material, used particularly in sugar refining and the bleaching of neutral solutions. It was composed of about 10% carbon and 90% calcium carbonate and phosphate; and (b) purified animal charcoal, prepared by digesting bone black in HCl, followed by water washes until all the calcium salt had been removed. This was a highly porous and expensive material used for bleaching neutral and acid solutions. It was also prepared by pyrolysing in closed vessels a mixture of potassium carbonate and the blood or fleshy parts of animals (Stenhouse, 1857).

Stenhouse was able to develop an economical substitute for purified carbon animal by combining alumina with ordinary vegetable charcoal. In his process 54 parts of commercial alumina sulfate (containing sulfuric acid) were dissolved in water and digested with 92.5 parts of finely divided ordinary wood charcoal. The wholly impregnated mixture was evaporated to dryness and heated to red-hot until all the water and acid had disappeared. The residue was bleaching charcoal, black, thoroughly impregnated with anhydrous alumina and containing near 7.5% of alumina (the amount needed to coat all the cells of the charcoal). This aluminized charcoal could be employed to bleach all acid solutions, except those containing much free sulfuric acid. It was very appropriate for bleaching tartaric and citric acids more cheaply than bone black charcoal (Stenhouse, 1857).

Stenhouse also prepared a substitute for purified animal charcoal by heating under appropriate conditions a mixture of calcium hydroxide, coal tar pitch, and coal tar. The resulting product was very porous and light and extremely appropriate for bleaching logwood solutions and impure gallic acid. Stenhouse wrote that according to his results bleaching charcoals could be classified into three classes: (1) charcoals such as the purified and coal tar varieties, which could be regarded as pure charcoals in an extremely high degree of division, and which bleached by their porosity alone; (2) Mordanted charcoals (e.g. aluminized charcoal), which decolorized solely by the mordants or bases which they contained; and (3) bone black, which was a composite charcoal, decolorizing partly by the large quantity of calcium phosphate and partly by the minutely divided charcoal it contained (Stenhouse, 1857).

Lichens

Stenhouse became interested in a variety of Orchella weed, which had been imported into London from Cape of Good Hope but had been rejected by orchil (*Rocella tinctoria*) manufacturers because of its low content of the compound generating the purple dye. Upon inspection, Stenhouse discovered that the weed contained a large amount of another crystalline principle, which did not react with ammonia. This led him to conduct a similar investigation of the several lichens commonly employed by the orchil manufacturers, among them, *Rocella tinctoria* from the west coast of South America and from the Cape of Good Hope, *Rocella Montagnei* from Angola, and *Lecanora tartarea* (Stenhouse, 1848a).

Stenhouse wrote that the South American variety of *Rocella tinctoria* was lichen from 15 to 20 cm long, having thick stems. In order to extract the active principle, he cut the lichen in small pieces and macerated them with a large amount of water for some hours and then added quicklime and left the mixture to rest. The liquid was then withdrawn and the process repeated several times. Addition of an excess of HCl precipitated the coloring principle as a white gelatinous mass. This mass was drained over a cloth filter, left to dry over a plate of gypsum, and then dissolved in warm alcohol. On cooling, the coloring principle of the lichen precipitated as small white prismatic needles arranged in stars. This impure material, which Stenhouse named *alpha orsellic acid*, was purified by dissolution in cold calcium hydroxide. Stenhouse mentioned that this procedure was the same as the one employed by Edward Schunck (1820-1903) to extract erythric acid from the Angola lichen (Schunck, 1846). According to Stenhouse alpha orsellic acid was insoluble in cold water, sparingly soluble in boiling water, quite soluble in cold alcohol and ether, and extremely soluble in boiling alcohol. It reddened litmus paper and neutralized the alkalis and alkaline earths forming soluble and crystallizable salts. It reacted promptly with a solution of calcium hypochlorite producing a temporary deep blood red solution, which after a minute or so changed to deep yellow. An ammonia solution of orsellic acid in contact with air assumed a bright red color, which on standing became darker and purple-colored. A chemical analysis indicated that alpha orsellic acid contained, by weight, 60.46% carbon, 4.93% hydrogen, and 34.61% of oxygen, corresponding to the formula $C_{32.15.13}$+H.O (Stenhouse, 1848a).

Stenhouse reported that neutralization and boiling of crude orsellic acid with additional calcium hydroxide produced a clear solution, which neutralized with HCl precipitated a new acid, which he named *orsellesic* *acid*. The purified acid crystallized as needle-shaped crystals arranged in stars, which reddened litmus paper and had a weakly acid and somewhat bitter taste. It was very soluble in cold and hot alcohol and boiled in water it decomposed into CO. and orcin (orcinol). When boiled with an excess of calcium hydroxide it produced orcin and calcium carbonate. Chemical analysis indicated that it contained, by weight, 57.27% carbon, 5.26% hydrogen, and 37.47% of oxygen, corresponding to the formula C_{16}H.O. +H.O. Boiling orsellic acid with alcohol produced and ether (orsellesic ether), which crystallized as long flat white needles containing, by weight, 61.38% carbon, 6.51% hydrogen, and 32.11% of oxygen, corresponding to the formula C_{16}H.O.+C.H.O (Stenhouse, 1848a).

Analysis of the Rocella tinctoria from the Cape of Good Hope showed that it contained two crystalline principles, one very similar to orsellic acid and another, slightly less acid, which Stenhouse named *beta orsellic acid* and *roccellinin,* respectively. These two acids were easily separated taking advantage of the fact that roccellinin was quite insoluble in cold and hot water while beta orsellic was very soluble in hot water. Beta orsellic acid was found to redden litmus paper, to be very soluble in cold and hot water and in ether, and to produce with calcium hypochlorite the same blood-red color as alpha orsellic acid. Chemical analysis indicated that it contained, by weight, 60.10% carbon, 5.19% hydrogen, and 34.71% of oxygen, corresponding to the formula $C_{34.17.14}$+H.O. This type of Rocella was found to contain a much larger quantity of roccellinin than of beta orsellic acid. Chemical analysis of roccellinin indicated that it contained, by weight, 62.91% carbon, 4.59% hydrogen, and 32.50% of oxygen, corresponding to the empirical formula $C_{38.17.15}$ (Stenhouse, 1848a).

The lichen *Rocella montagnei* was analyzed by the same procedure. Stenhouse separated the erythric acid and found that it contained, by weight, 57.34% carbon, 5.15% hydrogen, and 37.51% of oxygen, corresponding to the formula $C_{20.10}$O.+H.O. This acid reacted with ammonia and calcium hypochlorite in the same manner as described above; with the first reagent it yielded red colored compounds, and with the second a blood-red solution. Erythric acid reacted with alcohol and methanol producing the pertinent ethers, which crystallized from their water solution. Boiling a neutral solution of erythric acid with calcium hydroxide decomposed the acid into two new compounds, which Stenhouse named *erythreselic acid* and *pico-erythrin.* Stenhouse also reported the synthesis and properties of a new compound, *pseudo-orcin*, obtained by decomposing erythric acid and its derivatives by means of alkalis, and the analysis of the lichen *Evernia Prunastri*. From the latter he separated a new aid, which he named *evernic acid*. The latter was insoluble in cold water, slightly soluble in boiling water, and very soluble in cold and hot alcohol and in ether. Chemical analysis indicated that it contained, by weight, 61.89% carbon, 4.75% hydrogen, and 33.36% of oxygen, corresponding to the formula $C_{34.15.13}$+H.O (Stenhouse, 1848a).[24]

Stenhouse mentioned that the amount of coloring principle present in the lichens was a small fraction of the biomass, and, in addition, the sources of the lichen were located at far distances from the manufacturing sites. For this reason, he believed that the basic extraction should be conducted at the countries were the lichens grew, and thus save a large proportion of the shipping costs. For this purpose, it was enough to macerate the lichens, cut in in small pieces, in wooden vats with limewater. The resulting extract solution would then be neutralized with HCl or acetic acid to precipitate the active principle as a gelatinous mass. After separation, the precipitate would be deposited over cloths and dried at low heat. The dry material would then be exported to the dye manufacturing facilities in Europe. The last section of the paper described the preparation of additional derivatives such as evernesic acid, evernesic ether, bromo orceid, chloro orceid, and usnic acid (Stenhouse, 1848a).

A following publication dealt with the preparation of alpha- and beta-orcin (Stenhouse, 1848b). Alpha-orcin was normally prepared by boiling principles derived from the lichens (e.g., lecanoric acid, erythric acid, etc.) with an excess of lime or baryta water, followed by purification by boiling water and bleaching with animal charcoal. A typical chemical analysis of the purified orcin, dried at 15.5 .C, indicated that it contained, by weight, 59.61% carbon, 6.95% hydrogen, and 33.44% oxygen. Stenhouse remarked that orcin retained its crystallization water with firmness; nevertheless, it could be rendered anhydrous by heating to 100 .C, by recrystallization from water, or by drying under vacuum in the presence of sulfuric acid. The resulting anhydrous compound contained, by weight, 68.16% carbon, 6.35% hydrogen, and 25.49% oxygen; representing a loss of three molecules of water (Stenhouse, 1848b).

Stenhouse wrote that although beta-orcin could be prepared from usnic acid by several processes, he preferred the one based on the destructive distillation of dry crude usnic acid where beta-orcin sublimed and deposited as long yellow crystals, partly on the neck and sides of the retort, and mostly dissolved in a brown resinous liquid, which passed into the receiver. The beta-orcin was extracted from liquid by successive washes with boiling water, and the accumulated liquids concentrated to a syrup state and then left alone in a flat open vessel. The deposited brown crystals were pressed between blotting paper to eliminate the attached resin and colored matter, bleached with animal charcoal, and repeatedly crystallized from water. The purified crystals were hard and brittle, having a brilliant luster. According to Stenhouse the empirical formula of beta-orcin is $C_{38.24.10}$. This paper contains the crystallographic parameters of alpha- and beta-orcin, as carried on by William Hallowes Miller (1801-1880), professor of mineralogy at Cambridge University (Stenhouse, 1848b). In another paper Stenhouse added information about the active principles and derivatives of the lichens *Gyrophora pustulata and Lecanora tartarea*, as well as the preparation and properties of derivatives of the lichens described previously (e.g. bromo orcin, beta-orcin, and pseudo orcin (Stenhouse, 1849).

Stenhouse extracted the active principle of *Gyrophora pustulata* with milk of lime and precipitated it in a gelatinous state by neutralizing the solution with HCl. The reddish brown precipitate was washed with cold water, filtered, and dried at gentle heat, followed by repeated digestion with concentrated alcohol and bleaching with animal charcoal. Cooling of the alcoholic solution deposited the active principle, which Stenhouse named *gyrophoric acid*. This acid was almost insoluble in cold and boiling water and in ether and in alcohol. Boiled for a short time in an excess of alkali it decomposed into orcin and CO.; boiled with a small amount of alkali it decomposed into an intermediate compound, more soluble in water, and clearly exhibiting acid properties. Chemical analysis indicated that it contained, by weight, 61.02% carbon, 5.09% hydrogen, and 33.89% of oxygen, corresponding to the formula $C_{36.18.15}$. Boiling the acid with methanol or ethanol yielded the corresponding ether, accompanied by a large amount of a resinous matter, as well as orcin (Stenhouse, 1849).

Stenhouse used the same procedures to extract and purify the active principle of *Leconora tartarea*, as well as prepare the pertinent ethers. Chemical analysis indicated that it contained, by weight, 61.02% carbon, 5.09% hydrogen, and 33.89% of oxygen, corresponding to the formula $C_{36.18.15}$, exactly the same as that of gyrophoric acid (Stenhouse, 1848b). Stenhouse changed the name of pseudo orcin to *erythromannite* (erythromannitol, erythritol) to indicate in a clear manner its origin and characteristic properties. In particular, he mentioned that treatment of erythromannitol with fuming nitric acid yielded erythromannitol pentatanitrate, an explosive compound similar to mannitol tetratanitrate. Stenhouse gave a detailed description of the precautions to take when synthesizing this dangerous derivative (Stenhouse, 1848b).

In 1861 Oswald Hesse (1835-1917) published a long memoir about lichens where he proved that the color-yielding compound of the archil lichen from Angola was erythrin. He prepared and determined the properties of orsellinic ether and showed that these were identical with the ones reported by Stenhouse. In addition, he prepared what he termed dichloro- and dibromo-orsellinic ethers (actually alkyl derivatives) (Hesse, 1861). In 1862 Stenhouse repeated and confirmed the Hesse's halogenation experiments and determined that the formula of the dibrominated compound was $C_{20.10}$Br.O.. In this publication Stenhouse also reported the synthesis of the methyl ether, amyl orsellinate, tribromo-beta- orcin, and erythroglucine (today erythritol) (Stenhouse, 1862a).

Additional papers gave information about the extraction of the active ingredients of *Cludonia rangiferin* and *Usnea barbata* (Stenhouse, 1870a); the nitro substitution compounds of the orcins (Stenhouse, 1870b, 1871b); chlorine substitution compounds of the orcins (Stenhouse, 1871a, 1873a); chlorine and bromo substitution compounds of the orcins (Stenhouse, 1872b); iodo derivatives of the orcins (Stenhouse, 1872a, 1873c); amido derivatives of the orcins (Stenhouse, 1873b); pricorocellin and xanthorocellin, extracted from *Rocella fuciformis* (Stenhouse, 1877). betorcinol (Stenhouse & Groves, 1880); etc.

Alkaloids Artificial alkaloids

According to Stenhouse all attempts that had been done so far to synthesize the natural alkaloids, such as quinine, cinchonine, strychnine, etc., had failed, although chemists had been able to prepare a large number of artificial alkaloids quite similar to the natural ones (Stenhouse, 1850a). Chemists had also succeeded in synthesizing some of the artificial alkaloids, such as quinoline, narcogenine, and cotarnine, by chemical action on the natural ones. Stenhouse was surprised that no one had considered the possibility of obtaining alkaloids using as starting material the highly nitrogenated principles (e.g. vegetable albumen, fibrin, casein, etc.) found in all plants, known to be as rich in nitrogen (about 15%) as the corresponding animal compounds. Many highly nitrogenated compounds were already produced from coal, a raw material of vegetable origin. Stenhouse mentioned that it was very difficult to obtained vegetable albumen, fibrin or casein (legumin) in a pure state and for this reason he had decided to use as starting point the portions of common plants, which contained these materials in large percentage (Stenhouse, 1850a).

For his first experiments he selected the seeds of green beans (*Phaseoulus vulgaris*), known to contain about 20.8% of legumin and 1.35% of albumen, corresponding to about 22% of nitrogenous matter. The beans were pyrolyzed in cast iron cylinders and the distillate recovered by condensation. This process produced a large amount of combustible but condensable gas accompanied by a liquid distillate, strongly alkaline, very complex, and containing, among other substances, acetone, methanol, acetic acid, empyreumatic oils, tar, ammonia, and several organic bases. It was first treated with a large excess of HCl and then the clear liquid separated from the bottom layer of tar and empyreumatic materials. This liquid was then distilled to eliminate the acetone, methanol, most of the neutral and acid volatile empyreumatic oils, as well as converting the tar and fixed oils into resins. It was filtered again, neutralized with quicklime or sodium carbonate, and subjected to an additional distillation. The first distillate was a watery liquid, with oily alkaloids floating upon it, which increased but then diminished again. The united oily alkaloids from the first two distillates were purified by treatments with a strong KOH solution to remove the ammonia and water, and then rectified again. The boiling began at 108 °C; a small quantity passed over between 108° and 130 °C; a large quantity between 150° and 165 °C; and the last between 165° and 220 °C. The different distillates were further separated by repeated fractional distillation (Stenhouse, 1850a).

Stenhouse wrote that although these oily alkaloids had different boiling points, they had very similar properties: They were transparent and colorless liquids, lighter than water and having the pungent and slightly aromatic odor characteristic of this kind of compounds. They had a strong refractive power; they reddened turmeric and turned reddened litmus blue, fumed in contact with HCl, and were completely soluble in alcohol and ether. They formed a double salt with platinum dichloride; chemical analysis indicated that its formula was $C_{10}H.N$, HCl, PtCl.. Separation of the bases indicated that their content in carbon and hydrogen varied very little, although their boiling points were significantly different. Chemical analysis of the base passing between 150. and 155 .C indicated that it contained, by weight, 74.98% carbon, 7.49% hydrogen, and 17.53% nitrogen, corresponding approximately to the formula $C_{10}H.N$ (very similar to that of picoline) (Stenhouse, 1850a).

The following set of experiments was conducted with the oil cake of flax seeds (*Linum usitassimum*). Distillation of the cake yielded a smaller amount of distillate than green bean seeds. The liquid products had an offensive odor; they contained acetone, acetic acid, and a large amount of empyreumatic oils. Once again the bases were separated and found to form a different series from either the coal or the bone bases. Stenhouse did not analyze them but speculated that some of the bases obtained from flax were identical to those obtained from green beans (Stenhouse, 1850a).

Stenhouse also reported the results of similar pyrolysis experiments conducted with wheat flour, peat from the moors in the neighborhood of Glasgow, wood, and guano. The liquid obtained from wheat was now strongly acid from the large quantity of acetic acid it contained. It did not contain aniline or quinoline and distilled at a lower temperature than the one obtained from the previous two series of experiments. The peat distillate was very neutral and did not contain aniline and quinoline. Stenhouse was surprised to find that the wood distillate contained scarcely ammonia or any other organic bases, a result, which seemed to indicate that the stems and trunks of trees appeared to contain very little nitrogenous matter. The guano distillate was strongly ammoniacal and its properties were similar to the ones obtained from green beans and flax, a result that lead Stenhouse to generalize his results as follows: "whenever ammonia is generated in large quantity from complex, either animal or vegetable substances, it is always accompanied by the formation or a larger or smaller amount of volatile organic bases"(Stenhouse, 1850a).

An addendum to the above paper described the production of bases by putrefaction of nitrogenated matter and from creeping cedar (*Lycopodium*). Stenhouse took a certain amount of horseflesh, cut in small pieces and repeatedly boiled with water, and left to putrefy in a warm place for nears a month. At the end of this period, the meat was full of maggots. It was then treated with a large amount of aqueous HCl and repeatedly agitated with water. The resulting liquid was concentrated, filtered to remove the accompanying flocculent and albuminous matter, neutralized with sodium carbonate, and distilled. A highly alkaline liquid passed over, consisting mainly of ammonia carbonate and a small amount of organic bases. Repeated distillation over NaOH yielded a light colorless oily fluid consisting of one or two bases, strongly alkaline, having an agreeable aromatic odor and being very soluble in water. Stenhouse was surprised that it did not contain any aniline (Stenhouse, 1850a).

Stenhouse boiled a quantity of *Semen lycopodii* with a strong solution of NaOH and then evaporated the resulting liquid to dryness. The residue was pyrolyzed in an iron retort and the ensuing products collected as before. These were found to contain a considerable amount of ammonia and a large quantity of basic oil, slightly soluble in water and having a very peculiar and very pungent odor. This oil neutralized acids and was clearly very different from the one separated from the other vegetables (Stenhouse, 1850a).

Quinic acid

According to Stenhouse no analytical procedure was available for detecting the presence of quinic acid (Stenhouse, 1845a). Since this acid was probably present in the state of calcium quinate in all the barks that contained the alkaloids quinine and cinchonine, an adequate analytical tool would help in differentiating true barks from false ones. Stenhouse developed a proper analytical technique based on the fact that the decomposition of quinic acid generated quinone, a unique byproduct, easily detectable by standard methods. His procedure was as follows: a sample of the bark being tested is macerated with dilute sulfuric acid and then precipitated with a slight excess of sodium or potassium carbonate. The dark colored precipitate is separated by filtration and then distilled with a great excess of NaOH or KOH. Quinone will pass over if the bark contains quinine or cinchonine. This compound is easily identifiable by its unique taste and smell and its strongly noticeable alkaline properties. It is nearly insoluble in water, unless first neutralized by an acid, when it readily dissolves; but it is immediately precipitated in oily drops on the addition of an alkali. Stenhouse remarked that his test only indicated the presence one or both alkaloids; these would then be identified by the available analytical procedures (Stenhouse, 1845a).

Sparteine

Stenhouse discovered sparteine in 1851 while studying the action of nitric acid on a variety of vegetables, among them, balsam poplar (*Populus balsamifera*), black poplar (*Populus nigra*), crack willow (*Salix russelliana*), mahogany wood (*Swietenia mahogani*), apple tree (*Pyrus malus*) hawthorn (*Cratargus oxyacantha*), common elder (*Sambucus nigra*), the root of turmeric (*Curcuma longa*), and common broom (*Spartium scoparium*), a leguminous shrub growing in Western Europe (Stenhouse, 1851).

A quantity of the branches of balsam poplar was cut into small pieces an exhausted with boiling water. The extract was concentrated by evaporation and then treated with dilute nitric acid for several hours. The acid solution was evaporated to dryness, the residue extracted with water, the solution neutralized with potassium carbonate, and again partially evaporated. The resulting precipitate was found to be potassium nitropicrate, accompanied by the potassium salt of a new acid, which Stenhouse named *nitropopulic acid*. The remaining mother liquor was found to contain potassium oxalate and nitrate. Stenhouse isolated nitropopulic acid, determined its properties and formula, $C_{14}H.N.O_{13} + H.O$, and also prepared the nitropopulates of potassium, sodium, barium, silver, and lead. Similar results were obtained with black poplar. Stenhouse found that the extract of common broom yielded nitropicric acid and exhibited some peculiar properties that led him to make a more detailed study of this bush (Stenhouse, 1851).

For this purpose, he cut the shrub into small pieces and extracted them with a large amount of boiling water for several hours. The extract was concentrated to about a tenth of its bulk and left in a cool place for twenty-four hours; after that time, it had transformed into a gelatinous mass, which was put on a cloth filter and washed with little cold water. The resulting jelly consisted mainly of a crystalline coloring substance (*scoparin*) contaminated with chlorophyll and ferric oxide derived from the cooking vessel, and a small amount of a volatile organic base, which gave the jelly its extreme bitter taste (Stenhouse named it *sparteine*). The gelatinous mass was boiled with water acidulated with HCl, then filtered through cotton and washed with cold water, and finally evaporated to dryness on a water bath. The impure scoparin was reduced to powder, dissolved in boiling water, filtered, and the resulting solution dried at room temperature or under vacuum. The resulting solid scoparin was an amorphous brittle mass, pale yellow or greenish yellow, slightly soluble in cold water and wine spirit. It dissolved readily in caustic and carbonated alkalis. Further purification with alcohol rendered a tasteless, odorless, and neutral solid, which dissolved easily in caustic and carbonated alkalis, and somewhat less in concentrated acids. A solution of calcium hypochlorite changed scoparin to a deep green color, probably by oxidation. Chemical analysis indicated that it contained by weight, 58.09% carbon, 5.06% hydrogen, and 36.88% oxygen, corresponding to the empirical formula $C_{21.11.10}$. Stenhouse believed that these results showed that scoparin belonged to the class coloring matters (Stenhouse, 1851).

The next experiments were devoted to separating and purifying sparteine, the principle contained in the acid mother liquor from the crude scoparin. This liquid was distilled with an excess of sodium carbonate; the sparteine that passed over slowly collected as colorless basic oil at the bottom of the aqueous liquid in the receiver. The ammonia accompanying the scoparin was eliminated by successive washes with cold water. Stenhouse wrote that sparteine was a viscous colorless liquid, originally transparent, and then, after remaining in contact with water, becoming slightly opalescent. Sparteine, when exposed to air it gradually acquired a brownish yellow color. This principle was considerably heavier than water, with a clear alkaline behavior, and forming bitter salts with acids. Boiled for some time with an excess of concentrated HCl it decomposed partially and acquired an odor resembling that of mice. Chemical analysis indicated that it contained, by weight, 76.91%

carbon, 11.10% hydrogen, and 11.99% nitrogen. Stenhouse gave a detailed description of the preparation, properties, and crystallographic characteristics of sparteine nitropicrate, sparteine chloroplatinate, and the double chloride of mercury and sparteine (Stenhouse, 1851).

Stenhouse reported that sparteine had powerful narcotic properties, although inferior to nicotine or coniine: one drop dissolved in acetic acid and administered to a rabbit, first produced excitement, followed by stupor lasting for five or six hours. Two hundred and sixty milligrams administered to a full-grown rabbit produced violent excitement, followed by death after three hours. Sparteine also acted as a powerful diuretic, the dose for a grown- up person being from 0.20 to 0.26 g, repeated three times successively every four hours (Stenhouse, 1851).

Quinidine

Stenhouse wrote that in 1833 Étienne Ossian Henry (1798-1873) and Auguste Pierre Delondre (1790-1865) reported for the first time the existence of a new alkaloid, which they named *quinidine,* in the product then sold under the name commercial quinidine (Stenhouse, 1862b; Henry and Delondre, 1833). The latter was found to be chiefly a mixture of quinidine, quinine, and resinous matters obtained from the mother liquors of the manufacture of quinine sulfate. J. van Heijningen was the first to separate quinidine from the mixture and prepare it in a pure and crystalline state. Van Heijningen named it *b-quinine* (Heijningen, 1849). The lack of information about the salts of quinidine led Stenhouse to prepare a number of them and study the action of ethyl iodide upon the alkaloid itself (Stenhouse, 1862b). Thus, he reported the preparation, properties, and formulas of quinidine platinum salt, quinidine gold salt, silver nitrate salt, zinc chloride salt, mercury(I) chloride salt, quinidine oxalate, and quinidine picrate. He reported that ethyl iodide reacted with readily with quinidine producing the iodide of ethyl quinidine. All the above results indicated that quinidine did not contain replaceable hydrogen, agreeing with quinine and cinchonine, the alkaloids with which it was associated. Stenhouse also reported the preparation, properties, and formula of the double tartrates of a variety of alkaloids with antimony, e.g. quinidine, strychnine, brucine, and berberine (Stenhouse, 1862b).

Wrightine

Stenhouse wrote that the tree *Wrightia antidysenterica,* belonging to the order apocynaceœ, was indigenous to various parts of India. Its bark and seeds were introduced in Europa in the middle of de 18th century as a valuable medicine in dysentery, diarrhea, and fever. In 1864 Stenhouse reported the analysis of the seed contents and the discovery of its active component (Stenhouse, 1864). For this purpose, he first pulverized the seeds and treated them with carbon disulfide to remove the fatty matter.

This fatty matter was found to be a fixed oil, which did not solidify even at a temperature well below 0 .C. Digested with caustic alkalis it produced a soap solution, which upon acidification precipitated the fatty matter as a semi solid.

The defatted seeds were extracted with boiling alcohol and the alcoholic solution evaporated to dryness. The residue was composed of the active principle, which Stenhouse named *wrightine*(conessine) mixed with fatty matter, gum, and other impurities. The crude wrightine was treated with dilute HCl, concentrated by heating, and neutralized with sodium carbonate. The purified principle was filtrated and washed with cold water. Stenhouse reported that wrightine was a bitter white crystalline substance, moderately soluble in boiling water and in boiling dilute alcohol, and slightly soluble in ether and in carbon disulfide. It readily dissolved in dilute HCl, sulfuric, nitric, acetic, and oxalic acids. Concentrated nitric acid dissolved it releasing red fumes and decomposing into oxalic acid, without formation of picric acid. Ignited with a mixture of calcium oxide and sodium hydroxide it released alkaline vapors and basic oil, which solidified to a resin on cooling. Digestion of a solution in acetic with nutgalls liquor produced a flocculent precipitate, which was soluble in HCl (Stenhouse, 1864).

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Appendix

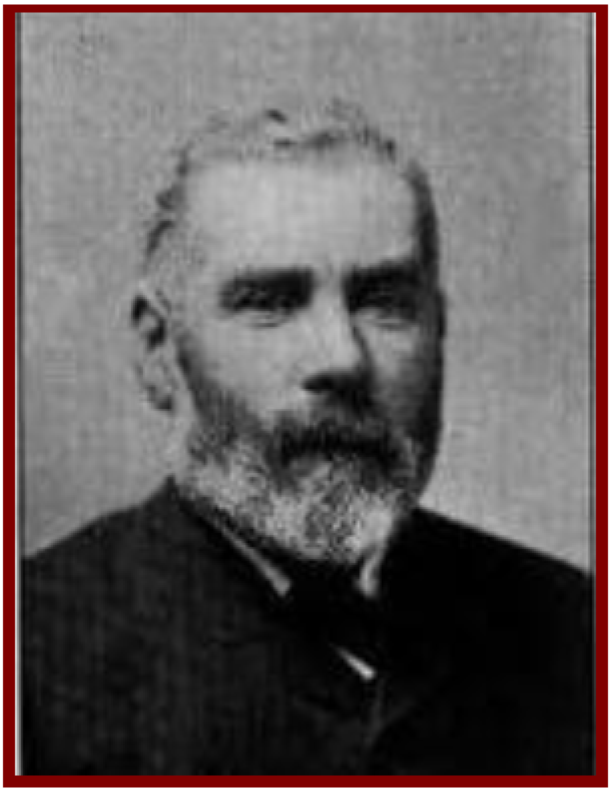

Figure 1
John Stenhouse (1809-1880).

Figure 2
Stenhouse's gas mask.

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