"NATURAL PRESERVATIVES"

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Cosmetics and Toiletries: August 2003

SUMMARY

This paper looks at the theoretical development of a natural preservative system using a data base on medicinal plants as a source of reference. The legal aspects of this concept are considered. The traditional methods of preservation, many taken from the food industry are summarised. The use of alcohol, glycerine, sugar, salt, dessication, anhydrous systems and temperature are amongst examples considered. The commercial solutions are examined.

KEY WORDS

Natural preservation, traditional preservation, legal status.

INTRODUCTION

The subject of natural preservatives is one that probably has more academic interest than practical or economic virtue. However, it does have a wonderful marketing angle which may justify the higher raw material costs.

The paper reviews the most commonly used methods of preservation that are already available to the formulator. The food and beverage industry may be called upon for many of these examples.

LEGAL POSITION

No preservative may be used which does not appear in Annex VI Part 1 or 2 of the EEC Cosmetic Directive 76/768/EEC - including 7th. amending Commission Directive 94/32/EC.

However, there is no legislation for those natural materials, which, when used for their beneficial effect on the skin, may coincidentally have a positive effect on the total preservative requirement of the formulation. Of course, no material appearing in Annex II may be considered.

The food industry often uses a preservation technique known as the “hurdle approach”, where there are a number of different methods that might eliminate organisms on their own if used at a high level, but which in a food might make the product unpalatable. The idea of using a whole variety of these “hurdles” to slowly weaken each organism, but at individual levels that would be ineffective is an almost alien concept to the cosmetic and toiletry industry.

SUGAR

High levels of sugar can preserve against spoilage organisms, this may be seen in jams, preserves, certain sweet pickles and marmalades. This is also an important factor in the preservation of boiled sweets and chocolates etc. Increasingly, it will be noticed that many products now have to be kept in the refrigerator of freezer once opened, because sugar has been replaced by artificial sweetener which is cheaper and healthier to eat, but which compromises the self-preservation of the product.

HONEY

Honey in its undiluted form is also a natural preservative and, indeed, there are many learnéd papers citing honey as a viscous barrier to bacteria and infection.

ALCOHOL

Not all organisms are bad! The production of alcohol from sugar by yeast is an industry in its own right. A wine carefully produced using sterilised equipment and fermented to 13% by volume will just about resist further infection from external organisms, once the ferment has completed. It is during the time of the fermentation process that the fermenting must is vulnerable to infection. The naturally produced fermentation grade alcohol can be concentrated by distillation and used as a natural preservative in toners, aftershaves and colognes. The purist would argue that the denaturant present in the alcohol is not "natural" and they would be right. The need to return to quassin, the bitter substance present in quassia (*Picraena excelsa*), might be a solution, however, the Customs & Excise might not see your antique solution to denaturing with quite the same enthusiasm.

HEAT

Heating, cooking and pasteurisation is another natural form of preservation that will sterilise products, especially where that product is designed as a one-shot use product - for example, a phial or a sachet. Alternatively, once opened, the product can be stored in the fridge of freezer to prevent microbiological degradation.

DESICCATION

Removing water from a product or making it totally dehydrated will greatly reduce the possibility of spoilage, however, it must be recognised that the presence of spore-bearing organisms could become active once that water is reintroduced.

ANHYDROUS

In a similar vein, one could make products with materials that do not contain any traces of water, i.e. to deliberately design and formulate a totally anhydrous product. However, creams that can be finished by the consumer, by introducing water to the blend of oils, fats and waxes are prone to the same restrictions as the dessicated products.

SALT

The use of extreme levels of salt as used by the ancient mariners to preserve their meat is effective and it very likely that the preservation of the Egyptian mummies was, in part, achieved by the 40 day treatment in natron (a concentrated brine solution that osmotically drained the tissues of water).

COLD

Placing a product in the cold merely 'stops the clock' on microbiological growth and this is perfectly fine, provided the product was sterile when it was placed in the cold and/or had sufficient preservative 'mass' to counter any new organisms subsequently introduced.

ACID pH

The preservative activity can be boosted by operating at as low a pH as possible. Natural acidity could be obtained from one of the many of the alpha hydroxy acids (AHAs) which are obtained from citrus species, where the major components are citric and malic acids.

CHELATING AGENTS

In addition to formulating at low pH, chelating agents such as ferulic acid extracted from rice bran, could be added to enhance the activity of the natural preservative.

ANTIOXIDANTS

Antioxidants such as natural tocopherol and ascorbic acid will further aid in preservation, as well as reducing the potential rancidity.

GLYCERINE

High levels of vegetable glycerine, up to 15-20%, will also have a preservative effect, similar to that effect obtained by the use of high levels of sugar.

EMULSION FORM

It has been argued that the formula comprised of a water-in-oil emulsion, where the oil is the continuous phase is far less likely to be subject of attack by spoilage organisms. This might be true, but it certainly does not exclude the use of a preservative system. It does, however, form another link in the hurdle approach to preservation.

EMULSIFIER TYPE

A material was marketed many years ago called Lauricidin, which was Glyceryl Laurate and was said to mimic the sterile and protective action found in a mother's milk (as well as bovine). It had been found that the properties that determine the anti-infective action of lipids are related to their structure: e.g., free fatty acids & monoglycerides. The monoglycerides are active; diglycerides and triglycerides are inactive. Of the saturated fatty acids, lauric acid has greater antiviral activity than either caprylic acid (C_8), capric acid (C_{10}), or myristic acid (C_{14}). Lauric acid is one of the best "inactivating" fatty acids, and its monoglyceride is even more effective than the fatty acid alone.

Once again the system has been shown to work, but the formulating is difficult and to a high degree unpredictable. It might be a good solution perhaps for those with a large research department and plenty of human resources.

PLANTS SELF-PRESERVATION

Plants in the wild do not go mouldy, and yet they are in an environment that predisposes them to suffer from the infestation of all manner of spoilage organisms. Yeasts, moulds and bacteria abound in the soil, all working to breakdown dead plant material and provide fresh humus for those plants living in the soil. Living plants resist the natural forces of disintegration.

The chemicals present in all parts of the plant protect it from the environment. However, examples can be seen where tampering with the plant leads to a reduction in the efficacy of this natural mechanism.

It is concluded, that the chemical constituents within each plant clearly differ in composition. Furthermore, that there may be in certain species a chemical or group of chemicals present in the plant that is capable of killing micro-organisms. This chemical composition varies according to whether the plant is alive or dead, and in certain/most plants will vary according to season.

In many cases, when these plants are extracted, it is found that the extracts are capable not only of resisting certain spoilage organisms, but in some cases can actively act to destroy them. The time and speed of extraction of the fresh plant is often critical if the preservative activity is to be retained.

COMMERCIAL PRODUCTS

There are a number of natural preservatives available on the market that is not strictly speaking legal, since they have no entry in Annex VI as a permitted preservative. However, the use of a plant for its marketing claim, or for other functional benefits smudges the issue. One may use a number of plant derivatives as fragrance components and coincidentally achieve a lower overall preservative requirement for the product in which they are used.

There are many cases where plants may contain paraben-type compounds in addition to other functional actives and the difficulty is to decide whether the botanical is being used as a preservative or for other legitimate and perfectly legal benefits.

A REVIEW OF THE SOLUTIONS ALREADY PRESENT ON THE MARKET.

In days of old, wine and water was stored in silver vessels because it had been observed that the keeping time vastly improved when compared to earthernware jugs and pots. This is somewhat surprising, because one might have expected that the glazes (often rich in lead) on those pots might have further aided preservation!

Silver Chloride

The modern preservative is comprised of silver chloride (20%) deposited on a substrate of titanium dioxide. It does appear in Annex VI, but is prohibited for use in children's products under three years of age. It is not allowed in oral products and those products intended for application around the eyes and lips. It is limited to 0.004% when calculated as silver chloride.

Nature identicals

There are a number of materials that are already allowed in the legislation and which occur naturally in nature, these include benzoic acid (limit 0.5% as the acid) and benzyl alcohol (limit 1%). They can be obtained naturally from natural sources such as balsamic resins, but the price is ludicrously expensive. Benzoic acid is moderately good against Gram+ve bacteria, yeast and moulds, but moderately poor against Gram-ve bacteria, while benzyl alcohol is good to very good against Gram+ve, moderately poor against Gram-ve, poor versus fungi and moderately poor against yeast.

Sorbic acid (and one supposes one could include its salt potassion sorbate) is found in nature (originally from *Sorbus aucuparia* or Rowanberry) but again purchase synthetically and can be used up to 0.6%. It is moderately effective against all bacteria and good against fungi and yeasts.

A two-pack system consisting of lactoperoxidase, glucose oxidase and glucose does not appear in Annex VI but has found a good following amongst the green brigade. It is very fiddly to work with and has to be premixed just prior to addition to the finished batch. Its mechanism is said to mimic the conditions that keep a cow's udder free of infection whilst it is suckling its calf.

THE "ILLEGAL" PRESERVATIVES

Citrus Seed extracts

There are other dodges used by the 'green' formulators in their quest to avoid the preservatives listed in Annex VI that do not occur in nature. Citrus fruits have always been a useful source of alpha hydroxy acids, of fragrant essential oils and useful astringents.

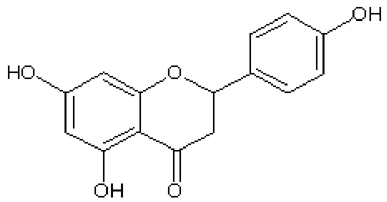


Fig.1 Naringenin

Everything in the fruit is useful, the juice for its vitamin C claims, the peel gives a fragrant essential oil and claims of "zest", the flowers yield an exquisite and very expensive essential oil called neroli, and the seeds yield an antibacterial, which is either hesperedin or naringenin depending on the citrus species chosen.

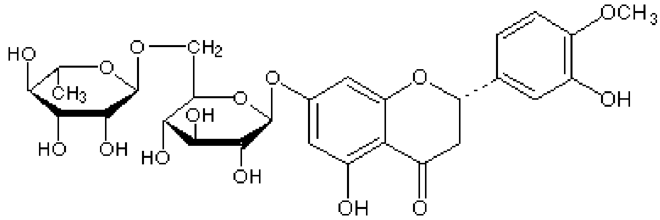


Fig.2 Hesperidin

This can be slipped in with other citrus components and is conveneiently lost amongst the myriad of exotic ingredients. As if by magic, the need for a preservative has disappeared. It is not simple to formulate with these types of materials and you have to do a lot of experiments, since not all systems are compatible, but success can be achieved.

Tree Lichen extracts

The tree lichen (*Usnea barbata*) contains usnic acid which is a fairly powerful agent against yeast and moulds.

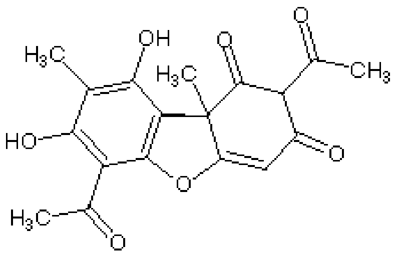


Fig.3 Usnic acid

It comes as no surprise therefore, that when this extract is used at a reasonable concentration that these spoilage organisms are not able to grow. The traditional use of this material for infections of the feet is well justified.

Japanese Honeysuckle extracts

A plant preservative that is based on the Japanese Honeysuckle (*Lonicera japonica*) is available that is described as being a complex mixture of esters of lonicerin and natural *p*-hydroxy benzoic acid.

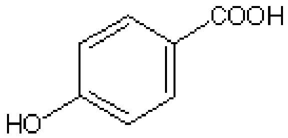


Fig.4 *p*-Hydroxy benzoic acid

Clearly this is a naturally occurring paraben, and we would expect this material to have antimicrobial properties.

Formosan Hinoki Tree

Hinokitiol is a white crystalline acidic substance first isolated from the essential oil of Formosan Hinoki (*Chamaecyparis taiwanensis* Masamune et Suzuki) by Nozoe in 1936. This substance was also found in the essential oil of Aomori Hiba tree (*Thujopsis dolabrata* SIEB et ZUCC) at a later date.

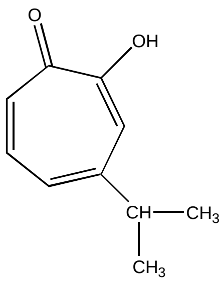
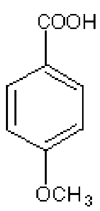


Fig.5 Hinokitiol

Though the natural form of hinokitiol is no longer available, the nature identical form is still made. It may be a surprise to learn that this material is listed as a hair conditioning agent in the CTFA Ingredient Dictionary. It is one of those unfortunate events where one was looking for a conditioning effect and then was annoyed to discover that the anticipated preservative system was superfluous to requirement. It is also unusual in that it has a 7-membered ring and is quite unlike any other preservative one normally encounters.

The Parfum (Fragrance)

Another clever idea is to look at essential oils and then isolate one or two of the



components that coincidentally have antimicrobial activity. Since these components came from an essential oil, they must be perfumery based materials and so can be listed as parfum or fragrance.

Fig.6 Anisic acid

The two largest commercial players at this time are anisic acid or 4-methoxy benzoic acid (the similarity to a paraben is outstanding) and levulinic acid or 4-oxopentanoic acid. Anisic acid is found in Aniseed (*Pimpinella anisum*) amongst many sources, and levulinic acid has been found as a by-product in the production of diosgenin from Wild Yam (*Dioscorea villosa*).

This area could be exploited far more, because there are many other essential oil components that have anti-bacterial properties.

Perillic acid

A material that was presumably first found in *Perilla frutescens* or the Japanese Shiso oil is perillic acid. The perillaldehyde present has already been found effective against *Acnes propionibacterium* and *Staphylococcus aureus*.

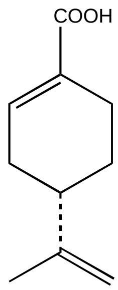


Fig. 7 Perrilic acid

This material is made commercially by the convertion from limonene using a biotechnology process. It has been found to have good activity against Gram+ve and Gram-ve bacteria.

PACKAGING CONSIDERATIONS

We have considered the base and also considered the additives that one could add in order to reduce or eliminate spoilage organisms in our products. The last piece of the jigsaw is the packaging. Wide neck jars with shives (the plastic discs that cover the neck) are probably the worst news for the microbiological integrity of a product. Those covers allow water to condense on the surface and then enrich the organisms. The cardboard seal in the lid is another microbial sponge just waiting to act as a growth medium.

Tubes are far better (which is why they are more widely used in the paharmaceutical industry). The nozzle offers a smaller and more discrete surface for contamination. There are now tubes that have non-return valves, so that once pressed the tube cannot relax to permit the ingress of air. Notice how tubes for eye products have long tapering nozzles with a small pin hole for delivery of product. This is good microbiological sense.

The new generation of pots does not allow the consumer to insert fingers of high contamination. There are pots with nozzles and sealed flat surfaces that have airless pistons that follow the product to completion. The product is offered to the consumer at a push and those days of scooping out are over, especially with the 7th amendment demanding a use after opening period to be declared.

It could be argued that in these sealed and hygienic environments that the need for a microbial challenge test is over, since the consumer and the air will never enter the product during its active life. The preservative requirement will be a fraction of that required for a wide-necked cream jar.

The most secure pack is a single application pack, the sachet, the blister pack and the single shot capsule. These are technologies that come to us from the fast food and pharmaceutical industry. You use it all or throw away the residue – it is the perfect preservative free environment and the worst example of wastefulness.

Conclusions

There is a move towards “preservative-free”, which is being achieved by many means. It is hoped that this overview has provided an insight into some of the techniques available.