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TABAKPRODUKT SOWIE HERSTELLUNG UND VERWENDUNGEN DAVON

PRODUIT DE TABAC, SA PRÉPARATION ET SES UTILISATIONS

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Description

Field of the Invention

[0001] The invention relates generally to smokeless tobacco, tobacco derivative or tobacco substitute products incorporating cyclodextrins or cyclodextrin derivatives. More specifically, the invention relates to smokeless tobacco, tobacco derivatives, or tobacco substitute products comprising cyclodextrins or cyclodextrin derivatives which are incorporated in or bound to a cellulosic material.

Background of the Invention

[0002] Cyclodextrins are cyclic oligosaccharides consisting of 1,4-α-glucoside monomers. They exist naturally as α-, β-, and γ-cyclodextrins consisting of 6, 7, and 8 glucose monomers in a ring, respectively. Their respective internal diameters are 0.57, 0.78, and 0.95 nm; each has a torus depth of about 0.78 nm. The toriod shape offers unequal opening sizes for the inner cavity. The smaller opening exposes a primary hydroxyl group to the surrounding solvent while the larger opening exposes a secondary hydroxyl group. The presence of these hydroxyl groups results in the exterior surface of the toroidal shaped molecule having a hydrophilic character, while the interior of the toroid is less hydrophilic and may be considered as a hydrophobic cavity.

[0003] Consequently, the interior of the toroid can host hydrophobic molecules, or hydrophobic chemical moieties, while the exterior allows the complex to be solubilised in an aqueous environment. In the liquid phase hydrophobic molecules or moieties can be used to form strong inclusion complexes with cyclodextrins or cyclodextrin derivatives. For example it has been shown that the aqueous solubility of vanillin is much higher in the presence of β-cyclodextrin, present at a molecular ratio of 1:1, compared to when β-cyclodextrin is absent from the solution (Karathanos et al. Food Chemistry 101, pp 652-658). Furthermore, from analytical measurements it may be concluded that the molecule of vanillin inside the cyclodextrin cavity is protected from oxidation.

[0004] This ability to form inclusion complexes yet remain water soluble has helped make cyclodextrins a subject of considerable interest. Complexes can be administered to an area of interest, be it a body organ or a component of a product, whereupon the molecules inside the cyclodextrin are released by various factors such as heat, enzymatic activity, and pH change. Cyclodextrins are also relied upon to scavenge or filter out certain molecules, often toxic molecules. Environmental clean-up operations can utilize the ability of cyclodextrins to complex with heavy metals such as cadmium, removing these materials from a contaminated area.

[0005] Cyclodextrin derivatives are also widely used. For example, 2-hydroxypropyl-β-cyclodextrin is used to formulate drug complexes which facilitate the aqueous solubility of certain pharmaceutically-active compounds. One application for cyclodextrin derivates is to complex them with nicotine then incorporate that complex into chewing gum, providing a smoking cessation aid as described in WO 91/09599. A chewing gum could alternatively offer flavour complexed in the cyclodextrin. Another use of cyclodextrins and derivatives thereof complexed with flavour particles is their application to smoking products. Flavourant use is common in the tobacco field, a wide variety of flavourants are known and flavours are continually being developed.

[0006] Flavourants are traditionally added to whole tobacco, reconstituted tobacco, wrapping paper, cigarette filters, or packaging, often to affect the flavour of the product in use but also to improve the aroma of the unused product or that experienced by persons in the vicinity of the product during use. One manufacturing and packaging challenge presented by many known flavourants is that they tend to be highly volatile and easily sublime. One solution has been to complex the flavourant with a cyclodextrin. For example, US 5,144,964 proposes a water-soluble molecular inclusion complex of a β-cyclodextrin derivative and a lipophilic organic flavourant compound which can be incorporated in the wrapping paper for a cigarette.

[0007] Despite the known uses of cyclodextrins, there remains an unmet need in the art to provide further, advanced uses for these powerful compounds.

Summary of the Invention

[0008] It is therefore an object of the present invention to provide a new product incorporating cyclodextrins or cyclodextrin derivatives, namely, smokeless oral tobacco products.

[0009] It is a further object of the present invention to provide a new product incorporating cyclodextrins or cyclodextrin derivatives complexed with flavourants and provided in a smokeless oral tobacco product.

[0010] According to an embodiment of the invention, a smokeless oral tobacco product is provided, which comprises at least one of tobacco, a tobacco derivative, or a tobacco substitute and a cellulosic material. The cellulosic material comprises at least one cyclodextrin or cyclodextrin derivative. The tobacco can be encapsulated in a cellulosic wrapper. The cellulosic material may be, for example, fibrous, a woven web, or a non-woven web.

[0011] The cyclodextrin or cyclodextrin derivative may be chemically attached to the cellulosic material. A spacer group may be located between the cellulosic material and the cyclodextrin or cyclodextrin derivative. A complex agent may be complexed with the cyclodextrin or cyclodextrin derivative, such complex agent being any agent which can be located in the cavity of the cyclodextrin or cyclodextrin derivative or otherwise provided in or on such as by chemical bonding. Examples of complex agent include flavourants, aroma modifiers, and antimicrobial agents.

[0012] Flavourants can comprise monoterpene flavourant, monoaromatic flavourant, or polyaromatic flavourant, and examples include (+), (-)-limonene, cinnamaldehyde, cinnamonitrile, euginol, cis-isoeuginol, trans-isoeuginol, eugenyl acetate, eugenol methyl/ethyl esters, trans-anethole, cis-anethole, menthol, isomenthol, neomenthol, (+)-menthone, (-)-menthone, (+)-citronellal, S(+)-carvone, R(-)-carvone, trans-methyl cinnamate, cis-methyl cinnamate, vanillin, capsaicin, phenylpropanoids, aspartame, chocolate, coffee, pyrazines, salt, γ-Glu-Tyr, γ-Glu-Phe, orinithyl containing peptides, aromatic aldehydes, aromatic aldehydes derivatized as acetals, and lactones.

[0013] Aroma modifiers can comprise, for example, maltol, ethyl maltol, cis-jasmone, methyl jasmonate, geraniol, nerol, geranyl esters, neryl esters, (+)-citronellol, (-)-citronellol, citral, (+)-limonene, (-)-limonene, and monoterpenes.

[0014] An example of an antimicrobial agent is hinokitol.

[0015] According to another embodiment, a cyclodextrin or cyclodextrin derivative is used in the preparation of a smokeless oral tobacco product, wherein the product comprises tobacco. Alternatively, a cyclodextrin or cyclodextrin derivative complexed with at least one flavourant can be used in the preparation of a smokeless oral tobacco product, wherein the product comprises tobacco. The product can further comprise a cellulosic material, in which case the cyclodextrin or cyclodextrin derivative is complexed to the cellulosic material such as by chemical attachment.

[0016] According to another embodiment, a method for complexing at least one cyclodextrin or cyclodextrin derivative with a material in or formed by a smokeless oral tobacco product is provided which comprises the steps of providing a smokeless oral tobacco product comprising at least one cyclodextrin or cyclodextrin derivative, contacting the product with moisture to moisten the product, and allowing the material to complex with the cyclodextrin or cyclodextrin derivative. Where the cyclodextrin or cyclodextrin derivative comprises at least one flavourant the method can further comprise the step of allowing the flavourant to be released from the cyclodextrin or cyclodextrin derivative after the contacting step. Examples of materials complexed according to this embodiment include benzo(a)pyrene and cadmium.

[0017] As used herein, the term "cellulosic material" means a material consisting wholly or in part of natural or synthetic cellulose $(C_6H_{10}O_5)_n$, a long chain polymeric polysaccharide carbohydrate of β-glucose, for example lignocellulose, flax fibres, hardwood pulp, softwood pulp, hemp fibres, esparto fibres, kenaf fibres, jute fibres, and sisal fibres. It also means a material consisting wholly or in part of cellulose derivates, wherein the hydroxyl groups of cellulose have been partially or fully reacted with any appropriate entity. Examples of derivatives include cellulose esters such as cellulose acetate or cellulose triacetate. The term also encompasses mixtures of more than one type of cellulosic material as well as materials which have undergone treatments to improve performance or appearance, such as bleaching.

[0018] "Cyclodextrin(s)" "cyclodextrin derivative" or "CD" means any molecule from the class of naturally-occurring or synthetic cyclodextrins. It further encompasses molecules or portions thereof derived from cyclodextrins or synthesized to resemble cyclodextrins in whole or in part. Such cyclodextrins or cyclodextrin derivatives are toroidal, chiral structures having a hydrophilic, water-soluble outer surface comprising hydroxyl groups and a less hydrophilic or hydrophobic internal cavity. A cyclodextrin as denoted herein could refer to an α, β or γ cyclodextrin, a methyl substituted cyclodextrin, an ethyl substituted cyclodextrin , an alkyl substituted cyclodextrin with straight chain or branch chain alkyl groups, a hydroxyalkyl substituted cyclodextrin (e.g. 2-hydroxypropyl cyclodextrin , an anionic cyclodextrin, a cationic cyclodextrin, a quaternary ammonium cyclodextrin, an amphoteric cyclodextrin, or mixture of the same).

[0019] "Flavour" or "Flavourant" refers to any compound or chemical entity which may stimulate a taste sensation when consumed or when placed in the oral cavity of a user. Stimulation may be in the form of actual taste stimulation or perceived taste stimulation (simulation), such as that provided by scented materials. Examples of flavours include but are not limited to citrus ((+), (-)-limonene), fruit (benzaldehyde) aromatic and spice (cinnamon could be cinnamaldehyde, green leafy odour could be cis-3-hexenal, clove could be euginol, other monoterpene flavourants), mint (mentha flavours such as menthol, isomenthol, neomenthol), pepper (S(+)-carvone), dill (R(-)-carvone), ginger (phenylpropanoids), vanilla (vanillin and other aromatic aldehydes), sweet (sweeteners such as aspartame), chocolate and coffee (pyrazines), liquorice, salt (γ-Glu-Tyr, γ-Glu-Phe, orinithyl containing peptides). Flavourants which can achieve desired flavours can be natural or synthetic and include but are not limited to the above examples.

[0020] To achieve a flavour sensation or in addition to flavourant, aroma modifier compounds may be complexed to cyclodextrins according to the invention. Examples of aroma modifiers include but are not limited to maltol and ethyl maltol, cis-jasmone, methyl jasmonate, geraniol, nerol, geranyl and neryl esters, (+)-citronellol, (-)-citronellol, citral, (+)-limonene, (-)-limonene, monoterpene aroma compounds.

[0021] By using flavourants it can be possible to provide not only a product with improved flavour, but also one which has additional benefits over existing products. For example, flavourants which mimic the taste of salt can be used to provide a reduced salt product, and artificial sweeteners can be used to provide a reduced calorie product.

[0022] In addition to or instead of flavourants other complex agents can be provided with the cyclodextrins of the

present invention. For example, use of an anti-microbial agent such as hinokitol can increase shelf-life and/or provide a product which can be suitably stored under less stringent conditions. Complex agents such as anti-refrigerants or preservative agents could be used to improve product stability and/or minimize undesired limitations on storage and transport conditions. The complex agents used with the present invention thus give the blender greater latitude in the use of flavourants, buffers, additives and moisture when preparing the tobacco or tobacco substitute.

[0023] Smokeless oral tobacco products are a class of tobacco products which are intended for oral administration. Such products are inserted in the mouth of the user and retained for a period of time, often for between 5 and 60 minutes. The product may be actively chewed or allowed to remain in the mouth without mastication. The user may expectorate saliva during use or not. The tobacco portion may comprise loose tobacco leaves or leaves which are chopped, shredded, or pulverized, alternatively, the tobacco may be compressed into a plug. Chopped, shredded or pulverized tobacco may be provided in a pouch, which pouch is inserted orally.

[0024] Thus "smokeless oral tobacco product" is used herein to denote any tobacco product which is not intended for combustion but instead designed to be placed in the oral cavity of a user for a limited period of time, during which there is contact between the user's saliva and the product. The term encompasses conventional products such as Swedish-style snus and American-style chewing tobacco, as well as less conventional and forthcoming products.

[0025] "Spacer group" or "SG" is used herein to describe any of a class of molecules which can be used to create a physical or chemical span between a cyclodextrin and cellulosic material. Spacer entities are well known in the art; see, for example, WO 06/53628. A spacer group located between a cyclodextrin and cellulosic material thus could be represented CD-SG-cellulosic material wherein SG could be an alkylene with up to 10 carbon atoms which may be unsubstituted, mono or polysubstituted by halogens, alternatively one or more non-adjacent CH_2 groups could be replaced, in each case independently from one another, with O, S, NH-NR, CO, COO, OCO, OCO-O, S, CO, CO-S, CH=CH, or C≡C in such a manner that O and/or S atoms are not linked directly to each other. Examples of spacer entities include $(CH_2)_p$ and $(CH_2CH_2O)_q$ where p is an integer from 2 to 6 and q is an integer from 1 to 3. In some embodiments the spacer group could be an imidazolidone moiety or $(CH_2)_r$ or $(CH_2O)_r$ where r is an integer between 1 and 5.

[0026] "Tobacco, tobacco derivative, or tobacco substitute" as used herein includes pure tobacco and reconstituted tobacco. It includes derivatives of tobacco such as specific compounds, e.g., nicotine, whether extracted from actual tobacco or otherwise produced, as well as structural derivatives such as the fibrous portion of a tobacco leaf. Tobacco substitutes can comprise individual chemical entities as well as complex chemical solutions which, when appropriately prepared, physically resemble actual tobacco.

Detailed Description

[0027] Unless specifically noted, all materials and equipment are standard, commercially available products.

[0028] As noted previously herein, the invention is directed to smokeless oral tobacco products which incorporate at least one cyclodextrin or cyclodextrin derivative. Smokeless oral tobacco products, particularly those comprising natural tobacco, contain compounds or release compounds in use that may present a risk of injury to the user after extensive and extended use of the product. Technologies for identifying and extracting such compounds from the natural tobacco have progressed; however, it can be preferable, perhaps particularly so for newly-identified compounds, to provide a way to remove the compounds during use of the product so as to minimize the complex steps related to preparing the tobacco for inclusion in a product.

[0029] The cyclodextrins of the present invention thus provide a novel means for complexing with potentially harmful compounds, before the compounds can be carried away with the user's saliva and move freely about the oral cavity. It is therefore advantageous to provide the cyclodextrins in a manner so that they are bound to one or more substrates that will be expectorated after use of the product, thereby removing the cyclodextrin-compound complex from the mouth of the user.

[0030] According to an embodiment of the invention cyclodextrins are attached, for example by chemical bonds, to cellulosic material. That material is then incorporated into the smokeless oral tobacco product, e.g., a filler material or as a wrapper for a pouch-like product. Attachment of cyclodextrins is a routine matter, technology related to their applicability in chromatography provide numerous examples of the process.

[0031] Where chemical bonds are used, so that the cyclodextrin is not subject to interference from the cellulosic material to which it is attached, a spacer group can be provided. This ensures the cavity of the cyclodextrin is free to interact with the surrounding solution either to release a complexed compound or to remove a target molecule from free solution.

[0032] Cyclodextrins are known in the art, as are methods and materials for selecting particular cyclodextrins based on the molecule to be contained within the cavity. For example, in use it can be expected that certain smokeless oral tobacco products release polyaromatic hydrocarbons such as benzo(a)pyrene, a molecule which is suspected of potentially causing harm for long-term heavy users. Benzo(a)pyrene has been calculated to be 0.88 nm across its wide axis. It is thought that benzo(a)pyrene cannot form an inclusion complex with α-cyclodextrin, but that it forms a stable

1:1 host-guest complex with β- cyclodextrin and a 1:2 host-guest complex with γ- cyclodextrin (Fielden and Packham, J.Chromatog. 516(1990) 355-364).

[0033] To remove benzo(a)pyrene from a product during use it can be preferred to take advantage of its high propensity to complex within the γ-cyclodextrin cavity. Once complexed, benzo(a)pyrene is unlikely to return to free solution, i.e., the user's saliva, as it is an extremely hydrophobic molecule. By providing the cyclodextrins in or attached to cellulosic material one ensures that both the cyclodextrins and the molecules they have complexed with are expectorated after use of the product.

[0034] Instead of or in addition to providing the cyclodextrin with an empty cavity, the invention further provides complexing the cyclodextrins with one or more flavourants which will be released by the cyclodextrin during use, after which the cyclodextrins present an empty cavity for complexing with a compound of interest present or generated in the tobacco portion of the product. This provides the added benefit of flavour release while still reaping the benefit of reducing the release of certain compounds into the oral cavity of the user.

[0035] This aspect of the invention takes advantage of the fact that many flavourants or other additives, which are also within the scope of the invention, are small mono-aromatic compounds which form transient complexes with cyclodextrins and are readily released upon contact with moisture such as saliva. γ-cyclodextrin presents a large cavity from which a small compound would more rapidly disassociate, providing an open cavity into which another molecule such as benzo(a)pyrene could complex.

[0036] According to an embodiment of the invention, β-cyclodextrin could be a preferred cyclodextrin for the complexation of flavourants and aroma molecules because it presents a cavity size which is ideal for a large number of flavourant and aroma molecules. The bi-aromatic ring compounds in particular would be held stably in the cyclodextrin complex until conditions are such that they solubilize. This would allow for a high moisture content in the product which would not interfere with the inclusion complex, only upon use where the user's saliva causes a much higher degree of wetting would sufficient solution be available to release the flavourant. The cyclodextrins would then be free to complex with other compounds. Particularly drawn to the cyclodextrins would be hydrophobic molecules such as those which might potentially cause harm to the user if allowed to pass into the saliva and be carried around the oral cavity freely.

[0037] Another feature of the invention is that molecules complexed by cyclodextrins are presumably more resistive to decomposition, degradation and alteration. It is known, for example, that the propensity for the flavourant vanillin to undergo oxidation is lowered while it is complexed to a cyclodextrin.

[0038] According to an embodiment of the invention, α-cyclodextrins could preferably be used where the flavourant of interest is a small molecule, such as a mono-aromatic flavour compound containing one phenyl-sized moiety, for example, phenylacetaldehyde dimethyl acetal. Release from the inclusion complex would be slow and sustained over a period corresponding to the average time of product use.

[0039] Approximate ranges which can be employed when practicing the present invention can be readily determined by a skilled person. For example, benzo(a)pyrene is known to be present in certain smokeless tobacco products in amounts ranging from approximately 0.1-10 μg/kg (e.g., a product with 1μg/kg could release 4 mmole/kg into the user's mouth). So where a 1:1 complex between benzo(a)pyrene and a cyclodextrin is assumed, and no other molecule is believed to complex with the cyclodextrin, 0.4-40 mmole/kg cyclodextrin could be provided in an effort to complex all benzo(a)pyrene from the product. To compensate for less than efficient complexing and the possibility of other molecules forming complexes with certain of the cyclodextrins, one may choose to use, for example, ten or twenty times the base amount of cyclodextrin calculated, in this example, 4.0-800 mmole/kg.

[0040] Because the ratio of cellulosic material to tobacco is eminently variable, the amount of cyclodextrin relative to the tobacco and tobacco constituents can easily be manipulated. The cellulosic material may be provided, e.g., as fragments, fibres, leaves or sheets blended in the tobacco or as a moisture-permeable wrapper encapsulating the tobacco.

[0041] Cyclodextrins may be provided interstitially within or bonded to the cellulosic material in a random pattern or in a specific pattern such as rows. Where the cellulosic material forms a wrapper for a tobacco pouch, the cyclodextrins may be provided on the side of the pouch facing the user or the side facing the tobacco during use, or a mixture of both. Methods of providing the cyclodextrins in the cellulosic material as well as densities, locations and the like can be optimized depending on factors such as the molecule the cyclodextrin is designed to capture and its relative amounts in the product, how and where that molecule is released, the timing of the release, and the like.

[0042] Where flavourants or other additives are provided as an inclusion complex with cyclodextrins, they may be provided in a range such that perhaps about 5% of the cyclodextrins are complexed, or 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, or 100% are complexed. A smokeless oral tobacco product may incorporate all of its flavourant or additive in the cyclodextrin complex, or only a portion of its overall flavourant or additive may be present in complex with cyclodextrin and the remainder provided according to conventional means. For example, cyclodextrin immobilized on a cellulosic wrapper may include 0.85 mol/mol (+)-limonene or 0.95 mol/mol hinokitiol.

[0043] A variety of conditions can be used to attach β-, γ-hydroxypropyl, and/or γ-cyclodextrins to cellulose powder via a spacer or linker group.

Example 1 Cyclodextrin linked to Cellulose Powder with Epichlorohydrin

[0044] Two samples were prepared using aqueous potassium carbonate to attach epichlorohydrin and cyclodextrin to cellulose.

[0045] A mixture of cellulose (50g), epichlorohydrin (5g), potassium carbonate (10g) and β-cyclodextrin (10g) in water (200ml) were stirred at 50°C for 5 hours. The mixture was cooled, filtered, washed exhaustively with water and dried *in vacuo* to give the first sample, PD906 (50.1g). The second sample was prepared by stirring a mixture of cellulose (50g), epichlorohydrin (5g), potassium carbonate (10g) and γ-cyclodextrin (10g) in water (200ml) at 75°C for 14 hours. The mixture was cooled, filtered, washed exhaustively with water and dried *in vacuo* to give sample PD907 (50g).

[0046] Two samples were prepared using potassium carbonate and butanone to attach epichlorohydrin and cyclodextrin to cellulose.

[0047] A mixture of cellulose (50g), epichlorohydrin (5g), potassium carbonate (10g) and β-cyclodextrin (10g) in 2-butanone (200ml) were stirred at reflux (80°C) for 6 hours. The mixture was cooled, filtered, washed exhaustively with water and dried *in vacuo* to give sample PD911 (46.2g). For the second sample in this class a mixture of cellulose (50g), epichlorohydrin (5g), potassium carbonate (10g) and γ-cyclodextrin (10g) in 2-butanone (200ml) were stirred at reflux (80°C) for 6 hours. The mixture was cooled, filtered, washed exhaustively with water and dried *in vacuo* to give sample PD912 (47.1g).

[0048] Two samples were prepared using aqueous sodium hydroxide to attach epichlorohydrin and cyclodextrin to cellulose.

[0049] A mixture of cellulose (50g), epichlorohydrin (7g), sodium hydroxide (6g) and β-cyclodextrin (10g) in water (200ml) were stirred at 50°C for 2 hours then at room temperature overnight. The mixture was cooled, filtered, washed exhaustively with water (very slow filtration) and dried *in vacuo* to yield sample PD913 (49.4g). The second sample of this type was created when a mixture of cellulose (50g), epichlorohydrin (7g), sodium hydroxide (6g) and γ-cyclodextrin (10g) in water (200ml) were stirred at 50°C for 2 hours then at room temperature overnight. The mixture was cooled, filtered, washed exhaustively with water (very slow filtration) and dried *in vacuo* to give sample PD914 (50.8g).

[0050] On drying, both of samples PD913 and PD914 were very hard to crush in a mortar and pestle. The samples were thus only semi-crushed.

[0051] Where epichlorohydrin is used as the linker group, methods using 2-butanone/potassium carbonate tend to produce more tanned cellulosic material whereas methods relying upon aqueous sodium hydroxide reactions generally afford the whitest material. In some downstream applications, a whiter or brighter cellulose material may be favoured.

Example 2 Cyclodextrin linked to Cellulose Powder with Imidasolidone

[0052] In these thermal reactions, the general procedure followed was: addition of an aqueous (deionised water) or aqueous methanolic solution of CD/imidazolidone/catalytic magnesium chloride/citric acid to cellulose powder (microcrystalline size) followed by evaporation of the slurry (circa 75°C *in vacuo*) and heat treatment of residue (circa 160°C either in air or under a nitrogen atmosphere). The cooled material was exhaustively washed with water and dried at 65-75°C *in vacuo.*

[0053] The experimental conditions were generally similar to those disclosed in US Patent No. 7,109,324. As noted therein, magnesium chloride was added to optimize CD-cellulose bonding and citric acid was added to keep pH at 5.

[0054] A solution of β-CD (5g), imidazolidone (5g), magnesium chloride hexahydrate (1g), citric acid (100mg) in deionised water (50ml) was mixed with cellulose to form a paste. This was placed in a glass dish in a 155-180°C oven (temperature gradient from front to back). After 45 minutes, weight check indicated all the water had evaporated and the mixture was left for a further 5 minutes. Cooled, washed exhaustively with water and dried *in vacuo* at 65-75°C to yield sample PD908 (48g).

[0055] A solution of γ-CD (5g), imidazolidone (5g), magnesium chloride hexahydrate (1g), citric acid (100mg) in deionised water (50ml) was mixed with cellulose to form a paste. The mixture was pre-dried *in vacuo* at 75°C before heating in an oil bath up to 180°C (oil bath temperature) in a magnetically stirred glass flask until the temperature of the air inside the flask reached 160°C. Cooled, washed exhaustively with water and dried *in vacuo* at 65-75°C to give sample PD909 (46.6g).

[0056] A solution of γ-CD (5g), imidazolidone (5g), magnesium chloride hexahydrate (1g), citric acid (100mg) in deionised water (50ml) was mixed with cellulose to form a paste. The mixture was pre-dried *in vacuo* at 75°C before heating in an oil bath to 160-164°C for 5 minutes (temperature of solid ~150°C) in a magnetically stirred glass flask. Cooled, washed exhaustively with water and dried *in vacuo* at 65-75°C to give sample PD910 (49.2g).

[0057] A solution of γ-CD (5g), imidazolidone (5g), magnesium chloride hexahydrate (1g), citric acid (100mg) in methanol (50ml)/water (30ml) was mixed with cellulose to form a paste. The mixture was pre-dried *in vacuo* at 75°C before heating in an oil bath up to 180°C (oil bath temperature) in a magnetically stirred glass flask until the temperature of the air inside the flask reached 160°C. Cooled, washed exhaustively with water and dried *in vacuo* at 65-75°C. After drying,

the material was placed in a magnetically stirred glass flask then put in a 175°C oil bath under a stream of nitrogen for 15 minutes. The reaction was placed under nitrogen to see if this would affect material tanning. The sample produced was PD911 (46.2g).

[0058] A solution of γ-HP-CD (5g), imidazolidone (5g), magnesium chloride hexahydrate (1g), citric acid (100mg) in deionised water (50ml) was mixed with cellulose to form a paste. The mixture was pre-dried *in vacuo* at 75°C before heating under nitrogen in an oil bath up to 175°C (oil bath temperature) in a magnetically stirred glass flask for 20 minutes. Cooled, washed exhaustively with water and dried *in vacuo* at 65-75°C to give sample PD917A (48.5g).

[0059] A solution of γ-HP-CD (5g), imidazolidone (5g), magnesium chloride hexahydrate (1g), citric acid (100mg) in deionised water (50ml) was mixed with cellulose to form a paste. The mixture was pre-dried *in vacuo* at 75°C before heating under nitrogen in an oil bath up to 175°C (oil bath temperature) in a magnetically stirred glass flask for 20 minutes. Cooled, washed exhaustively with water and *dried in vacuo* at 65-75°C. The dried paste was slurried in methanol (150ml), dried at 60°C *in vacuo,* then heated under nitrogen in a 175°C oil bath for 20 minutes. The sample produced was PD917B (49g).

[0060] The final two thermal reactions were undertaken using similar proportions of additives to cellulose as described in US Patent No. 7,109,324. The mixture was heated to lower temperature to observe the effect on material tanning.

[0061] A solution of γ-CD (1.75g), imidazolidone (4g), magnesium chloride hexahydrate (1g) and citric acid (40mg) was made up in deionised water (20ml) and methanol (100ml). The paste was dried in vacuo at 65°C then heated in a 160-165°C oil bath for 15 minutes. Cooled, washed exhaustively with water and dried *in vacuo* at 65-75°C to yield sample PD918 (47.8g).

[0062] A solution of γ-HP-CD (1.75g), imidazolidone (4g), magnesium chloride hexahydrate (1g) and citric acid (40mg) was made up in deionised water (20ml) and methanol (100ml). The paste was dried in vacuo at 65°C then heated in a 160-165°C oil bath for 15 minutes. Cooled, washed exhaustively with water and dried *in vacuo* at 65-75°C to yield sample PD919 (45.8g).

[0063] Tanning was observed for most of the thermal reactions - the least coloured samples from those described above were PD916 and PD919.

Example 3 Removal of Benzo(a)Pyrene by Derivatised Cellulose

[0064] A feature of the invention was displayed using derivatised cellulose to remove B(a)P from an aqueous solution. This also had the effect of confirming the variety of cyclodextrin entities described above were successfully bound to cellulose.

[0065] Because of the complex nature of tobacco extract, replete with numerous substances, it can be difficult to quantify molecules such as B(a)P which are present at low concentrations in the matrix: This problem is particularly acute with fluorescence measurements because sometimes the matrix can affect the measurement; this phenomenon is known as fluorescence quenching. For this reason fluorescence determinations often require extensive sample clean-up to minimize the deleterious affects of the matrix.

[0066] To avoid problematic fluorescence quenching and clean-up procedures, the following experiments were conducted without a tobacco matrix. This allowed the cyclodextrins - cellulose compounds to be directly assessed for their ability to complex B(a)P molecules out of an aqueous environment, thus reducing the concentration of B(a)P in the sample.

[0067] In brief, mini-columns containing a bed of either the cyclodextrin derivatised cellulose or pure cellulose were prepared. A small quantity of a solution of B(a)P in acetonitrile was placed at the head of this column followed by larger amounts of water. The water was allowed to flow through the column without assistance under gravity and the resultant eluent was collected and analysed for B(a)P.

Preparation of Mini-Columns

[0068] Glass Pastuer pipettes 150 mm long (Fisher Scientific, Fisherbrand: FB50251) were plugged with a small amount of untreated glass wool (Supelco: 2-0384, lot: 1561-18). The glass columns were weighed with the glass wool plug, following which a quantity of either the cyclodextrin derivatised cellulose or untreated cellulose (control, from the same batch as used for the preparation of the CD-derivatised cellulose samples) was added into the column. The material was dry packed without any compaction; approximately 30 mm of solid material was added into each column. The column was kept vertical and tapped gently to ensure the bed contained no air pockets, and to see that the head of the bed was approximately horizontal. The column was weighed after packing to calculate the weight of the bed. Details are described below in Table 1.

Table 1

Sample Material	Replicate Number	Weight of column (g)	Weight of column + bed material (g)	Calculated weight of bed material (g)
Cellulose	1	2.8451	3.1585	0.3134
	2	2.9729	3.266	0.2931
	3	2.7864	3.1046	0.3182
	4	2.8579	3.1676	0.3097
PD917A	1	2.9121	3.1876	0.2755
	2	2.9663	3.2152	0.2489
	3	2.8856	3.1082	0.2226
	4	2.9948	3.2284	0.2336
PD908	1	3.0032	3.2229	0.2197
	2	2.8852	3.1294	0.2442
	3	2.9489	3.2839	0.3350
	4	2.9338	3.1794	0.2456
PD909	1	2.8405	3.1054	0.2649
	2	2.9568	3.236	0.2792
	3	2.7631	3.0132	0.2501
	4	2.8071	3.1043	0.2972
PD912	1	2.9202	3.1567	0.2365
	2	2.9355	3.1815	0.2460
	3	2.8662	3.0607	0.1945
	4	2.8119	3.0229	0.2110

Application of B(a)P Solution

[0069] 100 μL of a 500 ng/mL (50ng) solution of B(a)P in acetonitrile (Stock Standard Solution) was carefully pipetted onto the inner surface of the glass column. This solution was incorporated into the top 3-5 mm of the absorbent bed.

Elution of B (a)P from Column

[0070] 1000 μL of water was slow discharged by pipette down the inside of the column. This addition progressively hydrated the dry material of the bed as well as mobilized the B(a)P. Eventually water droplets appeared at the base of the column which were collected in a 20 mL glass vials. Approximately, 8-11 minutes were required for the water to drain to the level of the top of the bed. After this a further 1000 μL of water was slow discharged by pipette down the inside of the column. All of the water eluent was collected and submitted for B(a)P analysis. Approximately 25-30 minutes was allowed for liquid to drain out of the column.

Preparation of 100% recovery sample

[0071] In order to check the efficacy of the system a 100% recovery sample was also produced. This sample was not subjected to any column environment; the B(a)P added would be expected to be conserved. In this sample 100 μL of a 500 ng/mL (50ng) solution of B(a)P in acetonitrile was mixed with 2000 μL water in 20mL vial.

Analysis of Eluent

[0072] Reverse phase HPLC was used with Fluorescence detection. The column used was 125 x 4.60 mm 5 micron

(Envirosep PP, Phenomenex), thermostated at 30°C. The mobile phase was water/acetonitrile proportioned under the gradient regime detailed in Table 2.

Table 2

Time (minutes)	Flow (mL/min)	% water	% acetonitrile
0.00	2.00	60.0	40.0
2.00	2.00	60.0	40.0
25.00	2.00	0.0	100.0
27.00	2.00	0.0	100.0
30.00	2.00	60.0	40.0

[0073] The wavelength of excitation was 378nm and the wavelength of detection was 405nm. B(a)P elution was after about 20.5 min. Injection volume was 50 μL. The results are summarised in Table 3.

Table 3

Sample Material	Replicate	B(a)P units	Average B(a)P units	Standard Deviation
Cellulose	1	6974	6112.25	1239
	2	4814		
	3	7350		
	4	5311		
PD917A	1	2086	2914	790
	2	2702		
	3	3982		
	4	2886		
PD908	1	3641	2780.25	1091
	2	3228		
	3	3068		
	4	1184		
PD909	1	3671	4181.75	1209
	2	3972		
	3	5924		
	4	3160		
PD912	1	7985	7381.5	1614
	2	8311		
	3	4970		
	4	8260		
Recovery sample	1	7155	6877.5	1019
	2	8108		
	3	6562		
	4	5685		

[0074] As detailed in previous Examples,

PD917A was a gamma hydroxypropyl cyclodextrin cellulose derivative;
PD908 was a beta cyclodextrin cellulose derivative;
PD909 was a gamma cyclodextrin cellulose derivative; and
PD912 was a beta cyclodextrin cellulose derivative.

[0075] The results show that there is a small loss of B(a)P using the pure cellulose column compared to the recovery sample. However, in the CD-derivatised cellulose columns there is a far more dramatic reductions in the amounts of B (a)P eluting from the column for samples PD908, PD909 and, in particular, PD917A. In the case of PD912 no reduction in B(a)P was observed.

[0076] The high degree of B(a)P reduction shown by sample PD917A supports the particularly inventive nature of using gamma cyclodextrin to complex B(a)P. As shown above, cyclodextrin-cellulose derivatives remove B(a)P in an aqueous environment.

[0077] Examples 1-3 describe methods to provide inventive materials, and the following Examples 4-8 demonstrate a few of the ways in which the inventive materials can be incorporated in products.

Example 4 Smokeless Oral Tobacco Product with Cellulosic Material

[0078] Smokeless tobacco for oral administration is provided. For example, a commercial blend of tobaccos can be cut to the suitable size and shape for a loose leaf chewing tobacco product. The cut tobacco can then be cased with an aqueous mixture of flavouring materials and sweetening agents to give a cut and cased tobacco containing approximately 50 percent moisture. The treated tobacco can be arranged on a conveyor belt or loaded onto sheets and moved through or placed in a dryer. The dryer may heat the tobacco to about 70°C, briefly, to reduce its moisture content to about 25 percent. Subsequent processing of the tobacco can be conventional such as application of a top flavouring solution and temporary storage to allow equilibration of the top flavouring additives throughout the tobacco mass.

[0079] Top flavouring can serve the dual purpose of both adding a top note to the tobacco itself and presenting a number of unassociated flavour molecules in the mixture. These molecules could be expected to migrate toward cyclodextrins provided in proximity to the flavoured tobacco and complex with them. Moist conditions favour the formation of an equilibration throughout the tobacco mass and nearby cellulosic material comprising cyclodextrins.

[0080] In addition, or instead of application of a top flavouring solution, cyclodextrins previously complexed with flavourant can be provided. Where flavourant-complexed cyclodextrins are used, it can be found that flavourant migration occurs in two directions: some of the complexed flavourant will disassociate and migrate toward the tobacco whereas certain of the tobacco-associated flavourant will complex with the recently-emptied cyclodextrins.

[0081] As noted above, either or both of pre-complexed or 'empty' cyclodextrins could be employed. For example, fibrous cellulosic material is dipped in a water bath containing 15 mM β-cyclodextrin and 15 mM imidazolidone. After dipping it is subjected to oven hearting at 150°C for 1-5 minutes. Where α-cyclodextrin is used, one may increase the concentration to about 130 mM and where γ-cyclodextrin is used, to about 170 mM.

[0082] The procedure results in cyclodextrin linked with imidazolidone (spacer group) through the formation of ether (hemiacetal) bonds between the imidazolidone and the hydroxyl group(s) on the cyclodextrin. The imidazolidone is attached to the cellulose by the formation of ether bonds between it and hydroxyl groups present on the cellulose. As such, cellulosic material is provided having a covalently bonded spacer group which in turn is linked to a cyclodextrin.

[0083] The cyclodextrin-cellulosic material is cut to approximately the same size as the tobacco pieces and blended with the tobacco. Moisture, pH, and other parameters are adjusted as necessary to provide a stable, useable product. For example, buffering agents may be used to produce a pH of above about 6.5, or above about 7.5. The blend is packaged into moisture proof containers.

[0084] When the product is used, moisture liberates molecules. Benzo(a)pyrene and other large polyaromatic hydrocarbons in the tobacco will be drawn to the relatively hydrophobic, suitably-sized inner cavity of the cyclodextrin to form an inclusion complex. The hydrocarbons thus bound will be removed from the moist product and, while in the mouth of a user, the hydrocarbons will not be bioavailable.

Example 5 Smokeless Oral Tobacco Product Comprising Cellulosic Wrapper

[0085] This embodiment of the invention comprises a pouch-type product which can be similar to portioned Swedish-style snus products. That is, as a pouch containing tobacco products intended to fit into the gingival fold of the mouth. A non-woven fabric can be used as a package material for such pouches.

[0086] In order to prepare the cyclodextrin-fabric complex, cyclodextrin derivatised with a spacer group having a reactive entity at the non-cyclodextrin end of the spacer group is obtained (for example, monochlorotriazinyl-β-cyclodextrin, Wacker GmbH, Germany). The reactive entity is allowed to interact with the fabric thus bonding the spacer group to the fabric.

[0087] A unit of pulverized tobacco suitable for an individual dose, for example 0.05-2.0 g (dry weight) is placed on

the cellulose-bonded fabric and a pouch is formed. To increase the amount or to alter the location of the cyclodextrins in the product, pieces of cellulosic material incorporating cyclodextrins may be blended with the tobacco prior to its addition to the pouch. Conventional snus or tea bag filling equipment may be used. The pouch may be sealed shut, for example by heat sealing. Where different cellulosic materials are substituted, e.g., long fibre cellulose materials, a heat weldable binder may be added to the material to facilitate heat sealing. The product is stored in a moisture-proof container, possibly under refrigeration, prior to use.

[0088] By way of example, a mini snus product typically contains 0.5 g tobacco. To complex the benzo(a)pyrene present in that dose of tobacco, 1.9-19 mg α-cyclodextrin (MW 972) could be attached to the fabric. Alternatively, 2.3-23 mg β-cyclodextrin (MW 1135) could be attached to the fabric. Alternatively, 2.6-26 mg of γ-cyclodextrin (MW 1297) could be attached to the fabric. A mix of two or more cyclodextrins could be employed.

Example 6 Smokeless Oral Tobacco Product Comprising Cellulosic Wrapper

[0089] In order to prepare a flavourant-cyclodextrin-cellulose complex, cyclodextrin derivatised with a spacer group having a reactive entity at the non-cyclodextrin end of the spacer group is obtained (for example, CAVAMAX W7 CITRAL, Wacker GmbH, Germany). This reactive entity is designed to react with cellulose wherein the spacer group is bonded to the cellulosic material and provides a lemon flavourant to the resultant product. A sheet of cellulosic material in web form is used.

[0090] Through extraction processes or chemical synthesis, select components of tobacco are provided such as nicotine. These tobacco extracts are applied to cellulosic or synthetic tobacco-like material which is then incorporated into a pouch-like object formed by folding the sheet of cellulosic web around the cellulosic or tobacco like material.

[0091] A pouch so provided does not contain whole, natural tobacco but rather natural or synthetic tobacco extracts. During use, moisture permeating the pouch will encourage the lemon flavourant to disassociate from the cyclodextrin and pass out of the pouch and into the surrounding area. Simultaneously, molecules present in the extracts or formed by the extract when moistened are transported with the moisture through the sheet of cellulosic material are attracted to the relatively hydrophobic inner cavities of the cyclodextrins, thus prevented from exiting the pouch or from remaining in the pouch unbound.

Example 7 Smokeless Oral Tobacco Product Comprising Cellulosic Wrapper

[0092] A unit of cellulosic material in web form is provided. 4-40 mg of β-cyclodextrin is bound to the cellulosic web. 1.0 g of standard smokeless tobacco is placed on the cellulosic web and a sealed pouch is formed.

[0093] As standard smokeless tobacco is expected to comprise about 0.1-0.3 mg/kg cadmium, the amount of β-cyclodextrins is selected to correspond to this amount. Thus during use an amount of cadmium is released from the tobacco product, a portion of which will be subsequently bound by the β-cyclodextrins. Cadmium exposure may be disfavoured; complexation by β-cyclodextrins will reduce the user's exposure to the substance. The most common oxidation state of cadmium is +2, therefore cadmium is at times represented as cadmium(II). Any state and any form of cadmium could be encompassed by the present invention.

Example 8 Smokeless Oral Tobacco Product Comprising Cellulosic Wrapper

[0094] A sheet of cellulosic material in web form is provided, a spacer group and subsequently a cyclodextrin derivative are bound to the cellulosic web. The cellulosic web is treated with a mixture of nicotine and flavourants to provide nicotine- and flavourant-cyclodextrin inclusion complexes.

[0095] A suitable amount of tobacco in the desired physical form is added to the sheet, which is then folded to form a pouch and sealed. In use, moisture permeating the pouch will encourage the nicotine and flavourant to disassociate from the cyclodextrin and pass out of the pouch. Compounds present in or formed by the tobacco are similarly transported by moisture towards the outside of the pouch, however, due to the suitably-sized, relatively hydrophobic cavity offered by the bound cyclodextrin they are drawn into an inclusion complex and do not pass out of the pouch.

[0096] Because small, mono-aromatic compounds typically will not be able to form long-lasting complexes with cyclodextrins they will be rapidly released from the inclusion complexes when moistened, providing nicotine and flavour to the user while making the cyclodextrins available to bind with larger molecules of interest. A mixture of different cyclodextrins may be used in this configuration, to provide an extended release profile for the product.

[0097] As compared with other exemplary products, this configuration may require stricter formulation and storage controls to ensure low moisture and appropriate pH which would encourage stability of the initial inclusion complexes until use.

[0098] The foregoing description and examples have been set forth merely to illustrate the invention and are not intended to be limiting. Since modifications of the described embodiments may occur to persons skilled in the art, the

invention should be construed broadly to include all variations within the scope of the appended claims and equivalents thereof.

Claims

1. A smokeless oral tobacco product, comprising:

   at least one of tobacco, a tobacco derivative, or a tobacco substitute; and
   a cellulosic material,
   characterised in that said cellulosic material comprises at least one cyclodextrin or cyclodextrin derivative, preferably wherein the product comprises a wrapper encapsulating said tobacco, tobacco derivative, or tobacco substitute; and said wrapper comprises said cellulosic material.

2. A product according to claim 1, wherein said cellulosic material is:

   (a) fibrous; or
   (b) a woven or non-woven web.

3. A product according to either of claims 1 or 2, wherein said cyclodextrin or cyclodextrin derivative is:

   (a) chemically attached to said cellulosic material, preferably wherein a spacer group is located between said cellulosic material and said cyclodextrin or cyclodextrin derivative; or
   (b) predominantly γ-cyclodextrin or a derivative thereof, preferably wherein said cyclodextrin or cyclodextrin derivative is γ-cyclodextrin or a derivative thereof.

4. A product according to either of claims 1 or 2, wherein at least a portion of said cyclodextrin or cyclodextrin derivative is complexed with at least one complex agent, preferably wherein complexes of said cyclodextrin or cyclodextrin derivative and said complex agent are chemically attached to said cellulosic material.

5. A product according to claim 4, wherein said cyclodextrin or cyclodextrin derivative is predominantly β-cyclodextrin or a derivative thereof, preferably wherein said cyclodextrin or cyclodextrin derivative is β-cyclodextrin or a derivative thereof.

6. A product according to claim 4, wherein said cyclodextrin or cyclodextrin derivative is predominantly α-cyclodextrin or a derivative thereof.

7. A product according to any one of claims 4-6, wherein said complex agent comprises at least one flavourant, aroma modifier or antimicrobial agent, preferably wherein said complex agent comprises:

   (a) a flavourant and said flavourant is selected from the group consisting of: (+), (-)-limonene, cinnamaldehyde, cinnamonitrile, euginol, cis-isoeuginol, trans-isoeuginol, eugenyl acetate, eugenol methyl/ethyl esters, trans-anethole, cis-anethole, menthol, isomenthol, neomenthol, (+)-menthone, (-)-menthone, (+)-citronellal, S(+)-carvone, R(-)-carvone, trans-methyl cinnamate, cis-methyl cinnamate, vanillin, capsaicin, phenylpropanoids, aspartame, chocolate, coffee, pyrazines, salt, γ-Glu-Tyr, γ-Glu-Phe, orinithyl containing peptides, aromatic aldehydes, aromatic aldehydes derivatized as acetals, and lactones;
   (b) an aroma modifier and said aroma modifier is selected from the group consisting of: maltol, ethyl maltol, cis-jasmone, methyl jasmonate, geraniol, nerol, geranyl esters, neryl esters, (+)-citronellol, (-)-citronellol, citral, (+)-limonene, (-)-limonene, and monoterpenes; or
   (c) an antimicrobial agent and said antimicrobial agent comprises hinokitol.

8. A product according to claim 7, wherein said complex agent comprises a flavourant and said flavourant comprises:

   (a) at least one monoterpene flavourant;
   (b) at least one monoaromatic flavourant; or
   (c) at least one polyaromatic flavourant.

9. Use of at least one cyclodextrin or cyclodextrin derivative in the preparation of a smokeless oral tobacco product,

characterized in that said product comprises tobacco.

10. Use of at least one cyclodextrin or cyclodextrin derivative complexed with at least one flavourant in the preparation of a smokeless oral tobacco product, **characterized in that** said product comprises tobacco.

11. Use according to either one of claims 9 or 10, wherein said product further comprises a cellulosic material and wherein said at least one cyclodextrin or cyclodextrin derivative is complexed to said cellulosic material, preferably wherein said at least one cyclodextrin or cyclodextrin derivative is chemically attached to said cellulosic material, and preferably wherein said tobacco is encapsulated in said cellulosic material.

12. Use according to any one of claims 9-11, wherein said at least one cyclodextrin or cyclodextrin derivative is selected from the group consisting of β-cyclodextrin, β-cyclodextrin derivative, γ-cyclodextrin, γ-cyclodextrin derivative, α-cyclodextrin, and α-cyclodextrin derivative.

13. A method for complexing at least one cyclodextrin or cyclodextrin derivative with a material in or formed by a smokeless oral tobacco product, comprising the steps of:

providing a smokeless oral tobacco product comprising at least one cyclodextrin or cyclodextrin derivative;
contacting said product with moisture to moisten said product; and
allowing the material to complex with said cyclodextrin or cyclodextrin derivative,
preferably wherein said cyclodextrin or cyclodextrin derivative comprises at least one flavourant, further comprising the step of allowing said flavourant to be released from said cyclodextrin or cyclodextrin derivative after said contacting step.

14. A method according to claim 13, wherein said material is:

(a) a polyaromatic hydrocarbon, preferably wherein said polyaromatic hydrocarbon is benzo(a)pyrene; or
(b) cadmium.

15. A method according to either of claims 13 or 14, wherein said product comprises a cellulosic material; and said cyclodextrin or cyclodextrin derivative is attached to said cellulosic material, preferably wherein said cyclodextrin or cyclodextrin derivative is chemically attached to said cellulosic material and preferably wherein a spacer group is located between said cellulosic material and said cyclodextrin or cyclodextrin derivative.

Patentansprüche

1. Rauchloses orales Tabakprodukt, das Folgendes umfasst:

mindestens ein Material von Tabak, einem Tabakderivat oder einem Tabakersatz und
ein Cellulosematerial,
dadurch gekennzeichnet, dass das Cellulosematerial mindestens ein Cyclodextrin oder Cyclodextrinderivat umfasst,
vorzugsweise wobei das Produkt eine Hülle umfasst, die den Tabak, das Tabakderivat oder den Tabakersatz einkapselt;
und die Hülle das Cellulosematerial umfasst.

2. Produkt nach Anspruch 1, wobei das Cellulosematerial Folgendes ist:

(a) faserförmig oder
(b) eine gewebte oder Vliesbahn.

3. Produkt nach Anspruch 1 oder 2, wobei das Cyclodextrin oder Cyclodextrinderivat Folgendes ist:

(a) chemisch an das Cellulosematerial angelagert, vorzugsweise wobei eine Abstandsgruppe zwischen dem Cellulosematerial und dem Cyclodextrin oder Cyclodextrinderivat angeordnet ist; oder
(b) vorwiegend γ-Cyclodextrin oder ein Derivat davon, vorzugsweise wobei das Cyclodextrin oder Cyclodextrinderivat γ-Cyclodextrin oder ein Derivat davon ist.

4. Produkt nach Anspruch 1 oder 2, wobei mindestens ein Teil des Cyclodextrins oder Cyclodextrinderivats mit mindestens einem Komplexbildner komplexiert ist, vorzugsweise wobei Komplexe des Cyclodextrins oder Cyclodextrinderivats und der Komplexbildner chemisch an das Cellulosematerial angelagert sind.

5. Produkt nach Anspruch 4, wobei das Cyclodextrin oder Cyclodextrinderivat vorwiegend β-Cyclodextrin oder ein Derivat davon ist, vorzugsweise wobei das Cyclodextrin oder Cyclodextrinderivat β-Cyclodextrin oder ein Derivat davon ist.

6. Produkt nach Anspruch 4, wobei das Cyclodextrin oder Cyclodextrinderivat vorwiegend α-Cyclodextrin oder ein Derivat davon ist.

7. Produkt nach einem der Ansprüche 4 bis 6, wobei der Komplexbildner mindestens einen Geschmackstoff, einen Aromaverbesserer oder ein antimikrobielles Mittel umfasst, vorzugsweise wobei der Komplexbildner Folgendes umfasst:

(a) einen Geschmackstoff, und der Geschmackstoff ist aus der Gruppe bestehend aus folgenden ausgewählt: (+)-, (-)-Limonen, Cinnamaldehyd, Cinnamonitril, Euginol, cis-Isoeuginol, trans-Isoeuginol, Eugenylacetat, Eugenolmethyl-/-ethylestern, trans-Anethol, cis-Anethol, Menthol, Isomenthol, Neomenthol, (+)-Menthon, (-)-Menthon, (+)-Citronellal, S(+)-Carvon, R(-)-Carvon, trans-Methylcinnamat, cis-Methylcinnamat, Vanillin, Capsaicin, Phenylpropanoiden, Aspartam, Schokolade, Kaffee, Pyrazinen, Salz, γ-Glu-Tyr, γ-Glu-Phe, orinithylhaltigen Peptiden, aromatischen Aldehyden, als Acetale derivatisierten aromatischen Aldehyden und Lactonen;
(b) einen Aromaverbesserer, und der Aromaverbesserer ist aus der Gruppe bestehend aus folgenden ausgewählt: Maltol, Ethylmaltol, cis-Jasmon, Methyljasmonat, Geraniol, Nerol, Geranylestern, Nerylestern, (+)-Citronellol, (-)-Citronellol, Citral, (+)-Limonen, (-)-Limonen und Monoterpenen; oder
(c) ein antimikrobielles Mittel, und das antimikrobielle Mittel umfasst Hinokitol.

8. Produkt nach Anspruch 7, wobei der Komplexbildner einen Geschmacksstoff umfasst und der Geschmackstoff Folgendes umfasst:

(a) mindestens einen Monoterpen-Geschmackstoff;
(b) mindestens einen monoaromatischen Geschmackstoff oder
(c) mindestens einen polyaromatischen Geschmackstoff.

9. Verwendung mindestens eines Cyclodextrins oder Cyclodextrinderivats bei der Herstellung eines rauchlosen oralen Tabakprodukts, **dadurch gekennzeichnet, dass** das Produkt Tabak umfasst.

10. Verwendung mindestens eines Cyclodextrins oder Cyclodextrinderivats, das mit mindestens einem Geschmackstoff komplexiert ist, bei der Herstellung eines rauchlosen oralen Tabakprodukts, **dadurch gekennzeichnet, dass** das Produkt Tabak umfasst.

11. Verwendung nach Anspruch 9 oder 10, wobei das Produkt weiterhin ein Cellulosematerial umfasst und wobei das mindestens eine Cyclodextrin oder Cyclodextrinderivat mit dem Cellulosematerial komplexiert ist, vorzugsweise wobei das mindestens eine Cyclodextrin oder Cyclodextrinderivat chemisch an das Cellulosematerial angelagert ist und vorzugsweise wobei der Tabak in dem Cellulosematerial eingekapselt ist.

12. Verwendung nach einem der Ansprüche 9 bis 11, wobei das mindestens eine Cyclodextrin oder Cyclodextrinderivat aus der Gruppe bestehend aus β-Cyclodextrin, β-Cyclodextrinderivat, γ-Cyclodextrin, γ-Cyclodextrinderivat, α-Cyclodextrin und α-Cyclodextrinderivat ausgewählt ist.

13. Verfahren zum Komplexieren von mindestens einem Cyclodextrin oder Cyclodextrinderivat mit einem Material in einem rauchlosen oralen Tabakprodukt oder das von einem rauchlosen oralen Tabakprodukt gebildet wird, wobei das Verfahren die folgenden Schritte umfasst:

Bereitstellen eines rauchlosen oralen Tabakprodukts, das mindestens ein Cyclodextrin oder Cyclodextrinderivat umfasst;
Inkontaktbringen des Produkts mit Feuchtigkeit, um das Produkt zu befeuchten; und
Komplexierenlassen des Materials mit dem Cyclodextrin oder Cyclodextrinderivat,
vorzugsweise wobei das Cyclodextrin oder

Cyclodextrinderivat mindestens einen Geschmackstoff umfasst, wobei das Verfahren weiterhin den Schritt des Zulassens, dass der Geschmackstoff aus dem Cyclodextrin oder Cyclodextrinderivat nach dem Schritt des Inkontaktbringens freigesetzt wird, umfasst.

14. Verfahren nach Anspruch 13, wobei das Material Folgendes ist:

(a) ein polyaromatischer Kohlenwasserstoff, vorzugsweise wobei der polyaromatische Kohlenwasserstoff Benzo(a)pyren ist; oder
(b) Cadmium.

15. Verfahren nach Anspruch 13 oder 14, wobei das Produkt ein Cellulosematerial umfasst und das Cyclodextrin oder Cyclodextrinderivat an das Cellulosematerial angelagert ist, vorzugsweise wobei das Cyclodextrin oder Cyclodextrinderivat chemisch an das Cellulosematerial angelagert ist und vorzugsweise wobei eine Abstandsgruppe zwischen dem Cellulosematerial und dem Cyclodextrin oder Cyclodextrinderivat angeordnet ist.

Revendications

1. Produit de tabac oral sans fumée, comprenant :

au moins un élément parmi du tabac, un dérivé de tabac ou un substitut de tabac ; et
un matériau cellulosique,
caractérisé en ce que ledit matériau cellulosique comprend au moins une cyclodextrine ou un dérivé de cyclodextrine,
de préférence dans lequel le produit comprend une cape encapsulant ledit tabac, dérivé de tabac ou substitut de tabac ; et ladite cape comprend ledit matériau cellulosique.

2. Produit selon la revendication 1, dans lequel ledit matériau cellulosique est :

(a) fibreux ; ou
(b) un tissu tissé ou non tissé.

3. Produit selon l'une ou l'autre des revendications 1 ou 2, dans lequel ladite cyclodextrine ou ledit dérivé de cyclodextrine est :

(a) chimiquement relié audit matériau cellulosique, de préférence dans lequel un groupe espaceur est situé entre ledit matériau cellulosique et ladite cyclodextrine ou ledit dérivé de cyclodextrine ; ou
(b) principalement de la γ-cyclodextrine ou un dérivé de celle-ci, de préférence dans lequel ladite cyclodextrine ou ledit dérivé de cyclodextrine est la γ-cyclodextrine ou un dérivé de celle-ci.

4. Produit selon l'une ou l'autre des revendications 1 ou 2, dans lequel au moins une portion de ladite cyclodextrine ou dudit dérivé de cyclodextrine est complexée avec au moins un agent complexe, de préférence dans lequel des complexes de ladite cyclodextrine ou dudit dérivé de cyclodextrine et dudit agent complexe sont chimiquement reliés audit matériau cellulosique.

5. Produit selon la revendication 4, dans lequel ladite cyclodextrine ou ledit dérivé de cyclodextrine est principalement de la β-cyclodextrine ou un dérivé de celle-ci, de préférence dans lequel ladite cyclodextrine ou ledit dérivé de cyclodextrine est la β-cyclodextrine ou un dérivé de celle-ci.

6. Produit selon la revendication 4, dans lequel ladite cyclodextrine ou ledit dérivé de cyclodextrine est principalement de la α-cyclodextrine ou un dérivé de celle-ci.

7. Produit selon l'une quelconque des revendications 4 à 6, dans lequel ledit agent complexe comprend au moins une essence, un modificateur d'arôme ou un agent antimicrobien, de préférence dans lequel ledit agent complexe comprend :

(a) une essence et ladite essence est sélectionnée parmi le groupe constitué de : (+), (-)-limonène, cinnamaldéhyde, cinnamonitrile, euginol, cis-isoeuginol, transisoeuginol, acétate d'eugényle, esters de méthyle/éthyle

d'eugénol, trans-anéthole, cis-anéthole, menthol, isomenthol, néomenthol, (+)-menthone, (-)-menthone, (+)-citronellal, S(+)-carvone, R(-)-carvone, trans-méthylcinnamate, cis-méthylcinnamate, vanilline, capsaïcine, phénylpropanoïdes, aspartame, chocolat, café, pyrazines, sel, γ-Glu-Tyr, γ-Glu-Phe, peptides contenant de l'ornithyle, aldéhydes aromatiques, aldéhydes aromatiques dérivés en tant qu'acétals et lactones ;
(b) un modificateur d'arôme et ledit modificateur d'arôme est sélectionné parmi le groupe constitué de : maltol, maltol éthylique, cis-jasmone, jasmonate méthylique, géraniol, nérol, esters de géranyle, esters de néryle, (+)-citronellol, (-)-citronellol, citral, (+)-limonène, (-)-limonène et monoterpènes ; ou
(c) un agent antimicrobien et ledit agent antimicrobien comprend de l'hinokitol.

8. Produit selon la revendication 7, dans lequel ledit agent complexe comprend une essence et ladite essence comprend :

(a) au moins une essence de monoterpène ;
(b) au moins une essence monoaromatique ; ou
(c) au moins une essence polyaromatique.

9. Utilisation d'au moins une cyclodextrine ou un dérivé de cyclodextrine dans la préparation d'un produit de tabac oral sans fumée, **caractérisée en ce que** ledit produit comprend du tabac.

10. Utilisation d'au moins une cyclodextrine ou un dérivé de cyclodextrine complexé avec au moins une essence dans la préparation d'un produit de tabac oral sans fumée, **caractérisée en ce que** ledit produit comprend du tabac.

11. Utilisation selon l'une ou l'autre des revendications 9 ou 10, dans laquelle ledit produit comprend en outre un matériau cellulosique et dans laquelle ladite au moins une cyclodextrine ou ledit au moins un dérivé de cyclodextrine est complexé avec ledit matériau cellulosique, de préférence dans laquelle ladite au moins une cyclodextrine ou ledit au moins un dérivé de cyclodextrine est chimiquement relié audit matériau cellulosique, et de préférence dans laquelle ledit tabac est encapsulé dans ledit matériau cellulosique.

12. Utilisation selon l'une quelconque des revendications 9 à 11, dans laquelle ladite au moins une cyclodextrine ou ledit au moins un dérivé de cyclodextrine est sélectionné parmi le groupe constitué de la β-cyclodextrine, d'un dérivé de β-cyclodextrine, de la γ-cyclodextrine, d'un dérivé de γ-cyclodextrine, de la α-cyclodextrine et d'un dérivé de α-cyclodextrine.

13. Procédé de complexation d'au moins une cyclodextrine ou un dérivé de cyclodextrine avec un matériau dans ou formé par un produit de tabac oral sans fumée, comprenant les étapes consistant à :

fournir un produit de tabac oral sans fumée comprenant au moins une cyclodextrine ou un dérivé de cyclodextrine ;
mettre en contact ledit produit avec de l'humidité pour humidifier ledit produit ; et
permettre au matériau de complexer avec ladite cyclodextrine ou ledit dérivé de cyclodextrine, de préférence dans lequel ladite cyclodextrine ou ledit dérivé de cyclodextrine comprend au moins une essence, comprenant en outre l'étape consistant à permettre à ladite essence d'être libérée depuis ladite cyclodextrine ou ledit dérivé de cyclodextrine après ladite étape de mise en contact.

14. Procédé selon la revendication 13, dans lequel ledit matériau est :

(a) un hydrocarbure polyaromatique, de préférence dans lequel ledit hydrocarbure polyaromatique est le benzo (a)pyrène ; ou
(b) du cadmium.

15. Procédé selon l'une ou l'autre des revendications 13 ou 14, dans lequel ledit produit comprend un matériau cellulosique ; et ladite cyclodextrine ou ledit dérivé de cyclodextrine est relié audit matériau cellulosique, de préférence ladite cyclodextrine ou ledit dérivé de cyclodextrine est chimiquement relié audit matériau cellulosique et de préférence dans lequel un groupe espaceur est situé entre ledit matériau cellulosique et ladite cyclodextrine ou ledit dérivé de cyclodextrine.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 9109599 A **[0005]**
- US 5144964 A **[0006]**
- WO 0653628 A **[0025]**
- US 7109324 B **[0053] [0060]**

Non-patent literature cited in the description

- **Karathanos et al.** *Food Chemistry,* vol. 101, 652-658 **[0003]**
- **Fielden ; Packham.** *J.Chromatog.,* 1990, vol. 516, 355-364 **[0032]**