

This invention relates to a process for the production of a substantially odourless and neutral-tasting, antioxidant spice extract and to the use of this extract.

5 It is known that certain spices, such as rosemary and sage, have a high content of antioxidants. Processes have already been developed in the prior art to free the spices from all those components which do not contribute to the antioxidant activity. EP 38959 relates to a process for the production of antioxidant and antibacterial preserva-
10 tives, in which the base material, such as rosemary, is extracted with a mixture of polar and non-polar solvents, for example ethanol and n-hexane, to obtain the ready-to-use spice extract. The disadvantage of this process is that it does not give a spice extract totally freed from
15 its bitterness and all its odoriferous components. The same may be said of GB-PS 2,184,341 which relates to a process for extracting rosemary and sage in which the antioxidant materials are extracted both with non-polar solvents and with polar solvents. FR-PS 2 192 852 relates
20 to a process for extracting flavours and perfumes, but not antioxidants, in which the vegetable material is extracted with a non-polar fluorinated hydrocarbon and simultaneously or successively with a polar solvent. US-PS 4,450,097
25 relates to a process for the production of an antioxidant from rosemary, in which the spice is extracted with a non-polar solvent, the extract is subjected to steam distillation and the residue thus obtained is extracted with an aqueous alkaline solution having a pH value of at least 10.5. The disadvantage of this process is that it does not
30 enable all the antioxidant material to be extracted from the rosemary.

The object of the process according to the invention is to prepare an odourless, neutral-tasting spice extract which may be considered for a wide variety of applications
35 by utilizing the preservative character of the spice

extract.

The present invention relates to a process for the production of a substantially odourless and neutral-tasting antioxidant spice extract, in which the spice is subjected to at least one extraction with a non-polar solvent, the
5 spice thus treated is subjected to at least one extraction with a polar solvent and the extract containing the polar solvent is concentrated and dried to obtain the spice extract.

10 In one embodiment which enables the degree of extraction of antioxidant materials to be increased, the extract obtained with the non-polar solvent may be treated. In this case, the extract is mixed with a basic aqueous solution, the aqueous phase is recovered, acidified and
15 extracted with dichloromethane and the extract obtained is mixed with the phase obtained from the extraction with the polar solvent and the mixture obtained is evaporated and dried to obtain a spice extract having a high content of antioxidant material. The treatment of the spice with a
20 non-polar solvent enables virtually all the odoriferous constituents of the spice to be extracted. The subsequent treatment of the non-polar extract with a base enables the antioxidant components to be recovered. The base used is preferably sodium hydroxide. The extraction of the spice
25 with a polar solvent enables all the remaining components responsible for the antioxidant character to pass into the polar phase.

This embodiment of the process according to the invention gives a substantially odourless and colourless
30 extract which contains all the antioxidant constituents available in the spice by virtue of the fact that an antioxidant product is reconstituted from two extracts which themselves show antioxidant properties.

In the context of the invention, non-polar solvents
35 are understood to be optionally branched, optionally

cyclized, saturated C_{5-8} hydrocarbons and mixtures thereof, volatile aromatic hydrocarbons and chlorinated solvents, while polar solvents are understood to be C_{1-4} alcohols, volatile ketones, acetone, methyl ethyl ketone and solvents of the ether and ester type. Hexane is preferably used as the non-polar solvent and ethanol as the polar solvent.

The spice subjected to the treatment according to the invention may be both the whole spice and also spice residues, i.e. spices which have been subjected to steam distillation.

Depending on the starting product and the type of application envisaged, the spice is subjected to between 1 and 7 extractions with hexane and, similarly, to between 1 and 7 extractions with ethanol. These extractions normally take place between ambient temperature and the boiling point of the solvent, preferably at a temperature in the range from 20 to 30°C, with a ratio of spice to hexane and spice to ethanol for each extraction of from 1:1 to 1:10 (weight/volume). The extractions both with hexane and with ethanol are carried out over a period of from 30 minutes to 3 hours.

In order not to degrade the antioxidant materials, these extractions are carried out in the presence of an inert gas, for example nitrogen.

The process according to the invention gives a spice extract having a high content of antioxidant material. However, this extract is green in colour. In some cases, it is of advantage, depending on the application envisaged, to prepare a colourless spice extract. In this case, the last extraction with ethanol is followed by decoloration with active carbon. This decoloration is carried out with an active carbon content of from 10 to 20% by weight, based on the end product. It has been found that the antioxidant power is less pronounced after decoloration than in a non-decoloured spice extract. Finally, the ethanol phase has

to be concentrated and dried. The drying step is preferably carried out in vacuo over a period of about 10 hours at a temperature below 60°C in order not to degrade the antioxidants present. In one variant, water is added to the concentrated ethanol solution and the drying step is carried out by spray-drying so that the spice extract is obtained in the form of a fine powder. The spices treated in accordance with the invention are rosemary and sage. Since the powder obtained by the process according to the invention has virtually no odour or taste, it may be considered for virtually any application both in the food industry and in the cosmetics and pharmaceutical field. It is incorporated in a quantity of 0.01 to 0.5% by weight, based on the weight of the product to be stabilized.

The process according to the invention is carried out either continuously or in batches, in countercurrent or by percolation.

The process according to the invention is illustrated by the following Examples.

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Example 1 (Batch process)

500 g rosemary residue (rosemary leaves which have been subjected to steam distillation are extracted for 2.5 h at ambient temperature with 2.5 l hexane in a tank equipped with a mixer. After filtration, the extraction is repeated a second time under the same conditions. The two filtrates are combined and concentrated to a volume of 400 ml. This hexane extract is carefully stirred in a gentle stream of nitrogen with 400 ml of an aqueous sodium hydroxide solution (2-normal). After 10 minutes, the aqueous phase is separated from the organic phase and immediately acidified with concentrated sulfuric acid and then extracted with dichloromethane to recover the antioxidant material. This treatment of the extract with hexane is repeated a second time under the same conditions and the two result-

ing dichloromethane extracts are combined.

The residue of rosemary extract treated with hexane as described above is extracted with 2.5 l ethanol while mixing under nitrogen for 2.5 h at ambient temperature. The alcoholic extract is filtered and decoloured with 5 g active carbon while mixing under nitrogen for 2.5 h at ambient temperature. After filtration on Celite, the extract is combined with the dichloromethane extract of the non-polar fraction and the resulting mixture is concentrated in a rotary evaporator and finally evaporated to dryness in a vacuum oven. 57 g of powder-form rosemary extract are obtained (yield: 11.4%).

Example 2

The procedure is as in Example 1, except that the ethanol extract is not decoloured with active carbon. The resulting rosemary extract corresponds to a yield of 12.4%.

Example 3 (Batch process)

1 kg ground rosemary residue is mixed with 5 l hexane in a tank equipped with a mixer. After extraction under nitrogen for 2.5 h at ambient temperature, the hexane extract is filtered. The hexane phase is discarded and the operation is repeated under the same conditions as before. The residue thus recovered is mixed with 5 l ethanol mixed with 5% methanol. After extraction under nitrogen with stirring for 2.5 h at ambient temperature, the product is filtered to recover 4.7 l alcohol containing the antioxidant materials. The alcohol extract is then decoloured with 20 g active carbon for 2.5 h under nitrogen at ambient temperature. After filtration, 4.6 litres ethanol remain and are concentrated in a rotary evaporator to 0.4 l and, finally, evaporated in vacuo (16.10^2 or 12 mm Hg) to dryness for 15 h at 50°C. 96.5 g of powder-form rosemary extract are obtained (yield 9.65%).

Example 4 (Countercurrent process)

1 l hexane is mixed with 1 kg ground rosemary residue. 4 l hexane which have already been used to extract two other batches of rosemary and contain 21 g waxes are then
5 passed over the resulting mixture. After this extraction, the 4 litres of hexane contain 47 g waxes. A second extraction is carried out with 4 litres hexane which have already been used to extract another batch of rosemary and contain 8 g waxes. Thereafter, this volume of hexane
10 contains 21 g waxes. A third extraction is carried out with 4 litres of fresh hexane which thereafter, contain 8 g waxes. The rosemary residue is left to dry and is then mixed with 1 l ethanol. 3 l ethanol which have already been used to extract another batch of rosemary are then
15 passed over this mixture, containing 45 g rosemary extract before passage and 105 g of rosemary extract thereafter. A second extraction is carried out with 3 l fresh ethanol which then contains 45 g crude extract. The rosemary thus extracted is discarded. The 3 l ethanol containing 105 g
20 extract are then decoloured with active carbon, filtered, concentrated and evaporated to obtain 95 g of powder-form rosemary extract ready for use (yield 9.5%).

Example 5 (Percolation process)

25 500 g of rosemary residue are placed in a chromatography column. 1,250 ml hexane are added and the rosemary residue is extracted by percolation, the hexane being recirculated through the column for 30 minutes (throughput: 750 ml/h). The hexane containing the waxes is then drained
30 for 15 minutes and the resulting 750 ml extract are replaced by fresh hexane. The operation is repeated 6 times in the same column. The residue is left to dry in a gentle stream of nitrogen and is extracted in the same column by percolation with 1,250 ml ethanol recirculated for 30
35 minutes at ambient temperature. The ethanol is then

drained for 15 minutes and the resulting 750 ml extract are replaced by fresh ethanol. This extraction with ethanol is repeated six times. The seven ethanol extracts are combined, concentrated to half the volume, decoloured for 2.5 h on active carbon and, after filtration, dried in vacuo. The rosemary extract obtained (52.5 g dry powder) corresponds to a yield of 10.5%.

Example 6

The procedure is as in Example 3 without decoloration of the ethanol extract. Yield: 10.5%.

Example 7

The procedure is as in Example 3, except that sage (distilled with steam) is used as the starting material. Yield 12.4%.

The following Table shows the yields, antioxidant activities and organoleptic properties of the extracts obtained in accordance with Examples 1 to 7. These data are compared with those of three extracts of rosemary or sage residue which have been obtained simply by extraction with ethanol (ratio of spice to ethanol 1:5 (weight/volume)) for 2.5 h at ambient temperature with or without decoloration.

Table

Extract	Extraction yield % by weight	Anti- oxidant index (a)	Anti- oxidant value (b)	Odour (c)	Bitter- ness (c)	Colour
Ex. 1	11.4	4.3	49.2	-	-	Beige
Ex. 2	12.7	4.9	62.2	-	-	Greenish
Ex. 3	9.65	3.7	35.7	(+)	-	Yellowish
Ex. 4	9.5	3.6	34.2	-	-	Beige
Ex. 5	10.5	3.5	36.75	-	-	Beige
Ex. 6	10.5	4.2	44.1	-	-	Greenish
Ex. 7	12.4	4.8	59.5	+	+	Green
Ethanollic extract of rosemary residue	11.9	3.9	46.4	+++	++	Dark Green
Decoloured ethanollic extract of rosemary residue	10.1	3.6	36.35	++	++	Green
Ethanollic extract of sage residue	14.2	4.4	62.5	+++	++	Dark green

(a) Antioxidant index: Rancimat test (500 ppm extract, chicken fat, 110°C, air: 20l/h)

(b) Antioxidant value: Product of EY x AI
EY = extraction yield
AI = antioxidant index

(c) Evaluation criteria - virtually no odour/no bitterness
+ some odour/slightly bitter
++ odoriferous/bitter
+++ highly odoriferous/very bitter

**CLAIMS**

1. A process for the production of a substantially odourless and neutral-tasting antioxidant spice extract, characterized in that the spice is subjected to at least one extraction with a non-polar solvent, the spice thus treated is subjected to at least one extraction with a polar solvent and the extract containing the polar solvent is concentrated and dried to obtain the spice extract.
2. A process as claimed in claim 1, characterized in that the extract obtained with the non-polar solvent is treated with a basic aqueous solution, the aqueous phase is recovered, acidified and extracted with dichloromethane and the extract obtained is mixed with the phase obtained from the extraction with the polar solvent.
3. A process as claimed in claim 1 or 2, characterized in that the non-polar solvent is hexane while the polar solvent is ethanol.
4. A process as claimed in claim 3, characterized in that between 1 and 7 extractions are carried out with hexane.
5. A process as claimed in claim 3, characterized in that between 1 and 7 extractions are carried out with ethanol.
6. A process as claimed in claim 4 or 5, characterized in that the extractions with hexane and ethanol are carried out at a temperature in the range from 20 to 30°C.
7. A process as claimed in any of claims 4 to 6, characterized in that each extraction with hexane and with ethanol is carried out over a period of from 30 minutes to 3 hours.
8. A process as claimed in any of claims 4 to 7, characterized in that the extractions with hexane and with ethanol are carried out in the presence of an inert gas.
9. A process as claimed in any of claims 4 to 8, characterized in that each extraction is carried out with a ratio by weight/volume of spice to hexane and spice to ethanol of from 1:1 to 1:10.



10. A process as claimed in any of claims 1 to 9, characterized in that the last extraction with ethanol is followed by decoloration with active carbon.
- 5 11. A process as claimed in any of claims 1 to 10, characterized in that the spices treated are selected from the group consisting of sage and rosemary.
- 10 12. The use of the antioxidant spice extract capable of being obtained by the process claimed in any of claims 1 to 11, characterized in that it is incorporated in food, cosmetic or pharmaceutical products in a content of from 0.01 to 0.5% by weight.