PAPRIKA EXTRACT
Chemical and Technical Assessment (CTA)

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1. Summary

Paprika extract is an extract of the fruits of the genus Capsicum. Capsicums are a widely consumed natural foodstuff used as a vegetable, spice or colour. The variety used to manufacture paprika extract for food colouration is *Capsicum annuum*. Colour extracts have a very low content of capsaicin in contrast to the extracts used as flavouring agents. Paprika extract primarily consists of carotenoid pigments and extracted or added vegetable oil. In addition to carotenoids and capsaicinoids the extract contains mainly oil and neutral lipids including tocopherols derived from the fruit tissues and seeds of the dry raw material. Traces of volatile compounds may also be present; however, most of them are removed during processing when solvents are removed. Some fatty acids are also present as esters of carotenoids. Capsanthin and capsorubin are the main compounds responsible for the red colour. Extracts are slightly viscous, homogenous red liquids with good flow properties at room temperature and are used to obtain a deep red colour in any food that has a liquid/fat phase. Typical use levels are in the range of 10 – 60 mg /kg finished food, calculated as pure colouring matter. At the 69th meeting, paprika extract was evaluated as a colour, but the assessment was not finalized.

2. Introduction

Paprika oleoresin as a spice was evaluated by JECFA at its 14th meeting. No ADI was established because it was recognized that the use of this material was self-limiting for technological and organoleptic reasons. At its thirty-second Session, the Codex Committee on Food Additives and Contaminants requested clarification of this evaluation from the Committee. At its 55th meeting, JEFCA did not evaluate the available data on paprika oleoresin, but reviewed the previous evaluation of this substance, which stated that "oleoresins of paprika ... are derived from a widely consumed natural foodstuff, and there were no data indicative of a toxic hazard. The use of oleoresins as a spice was self-limiting and obviates the need for an ADI". The committee interpreted this statement to mean that the use of paprika oleoresin as a spice is acceptable.

At the 69th meeting, paprika extract was evaluated as a colour, but the assessment was not finalized. Data is needed on the composition and capsaicin content of batches of paprika extract for use as a colour produced by a variety of manufacturers. Also, information is needed as to whether the material used in the toxicological tests submitted was representative of all the products in commerce. If not, additional toxicological data on representative material would be needed for the evaluation of paprika extract for use as a colour.

3. Description

The genus *Capsicum*, which originates from Central and Southern America, belongs to the Solanaceae family and includes major types of chilli peppers. It includes all the peppers, from the mildest bell pepper to the hottest habanero. There are five domesticated species: the three most wide-spread are *C. annuum, C. frutescens, C. chinense*, together with *C. pubescens* and *C. baccatum* var. *pendulum*. The first to be introduced worldwide was *C. annuum*, originating from Mexico. It is divided into two categories: sweet (or mild) peppers and hot (or chilli) peppers, though modern

plant breeding removed that distinction. At present, *C. annuum* is the most wide-spread in terms of household consumption and industrial processing.

Paprika extracts are extensively used in food industry as natural flavouring but also as colouring agent for many foods such as spicy culinary, meat products, cheese food coatings, popcorn oil and cheeses. In addition, it is used dried or fresh in various pharmacological preparations. It has a long history as a source of biologically active compounds, such as flavonoids, phenols, carotenoids, capsaicinoids and vitamins. Capsicum fruits contain colouring pigments, pungent principles, resins, protein, cellulose, pentosans, mineral elements and very little volatile oil, while seeds contain fixed (non-volatile) oil. The fixed oil mainly consists of triglycerides (about 60%) of which linoleic acid and other unsaturated fatty acids predominate.

Xanthophyll biosynthesis in the pepper fruit involves two biosynthetic pathways, one or the other dominant depending on the ripeness stage. During ripening, carotenoid chromoplast pigments are synthesized and esterified to fatty acids. The total or partial esterification of most carotenoids gives them a high stability against possible thermo- and photo-oxidation reactions.

Paprika preparations are manufactured by solvent extraction from the pepper fruit of the genus *Capsicum annuum*, exclusively. There are two types of products prepared:

- Oleoresin capsicum: obtained from the longer, moderately pungent Capsicum used in the production of red pepper. Commercial red pepper oleoresins are mainly used as a spice supplied in pungency ratings between 80 000 and 500 000 Scoville units (approximately 0,6-3,9 % capsaicin w/w) and a wide range of colour. In the market place practice has shown that 1 kg of 200 000 Scoville units oleoresin replaces 10 kg of good quality red pepper.

- Paprika extract: obtained from varieties of *C. annuum* from which paprika powder is produced. It has a high colour value, but little or no pungency. Commercial paprika oleoresin is available in different colour strengths up to 150 000 colour units (equivalent to 10.8% total carotenoids). In the market place practice has shown that 1 kg of paprika extract replaces 12-15 kg of paprika powder with respect to colour intensity.

No relationship between pungency and colour intensity has been reported.

Paprika extract primarily consists of carotenoid pigments and fruit oil. Commercially available products are standardized by the addition of food grade vegetable oils to give a minimum total carotenoid content of 7%. Capsanthin and capsorubin are the main compounds responsible for the red colour (min. 30% of the total carotenoids). The extracts are slightly viscous, homogenous red liquids with good flow properties at room temperature. They give a deep red colour in any food that has a liquid/fat phase. Paprika extract used to colour foods has, in contrast to the oleoresin used as a flavouring agent, a very low content of capsaicin and hence little or no pungency.

The lipid fraction of fresh and dried chillies is extracted by common solvents used in the production of extracts. Ether-soluble substances comprise approx. 20% of dry chillies of which only a small faction is volatile. Using less polar solvent(s) (e.g. hexane) the proportion of neutral lipids increases at the expense of the polar lipids. The oil from bell pepper contains more than 80% neutral lipids (the remaining being polar lipids); the main fatty acid is linolenic acid, followed by saturated fatty acids. The seeds have significantly higher proportion of unsaturated fatty acids (mainly linolenic acid). Hexane extracts from red and green peppers are similar to the normal lipid constituents occurring in edible plant tissues.

Volatile compounds or essential oil constitutes between 0.1 to 2.6 % of paprika; in the final extract the fraction may be lower depending on the route of removal of the extraction solvents.

4. Method of manufacture

4.1. Manufacturing principle

Paprika extract is manufactured by solvent extraction of the dried Capsicum pods. On harvesting, the pods have a moisture content of up to 90% which has to be reduced to at least 10%. The drying operation is carried out by sun-drying, in hot air-dryers or in drying chambers.

Prime extract
Paprika oleoresin (which includes paprika and chilli) is manufactured by solvent extraction of the dried Capsicum pods, followed by solvent removal. Typically, one kg of pods yields 90 to 120 g of extract.

The pigment concentration in the extract depends mainly on two parameters, the composition of the fruit and the extraction technique employed. With respect to the fruit, the organic solvent will extract all of the lipophilic compounds, which are the pigments and the oil from the pepper pericarp. The oil is present in much higher quantity than the pigments. In addition, the pigments are located in cellular structures that are more difficult to access for the solvent. The oil is easily extracted at the early stage of the process and subsequently becomes richer in pigments. At the end of this process the solvent(s) is/are evaporated.

New extraction methods have been investigated, e.g. fractionation of paprika extract by extraction with supercritical carbon dioxide. Higher extraction volumes, increasing extraction pressures, and similarly, the use of co-solvents such as 1% ethanol or acetone resulted in higher pigment yields. Pigments isolated at lower pressures consisted almost exclusively of β-carotene, while pigments obtained at higher pressures contained a greater proportion of red carotenoids (capsorubin, capsanthin, zeaxanthin, β-cryptoxanthin) and small amounts of β-carotene. It is unknown to which extent these new extraction methods are commercially utilized.

Further processing
The prime extract can undergo a second extraction process with the objective to remove some or all of the capsaicinoids, which will yield:
- (i) purified capsaicin for commerce and to standardise other Capsicum extracts and
- (ii) a resin which contains less capsaicin than the prime extract and which may be sold as colour or as a spice oleoresin depending on the analytical results and its flavour characteristics.

The prime extract, if low in capsaicin, can be subject to further processing to reduce the flavour and aroma and thus yield a colour extract.

The final extracts are standardized by either adding food-grade oils or turned into water-dispersible formulations by adding food emulsifiers.

5. Characterization

5.1. Composition of paprika extract

Carotenoids
There has been extensive research into isolation and characterization of the Capsicum colour. in one study, 34 of 56 the detected carotenoids were identified, including beta-carotene, cryptoxanthin, violoxanthin, capsanthin and capsorubin. Xanthophylls occur primarily as fatty acid esters in the pods and oleoresin preparations. Small amounts of free carotene and xanthophyll pigments can also be found.

The total carotenoid content of the ripe fruits of *Capsicum annuum* var. *lycopersiciforme rubrum* was about 1.3 g/100 g of dry weight, of which capsanthin constituted 37%, zeaxanthin was 8%, cucurbitaxanthin A was 7%, capsorubin constituted 3.2%, and β-carotene accounted for 9%. The remainder was composed of capsanthin 5,6-epoxide, capsanthin 3,6-epoxide, 5,6-diepikarpoxanthin, violaxanthin, antheraxanthin, β-cryptoxanthin, and several cis isomers and furanoid oxides.

Capsanthin and capsorubin are the major carotenoids in the ripe fruits. Capsanthin can contribute up to 60% of the total carotenoids. Capsanthin and capsorubin increase proportionally with advanced stages of ripeness with capsanthin being the more stable of the two. The amount of carotenoids in fruit tissue depends on factors such as cultivar, maturity stage, and growing conditions.

From the first stages of ripening, the fraction of totally esterified pigments makes up almost 50% of the total carotenoid content. The proportion of the partially esterified pigment fraction (zeaxanthin monoester, capsanthin monoester, and capsorubin monoester) in the total carotenoid content increases, with a gradual decrease in the fraction of free pigments (beta-cryptoxanthin, beta-carotene, zeaxanthin, capsanthin, and capsorubin). In the fully ripe stage, a balance is reached between the three esterification fractions (free, partially esterified, and totally esterified), which seems to be largely independent of variety.

The highest concentrations of carotenoid esters are found in red chilli (*Capsicum frutescens*; 17.1 mg/100 g) and orange pepper (*Capsicum annuum*; 9.2 mg/100 g). Yellow chilli (*Capsicum frutescens*), and yellow pepper (*Capsicum annuum*) contained lesser carotenoid ester amounts (6.8, 3.2, and 2.1 mg/100 g, respectively). Both mono-esters and di-esters have been described with varying fatty acid components. Capsanthin occurs in the un-esterified form, as mono-ester and as di-ester whereas capsorubin only occurred as di-ester. β–cryptoxanthin was only found in un-esterified form.

Table 1: Content of carotenoids in *Capsicum annuum* sorted by degree of esterification.

Form	Xanthophyll	Content (% of total carotenoids)
Free	β-Cryptoxanthin	-
	Cryptoxanthin	6.1
	Lutein	-
	Violaxanthin	8.5
	Capsanthin	2.9
	Neoxanthin	2.4
	Total	19.9
Monoester	β-Cryptoxanthin	14.6
	Zeaxanthin	3.7
	Capsanthin	7.6
	Total	25.9
Diester	Antheraxanthin	11.0
	Capsanthin-5,6-epoxid	2.1
	Capsanthin	28.8
	Capsorubin	12.2
	Total	54.1

The composition of paprika extracts manufactured by different methods has been studied. Paprika extract produced with organic solvents may contain high levels of unsaturated fatty acids. In addition to fatty acids they also contain high quantities of tocopherols (0.9-1%). The main pigments of the extracts were identified as esters of lauric, mystiric and palmitic acid. At the end of the extraction process the solvents are evaporated which causes heat degradation of carotenoids. The extraction of

carotenoids by traditional methods is often complicated by their susceptibility to isomerization and degradation.

The drying operation influences the carotenoid content of the end product. The first studies on the effects of drying on the initial carotenoid concentration of the fruit were carried out on the varieties most common at that time, *Bola* and *Agridulce*. The impact of the drying procedure on the carotenoid content depended on the variety of pepper used. Drying in industrial hot air-dryers reduced total carotenoid concentration in both varieties. The carotenoid richness in the *Capsicum annuum* varieties *Jaranda* and *Jariza* has also been characterized.

5.2. Other constituents

Capsaicinoids

The pungent compounds of the Capsicum fruit are called capsaicinoids (capsaicin and its analogs). More than 10 capsaicinoids occur in red peppers as minor components. The following five have been reported as the major components of most Capsicum species: capsaicin, dihydrocapsaicin, nordihydrocapsaicin, homocapsaicin, and homodihydrocapsaicin. They represent approximately 95% or more of the total capsaicinoid content. Using mass spectroscopy, the following distribution of capsaicinoids in *Capsicum annuum* was determined: capsaicin (69%), dihydro- capsaicin (22%), nordihydrocapsaicin (7%), homocapsaicin (1%), and homodihydrocapsaicin (1%).

It has been reported that the fruit of a nonpungent cultivar of *Capsicum annuum*, named CH-19 Sweet, contains only a small amount of capsaicinoids but have considerable capsaicinoid-like substances. The structures of two major compounds were determined to be 4-hydroxy-3-methoxybenzyl (E)-8-methyl-6-nonenoate and 4-hydroxy-3-methoxybenzyl 8-methylnonanoate. They were named capsiate and dihydrocapsiate, respectively. The acyl residues of capsiate and dihydrocapsiate were the same as those of capsaicin and dihydrocapsaicin, respectively, although their aromatic portions were not vanillylamine such as capsaicinoids but vanillyl alcohol. They had no pungency upon oral tasting. A new capsiate-like substance, named nordihydrocapsiate, has been isolated from an extract from CH-19 Sweet. The structure was determined to be 4-hydroxy-3-methoxybenzyl 7-methyloctanoate by spectroscopic methods. Preliminary work had indicated the existence of several capsiate-like substances as minor components in the CH-19 Sweet cultivar.

Paprika extracts intended for use in food colouring contain capsaicinoids and capsaicinoid-like substances in small quantities.

Glycosides

In polar n-butanol extracts from ripe fruits of *Capsicum annuum L.* var. *acuminatum*, three glycosides, capsosides A and B and capsianoside VII were identified, although the substances were found at very low levels. Four new acyclic diterpene glycosides named capsianosides, were isolated from the fresh sweet pepper fruits of *Capsicum annuum* and their the chemical structures and absolute configurations were established. Due to their polarity it is unlikely that such glycosides are present in paprika extract which is obtained by hexane extraction.

Glycolipids

Five major glycolipid classes (acylated steryl glucoside, steryl glucoside, monogalactosyldiacylglycerol, digalactosyldiacylglycerol, and glucocerebroside) were isolated from fruit pastes of red bell pepper. The molecular species of each glycolipid were characterized. The molecular species of steryl glucoside were β-sitosteryl and campesteryl glucosides, and those of the acylated steryl glucoside were their fatty acid esters. The dilinolenoyl species was predominant in monogalactosyldiacylglycerol in addition to small amounts of another five molecular species, whereas digalactosyldiacylglycerol consisted of seven molecular species varying in their degree of unsaturation. The glucocerebroside class contained at least seven molecular species, which were characterized. Due to their amphiphilic properties it is unlikely that such glycolipids are present in paprika extract which is obtained by hexane extraction

6. Functional uses

6.1 Technological function

Paprika extract has an extensive use in food industry as a natural colouring agent for foods such as spicy culinary, meat products, cheese food coatings, popcorn, oil & cheeses. Depending on the nature of the food (moisture, fat content, texture, background colour) colour saturation is achieved at the use level of approximately 100 mg/kg (ppm) colouring matter. Increasing the quantity of paprika extract has no further benefit, neither for the appearance nor for the taste of the food. As a result, the use of paprika extract as a colour is self-limiting.

6.2 Food categories and use levels

The results of the NATCOL survey of use levels of paprika extract are summarised in Annex I of this document. Use levels of paprika extract were provided for each food category. Because different use levels correspond to different colour hues, respondents were asked to provide range of use levels and a typical value, representing the most common use level. The data provided by individual paprika extract producers have been combined. Paprika extract producers were asked to provide use levels standardised to a 100,000 colour units, which corresponds to a total carotenoid concentration of 7.2%. This factor was used to derive the total carotenoid concentrations in each foodstuff.

7. Reactions and fate in food

At room temperature and exclusion of light, cis-trans isomerization of the carotenoids easily occurs. Under light exposure and room temperature, carotenoid structures are broken down, and the molecules lose all their nutritional, medical and colourant properties. It has been established in model systems that carotenoids are degraded in a sequence of reactions.

Although the paprika extract is a complex mixture of different carotenoids in oil, the decolouration reaction can be studied using a simple approach. The whole carotenoid content disappears following a first order reaction depending on time and temperature. Loss of red and yellow pigments it temperature-dependent.

Processing of Capsicum annuum into paprika extract involves some operation units where heating is the driving force to transform the raw material Several studies have been performed to determine degradation kinetics and the effect of thermal processing in the carotenoid profile present in that processed product. Some possible degradation products were detected, although their contribution to the total carotenoid profile was not significant. The high-temperature treatment modified the carotenoid profile, yielding several degradation products. Taking into account structures of the identified degradation products, the cyclization of polyolefins could be considered as the general reaction pathway in thermally induced reactions, yielding also xylene as byproduct and the corresponding nor-carotenoids.

8. References

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Annex I

Results of NATCOL survey of Paprika Oleoresin usage (Table 3, NATCOL submission, 2007).

Food Category No.	Food Category	Use Levels mg/kg Oleoresin			Use Levels mg/kg Total carotenoids		
		Range		Typical	Range		Typical
		Min	Max		Min	Max	
1.1.2	Dairy-based drinks, flavoured and/or fermented (e.g., chocolate milk, cocoa, eggnog, drinking yoghurt, whey-based drinks)	14	183	131.5	1.0	13.2	9.5
1.4.4	Cream analogues	61	183	166	4.4	13.2	12.0
1.5.2	Milk and cream powder analogues	70	490	195	5.0	35.3	14.0
1.6.2	Ripened cheese	30	122	111	2.2	8.8	8.0
1.6.2.1	Ripened cheese, incl. rind	61	183	166	4.4	13.2	12.0
1.6.4.1	Plain processed cheese	19	144	50	1.4	10.4	3.6
1.6.4.2	Flavoured processed cheese	50	200	75	3.6	14.4	5.4
1.6.5	Cheese analogues	50	141	95	3.6	10.2	6.8
1.7	Dairy-based desserts (e.g., pudding, fruit or flavoured yoghurt and ice cream)	4	490	192.5	0.3	35.3	13.9
2.2.1	Fat emulsions containing at least 80% fat	40	200	150	2.9	14.4	10.8
2.2.2	Fat emulsions containing less than 80% fat	100	400	300	7.2	28.8	21.6
2.3	Fat emulsions mainly on type oil-in-water, including mixed and/or flavoured products based on fat emulsions (excluding desserts 2.4)	50	400	250	3.6	28.8	18.0
2.4	Fat-based desserts excluding dairy-based dessert products of food category 1.7.	10	250	150	0.7	18.0	10.8
3.0	Edible ices, including sherbet and sorbet - water-based only (excluding dairy based 1.7, vegetable based 2.7)	14	210	57.5	1.0	15.1	4.1
4.1.2.3	Fruit in vinegar, oil, or brine (e.g. pickled fruits)	28	630	97.3	2.0	45.4	7.0
4.1.2.6	Fruit-based spreads (e.g., chutney) excluding products of food category 4.1.2.5	28	630	97.3	2.0	45.4	7.0
4.1.2.8	Fruit preparations, including pulp, purees, fruit toppings and coconut milk	28	630	100	2.0	45.4	7.2
4.1.2.8	Jams, jellies, marmalades	28	630	100	2.0	45.4	7.2
4.1.2.9	Fruit-based desserts, including fruit-flavoured water-based desserts but excluding edible ice 3.0 and frozen dairy desserts 1.7	10	150	100	0.7	10.8	7.2
4.1.2.10	Fermented fruit products	28	630	47.5	2.0	45.4	3.4
4.1.2.11	Fruit fillings for pastries excluding purees 4.1.2.8	28	630	97.3	2.0	45.4	7.0
4.2.2	Processed vegetables (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera), seaweeds, and nuts and seeds	45	96	97.3	3.2	6.9	7.0
5.2	Confectionery including hard and soft candy, nougat, etc. other than food categories 05.1, 05.3 and 05.4	10	400	150	0.7	28.8	10.8
5.3	Chewing gum	10	150	100	0.7	10.8	7.2

Food Category No.	Food Category	Use Levels mg/kg Oleoresin			Use Levels mg/kg Total carotenoids		
		Range		Typical	Range		Typical
		Min	Max		Min	Max	
5.4	Decorations (e.g., for fine bakery wares), toppings (non-fruit) and sweet sauces	305	811	500	22.0	58.4	36.0
6.3	Breakfast cereals, including rolled oats	61	500	400	4.4	36.0	28.8
6.4.3	Pre-cooked pastas and noodles and like products	1.2	1000	800	0.1	72.0	57.6
6.5	Cereal and starch based desserts (e.g., rice pudding, tapioca pudding)	20	490	200	1.4	35.3	14.4
6.6	Batters (e.g., for breading or batters for fish or poultry)	25	1250	200	1.8	90.0	14.4
7.1.2	Crackers, excluding sweet crackers	20	200	50	1.4	14.4	3.6
7.1.4	Bread-type products, including bread stuffing and bread crumbs	100	3780	275	7.2	272.2	19.8
7.2	Fine bakery wares (sweet, salty, savoury) and mixes	61	520	343	4.4	37.4	24.7
8.3	Processed comminuted meat, poultry, and game products (sausages)	20	800	125	1.4	57.6	9.0
8.4	Edible casings (e.g., sausage casings)	0	108	50	0.0	7.8	3.6
9.2	Processed fish and fish products, including molluscs, crustaceans, and echinoderms	20	2000	760	1.4	144.0	54.7
10.4	Egg-based desserts (e.g., custard)	10	200	150	0.7	14.4	10.8
11.4	Other sugars and syrups (e.g., xylose, maple syrup, sugar toppings)	30	300	150	2.2	21.6	10.8
12.2.1	Herbs and spices	100	1000	350	7.2	72.0	25.2
12.2.2	Seasonings and condiments (important to distinguish between C, F, S)	5	5000	205	0.4	360.0	14.8
12.4	Mustards	20	300	115	1.4	21.6	8.3
12.5	Soups and broths	10	1000	215	0.7	72.0	15.5
12.6	Sauces and like products	10	400	77.5	0.7	28.8	5.6
12.7	Salads (e.g., macaroni salad, potato salad) and sandwich spreads excluding cocoa- and nut-based spreads of food categories 4.2.2.5 and 05.1.3	5	300	102.5	0.4	21.6	7.4
12.9	Protein products	60	60	60	4.3	4.3	4.3
12.9.1.1	Soy bean beverage	14	350	97.3	1.0	25.2	7.0
14.1.3.2	Vegetable nectar	5	20	20	0.4	1.4	1.4
14.1.4	Water-based flavoured drinks, including "sport," "energy," or "electrolyte" drinks and particulated drinks (dairy based 1.1.2, soy based 12.9 and 12.10)	14	420	97.3	1.0	30.2	7.0
15.1	Snacks - potato, cereal, flour or starch based	20	1040	500	1.4	74.9	36.0
15.2	Processed nuts, incl. coated nuts	100	200	150	7.2	14.4	10.8
16.0	Composite foods - foods that could not be placed in categories 1 - 15	0.4	1000	255	0.0	72.0	18.4