EXTRACTION OF VOLATILE AND FIXED OIL PRODUCTS FROM HOT PEPPERS

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Pungent peppers belonging to the family Solanaceae and classified as the variety *Capsicum annum L. var. Annum* are widely cultivated in the Caribbean. They are renowned for their flavours, which originate from both the volatile oil (flavour) and the fixed oil (pungency), and are marketed both as fresh and dried products.

The work described in this paper is aimed at developing processes for the extraction of these two products using supercritical carbon dioxide using a bench scale Supercritical Fluid Extraction (SFE) unit. Experiments were carried out using peppers from a single source. Analysis of the fixed oils was by HPLC after identifying the components using NMR, the major group of components being the capsaicinoids. The analysis of the volatile oils was by GC, after identifying the components using GCMS.

In the initial series of experiments on fresh peppers, experiments were carried out over ranges of temperature (35^{o}C to 70^{o}C) and pressures (100 to 550bar). Fixed oil yields were 0.2 to 0.3%, based on wet weight, showing no significant trends with the variables. Capsaicinoid contents were up to 75%. Yields from the dried material were an order of magnitude higher, as may be expected, but with lower capsaicinoid contents. These results were similar to those from standard solvent extraction using acetone. In the third series of experiments attempts were made to collect the volatile and fixed oils separately by pressure variation, but because the fixed oils are released to some extent at lower pressures, this could only be done by modifying the collection system. Fixed oil composition with time results are presented, both with and without using acetic acid as entrainer, these demonstrating the benefits of using the entrainer. The major components of the volatile product are also identified.

INTRODUCTION

The word ‘pepper’ is used to describe a group of spices associated with two different kinds of plants from two unlike species. Thus the original peppers used in International Trade belong to the genus *Piper N.O. Piperaceae*, this species being a climbing vine. Chillies and other types come from the bushy *Capsicum* species (family – Solanaceae). The work described in this paper is associated with the latter species, for which four broad categories have been identified. Of particular interest is the variety *Capsicum Annum L.* (also known as Scotch Bonnet and Bell peppers), which grows in abundance in the Caribbean. It is of particular importance as a food flavouring, the specific flavours being characterised by both the volatile oil and the fixed oil. The volatile oil provides the basic flavour and the fixed oil gives the pepper pungency. In addition, however, the pungency which is created by the presence of capsaicinoids (Molecular Formula $C_{18}H_{27}NO_3$ – IUPAC name 8-methyl-N-

vanyllyl-6-noneamide), constitutes the active ingredient in pepper sprays used for personal security.

The work described in this paper is aimed at developing processes for the extraction of these two products using supercritical carbon dioxide. Previously reported work[1] has concentrated on the extraction of the pungent principle from dried peppers. It has been established [2], however, that the volatile oils are driven off during the predrying process.

MATERIALS AND METHODS

Raw Materials

Fresh peppers of the variety *Capsicum Annum L. var. annum* were obtained from a farmer in Central Trinidad. The peppers were stored in the chilling compartment of a refrigerator prior to processing if they were processed within a few days of purchase. Otherwise they were stored in the freezer.

Equipment and Methods

When the peppers were predried prior to extraction, the drying was carried out to equilibrium moisture content at 45^{o}C in a fan blown Lab Line Environette tray drier.

Supercritical extraction was carried out in a bench-top scale Applied Separations (Penn. USA) Spe-ed unit. A 100ml stainless steel extraction vessel was used in the investigation, this being packed with ~30gms of diced pepper for each run. The carbon dioxide flow rate was fixed at 2.5 litres per minute. Three series of experiments were carried out as follows:

- To investigate the effect of temperature and pressure on the yield and fixed oil composition of fresh peppers
- To see if predrying the peppers affected extraction and to compare the results with standard solvent extraction using acetone
- To attempt to collect the volatile components separately from the fixed oil and to investigate the extract composition with time. The potential use of an entrainer, i.e. acetic acid, was also investigated.

The SFE equipment did not have entrainer injection facilities, so the acetic acid was added to the extraction vessel with the initial charge of peppers.

All moisture contents were measured using the Dean and Stark toluene distillation technique.

Analysis of Volatile constituents

The composition of the volatile oils was determined using a HP5890 Series 2 Gas Chromatograph using an FID detector. Separations were performed using a 60m Supelco SPB-50 (50% diphenyl 50% dimethylsiloxane) capillary column. Identification of the specific components was carried out in a commercial analytical laboratory using GCMS.

Analysis of Fixed Oils

Quantitative analysis of the capsaicinoid contents of the fixed oil samples was carried out using a HP1090 HPLC with an ultraviolet diode array detector in conjunction with a HP Series 3396 Series 2 integrator. The mobile phase was a mixture of Methanol:water:acetic

acid in the ratio 70:28:2, utilising a ready-packed column of Econosil. A commercial capsaicin standard was used for comparative purposes.

RESULTS AND DISCUSSION

In the initial series of experiments on fresh peppers, experiments were carried out at extraction temperatures varying from 35C to 70^{o}C and extraction pressures varying from 100 to 550 bar. No attempt was made to collect the volatiles in this series of experiments. The results are shown in Table 1 below:

Table 1 : Extraction Yield and Total Capsaicinoid Content from fresh Peppers as a Function of Extraction Temperature and Pressure

Temperature (^{o}C)	Pressure (Bar)	Extraction Yield (% wt basis)	Capsaicinoid Content (% of extract)
40	100	0.23	44.1
40	200	0.31	54.4
40	300	0.19	61.4
40	400	0.19	49.6
40	500	0.24	48.3
40	550	0.25	51.2
35	200	0.20	67.9
45	200	0.17	62.0
50	200	0.19	62.0
60	200	0.21	65.4
70	200	0.20	74.5

Reference to Table 1 shows that yields of fixed oil were between 0.19% and 0.31% by weight based on wet material, there being no significant trends with the variables investigated. Differences between experiments were probably as a result of raw material variation, together with the difficulties of extracting from materials with a high moisture content, ~90% w.b. The capsaicinoid contents are given in Table 1 as the sum of the measured Capsaicin and Dihydrocapsaicin values, with the normal weight ratio being ~70/30. Reference to Table 2 shows no significant changes in capsaicinoid content with varying pressure. It may however be significant that the highest value at 74.5% was at an extraction temperature of 70^{o}C, bearing in mind that the melting point of capsaicin is 65^{o}C.

The second series of experiments was on peppers which had been dried to close to equilibrium moisture content at 45^{o}C. It had previously been established that the volatile oils are driven off during drying [2], so no attempt was made to collect the oils during this series of experiments either. The objectives of this series of experiments were:

- To compare the SFE extractions of wet and dried peppers.
- To compare the SFE extraction of dried peppers with the standard solvent extraction technique using acetone.

The results are shown in Table 2 where it is seen that the extraction yields were a magnitude higher than those for fresh peppers. This is predictable, because the moisture content of fresh

peppers was ~90% w.b, whereas that of the dried peppers was ~10% w.b. When converted to a common basis e.g. dry weight basis, the extraction yields using dried peppers were similar to those from wet peppers. Reference to Table 2 shows the yields using standard acetone extraction to be slightly higher than SFE, whereas capsaicinoid contents were similar. Comparison of the capsaicinoid contents of the extracts from the fresh and dried peppers were, however significantly different; with the capsaicinoid contents of the extracts from fresh peppers being significantly higher.

Table 2: Comparison of Extraction Yield and Total Capsaicinoid Content from Dried Peppers by SFE using Carbon Dioxide and Solvent Extraction using Acetone

Extraction Process	Extraction yield (% wt basis)	Capsaicinoid Content (% of extract)
SFE	2.2	17.7
SFE	2.5	26.2
SFE	2.7	14.0
Acetone	3.7	19.6
Acetone	3.5	14.0

The third series of experiments was carried out on fresh peppers with the following objectives:

- To attempt to collect the volatile oil and fixed oil separately
- To examine the extract composition relationship with time
- To investigate the potential for the use of an entrainer to improve extraction

The results from two such experiments are shown in Tables 3 and 4, the first experiment being without the addition of an entrainer, and the second one where the initial charge of peppers was mixed with 5% by weight of acetic acid as entrainer. In each case the experiment was started at a pressure of 100bar and temperature 40^{o}C, but both temperature and pressure were increased in steps during the course of the experiment. Reference to Tables 3 and 4, shows that some capsaicin is extracted, even under the least severe conditions. Because of this, a modification was made on the apparatus such that the volatile oil could be collected separately from the fixed oil. The quantum was sufficient for GC analysis but not enough to calculate a yield. The major components identified were as follows:

Butanoic acid, 3-methyl
Iso-valeric acid
n-hexyl isobutyrate
hexyl 2-methyl butyrate
butyl 2-methyl butanoate
cis-3-hexenyl isobutyrate
hexyl isovalerate
Hexyl-n-valerate pentanoic acid
Cis-3-hexenyl (3) 2-methyl butanoate
Hexanoic acid, (3)-hexyl ester
Delta-cadinene naphthalene

Reference to Table 3 shows that there was a fair proportion of capsaicinoids in the initial extract even at the lower temperature and pressures. This proportion increased with time until after about 3 hours or so the extract consists mainly of capsaisins. After about 4 hours the capsaicin concentration dropped off with time, the extract presumably being made up of higher boiling components.

Table 3: Extraction from Fresh Peppers with Successive Increase of Temperature and Pressure – No Entrainer

Presssure (Bar)	Temperature (^oC)	Time (mins)	Extraction Yield (% wt basis)	Capsaicinoid Content (% of extract)
100	40	75	0.118	23.1
150	40-50	90	0.045	41.1
200	50-60	75	0.019	92.2
250	60-70	60	0.091	14.8
300	70	30	0.040	2.9

Reference to Table 4, however, shows similar trends, but seemingly with the capsaicinoids being extracted slightly earlier, this presumably being caused by the presence of the entrainer aiding the solubility of the capsaicinoids in the carbon dioxide.

Table 4: Extraction from Fresh Peppers with Successive Increase of Temperature and Pressure – Acetic Acid Entrainer at the 5% Level by Weight of Charge

Pressure (Bar)	Temperature (^oC)	Time (mins)	Extraction Yield (% wt basis)	Capsaicinoid Content (% of extract)
100	40-50	60	0.065	47.0
130	50-60	45	0.040	57.5
150	60-70	45	0.010	87.4
175	70-75	45	0.003	98.8
250	75	45	0.106	0.8

Surprisingly the overall yield without entrainer was slightly higher at 0.31% than that with the entrainer at 0.23%. Further reference to Table 4 shows that the extraction may not have been quite complete in the latter case.

CONCLUSIONS

It may be concluded that the use of Supercritical Fluid Extraction offers a credible alternative to the extraction of the pungent principles from hot peppers. Direct comparison of extraction results with SFE to those using solvent extraction from dried peppers show similar results. If, however, fresh peppers are used capsaicinoid compositions in the extracts are much higher, and, in addition, there is the potential for retaining the volatile components, thereby improving the product as a food flavouring product. Initial results on the SFE of the pungent extracts from hot peppers have shown that variation of temperature and pressure have little effect on the quantum and composition of the extract. They also show that the capsaicinoid content of

the extract increases with time until it reaches a maximum after about 3 hours. After this time the capsaicinoid content in the extract drops off. The investigation has shown that the use of SFE could have good commercial potential in producing high quality extracts from hot peppers. Much further work however is necessary.

REFERENCES

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