

Extraction of Chili, Black Pepper, and Ginger with Near-Critical CO₂, Propane, and Dimethyl Ether: Analysis of the Extracts by Quantitative Nuclear Magnetic Resonance

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Ginger, black pepper, and chili powder were extracted using near-critical carbon dioxide, propane, and dimethyl ether on a laboratory scale to determine the overall yield and extraction efficiency for selected pungent components. The temperature dependency of extraction yield and efficiency was also determined for black pepper and chili using propane and dimethyl ether. The pungency of the extracts was determined by using an NMR technique developed for this work. The volatiles contents of ginger and black pepper extracts were also determined. Extraction of all spice types was carried out with acetone to compare overall yields. Subcritical dimethyl ether was as effective at extracting the pungent principles from the spices as supercritical carbon dioxide, although a substantial amount of water was also extracted. Subcritical propane was the least effective solvent. All solvents quantitatively extracted the gingerols from ginger. The yields of capsaicins obtained by supercritical CO₂ and dimethyl ether were similar and approximately double that extracted by propane. The yield of piperines obtained by propane extraction of black pepper was low at ~10% of that achieved with dimethyl ether and CO₂, but improved with increasing extraction temperature.

KEYWORDS: Spices; ginger; black pepper; chili; extraction; near-critical; pungent; gingerol; piperine; capsaicin; quantitative NMR

INTRODUCTION

Chili, *Capsicum* species (family Solanaceae), ginger, *Zingiber officinalis* Roscoe (family Zingiberaceae), and pepper, *Piper nigrum* L. (family Piperaceae), are the classic pungent spices used for food flavoring. Ginger is also used medicinally (1), and chili compounds are used for pain relief (2). Concentrated extracts of the aroma, flavor, and coloring compounds (oleoresins) are important commercial products that have generally been prepared with liquid solvents such as ethanol, acetone, and dichloroethane (3–5). The extraction of spices with supercritical carbon dioxide (SCO₂) has been widely reported on a laboratory and pilot scale for ginger (6, 8–15), black pepper (16–19), and chili (20–29) and is now carried out on an industrial scale (8, 14). There are a small number of publications on the extraction of spices with subcritical propane (26–29), and only two reports of the use of dimethyl ether for the extraction of nutmeg (30, 31).

Extraction of spices using SCO₂ is generally carried out with two-stage separation of extracts into a pungent oleoresin and an essential oil fraction. Ginger is the easiest of the spices to extract in terms of pressure and temperature, and liquid CO₂ is sufficient to extract the pungent principles (14). Chili can be extracted at moderate supercritical pressures and temperatures (6–8, 20–24), especially if small amounts of cosolvent are used (22, 25), and the capsaicins are relatively soluble in SCO₂ (32, 33). Chili extract also contains fatty oil and a mixture of carotenoids (20, 21). It is likely that the fatty oil acts as a cosolvent for the capsaicins (25). Black pepper is the most difficult to extract and requires high pressures and moderate to high temperatures (6, 7). The extract is viscous, pasty, and semisolid and thus difficult to recover from separation vessels. A substantial yield of essential oil can also be obtained, either by two-stage separation of extract after supercritical extraction or simply by extraction using liquid CO₂, as piperine is not extracted at these conditions (13, 18).

Illés and co-workers (26–29) have reported the extraction of a number of spices using subcritical propane, including both mild (27) and pungent (28, 29) paprika. The yields of key extractables were compared with those obtained by supercritical carbon dioxide. Propane was found to be an effective solvent

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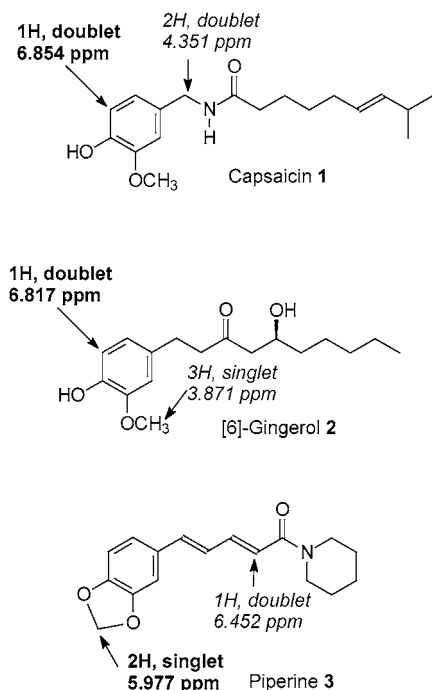


Figure 1. Structures of pungent compounds and ^1H NMR signals used for quantitative analyses: **boldface** type indicates main signal; *italic* type indicates check signal.

for fatty oils, tocopherols, and carotenoids (27–29) and a poor solvent for capsaicins (28–29), whereas carbon dioxide was a good solvent for capsaicinoids, fatty oils, and tocopherols but not carotenoids. Propane has been promoted as a cost-effective alternative to SCO_2 due to the lower operating pressures and lower energy consumption required for the extraction of spices, with the inherent assumption that all spices could be extracted using propane (34).

Dimethyl ether is another alternative to SCO_2 that has similar advantages to propane with respect to operating pressures and compatibility as a food grade solvent. The work reported herein compares propane and dimethyl ether with SCO_2 for extraction of the pungent principles of ginger, chili, and black pepper. These spices represent the spectrum of ease of extraction, from ginger as the easiest to black pepper as the most difficult.

The pungent components in these spices are capsaicin (1) and related compounds in chili (3), [6]-gingerol (2) and related compounds in ginger (5), and piperine (3) and related compounds in black pepper extracts (4) (**Figure 1**). Quantitative analyses of these compounds are generally done by HPLC (35). However, this can require extensive preanalysis preparation to remove compounds that could damage HPLC columns. It was considered that high-field ^1H NMR spectroscopy could provide a faster method, quantifying the characteristic aromatic signals of 1–3 and related pungent compounds. Evilia (36) has recently reviewed theoretical and practical factors in quantitative NMR spectroscopy. Pauli (37) has also discussed this method for the analysis of natural product reference compounds. ^1H NMR spectroscopy has been used for rapid quantitative analyses of pungent sesquiterpene dialdehydes in leaves of the New Zealand pepper tree, *Pseudowintera colorata* (38), and that method has been further developed for this work.

MATERIALS AND METHODS

Spices, Solvents, and Reference Compounds. Australian and African dried ginger samples were supplied by Buderim Ginger (Buderim, Australia). Ground chili and whole black peppercorns were purchased from a local supplier. Ginger and pepper were ground before extraction in a Wiley knife mill to an average particle size of 0.5 mm as determined by sieve analysis. Moisture contents (% w/w) of the spice samples were as follows: Australian ginger, 8.8; African ginger, 10.5; chili, 6.7; and pepper, 8.8. Moisture contents of the ground spice samples were obtained by measuring the loss of mass upon drying overnight in an oven at 80 °C. Acetone was redistilled before use. Industrial grade (>99.5%) CO_2 was supplied by BOC (New Zealand) Ltd., unodorized propane by Propane Gas Ltd. (New Zealand), and dimethyl ether by Aerosol Products Ltd. (New Zealand). Deuterated chloroform (Aldrich, Auckland, New Zealand) was 99.8 atom % D, and dimethylformamide (BDH, Palmerston North, New Zealand) was of Analar grade. Capsaicin (Sigma, Auckland, New Zealand) was labeled 98% pure, piperine (Aldrich) 97% pure, and [6]-gingerol (Chromadex, Santa Ana, CA) >95% pure.

Extractions. Soxhlet extractions with acetone (75 mL) were carried out on each spice (2.0 g) for 2 h, after which time no more pigments were being extracted. The solvent was removed by rotary evaporation at room temperature.

Supercritical and subcritical extractions were carried out in the laboratory scale apparatus shown schematically in **Figure 2**, which had previously been used for the extraction of a variety of seed oils using

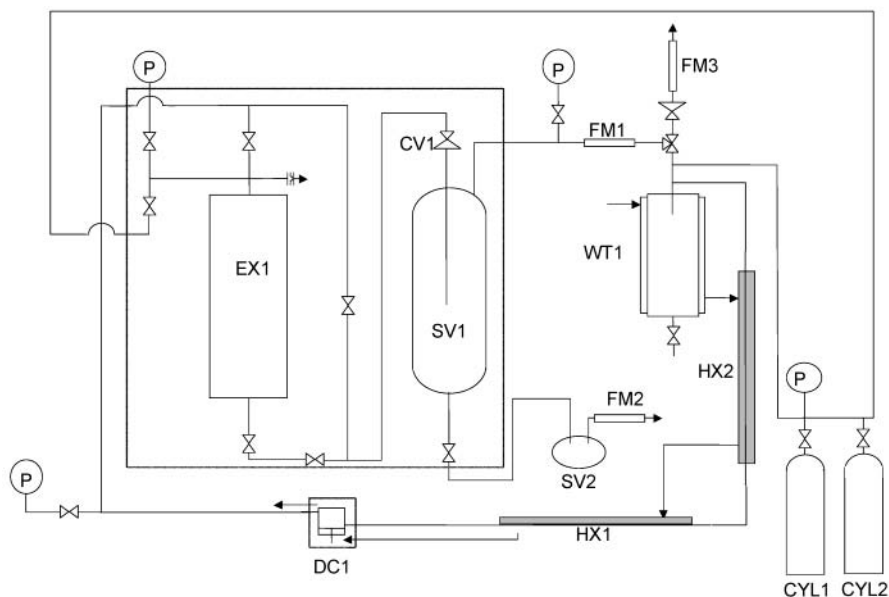


Figure 2. Schematic of laboratory scale supercritical extraction plant.

supercritical CO₂ and subcritical propane (39). The apparatus consists of an air-driven remote head diaphragm compressor (DC1), a 0.5 L autoclave (EX1), a 1 L separation vessel (SV1), a mass flow meter (FM1), and a water trap (WT1). Ground spice was added to a preweighed basket, which was then reweighed and placed in the extraction vessel (EX1). This was then closed and filled with the solvent up to the cylinder pressure. Simultaneously, the water bath around EX1 was taken to the extraction temperature using a steam/water mixer. EX1 was taken to the extraction pressure before flow was initiated. The flow path for extraction was as follows. Liquid extraction solvent (make up to account for losses) was withdrawn from the cylinder (CYL1) and then passed through WT1 and subcoolers (HX1 and HX2) before entering DC1. WT1 was cooled by glycol/water passed through an external jacket. DC1 was placed in an oil bath cooled by a glycol/water coil. The glycol/water was chilled by an external refrigeration system. The liquid extraction solvent was compressed to the operating pressure by DC1 and then passed through EX1 and the bed of ground spices. The solvent and dissolved extract then passed through a micrometering valve (CV1), where the pressure was reduced to the cylinder pressure. Extract was precipitated into the separation vessel (SV1). The solvent was boiled and superheated before leaving SV1. The gaseous solvent then passed through mass flow meter (FM1), a water trap (WT1) (which also served as a condenser), and a subcooler heat exchanger (HX1) before being recycled to the compressor. Samples were withdrawn from SV1 at regular time intervals. The solvent usage, temperature, and pressures at various parts of the apparatus were also recorded at the same time interval to give solvent loading (amount dissolved in the solvent) as a function of solvent usage. SC₂ experiments were carried out until the amount of extract recovered per time interval was <0.1 g or the extract was almost entirely water. Propane and dimethyl ether experiments were carried out for 25 min, as previous experiments on a variety of seeds had shown that this length of time was more than sufficient for complete extraction (39). As in the previously reported work (39), there were difficulties in getting quantitative recovery of extract from SV1 due to freezing of the extract resulting from flashing of dissolved solvent in the extract after pressure release. An additional separator SV2 was required to enable venting of this potentially flammable gas through a flow meter FM2 and outside vent. At the conclusion of the run, the extraction vessel was vented back to the cylinder down to the cylinder pressure via the separation vessel and water trap. CO₂ could then be vented to the atmosphere. When propane or dimethyl ether was used, the extraction vessel was then repressurized up to 50 bar using nitrogen. The combined mixture of solvent gas and nitrogen (now below the flammability limit) was then vented to the atmosphere. The extraction vessel was opened and the extraction basket weighed to obtain the mass loss from the solids. A solvent wash of the extractor and SV1, followed by evaporation of the solvent under vacuum from a preweighed round-bottom flask, was performed to complete the mass balance over the experiment (total mass of extract recovered during the extraction + mass recovered from the solvent wash = mass lost from the extraction basket).

NMR Analyses. A subsample of each extract (10–24 mg) was dissolved in CDCl₃ (containing 0.05% v/v dimethylformamide as an internal standard and tetramethylsilane as a chemical shift reference, set as 0.00 ppm) to a concentration of 10 mg/mL, and 0.7 mL was filtered into a 5 mm diameter NMR tube. ¹H NMR spectra were recorded on a Varian Inova instrument at 500 MHz, 128 transients each, temperature of 297 K, digital resolution of 0.087 Hz, and a pulse width of 80°. A total of 12.5 s between radiofrequency pulses was used to obtain fully relaxed spectra. Each sample was shimmed to give typical half-height line widths of 0.4–0.6 Hz. Before analysis of each spectrum, the data were phase corrected, and a spline fit baseline correction ensured a flat baseline. A macro was developed to locate and integrate with preset parameters the chosen peaks (**Figure 1**) of capsaicin **1** (integration range of **main peak** = 6.850–6.860 ppm, **check peak** = 4.347–4.361), [6]-gingerol **2** (6.813–6.820, 3.868–3.874), and piperine **3** (5.975–5.979, 6.446–6.454). These integrals were compared to the integrated value of the dimethylformamide singlet at 8.02 ppm (integration range = 8.006–8.030 ppm).

Six-point calibration curves (from 4 to 0.125 mg/mL) gave good linear responses: $R^2 = 0.9989$ for capsaicin, $R^2 = 0.9972$ for

[6]-gingerol, and $R^2 = 0.9991$ for piperine. NMR analyses of the standards showed no important impurities, so no allowance was made in the calibration curves for the suppliers' stated purities. The detection limits will depend on the signals of other compounds present, but the signal-to-noise ratios of the selected signals at the lowest calibration concentration of 0.125 mg/mL were about 30:1 for **1**, 20:1 for **2**, and 100:1 for **3**. Triplicate analyses of single spice extracts gave relative standard deviations of ±8% for capsaicins level, ±6% for gingerols level, and ±3% for piperine level.

The volatiles content of extracts of herbs and spices is normally determined by steam distillation. Because of the difficulty of getting reliable weights of the volatile or nonvolatile fractions of very small samples using normal steam distillation, dry air evaporation was used to remove the volatiles at 100 °C. A sample (~1 g, weighed to ±1 mg) of each extract was spread evenly over the walls of a 4 mL vial that was then immersed in an oil bath set at 100°C. A stream of dry air (100 mL/min) was blown through the vial from a fine tube lowered as close to the bottom of the vial as possible. Evaporation was continued until the nonvolatile fraction in the vial achieved constant weight (~12–18 h). The volatiles fraction includes both essential oil and water.

RESULTS AND DISCUSSION

Development of the Analysis Technique. Dimethylformamide was chosen as the internal standard for quantitative NMR analyses because it is readily available and nonvolatile and has a proton signal (at 8.016 ppm) that was found to be clear of any signals in the spice extracts. ¹H NMR signals of the pungent compounds capsaicin (**1**), [6]-gingerol (**2**), and piperine (**3**) were chosen to be clear of any other signals in the spice extracts (**Figure 1**). This was supported by showing that the ratio of the main signal to a check signal (**Figure 1**) was similar for the extracts and for the pure reference compounds. The analytical methods developed showed good linear calibrations, sufficient sensitivity for the spice extracts, and acceptable repeatability. The calibration factors were within 15% of those calculated on the basis of molar ratios of dimethylformamide to pungent compounds. Therefore, it would be possible to use this approach for quantitative NMR analyses without having pure reference compounds, with somewhat lower accuracy in quantification.

The ¹H NMR signals of capsaicin (**1**) chosen for integration (**Figures 1** and **3**) would include the corresponding signals of other capsaicins, which contribute to the pungency of *Capsicum* species. The most important of these is dihydrocapsaicin, which can be 20–50% of the total capsaicins (3). However, because capsaicin and dihydrocapsaicin have equal pungency (3) and differ little in molecular weight, this method will give a good estimate of both total capsaicins and total pungency. Similarly, the ¹H NMR signals of [6]-gingerol (**2**) chosen for integration (**Figures 1** and **4**) would include the corresponding signals of [8]- and [10]-gingerol, which are also found in ginger (5). Although it is not clear how these homologues compare in pungency (5), our results are taken as giving levels of total gingerols. There is less ambiguity about the quantitation of piperine (**3**) (**Figures 1** and **5**), because it comprises >95% of the total pungent alkaloids present (4).

Extraction of African and Australian Ginger. Liquid acetone extractions of Australian and African dried ginger rhizome gave extract yields of 7.8 and 5.3%, respectively (**Table 1**), within the range of 3.5–10% of oleoresin yields reported (5). ¹H NMR spectra of these two extracts showed that gingerols were the major components in each, at 30.4 and 20.9% w/w, respectively, calculated as [6]-gingerol (**2**). The expected level of gingerols in ginger oleoresin is 16–24% (14). The ¹H NMR spectra also showed broad singlets at 1.681 and 1.602 ppm

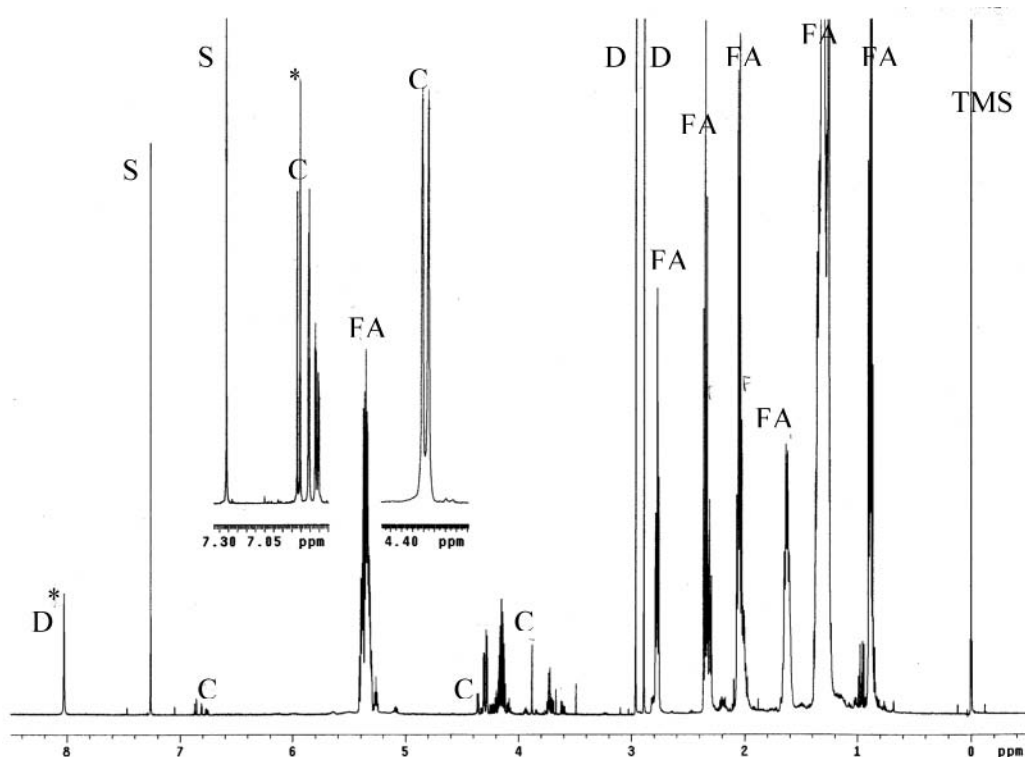


Figure 3. ^1H NMR spectrum of a chili extract, plus two expanded regions, showing peaks* used for quantitative analyses: D, dimethylformamide; S, solvent (CHCl_3 in CDCl_3); C, capsaicins; FA, fatty acid; TMS, tetramethylsilane.

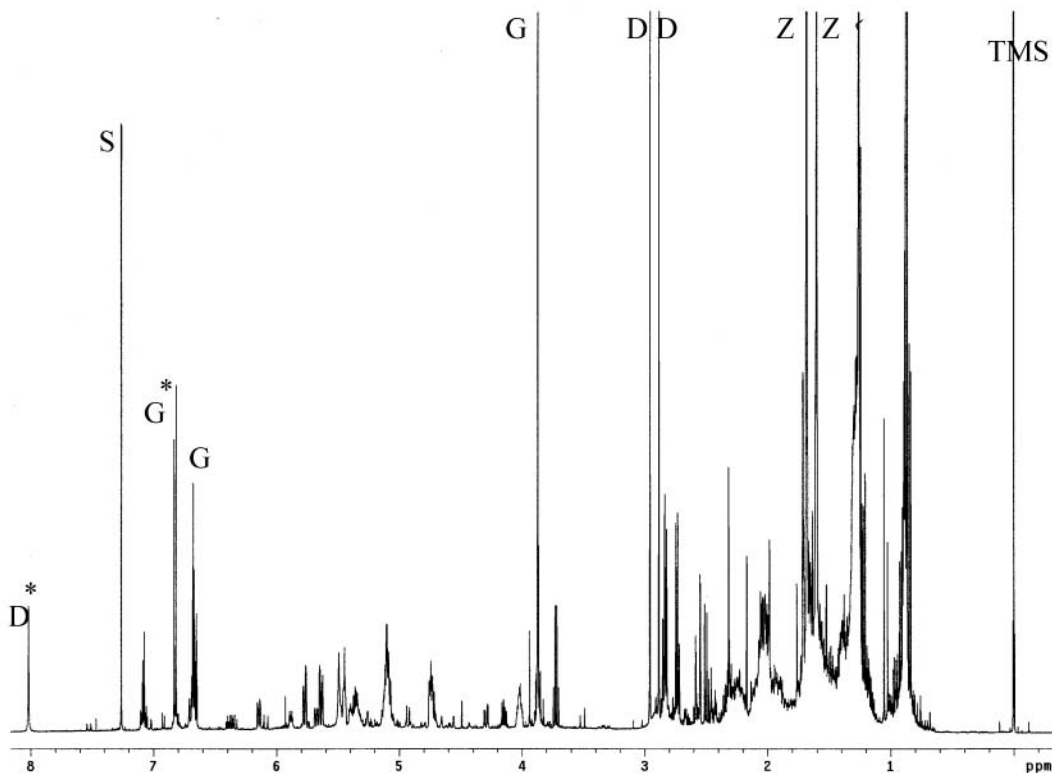


Figure 4. ^1H NMR spectrum of a ginger extract, showing peaks* used for quantitative analyses: D, dimethylformamide; S, solvent (CHCl_3 in CDCl_3); G, gingerols; Z, zingiberene; TMS, tetramethylsilane.

appropriate for allylic methyl signals in zingiberene (33), the main sesquiterpene in ginger extracts (5), plus a range of signals due to other components (**Figure 4**).

These two ginger samples were also extracted with SCO_2 at 300 bar and 313 K and with propane and dimethyl ether, both at 40 bar and 305 K. The total yields of extracts and contents

of gingerols and nonvolatiles (taken to be oleoresin) of the extracts are given in **Table 1**. The yield of extract was consistently higher for the African ginger sample than for the Australian, but there was no corresponding pattern in the contents of oleoresin and gingerols. All of the extracts gave NMR spectra that showed a similar mix of components.

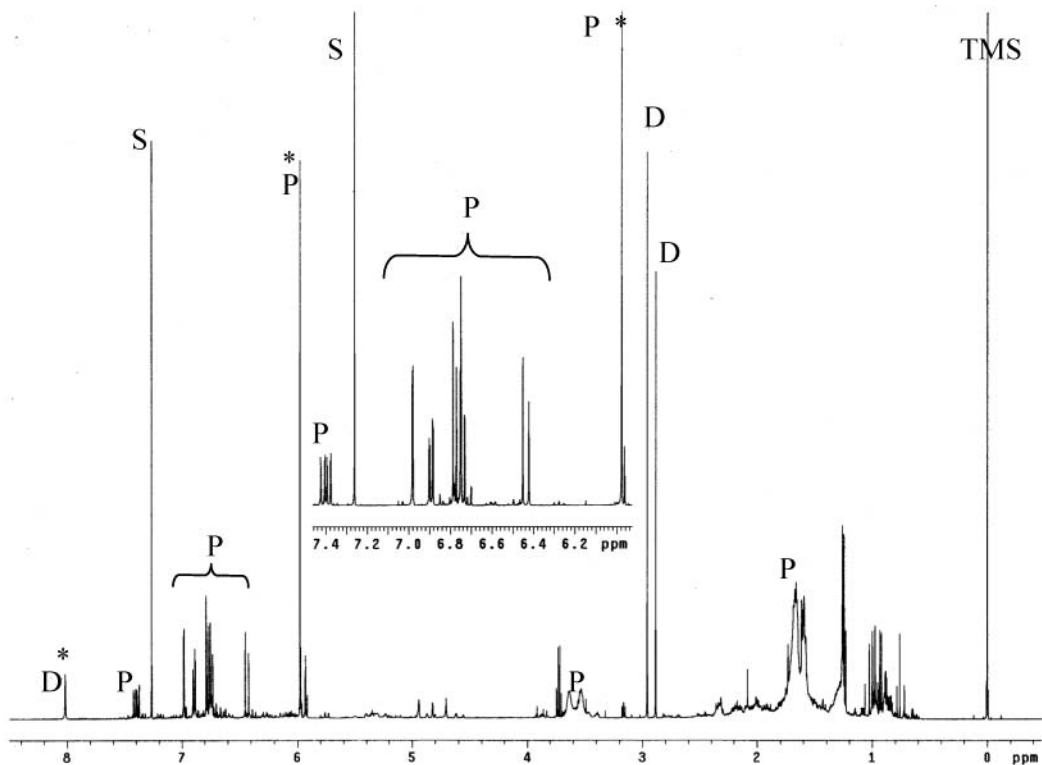


Figure 5. ^1H NMR spectrum of a pepper extract, plus an expanded region, showing peaks* used for quantitative analyses: D, dimethylformamide; S, solvent (CHCl_3 in CDCl_3); P, piperine; TMS, tetramethylsilane.

Table 1. Total Extract Yields and Gingerol and Oleoresin Contents of African and Australian Ginger Extracts

solvent	extract yield, g/kg of ginger		gingerol (oleoresin) content, g/kg of extract	
	African	Australian	African	Australian
acetone	78	53	304 (ND ^a)	219 (ND)
SCO_2 ^b	84	41	244 (554)	209 (577)
propane ^c	41	27	259 (613)	284 (569)
DME ^{c,d}	102	78	175 (567)	193 (463)

^a Not determined. ^b 300 bar and 313 K. ^c 40 bar and 305 K. ^d Dimethyl ether.

Within each ginger type, propane gave the lowest total extract yields and dimethyl ether the highest (**Table 1**). This was partly due to the coextraction of water, which is included in the reported yields. Dimethyl ether was found to extract a considerable amount of water, substantially more than SCO_2 , even though much larger masses of CO_2 were used. Dimethyl ether and water have high mutual solubilities (30, 31, 41, 42). The cumulative yields of extracts of both African and Australian ginger as a function of solvent usage (kg of solvent/kg of spice) are shown in **Figure 6**. The yields for SCO_2 shown in **Figure 6** differ from those reported in **Table 1** because the curves were truncated at the point where no further oleoresin was extracted. Further water without oleoresin was obtained from SV1 at the end of the experiment, giving the increase in total yield. Extraction was complete for propane and dimethyl ether usages of <1 kg/kg of spice, whereas SCO_2 required >15 kg/kg.

Ginger (and black pepper) extracts contain a high amount of volatiles (obtainable from **Tables 1** and **3** as the difference between 1000 and the oleoresin yield in g/kg of extract). SCO_2 offers flexibility in the splitting of the extract into oleoresin and essential oil fractions by using two-stage pressure reduction (13). This flexibility is difficult to achieve with propane or dimethyl ether. To enable two-stage separation of the extract,

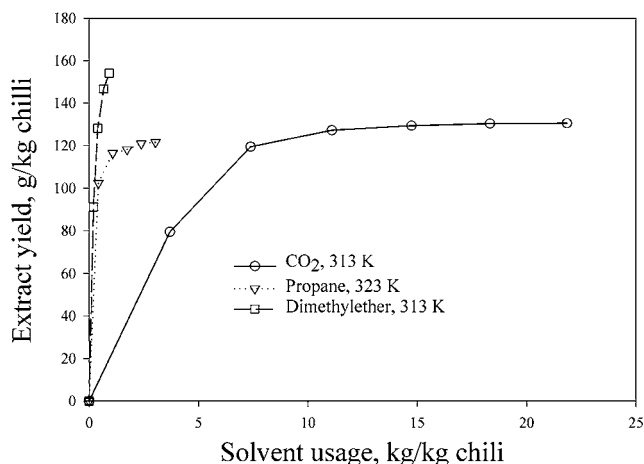


Figure 6. Extraction curves for African and Australian ginger using CO_2 , propane, and dimethyl ether.

Table 2. Total Extract Yields and Capsaicin Contents of Chili Extracts

solvent	extract yield, g/kg of chili				capsaicin content, g/kg of extract			
	308 K	313 K	323 K	333 K	308 K	313 K	323 K	333 K
acetone	160				20			
SCO_2 ^a		131				19		
propane ^b	138	123	121	122	8	11	9	10
DME ^{b,c}	154	189	158	188	19	14	15	14

^a 300 bar. ^b 40 bar. ^c Dimethyl ether.

propane and dimethyl ether must be heated to a temperature near the critical temperature, at which the oleoresin is no longer soluble but the essential oil is still soluble, and then further heated to above the critical point, or alternatively cooled, depressurized, and boiled to recover the essential oil. As the critical temperature of propane and dimethyl ether is relatively

Table 3. Total Extract Yields, Piperine, and Oleoresin Contents of Black Pepper Extracts

solvent	extract yield, g/kg of pepper				piperine (oleoresin) content, g/kg of extract			
	308 K	313 K	323 K	333 K	308 K	313 K	323 K	333 K
acetone	100				526 (ND ^a)			
SCO ₂ ^b		130				244 (589)		
propane ^c	51	45	45	54	22 (460)	37 (469)	50 (402)	55 (ND)
DME ^{c,d}	147	148	187	181	266 (839)	267 (846)	190 (563)	269 (423)

^a Not determined. ^b 300 bar. ^c 40 bar. ^d Dimethyl ether

high compared to that of CO₂, considerable heat input is required and some thermal degradation may occur. Additional heating to recover essential oil is probably impractical, as the increasing vapor pressure of the essential oil components will ensure incomplete recovery of extract. Cooling, depressurization, and boiling will then be required, which again involve a large energy input.

Extraction of Chili. Preground chili extracted with liquid acetone gave a yield of 16.0% (Table 2), at the top end of the range of 8.7–16.5% reported (3). The ¹H NMR spectrum of this extract showed capsaicins at 2.0% w/w. Yao et al. (20) obtained capsaicins concentrations of ~3% from Scotch bonnet peppers, which are among the hottest chilies. The ¹H NMR spectrum (Figure 3) was dominated by signals appropriate for linoleic acid, the main fatty acid in chili and chili extracts (3).

Chili was extracted using all three near-critical solvents under the same conditions as for ginger. Additional tests were performed at 40 bar and 313, 323, and 333 K for both propane and dimethyl ether to establish any temperature dependence of extraction yield and content of capsaicins. The extract yields and capsaicins contents are reported in Table 2; volatiles contents were very low at ~2% by mass and are thus not reported. All of the extracts gave NMR spectra dominated by fatty acid signals. Total extract yields were highest for dimethyl ether. Capsaicin contents were similar for SCO₂ and dimethyl ether, whereas the capsaicins contents of the propane extracts were around half to two-thirds of those obtained with the former solvents. The presence of nitrogen in capsaicins and the resultant increase in polarity over gingerols appears to reduce the effectiveness of propane, the most nonpolar of the solvents. Gnayfeed et al. (28) and Daood et al. (29) also found propane to be a poor to medium solvent for extracting capsaicins from pungent paprika.

The extract yields as a function of solvent usage are shown in Figure 7. Again, propane and dimethyl ether usage required to achieve complete extraction was substantially less than for SCO₂. There was little effect of temperature on either the total yield or the yield of capsaicins for both propane and dimethyl ether.

The extracts also contained carotenoid pigments (22–25). The extract obtained with SCO₂ was a bright red color, whereas those obtained with propane or dimethyl ether were dark red. The residue after extraction was pink with SCO₂ and practically decolorized using propane or dimethyl ether. Although the quantitative yields of carotenoids were not determined, the results were qualitatively similar to those obtained for the extraction of carotenoids from paprika using SCO₂ and propane (26–29). Dimethyl ether resulted in the most complete extraction of both pungent components and pigments. As with ginger, some extraction of water was observed with dimethyl ether, whereas a small amount of water was observed with SCO₂ and no water with propane.

Extraction of Black Pepper. Liquid acetone extraction gave a yield of 10.0% (Table 3), in the range of 5–15% reported

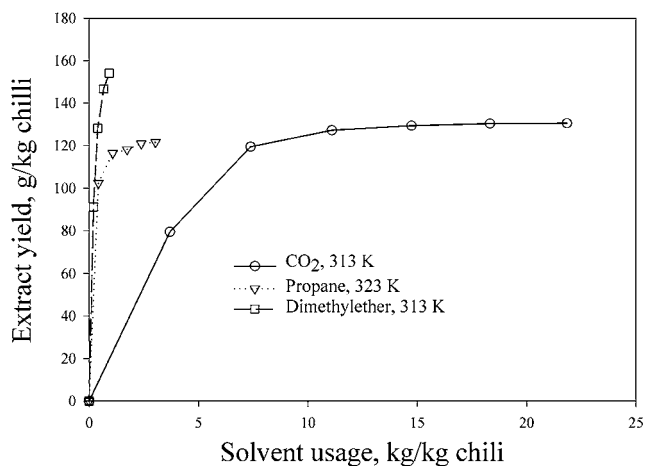


Figure 7. Extraction curves for chili powder using CO₂, propane, and dimethyl ether.

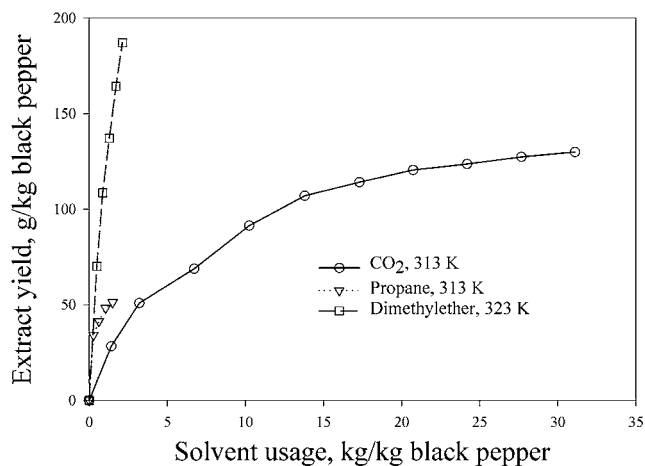


Figure 8. Extraction curves for black pepper using CO₂, propane, and dimethyl ether.

(4). The ¹H NMR spectrum of this extract was dominated by the signals of piperine (3) (Figure 5) at a calculated content of 52.6% w/w. This is similar to the contents reported by Stahl et al. (6) of 44% and by Sovová et al. (18) of 50–54%. There were only relatively low levels of aliphatic and allylic methyl signals due to monoterpene hydrocarbons in the 0.7–1.7 ppm region of the NMR spectrum. The monoterpenes, a major part of pepper volatile oil (4), may have been evaporated together with the acetone solvent.

Black pepper was extracted using the same solvents, pressures, and temperatures, including the extra temperature series, as for chili. The total yields and piperine and oleoresin contents are reported in Table 3. The NMR spectra of the SCO₂ and dimethyl ether extracts showed stronger signals in the 0.7–1.7 ppm region than in the acetone extract, and the propane extracts were dominated by signals in this region, indicating high

monoterpene levels. Propane gave substantially lower extract yields and piperine contents than either dimethyl ether or SCO₂ and somewhat lower oleoresin yields. The piperine content of the propane extracts increased with temperature but was still only ~20% of the contents of the dimethyl ether or SCO₂ extracts, which were on average 250 mg/g (25% by mass).

The extract yields as a function of solvent usage are shown for all three solvents in **Figure 8**. Again, complete extraction was achieved with very small solvent usages for propane and dimethyl ether, although the yield was also very small for propane. The extract obtained with SCO₂ was pasty, yellow, and semisolid, as found by previous workers (6–8, 18). The extracts obtained with dimethyl ether were yellow/black and liquid at room temperature. A large amount of water was also extracted by dimethyl ether, resulting in a dilution of the essential oil and piperine contents. The extracts obtained with propane were mobile and lightly colored. The solid residues after extraction were partly decolorized by dimethyl ether, with some black pigment and all yellow oleoresin removed. In contrast, only the yellow color had been removed by SCO₂, and the residues were virtually unchanged in appearance after propane extraction.

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