

## LITERATURE CITED

- Aharonson, N.; Ben-Aziz, A. *J. Assoc. Off. Anal. Chem.* 1973, 56, 1330.
- Association of Official Analytical Chemists "Official Methods of Analysis", 12th ed.; AOAC: Washington, DC, 1975; p 801.
- Ebel, S.; Herold, G. *Dtsch. Lebensm. Rundsch.* 1974, 70, 133.
- Farrow, J. E.; Hoodless, R. A.; Sargent, M.; Sidwell, J. A. *Analyst (London)* 1977, 102, 752.
- Jacob, T. A.; Carlin, J. R.; Walker, R. W.; Wolf, F. J.; Vanden-Heuvel, W. J. A. *J. Agric. Food Chem.* 1975, 23, 704.
- Maeda, M.; Tsuji, A. *J. Chromatogr.* 1976, 120, 449.
- Mestress, R.; Campo, M.; Tourte, J. *Ann. Falsif. Expert. Chim.* 1970, No. 691, 160.
- Mihara, M.; Kondo, T.; Tanabe, H. *Shokuhin Eiseigaka Zasshi* 1973, 14, 179.
- Miller, V. L.; Gould, C. J.; Csonka, E. *J. Agric. Food Chem.* 1974, 22, 90.
- Norman, S. M.; Fouse, D. C.; Craft, C. C. *J. Agric. Food Chem.* 1972, 20, 1227.
- Nose, N.; Kobayashi, S.; Tanaka, A.; Hirose, A.; Watanabe, A. *J. Chromatogr.* 1977, 130, 410.
- Ott, D. E. *J. Assoc. Off. Anal. Chem.* 1975, 58, 160.
- Otteneder, H.; Hezel, U. *J. Chromatogr.* 1975, 109, 181.
- Tanaka, A.; Fujimoto, Y. *J. Chromatogr.* 1976, 117, 149.
- Thornburg, W. W. "Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives"; Zweig, C., Ed.; Academic Press: New York, 1963; Vol. I, 99.
- Tjan, G. H.; Jansen, J. T. A. *J. Assoc. Off. Anal. Chem.* 1979, 62, 769.
- VandenHeuvel, W. J. A.; Wood, J. S.; Di Giovanni, M.; Walker, R. W. *J. Agric. Food Chem.* 1977, 25, 386.

Received for review May 5, 1980. Accepted July 23, 1980.

## Extraction of Seed Oils with Liquid and Supercritical Carbon Dioxide

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Vegetable oils can be extracted from crushed seeds with liquid or supercritical carbon dioxide. The yields obtained depend upon the pressure and the temperature employed during extraction as well as the size and shape of the seed particles. Oil fractions differing in color, taste, and odor can be recovered at various pressures and temperatures. Parameters influencing the extraction and fractionation of soybean, sunflower seed, and rapeseed oils are described.

Pressing as well as extraction with organic solvents is used widely in the production of vegetable fats and oils. The yields obtained by pressing are not as high as those achieved by extracting oil seeds. Therefore, pressing of intact or ground seeds, a most convenient process, is often followed by extracting the resulting press cake with hot organic solvents, such as petroleum hydrocarbons, for nearly quantitative recovery of the seed oils. Solvent extraction alone is used, e.g., in the commercial production of soybean oil.

The present communication describes the results of studies aimed at substituting organic solvents by liquid or supercritical gases, particularly carbon dioxide, for the extraction of oils from soybeans, sunflower seeds, and rapeseeds at fairly low temperatures.

The complete removal of organic solvents used for extracting seed oils is mandatory, if the oil is to be used for human consumption. Liquid and supercritical carbon dioxide offer the advantage of being easily removable from the extracted oil. In contrast to organic solvents and some of their contaminating components, carbon dioxide is nontoxic, and it cannot easily lead to environmental pollution. Moreover, this inexpensive gas is available on an unlimited scale both from renewable organic resources and from inorganic material including various minerals.

As in the extraction with organic solvents, the efficiency of extraction with liquid and supercritical carbon dioxide is dependent upon its amount and the time it is in contact with the ground seeds. The yield of oil is also influenced

by the size and physical structure of the seed particles. In working with liquid and supercritical gases, pressure and temperature during extraction and recovery of the oil are parameters that should receive special attention.

The principle of the equipment used for the extraction of seed oils with liquid and supercritical carbon dioxide, as shown in Figure 1, is simple. Gaseous carbon dioxide is condensed in a diaphragm compressor, C, to a pressure of 350 bar, p<sub>1</sub>; even higher pressure, up to 700 bar, can be obtained by employing a second compressor. The liquid or supercritical carbon dioxide flows through an extraction vessel, E, containing crushed seeds. The extracted oil is recovered from its solution by lowering the pressure in two stages, in a first trap, S<sub>1</sub>, to ~200 bar, p<sub>2</sub>, and in a second trap, S<sub>2</sub>, to 30-65 bar, p<sub>3</sub>, that is, below the critical pressure of carbon dioxide. The gas released is again condensed in the compressor, C, thus closing the cycle. Further details of the construction and operation of the equipment used are described under Experimental Section.

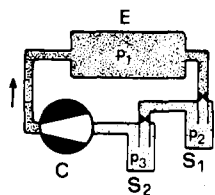
### EXPERIMENTAL SECTION

**Materials.** Seeds of soya, *Glycine max* var. Corsoy, were obtained from the American Soybean Council, St. Louis, MO, those of sunflower, *Helianthus annuus* var. Fransol, from the International Sunflower Association, Zevenaar, The Netherlands, and those of rape, *Brassica napus* var. Rapora, from Norddeutsche Pflanzenzucht Hans-Georg Lembke K.G., Hohenlieth, Germany.

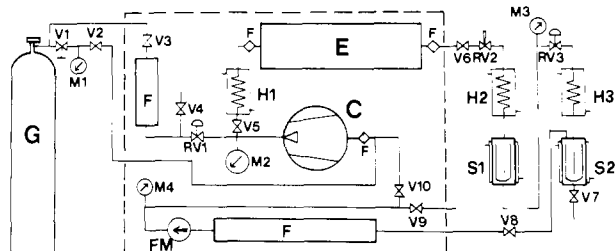
**Analytical Procedures.** Oils were extracted by treating the ground seeds (60-100 mesh) in a Soxhlet apparatus with hexane for 5 h. After evaporation of the solvent, the oil content of the seeds was determined gravimetrically.

The oils extracted with hexane as well as those obtained by extraction with liquid or supercritical carbon dioxide were analyzed by thin-layer chromatography on silica gel

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**Figure 1.** Principle of the experimental design employed in extracting seed oils with liquid and supercritical carbon dioxide. C, compressor; E, extraction vessel; S1 and S2, separators (traps); p1, p2, and p3, pressure in various parts of the apparatus.



**Figure 2.** Apparatus used for extraction with liquid or supercritical carbon dioxide. For details of construction and operation, see the text.

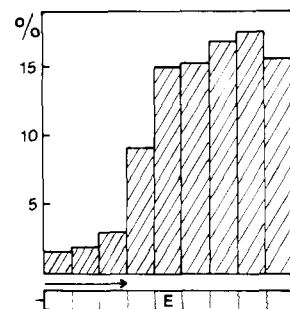
G (E. Merck A.G., Darmstadt, Germany) with hexane-diethyl ether-acetic acid (80:20:1 v/v) as the solvent and a 0.1% aqueous 2',7'-dichlorofluorescein solution or iodine vapor as the indicator (Mangold and Malins, 1960).

Aliquots (10 mg) of the oils extracted with hexane or liquid or supercritical carbon dioxide were subjected to methanolysis (Chalvardjian, 1964); the resulting methyl esters were purified by thin-layer chromatography in the above solvent system. The fatty acid composition of the various oils was determined by gas chromatography with a Perkin-Elmer F22 instrument using a glass column, 2 m  $\times$  2.5 mm, packed with 10% Silar 5 CP on Gas-Chrom Q, 80–100 mesh, at a temperature of 200 °C, with nitrogen as the carrier gas.

**Apparatus.** The design of the equipment used is shown in Figure 2. Gaseous carbon dioxide of high purity is obtained from a storage tank, G, via a reducing valve, V1; its pressure is indicated by a manometer, M1. A membrane compressor, C (Type MK 35002), (Andreas Hofer Hochdrucktechnik GmbH, Mühlheim-Ruhr, Germany) is used up to a pressure of 350 bar. By the addition of a second compressor (Type MK 1000; Nova Werke AG, Effretikon, Switzerland), pressures up to 700 bar can be obtained. The second compressor, the extraction vessel, and some connecting parts are enclosed in a thermostated and soundproof insulated casing.

The jackets of the heat exchangers H1, H2, and H3, as well as those of the separators S1 and S2 are filled with water that is kept circulating by a pump. Several filters, F, are used to purify the gas stream.

The pressure used during extraction, p1, is adjusted by a pressure regulator, RV1 (Circle Seal, Anaheim, CA) and checked by the manometer M2. The excess output of the compressor is fed back into the gas tank, G. The flow rate of carbon dioxide through the extraction vessel, E, is regulated by the valve RV2 (C.T. GmbH, Hamburg, Germany) through which the gas is allowed to expand. The pressure in the preseparator, S1, is kept constant by the pressure regulator RV3; it can be read off the manometer M3. The flow rate of carbon dioxide is measured by a flow meter FM (Brooks Instrument GmbH, Pinneberg, Germany) that is installed after the two separators S1 and S2. The oil dissolved is precipitated from the gaseous phase, which means that the temperature in the



**Figure 3.** Distribution of residual oil (percent) in various segments of a bed of ground soybeans contained in the extraction vessel E, after treatment with carbon dioxide. For experimental conditions, see the text.

preseparator, S1, is kept above the critical temperature of carbon dioxide and in the final separator, S2, above its liquefaction temperature. Thus, extracts free of water can be obtained at temperatures exceeding 40 °C.

**Extraction with Liquid or Supercritical Carbon Dioxide.** The ground seeds to be extracted (50–300 g) are filled in the extraction vessel, E, and stamped down carefully. In order to remove air, the entire installation is rinsed repeatedly with carbon dioxide at a pressure of  $\sim$ 10 bar. During this operation, the valves V5, V6, RV2, and V8 are kept open, whereas V7, V9, and V10 are closed; the gas is released via V9 while V2 is kept closed. When the apparatus has reached the desired temperature, it is filled with carbon dioxide in several steps. First, the pressure adjusted at V1 is established throughout the installation by opening V2 and V10. The compressor, C, is then started, V5 being closed and V3 being open, and its output pressure is increased by the pressure regulator RV1. When the desired pressure is reached, V5 is opened and thus the extraction vessel, E, is filled with carbon dioxide. If the oil is to be precipitated in two steps, V6 and RV2 are kept open, for a while, and the pressure desired for trapping it in S1 is adjusted at RV3. The valve V6 is closed when this pressure is reached.

Extraction is started by opening valve V6 and adjusting the flow rate of carbon dioxide at RV2. The extracted oil is collected in test tubes that are placed in the separators S1 and S2. For fractional recovery of the oil, the extraction process can be interrupted for a few minutes. Alternatively, the extract can be withdrawn through valve V7. Such a valve may be installed also at S1; in this case, the gas outlet is fitted on top of the separator. After separation, the gas is released through the sorption filter F and the flow meter FM. After the extraction process is terminated, the valve V5 has to be closed, thereby reducing the output pressure of the compressor to a pressure slightly above that prevailing in the gas tank, G, and pumping the excess carbon dioxide back into this tank. Valves V5 and V10 are then closed, and the gas remaining in the apparatus is released through V9.

## RESULTS

**Extraction of Seed Oils with Carbon Dioxide.** In order to assess the solubility of seed oils in carbon dioxide, ground soybeans were treated at a pressure of 200–250 bar and a temperature of 40 °C with supercritical carbon dioxide for 60 min. The contents of the extraction vessel were cut into nine segments of equal length, and, after extraction with hexane, the oil that had remained in each section was determined gravimetrically. Figure 3 shows the distribution of oil over the nine zones.

It is evident that, after 60-min extraction with carbon dioxide, the oil content of the first two zones amount to

Table I. Extraction and Stepwise Recovery of Seed Oils

extraction pressure, bar	temp, °C	first fraction		yield, %	second fraction, yield, %	total yield of oil, %
		pressure, bar	temp, °C			
300	50	Decrease in Pressure (Rapeseeds)		28.4	4.4	32.8
		180	50			
300	40	Increase in Temperature (Sunflower Seeds)		34.5	11.7	46.2
		300	75			
200	20	200	75	36.7	4.3	41.0
Decrease in Pressure and Increase in Temperature (Sunflower Seeds)						
300	40	200	60	36.7	8.8	45.5
350	40	90	50	30.7	0.6	31.3

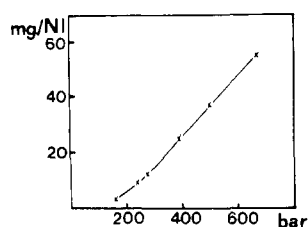


Figure 4. Solubility of sunflower seed oil in carbon dioxide at various pressures and a temperature of 40 °C.

less than 2%, each, whereas from the fifth zone on the oil level remaining in the ground seeds amounts to 15–17%. Thus, it can be presumed that in the initial phase of extraction a saturated solution of oil in carbon dioxide is attained.

The initial treatment with carbon dioxide yielded 6% of oil and the subsequent extraction of the ground soybeans afforded another 10.1%.

Additional experiments showed that over a wide range of flow rates the concentration of oil in carbon dioxide is independent of the flow rate of the gas. The pressure of carbon dioxide during extraction, however, is of great significance. By use of sunflower seeds as an example, Figure 4 shows that, at a temperature of 40 °C, the concentration of oil in supercritical carbon dioxide increases with increasing pressure during extraction. From ~300 bar on, this increase in the concentration of the oil as a function of the pressure of carbon dioxide proceeds in a linear fashion; at 700 bar it reaches a value of 55 mg/NL, which corresponds to ~3%, by weight (1 NL = 1 L of gas at 293 K and 1 atm).

Not only the solubility of an oil in supercritical carbon dioxide but also the solubility in liquid carbon dioxide increases with pressure, though at a different rate. As an example, Figure 5 shows the increase in concentration of soybean oil when the seeds are treated either with supercritical (curve 1) or with liquid carbon dioxide (curve 2).

Obviously, at pressures below 250 bar, the concentration of oil is higher in liquid carbon dioxide whereas above 250 bar its concentration is higher in supercritical carbon dioxide. Apparently, the effect of pressure on the solubility of a seed oil is much more pronounced when supercritical carbon dioxide is used for its extraction. The concentration of oil in supercritical carbon dioxide is a decisive factor in the amount of carbon dioxide needed for the extraction of the oil from a certain amount of seeds. By use of sunflower seeds (100 g) as an example, Figure 6 shows the yields of oil at pressures of 660–700 and 250–280 bar, respectively, and at a temperature of 40 °C, as well as the concentration of oil in carbon dioxide at these pressure ranges.

It is obvious that, at a pressure of 660–700 bar and a temperature of 40 °C, the extraction of 40 g of oil requires

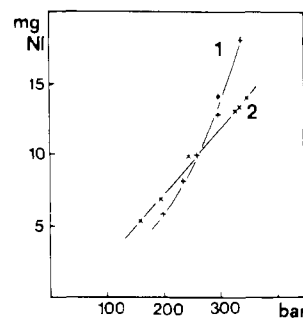


Figure 5. Solubility of soybean oil in supercritical (curve 1) and liquid (curve 2) carbon dioxide at various pressures and at temperatures of 40 and 20 °C, respectively.

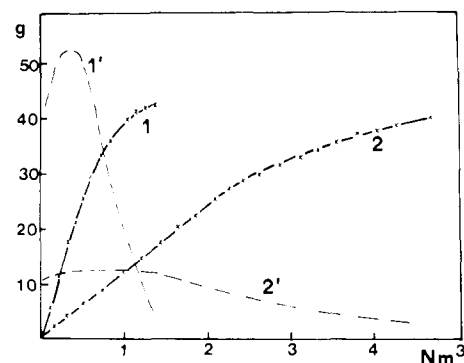


Figure 6. Yields of sunflower seed oil at pressures of 660–700 bar (curve 1) and 250–280 bar (curve 2) and a temperature of 40 °C. The concentration of oil in carbon dioxide at the two pressure ranges is given by curves 1' and 2'.

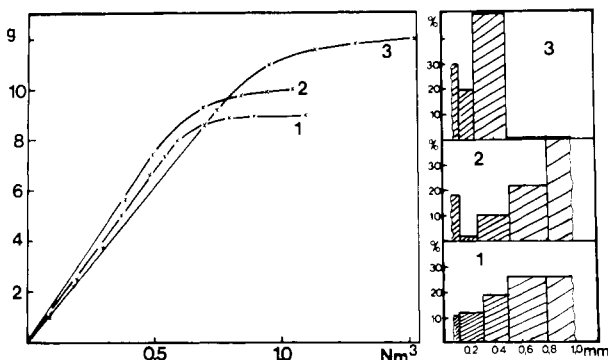
~1.1 Nm<sup>3</sup> of carbon dioxide (curve 1) whereas at 250–280 bar and 40 °C the extraction of 40 g of oil requires more than 4 times this amount of carbon dioxide (curve 2) (1 Nm<sup>3</sup>, at 293 K, 1 atm, corresponds to ~1.8 kg of carbon dioxide). At the higher pressure, the concentration of oil in carbon dioxide decreases rapidly after ~0.7 Nm<sup>3</sup> have flown through the bed of ground seeds (curve 1') whereas at the lower pressure the concentration of oil in carbon dioxide remains fairly constant until ~1.5 Nm<sup>3</sup> have been used (curve 2'). Thus, an increase in pressure to over 300 bar can obviously be of advantage, a fact which is in contrast to our experiences so far. We assume the following two reasons to be responsible: a different solubility behavior of the lipids and a relatively high oil content of the seeds.

As an increase in the pressure of carbon dioxide leads to an increase of the solubility of an oil, a decrease in pressure after extraction should be useful for recovering the oil. It should be possible to achieve the same effect by increasing the temperature of the solution. The data given in Table I show how a stepwise decrease in pressure, an increase in temperature, or both can be used to recover

Table II. Extraction and Recovery of Seed Oils

seeds	extraction with hexane, <sup>a</sup> yield, %	extraction with carbon dioxide				
		pressure, bar	temp, °C	time, min	yield, %	residual oil %
soybeans	19.9	280	20	150	16.6	3.3
		300	40	120	16.4	3.1
sunflower seeds	38.4	250-300	20	150	35.0	1.5
		320-350	40-50	150	36.0	2.3
rapeseeds	40.1	320	17	180	38.2	4.5
		350	40	180	39.3	3.9

<sup>a</sup> Extraction was carried out in a Soxhlet apparatus.



**Figure 7.** Yields of oil extracted from ground soybeans of different size and shape (1, 2, and 3) (left). The distribution of particle sizes in samples 1, 2, and 3 is given (right). 1, 83 g of beans crushed in a laboratory grinder; 2, 80 g of beans crushed in a cross-beater mill; 3, 80 g of beans crushed in a laboratory grinder.

an oil in fractions. In all cases, final recovery was achieved below the critical pressure and at a temperature that yielded an oil free of water, that is, 30–65 bar and 40–55 °C.

Experiments with sunflower seeds showed that even at supercritical pressures the oil can be recovered in a large amount by increasing the temperature. In a continuous technological process, recovering an oil solely by increasing the temperature would offer the advantage of requiring less energy than would be needed if the same effect were accomplished by decreasing the pressure. The data given in Table II show that both liquid and supercritical carbon dioxides can be used to extract almost all of the oil that can be obtained from various seeds by conventional extraction with hexane.

As in all extraction processes, the seeds have to be ground to assure a satisfactory extraction of the oil. Thus, it is almost impossible to recover any oil by treating intact rapeseeds with liquid or supercritical carbon dioxide; between 96 and 98% of the oil can be extracted, however, from rapeseeds that have been ground to 40–120 mesh.

It should be noted that not only the size of the ground seed but also their shape affect the yields of oil. As an example, Figure 7 demonstrates the differences in the time course of extraction as well as the yield of oil when soybeans ground by different methods are treated with liquid or supercritical carbon dioxide.

Gas-chromatographic analyses of the methyl esters of the constituent fatty acids of oils extracted with hexane or carbon dioxide showed no significant differences.

Samples of soybean, sunflower seed, and rapeseed oils that were obtained by a stepwise process differed greatly in their color, taste, and odor. Some pertinent observations are summarized in Table III.

**Table III.** Characteristic Properties of Seed Oils Extracted and Recovered under Different Experimental Conditions

source of oil	fractions	characteristics
soybeans	(1) 200 bar, 40 °C	clear yellow oil, odorless
	(2) 40 bar, 40 °C	turbid yellow oil, maltlike odor
sunflower seeds	(1) 150 bar, 40 °C	clear light yellow oil, colorless
	(2) 40 bar, 40 °C	turbid brown oil, acidic odor
rapeseeds	(1) 180 bar, 50 °C	clear yellow oil, slightly bitter taste, odorless
	(2) 45 bar, 50 °C	turbid yellow oil, bitter taste, mustardlike odor

It is noteworthy that the fractions obtained by separation from the miscella at relatively high pressure were clear and less colored than those that were isolated at much lower pressures. Moreover, the fractions isolated at "high" pressures had superior organoleptic properties as compared to those obtained at "low" pressures.

Instead of separating most of the oil from the solution at a fairly high pressure and the rest at a much lower pressure, the opposite sequence may be applied to the same end. Thus, extraction of sunflower seeds with carbon dioxide at 150 bar and a temperature of 40 °C yielded a turbid yellow oil having a definite odor; subsequent extraction of the major portion at 330 bar and the same temperature afforded a clear, yellow, and almost odorless oil.

The method can be used also for refining sunflower oil by treating it with carbon dioxide at a pressure of 150 bar and a temperature of 40 °C. The oil obtained as a residue was clear and light yellow whereas the fraction that had been washed out was turbid and brown.

These results demonstrate the efficiency of the use of liquid and supercritical carbon dioxide both for extracting and refining seed oils.

## DISCUSSION

The method of extracting natural products with liquified or supercritical gases is still in a state of development. In a few cases the experience gained in work on the laboratory scale have been scaled up to pilot plant and even technical applications (Schneider et al., 1980).

The results of our study on the extraction of seed oils by means of liquid and supercritical carbon dioxide permit an evaluation of the factors that have to be considered in trying to apply the method on a large scale.

We have shown that the amount of carbon dioxide needed depends to a large extent on the pressure and

temperature used during extraction. In our experience, liquid and supercritical carbon dioxides at pressures of at least 250 bar and a temperature of 20 and 40 °C, respectively, are equally suitable for the extraction of oilseeds. At pressures over 300 bar, however, liquid carbon dioxide is inferior to supercritical carbon dioxide with regard to dissolving power. Moreover, still higher pressures reduce the amount of carbon dioxide required to extract a certain amount of oil. Thus, the extraction of 40% oil of sunflower seed at 260 bar requires 47 NL/g of seeds whereas at 700 bar only 11 NL of carbon dioxide/g of seeds is needed. Other natural products are, as a rule, best extracted at pressures below 200 bar.

The yields of oil that can be extracted with liquid or supercritical carbon dioxide are comparable to those obtained by conventional solvent extraction. The use of carbon dioxide offers the advantage, however, that the quality of the extracted oil can be influenced by varying the parameters of the extraction process. Moreover, the oils obtained by extraction with liquid or supercritical carbon dioxide are of course free of organic solvents, whose complete removal is a time- and energy-consuming process in present-day oil technology. Last but not least, extraction with carbon dioxide at ambient temperature is quite obviously of great advantage if the seed proteins are to be recovered because extraction with hot organic solvents invariably leads to pronounced denaturation of these proteins.

The use of liquid and supercritical gases including carbon dioxide for the extraction of compounds of "high molecular weight" has been suggested, more than 40 years ago, in some patents (Pilat and Godlewicz, 1936a,b). The same principle has been recommended for extracting fats and oils (Dickinson, 1947; Groll, 1953; Palmer and Fanwood, 1950), yet practical applications have not been described.

In the sixties, the idea of extracting lipids and other natural products with liquid or supercritical carbon dioxide has gained new impetus (Zosel, 1964). It has been demonstrated that lipids can be extracted from copra, sunflower seeds, soybeans, and shelled peanuts with carbon dioxide at pressures ranging from 280 to 350 bar (Vitzthum and Hubert, 1972). Moreover, it has been shown that the constituents of lipid mixtures that usually are separated by vacuum distillation at fairly high temperatures can be resolved under much milder conditions by fractional recovery from their solution in supercritical gases. The use

of a "carrier" has been recommended for the efficient fractionation of complex mixtures (Peter et al., 1976).

Systematic studies have been facilitated by the development of an apparatus for the extraction of natural products with supercritical carbon dioxide on a microscale (Stahl and Schilz, 1976). By means of this piece of equipment, it has been found recently that in the pressure range from 80 to 200 bar a solubility can be reached which is sufficient for the extraction of many nonpolar compounds. For polar, almost insoluble substances, extending the pressure up to 2500 bar does not lead to substantial improvements (Stahl et al., 1978). However, we found that in a preparative extraction plant (Schütz, 1979) terpenes, for example, can be completely extracted in the range up to 160 bar (Stahl and Schütz, 1978). Contrary to these results, it has been shown that the solubility of lipids increases steadily in the range above 160 bar (Schilz, 1978).

#### ACKNOWLEDGMENT

We thank A. Hübgen, who has built the apparatus used in the present investigation.

#### LITERATURE CITED

- Chalvardjian, A. *Biochem. J.* **1964**, *90*, 518.  
Dickinson, J. T. U.S. Patent 2 660 590, 1947.  
Groll, H. P. A. German Auslegeschr. 1 079 636, 1953.  
Mangold, H. K.; Malins, D. C. *J. Am. Oil Chem. Soc.* **1960**, *37*, 383.  
Palmer, G. H.; Fanwood, N. J. U.S. Patent 2 658 907, 1950.  
Peter, S.; Brunner, G.; Riha, R. *Fette, Seifen, Anstrichm.* **1976**, *78*, 45.  
Pilat, S.; Godlewicz, M. U.S. Patent 2 188 012, 1936a.  
Pilat, S.; Godlewicz, M. U.S. Patent 2 188 013, 1936b.  
Schilz, W. Ph.D. Thesis, Saarbrücken, 1978.  
Schneider, G. M.; Stahl, E.; Wilke, G., Eds. "Extraction with Supercritical Gases"; Verlag Chemie: Weinheim, Germany, 1980.  
Schütz, E. Ph.D. Thesis, Saarbrücken, 1979.  
Stahl, E.; Schilz, W. *Chem.-Ing.-Tech.* **1976**, *48*, 773.  
Stahl, E.; Schilz, W.; Schütz, E.; Willing, E. *Angew. Chem.* **1978**, *90*, 778.  
Stahl, E.; Schütz, E. *Arch. Pharm. (Weinheim, Ger.)* **1978**, *331*, 992.  
Vitzthum, O. G.; Hubert, P. German Offen. 2 127 596, 1972.  
Zosel, K. German Auslegeschr. 1 493 190, 1964.

Received for review March 5, 1980. Accepted July 28, 1980. This research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.