Petroleum-Free Extraction of Oil from Soybeans with Supercritical CO_2

J.P. FRIEDRICH, G.R. LIST and **A.J. HEAKIN**, Northern Regional Research Center,
ARS, USDA, Peoria, IL 61604

ABSTRACT

Full-fat soyflakes are readily extracted with supercritical carbon dioxide (SC-CO_2) at pressures of 3,000-10,000 psig and 50 C. Under these conditions, SC-CO_2 has the density of a liquid and the diffusivity of a gas. Therefore, equilibrium solubility is readily achieved in a short-path batch extractor which permits high gas flow rates. Soybean oil extracted with SC-CO_2 is lighter in color and contains less iron and about one-tenth the phosphorus of hexane-extracted crude oil from the same beans. The lower phosphorus content is reflected in a chromatographic refining loss of 0.6% compared to 1.9% for hexane crude. Refined oils from hexane and SC-CO_2 extraction had equivalent odor and flavor scores initially and after 4 days' storage at 60 C. Carbon dioxide, an ideal solvent for extraction of food products, is low-cost and readily available from fermentation processes and could free over 20 million gallons of costly hexane per year for essential energy uses.

INTRODUCTION

Over one billion bushels (30 million tons) of soybeans are crushed each year for domestic use. Hexane has long been the preferred solvent for extracting the 6 million tons of oil from these beans. Recently, economic and social factors have revived interest in government and industry to seek cheaper and safer solvents. Ethanol and isopropanol have been suggested, but ethanol is not an effective solvent at the concentration of its water azeotrope and further rectification is costly. Likewise, isopropanol has a higher boiling point and therefore is difficult to remove from both oil and flakes.

Supercritical fluids technology may be a viable alternative to current extraction methods. Supercritical fluids (SCF) are often called dense gases (1). Technically, an SCF is a gas existing above its critical temperature and critical pressure, as defined in the phase diagram of the pure substance. A gas, at or above its critical temperature, increases in density dramatically when it is compressed. Therefore, under a given set of conditions, an SCF may possess the density (solute holding capacity) of a liquid while maintaining the diffusivity of a gas. The solvent properties of SCF have been recognized for over 100 years (2) but commercial applications have been slow in developing, possibly due to the sophisticated and expensive high pressure equipment and technology required. Although pressures to 3,000 atm are common in the chemical industry today, applications have been in liquid systems operated in a continuous manner. With the rapidly escalating costs and uncertain availability of petroleum solvents (3,4), and with the potential health- and safety-related problems of both hydrocarbon and chlorinated hydrocarbon solvents, the social and economic environment has stirred renewed interest in SCF. Decaffeination of coffee apparently is the only current commercial large-scale SC-CO_2 process (5). A recent review (6) lists 21 patents related to SCF extraction of food products.

SC-CO_2 is an ideal solvent because it is nontoxic, nonexplosive, cheap, readily available and easily removed from the extracted products. The extraction of oil seeds, including soybeans, with SC-CO_2 has been reported (7-9), but analytical and organoleptic data comparing SC-CO_2- and hexane-extracted oils are needed to properly evaluate the potential of SC-CO_2 extraction and processing. A preliminary communication (10) from this laboratory reported the extraction of soybeans with SC-CO_2 at 5,000 psig and 50 C. Analyses of crude soybean oil obtained under these conditions were compared with those of hexane-extracted oil from the same beans.

This study is a full report of this work and extends the previous extraction parameters, follows the fate of some of the minor constituents during the course of the extraction and compares orgaoleptic properties of refined SC-CO_2 and hexane crude oils.

EXPERIMENTAL PROCEDURES

Materials

Commercial-grade carbon dioxide was obtained in 60-lb cylinders from Matheson (Joliet, IL). Soybeans were obtained commercially, as well as crude oil extracted from the same beans.

These beans (9.8% moisture) were cracked, dehulled and flaked without further treatment to produce flakes with a thickness of .015-.020 in. These flakes were stored at -20 C to prevent enzymatic deterioration until they were extracted.

Analytical Methods

AOCS official methods (11) were used for the analyses. Individual methods are referenced in Table I.

Extraction Equipment and Procedures

Hardware for the SC-CO_2 extraction system described next was purchased from the following manufacturers: 10,000 psi double-ended diaphragm compressor (Superpressure Equipment Co., Silver Spring, MD); back pressure relief valve (Haskel Inc., Burbank, CA); instantaneous flow meter (Fischer and Porter Co., Warminster, PA); dry test flow totalizer (Singer Am. Meter Div., Philadelphia, PA); high pressure tubing, shut-off valves, micrometering valves, check valves, filters, fittings, adapters, pressure gauges, extraction cylinder and receiver (Autoclave Engineers, Erie, PA); and heating mantles and tapes (Glas-col, Terre Haute, IN).

A flow diagram of the extraction apparatus is shown in Figure 1. One or more cylinders of commercial-grade CO_2 (A) are placed on a 1,000-lb-capacity scale (B) with ½ oz sensitivity. The cylinders are wrapped with heating tapes controlled by an electric contact face on the cylinder pressure gauge (TP). Cylinder pressure is maintained at 1,200-1,250 psig, providing a nearly constant suction pressure for the compressor. The pressure gauge and cylinders are protected by a 1,500-psi rupture disc (RD-1). The gas passes through 1/8 in., 11,000 psi, 304 SS tubing and check valve (CV) to a 5-μ particulate filter (F-1), which protects the compressor diaphragms from scale and other foreign matter. The 10,000-psi, double-end, air-driven compressor (C) delivers about 19 standard L/min at 8,000 psi with a suction pressure of 1,000 psig. The gas pressure is controlled by a variable (2,000-25,000 psig) back pressure relief valve (RV). The temperature (TC-1) and regulated pressure (RP) of the gas are measured prior to entering the manifold

TABLE I

Comparison of $SC\text{-}CO_2$- and Hexane-Extracted Crude Soybean Oil

Analyses	AOCS Method[a]	Hexane	$SC\text{-}CO_2$
Yield	Ac 3-44	19.0	18.3
Residual oil (%)	Ac 3-44	0.7	2.1
Chromatographic refining loss (%)	Ca 9f-57	1.9	0.6
Free fatty acid (%)	Ca 5a-40	0.6	0.3
Peroxide value (meq/kg)	Cd 8-53	<0.1	<0.1
Unsaponifiables (%)	Ca 6a-40	0.6	0.7
Fe (ppm)	Ca 15-75	1.45	0.3
Phosphorus (ppm)[b]		505	45

[a] *AOCS Official and Tentative Methods* (11) (1975).

[b] Phosphorus determination by atomic absorption (13).

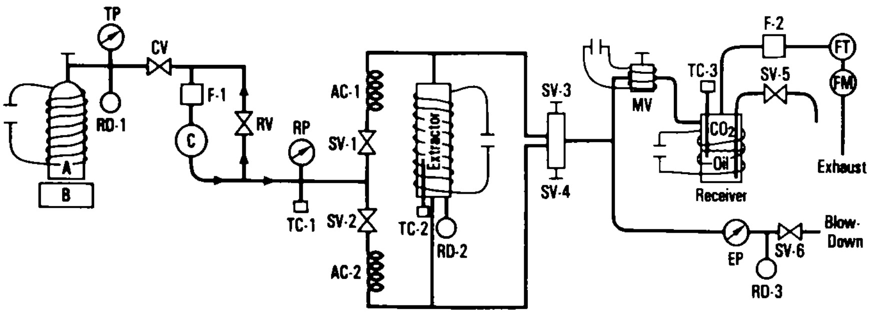

FIG. 1. Supercritical carbon dioxide extraction apparatus: (A) CO_2 cylinder, (B) balance, (TP) tank pressure, (RD1-3) rupture disc assemblies, (CV) check valve, (F1&2) gas filters, (C) diaphragm compressor, (RV) back pressure regulating valve, (RP) regulated gas pressure (TC1-3) thermocouples, (SV1-6) shut-off valves, (AC1&2) gas coolers, (MV) micrometering valve, (FM) flow meter, (FT) flow totalizer and (EP) extractor pressure.

leading to the extractor. The 2-L extractor (2-7/16 in id × 29-1/4 in long) is a hydraulic cylinder made of 4340 steel with a working pressure of 15,000 psi at room temperature. The head, which contains gas inlet, thermocouple (TC-2), rupture disc (RD-2) and glass wool particulate filter, is threaded into the cylinder and sealed with a standard O-ring closure. The compressed gas is then allowed to flow through the vertically mounted extractor in either direction by opening and closing the appropriate shut-off valves (SV-1, 2, 3 and 4). If the compressed gas temperature is above that required for the extraction (temperature varies with pressure), the gas is passed through an air cooler (AC-1 or 2) prior to entering the temperature-controlled extractor. The oil-laden gas leaves the extractor and passes through a temperature-controlled micrometering valve (MV) into a temperature-controlled, 1-L receiver. The receiver is slightly above atmospheric pressure, so the pressure drop across MV results in rapid cooling. Without applied heat, the extracted oil would freeze in MV and make flow control impossible.

The oil and gas phases separate in the receiver. The oil settles to the bottom and can be withdrawn as desired through (SV-5). The CO_2 is passed through a filter (F-2) to remove entrained oil (<0.5% under all extraction conditions tried) and then through an instantaneous flow meter (FM) and a flow totalizer (FT) before being exhausted. Any pressure drop across the extractor is shown by a difference between regulated pressure (RP) and extractor pressure (EP). Likewise, any CO_2 leak in the system is indicated by a difference between the CO_2 weight loss measured at (B) and the total flow through the system (FT). A final rupture assembly (RD-3) is placed just ahead of the blowdown valve (SV-6) for the entire system. During the extraction, the micrometering valve (MV) is adjusted until the desired flow (within compressor capacity) is indicated on the instantaneous flow meter (FM). The excess compressor capacity is then recycled through the backpressure valve.

Extraction of Soybean Flakes

One kg of full-fat soybean flakes was removed from cold storage and poured into the 2-L extractor. Some packing was required because of the low bulk density (0.4-0.5 g/cc) of the flakes. The extractor was sealed and brought to 8,000 psig while it was being heated to a controlled 50 C with heating tape. The temperature of the compressed gas was about 70 C and was passed through an air cooler prior to entering the top of the extractor. The micrometering valve was opened slowly until the reactor pressure began to drop and then closed slightly to bring the pressure back up to 8,000 psig. This procedure allowed maximal flow with only enough recycle gas to insure a stable pressure. With a CO_2 cylinder pressure of 1,100-1,200 psi, a flow of 15-18 standard L/min was maintained. The receiver was heated (60 C) to remove extracted water from the recovered oil. Oil was completely withdrawn from the receiver at various times, and the weight of oil and CO_2 consumed were recorded. Oil solubility (g oil collected/g CO_2 consumed) was calculated from these data, and the oil fractions were later analyzed for minor constituents. When the extraction rate began to drop, the CO_2 flow rate was decreased by 7-10 L/min, and the extraction was continued until less than 1 g of oil/hr was obtained. The extractor was depressurized and allowed to stand overnight because the nitrile rubber O-ring closures absorb CO_2 and cannot be easily removed until they decompress in place for several hours. The head was removed and the flakes were transferred pneumatically. A total of 183 g of oil and 783 g of flakes (8.1% moisture) was obtained.

The hexane-extracted oil was degummed, alkali-refined, bleached and deodorized by conventional methods (12).

RESULTS AND DISCUSSION

Extraction curves (Fig. 2) show the increase in extraction efficiency with increase in pressure from 5,000 psig to 8,000 psig at 50 C. The straight-line (constant extraction rate) portion of the curves indicates that equilibrium solubility is readily established and maintained until nearly 90% of the oil is extracted. During this portion of the extraction, the rate-limiting factor is the gas flow or compressor capacity. However, extremely high flow rates can result in packing and cause an undesirable pressure drop across the column. Passing the SC-CO_2 under the same conditions and at the same rate through an extractor of roughly one-sixth the cross-sectional area of the larger extractor increased the linear velocity 6-fold and resulted in packing. These results indicate that the ratio of length to cross-sectional area is also important in maximizing extraction efficiency. As the flakes reach low oil levels (last 10% of the oil), it is more efficient to reduce CO_2 flow rate because the extraction rate is not improved by operating significantly below equilibrium solubility conditions.

The solubility of soybean lipids in SC-CO_2 is strongly influenced by pressure (Fig. 3). The 50 C solubilities at pressures above 6,000 psig are less, and those below 6,000 psig are greater than those for similar extraction at 60 C. This cross-over of the solubility curves may be related to the densities of the SC-CO_2. Between its critical pressure (1,070 psig) and 6,000 psig, CO_2 is quite compressible. The density, which is related to solute holding power, changes rapidly in this range, whereas above 6,000 psig, the density does not change as rapidly. Therefore, the expected increase in solubility with increase in temperature would be observed at the higher pressures; but at the lower pressures, the increased solubility effect due to temperature may be overcome by the decrease in density and related decrease in solute holding power. On this basis, extraction efficiency should be maximized at the highest temperature that is consistent with product integrity and at the highest practical pressure exceeding about 6,000 psig.

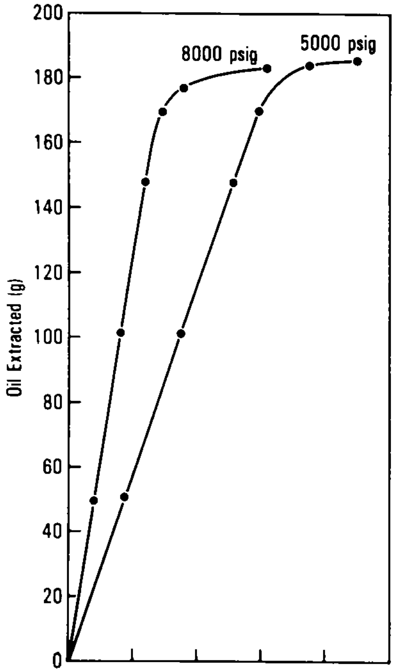

FIG. 2. Effects of pressure on the extraction efficiency of soybean flakes at 50 C.

The insolubility of phospholipids in SC-CO_2 is evidenced by the low phosphorus content of all oil fractions (Fig. 4). As expected, some fractionation takes place with increasing concentrations of phosphorus appearing in the smaller final 2 fractions. The sparing solubility of phospholipids in SC-CO_2 is further substantiated by the significantly lower chomatographic refining loss compared to hexane-extracted oil (Table I). Therefore, the slightly lower oil yield (18.3%)

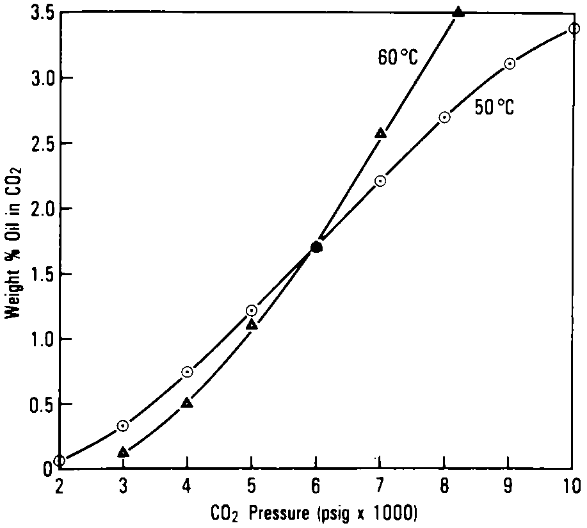

FIG. 3. Effects of temperature and pressure on solubility of soybean oil in supercritical carbon dioxide. Data points on curves represent an average of 2 or 3 determinations.

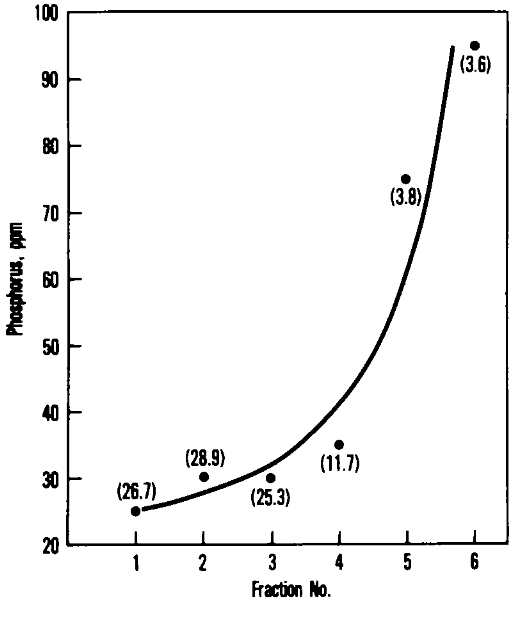

FIG. 4. Phosphorus content of soybean oil fractions extracted with supercritical carbon dioxide at 8,000 psig and 50 C. Numbers in parentheses are the percentages of the total oil represented by each fraction.

and higher residual oil content of the flakes (2.1%) from SC-CO_2 extraction compared to hexane extraction (19 and 0.7%) are somewhat misleading. The hexane-extracted oil contains about 1.5% phospholipids (13) based on the accepted calculation (% phosphorus × 31.7), whereas the SC-CO_2-extracted oil contains about 0.13% on the same basis. Likewise, the residual oil from the SC-CO_2-extracted flakes is very high in phosphorus (2,500-3,000 ppm).

Fractionation also is observed with the unsaponifiables (Fig. 5); However, there is no significant difference in total unsaponifiables between SC-CO_2- and hexane-extracted oils (Table I). Free fatty acids, because of their lower molecular weight, would be expected to concentrate in the earlier oil fractions; although this is observed through the first 3 fractions (Fig. 6), the final 3 fractions show increases. These acids have not been isolated or identified. They constitute a very small percentage of the free acids in the oil and, based on their lower solubility in SC-CO_2, may have higher molecular weight or more functionality than typical FFA. The iron content of commercially extracted hexane crude oil is significantly higher than SC-CO_2 crude oil (Table I). Like the phosphorus, the iron content of hexane oil is reduced to the same levels found in SC-CO_2 oil by degumming and alkali refining (Table II).

The refined, bleached and deodorized (RBD) SC-CO_2 oil has good quality (Table III). The odor and flavor scores initially and after 4 days' storage at 60 C are not significantly different than the RBD oil obtained from degummed hexane crude oil. SC-CO_2 extraction, therefore, has the advantages of using a safe, readily available, low-cost solvent and of eliminating a processing step (degumming) and its attendant oil losses without sacrificing quality of the finished oil. SC-CO_2 is also a more versatile solvent than hexane in that its solvent properties are affected significantly by changes in pressure and temperature. Evaluation of the meals and extraction of other seed oils will be the subject of future publications.

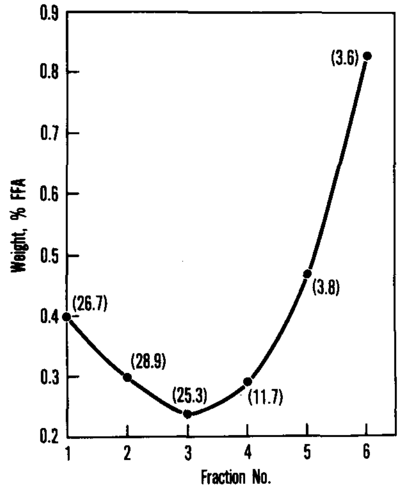

FIG. 6. Free fatty acid content of soybean oil extracted with supercritical carbon dioxide at 8,000 psig and 50 C. Numbers in parentheses are the percentages of the total oil represented by each fraction.

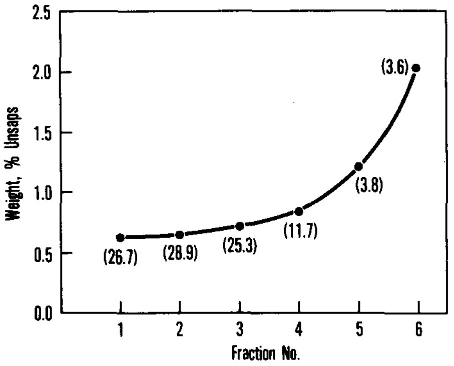

FIG. 5. Unsaponifiable content of soybean oil fractions extracted with supercritical carbon dioxide at 8,000 psig and 50 C. Numbers in parentheses are the percentages of the total oil represented by each fraction.

TABLE II

Effect of Oil Processing on Phosphorus[a] and Iron Contents

Processing step	Hexane Fe (ppm)	Hexane P (ppm)	SC-CO_2 Fe (ppm)	SC-CO_2 P (ppm)
Crude	1.45	505	0.3	45
Degummed	0.69	63	—	—
Refined	0.11	28	0.07	35
RB[b]	0.09	25	0.08	25
RBD[c]	0.09	12	0.11	20

[a] Phosphorus determination was by atomic absorption (14). Values for refined, RB and RBD oils are near lower detection limits for AA method.

[b] Refined and bleached.

[c] Refined, bleached and deodorized.

TABLE III

Odor and Flavor Scores and Descriptions[a] for Hexane- and SC-CO_2-Extracted Soybean Oil

Descriptions		Odor Hexane		Odor SC-CO_2	Flavor Hexane		Flavor SC-CO_2
	O-Time:	8.6	NS[b]	7.8	7.5(0.0)[c]	NS	7.8(0.0)
Buttery		0.2		0.2	0.7		0.5
	4 days, 60 C:	7.6	NS	7.1	6.6(1.3)	NS	6.0(1.7)
Buttery		0.6		0.9	0.6		0.9
Beany		0.3		0.3	0.3		0.4
Grassy		—		—	0.3		0.5
Rancid		0.3		0.3	0.4		0.2
Nutty		—		—	0.3		—

[a] Ref. 15.

[b] No significant difference.

[c] Peroxide values (meq/kg).

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Glyceride Composition of Processed Fats and Oils As Determined by Glass Capillary Gas Chromatography

R.P. D'ALONZO, W.J. KOZAREK and **R.L. WADE**, The Procter & Gamble Company, Cincinnati, OH 45241

ABSTRACT

Refined and bleached fats and oils can be analyzed directly by high-temperature glass capillary column gas chromatography after derivatization of the fatty acids, mono- and diglycerides with BSTFA [(N,O)-bis(trimethyl silyl) trifluoroacetamide]. The intact glycerides are separated on the basis of volatility to provide characteristic carbon number profiles (CNP). Quantitative information on mono-, di- and triglycerides, as well as free fatty acids, is obtained from a single, rapid separation. Profile values are reported for 13 different processed fats and oils. The analysis performed in the split-injection mode maintains column integrity after numerous separations, while producing acceptable relative standard deviations.

INTRODUCTION

The gas chromatographic (GC) separation of triglycerides according to their total number of carbon atoms has been done for nearly 20 years (1-4). In this laboratory, a procedure has been established to extend the carbon number profile (CNP) analysis to mixtures of fatty acids, mono- and diglycerides after derivatization with BSTFA, in addition to the triglyceride profiling. This procedure has used short-packed columns with on-column injection, but recently has been replaced by glass capillary columns with split injection. Several workers have identified the advantages of glass capillary chromatography for this type of application (5-8).

We have reported previously the details on the analysis of soybean oil by capillary GC (8). The same procedure has been applied to the quantitative CNP analysis of 13 refined and bleached fats and oils, and the results are reported here.

EXPERIMENTAL

Equipment

A Hewlett-Packard Model 5880A (level 2) gas chromatograph, equipped with a flame ionization detector and capillary inlet system, was used for all separations. The chromatograph was interfaced to a Hewlett-Packard Model 3351B data system with 32K memory for data processing and report formating.

Reagents

BSTFA [(N,O)-bis(trimethyl silyl) trifluoroacetamide] (Pierce Chemical Company) was used as a derivatizing reagent for the free fatty acids, mono- and diglycerides to form the corresponding trimethyl silyl esters and ethers. Derivatization prevents both glyceride rearrangement side reactions and peak tailing. Reagent-grade methylene chloride (MC/B Manufacturing Chemists, Inc.) and all glyceride reference standards (Applied Science Division) were used as received.

Preparation of Glyceride Standard Mixtures

A primary mixture of glycerides used to determine response factors was prepared by dissolving known amounts of pure fatty acids, mono-, di- and triglycerides in 100 mL of methylene chloride according to Table I. The mixture is stable for several weeks under refrigeration. For samples containing components for which there were no corresponding reference standards, an average response factor obtained from neighboring reference peaks was assigned to the unknown. For example, the average response factor of the

TABLE I

Composition of Primary Glyceride Standard Mixture

Amount (mg)	Component	Notation
50	Palmitic acid	C16A
50	Stearic acid	C18A
50	Monopalmitin	C16M
50	Monostearin	C18M
50	Dipalmitin	C32D
50	Palmitostearin	C34D
50	Distearin	C36D
150	Tripalmitin	C48T
150	Dipalmitostearin	C50T
150	Distearopalmitin	C52T
150	Tristearin	C54T