

## A Comparative Study of the Composition of Lipids Associated with Starch Granules from Various Botanical Sources

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Lipids from highly purified wheat, rice, corn, fababean, lentil, potato and cassava starches were extracted by acid hydrolysis and by selective solvent extraction with chloroform-methanol 2:1 v/v [CM] at ambient temperature, followed by n-propanol-water 3:1 v/v [PW] at 90-100°C. The acid hydrolyzed extracts which represented the total starch lipid [TSL] content ranged from 0.1% (potato) to 0.8% (corn). The combined action of CM and PW resulted in almost complete removal of starch lipids (>98.6%) from most of the starches, the exception being wheat, where the solvent extraction efficiency (% TSL) was 96.3%. The free lipids in the CM extracts (% TSL) ranged from 5.0% (corn) to 62% (fababean), whereas the free and bound lipids in the PW extracts ranged (% TSL) from 44.2% (potato) to 94.8% (corn). Neutral lipids (NL) formed the major lipid class in the CM extracts of all starches, while in PW extracts these were NL in corn and cassava, NL and phospholipids (PL) in potato, and PL in wheat, rice and fababean. There was a great variation among the starches with respect to the major components of the lipid classes in both CM and PW extracts. Monoacyl lipids were most abundant in cereal starches (>78% TSL). The fatty acid composition of NL, GL and PL in CM and PW extracts was determined.

#### INTRODUCTION

Lipids associated with isolated cereal starch granules have been found to occur on the surface as well as inside the granule (Morrison, 1981). The surface lipids are mainly triglycerides (TG), followed by free fatty acids (FFA), glycolipids (GL) and phospholipids (PL), and they include those that may have been present on the granule surface in situ within the plant tissue and the non-starch lipids, which are absorbed into the surface layer of starch granules during isolation procedures (Morrison, 1981; Galliard & Bowler, 1987). The non-starch lipids occur as spherosomes and as components of membranes and organelles associated with storage protein (Morrison, 1981). Since it is not possible to distinguish between these two types of surface lipids on the basis of solvent extraction techniques, it has been suggested that all lipids found on the surface have to be considered as starch lipids (Galliard &

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Food Chemistry 0308-8146/91/\$03.50 © 1991 Elsevier Science Publishers Ltd, England. Printed in Great Britain Bowler, 1987). The internal lipids of cereal starches are predominantly monoacyl lipids, with the major components being lysophospholipids (LPL) and FFA (Hargin & Morrison, 1980; Morrison, 1981). It is likely that both surface and internal lipids may be present in the free state as well as bound to starch components, either in the form of amylose inclusion complexes (Acker, 1977) or linked via ionic or hydrogen bonding to hydroxyl groups of the starch components. Free lipids are easily extractable by solvent systems at ambient temperatures (Morrison, 1981), whereas prolonged extraction (> $2.5 \times 10^5$  h) with hot aqueous alcoholic solvent systems (Morrison, 1981) or disruption of the granular structure by acid hydrolysis (Goshima *et al.*, 1985) is required for the efficient removal of bound lipids.

Starch damage has been shown to occur during isolation of cereal starches (Evers *et al.*, 1984). The type of damage may range from cracks, cuts and other abrasions on the surface to cleavage of amylose and amylopectin. Therefore, there is always a possibility that cross-contamination of surface (free and bound) with internal (free and bound) lipids, and vice versa, could occur respectively during cold and hot solvent extractions. It is our opinion that classification of starch lipids as surface and internal is valid only if the starch granules were highly purified (60–80 mg N 100 g<sup>-1</sup> dry starch) and were undamaged. However, since the latter criterion is very difficult to achieve in practice, an alternative classification based on solvent (cold and hot) extractability would be more meaningful.

Although the lipids of cereal starches have been well characterized (Ito et al., 1979; Hargin & Morrison, 1980; Maningat & Juliano, 1980; Goshima et al., 1985; Morrison & Coventry, 1985; Morrison & Azudin, 1987), those of legumes (Hoover et al., 1988), tubers (Goshima et al., 1985) and root (Rogols et al., 1969) starches have received only scant attention. Furthermore, many authors (Ito et al., 1979, Maningat & Juliano, 1980; Goshima et al., 1985) have characterized internal cereal starch lipids without reporting the level of starch damage. Therefore, the extent of purity of their internal lipid preparations cannot be properly ascertained. In addition, some of the studies on cereal and tuber starch lipids have been performed using techniques that are effective in removing only free lipids (Melvin, 1979; Maningat & Juliano, 1980; Choudhury & Juliano, 1980a,b; Eliasson et al., 1981).

The objective of this study was to investigate the amount and composition of the lipids associated with highly purified starch granules from various botanical sources, using selective solvent extraction techniques and acid hydrolysis. It is hoped that the results may give a deeper insight into the changes in pasting and gelling properties that occur when starches are modified by altering their lipid composition (Melvin, 1979; Goshima *et al.*, 1984).

## MATERIALS AND METHODS

#### Materials

Wheat corn, rice and potato starches were obtained from Sigma Chemical Co., St. Louis, Mo, USA. Cassava starch was obtained from National Starch and Chemical Corporation, Bridgewater, NJ, USA. Seeds of lentil (*Lens culinaris Medicus*) and fababeans (*Vicia faba* L) were obtained from a local supplier. Ten percent SP-2330 (68% cyanopropyl silicone) on 100/120 Chromosorb<sup>®</sup> W AW was purchased from Sulpelco Inc., Bellefonte, PA, USA. Silica gel G was from Fisher Scientific Ltd, Ontario, Canada. Other chemicals and solvents were analytical grade. Solvents were distilled from glass before use.

#### Methods

Standard AACC methods (1983) were used for the determination of moisture, nitrogen and starch damage on purified starches. Amylose content was determined by the blue-value method (Gilbert & Spragg, 1965). Calculation for amylose content was by the equation of Kawamura (1969).

#### Starch isolation and purification

Isolation of starches from the legume seeds and purification of all starches were carried out by procedures outlined in an earlier publication (Hoover *et al.*, 1988).

#### Lipid extraction and analysis

Wheat starch (5 g dry basis) was used for comparing the lipid extraction efficiency of various solvent systems. Extraction at ambient temperatures (25-27°C) was with 100 ml each of chloroform-methanol 2:1 v/v (CM) and water saturated n-butanol (WSB) under vigorous agitation in a wrist action shaker for 1 h. At elevated temperatures (90-100°C) lipids were obtained by Soxhlet extraction (12 h) with 100 ml each of n-propanol-water 3:1 v/v (PW) and WSB. However, in the determination of lipid composition, all starches were subjected to the following extraction procedures: (A) starches (5 g dry basis) were extracted under vigorous agitation in a wrist action shaker with CM at 25-27°C for 1 h; (B) the residues from CM extraction were solvent extracted with PW (90-100°C) for 12 h; (C) the native starches were hydrolyzed with 24% HCl at 70-80°C for 30 min, and the hydrolyzate then extracted three times with n-hexane (Goshima et al., 1985).

The crude lipids extracts from the above were purified by extraction with chloroform/methanol/water (1:2:0.8 v/v/v) and forming a biphasic system (chloroform/methanol/water (1:1:0.9 v/v/v)) by addition of chloroform and water (Bligh & Dyer, 1959); the chloroform layer was diluted with benzene and brought to dryness on a rotary evaporator. The purified lipids were fractionated by silicic acid column chromatography into neutral lipids (NL), glycolipids (GL) and phospholipids (PL) and each fraction was examined by TLC on precoated silica gel plates in the following solvent systems: (1) petroleum ether/diethyl ether/acetic acid (70:30:1 v/v/v); (2) chloroform/methanol/water (65:25:4 v/v/v); (3) chloroform/methanol/conc ammonia (65:35:5 v/v/v); (4) chloroform/methanol/acetone/diethylamine/H2O (120:35:37:6:4 v/v/v), and (5) chloroform/ acetone/methanol/acetic acid/water (10:4:2:2:1 v/v/v/v).

NL were separated by development in solvent system 1. Polar lipids were separated by one or two dimensional TLC using systems 2 and 3. The GL were resolved in solvent system 4 while the PL were resolved in solvent system 5. Lipids were detected on TLC plates by charring with 50%  $H_2SO_4$  or by spraying with specific spray reagents (Kates, 1972). Identification of polar lipid components was established by the use of specific spray reagents (Kates, 1972) and comparison of their  $R_f$  values with those of authentic samples.

A Pharmacia Ultrascan XL enhanced laser (helium-

neon) densitometer (Model LKB 2222-20, Uppsala, Sweden) and a Pharmacia XL software (code 2400) system was used to determine the percentage distribution of the lipid constituents within each lipid class. Lipid components were visualized using 50% H<sub>2</sub>SO<sub>4</sub>.

Fatty acid methyl esters (FAME) were prepared by transmethylation of the lipid fraction or component in 6% H<sub>2</sub>SO<sub>4</sub> in 99.9 mole% methanol at 65–70°C for 15 h (Keough & Kariel, 1987). After extraction of the methyl esters and their dissolution in CS<sub>2</sub>, the FAME were analyzed in a 30 m × 0.25 mm column coated with SP 2330 in a Perkin-Elmer 8310 gas chromatograph. Oven temperature was 180°C and the injection port and flame ionization detector temperatures were 230° and 250°C, respectively. The flow rate of the helium carrier gas was 25 ml min<sup>-1</sup>.

Identification of the FAME was based on comparison of retention times of samples and standards (Supelco Inc.). Quantitation was accomplished with the data handling and control unit of the instrument. All determinations were performed in triplicate and the mean values were reported.

#### **RESULTS AND DISCUSSION**

The nitrogen content of isolated starches represents the contributions from endosperm storage proteins, LPL and proteins located inside starch granules (Morrison, 1981). The nitrogen contents of the purified starches were in the range 0.01-0.04% (dry basis) (Table 1), indicating the absence of endosperm proteins and, by implication, most of the non-starch lipids (Morrison, 1981). The lipid extracting ability of solvent systems at ambient and elevated temperatures (Fig. 1) was determined on wheat starch due to its high LPL content (Hargin & Morrison, 1980). LPL occurs in the starch granule mainly in the form of amylose–lipid complexes (Acker, 1977) and is thus not easily extractable by lipid



Fig. 1. Solvent extraction of lipids from wheat starch.

solvents (Wren & Merryfield, 1970; Morrison & Coventry, 1985). Neither CM nor WSB was capable of extracting significant amounts of lipids at 25°C (Fig. 1). At this temperature, the extraction ability of CM was slightly superior to that of WSB. However, higher yields were obtained when the residues from CM and WSB extractions (at 25-27°C) were subjected to lipid removal at 90-100°C by PW and WSB, respectively. After 7 h, PW had extracted 16.2% more lipid than WSB (Fig. 1). Although there was hardly any increase in extracted lipid after 7 h with PW, the yield of lipid continued to increase with WSB, and reached a plateau after 12 h. However this yield was still 4.3% less than that obtained with PW during this same time period (Fig. 1). Thus, due to their superior extraction ability, CM and PW were used, respectively, at ambient and elevated temperatures to characterize the starch lipids.

#### Total starch lipids (TSL)

The TSL obtained by acid hydrolysis are presented in Table 1. They ranged from 0.1% (potato) to 0.8% (corn).

Starch source	Moisture (%)	Nitrogen (%)	Starch damage (%)	Amylose content (%)	Lipids (mg/100 g dry starch)			
					Acid	Solvent extracted		
					hydrolyzed <sup>b</sup>	CM <sup>c</sup>	PWd	
Wheat	10.7	0.04	0.8	28.5	704	38.0	639.9	
Rice	10.7	0.02	0.7	27.2	760	<b>48</b> ·4	710·8	
Corn	9.4	0.03	0.9	26.0	796	39.7	755·9	
Fababean	7.4	0.04	0.7	32.0	234	144.6	86.2	
Lentil	10.9	0.02	0.6	38.6	136	30.0	105.8	
Potato	14.5	0.03	1.2	20.5	107	17.3	89.3	
Cassava	12.1	0.01	0.4	20.6	188	<b>78</b> ⋅6	109.0	

Table 1. Physical Characteristics of Some Cereal, Legume, Tuber and Root Starches

<sup>a</sup> Values are averages of three determinations.

<sup>b</sup> Lipids obtained by acid hydrolysis (24% HCl) of native starches at 70-80°C for 30 min.

c Lipids extracted by chloroform-methanol 2:1 (v/v) at 25-27°C.

<sup>d</sup> Lipids extracted by propanol-water 3:1 (v/v) at 90-100°C from the residue left after CM extraction.



Fig. 2. The neutral lipid content in CM and PW extracts.

#### Solvent extracted starch lipids (SEL)

SEL refers to the starch lipids obtained by the combined action of CM and PW. The sequential use of these two solvents resulted in complete removal of starch lipids (> 98.6%) from most of the starches, the exception being wheat, where the total solvent extraction efficiency was 96.3% (Table 1). Comparisons between results of this study and some of those cited are difficult because of differences in extraction procedures and solvents.

#### CM extracted starch lipids

The lipid content in these extracts followed the order: legumes > cassava > potato > cereals. The values (% TSL) were 5.4% (wheat), 5.3% (rice), 5.1% (corn), 55.7% (fababean), 23.8% (lentil), 18.0% (potato) and 42% (cassava). Since the degree of penetration of CM into the granule interior and its capacity to extract bound lipids is negligible at ambient temperatures, the extracted lipids probably represent to a large extent the free surface lipids. However, since the granules were



Fig. 3. The glycolipid content in CM and PW extracts.



Fig. 4. The phospholipid content in CM and PW extracts.

slightly damaged, the probability of contamination with free internal lipids cannot be ruled out.

The lipid classes generally followed the order: NL > PL > GL, except in wheat and rice, where it was NL > GL > PL (Figs 2-4). The concentration (% SEL) of NL ranged from a low of 2.6% in rice to a high of 30.3% in fababean (Tables 1-2). The major NL (Table 2) fractions (% total NL) were FFA in wheat (43%); free sterols (FS) in rice (61.5%), corn (60%) and cassava (39%); TG in fababean (41%); and sterol esters (SE) in lentil (75.5%) and potato (69%). The GL concentration (% SEL) ranged from a low of 1.3% in rice to a high of

13% in fababean. GL were not detected in corn, lentil and potato (Tables 1–3). The major GL (Table 3) fractions (% total GL) were digalactosyldiglyceride (DGDG) in wheat (69%) and rice (46%); cerebroside II (CE 11) in fababean (51%), and monogalactosylmonoglyceride (MGMG) in cassava (42%). The PL concentration (% SEL) ranged from a low of 1·1% in rice to 19·3% in fababean (Tables 1, 4). The major PL (Table 4) fractions (% total PL) were phosphatidylcholine (PC) in wheat (62·2%) and lentil (46%), and LPC in corn (37·3%), rice (60·5%), fababean (41%) potato (100%) and cassava (100%).

Table 2. Composition of Neutral Lipids Associated with Some Cereal, Legume, Tuber and Root Starch Granules.

Starch source	Extraction method	Total neutral <sup>a</sup> lipids (mg/100 g dry starch)	Neutral lipid composition <sup>b</sup> (mg/100g dry starch)							
			FFA	MG	DG	TG	FS	SEc		
Wheat	СМ	19.9	8.5	0.3	1.7	5.8	3.2	0.4		
	PW	34.9	19-1	1.6	5.2	1.7	3.4	3.9		
Rice	СМ	20.0	6.4	0.3	0.7	trd	12.3	0.3		
	PW	192	140	9.6	19.2	6.3	11.6	5-3		
Corn	СМ	30.6	0.9	0.6	0.7	1.2	18.3	8.9		
	PW	440	348	22.2	23.2	18-3	12.3	16.0		
Fababean	CM	70.0	10.9	tr	7.1	28.5	17.8	5.7		
	PW	30-0	6.8	1.6	0.3	13.4	4.1	3.8		
Lentil	CM	20.0	tr	tr	2.8	tr	2.1	15.1		
	PW	48-4	12.1	tr	5.3	8.5	10.7	11.8		
Potato	СМ	9.7	1.4	tr	tr	1.6	tr	6.7		
	PW	39.5	23.2	tr	tr	7.1	9-2	tr		
Cassava	СМ	39.8	9.4	<b>4</b> ·2	tr	3.6	15.5	7.1		
	PW	59.9	tr	3.9	3.3	12.2	24.4	16-1		

<sup>a</sup> Values are averages of three determinations.

<sup>b</sup> Based on densitometric absorbance.

<sup>c</sup> FFA, free fatty acid; MG, monoacylglycerol; DG, diacylglycerol; TG, triacylglycerol; FS, free sterol; SE, sterol ester.

<sup>d</sup> trace = less than 0.5% of total neutral lipid.

Starch source	Extraction method	Total glycolipids <sup>a</sup> (mg/100 g dry starch)	Glycolipid composition <sup>b,c</sup> (mg/100 g dry starch)							
			MGMG	MGDG	DGDG	DGMG	CE I	CE II	Unknown	
Wheat	СМ	9.9	trd	tr	6.8	tr	tr	1.9	1.2	
	PW	18.9	3.8	1.7	5.6	7.8	tr	tr	tr	
Rice	CM	9.8	2.4	tr	4.5	tr	2.9	tr	tr	
	PW	77.8	39-1	tr	8.6	<b>30</b> ·1	tr	tr	tr	
Corn	СМ						A1944			
	PW	47.0	18.2	7.5	11.3	8.5	tr	1.5	tr	
Fababean	СМ	30.0	tr	tr	6.4	tr	8.4	15.2	tr	
	PW	9.7	2.3	4.9	tr	tr	tr	2.5	tr	
Lentil	СМ									
	PW	30.0	tr	2.6	tr	15.8	tr	11.6	tr	
Potato	СМ	W7								
	PW	10.0	tr	tr	tr	7.2	tr	tr	2.8	
Cassava	СМ	9.8	4.1	tr	3.8	tr	tr	tr	1.9	
	PW	19.7	2.3	4.1	6.1	3.7	tr	3.3	0.2	

Table 3. Composition of Glycolipids Associated with Some Cereal, Legume, Tuber and Root Starch Granules

<sup>a</sup> Values are averages of three determinations.

<sup>b</sup> Based on densitometric absorbance.

MGMG, monogalactosylmonoglyceride; MGDG, monogalactosyldiglyceride; DGDG, digalactosyldiglyceride;

DGMG, digalactosylmonoglyceride; CE 1, cerebroside I; CE II, cerebroside II.

<sup>d</sup> trace = less than 0.5% of total glycolipid.

The major fatty acid in NL fractions was palmitic (16:0) in wheat, corn, fababean, potato and cassava, and linoleic (18:2) in rice and lentil, while in GL fractions, it was 18:2 in cereal starches, and 18:1 (oleic) and 16:0 in fababean and cassava, respectively. However, in PL fractions all starches had 16:0 as their major fatty acid (Table 5).

## PW extracted starch lipids

Lipids obtained by extraction of the CM residues with hot PW are presented in Figs 2–4. These lipids probably represent most of the free and bound lipids in the granule interior and some bound lipids that may have been present on the granule surface. They ranged (%

Table 4. Composition of Phospholipids Associated with Some Cereal, Legume, Tuber and Root Starches

Starch source	Extraction method	Total phospholipids <sup>a</sup> (mg/100 g dry starch)	Phospholipid composition <sup>b</sup> (mg/100 g dry starch)							
			LPC	LPE	PC	PE	PS	PG	PAc	
Wheat	СМ	8.2	tr <sup>d</sup>	tr	5.1	3.1	tr	tr	tr	
	PW	586-1	482	75.2	19.9	tr	tr	tr	9.0	
Rice	CM	8.6	5-2	tr	3.4	tr	tr	tr	tr	
	PW	437-1	311	88.6	12.8	10.4	6.1	tr	8.2	
Corn	CM	9.1	3.4	2.4	3.3	tr	tr	tr	tr	
	PW	268.9	153	65.8	14.3	35.8	tr	tr	tr	
Fababean	CM	44.6	18-3	15.6	tr	7·9	tr	tr	2.8	
	PW	46.5	16-1	6.3	24.1	tr	tr	tr	tr	
Lentil	CM	10.0	2.8	tr	4.6	tr	tr	tr	2.6	
	PW	27.4	7.3	2.3	11.3	tr	tr	tr	6.5	
Potato	СМ	7.6	7.6	tr	tr	tr	tr	tr	tr	
	PW	39.8	31.8	1.7	2.4	3.9	tr	tr	tr	
Cassava	CM	29.0	29.0	tr	tr	tr	tr	tr	tr	
	PW	29.4	5.8	11.5	2.2	9.9	tr	tr	tr	

<sup>a</sup> Values are averages of three determinations.

<sup>b</sup> Based on densitometric absorbance.

<sup>c</sup> LPC, lysophosphatidylcholine; LPE, lysophosphatidylethanolamine; PC, phosphatidyl-choline; PE, phosphatidylethanolamine; PS, phosphatidylserine; PG, phosphatidyl-glycerol; PA, phosphatidic acid.

d trace = less than 0.5% of total phospholipid.

Starch source	Lipid class and extraction medium	Fatty acid composition (area %)							
	extraction medium	16:0	18:0	18:1	18:2	18:3	20:0	Other <sup>a</sup>	
Wheat	Neutral lipids								
	CM ·	43.1	5.7	6.9	40·3	2.6	1.1	0.3	
	Glycolipids	43.0	0.1	/•1	3/.8	1.3	0.9	v∙o	
	CM	42.2	3.9	9.8	42.6	0.1	0.9	0.5	
	PW Phospholipids	39.6	<b>6</b> ∙1	10-1	41.5	0.2	2.1	0.1	
	CM	<b>46</b> ·7	3.5	10.4	38.7	0.1	0.4	0.2	
	PW	<b>39</b> ·7	3.2	7.3	<b>4</b> 7·9	1.3	0.5	0.1	
Rice	Neutral lipids	20.2	2.5	12.5	51.6	14	1.2	0.6	
	PW	30.3	2·1	8.1	57.9	1.4	0.2	0.0	
	Glycolipids	22.0		<b>7</b> 1	40 C	0.4	1.6	0 <b>7</b>	
	CM PW	33·8 41·1	/·/ 4.9	7·1 9·5	48∙5 43•1	0.6 0.8	1.0 tr <sup>b</sup>	0.7	
	Phospholipids						••		
	CM PW	43·6 52·6	4.9 2.4	6·9 12.7	41·5 30·9	0·8 0·7	1.6 tr	0·7 0·7	
Corn	Neutral linids	52.0	24	12 /	507	07		07	
Com	CM	35.5	6.7	9.8	44·3	2.1	1.3	0.3	
	PW	37.3	5.3	10-3	<b>4</b> 2·7	2.8	0·7	0.9	
	PW	35.2	7.5	12.8	<b>41</b> ·8	2.2	tr	0.5	
	Phospholipids	10.0		0 <b>f</b>	<b>3</b> 0 (			0.4	
	CM PW	42·8 38·7	5·5 5·8	9·5 8·4	38·6 44·3	2.1	l∙l tr	0·4 0·5	
Fahabean	Neutral linids								
1	CM	35.5	10.7	28.9	17.8	6.6	tr	0.5	
	PW Glycolinids	34.2	8.3	30.5	20.3	4.5	1.4	0.8	
	CM	26.5	11.9	28.5	26.6	<b>6</b> ·1	tr	0.4	
	PW Dhosphalinida	29.6	13.1	21.5	26.3	7∙4	1.8	0.3	
	CM	51-1	8.2	22.3	16-3	0.1	1.4	0.6	
	PW	35.5	10.9	29.1	20.9	2.5	0.9	0.2	
Lentil	Neutral lipids	22.6	4.0	10.0	26.0	141	1.2	0.4	
	CM PW	23·6 36·5	4·8 8·2	18·9 29·1	30·8 22·3	14·1 2·5	1.4	U∙o tr	
	Glycolipids						•		
	CM PW	30·6 42·9	6·7 5·8	13·6 26·6	35-2 17-7	13.8	tr 2.9	0·1 0·5	
	Phospholipids	42 )	50	20 0	1, ,	50	2 /	05	
	CM	34.8	8.1	11.2	30.7	12.8	1.8	0.6	
Deteta	r w	30.1	5.2	13.3	34.1	15.2	1.2	0.2	
Potato	CM	36.1	7.3	28.8	14.4	12.5	tr	0.9	
	PW	38.2	9.2	30.1	15.8	6.3	tr	0.4	
	Glycolipids PW	39-1	6.2	25.8	18.2	9.2	0.8	0.7	
	Phospholipids			20 0				• •	
	CM PW	44·9 40·4	9.7 6.4	17·5 22·2	16·9 18·5	8·4 11-8	1.9 0.4	0.7	
Cassava	Neutral linids				200		0.		
~u00u + 4	CM	32.4	10.8	28.6	17.5	9.5	0.4	0.8	
	PW Clycolinida	37.1	8.4	36.8	10.5	<b>6</b> ·1	0.8	0.3	
	CM	36.6	5.5	30.9	13.9	10.9	1.6	0.6	
	PW Phasehalisida	35.9	6.3	33.9	16.9	5-2	1.5	0.3	
	CM	<b>4</b> 3·8	3.9	24.6	20.7	6.3	tr	0.7	
	PW	39.2	2.8	<b>26</b> ·7	22.3	8.8	tr	0.5	

# Table 5. Fatty Acid Distribution of the Major Lipid Classes in Chloroform-Methanol and Propanol-Water Extracts of some Cereal, Legume, Tuber and Root Starch Granules

<sup>a</sup> Includes 14:0 and 22:0. <sup>b</sup> Trace = less than 0.1%.

TSL) from 44.2% (potato) to 94.8% (corn). These results contradict the findings of Milligan and Morrison (unpublished results) who showed that potato and legume starches are devoid of internal lipids. It is difficult to explain this discrepancy due to a lack of data with regard to solvent systems and extraction times.

The lipid classes followed the order: PL > NL > GLin wheat, rice and fababean; NL > PL > GL in corn and cassava; and NL = PL > GL in potato (Figs 2-4). The NL content was found to vary widely even among starches belonging to the same species. In cereal starches, these values (% SEL) were, respectively, 5·1, 26·1 and 55·2% in wheat, rice and corn, and in legume starches these were 11·5% (lentil) and 30·8% (fababean). The corresponding values for potato and cassava were, respectively, 36·4 and 31·5%.

The major NL (Table 2) fractions (% total NL) were FFA in wheat (55%), rice (71.4%), corn (79.0%), lentil (25%) and potato (59%); TG in fababean (45%); and FS in cassava (41%). The GL contents also differed widely among cereal and legume starches. The values (% SEL) were 2.8% (wheat), 10.4% (rice), 5.9% (corn), 3.8% (fababean) and 23.1% (lentil). The corresponding values for potato and cassava were 9.0 and 10%, respectively (Tables 1, 3). The major GL (Table 3) fractions (% total GL) were DGDG in wheat (41.2%) and MGMG in rice (50.2%) and corn (38.7%). In legume starches these were MGDG in fababean (50.5%) and DGMG in lentil (52.7%). DGMG and DGDG formed the major GL in potato (100%) and cassava (31%), respectively. Cereal starches exhibited wide variations in their PL levels (Tables 1,4). The values (% SEL) were 86.2% (wheat), 58.3% (rice) and 34% (corn). These variations were similar to those seen in NL and GL fractions. However, the PL levels of legume starches were fairly close with values of 18.5 and 21% for fababean and lentil, respectively. The corresponding values for potato and cassava were 36.4 and 16%, respectively. The major PL (Table 4) fractions (% total PL) were LPC in wheat (82%), rice (71%), corn (57%) and potato (80%), PC in fababean (52%) and lentil (41%), and LPE in cassava (39%).

The major fatty acids in NL, GL and PL fractions of all starches were identical to those observed in CM extracts (Table 5). However, there were slight variations in their area percentages (Table 5). The monoacyl lipid content in both CM and PW extracts of wheat, rice and corn amounted to, respectively,  $85 \cdot 2$ ,  $83 \cdot 2$  and  $78 \cdot 2\%$  of the TL extract (Tables 2-4). These values are in general agreement with those reported by Hargin and Morrison (1980) and Ito *et al.* (1979) on wheat and rice, respectively. The corresponding values for the other starches were  $33 \cdot 3\%$  (fababean),  $29 \cdot 6\%$  (lentil), 68% (potato) and  $39 \cdot 3\%$  (cassava). Since it is the monoacyl lipids that interact most strongly with the amylose helix, their removal by defatting would therefore result in greater functionality changes in starches from cereals and potato than those from legumes and cassava. Work is now in progress to study the effect of defatting on the thermal and rheological properties of these starches.

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