WHEAT LIPID COMPOSITION[1]

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ABSTRACT

The structure, composition and distribution of the principal lipid classes in wheat are described, and data are given for tocols, tocotrienols, triterpene alcohols, sterols, fatty acids, simple glycerides, galactosyldiglycerides and phosphoglycerides in whole wheat, bran, germ, and flour. Lipids exist in flour as amylose-complexed monoacyl lipids in starch granules (starch lipids) and as triglycerides, diacylglycerides and free fatty acids outside the starch granules (nonstarch lipids). Starch lipids are effectively inert and nonstarch lipids participate in physical, chemical and biochemical processes in flour and dough.

Wheat lipids have been studied intensively for more than half a century, but despite this, the gaps in the information in the literature are substantial.

Lipids are distributed throughout the wheat kernel (Table I) as structural components of biomembranes and organelles and as spherosomes (membrane-bound oil droplets <5 μm in diameter) in oil-rich tissues such as the aleurone, scutellum and embryonic axis. The classes of wheat lipids are the same as those in other cereals and are typical plant lipids (1–3). Except for the starch lipids that are more saturated, the fatty acids in the total lipids and in the major lipid classes have similar compositions (Table II).

MINOR LIPIDS

Wheat has more tocopherols with higher vitamin E activity than any other cereal. The tocopherols (Fig. 1) are unevenly distributed, and their order of

TABLE I
Distribution of Crude Fat in the Wheat Kernel[a]

Tissue	Proportion of Whole Kernel (%)	Crude Fat (%)
Whole grain	100	2.1 – 3.8
Bran	...	5.1 – 5.8
Pericarp	5.0– 8.9	0.7 – 1.0
Testa, hyaline	0.2– 1.1	0.2 – 0.5
Aleurone	4.6– 8.9	6.0 – 9.9
Endosperm	74.9–86.5	0.75– 2.2
Scutellum	1.1– 2.0	12.6 –32.1
Embryonic axis	1.0– 1.6	10.0 –16.3

[a]From Morrison (2).

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abundance differs in each kernel fraction (Table III). Germ is an exceptionally rich source of α-tocopherol (highest vitamin E activity); bran and bran oil contain mostly β-tocotrienol. Tocopherols in white flour are partly destroyed by flour-bleaching agents such as benzoyl peroxide and chlorine dioxide (4) and by lipoxygenase oxidation in intensively mixed doughs (5).

Detailed analysis of the unsaponifiable matter in wheat germ oil (6,7) shows that most of the intermediates in the sterol biosynthetic pathway are present (Fig.

TABLE II
Fatty Acid Composition of Total Lipids of Wheat Fractions and Major Lipid Classes of Wheat Flour[a]

Source	16:0 (% Wt.)	18:0 (% Wt.)	18:1 (% Wt.)	18:2 (% Wt.)	18:3 (% Wt.)
Total lipids					
Whole wheat	17–24	1–2	8–21	55–60	3–5
Bran	18–28	1–4	17–24	41–58	1–6
Germ	18–24	<2	8–17	54–57	4–9
Flour, nonstarch fraction	16–21	<2	12–13	60–66	4–5
Flour, starch fraction	35–54	<2	7–14	44–52	1–4
Flour, nonstarch lipid classes					
Steryl ester	30–44	2–4	8–10	39–43	2–4
Triglyceride	13–20	<2	13–17	57–65	4–7
Diglyceride, monoglyceride	14–24	1–2	10–16	57–66	3–6
Free fatty acid	18–28	1–2	9–12	56–74	3–6
Esterified steryl glucoside	30–38	4–9	9–18	35–49	3–5
Monogalactosyldiglyceride	5–11	<1	7–10	74–82	3–6
Digalactosyldiglyceride	10–16	1–2	5–8	69–74	4–7
Phosphoglycerides (all)	18–23	1–3	5–15	60–65	1–4
Flour, starch lipid classes					
Nonpolar classes, free fatty acids	35–41	3–6	14–18	36–43	2–4
Glycolipids	19–24	2–5	9–11	59–63	3–5
Lysophospholipids	36–37	<2	7–9	49–51	2–4
Lysophosphatidylcholine	34–36	<1	6–10	50–55	2–4

[a]Unpublished data from our laboratory and data from Morrison (2).

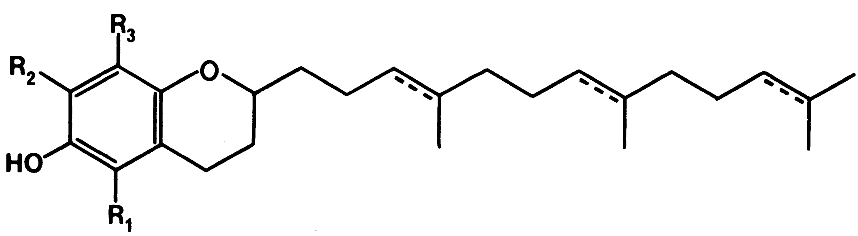

Fig. 1. Tocopherols in wheat (2). Tocols have saturated side chains and tocotrienols have triunsaturated side chains. R_1, R_2, and $R_3 = CH_3$ in α-tocopherol and α-tocotrienol, $R_2 = H$ and R_1, $R_3 = CH_3$ in β-tocopherol and β-tocotrienol.

2, Table IV). There are no comparable analyses for other kernel fractions. β-Sitosterol is always reported as the major sterol, but discrepancies between analyses of the minor sterols are often substantial and may be attributed to inadvertent inclusion of variable quantities of pentacyclic triterpene alcohols, 4,4-dimethyl sterols and 4-methyl sterols (2).

The sterols occur mainly as free sterols and steryl esters (Fig. 3), with only small amounts of steryl glucoside and 6-0-acyl steryl glucoside (ESG). In *Triticum durum* and in L-phenotypes of *T. aestivum*, levels of steryl esters that contain primarily linoleate (L) and other unsaturated acids are comparatively low and the levels of free sterols are comparatively high. In normal *T. aestivum*

TABLE III
Composition of Tocopherols in Whole Wheat and Wheat Fractions[a]

Fraction	α-T[b] (mg/100 g)	α-T-3[c] (mg/100 g)	β-T[d] (mg/100 g)	β-T-3[e] (mg/100 g)	γ-T[f] (mg/100 g)	Total (mg/100 g)
Whole wheat	0.9 −1.8	0.3–0.7	2.5 −3.6	2.5 −3.6	...	4.9–5.8
Germ lipid	110–180	2.6–8.8	61–81	9–18	10–20	192–264
Germ oil	133–149	...	40–90	48–61	...	268–305
Bran	1.6 −3.3	1.1	1.0 −1.3	2.9 −5.4	...	...
Bran oil	18–27	29–43	9–14	161–178	...	228–244
Patent flour	0.26–0.34	0.14	0.20–0.22	1.04–2.18	...	1.5–2.8

[a]From Morrison (2).
[b]α-T = α-tocopherol.
[c]α-T-3 = α-tocotrienol.
[d]β-T = β-tocopherol.
[e]β-T-3 = β-tocotrienol.
[f]γ-T = γ-tocopherol.

TABLE IV
Composition of Triterpene Alcohols and Sterols in Wheat Germ Oil[a]

Pentacyclic Triterpene Alcohols and 4,4-Dimethyl Sterols	%	4-Methyl Sterols	%	4-Desmethyl Sterols	%
Pentacyclic					
α-Amyrin	8	Obtusifoliol	6	Cholesterol	Trace
β-Amyrin	18	Gramisterol = 24-methylene lophenol	41	Brassicasterol	Trace
				Stigmasterol	Trace
4,4-Dimethyl					
Cycloartanol	3	Citrostadienol =	46	Δ^5-Avenasterol	6
Cycloartenol	17	24-ethylidene lophenol			
				Δ^7-Stigmastenol	3
24-Methylene cycloartanol	44			Δ^7-Avenasterol	2
Cyclobranol	3	3 Unknown	7	Campesterol	22
Unknown	2			Sitosterol	67

[a]From Itoh and co-workers (6,7).

(PL-phenotype), the steryl esters contain much more palmitate (P) in addition to the other acids and correspondingly less free sterol (2,8). These differences between the PL and L phenotypes appear to be confined to the endosperm lipids

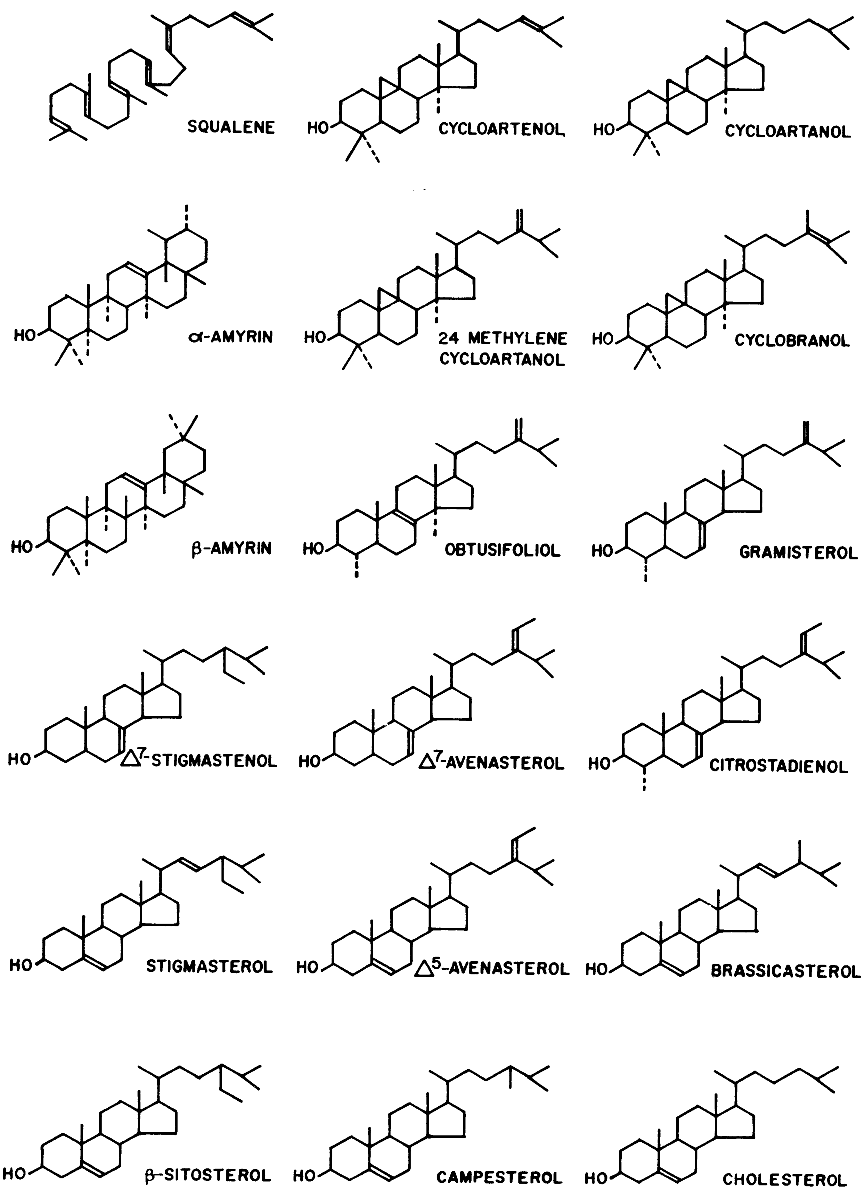

Fig. 2. Squalene, triterpene alcohols, 4,4-dimethyl sterols, 4-methyl sterols, and 4-desmethyl sterols in wheat and other cereals (2).

(8). Other genetic differences in the quantities of purothionins (petroleum-soluble lipoproteins), together with the sterol/steryl ester pattern, should permit unequivocal identification of *T. durum* and *T. aestivum* (9).

The carotenoid pigments in wheat contain only 2–12% β-carotene, and the remainder is mostly the dihydroxyxanthophyll pigment lutein (1). The proportions of free lutein and lutein esterified with one or two fatty acids vary considerably in *T. durum* and *T. aestivum* and in different parts of the kernel.

The sphingolipids comprise a series of ceramide monohexosides, dihexosides,

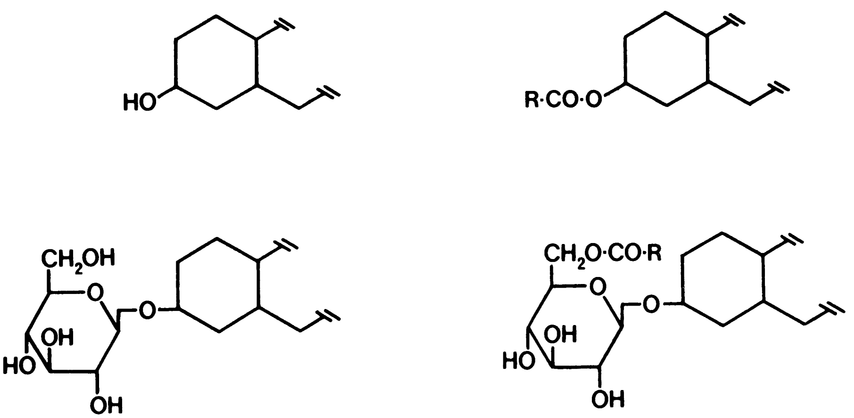

Fig. 3. Sterol lipids in wheat (2). Free sterol (top left; rest of structure as in Fig. 2), steryl ester (top right), steryl-β-D-glucoside (bottom left) and steryl-β-D-[6-0-acyl]-glucoside or esterified steryl glucoside (bottom right).

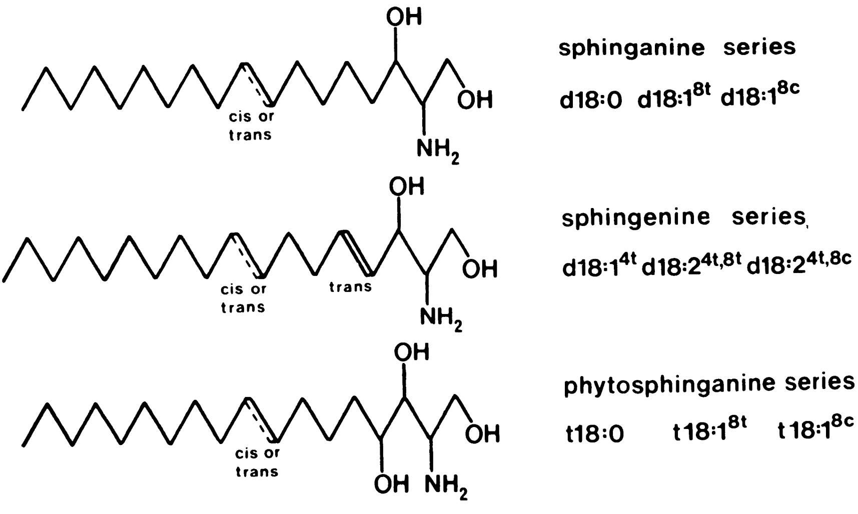

Fig. 4. Long-chain bases in wheat sphingolipids (2). Only C_{18} structures are shown, but other chain lengths also occur (10–12).

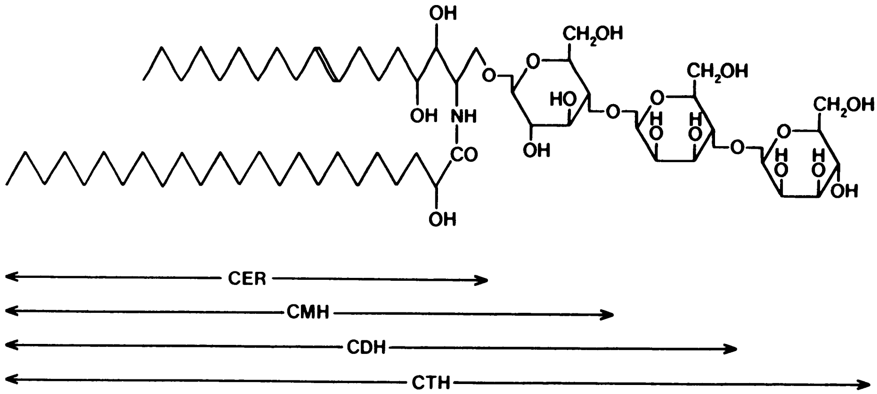

Fig. 5. Ceramide hexosides in wheat (2). The structure shown is 0-β-D-mannopyranosyl-(1→4)-0-β-D-mannopyranosyl-(1→4)-0-β-D-glucopyranosyl-(1-1′) ceramide. Ceramide dihexosides (CDH) and ceramide monohexosides (CMH) have similar structures but lack one or two terminal mannose residues, respectively. The fatty acid in the ceramide portion is 2-hydroxytetradecanoic acid, but other 2-hydroxy acids and small amounts of normal fatty acids also occur. (CER = ceramide, CTH = ceramide trihexosides.)

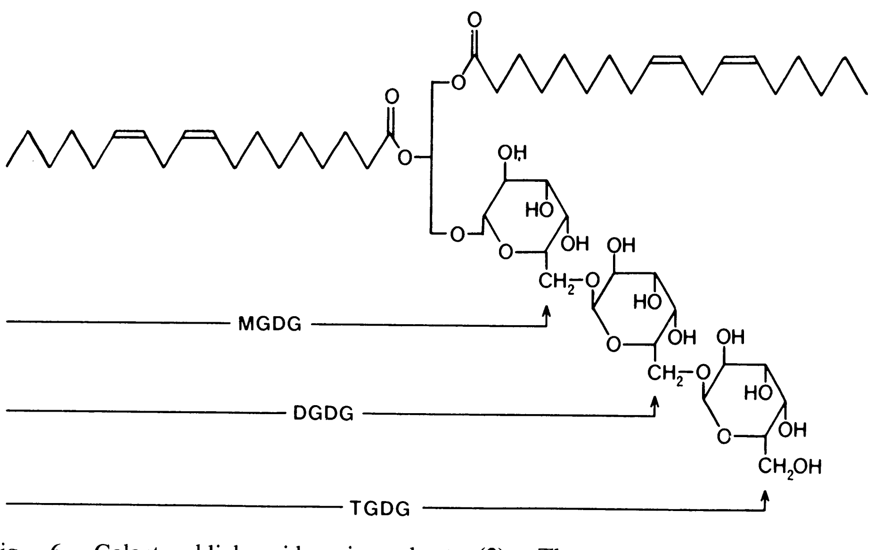

Fig. 6. Galactosyldiglycerides in wheat (2). The structure shown is the trigalactosyldiglyceride (TGDG), 1,2-diacyl-3-0-(α-D-galactopyranosyl-(1→6)-0-α-D-galactopyranosyl-(1→6)-0-β-D-galactopyranosyl)-*sn*-glycerol. Digalactosyldiglyceride (DGDG) and monogalactosyldiglyceride (MGDG) have similar structures but lack one or two terminal galactose residues, respectively. The principal molecular species contains two linoleic acid residues, as shown, but minor molecular species contain one or two other fatty acids (15) (Table II).

and trihexosides (10–12). The fatty acids are mostly 2-hydroxy acids, and the bases consist of sphinganine (d:o), sphingenine (d:1^{4t}), and phytosphinganine (t:o) series, sometimes with additional *cis* or *trans* unsaturation at position-8 (Fig. 4). The sugars are β-glycosidically linked in the ceramide-glucose-mannose-mannose sequence (Fig. 5).

SIMPLE GLYCERIDES

Triglyceride is the principal lipid in all kernel fractions except starch. Free fatty acids, monoglyceride and diglyceride reach low levels about three to six days before the wheat is dead ripe and then increase slightly (13,14).

The stereospecific distribution of fatty acids in flour triglyceride *appears* to conform to a 1-random, 2-random, 3-random distribution, with fatty acids in the 2-position much more unsaturated than those in the 1-position and 3-position (15). The distribution of fatty acids in the diglyceride isomers suggests that they originate from a 1,2-diacyl-*sn*-glycerol of the type that would be intermediate in biosynthesis of all wheat glycerides (15).

Free fatty acids comprise about 5% of the lipids in new flour but can reach 70% of the total in extremely old flour (1,2,16). Free fatty acids are formed by lipolysis of all accessible simple glycerides, galactosyl glycerides and phosphoglycerides (17). The enzymes are probably native flour acyl-hydrolases, supplemented with large and variable amounts of enzymes from contaminating molds.

GLYCOSYL GLYCERIDES

The glycosyl glycerides (Fig. 6) usually are described as monogalactosyldiglyceride, digalactosyldiglyceride, and 6-0-acyl monogalactosyldiglyceride

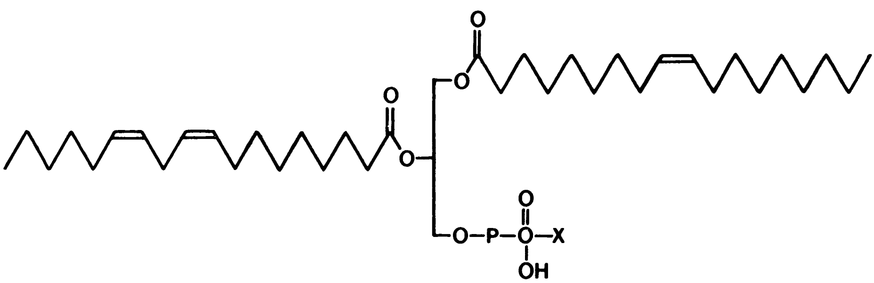

Fig. 7. Phosphoglycerides in wheat (2). In N-acyl phosphatidylethanolamine (APE) X = $-O{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}R$, where R is fatty acid, phosphatidic acid (PA) X = $-OH$, phosphatidylethanolamine (PE) X = $-O{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, phosphatidylglycerol (PG) X = $-O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2OH$, phosphatidylcholine (PC) X = $-O{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_3)_3$, phosphatidylserine (PS) X = $-O{\cdot}CH_2{\cdot}CH(COOH){\cdot}NH_2$, and phosphatidylserine (PS) X = $-O{\cdot}CH_2{\cdot}CH(COOH){\cdot}NH_2$, and phosphatidylinositol (PI) X = *myo*-inositol. The principal molecular species contains oleic acid in position-1 and linoleic acid in position-2, but other molecular species contain different combinations of fatty acids (15) (Table II). In the lysophospholipids, the fatty acid usually is missing from the 2-position of the glycerol.

(EMGDG), although as much as 20% of the sugar in these lipids may be glucose. There also are small amounts of the corresponding galactosylmonoglycerides and trigalactosyldiglyceride (1,2). The fatty acids esterified to the sugar of EMGDG (and of ESG) are comparatively saturated and resemble those in the steryl ester. The 2-position fatty acids of the galactosyldiglycerides are highly unsaturated, containing 83% linoleic acid and 7% linolenic acid (15).

PHOSPHOGLYCERIDES

Phospholipase-D in tissues such as bran complicates analysis of the already complex phosphoglycerides (Fig. 7). Unless inactivated, the enzyme can form significant amounts of phosphatidic acid, phosphatidyl methanol or phosphatidyl butanol as artifacts during solvent extraction of the phospholipids (18,19). Phosphatidic acid is normally present only in trace amounts, and the others are not natural phosphoglycerides.

The principal phospholipids in whole kernels, bran, and endosperm are listed in Table V. The high lysophosphatidylcholine content in endosperm is from starch lipids, and not from degradation of phosphatidylcholine. N-acyl phosphatidylethanolamine is sometimes wrongly described as phosphatidic acid, and N-acyl lysophosphatidylethanolamine as phosphatidylglycerol or diphosphatidylglycerol.

LIPIDS IN FLOUR AND STARCH

Flour contains all the endosperm lipids plus a small proportion of germ (and perhaps aleurone) lipids transferred to the flour during milling (20,21). Flour lipids also may be regarded as consisting of true starch lipids and all the other lipids that are collectively termed nonstarch lipids (22).

TABLE V
Composition of Phospholipids in Whole Wheat, Dissected Bran and Endosperm

Phospholipid	% of Total Lipid Phosphorus		
	Whole Kernels[a]	Bran[b]	Endosperm[b]
N-acyl phosphatidylethanolamine	11.0	4.8	8.65
N-acyl lysophosphatidylethanolamine	13.2	4.0	6.85
N-acyl glycerylphosphorylethanolamine	...	...	4.75
Phosphatidic acid	Trace	5.15	...
Phosphatidylethanolamine	11.6	4.6	0.5
Phosphatidylserine	3.3	...	...
Phosphatidylcholine	45.5	25.2	3.05
Phosphatidylinositol	...	9.15	0.9
Lysophosphatidylethanolamine	1.6	...	8.4[c]
Lysophosphatidylcholine	14.0	34.5	65.35
Others	...	14.4	1.25

[a]From DeLaRoche and co-workers (19).
[b]Average of two determinations, from Colborne and Laidman (18).
[c]Contains some phosphatidylserine.

TABLE VI
Composition of Nonstarch Lipids from Winter Wheat Flour and of Lipids from Purified Starch from the Flour[a]

Lipid	Flour, Nonstarch Lipids (mg/100 g)[b]	Starch Lipids (mg/100 g)[b]
Steryl ester	43	2
Triglyceride	909	15
Diglyceride	67	7
Monoglyceride	53	8
Free fatty acid	64	27
Esterified steryl glycoside	18	3
Monogalactosyldiglyceride	115	4
Monogalactosylmonoglyceride	17	10
Digalactosyldiglyceride	322	11
Digalactosylmonoglyceride	52	24
N-acyl phosphatidylethanolamine	95	NIL
N-acyl lysophosphatidylethanolamine	33	NIL
Phosphatidyl-ethanolamine,-glycerol	19	NIL
Phosphatidylcholine	96	NIL
Phosphatidyl-serine,-inositol	9	NIL
Lysophosphatidylethanolamine	7	104
Lysophosphatidylglycerol	5	23
Lysophosphatidylcholine	29	783
Lysophosphatidyl-serine,-inositol	...	26
Total non polar lipids	1154 (59%)	62 (6%)
Total glycolipids	506 (26%)	49 (5%)
Total phospholipids	293 (15%)	936 (89%)
Total lipids	1953	1047

[a]From Morrison and co-workers (22).
[b]All results reported on dry basis.

TABLE VII
Free Lipids in Flour and Freeze-Dried Doughs[a]

Lipid	Flour (mg/100 g)[b]	Aerobic Dough (mg/100 g)[b]	Anaerobic Dough (mg/100 g)[b]
Steryl ester	66	49	49
Triglyceride	656	325	246
Diglyceride	77	54	56
Free fatty acid	78	9	11
Monoglyceride	13	} 8	} 6
Esterified monogalactosyldiglyceride	14		
Esterified steryl glycoside	12	9	6
Polar lipids	171	10	8

[a]Data from Mann and Morrison (24).
[b]All results reported on dry basis.

True starch lipids exist as amylose-inclusion complexes throughout starch granules (2,23). The nonstarch lipids consist of all the other endosperm lipids and adventitious lipid outside the starch granules and thus include any lipids associated with residues of the amyloplast membrane on the starch granules' surfaces. Nonstarch lipids are mostly fully acylated glycerides (Table VI).

Nonstarch lipids in flour are readily extracted at ambient temperatures with the commonly-used polar solvent mixtures (23), but starch lipids are not extracted unless the structure of the starch granules has been disturbed by swelling with water (as in dough) or by freeze-drying, in which case slight leakage will occur. Starch lipids can only be extracted quantitatively with hot butanol-water mixtures (22,23).

Free lipids are the nonstarch lipids that can be extracted with light petroleum or diethyl ether, and bound lipids are the remaining nonstarch lipids that can be recovered only with cold polar solvent mixtures. Unfortunately some contamination with starch lipids is likely on prolonged extraction with cold polar solvent mixtures, especially when freeze-dried dough is used. Typical analyses are shown in Table VII.

If precautions are taken to remove all traces of gluten and residues of associated nonstarch lipids, the starch lipids are exclusively monoacyl lipids (Table VI). Saturated monoacyl lipids form amylose-inclusion complexes more readily than do unsaturated lipids, so it is surprising that the starch lipids contain 52–67% *cis*-unsaturated acids (22,23). Conceivably, these lipids enter the helix during amylose biosynthesis and the shape of the helix is modified to contain the bent fatty acid chain.

Nonstarch lipids are comparatively accessible and participate in all the physical, chemical and biochemical reactions involving lipids in flour and dough (1,2). In contrast, starch lipids are in a highly protected environment and probably are not affected by normal flour treatment.

This difference is illustrated by our recent work (25) showing that chlorine attacks about 60% of all unsaturated fatty acids in nonstarch lipids but does not affect starch lipids during gas treatment of high-ratio cake flour. Lipids in starch also are exceptionally stable against autoxidation and show little change after the starch has been stored aerobically at 70° C for one month.

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