

Lipids

Tuesday, October 21, 2014 8:51 PM

Family of compounds that includes triglycerides, phospholipids, and sterols
Contain C, H, O – more C&H than O >> more energy from breakage of C- H bonds (great food supply)

Fats – triglycerides that are solid at room temp

Oils – triglycerides that are liquid at room temp

Dietary fat- includes all lipids contained in food

Visible fat – butter, margarine, oil, salad dressing

Invisible fat – meat fibers (depends on leanness), Milk, dairy (depends on processing), whole grain (in germ), nuts (large amount of fat), baked goods, fruits (avocados 16%, olives 30%)

- Plant based → cottonseed, linseed, canola, sunflower, olives, palm, nuts, seed (8% of total fat intake)
- Animal Sources → meat, fish, eggs, dairy (42 % of total fat intake)

Palatability

- Texture and flavor of food
- “Mouth feel”
- Tenderness of baked goods
- Carry flavor and aroma compounds

Ontario food survey – Fat highlights

Mean total fat intake:

- Men (18 to 74 years) = 87 g/day
- Women (18 to 74 years) = 56.5 g/day

Mean saturated fat intake:

- Men (18 to 74 years) = 29 g/day
- Women (18 to 74 years) = 19 g/day

1. Triglycerides

- Triacylglycerides

- Main form of dietary fat (95%) and body fat (in tissues and adipose)
- 1 glycerol molecule bonded to 3 fatty acid molecules
Glycerol → 3 carbon chain and 3 hydroxyl groups
Fatty acids → methyl end and carboxyl end
→ Types of fatty acids are determined by: length of carbon chain, and # C=C double bonds (saturation)

- Formed by condensation broken down by hydrolysis
- 2 fatty acids- diglyceride
- 1 fatty acid- monoglyceride

Glycerol – carboxyl group binds to glycerol

- The carboxyl group at the end of each fatty acid is also water soluble
- Carbon chain is not water soluble
- Insoluble ends position themselves away from water

Unsaturated fatty acid

- A fatty acid that lacks H atoms and has at least 1 C=C bond

Saturated fatty acid

- A fatty acid that carries the max # of H atoms

Trans fatty acid

- Contains C=C in trans configuration

Characteristics of FAs

1) Chain length

- <10 carbons = short chain fatty acids (rare)
- 10-14 carbons = medium chain fatty acids
- >16 carbons = long chain

- Degree of saturation
- # of C=C bonds determines → solid or liquid at room temp, melting point, stability

Fatty Acid Nomenclature

- Oleic acid (18:1) # Cs in chain: # double bonds
- Oleic acid (18:1n-9) "n-#" notation gives location of the double bonds from methyl end of FA
- If > 1 double bond written as 18:2n=9,12
- Oleic acid (18:1;9) → means same as above without "n"

Saturated Fats and Fatty Acids

- Saturated fatty acid: An FA with the maximum # of H atoms (no C=C bond) eg. Stearic acid (18:0)
- Saturated fat: consists primarily of saturated fatty acids eg. Butter

Saturated Fatty Acids

- Usually solid at room temp > 10 C
- Tropical oils: coconut, palm, palm kernel are not solid at room temp (contain lots of SCFAs)
- Stearic (18:0), palmitic (16:0) myristic (14:0), lauric (12:0)
- Much more stable than unsaturated fatty acids (10x more stable than MUFAs, 100x more stable than PUFAs)

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Unsaturated Fatty Acids

- Monounsaturated fatty acid (MUFA)- a fatty acid that lacks 2 H atoms and has 1 C=C bond eg. Oleic acid (18:1)
- Monounsaturated fat: a fat containing mostly MUFAs (1 C=C) eg. Olive oil, canola oil, peanuts
- Unsaturated Fat: a fat in which most of the fatty acids are unsaturated
 - Lower melting point than saturated Fats
 - C=C bonds create "cis" kinks in molecules (means that you cannot pack them tightly as saturated Fats which takes less heat to disrupt their structure > liquid form)
 - two types: monounsaturated and polyunsaturated
- ▶ Polyunsaturated fatty acid (PUFA) - a fatty acid that lacks 4 or more H atoms > 2 C=C
 - E.g., linoleic (18:2); linolenic acid (18:3)
 - Polyunsaturated fat - a fat containing mostly PUFAs (> 2 C=C)
 - E.g., vegetable oils

- ▶ Must be a minimum of 12 C long to contain a C=C
- ▶ Each double bond occurs 3Cs farther along the chain
- ▶ # of C=C restricted by chain length
- ▶ Maximum of 6 C=C in dietary fatty acids
- ▶ Human enzymes **cannot insert C=C** below C9

→ liquid at room temp

Unstable C=C bonds react with oxygen to form peroxides

- Results in rancid taste and smell

Remedy:

- Add antioxidants (Vitamins A, C, E, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT))
- Vacuum seal
- Saturate the C=C bonds (hydrogenation)

3- Fatty Acids

- Omega 3, w-3, n-3
- PUFAs with their first C=C between 3rd and 4th carbons (from methyl end)
- Constituents of phospholipids

Essential Fatty Acids

- Fatty acids that are not made in sufficient amounts to meet physiological needs
- Linoleic and linolenic acid
- Required for → cell membranes
- Production of → Eicosanoids which regulate blood pressure, blood clotting and blood lipid levels

A - linolenic acid (18:3; n-3,6,9)

- Sources → soy, leafy vegetables, flax seed, canola, linseed, walnuts, wheat germ, soy oil, vegetables and fish oils
- Converted to EPA and DHA

Eicosapentaenoic acid (EPA) → 20:5, n-3, 6,9,12,15

- Sources: fish, human milk

Docosahexanoic acid (DHA) → 22:6 or n- 3 6 9 12 15 18

Docosahexaenoic acid (DHA) / 22:6 n-3, 5, 8, 11, 14, 17, 20

- Sources: fish, human milk

Omega-6, n-6 FAs

- PUFAs with a C=C between carbons 6 and 7 (from methyl end)
- NB component of phospholipids, body tissues

Linoleic acid (18:2, n-6,9)

- Sources → vegetable oils, meats, nuts, grains, leafy vegetables
- Converted into → Arachidonic acid (20:4, n-6,9,12,15)
- Sources → meat, liver, peanut

Omega 9

- PUFA's with the C=C between 9 and 10
- Eg. Elaidic acid found in hydrogenated (vegetable oils) and ruminant fats

An unsat FA can be in trans or cis configuration

Trans → H atoms are on opposite sides of the C=C

Cis → H atoms are on the same side of C=C

Most common configuration in nature (lower melting point)

Trans configuration of unsat FA

- Few found in nature
- Milk, beef and lamb
- Small amounts in some veg oils
- Most trans fat in foods produced by partial hydrogenated
→ Bubble H through unsaturated oils and breaks may C=C bond and some are changed to the trans

CLA (conjugated linoleic acid) → weight loss possible, not all trans fat are bad some protective effects

Total Hydrogenation

- A chemical process by which hydrogen's are added to MUFAs and PUFAs to reduce the # of double bonds

- Makes more saturated (solid) and more resistant to oxidation
- This now becomes a saturated fatty acid

Partial Hydrogenation

- Breaks some C=C bonds and adds hydrogen's
- Changes the configuration of H atoms at some C=C from cis to trans
- Results in a trans fatty acid

Trans fatty acids in foods

- Raises melting points
- Margarine and shortening → partially hydrogenated
- Found in baked good, peanut butter, fried foods and snacks
- Elaidic acid (**C18:1, n-9 trans**) has a melting point of 44 degrees Celsius
- Oleic acid (**C18: 1, n-9, cis**) has a melting point of 13 degrees Celsius
- **Why make TFAs?**
- Studies show total TFA intake is 2 to 3% of total energy intake (about 5 g/day)
- 40% decrease in past 10 years

WHO recommends TFA <1% of total energy intake

Trans Fat Task Force recommended TFA <2% of total fat in veg oils and <5% of total fat content in all other foods

**Two types of polyunsaturated fats are essential → omega 3, and omega 6

Ratio of omega 6:3, should be 1:1, 4:1

Typical diet right now is 11:1 – 30:1

Omega 3- aim for 500 mg a day

Avoid omega 3-6-9 wont correct imbalance of ratio

2. Phospholipids

- Glycerol + 2FAS + a nitrogen containing compound + a phosphate group
- 2% of total fat intake in our diets
- PO₄ group & N compound form a hydrophilic head
- Fatty acids form hydrophobic tail

- Found naturally in food, added as emulsifiers

Roles

- Major component of cell membrane
- Allow lipids to pass through membranes
- Emulsify- suspend lipids in body fluids
- Phosphatidylcholine, phosphatidylserine, phosphatidylglycerol

3. Sterols

- Composed of C, H, O atoms
- Arranged in rings with various side chains
- Don't contain fatty acids *
- Roles → production of bile, sex hormones, adrenal hormones, vitamin D, cholesterol (cholesterol is very important)
- Sources → plant and animal foods

Focus on cholesterol

- Only in animal fat and animal products
- Manufactured by liver, small intestine, and body cells

Cholesterol

Dietary cholesterol: cholesterol found food

Blood cholesterol: level of cholesterol found in blood (can originate from exogenous- outside body and endogenous- inside the body)

**Dietary CH has little influence on blood CH → saturated fat has much greater effect on cholesterol

Not an essential nutrient

Absorb 40-60% of dietary CH

Dietary cholesterol is absorbed by chylomicrons > lymph > blood

Carried in blood by various lipoproteins

Phytosterols

- Chemically related to cholesterol in plants

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- Saturated phytosterols inhibit CH absorption
- Only occur naturally in few foods → produced commercially
- Average intake is 250mg/day and very poorly absorbed
- 1.6 to 2.0 g/day of plant sterols can lower blood CH levels by 5-10%
- “Becel proactive”

Lipid digestion and absorption

- Most dietary fats are triglyceride
- Emulsification and digestion by lipases
- 50% becomes free fatty acids and glycerol and 50% becomes MG and DG and free fatty acids

Lipid absorption

- ▶ Absorbed by **microvilli** > **blood**:
 - Glycerol, short chain FA (< 10 Cs), medium chain FA (10-14 Cs)
 - Form **micelles** > diffuse into microvilli > enter lymph
 - Long chain FAs, MGs
 - Form **chylomicrons** > absorbed by **exocytosis** > lymph:
 - TGs (formed from long chain FAs, MGs, glycerol), cholesterol, phospholipids

Lipoproteins

- ▶ Carry TGs, phospholipids, & cholesterol in different proportions
- ▶ 4 types (vary by **size** and **density**)
 - **Chylomicrons**
 - **Very low density lipoproteins (VLDL)**
 - **Low density lipoproteins (LDL)**
 - **High density lipoproteins (HDL)**
 - All contain **PROTEIN** and **LIPID** → the more protein (apolipoproteins), the **higher** the density

Chylomicrons – lowest density

- ▶ Largest lipoprotein, **lowest** density (least protein)
- ▶ Carry dietary lipids: TGs (medium & long chain FAs), MGs, glycerol, cholesterol, phospholipids throughout body for **metabolism & storage**
- ▶ **Formed in GI tract** > lymph > thoracic duct >> blood

- ▶ Surface > **hydrophilic**; core > **hydrophobic**
- ▶ **Lipoprotein LIPASE** on cells breaks chylomicrons into **free FA, glycerol and MGs**
- ▶ Cells remove lipids from chylomicrons as they pass > chylomicrons **reduce** in size (**get smaller**)

VLDLs

- ▶ Formed in the **liver**
- ▶ Carry **lots of TGs** (exogenous & endogenous) and little **cholesterol**
- ▶ Body cells remove TGs as VLDL pass >> VLDLs shrink >> VLDLs **pick up cholesterol** and become **LDLs**
- ▶ **Lipoprotein lipase** in body cells breaks down **VLDLs** into free FAs and MGs

LDLs

- Formed from **VLDLs**
- ▶ Carry lots of **cholesterol** and little **triglyceride (TG)**
- ▶ “Less” healthy (want “low”)
- ▶ **LDLs associated with CVD**
- ▶ Cells **remove** cholesterol, TGs & phospholipids
- ▶ Carry cholesterol **TO** the body cells

HDLs- highest density

- ▶ Formed from **chylomicrons & VLDLs**
- ▶ “Healthy”, want “high” amounts in body
- ▶ **HDLs associated with decreased CVD risk**
- ▶ Transport cholesterol & phospholipids **TO the liver** for **breakdown or excretion**

Cholesterol myth

- ▶ There is no such thing as “good” and “bad” cholesterol – there is only one kind of cholesterol
- ▶ LDLs & HDLs vary in the **amount** of cholesterol they carry
- ▶ LDLs & HDLs also vary in the **direction** in which they carry cholesterol
- ▶ (thus, one is better than the other!)

Lipid metabolism

Potential fates of lipids:

1. Used as immediate **energy**
2. Stored in **adipose** tissue
3. *Becomes part of **cell membranes** ...
4. *Used to produce necessary compounds such as cholesterol, bile, and hormones...

Coenzymes involved in energy metabolism

- ▶ FADH_2 – Flavin adenine dinucleotide (reduced form – gains electrons)
- ▶ NADH - Nicotinamide adenine dinucleotide (reduced form – gains electrons)
- ▶ FADH_2 & NADH become source of ATP (reoxidized – donates e^- to ETC)
- ▶ Acetyl CoA enters CAC ...

Lipids as an energy source

- ▶ Oxidation of **palmitic acid (C16)** outside the body yields 2340 kcal
- ▶ Oxidation inside the body yields 940 kcal max (recall: e^* used in oxidation!)
- ▶ Oxidation of FAs > **40% efficient** (same as glucose)
- ▶ Overall lipid oxidation >>> **ATP + CO_2 + H_2O**
- ▶ **Beta-oxidation** pathway (**mitochondria**) & its variants
- ▶ Successive cleavage of **pairs of C atoms**

Fatty Acid Oxidation

- ▶ β -oxidation- primary pathway for oxidation of saturated FA
- ▶ FA > 22 C long oxidized via modified β -oxidation called peroxisomal pathway
- ▶ Unsaturated FA oxidized via another modified β -oxidation pathway, use 2 ATP per C=C

Energy Balance Sheet

For 1 **18C saturated** fatty acid:

9 2C fragments join with 9 CoA to form 9 Acetyl CoA and enter **CAC** (if sufficient CHO intake) > **27 NADH + 27H⁺ + 9 FADH₂ + 9 GTP**

From β -oxidation:

• **9 FADH₂**

- ▶ **8 FADH₂**
- ▶ **8 NADH + 8H⁺**
- ▶ **2 ATP used to begin oxidation**

RECALL:

3 ATP per 1 NADH oxidized

2 ATP per FADH₂ oxidized

GTP does not enter oxidative phosphorylation (ETC) = directly phosphorylated

1 ATP per GTP

How does fat and glucose metabolism compare?

- ▶ One 18C saturated fatty acid yields 146 ATP
- ▶ Three 6C glucose (total 18C) yields 114 ATP

ATP yield per Carbon:

18 C FA = 8.1 ATP per C

18 C glucose = 6.3 ATP per C

Why is there more ATP from fat?

- ▶ FAs are all hydrocarbon except for the carboxyl group – they exist in a highly reduced state
- ▶ Glucose is already partly oxidized due to the presence of its hydroxyl (OH) groups

From B- oxidation

- ▶ 1 NADH + 1 H⁺ AND 1 FADH₂ per β-oxidation reaction
- TIMES **9** β-oxidation reactions =
- ▶ 9 NADH + 9 H⁺
- ▶ 9 FADH₂
- ** Remember the 2 ATP used to start β-oxidation

Fates of Acetyl CoA

(1) Enter CAC/TCA cycle if:

- ▶ Body cells **require energy**
- ▶ **Sufficient carbohydrate** to run CAC

- Need **oxaloacetate** – required for step 1
- Oxaloacetate is a **carbohydrate derivative** (arises from glycolysis (formed from pyruvate) and can be used to produce glucose)

(2) Produce ketone bodies:

- ▶ Some **ketone** bodies are ALWAYS produced – acetoacetate is preferred fuel source of heart muscle & renal cortex
- ▶ Adipose around the heart provides ketones from CHO

Ketone Bodies

Fasting or ketogenic {low CHO, high fat} weight loss diets, uncontrolled diabetes:

- ▶ Insufficient oxaloacetate to react with excess Acetyl CoA (from FA beta oxidation) > ketone bodies
- ▶ Ketone bodies (water soluble) generated in liver > diffuse into blood >> used as energy source by many cells
- ▶ ≈1 week of fasting, some brain cells adapt > use ketone bodies
- ▶ Some brain cells still require glucose – protein still catabolized for gluconeogenesis >> continuing lean tissue loss

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Effects of Ketosis

- ▶ Blood ketone bodies (acetoacetate & beta-hydroxybutyrate are acidic) >> overwhelm buffering capacity of blood > ketoacidosis (lowering of blood pH)
- ▶ Body tries to restore pH by excreting H⁺ (accompanying loss of Na, K, & H₂O) in urine > acidic

H₂O / H⁺ / HCO₃⁻ / acetate

- ▶ Under low pH > hemoglobin binds less oxygen
- ▶ Severe dehydration
- ▶ 2° mineral imbalance (dangerous to those with weak heart)
- ▶ Coma > death (uncontrolled diabetes)
- ▶ Loss of:
- ▶ Appetite (true for any e* restriction)
- ▶ Weight (rapid) >> from **body water, glycogen stores, muscle mass** and adipose
- ▶ Body minerals
- ▶ Ketogenic Weight loss diets
- ▶ Adipose losses on ketogenic weight loss diets no greater than balanced weight loss diets providing same # kcal **WITHOUT** the danger of ketosis and **MINIMIZING** lean tissue loss
- ▶ Return to balanced diet – weight will be regained

Acetyl CoA and Cholesterol

- ▶ Acetyl CoA -- precursor of cholesterol
- ▶ Limit endogenous cholesterol production > limit total fat intake > less acetyl CoA available to synthesize cholesterol
- ▶ Best advice is to limit total fat intake to reduce blood CH
- ▶ This will limit both exogenous hypercholesterolemic saturated fat intake AND endogenous CH production therefore reducing blood CH

2. Storing excess lipids as adipose

- ▶ If sufficient carbohydrate to provide energy for cells:
 - Chylomicrons release free FAs AND lipoprotein lipase -- enzyme on surface of adipose cells hydrolyzes TAGs from blood >> parts enter fat cells >> reassembled & stored > lipogenesis
 - Less energy used to store dietary lipids as body fat than to store carbohydrate as body fat!