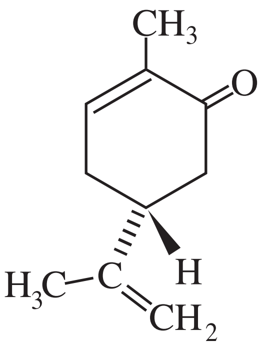
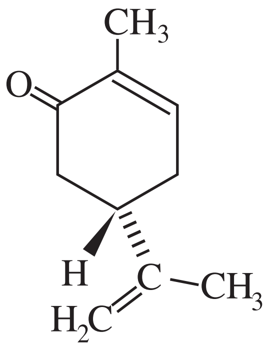
Super Models



(*R*)-carvone
Spearmint



(*S*)-carvone
Caraway

Hot and Spicy Molecules
Molecular Model Kit

⚠**Caution:** Atom centers and vinyl tubing are a choking hazard. Do not eat or chew model parts.

Kit Contents:
- 65 white 1-peg hydrogen atom centers
- 5 blue 3-peg nitrogen atom centers
- 14 red 2-peg oxygen atom centers
- 4 yellow 2-peg sulfur atom centers
- 3 yellow 4-peg sulfur atom centers
- 3 yellow 6-peg sulfur atom centers
- 40 black 4-peg carbon atom centers
- 13 black 3-peg carbon atom centers
- 138 clear, 1.25″ single bonds
- 18 clear, 4cm bonds (for double bonds)

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Hot and Spicy

Background:

A. **The sense of taste.**

The chemical sensors in our mouths and associated organs are sensitive to at least five basic taste sensations; sweet, sour, bitter, salty, and umami, which is associated with a "savory" sensation that is provoked by substances such as MSG.

Why is it then that we seem to experience a greater variety of taste when we eat? Other components of perceived tastes are due to 1) volatile compounds that we sense as odors and interpret as taste, 2) compounds such as menthol which produces a "cool" sensation, and 3) food texture.

The sensation of "hot" that one apprehends is due to chemical stimulation of pain nerve cell endings, on the trigeminal nerve, so "hot" is not really a taste but the same type of pain that one would feel if some thing of a high temperature or a caustic nature were placed in the mouth. Two of these irritating food substances are capsaicin in chili peppers and zingerone found in ginger.

The "hot" and spicy sensations provoked by the foods we eat are produced by a vast number of chemical substances in many categories of compounds such as terpenes and terpenoids, vanilloids, phenols or other substituted aromatics, aldehydes, and allyl glucosinolates and several other sulfur containing compounds. Many of these substances provide the plants that produce them with protection against being eaten by animals or infection by bacteria or fungi.

In some instances, a precursory chemical (e.g. sinigrin in black mustard, and alliin in onions and garlic) must be broken down by an enzyme to yield several smaller molecules which then impart the identifying flavor of the spice.

The number of spicy substances within one particular plant is usually large (a dozen or more); however, an individual spice can be characterized by the predominance of two or three of these chemicals. Because of the limitation of space, we will examine only a few compounds that contribute to the exciting flavors of foods.

B. A partial list of spice compounds.

Spice or plant	**Compounds**
1. Allspice	eugenol, thymol, cineole (eucalyptol), caryophellene
2. Anise	anethole, anise aldehyde, estragol
3. Bay	cineol, linalool, borneol, eugenol
4. Caraway	(*S*)-carvone, carveol (*R*)limonene
5. Cinnamon (Chinese)	Cinnamic aldehyde, benzoic acid, coumarin, umbelliferone, salicylic acid, cinnamic acid
6. Cinnamon (Cylon)	Cinnamic aldehyde, 3-phenyl-acrolein, eugenol

Spice or plant	Compounds
7. Clove	eugenol, caryophylline
8. Cress (several types)	gluconasturciin
9. Dill	carvone, pinenes, α-phellandrene
10. Garlic	alliin, allicin, dimethyl trisulfide, thiophene, ajoene
11. Ginger	Zingerberene, α-curcumene, citral, borneol, farnesene, linalool, zingerone
12. Juniper	pinenes, borneol, terpineol, geraniol, cadinene, caryophyllene
13. Lemon	(*R*)-limonene
14. Mustard (black)	sinigrin, nitriles, isothiocyanates, thiocyanates
15. Mustard (white)	sinalbin, nitriles, isothiocyanates, thiocyanates
16. Nutmeg	pinenes, camphene, p-cymene, safrole myrcene, terpinene, (*R*)-limonene, myristicene, elemicene
17. Onion	alliin, allicin, dimethyl disulfide
18. Oregano	thymol, pinenes, carvecrol
19. Peppermint	menthol, jasmone
20. Pepper (black)	piperene, myrcene camphene
21. Pepper (white)	piperene
22. Pepper (chili)	capsaicin
23. Rosemary	cineole, borneol, linalool, terpineol, camphor
24. Saffron	safrole, safranal
25. Sage	cineole, linalool, ocimene, borneol, pinenes, thujone
26. Spearmint	(*R*)-carvone
27. Tarragon	estragol, anethole, myrcene, ocimene
28. Thyme	iso-valeric acid, carvecrol
29. Vanilla	vanillin
30. Wintergreen	methyl salicylate

And just for the fun of it: cats like this one.

31. Catnip	nepetalactone

Constructing the molecular models:

If you have a working knowledge of chemical symbolism, skip section A, and go to B, where you will find instructions for making double bonds in your models.

A. Chemical symbolism.

It is expedient sometimes to show a complex biochemical structure in an abbreviated form. For example, cyclohexane (C_6H_{12}) can be drawn as a simple hexagon. A carbon atom is understood to be located where two lines intersect. We also assume two hydrogen atoms are bonded to each carbon, since carbon atoms always make four bonds. See Fig. 1.

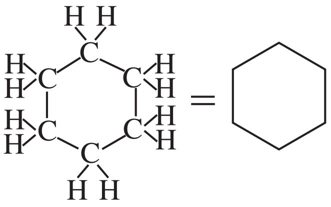


Fig. 1 A shorthand method of drawing a molecule of cyclohexane.

There are four methods of making a molecular diagram of a benzene ring. This also applies to a phenyl group which is benzene minus one hydrogen atom. This structure should be assembled by using six of the black, three-peg carbon atoms (see Fig. 2).

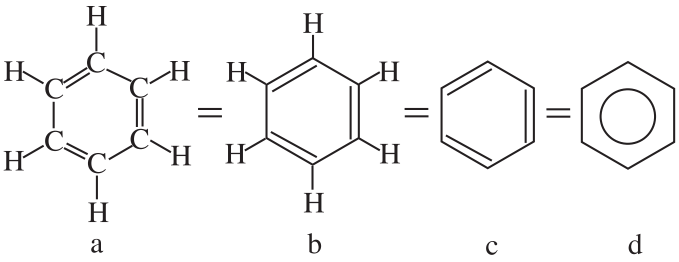


Fig. 2 Four ways to draw a benzene ring or a phenyl group.

The display of bonds and H atoms is also avoided in other structures as illustrated below. See Figs. 4, 5, 6, and 7.

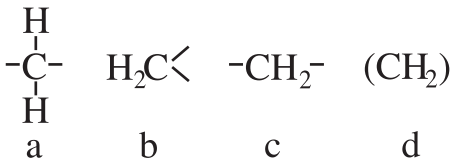


Fig. 4 Four examples of a methylene group.

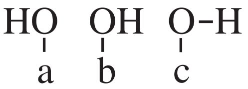


Fig. 5 Three examples of an hydroxyl, or hydroxy group.

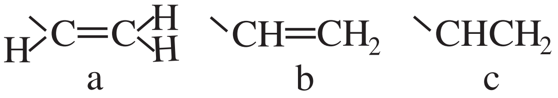


Fig. 6 Three examples of an alkene (double bonded carbons) group.

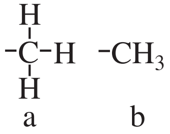


Fig. 7 Two examples of a methyl group.

Greater simplification is possible when we leave out carbon and hydrogen atoms as you can see in Fig. 8.

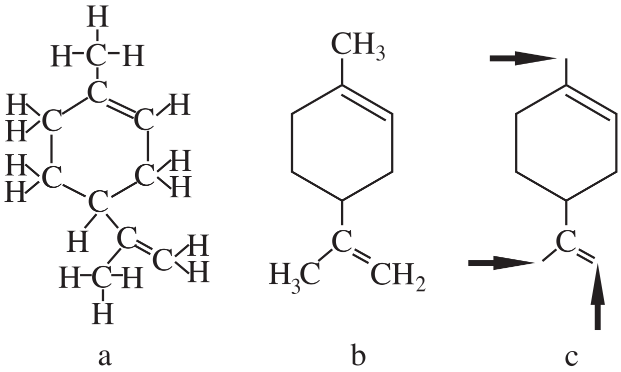


Fig. 8 From complex to simpler diagrams as we move from letter a to letter c.

Notice that at the “open” end of a bond, indicated by the arrows in the above diagram, you will find a carbon atom. Count the bonds shown attached to a carbon atom, subtract this number from four. The result is the number of hydrogen atoms you should attach to the carbon atom.

Count the numbers of carbons, hydrogens, oxygens, single bonds, double bonds, and the total number of bonds in the structural formula of elemicin below in Fig. 9.

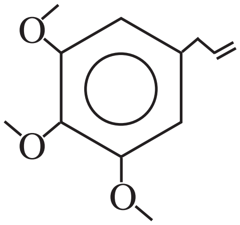


Fig. 9 Elemicin

Answers: carbons—12; hydrogens—16; oxygens—3; single bonds—31; double bonds—4; total number of bonds—35.

Next consider the method for simplifying the formulas of organic acids and aldehydes which are both composed of atoms of carbon, hydrogen and oxygen as you see below in expanded (a) and condensed (b) forms. See Fig. 10.

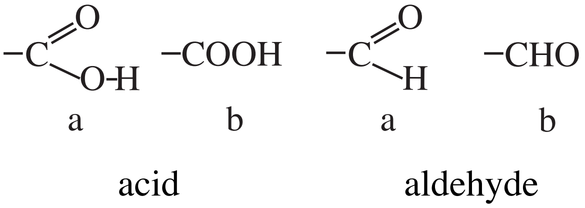


Fig. 10 Expanded and condensed forms of organic acids and aldehydes.

Before making the models, we should examine three more concepts that deal with molecular structure; one is enantiomers, the orientation of atoms around an atom of carbon that has four different groups bonded to it. The second is bicyclic compounds, and the third is conformations of ring structures.

We will start with enantiomers which are chiral molecules that have at least one chiral carbon. Chiral carbon atoms have four different atoms or groups of atoms bonded to them. In some instances, it is possible to have two different arrangements of the same four bonded groups on a carbon atom. A carbon atom of this description is known by several names such as stereogenic center, stereocenter, chirality center, asymmetric carbon, chiral carbon, or chiral center. We will call it a chiral carbon, and start our discussion of enantiomers (chirality) with some simple compounds. Fig. 11 has a list of symbols that will be helpful in visualizing molecular structures.

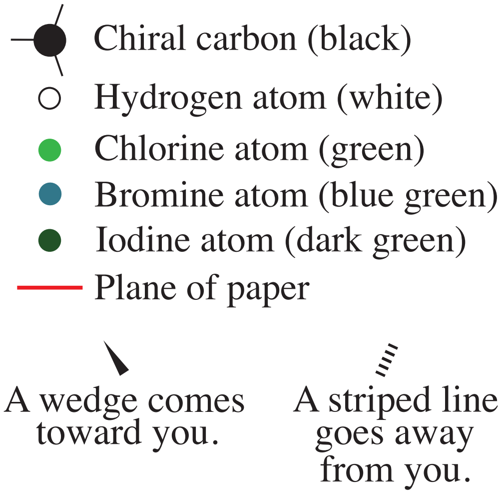


Fig. 11 Symbols for understanding chirality.

A molecule with two or more groups of the same type will not be chiral due to the presence of an internal plane of symmetry. The molecule will be in perfect alignment with its mirror image. The drawing at the top of Fig. 12 is a view of the molecule looking down on the chlorine atom.

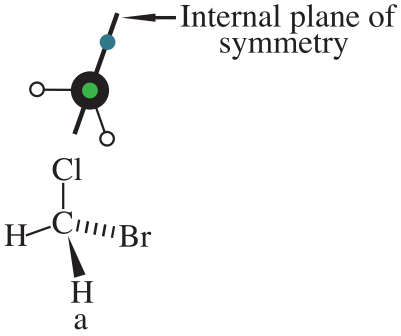


Fig. 12 A molecule with no chiral carbon and is not chiral.

A molecule with only one chiral carbon will not be in perfect alignment (be superimposable) on its mirror image. The molecule itself is called chiral. Chiral comes from the Greek word for hand, so chiral molecules have "handedness," (i.e. a left and a right handed form). Chiral molecules are called enantiomers.

In structural diagrams, solid lines are bonds that link atoms which lie in the plane of the paper; those that are in front of the plane are connected by solid wedges; and those that go behind the plane are bonded by a series of stripes. An asterisk (*) marks a chiral carbon.

Use the key presented in Fig. 11 to make a model of bromochloroiodomethane. Also make its enantiomer. See Fig. 13.

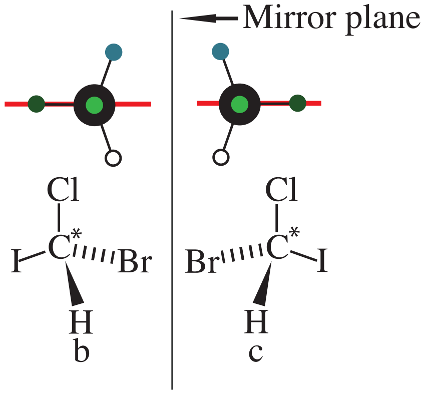


Fig. 13 Enantiomers of CHBrClI (bromochloroiodomethane).

At the top of Fig. 13, you see the view of the two molecules looking down on the chlorine atoms. Notice that "b" and "c" are mirror images of one another. The two different forms of CHBrClI share the same sets of chemical and physical properties with only a few exceptions which depend on chirality.

Now we would like to know which one is left handed and which one is right handed. In the following section we will learn the procedure for determining the "handedness" of "b" and "c."

B. Determining the stereochemistry of a chiral compound.

Step 1. Make sure that the atom with the lowest atomic weight on the chiral carbon is pointing away from you. In most, but not all, of the molecules you will encounter, it will be a hydrogen atom (at. wt. 1). In order to get "b" into the correct position, grab the chlorine of "b" and turn it clockwise 180° so that it looks like "e." See Fig. 14.

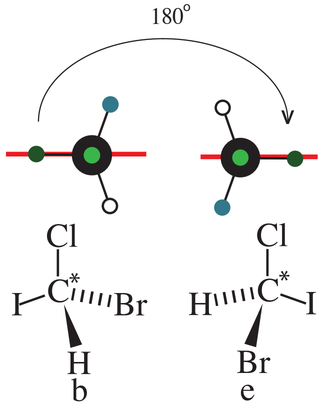


Fig. 14 Positioning –H behind the plane of the paper.

Step 2. Find the atomic weight of each other atom immediately bonded to the chiral carbon.

Step 3. Assign values from 1 to 4 to the atoms based on their atomic weights. The lower the weight, the lower the priority. Here, H = 4 (lowest priority). The other atomic weights are Cl = 35, Br = 80, I = 127. Therefore, Cl gets a 3, Br gets 2, and I is priority 1.

Step 4. We already placed H = 4 in back, so now we trace a path from 1 to 2 to 3. The path travels clockwise, so we have discovered that "b" is right handed. See Fig. 15.

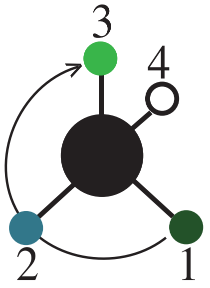


Fig. 15 Right handed CHBrClI.

Step 5. The way we indicate handedness is by naming a right handed molecule with the prefix (*R*)-, and a left handed molecule with the prefix (*S*)-. The CHBrClI with which we used to learn the procedure would then, be called (*R*)-bromochloroiodomethane. Its "c" enantiomer in Fig. 13 is called (*S*)-bromochloroiodomethane.

The same parts are present, just the way they are arranged in space is different.

In Fig. 16 there is a photograph of the isomers of bromochloroiodomethane. Which one is (*R*), and which one is (*S*)?

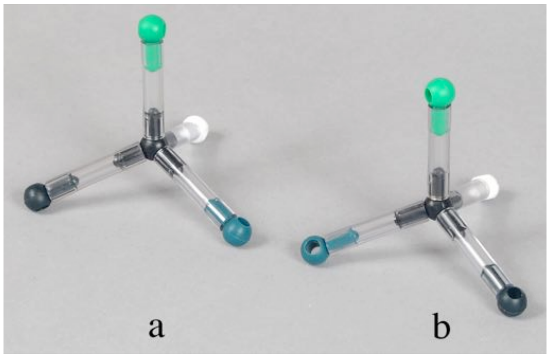


Fig. 16 Identify the chirality of "a" and "b."

Answers: "a" is the (*S*) isomer. "b" is the (*R*) isomer.

The following photograph in Fig. 17 has a problem which is a little more challenging. Which one is (*R*), and which one is (*S*)?

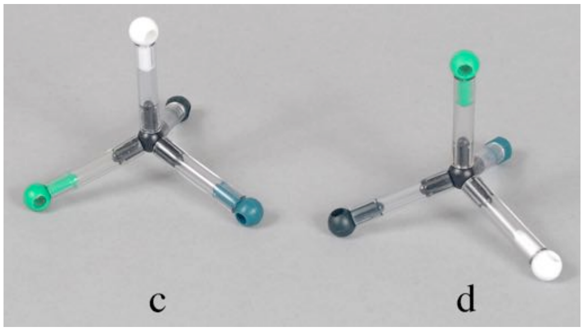


Fig. 17 Identify the chirality of "c" and "d."

There are three approaches you can try here. 1) Make models, and turn them to see the H in the back. 2) In your mind flip the pictures around so that the H is in the back, and then make your determination. 3) Again using your imagination, switch the H and any other atom so that the H is in the back. Determine the clockwise or counterclockwise path from 1 to 3. You will find the (*R*) or (*S*) answer, but since you made the allowable switch of atoms, you must switch your answer to the opposite chirality.

Answers: "c" is (*S*), and "d" is (*R*) .

The molecules you just looked at were quite simple, but the hot and spicy chemicals are more complex. Therefore we should learn about the chirality of molecules with greater complexity. Are there any chiral carbons in Fig. 18?

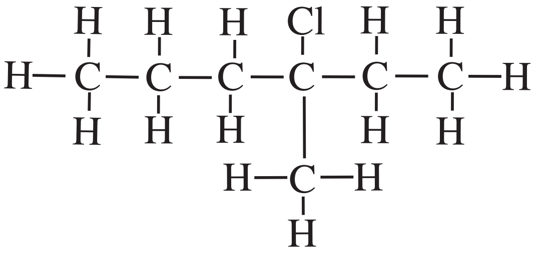


Fig. 18 Do you see any chiral carbons here?

Answer: Fig. 19 shows the only chiral carbon, marked with an asterisk (*).

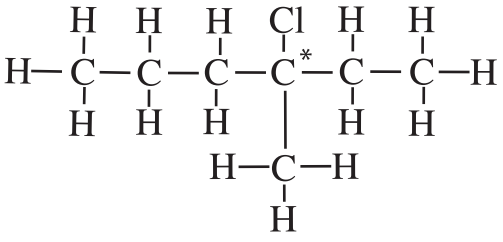
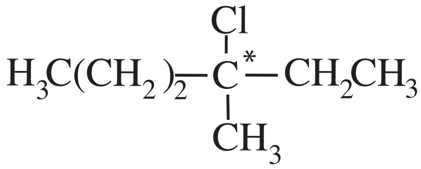


Fig. 19 3-chloro-3-methylhexane with one chiral carbon.

Converting the molecule in Fig. 19 to a condensed formula, we will see Fig. 20.



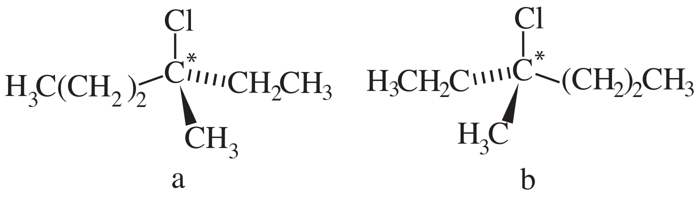
$$H_3C(CH_2)_2-\overset{Cl}{\underset{CH_3}{C^*}}-CH_2CH_3$$

Fig. 20 Condensed form of 3-chloro-3-methylhexane.

Using straight lines, dashes and a wedge, draw one of the isomers of 3-chloro-3-methylhexane. There are only two isomers of the compound, so you can not make a mistake.

An interesting fact you might want to know is that there are a maximum of 2^n isomers for a compound with n chiral carbons. However, some of the isomers may not exist. So, with one chiral carbon, there might be two isomers. With two chiral carbons, four isomers are possible, and so on.

Your structural formulas should look like the two enantiomers in Fig. 21.



a

b

Fig. 21 The two enantiomers of 3-chloro-3-methylhexane.

Is “a” (*R*), or (*S*)?

Answer: “a” is (*S*), so then “b” is (*R*).

Here is how we determined the answers. Inspection of the atoms immediately bonded to the C* shows that the Cl atom has the highest atomic weight (35), so Cl has highest priority value of 1. The other three atoms are tied at atomic weight 12 each. See Fig. 22.

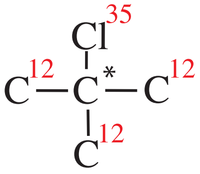


Fig. 22 The first step in finding chirality.

In order to break the tie among the other carbon atoms, we set up the following diagrams in Fig. 23.

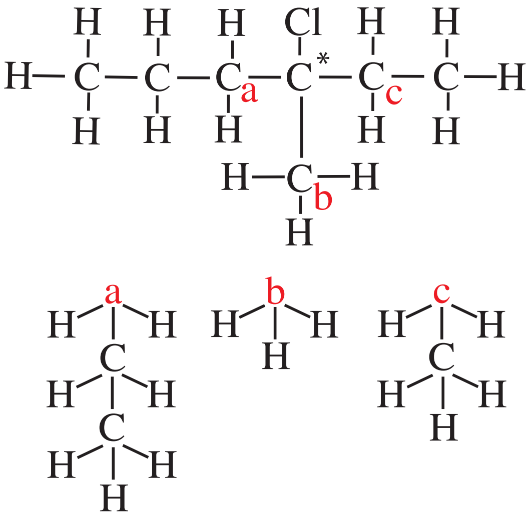


Fig. 23 Finding the distribution of mass.

“a” has the second most mass, so its priority is 2; “c” is next, and “b” has the lowest. $-CH_3$ should be placed in back of the plane of the paper in order to determine (*R*), and (*S*) enantiomers.

Finally, we will demonstrate the concept with (*R*)- and (*S*)-carvone. See Fig. 24.

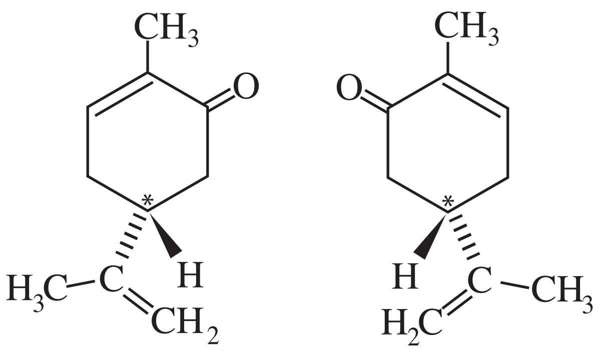


Fig. 24 Carvone.

Which one is (*R*), and which one is (*S*)? Flip the carvone that is on the right side of Fig. 24 so that it looks like Fig. 25. Then label the carbons as illustrated.

The chiral carbon is marked with an * as usual, and the H atom can immediately be assigned the lowest priority (4).

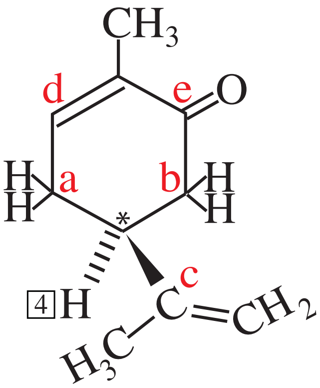


Fig. 25 Carvone set up for (*R*), (*S*) determination.

Fig. 26 Shows what is found following the bonds from “a” and from “b.”

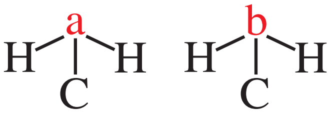


Fig. 26 The same results at “a” and “b.”

The atoms at “c” make up a group called methylethenyl. Because the group has a double bond, we must make some changes in its structure before we can determine its weight value.

The “c” carbon is joined with another carbon, c-prime (c´), through a double bond. Each carbon is treated as though it was bonded with **two** other carbon atoms, not one. On the right side of Fig. 27, the two additional carbon atoms are shown.

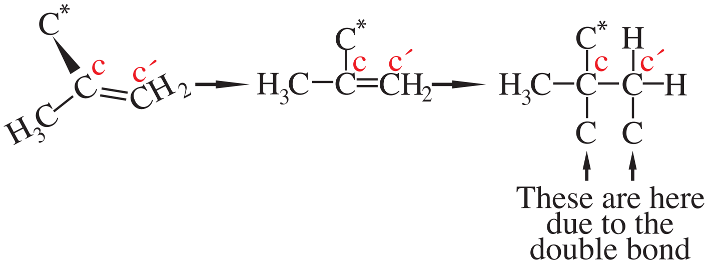


Fig. 27 Expanding methylethenyl to include extra carbon atoms.

Now we can better compare “a,” “b,” and “c.” “c” clearly has the highest priority of the three. Its priority is a 3. See Fig. 28.

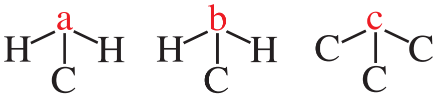


Fig. 28 With three carbons joined to it, “c” has the highest priority.

We still have a tie between “a” and “b” to break, so we use the same analytical technique on them as we used on “c.” See Figs. 29 and 30.

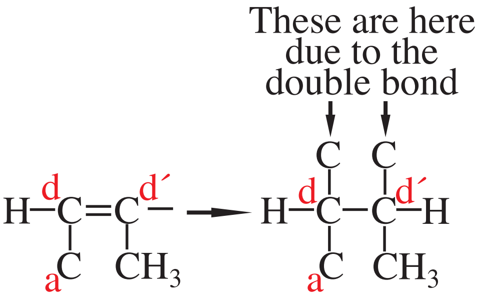


Fig. 29 Expanding groups around “d” to include extra carbon atoms.

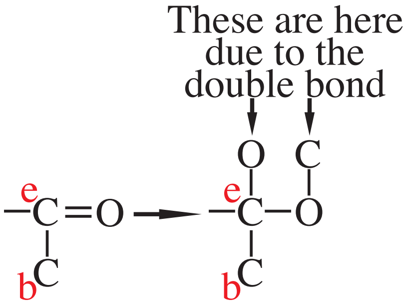


Fig. 30 Expanding groups around "e" to include an extra carbon and oxygen atom.

Fig. 31 is a summary of what we found in making Figs. 29 and 30.

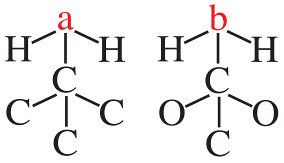


Fig. 31 Showing the preference of "b" as priority 2 and "a" as priority 3.

So, the structure we worked so hard on is the (*S*) enantiomer, the one that tastes like caraway seeds. The (*R*) enantiomer has the taste of spearmint. This is just one example of how important chirality is in biological molecules. See Fig. 32.

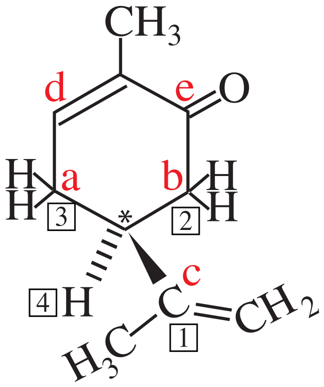


Fig. 32 (*S*)-carvone.

Many flavorful compounds listed below are bicyclic molecules. That is, they are composed of two rings of carbon atoms (sometimes with other elements as well) joined together. There are three ways to join rings: one is by bridging the two rings, a second way is by fusing the rings. We will not discuss the third way at this time because it doesn't apply to the molecules we investigate.

An example of a bridged system is the terpenoid derivative, borneol. Fig. 32 shows the molecule with the shortest bridging bonds in red.

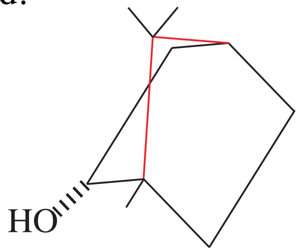


Fig. 32 Borneol, a bridged bicyclic.

An example of a fused system is the sesquiterpene derivative, δ-cadinene (δ is read, "delta"). Fig. 33 shows the molecule with its two fused carbons bonded in red.

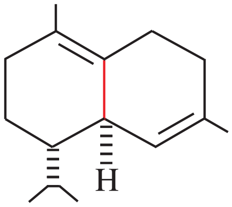


Fig. 33 δ-cadinene, a fused bicyclic.

B. **Making a double bond for a model.**

When making a double bond, connect two pegs of one atom to two pegs of the other atom with two of the long, thin tubes as you see below in Fig. 34.

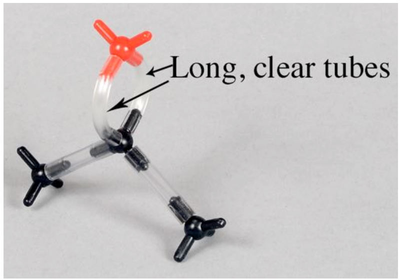


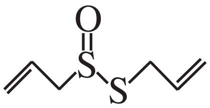
Fig. 34 How to make a double bond.

C. **Making molecular models.**

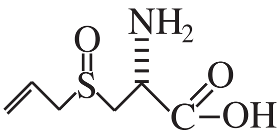
The following are skeletal structures of several spices. Where necessary, the stereochemistry is indicated with dashes and wedges.

1. Ajoene (ajo is the Spanish word for garlic) is formed when alliinase, an enzyme found in garlic, breaks down alliin. This happens when garlic cells are damaged.

2. Allicin, like ajoene, is found only after cellular damage in garlic. Allicin is also formed by the enzymatic action of alliinase on alliin.

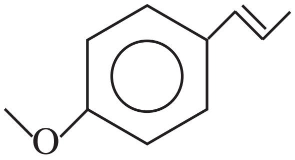


3. Alliin, a sulfoxide , is found in fresh garlic. The compound has no flavor or odor.



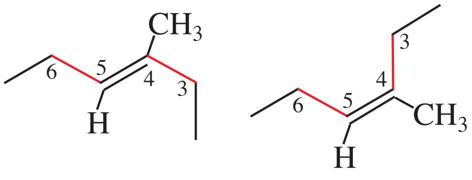
4. Allyl isothiocyanate (AITC) is formed by the action of the enzyme myrosinase on sinigrin. AITC is the pungent, tear producing chemical in mustard, wasabi and radishes.

5. Anethole is an aromatic (containing a benzene ring) compound. It has the flavor of anise, fennel, and licorice.

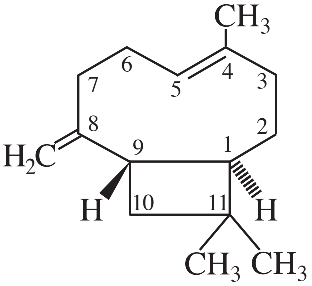


6. Caryophyllene is a fused bicyclic sesquiterpene. It is found in cloves, rosemary, hops, basil, oregano, cannabis, and black pepper.

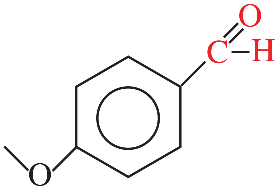
This model is difficult to build because it has two unusual features: one is the large, nine membered ring, and second, the other ring is a cyclobutane which has obvious bond angle strain. In addition care must be taken to make sure that the double bond at carbons 4-5 is in the *E* configuration <u>not</u> the *Z*. Observe the illustration below.



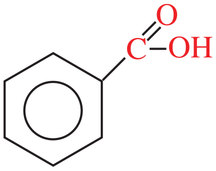
E *Z*



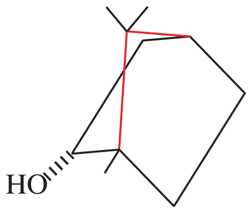
7. Anise aldehyde is an aromatic found in anise oil, fennel, and vanilla (to which it is a related compound). The aldehyde group is represented in red.



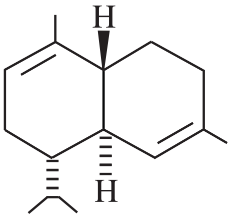
8. Benzoic acid, occurring naturally in many fruits and vegetables, adds tartness. It is also put into some foods and drinks as a preservative. It is an aromatic compound. The acid group is in red.



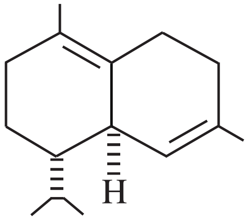
9. Borneol is a bridged, bicyclic monoterpenoid found in cinnamon, thyme, and cannabis. Both *R* and *S* forms are found in nature. The structure below is the *S* enantiomer. Upon oxidation borneol is converted to camphor. The one-carbon bridge bonds are shown in red.



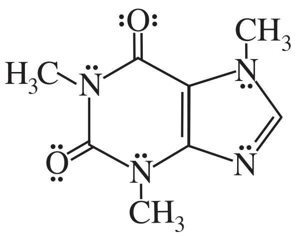
10. α-cadinene is a fused bicyclic sesquiterpene. Along with several other similar fused bicyclic sesquiterpenes it belongs to the cadinene family. It can be found in alcoholic beverages, and hops.



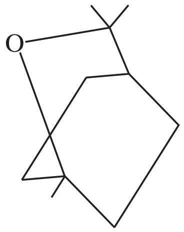
11. δ-cadinene is another member of the cadinene family. It is found in allspice, cubeb, or tailed, pepper, and citronella.



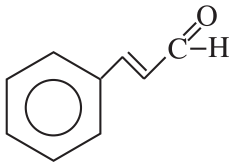
12. Caffeine is the popular bitter-tasting stimulant found in coffee, tea, and soft drinks (mainly colas). Caffeine, an alkaloid, is an analog of the purines found in DNA and RNAs.



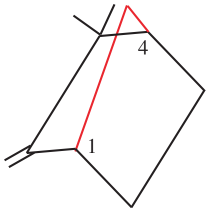
13. Cineole also known as eucalyptol is a monoterpenoid and a cyclic ether. It is one of about 599 cigarette additives. Natural sources are tea, bay leaves, cannabis, and mugwort.



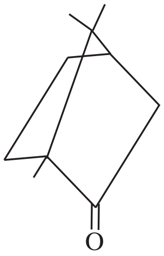
14. Cinnamaldehyde is an aromatic which is extracted from plants in the *Cinnamomum* genus. In addition to its use as a flavoring, cinnamaldehyde is applied to steel products as a corrosion inhibitor, and it has fungicidal properties when used on plant roots.



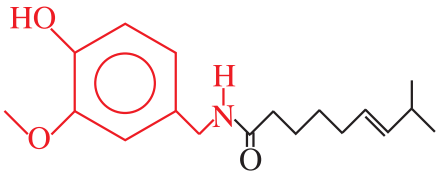
15. Camphene is a 1*R*, 4*S* bicyclic monoterpene. It is used in cola drinks, and it is found in ginger, valerian, citronella, and neroli oil.



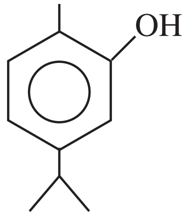
16. Camphor, a monoterpenoid, naturally exists in the R form pictured below. It is found in rosemary, the camphor-laurel evergreen tree. Beyond its use as a flavoring agent in Asian foods, it is widely used as an insect repellant and even as an embalming agent.



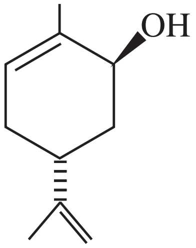
17. Capsaicin, the well known “hot” (piquant) spice of chili peppers is classified as a vanilloid. The vanillyl group is shown in red in the diagram below. There are some other capsaicinoids, but capsaicin is the most abundant in chili peppers. The hottest of the chili peppers is the so-called Dragon’s Breath which was developed in Wales. It scores the highest on the Scoville scale.



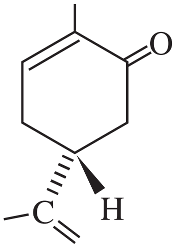
18. Carvacrol is an aromatic monoterpenoid with a benzene ring. It is found in thyme, oregano, savory, marjoram, and it is one of the many components of tequila.



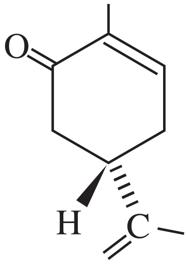
19. Carveol is a monoterpenoid, and it imparts the flavor of spearmint and caraway. It is found in caraway seeds, celery, black tea, dill, and blackcurrant berries.



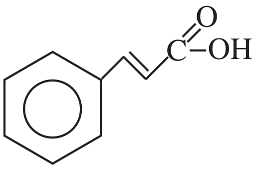
20. *R*-carvone (the right handed isomer) is a monoterpenoid giving the taste of spearmint. It is found in caraway seeds, *Mentha spicata* (wrinkled leaf mint), dill, and mandarin orange peel.



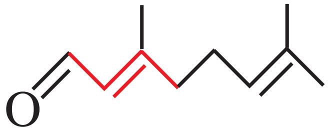
21. *S*-carvone (the left handed isomer) has the odor of caraway seeds. The *S* isomer is usually found along with the *R* molecule in all of its sources.



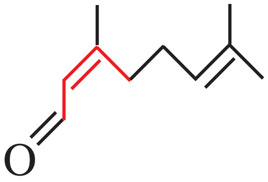
22. Cinnamic acid is an unsaturated carboxylic acid with a benzene ring. Pictured below is the trans isomer. This plant product is found in cinnamon.



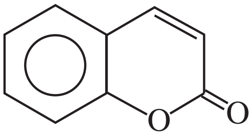
23. Citral A (geranial) is a monoterpenoid in the *E* configuration. It is found in apricots, lemons, oranges, lemongrass, lime, pimento and many other plant essential oils. The bonds in red emphasize the *E* configuration.



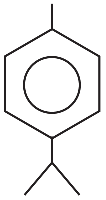
24. Citral B (neral) is the *Z* isomer of citral A. It is also a monoterpenoid, but its lemony flavor is not as intense as we find in geranial. The *Z* form is indicated by the red in the figure below.



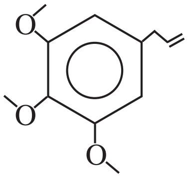
25. Coumarin (smells like new mown hay: used in perfumes). The benzene ring on the left is fused with a cyclic ester (a lactone) on the right. This type of structure is indicative of the benzopyrone family of chemicals. Coumarin is a component of apricots strawberries, black currants, and cherries. Mostly in Europe, sweet woodruff, containing coumarin is used as a flavoring in some alcoholic drinks, herbal tea, and jelly. Although coumarin is not an anticoagulant, it is used as a starting material to make some very powerful agents that prevent blood from clotting. One of these is warfarin.



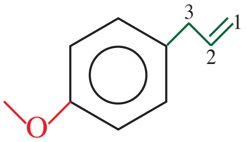
26. p-cymene is a monoterpene with two para (p-) substituted alkyl groups. Since it has the benzene ring, it can also be called an aromatic. It is found in the essential oils of cumin, thyme, bay leaf, basil leaf, anise, oregano, coriander, and mace.



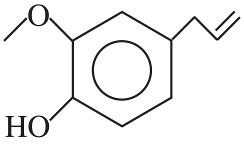
27. Elemicin is a substituted aromatic compound. It is found in nutmeg, mace, some species of *Cinnamomum*, and some types of tarragon.



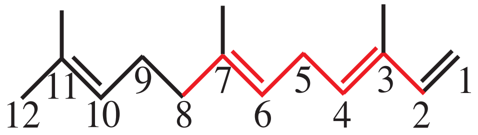
28. Estragole is a para- substituted aromatic. The benzene ring is bonded to a propene group shown in green and a methoxy group in red (forming an ether linkage). Estragole is an isomer of anethole which has the double bond between carbons 2 and 3. Estragole is found in anise, fennel, bay leaf, tarragon, and basil.



29. Eugenol is another substituted aromatic. It is found in clove oil, nutmeg, cinnamon, basil, and bay leaf.

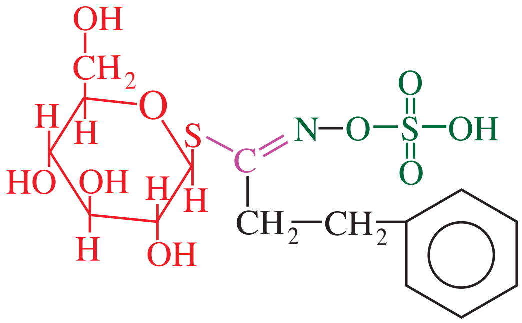


30. Farnesene is a sesquiterpene which can exist as any of six different isomers. (*E*, *E*)-α-farnesene is drawn below. α-farnesene may also be in the (*Z*, *Z*), (*Z*, *E*), or the (*E*, *Z*) form. β-farnesene, which has a different placement of one double bond, has two different stereo-isomers. (*E*, *E*)-α-farnesene is found on the surface of many fruits. It smells like green apples.



31. Geraniol is a monoterpenoid. It is used as the flavor of peach, raspberry, plum, grapefruit, red apple, lime, orange, lemon, watermelon, pineapple, and blueberry.

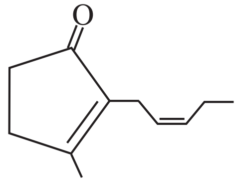
32. Gluconasturtiin is a glucosinolate, a chemical found most abundantly in the Cruciferae (Brassicaceae) family, and others as well. In the structure below, the central carbon atom is purple; the side phenethyl group is black; the nitrogen-sulfate is green; and the thioglucose is red. The pungent flavor of glucosinolates is due to the action of myrosinase, an enzyme, which releases allyl isothiocyanate. The latter then provides the pungent flavor.



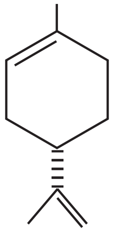
33. Isovaleric acid, alternatively known as 3-methylbutanoic acid and β-methylbutyric acid can be classified as a fatty acid. It is naturally produced by bacteria and yeast in wine and beer making. It is also found in cheeses.

$(CH_3)_2CHCH_2COOH$

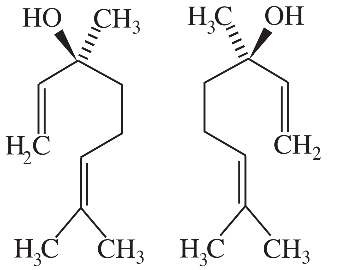
34. Jasmone is found naturally in the *cis* form (pictured below). It is found in citrus, peppermint oil, green tea and bergamot oranges. It is a monoterpene.



35. *R*-limonene, found in all citrus fruits is a monoterpene. In addition to adding a citrus flavor to foods, it has a wide variety of uses such as an insecticide, solvent, cleaning agent, paint stripper, etc..

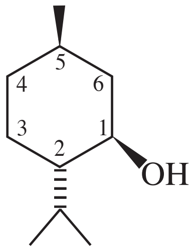


36. (*S*)- and (*R*)-linalool. Both isomers are monoterpenoids. It is produced in several species of plants, mainly by the mints, laurels, cinnamon, coriander, and citrus.



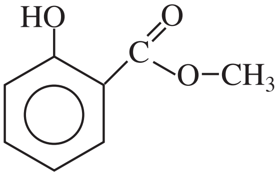
(*S*)-linalool (*R*)-linalool

37. Menthol is a monoterpenoid existing naturally as the (1*R*, 2*S*, 5*R*) isomer. Its sources are mint oils. has a “cool” taste:

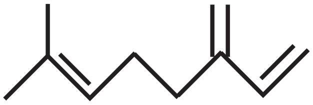


38. Methyl salicylate is an ester of the aromatic, salicylic acid, and the alcohol, methanol. It is produced by several plants in a few distinct families. The wintergreen plant, or box berry, *Gaultheria procumbens*, is one example of a good source of the ester.

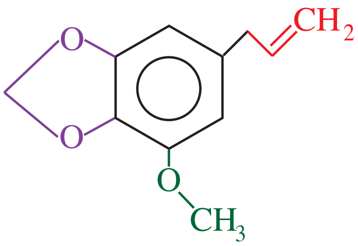
An interesting effect provoked by the crushing of Life Savers® wintergreen mints in a dark room is called tribo-luminescence. A very obvious light is emitted by the breaking and remaking of bonds in the mint as it is crushed.



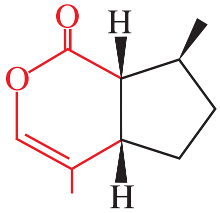
39. β-myrcene is a monoterpene made by many plants including bay, cannabis, parsley, ylang-ylang, cardamom, hops, mango, thyme, and lemon grass.



40. Myristicin is found in nutmeg. Small amounts are found in parsley, anise, and dill. This is an aromatic (benzene) ring (black) with a propylene group (red), a methoxy group (green), and a methylenedioxy group (purple) attached. A major source of myristicin in the human diet is soft drinks, mainly colas.

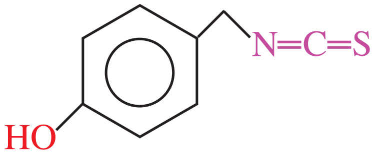


41. Nepetalactone, obtained from catnip, is a bicyclic monoterpenoid consisting of cyclopentane (black) fused to a δ-lactone (red).

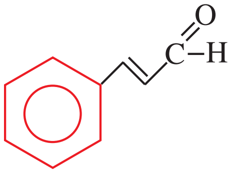


42. Ocimene is usually found as a mixture of three isomeric monoterpenes. Below is a skeletal diagram of α–ocimene. There are two β- isomers. Ocimenes are found in cannabis, allspice, and basil.

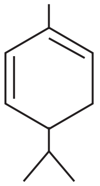
43. p-hydroxybenzyl isothiocyanate is a product of the action of the enzyme myrosinase on sinalbin. The aromatic benzene ring (black) has two group bonded in positions that are designated p-, or para to each other. The isothiocyanate is colored purple, and the hydroxyl group is red. Cf. sinalbin for the sources of p-hydroxybenzyl isothiocyanate



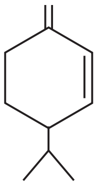
44. 3-phenyl acrolein, also known as cinnamaldehyde. The phenyl group (red) is a benzene ring bonded to another group, which in this case is called acrolein (black). Cinnamon comes from the bark of *Cinnamomum cassia* (Chinese cinnamon), and the bark of *Cinnamomum zeylanicum* (Ceylon Cinnamon).



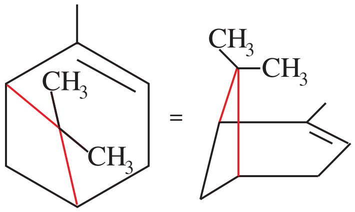
45. α-phellandrene and β-phellandrene are both monoterpenes, and both are found in allspice, garlic, and ginger.



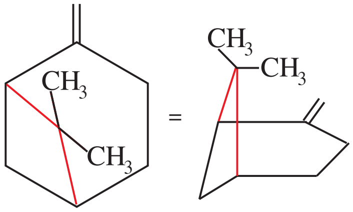
46. β-phellandrene. The only difference between the α- and the β- isomer is the position of a double bond. See above for other information about phellandrenes.



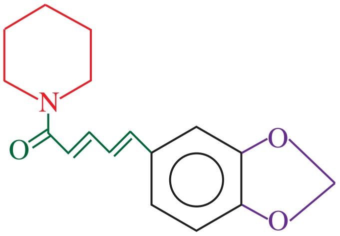
47. α-pinene is a bridged, bicyclic monoterpene with a structural isomer which appears below in number 48. As you can see, the difference between the two is the placement of a double bond. Each one has an *R*- and an *S*- isomer. The *S*- enantiomer is shown below. Both are found in pine nuts, lime peel, sage, ginger, nutmeg, mace, bitter fennel, and rosemary.



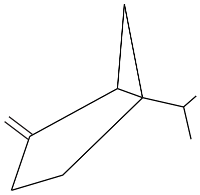
48. β-pinene. See α-pinene above for a description. The *S*- enantiomer is shown below.



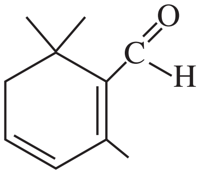
49. Piperine is classified as an alkaloid due to the presence of a basic nitrogen atom in the compound. Piperine is found in black pepper. The groups found in the molecule are piperidine (red), pentane-2,4-dieneal (green), benzene (black), and methylenedioxy (purple).



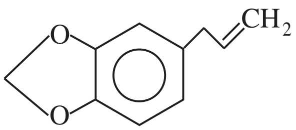
50. Sabinene is a bicyclic monoterpene with a cylcopentane ring fused to a cyclopropane ring. Sources include Norway spruce, black pepper, and *Myristica fragrans*, an evergreen. Sabinene adds flavor to nutmeg and ginger.



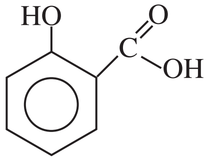
51. Safranal is found in tea, saffron, fig leaf, cumin seed, lemon, and other sources. It is a monoterpene.



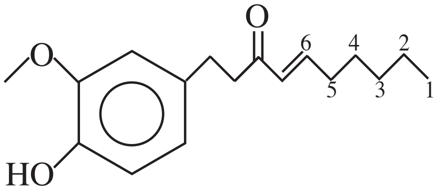
52. Safrole, minus a methoxy group, is identical to myristicin, q.v. It is found in sassafras, but the FDA has banned its inclusion in commercial sassafras. It is a component of anise, nutmeg, cinnamon, and black pepper. It is added to root beer and confections.



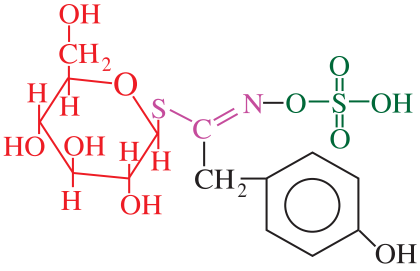
53. Salicylic acid, an orthophenolic acid is used as a food preservative, and it is also used to make acetylsalicylic acid (aspirin). Salicylic acid is found in the bark of willow trees and the meadowsweet plant.



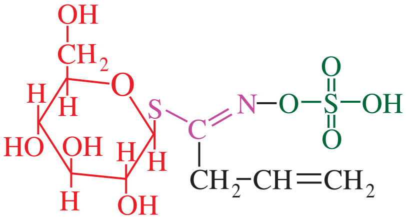
54. (6)-Shogaol is a pungent component of ginger with a substituted phenolic aromatic ring structure. The double bond on the carbon chain is at position 6, hence the name of this molecule. Several other shogaols exist, and they are named in a similar manner.



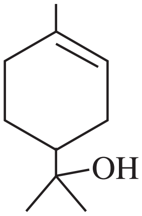
55. Sinalbin is a glucosinolate, similar in structure to gluconasturtiin. Sinalbin is found in white mustard which is in the Brassicaceae family. See number 32 above.



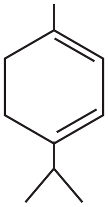
56. Sinigrin is another glucosinolate. It is found in Brussels sprouts, broccoli, black pepper seeds, etc.



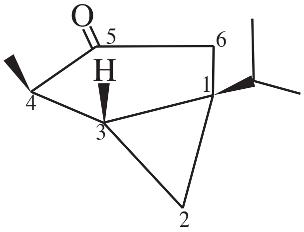
57. Terpineol is a monoterpenoid that can be found as four different isomers usually found together in one source, but α–terpineol is commonly the most abundant form. Terpineols found in cinnamon, pine oil, cajuput oil, black tea cannabis, oil of lime, and eucalyptus.



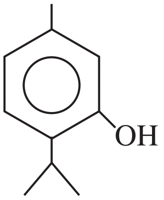
58. α-terpinene is one of four monoterpene isomers. The difference among the isomers is the location of a double bond. α-terpinene can be isolated from cardamom, marjoram, the tea tree, citrus fruits, eucalyptus, and juniper oils.



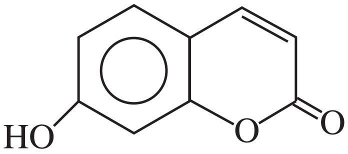
59. Thujone is a bicyclic-fused ring monoterpenoid with four different isomeric forms. The α- and β- isomers are diastereomers. There are two enantiomers of α-, and two enantiomers of the β- molecules. Thujone is found in sage, arborvitae, some junipers, grand wormwood, oregano, mugwort, tansy, and notably in the alcoholic beverage called absinthe. One of the isomers of α-thujone (1*S*, 4*R*, 5*R*) is drawn below.



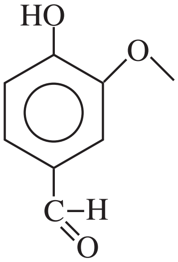
60. Thymol is a monoterpenoid phenol. A phenol is a benzene ring with an hydroxy group bonded to it. Thymol is found in thyme, bee balm, and oil of horsemint



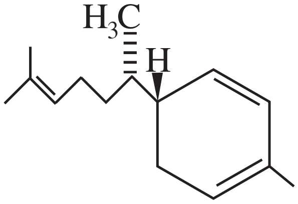
61. Umbelliferone is a phenolic-aromatic ring fused to a lactone. It is a member of the coumarin family. See Coumarin above. Umbelliferone can be obtained from carrots, correander, garden angelica, the bigleaf hydrangea, and asafetida which comes from the giant fennel. The name, umbelliferone comes from the parsley (carrot, celery) family name, Umbelliferae.



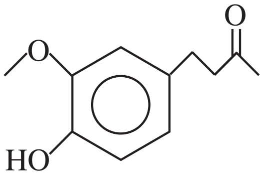
62. Vanillin is a phenolic aldehyde with an additional methoxy group. Vanillin provides the flavor of vanilla, and when present in small amounts olive oil, butter, raspberry, coffee, maple syrup, and lychee fruits. The extract from the vanilla bean is expensive and it contains hundreds of chemicals. Most vanilla purchased today is artificially produced.



63. Zingirberene, which is the main component of ginger, is a sesquiterpene.



64. Zingerone is another component of ginger. It is also found in cranberry, raspberry, and mango. It is a flavor additive in ginger ale, and ginger beer. Zingerone is a substituted phenol with a methoxy and a 2-butanone group.

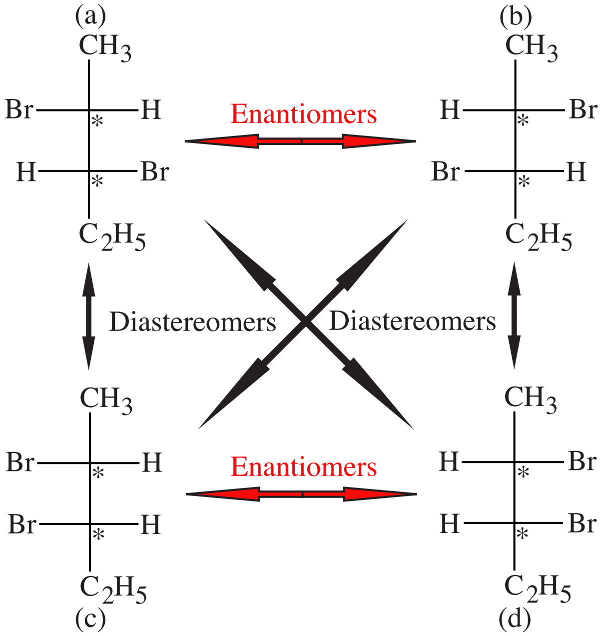


Glossary

Aromatic: Containing a benzene ring of six carbons with alternating double bonds.

Chiral carbon atoms: Carbon atoms with four different groups bonded to them.

Chiral molecules: Molecules that are not superimposable on their mirror images. An example follows. (a), (b), (c), and (d) are all chiral molecules with two chiral carbon atoms each (marked with asterisks).



Diastereomers: Stereoisomers that are not mirror images of each other. (a) and (c), and (a) and (d) are diastereomers. Also (b) and (c), and (b) and (d) are diastereomers. *Cis*- and *trans*- forms are also diastereomers of each other.

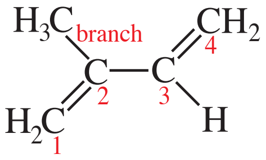
Enantiomer: A mirror image of a molecule which is not superimposable on itself. Using the above diagram again, (a) and (b) are enantiomers as are (c) and (d).

Ester: A molecule formed by the bonding of an acid (organic or inorganic) with an alcohol. The bond forms by a dehydration (loss of a water molecule) synthesis.

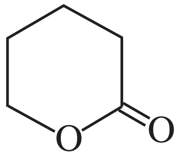
E-, *Z*- system: A method of determining the stereochemistry of double bonded carbon atoms when using *cis* and *trans* denotations do not adequately describe the configuration across the bond.

Glucosinolate: A complex molecule with a central carbon atom bonded to: 1) the sugar, thioglucose, 2) a nitrogen atom, which is bonded to a sulfate group, and 3) a hydrocarbon branch which is different in different glucosinolates.

Isoprene unit: The basic five membered chain of carbons used to build more complex molecules. A trick used by some people learning organic chemistry to remember the structure of isoprene is the phrase, “One, two, branch, three, four.”



Lactone: A lactone is a cyclic ester. An example follows.



R, *S* system: A method of determining the absolute configuration around a chiral carbon (a carbon atom with four different groups attached).

Scoville scale: This is a measure of the pungency (spicy heat) of foods in Scoville Heat Units (SHU). To run a test to determine SHU, five people deteremine whether they can sense the test foods presented to them in increasing dilutions. The test is very subjective.

Stereoisomers: Molecules that have the same chemical formula but different arrangements of the same atoms in space. The types of stereoisomers that are of interest here are *cis/trans* (*E, Z*), diastereomers, and enantiomers.

Terpene: Molecules constructed with one or more isoprene units.
  Hemiterpene: Made from one isoprene unit (has 5 carbons).
  Monoterpene: Made from two isoprene units (has 10 carbons).
  Sesquiterpene: Made from three isoprene units (has 15 carbons).
  Diterpene: Made from four isoprene units (has 20 carbons).
  Sesterterpene: Made from five isoprene units (has 25 carbons).
  Triterpene: Made from six isoprene units (has 30 carbons).
  Sesquarterpene: Made from seven isoprene units (has 35 carbons).
  Tetraterpene: Made from eight isoprene units (has 40 carbons).

Terpenoid: A terpene with oxygen as a member of the compound. These are also classified as hemi-, mono-, di-, etc., according to the number of isoprene units they contain.

Thioester: An ester made by combining an acid with a thioalcohol (e.g. CH_3SH which resembles the alcohol CH_3OH). Thio is a combining form meaning sulfur.