Module- 32: Clove: Oils & Oleoresin

32.1 Introduction

Cloves are the unopened flower buds of the evergreen tree *Eugenia caryophyllus*. The flowers develop in clusters of three to ten groups, each with three flowers per group. The young leaves are bright pink and change to a greenish yellow and harden. Cloves must be dried before they are stored and sold for market. The timing of harvest of the clove buds is critical. The buds should be harvested before the purple or crimson flowers start to develop. Clusters of flower buds are hand-picked from the branches. It is important that the branches are not removed or damaged as this will reduce the yield of future crops. The tree is native to the Moluccas (Spice Islands) a part of the Indonesian islands. Zanzibar and Pemba are now the world's largest producers of cloves.

32.2 Essential Oils & Oleoresins

Eugenol comprises 72-90% of the Essential oil extracted from cloves, and is the compound most responsible for the cloves' aroma. Other important essential oil constituents of clove oil include Acetyl eugenol, beta-caryophyllene, vanillin, crategolic acid, tannins such as bicornin, gallotannic acid, methyl salicylate (painkiller).

32.2.1 Eugenol

Eugenol is a phenylpropene, an allyl chain-substituted guaiacol. Eugenol is a member of the phenylpropanoids class of chemical compounds. It is a clear to pale yellow oily liquid extracted from certain essential oils especially from clove oil, nutmeg, cinnamon,basil and bay leaf. It is slightly soluble in water and soluble in organic solvents. It has a spicy, clove-like aroma. The name is derived from the scientific name for clove, *Eugenia aromaticum* or *Eugenia caryophyllata*. Eugenol is responsible for the aroma of cloves. It is the main component in the essential oil extracted from cloves, comprising 72–90% of the total.

32.2.2 beta-caryophyllene

β-caryophyllene is a natural bicyclic sesquiterpene that is a constituent of many essential oils, especially clove oil, the oil from the stems and flowers of *Syzygium aromaticum* (cloves), the essential oil of hemp *Cannabis sativa*, rosemary *Rosmarinus oficinalis* and hops. It is usually found as a mixture with isocaryophyllene (the *cis* double bond isomer) and α-humulene (obsolete name: α-caryophyllene), a ring-opened isomer. Caryophyllene is notable for having a cyclobutane ring, a rarity in nature.

32.2.3 Vanillin

Vanillin is a phenolic aldehyde, which is an organic compound with the molecular formula $C_8H_8O_3$. Its functional groups include aldehyde, ether, and phenol. It is the primary component of the extract of the vanilla bean. Synthetic vanillin, instead of natural vanilla extract, is now more often used as a flavoring agent in foods, beverages, and pharmaceuticals. Vanillin and ethylvanillin are used by the food industry; ethylvanillin is more expensive, but has a stronger note. It differs from vanillin by having an ethoxy group ($–O–CH_2CH_3$) instead of a methoxy group ($–O–CH_3$).

32.2.4 Biocornin

Biocarnin are the ellagitannins which are a diverse class of hydrolyzable tannins, a type of polyphenol formed primarily from the oxidative linkage of galloyl groups in 1,2,3,4,6-pentagalloyl glucose. Ellagitannins differ from gallotannins, in that their galloyl groups are linked through C-C bonds, whereas the galloyl groups in gallotannins are linked by depside bonds. Ellagitannins contain various numbers of hexa hydroxyl diphenoyl (HHDP) units, as well as galloyl units and/or sanguisorboyl units bounded to sugar moiety. In order to determine the quantity of every individual unit, the hydrolysis of the extracts with trifluoroacetic acid in methanol/water system is performed. Hexahydroxydiphenic acid, created after hydrolysis, spontaneously lactonized to ellagic acid, and sanguisorbic acid to sanguisorbic acid dilactone, while gallic acid remains intact.

32.2.5 Gallotannic acid

Gallotannic acid is a specific commercial form of tannin, a type of polyphenol. Its weak acidity (pK_a around 10) is due to the numerous phenol groups in the structure. The chemical formula for commercial tannic acid is often given as $C_{76}H_{52}O_{46}$, which corresponds with decagalloyl glucose, but in fact it is a mixture of polygalloyl glucoses or polygalloyl quinic acid esters with the number of galloyl moieties per molecule ranging from 2 up to 12 depending on the plant source used to extract the tannic acid. Commercial tannic acid is usually extracted from any of the following plant part: Tara pods (*Caesalpinia spinosa)*, gallnuts from *Rhus semialata* or *Quercus infectoria* or Sicilian Sumac leaves (*Rhus coriaria*). According to the definitions provided in external references such as international pharmacopoeia, Food Chemical Codex and FAO-WHO tannic acid monograph only tannins sourced from the above mentioned plants can be considered as tannic acid.

32.2.6 Methyl salicylate

Methyl salicylate (oil of wintergreen or wintergreen oil) is an organic ester that is naturally produced by many species of plants. Some of the plants which produce it are called wintergreens, hence the common name. This compound is used as a fragrance. It is also found in liniments (rubbing ointments). In 1843, methyl salicylate was first isolated (from the plant *Gaultheria procumbens*) by the French chemist Auguste André Thomas Cahours (1813-1891), who identified it

as an ester of salicylic acid and methanol**.** In pure form, methyl salicylate is toxic, especially when taken internally. A single teaspoon (5ml) of methyl salicylate contains 7g of salicylate, which is equivalent to more than twenty-three 300 mg aspirin tablets. The lowest published lethal dose is 101 mg/kg body weight in adult humans or 7.07 grams for a 70-kg adult. It has proven fatal to small children in doses as small as 4 ml.

SUGGESTED READINGS:

- Sepulveda, Leonardo; Alberto Ascacio, Raul Rodriguez-Herrera, Antonio Aguilera-Carbo, and Cristobal N. Aguilar (30 May 2011). "Ellagic acid: Biological properties and biotechnological development for production processes". *African Journal of Biotechnology* **10** (22): 4518–4523. Retrieved 12 November 2011.
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- Cahours, A. (1843) "Sur quelques réactions du salicylate de méthylène"(On some reactions of methyl salicylate), *Comptes rendus* … , **17** : 43-47.
- D. G. James, T. S. Price (August 2004). "Field-testing of methyl salicylate for recruitment and retention of beneficial insects in grapes and hops". *J. Chem. Ecol.* **30** (8): 1613–28.