Chapter 11

Gamboge- The bark exudate from *Garcinia* species

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Abstract

Garcinia bark exudates, known as gamboges, has been used as a pigment in Indian murals and European water colour-paintings. It has also been used for dyeing clothes and for colouring wood, metal and leather. Gamboge has several uses in traditional medicinal systems, especially as a purgative and also externally used for treating infected wounds. The major sources of gamboges are *Garcinia hanburyi* and *Garcinia morella*. Gamboge contains 70% to 80% yellow resin and 15% to 25% water soluble gum and the remaining portion is composed of esters, hydrocarbons, wax and ash. The characteristic bioactive compounds in gamboges were identified as caged xanthones, such as gambogic acid and morellin, that possess potential anticancer properties. This chapter provides a detailed account on history, distribution, chemistry and uses of gamboge.

Keywords: Gamboge, *Garcinia hanburyi, Garcinia morella,* Caged xanthones, Gambogic acid, Morellin

Introduction

Recently there has been an increased demand for plant derived natural products, mainly due to the safety concerns of the synthetic pigments, colouring agents and other additives that are essential ingredients in several industrial sectors such as cloth dyeing, food and nutraceutical. Among the different plant products, exudates are in high demand now, due to the low toxicity, abundant availability, biocompatibility, biodegradability and inertness compared to synthetic alternatives.

Gamboge, also known as camboge, is the exudate from the bark of *Garcinia* species. *Garcinia* species are perhaps known all over the world in ancient times by this value added product. The dried exudates are used as a pigment in Indian murals and European water-paintings and dyeing clothes and also for colouring wood, metal and leather. Though primarily gamboge was used as a colouring agent, several traditional medicinal uses were also attributed to the exudate. Recent phytochemical investigations showed the bark exudates as rich source of bioactive secondary metabolites such as caged xanthones. The present chapter summarises the history, traditional uses and phytochemistry of gamboge.

1. History of gamboge as a natural colouring agent

Plant exudates were used by ancient civilisations world over for various purposes and the usage can be traced back to about 3000 BC, where the Egyptian civilization used gum Arabica, the exudates from *Acacia*. The word gamboge comes from *Gambogia*, the Latin

word for Cambodia. Gamboge was used from ancient times to dye the clothes and also to make a transparent yellow varnish for the coloring of wood, metals and leather. The pigment was made more usable by mixing with other yellow pigments such as lemon yellow or alumnia. The color of gamboge is a deep tone of saffron, and gamboge is recognised as a distinct colour (Maerz and Paul, 1930). When used as a water colour, it gives a bright transparent golden yellow colour and is not a true pigment. In ancient India, gamboge had an important place among artists, herbalists and spiritual communities. The earliest evidence of the use of gamboge comes from artefacts of eighth century from East Asia, where the yellow colour is presumed to be derived from gamboge. *Garcinia* exudates were used to dye the robes of Buddhist monks (Lewington *et al.*, 1990). Gamboge was first brought to Europe, in 1603, by Admiral Van Neck, and used as a transparent oil color by Flemish painters (Chantarasriwong *et al*., 2010). John Smith in '*The Art of Painting in Oyl'*, published in 1701, describes a method for preparing the colour. The botanic artist William Hooker created the pigment 'Hooker's Green' that gives a special green to colouring leaves by mixing Green Malachite or Prussian blue and gamboge (Winter *et al.*, 1997). One can assume that since the gamboge faded so rapidly relative to iron blue, trees in some old artworks have become blue. A tradition of mural paintings in Kerala, south India, following the sixteenth century techniques, uses the exudates of *G. morella*, locally known as Eravikkara in Malayalam in combination with the leaves of *Indigofera tinctoria* to get different shades of green (Nayar *et al*., 1999). Jean Baptiste Perrin in his work on Brownian movement used a colloidal suspension of gamboge particles to investigate the phenomenon and derive a value for the Avogadro number in 1926 (Chantarasriwong *et al*., 2010).

2. Traditional medicinal uses of gamboge

The exudates from different *Garcinia* species were used therapeutically in traditional medicine, especially as emetics and cathartics (Majeed *et al*., 1994). Gamboge obtained from *Garcinia hanburyi* is used externally for infected wound and for pain and oedema in traditional Thai medicine. It has cathartic activity and is used in veterinary medicine as a drastic purgative. Gamboge is a laxative in doses of 10-15 cgm., produces abundant evacuations with violent colicky pains in doses of 30-50 cgm. It can cause vomiting, nausea and griping in high doses. It is also used as a vermifuge. It is usually combined with other purgatives such as aloe or calomel, to strengthen their effect. It is used in traditional medicine for the treatment of ulcers, skin infection, appetite suppression and to lower blood pressure (Panda, 2005). The resin of *G. morella* has purgative action and was mainly applied for intestinal complaints. The cathartic property of the exudate was made use for expelling tapeworms from the intestine. However, large doses are toxic, leading to gastro enteritis.

3. Extraction of gamboge

Gamboge is generally extracted by tapping of *Garcinia* species. The plant tissues of the Clusiaceae members were characterized by the presence of latex channels and different shades of yellow were reported for the exudates from *Garcinia* species (Nogueira *et al*., 2001). Generally trees of ten years old are tapped by making spiral incisions in the bark and traditionally collected in bamboo containers. The hard and brittle lumps of the solidified raw gamboge are dark yellow in color, which when pulverized, turns into a bright yellow powder. This powder is mixed with a variety of binders to make paints and varnishes.

4. Major sources of gamboge

The major sources of gamboge were *G. hanburyi* (Cambodia and Thailand), *G. morella* (India and Sri Lanka), and *G. elliptica* and *G. heterandra* (Myanmar). The chief trade supply was obtained from Siam in the form of cylindrical pieces or sticks and until recently, the gum resin of Siam was referred to *Garcinia cochin-sinensis* and that of Ceylon to *Hebradendron cambogioides*, while that of Southern India was supposed to be the produce of *Garcinia pictorial* (Watt,1890; Utpala and Nandakishore, 2016).

True gamboge of use in arts and medicine in India derives mainly from the gum resin of *G. morella* (**Figure 1**). The tree is distributed in Indo-Malay and Sri Lanka. All parts of the plant yield a thick yellow exudate.

Figure 1. *Garcinia morella* twig, seeds and bark

Table 1. Distribution of gamboge in different *Garcinia* species

Sl. No.	*Garcinia* species	Remarks
	G. anomala Planci. & Trian.	Gamboge is inferior in quality.
	G. cornea Linn.	Gamboge is inferior in quality.
	G. cowa Roxb.	Gamboges is inferior in quality, with paler colour than that of *G. morella* and is insoluble in water. Bark is used to extract a light yellow colour for colouring of the cloth for the garments of Buddist monks.
	G. eugeniaefolia Wall.	The exudate a green varnish
	G. gummi-gutta (L.) N. Robson	The tree yields a yellow, insoluble, very adhesive gum, which is valueless as a pigment on account of its insolubility in water
	G. hanburyi Hook. f.	Exudates is known as Siam gamboge and is used as a purgative and externally used for infected wounds in Thai traditional medicine.
	G. heterandra Wall.	This tree yields a superior kind of gamboge, so similar to the Gamboge of commerce. It readily forms an emulsion with water. Burmese priests occasionally use this gamboges to dye their robes and the Karens to dye their thread. The gum resin is occasionally employed as a medicine by Burman native practitioners.
	G. indica	The exudate is sparingly soluble in water, but it became

		insoluble when dried.
	G. mangostana Linn.	This species exudes gamboge of inferior quality
	G. morella Desrouss	This species produces the true gamboge of medicine and of the arts.
	G. speciosa Wall.	It yields an inferior gamboge.
	G. stipulata T. And.	The tree and fruit yield a yellow gum, but not used as gamboge.
	G. succifolia Kurz	The species yield inferior quality gamboge at very little yield.
	G. travancorica Beddome	Every portion of the tree yields an abundance of bright yellow gamboge.
	G. wightii T. Anderson	The gamboge of this species is very soluble and yields a good pigment.
	G. xanthochymus Hook. f.	This species yields a large quantity of inferior gamboge both from the stem and the fruit rind which is extensively used as a cotton dye in Assam. The exudate contains a larger proportion of gum than that derived from other species. The exudates are sparingly soluble in water, but it became insoluble when dried.

Figure 2 shows the exudates from 25 *Garcinia* species distributed in India. The colour of the exudates varies from white to different shades of yellow.

5. Chemistry of gamboge

Gamboge, being a well known commercial commodity of historical importance, had been a subject of intensive analytical investigation (Chantarasriwong *et al*., 2010; Utpala and Nandakishore 2016). Venkataraman (1973) has reviewed the chemistry of pigments from *Garcinia* species.

Exudates are a complex mixture of organic compounds that ooze out of plants through pores, or wounds. Gamboge is odorless but slightly acidic (Nayar *et al*., 1999). Exudates consist largely of gum, resin or latex, depending on the tree species. The exudates from *Garcinia* species are generally yellow translucent and sometimes white to reddish, which get solidified when exposed to air.

The resin portion of the exudates was separated through partition with ethyl acetate. The remaining aqueous portion represents gum content of the exudate. Gamboge contains about 70% to 80% yellow resin, 15% to 25% water soluble gum, and the remaining portion is composed of esters, hydrocarbons, wax and ash. In a recent report, *G. gummi-gutta* exudates contains 68% resin, while *G. indica* contains 60% resin followed by *G. xanthochyma* (40%) (Parthasarathy and Nandakishore, 2016**).** The brittle resin is deep orange colour in thin layers and when it is fine powdered, its colour is gamboge yellow. Gamboge resin is insoluble in water, but soluble in alcohol. It dissolves in a solution of caustic potash, forming a dark red liquid which gets precipitated by acids and lime water, and some metallic salts like lead, brown by protosulphate of iron and green by the nitrate of copper. The precipitates formed with the metallic salts are regarded as gambogiates of the respective metals, as they consist of the resin and the oxide of the metal.

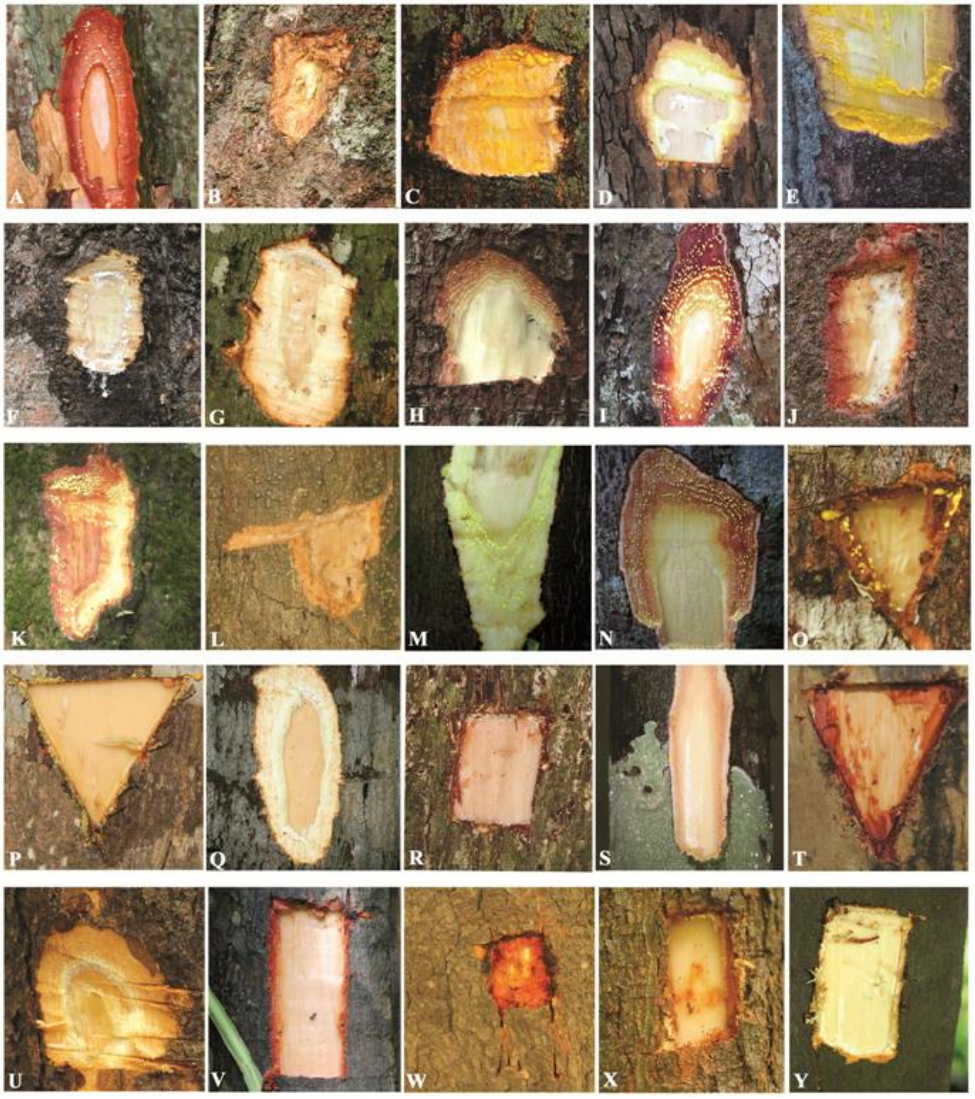
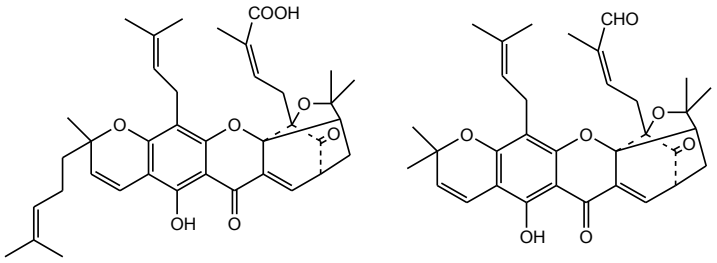


Figure 2. *Garcinia* bark exudates (**A.** *G. rubro-echinata*, **B.** *G. imberti*, **C.** *G. wightii*, **D.** *G. travancorica*, **E.** *G. morella*, **F.** *G. talbotii*, **G.** *G. pushpangadaniana*, **H.** *G. indica,* **I.** *G. gummi-gutta* var. *gummi-gutta,* **J.** *G. gummi-gutta* var. *papilla,* **K.** *G. gummi-gutta* var. *conicarpa,* **L.** *G. andamanica,* **M.** *G. assamica,* **N.** *G. anomala,* **O.** *G. cowa,* **P.** *G. dhanikariensis,* **Q.** *G. dulcis,* **R.** *G. hombroniana,* **S.** *G. kydia,* **T.** *G. speciosa,* **U.** *G. xanthochymus,* **V.** *G. cornea,* **W.** *G. livingstonei,* **X.** *G. mangostana,* **Y.** *G. spicata*)

(-) Gambogic acid has been identified as the principal pigment of gamboge derived from *Garcinia hanburyi*, while related investigations of the seeds and the resin of *Garcinia morella* led to the isolation of (-) morellin (**Figure 3**) (Rao, 1937; Lang and Katz, 1949; Yates *et al*., 1963). Both of the compounds belong to an interesting group of complex compounds known as caged xanthones, with unique 4-oxatricyclo [4.3.1.0] dec-2-one ring system. Gambogic acid occurs in nature as a mixture of epimers at the C2 center (C2R and

C2S) that can be separated by modern chromatographic and analytical techniques (Han *et al*., 2006). C2S Gambogic acid is also known as epigambogiac acid. *Garcinia hanburyi* has been reported as a rich source of such cytotoxic caged xanthones (Reutrakul *et al*., 2007). Many of such caged xanthones have been shown to possess anticancer and antitumor properties.



Gambogic acid Morellin

Figure 3. Structure of gambogic acid and morellin

6. Pharmacological activities of gamboge

The caged xanthone gambogic acid has been a centre of attraction for the pharmacological researchers as evident from the ever increasing number of publications over the compound (Chantarasriwong *et al*., 2010). The toxicity of gamboge was also noted early onwards and several accounts warn against licking brushes containing gamboge. Gambogic acid has been identified as a potent anti-tumor agent that inhibited cancer cell growth *in vitro* and *in vivo* with minimal toxicity to normal cells, in its pre-clinical trials (Kasibhatla *et al*., 2005). The unique caged xanthone structure is the basis of gambogic acid induced anti-cancer effects. Gambogic acid induced apoptosis has been reported in many cancer cell types including leukemia, cervical cancer, cholangio carcinoma, hepatoma, breast cancer, gastric cancer, glioblastoma and osteosarcoma (Zhao *et al*., 2004; Yu *et al*., 2006; Yang *et al*., 2007; Wang and Chen, 2012). Gambogic acid inhibits cell proliferation in multidrug-resistant cancer cells. It has also prevented cancer metastasis and angiogenesis, and has finished phase II clinical trials in China (Wang *et al*., 2011). The potent anticancer activity of gambogic acid is mainly attributed to its activation of the impaired apoptotic pathways in cancerous cells via down-regulation of telomerase (Guo *et al*., 2006). Morellin and gambogic acid have been reported as potential antibacterial compounds and exhibited high *in vitro* specific growth inhibitory effects on Gram-positive bacteria (Rao and Natarajan, 1950; Chantarasriwong *et al*., 2010).

Conclusions

Gamboge, the dried exudate from several *Garcinia* species, was used as a pigment in water paintings, dyeing cloths and also for coloring wood, metals and leather. Alternative products obtained from renewable sources, are getting prominence and the potential of gamboge as a natural substitute for colouring material is highly appreciated. Though historically known as source of coloring pigments, gamboge is now reputed as source of a new family of natural products, known as caged xanthones. The remarkable chemical structure, biosynthesis, biology and medicinal potential of the caged xanthones open up a new window to the potential utility of gamboge.

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