



Review

Tetraoxygenated naturally occurring xanthones

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Abstract

This review, with 350 references, gives information on the chemical study of 234 naturally occurring tetraoxygenated xanthones in 12 families, 53 genus and 182 species of higher plants, and two which are described as fungal and lichen metabolites. The value of these groups of substances in connection with pharmacological activity and therapeutic use of some species is described. The structural formulas of 135 isolated compounds, and their distribution, are also given. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Xanthone; Tetraoxygenated xanthones; Pharmacological activity; Fungus; Lichen; Biosynthesis

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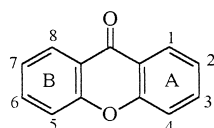
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1. Introduction

Xanthenes are secondary metabolites commonly occurring in a few higher plant families, and in fungi and lichens. Their taxonomic importance in such families and their pharmacological properties has aroused great interest (Cardona et al., 1990).

The symmetrical nature of the xanthone nucleus coupled with its mixed biogenetic origin in higher plants necessitates that the carbons be numbered according to a biosynthetic convention. Carbons 1–4 are assigned to the acetate-derived ring **A**, and carbons 5–8 to the shikimate-derived ring **B** (Bennett and Lee, 1989). The numbering system is based on xanthene-9-one as the basic skeleton (Gottlieb, 1968), and in cases where only ring **B** is oxygenated the lowest numbers are used, except for biosynthetic discussions (Bennett and Lee, 1989).



Xanthone basic skeleton

2. Classification

The xanthenes isolated so far may be classified into five major groups: simple oxygenated xanthenes, xanthone glycosides, prenylated and related xanthenes, xanthonolignoids, and miscellaneous xanthenes (Mandal et al., 1992). The simple oxygenated xanthenes can again be subdivided into six groups according to the degree of oxygenation, and we have previously reviewed trioxxygenated xanthenes (Peres and Nagem, 1997). In a continuation of our interest in these compounds, simple tetraoxxygenated xanthenes, as well as prenylated and related xanthenes with the same degree of oxygenation, are listed in this review (Tables 2–6).

3. Methods of isolation and structural investigations

Xanthenes are commonly separated by silica gel chromatography using different solvent mixtures (Harborne, 1973). Xanthenes are also separated and identified by comparison with authentic samples by TLC (Chawla et al., 1975) and by HPLC (Hostettmann and Guillardmod, 1976a,b; Hostettmann and McNair, 1976). The structures of simple oxygenated xanthenes have been established mainly from analysis of the UV, IR, MS and NMR spectroscopic data of these compounds (Roberts, 1961; Arends and Helboe, 1972; Arends et al., 1973; Sultanbawa, 1980).

Xanthenes can be detected by their colour in UV light with and without ammonia, or by using a general phenolic spray (Harborne, 1973). The UV spectrum varies in a characteristic manner, depending on the oxygenation pattern, and with the availability of a considerable amount of data, assignments can be readily made. By the use of AlCl_3 shifts for chelated hydroxyls, as well as sodium acetate, sodium hydroxide and boric acid shifts, considerable information on the position of hydroxyl groups can be obtained (Mesquita et al., 1968; Sultanbawa, 1980).

The use of IR spectroscopy in xanthone chemistry is generally limited to the detection of the carbonyl stretching frequency (Roberts, 1961; Mourão et al., 1966). For example, the effect of chelation on the IR carbonyl frequency of hydroxy-xanthenes may be a useful feature for analysis of spectra of substituted and extended xanthenes (Scheinmann, 1962; Chawla et al., 1973). The use of IR for detecting other functional groups, such as unchelated hydroxyl and methyl groups, has been described elsewhere (Roberts, 1961; Santesson, 1968a,b, 1969).

By introducing lichen samples into a mass spectrometer via a direct inlet system, Santesson (1968a,b) obtained mass spectra of volatile lichen substances. The method proved to be well suited for tentative identification of lichen xanthenes (Santesson, 1968a,b, 1969). Apart from discussion of the mass spectra of lichen xanthenes, no systematic investigation of the electron-impact-induced fragmentation of xanthenes appears to have been made, except by Arends et al. (1973) in their study of electron-impact-induced fragmentation of monohydroxy- and monomethoxyxanthenes. Mass spectrometry has not been applied extensively to the study of naturally occurring xanthenes, but the MS data available have been very valuable for preliminary examination (Barnes and Occolowitz, 1964).

The data obtained from ^1H NMR spectroscopic analysis are of great value in characterizing and identifying naturally occurring xanthenes (Mathis and Goldstein, 1964). Indeed, these have been used to determine the structure of substituents and for locating aromatic protons, through comparison with reference data and analysis of spin–spin coupling. Closer scrutiny of the chemical shifts of aromatic protons allows prediction of the oxygenation pattern (Barracough et al., 1970), and there are detailed NMR results for this class of compounds (Westerman et al., 1977).

^1H NMR and ^{13}C NMR spectroscopic analyses are the most useful tools in the structure elucidation of xanthenes (Chaudhuri et al., 1978). The ^{13}C NMR spectra of a great number of naturally-occurring xanthenes are reported, with all chemical shifts assigned (Castelão et al., 1977; Westerman et al., 1977; Frahm and Chaudhuri, 1979). Hambloch and Frahm (1980) introduced a computer program named SEOX 1, which

rapidly identifies unknown xanthenes with the help of additivity rules; this lends remarkable facility to structure elucidation.

4. Bioactivities of xanthenes

The study of xanthenes is interesting not only from a chemosystematic viewpoint, but also from a pharmacological point of view. Xanthenes possess antidepressant action and antitubercular activity, while xanthone glycosides exhibit depressant action. The choleric, diuretic, antimicrobial, antiviral and cardiostimulant action of some xanthenes has also been established (Hostettmann and Wagner, 1977; Suzuki et al., 1980, 1981; Kitanov and Blinova, 1987). The inhibition of type A and type B monoamine oxidases by a number of xanthenes has also been observed (Suzuki et al., 1980, 1981). And in spite of their restricted occurrence in the plant kingdom, some xanthenes are reported to possess antileukaemic, antitumour, antiulcer, antimicrobial, antihepatotoxic and CNS-depressant activities (Banerji et al., 1994). For example, bellidifolin (1,5,8-trihydroxy-3-methoxy-xanthone) was found to be a selective inhibitor of MAO A, whereas psorospermin, a dihydrofuranoxanthone epoxide, exhibits significant activity against leukaemia and in colon and mammary tumour models (Beerhues and Berger, 1994). In general, xanthenes and their derivatives have also been shown to be effective as allergy inhibitors and bronchodilators in the treatment of asthma (Balasubramanian and Rajagopalan, 1988).

A series of isoprenylated xanthenes isolated from moraceous plants showed interesting biological activities such as hypotensive effect, anti-rhinoviral activity, inhibition of the formation of some prostanoids and anti-tumour promoting activity (Hano et al., 1990). In a study of structure–activity relationships, it was found that 1,3,5,6-, 1,3,6,7-, 2,3,6,7- and 3,4,6,7-tetraoxygenated xanthenes possess antiplatelet effects, and that the mechanism of action of 1,3,6,7-tetraoxygenated xanthenes is due to both inhibition of thromboxane formation and phosphoinositide breakdown (Lin et al., 1993). Some xanthone dicarboxylic acids have shown a potent inhibition of the binding of leukotriene B₄ to receptors on intact neutrophils. Norathyriol showed anti-inflammatory effects mediated partly through the suppression of mast cell degranulation, and partly through (at least at higher doses) a non-selective blockade of the increase in vascular plasma exudation caused by various mediators (Lin et al., 1996). Bellidifolin, isolated from *Swertia japonica*, was found to be a potent hypoglycemic agent in STZ-induced diabetic rats by both oral and intraperitoneal administration (Basnet et al., 1995).

Recently, various bioactivities of xanthenes including cytotoxic and antitumour activities, anti-inflammatory activity, antifungal activity, enhancement of choline

acetyltransferase activity and inhibition of lipid peroxidase have been described (Iinuma et al., 1994). In 1994 Mehta et al., reported the total synthesis of novel xanthone antibiotics, cervinomycins A₁ and A₂, with promising activity against anaerobic bacteria, mycoplasma and some gram positive bacteria (Table 1).

5. Use of plant sources containing tetraoxygenated xanthenes

Anthocleista vogelli (Planch), Loganiaceae, is a small tree which grows in the tropical rain forest areas of west Africa. The stem bark is used in local medicine for curing fever, stomach ache and as purgative (Okorie, 1976).

Among *Calophyllum* species, *C. inophyllum* is the most widespread and has superior timber qualities, particularly in Malaysia (Al-Jeboury and Locksley, 1971). The balsam from the bark of *C. inophyllum* “Alexandrian Laurel” is an oleoresin and used as a cicatrificant, whereas an infusion or decoction of the leaves has been traditionally used as an eye remedy in Asian medicine (Basnet et al., 1995). Xanthenes from *C. inophyllum* produce CNS depression in rats and mice (Bennett and Lee, 1989). The tropical American tree *C. brasiliense* produces a strong and durable timber known as “Santa Maria” or “jacareuba” (King et al., 1953).

Canscora decussata Schult (Gentianaceae), an erect annual plant of height 0–6 m, finds use in indigenous medicine for a variety of purposes. The roots are used as a laxative, diuretic, for liver troubles, as a nerve tonic and in tuberculosis and fevers, while the aerial portions are used to treat cases of insanity, epilepsy and nervous debility (Ghosal and Chaudhuri, 1973; Okorie, 1976). The extract of *C. decussata* Schult is used in the treatment of certain mental disorders and tuberculosis (Ghosal and Chaudhuri, 1975).

The botanical source of the Taiwan folk remedy “Hwang-jin-guey” is the root and stem of *Cudrania cochinchinensis* (Lour.) Kudo and Masamune var. *gerontogea* (S. & Z.) Kudo and Masamune (Gottlieb et al., 1975). It was used in the treatment of neuralgia, rheumatics, hepatitis and contusions (Chang et al., 1994). Ethanolic extracts of the roots of this species also showed significant anti-inflammatory and liver protective effects, and the extract as well as isolated xanthone compounds exhibited anti-lipid peroxidative activities both in vivo and in vitro (Chang et al., 1995). *C. tricuspidata* (Carr.) Bur. (Japanese name “Hariguwa”, Moraceae) is a deciduous tree whose cortex and root bark have been used as a Chinese crude drug (Hano et al., 1990a,b,c).

Plant extracts obtained from genera *Eustoma* are used to treat various ailments, including constipation, nervous debility, tuberculosis, fever and anorexia (Sullivan et al., 1977).

Table 1
Natural source of tetraoxygenated xanthone

Family Asteraceae	
Genus <i>Senecio</i> — <i>S. mikanioides</i> [60]	<i>G. subelliptica</i> [103, 162, 163, 168, 169, 247, 248] <i>G. terpnophylla</i> [27] <i>G. thwaitesii</i> [135]
Family Betulaceae	
Genus <i>Alnus</i> — <i>A. glutinosa</i> [197]	Genus <i>Haploclathra</i> — <i>H. leiantha</i> [256, 257, 259] <i>H. paniculata</i> [258, 259]
Family Caryophyllaceae	
Genus <i>Saponaria</i> — <i>S. vaccaria</i> [192,193]	Genus <i>Hypericum</i> — <i>H. androsaemum</i> [263,176] <i>H. aucheri</i> [200] <i>H. canariensis</i> [54] <i>H. ericoides</i> [55, 117] <i>H. maculatum</i> [14] <i>H. patulum</i> [175, 176, 178, 179] <i>H. paturum</i> [177] <i>H. reflexum</i> [53] <i>H. roeperanum</i> [290] <i>H. sampsonii</i> [71]
Family Clusiaceae	
Genus <i>Allanblackia</i> — <i>A. floribunda</i> [226,227]	Genus <i>Kayea</i> — <i>K. stylosa</i> [131]
Genus <i>Archytaea</i> — <i>A. multiflora</i> [206]	Genus <i>Kielmeyera</i> — <i>K. candidissima</i> [98] <i>K. coriacea</i> [59] <i>K. ferruginea</i> [121] <i>K. rupestris</i> [74, 91] <i>K. speciosa</i> [120]
Genus <i>Bonnetia</i> — <i>B. dinizii</i> [270]	Genus <i>Lorostemon</i> — <i>L. coelhoi</i> [48] <i>L. negrensis</i> [48]
Genus <i>Calophyllum</i> — <i>C. austroindicum</i> [172] <i>C. apetalum</i> [165] <i>C. bracteatum</i> [312] <i>C. brasiliensis</i> [72,124,198,280] <i>C. calaba</i> [209,312] <i>C. canum</i> [57] <i>C. cordato-oblongum</i> [134] <i>C. cuneifolium</i> [130] <i>C. fragrans</i> [224] <i>C. inophyllum</i> [10,119,171,173,184, 208] <i>C. neo-ebudicum</i> [303] <i>C. ramiflorum</i> [39] <i>C. sclerophyllum</i> [182] <i>C. scribtilifolium</i> [183] <i>C. thwaitesii</i> [77] <i>C. tomentosum</i> [28, 191] <i>C. trapezifolium</i> [128] <i>C. walkeri</i> [77] <i>C. zeylanicum</i> [133]	Genus <i>Mammea</i> — <i>M. africana</i> [56] <i>M. acuminata</i> [330]
Genus <i>Caraipa</i> — <i>C. densiflora</i> [59, 214,215] <i>C. grandifolia</i> [104] <i>C. psidifolia</i> [104] <i>C. valioi</i> [104]	Genus <i>Mesua</i> — <i>M. ferrea</i> [337]
Genus <i>Cratoxylum</i> — <i>C. celebicum</i> [317,318] <i>C. cochinchinense</i> [36, 310] <i>C. formosanum</i> [166] <i>C. pruniflorum</i> [199]	Genus <i>Ochrocarpus</i> — <i>O. odoratus</i> [226]
Genus <i>Garcinia</i> — <i>G. cowa</i> [202,211,280] <i>G. densivenia</i> [339] <i>G. dioica</i> [179] <i>G. dulcis</i> [148, 164, 166, 167] <i>G. echinocarpa</i> [27] <i>G. eugenifolia</i> [184] <i>G. forbesii</i> [147] <i>G. mangostana</i> [20, 26, 92, 126, 152, 202, 275, 276, 298, 305, 306, 307, 308, 316, 328] <i>G. multiflora</i> [70] <i>G. nervosa</i> [12] <i>G. opaca</i> [118] <i>G. ovalifolia</i> [338] <i>G. pedunculata</i> [289] <i>G. polyantha</i> [12] <i>G. pyrifera</i> [12] <i>G. staudtii</i> [340]	Genus <i>Pentapthalangium</i> — <i>P. solomonse</i> [271] Genus <i>Poeciloneuron</i> — <i>P. pauciflorum</i> [56] Genus <i>Psorospermum</i> — <i>P. febrifugum</i> [2, 4, 138] Genus <i>Rheedia</i> — <i>R. benthamiana</i> [80] <i>R. brasiliensis</i> [82] <i>R. gardneriana</i> [83, 84] Genus <i>Symphonia</i> — <i>S. globulifera</i> [220, 221, 222, 223] Genus <i>Tovomitia</i> — <i>T. brasiliensis</i> [46] <i>T. macrophylla</i> [245, 269] <i>T. mangle</i> [237] <i>T. pyrifolium</i> [47, 245] Genus <i>Pentadesma</i> — <i>P. butyracea</i> [81] Genus <i>Vismia</i> — <i>V. guaramirangae</i> [132] <i>V. guineensis</i> [45]
Family Gentianaceae	
Genus <i>Blackstonia</i> — <i>B. perfoliata</i> [334]	Genus <i>Canscora</i> — <i>C. decussata</i> [66,107–109] <i>C. cachanlahuen</i> [335]
Genus <i>Centaurium</i> — <i>C. erythraea</i> [35, 190, 243, 261, 262, 327] <i>C. linarifolium</i> [114, 116, 272–274] <i>C. littorale</i> [35, 333] <i>C. pulchellum</i> [246]	Genus <i>Chironia</i> — <i>C. krebsii</i> [342] Genus <i>Erythraea</i> — <i>E. centaurium</i> [327]

Table 1 (continued)

Genus *Eustoma*—*E. grandiflorum* [319]

Genus *Fraseria*—*F. albicaulis* [314]

F. albomarginata [90]

F. caroliniensis [313]

F. speciosa [90]

Genus *Gentiana*—*G. algida* [51, 326]

G. barbata [285]

G. bavarica [156, 158]

G. bellidifolia [52, 233, 234, 235]

G. brachyphylla [155, 156]

G. campestris [52, 188]

G. cerastioides [187]

G. ciliata [239]

G. detonsa [187]

G. favrati [156]

G. germanica [52, 186]

G. karelinii [50, 326]

G. kochiana [136, 292]

G. lactea [302]

G. nivalis [155, 156]

G. ramosa [52, 186]

G. rostanii [156]

G. schleicherii [156]

G. strictiflora [187]

G. tenella [52]

G. utriculosa [156]

G. verna [153, 156]

Genus *Gentianopsis*—*G. paludosa* [349]

Genus *Halenia*—*H. asclepidea* [315]

H. campanulata [161]

H. corniculata [266, 286, 296]

H. elliptica [38, 87, 88, 322]

Genus *Hoppea*—*H. dichotoma* [110]

H. fastigiata [251–254]

Genus *Schultesia*—*S. lisianthoides* [328]

Genus *Swertia*—*S. bimaculata* [113]

S. calycina [295]

S. chirata [61, 79, 112, 231]

S. chirayita [22]

S. cuneata [196]

S. decussata [78, 292]

S. dilatata [329]

S. gracilescens [329]

S. hookeri [106]

S. erythrodicta [160]

S. iberica [85]

S. japonica [18, 19, 21, 33, 180, 189, 203]

S. lawii [19]

S. macrosperma [350]

S. mileensis [150, 219]

S. mussotii [31]

S. nervosa [329]

S. paniculata [13]

S. patens [149]

S. perennis [154, 292]

S. perfoliata [145]

S. petiolata [195, 207]

S. punicea [101]

S. purpurescens [8, 111]

S. racemosa [329]

S. speciosa [194, 238]

S. tetrapetala [7]

Genus *Veratrilla*—*V. baillonii* [348]

Family Gesneriaceae

Genus *Orphium*—*O. frutescens* [297]

Family Iridaceae

Genus *Iris*—*I. nigricans* [11]

Family Loganiaceae

Genus *Anthocleista*—*A. vogelli* [99]

Family Lytraceae

Genus *Lawsonia*—*L. inermis* [41, 42, 229]

Family Moraceae

Genus *Chlorophora*—*C. tinctoria* [122]

Genus *Cudrania*—*C. cochinchinensis* [62, 64]

C. javanensis [255]

C. tricuspidata [140, 141, 142, 264]

Genus *Maclura*—*M. aurantica* [17]

M. pomifera [75, 76, 86, 343–346]

Genus *Morus*—*M. insignis* [143, 144]

M. tinctoria [185]

Family Polygalaceae

Genus *Bredemeyera*—*B. brevifolia* [268]

Genus *Monnina*—*M. obtusifolia* [283]

M. sylvatica [31]

Genus *Polygala*—*P. arillata* [232]

P. nyikensis [236]

P. tenuifolia [100, 174, 181]

P. virgata [32]

Family Polypodiaceae

Genus *Athyrium*—*A. mesosorum* [265, 331, 332]

Fungus

Genus *Aspergillus*—*A. versicolor* [49, 151]

Lichen

Genus *Diploschistes*—*Diploschistes* sp [95]

Garcinia (Clusiaceae) is best known in Malaysia as a genus of fruit trees. The fruit of many species are edible and serves as a substitute for tamarinds in curries. Many species produce a yellow resin which is used in the making of varnishes and in treatment of wounds. Some species are used in traditional medicine and as a source of edible oils. Extracts and pure isolates of *Garcinia* species have been shown to exhibit significant antimicrobial and pharmacological activities (Goh et al., 1992).

Garcinia dulcis grows mainly in southeast Asia, and its leaves and seeds have been used in traditional medicine against lymphatitis, parotitis, struma and other disease conditions (Iinuma et al., 1996). The oil obtained from the seeds of *G. echinocarpa* is used for lighting lamps (Bandaranayake et al., 1975). *G. livingstonei* is a small to medium-sized tree producing edible fruits and growing at low altitude. It is found, particularly in South Africa, in riverine fringes and in open woodland. Extracts of the leaves and flowers are reported to exhibit antibiotic properties (Diserens et al., 1992). The fruit hull of *G. mangostana* L., the “Mangosteen” tree, is used in Thai folk medicine for healing skin infections and wounds, and for the relief of diarrhea (Mahabusarakam et al., 1987). It is fairly widespread in India, Sri Lanka and Burma, and is known for the sweet fruits called mangosteen. In the Ayurvedic system of medicine, the fruit hull of this plant finds wide application, mainly as an anti-inflammatory agent and in the treatment of diarrhoea (Balasubramanian and Rajagopalan, 1988).

Garcinia subelliptica is a small shrub 4–5 m in height or a large tree sometimes reaching 15–20 m, and has been extensively cultivated as a windbreak in the Yaeyama islands of Japan. Its bark has been utilized as a source of a yellow coloured dye (Fukuyama et al., 1991). The timber of *G. terpinophylla* is used for building purposes (Bandaranayake et al., 1975).

The roots and rhizomes of the yellow gentian (*Gentiana lutea*) have been much used for the production of a bitter tonic. Any medicinal value possessed by gentian preparations appears to be due to bitter, complex glycosides (Roberts, 1961). *Hoppea dichotoma* Willd. is used in the Ayurvedic system of medicine in the treatment of haemorrhoids, in cardiac disorders and in certain mental disorders (Ghosal et al., 1978).

A number of species of the genus *Hypericum* have been found to possess various biological properties. Among the activities is inhibition of monoamine oxidase (MAO; EC 1.4.3.4). MAO, which exists as two isoenzymes, MAO-A and MAO-B, plays a key role in the regulation of some physiological amines and is the target of inhibitors used as antidepressive drugs. The leaves and young twigs of *H. balearicum* contain lipophilic glandular products (Wollenweber et al., 1994). The xanthones of *H. brasiliense* inhibit MAO activity (Rocha et al., 1994); the stems, leaves and flowers of

H. ericoides are used in Valentian folk medicine (Cardona and Seoane, 1982), and ethanol extracts of the aerial parts of *H. mysorens* show antifungal action (Nattaya et al., 1996). Extracts of *H. perforatum* are widely used in Europe as a drug for depression treatment. *H. roeperanum*, a shrub or small tree growing in central, eastern and south tropical Africa, is employed, alone or in association with various plants or animal parts, to cure female sterility (Rath et al., 1996). *H. sampsonii* Hance is known as a tumour inhibiting plant in Formosan folk medicine (Chen and Chen, 1985).

Lawsonia inermis L. (“Henna”) is a plant used by ancient Egyptians for preserving mummies. It is presently used in India and Africa for dyeing hair and for staining hands and feet. It was also reported that the leaves are used for treating some skin diseases including Tinea of the legs (Mahmoud et al., 1980).

Mesua ferrea is commonly called ironwood in Malaya. The hard and durable trunkwood is used widely in agricultural tools and vehicles in southeast Asian countries (Chow and Quon, 1968). From the expressed oil of its seeds, two crystalline antibiotic principles have been isolated, mesuol and mesuone (Govindachari et al., 1967). In contrast to mangiferin, which is reported to be a CNS stimulant (Bhattacharya et al., 1972), xanthones from *M. ferrea* result in CNS depression in rats and mice (Bennett and Lee, 1989).

Monnina obtusifolia is used in the folk medicine of Ecuador as an antifungal, antitumoural, antipyorrhea and antiseptic and as a skin cleanser (Pinto et al., 1994).

The roots of *Polygala tenuifolia* are used as an expectorant, tonic and sedative agent under the names “Onji” in Japan and “Yuan zhi” in China (Ito et al., 1977; Ikeya et al., 1991). It is also effective in inhibiting congestive oedema in rats (Fujita et al., 1992).

Psorospermum febrifugum (Clusiaceae) is a woody plant of tropical Africa which has been used as a febrifuge, a leprosy treatment, a poison antidote, and a purgative. An ethanolic extract of *P. febrifugum* showed antileukaemic activity in vivo in the P388 lymphocytic leukaemia in mice and in vitro in the KB cell culture system (Kupchan et al., 1980). Six compounds isolated from the extract were found to exhibit significant in vitro cytotoxic activity against 9PS cells in culture, and another exhibited both in vitro cytotoxic and in vivo antitumour activity (Abou-Shoer et al., 1988, 1989a,b). One of these six xanthones exhibited significant cytotoxicity in the HT-29 human colon adenocarcinoma in vitro cell line (Abou-Shoer et al., 1993); the xanthone, sorospermin, isolated from *P. febrifugum*, exhibited cytotoxic and in vivo antitumour activity in the P388 mouse leukaemia, mammary (CD) and colon (C6) models (Habib et al., 1987).

Saponaria vaccaria is an annual herb growing as a weed in cultivated fields in northern Pakistan, and is widespread in the flora of Russia. It is reputed to possess

sudorific, emetic and laxative properties, and is also used in the indigenous system of medicine for the treatment of jaundice, rheumatism, hepatic eruption and venereal ulcers. It also shows toxicity against worms, and paramecium and other unicellular organisms (Kazmi et al., 1989).

Plants of the genus *Swertia* (Gentianaceae) have been used in traditional medicine for many years. Because these herbs taste extremely bitter and possess the ability to reduce fever, detoxify and act as choleric and liver tonics, they have been mainly used for the treatment of hepatic, choleric and inflammatory diseases, such as hepatitis, cholecystitis, pneumonia, osteomyelitis, dysentery, scabies, spasm, pain and neurasthenia. Both methanolic and dichloromethane extracts of *Swertia calycina* exhibit strong antifungal activity against *Cladosporium cucumerinum* and *Candida albicans* (Rodriguez et al., 1995).

Swertia chirata is widely distributed in India in the temperate Himalayas between 4000 and 10,000 ft, from Kashmir to Bhutan, and in Khasia Hills between 4000 and 5000 ft. It also grows abundantly in Nepal. The plant is well known for its use in the Indian system of medicine for a variety of purposes. The extract of the plant is used as a bitter tonic, stomachic, antimalarial and as a remedy for liver disorders, a febrifuge, an anthelmintic, a remedy for scanty urine, in epilepsy and for certain types of mental disorders (Ghosal et al., 1973). Recently, the hexane extract of the plant has been shown to possess promising hypoglycaemic activity (Chakravarty et al., 1994). *S. chirata* found a place among useful medicinal plants of east and southeast Asia as a bitter tonic, febrifuge, stomachic, laxative and blood purifier (Mukherjee and Mukherjee, 1987).

Swertia chirayita (Roxb. ex. Flem.) Karsh grows abundantly in the temperate regions of the Himalayas. It is used in India as a traditional remedy for chronic fever, anaemia, asthma and liver disorders, and as a bitter tonic. A recent report revealed hypoglycaemic activity in the hexane extract of this plant (Asthana et al., 1991).

The extract of *Swertia hookeri* is used by people for a variety of therapeutic purposes, e.g. in the treatment of microbial infections in man, in hypertension and as a mood enhancer (Ghosal et al., 1980). *S. japonica* Makino, a popular medicinal herb in Japan, usually grows in a cold climate. The whole plant has been widely used as a folk medicine for stomach complaints, and has a characteristic bitter taste. The *Swertia* herb has also been widely used in Ayurveda and Unani medicines as an anthelmintic, febrifuge and bitter tonic. The aqueous ethanolic extract of *S. japonica* and its fractions showed potent hypoglycaemic activity in STZ-induced diabetic rats (Basnet et al., 1994).

By using chemiluminescence assays (CL) Ashida et al. (1994) recently showed that a natural Japanese folk

medicine, named “Senburi” (*Swertia japonica* Makino), contained components with antioxidant activity. Antioxidant activities of six isolated xanthone derivatives are comparable to α -tocopherol and BHT (Ashida et al., 1994). In India, *S. chirata* decoctions are a commonly used household remedy for constipation and weak liver function in children. An infusion of the plant has been used by Hindu physicians as a bitter tonic, stomachic, febrifuge and anthelmintic. Its use has also been reported in Unani medicine as a substitute for official gentiana preparations.

Swertia macrosperma is a medicinal plant used as a febrifuge, an antidote and a stomach tonic by the indigenous population in the southwestern part of China (Zhou et al., 1989). *S. mileensis* and *S. mussoti* are especially efficacious for treating acute viral hepatitis, some preparations have been produced industrially in China.

Swertia petiolata is bitter in taste and is used for its laxative and antimalarial properties in the folk medicine of the high altitude Himalayan region (Khetwal et al., 1990). *S. punicea* grows in moist, mountainous areas in the central district of mainland China, and has been used in the folk medicine as a bitter stomachic (Fukamiya et al., 1990). Extracts of *S. purpurescens* Wall are very commonly used as a tonic and febrifuge in the indigenous system of medicine in India (Ahmad et al., 1973).

Vismia guineensis is a small tree growing in west tropical Africa, whose roots and bark are used as a remedy for skin diseases (Gunasekera et al., 1977).

6. Tetraoxygenated xanthones

The first reported naturally occurring tetraoxygenated xanthone is mangostin, isolated in 1855 from *Garcinia mangostana*; in spite of numerous attempts, its structure was not fully elucidated until more than 100 years later (Roberts, 1961). The first naturally occurring tetraoxygenated xanthone whose structure is described in the literature is 1,5,8-trihydroxy-3-methoxyxanthone, isolated from *S. japonica* in 1942 (Asahina et al., 1942).

The review by Roberts (1961) refers to the natural occurrence of seven tetraoxygenated xanthones, namely decussatin, jacareubin, mangostin, swerchirin, swertia-nol, swertinin and asperxanthone. Afzal et al. (1979) described 51 tetraoxygenated xanthones isolated from higher plants, and also described fungal and lichen metabolites. The review by Sultanbawa (1980) included 37 tetraoxygenated xanthones from tropical plants, isolated from different mentioned species, with a dramatic increase in the number of known natural tetraoxygenated xanthones.

In a review of *Hypericum* genus, Kitanov and Blinova (1987) listed only five simple tetraoxygenated xanthones; two years later, in a review of xanthones from

Table 2

Simple tetraoxygenated naturally occurring xanthenes

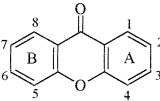
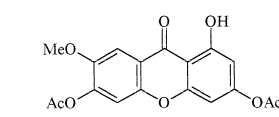
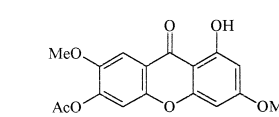
		<i>C. erythraea</i> [190] <i>C. linarifolium</i> [272] <i>C. pulchellum</i> [246] <i>Chironia krebisii</i> [342] <i>Eustoma grandiflorum</i> [319] <i>Gentiana barbata</i> [285] <i>G. bavarica</i> [156–158] <i>G. brachyphylla</i> [155, 156] <i>G. campestris</i> [52] <i>G. ciliata</i> [239] <i>G. detonsa</i> [187] <i>G. favrati</i> [156] <i>G. kochiana</i> [136–292] <i>G. nivalis</i> [155, 156] <i>G. ramosa</i> [52] <i>G. rostanii</i> [156] <i>G. schleicherii</i> [156] <i>G. tenella</i> [52] <i>G. utriculosa</i> [156] <i>G. verna</i> [156] <i>Gentianopsis paludosa</i> [349] <i>Orphium frutescens</i> [297] <i>Swertia bimaculata</i> [113] <i>S. calycina</i> [295] <i>S. chirata</i> [112–161] <i>S. decussata</i> [78] <i>S. dilatata</i> [329] <i>S. gracilescens</i> [329] <i>S. hookeri</i> [106] <i>S. iberica</i> [160] <i>S. lawii</i> [105] <i>S. mileensis</i> [150] <i>S. mussoitii</i> [321] <i>S. nervosa</i> [329] <i>S. paniculata</i> [13] <i>S. patens</i> [149] <i>S. perennis</i> [154] <i>S. perfoliata</i> [145] <i>S. punicea</i> [101] <i>S. purpurascens</i> [111] <i>S. racemosa</i> [329] <i>Schultesia lisianthoides</i> [328]
Laxanthone II (1) <i>Lawsonia inermis</i> [42–229]	 (1)	
Laxanthone III (2) <i>Lawsonia inermis</i> [41]	 (2)	
1-Hydroxy-2,3,5-trimethoxyxanthone (3) <i>Frasera albicaulis</i> [314] <i>F. albomarginata</i> [90] <i>F. caroliniensis</i> [313] <i>F. speciosa</i> [90] <i>Halenia asclepidea</i> [315] <i>H. campanulata</i> [161] <i>H. corniculata</i> [266, 286] <i>H. elliptica</i> [87] <i>S. millensis</i> [219] <i>S. tetrapetala</i> [7] <i>Veratrilla baillonii</i> [348]		
1-Hydroxy-2,3,7-trimethoxyxanthone (4) <i>F. caroliniensis</i> [313] <i>Halenia elliptica</i> [38, 87] <i>Veratrilla baillonii</i> [348]		
1-Hydroxy-3,4,5-trimethoxyxanthone (5) <i>Frasera albicaulis</i> [314]		
1-Hydroxy-3,4,7-trimethoxyxanthone (6) <i>Frasera albicaulis</i> [314] <i>F. albomarginata</i> [90]		
1-Hydroxy-3,5,6-trimethoxyxanthone (7) <i>Canscora decussata</i> [108] <i>Centaurium erythraea</i> [190] <i>Hopaea dichotoma</i> [110]		
1-Hydroxy-3,5,8-trimethoxyxanthone (8) <i>Centaurium littorale</i> [333] <i>Swertia chirata</i> [112–161] <i>S. hookeri</i> [106] <i>S. japonica</i> [189] <i>S. lawii</i> [105] <i>S. paniculata</i> [13] <i>S. perfoliata</i> [145]		
1-Hydroxy-3,6,7-trimethoxyxanthone (9) <i>Polygala tenuifolia</i> [174]		
1-Hydroxy-3,6,8-trimethoxyxanthone (10) (Ellipticol) <i>Halenia elliptica</i> [88]		
1-Hydroxy-3,7,8-trimethoxyxanthone (11) (Decussatin) <i>Anthocleista vogelli</i> [267] <i>Canscora decussata</i> [66] <i>Centaurium cachenlahuen</i> [335]		
		2-Hydroxy-1,3,7-trimethoxyxanthone (12) <i>Frasera albicaulis</i> [314] 2-Hydroxy-5,6,7-trimethoxyxanthone (13) <i>Hypericum ericoides</i> [55–117] 3-Hydroxy-1,2,4-trimethoxyxanthone (14) <i>Psorospermum febrifugum</i> [138] 3-Hydroxy-1,2,7-trimethoxyxanthone (15) <i>Polygala tenuifolia</i> [100] 3-Hydroxy-1,5,6-trimethoxyxanthone (16) <i>Haploclathra leiantha</i> [256] <i>Kielmeyera rupestris</i> [74, 91] 3-Hydroxy-1,7,8-trimethoxyxanthone (17) <i>Swertia paniculata</i> [13] 4-Hydroxy-2,3,6-trimethoxyxanthone (18) <i>Hypericum reflexum</i> [53] 5-Hydroxy-1,2,3-methoxyxanthone (19) <i>Schultesia lisianthoides</i> [328]

Table 2 (continued)

6-Hydroxy-1,3,5-trimethoxyxanthone (20) <i>Calophyllum austroindicum</i> [172]	1,5-Dihydroxy-3,8-dimethoxyxanthone (38) (Chiritol) <i>Swertia chirayita</i> [22]
7-Hydroxy-1,2,3-trimethoxyxanthone (21) (Onjixanthone I) <i>Polygala tenuifolia</i> [100, 174]	1,5-Dihydroxy-6,7-dimethoxyxanthone (39) <i>Caraipa densiflora</i> [215] <i>C. grandifolia</i> [104] <i>C. psidifolia</i> [104] <i>C. valioi</i> [104] <i>Tovomita brasiliensis</i> [46]
7-Hydroxy-1,3,8-trimethoxyxanthone (22) (Anthaxanthone) <i>Haploclathra leiantha</i> [257]	1,6-Dihydroxy-3,5-dimethoxyxanthone (40) <i>Canscora decussata</i> [108] <i>Centaurium linarifolium</i> [273, 274] <i>Chironia krebsii</i> [342] <i>Hoppea dichotoma</i> [110]
8-Hydroxy-1,3,5-trimethoxyxanthone (23) <i>Swertia bimaculata</i> [113] <i>S. mussotii</i> [321]	1,6-Dihydroxy-3,7-dimethoxyxanthone (41) <i>Iris nigricans</i> [11] <i>Polygala tenuifolia</i> [100–174]
1,2-Dihydroxy-5,6-dimethoxyxanthone (24) <i>Garcinia subelliptica</i> [247]	1,6-Dihydroxy-5,7-dimethoxyxanthone (42) <i>Caraipa densiflora</i> [214] <i>Hypericum canariensis</i> [54]
1,3-Dihydroxy-2,5-dimethoxyxanthone (25) <i>Bonnetia dinizii</i> [270] <i>Calophyllum apetalum</i> [165] <i>Centaurium linarifolium</i> [114] <i>Monnina obtusifolia</i> [283]	1,6-Dihydroxy-7,8-dimethoxyxanthone (43) <i>Bonnetia dinizii</i> [270] <i>Calophyllum trapezifolium</i> [128] <i>Polygala nyikensis</i> [236]
1,3-Dihydroxy-2,7-dimethoxyxanthone (26) <i>Veratrilla baillonii</i> [348]	1,6-Dihydroxy-7,8-dimethylenedioxyxanthone (44) <i>Caraipa densiflora</i> [215, 214]
1,3-Dihydroxy-2,8-dimethoxyxanthone (27) <i>Kielmeyera candidissima</i> [98]	1,7-Dihydroxy-2,3-dimethoxyxanthone (45) <i>Frasera speciosa</i> [90] <i>Halenia corniculata</i> [266–296] <i>H. elliptica</i> [322] <i>Polygala tenuifolia</i> [174, 100]
1,3-Dihydroxy-4,5-dimethoxyxanthone (28) <i>Frasera caroliniensis</i> [313] <i>F. speciosa</i> [90] <i>Swertia bimaculata</i> [113]	1,7-Dihydroxy-3,4-dimethoxyxanthone (46) <i>Polygala virgata</i> [32]
1,3-Dihydroxy-4,7-dimethoxyxanthone (29) <i>Frasera albicaulis</i> [314]	1,7-Dihydroxy-3,5-dimethoxyxanthone (47) <i>Hoppea fastigiata</i> [252]
1,3-Dihydroxy-5,6-dimethoxyxanthone (30) (Leiaxanthone) <i>Canscora decussata</i> [107] <i>Centaurium linarifolium</i> [116, 272] <i>Haploclathra leiantha</i> [256]	1,7-Dihydroxy-3,6-dimethoxyxanthone (48) <i>Calophyllum inophyllum</i> [208]
1,3-Dihydroxy-5,8-dimethoxyxanthone (31) <i>Swertia petiolata</i> [207]	1,7-Dihydroxy-3,8-dimethoxyxanthone (49) (Gentiacalein) <i>Gentiana barbata</i> [285] <i>G. bavarica</i> [156, 158] <i>G. brachyphylla</i> [155, 156] <i>G. ciliata</i> [239] <i>G. detonsa</i> [187] <i>G. favrati</i> [156] <i>G. karelinii</i> [50] <i>G. kochiana</i> [292] <i>G. nivalis</i> [155, 156] <i>G. rostanii</i> [156] <i>G. schleicheri</i> [156] <i>G. utriculosa</i> [156] <i>G. verna</i> [156] <i>Gentianopsis pludosa</i> [349] <i>Haploclathra leiantha</i> [256] <i>H. paniculata</i> [259] <i>Swertia dilatata</i> [329] <i>S. gracilescens</i> [329] <i>S. nervosa</i> [329] <i>S. perenis</i> [154] <i>S. punicea</i> [101]
1,3-Dihydroxy-6,7-dimethoxyxanthone (32) (Laxanthone I) <i>Lawsonia inermis</i> [42, 229]	
1,3-Dihydroxy-7,8-dimethoxyxanthone (33) (Swertinin) <i>Gentiana kochiana</i> [292] <i>Swertia decussata</i> [78] <i>Carapia inophyllum</i> [171]	
1,4-Dihydroxy-3,5-dimethoxyxanthone (34) <i>Centaurium erythraea</i> [261]	
1,5-Dihydroxy-2,3-dimethoxyxanthone (35) <i>Calophyllum thwaitesii</i> [77] <i>Calophyllum walkeri</i> [77] <i>Halenia elliptica</i> [322] <i>H. corniculata</i> [296] <i>Monnina sylvatica</i> [31] <i>Schultesia lisianthoides</i> [328]	
1,5-Dihydroxy-3,4-dimethoxyxanthone (36) (Tovopyrifolin-B) <i>Tovomita macrophylla</i> [245] <i>T. pyrifolium</i> [245, 47]	
1,5-Dihydroxy-3,7-dimethoxyxanthone (37) <i>Hoppea fastigiata</i> [254]	

Table 2 (continued)

<i>S. racemosa</i> [329]	<i>S. punicea</i> [150]
<i>S. speciosa</i> [238]	<i>S. racemosa</i> [329]
	<i>S. speciosa</i> [238]
1,8-Dihydroxy-2,6-dimethoxyxanthone (50)^a	1,8-dihydroxy-4,6-dimethoxyxanthone (54)^a
<i>Centaurium erythraea</i> [327]	<i>Erythraea centaurium</i> [327]
<i>C. linarifolium</i> [274]	<i>Swertia mileensis</i> [150]
1,8-Dihydroxy-3,5-dimethoxyxanthone (51)^a	2,4-dihydroxy-3,6-dimethoxyxanthone (55)
(Methylbellidifolin or Swerchirin)	<i>Hypericum reflexum</i> [53]
<i>Blackstonia perfoliata</i> [334]	2,5-dihydroxy-1,6-dimethoxyxanthone (56)
<i>Centaurium cachanlahuen</i> [335]	<i>Garcinia thwaitesii</i> [135]
<i>C. erythraea</i> [35, 190]	2,6-dihydroxy-1,5-dimethoxyxanthone (57)
<i>C. littorale</i> [35, 333]	<i>Garcinia sublliptica</i> [247]
<i>C. pulchellum</i> [246]	2,7-Dihydroxy-1,8-dimethoxyxanthone (58)
<i>Frasera albicaulis</i> [314]	<i>Cratoxylum formosanum</i> [166]
<i>F. albomarginata</i> [90]	3,8-Dihydroxy-1,2-dimethoxyxanthone(59)
<i>F. caroliniensis</i> [313]	<i>Cratoxylum formosanum</i> [166]
<i>Gentiana algida</i> [51]	<i>Calophyllum apetalum</i> [165]
<i>Gentiana bellidifolia</i> [233–252]	3,7-Dihydroxy-1,8-dimethoxyxanthone (60)
<i>G. karelinii</i> [326]	<i>Haploclathra paniculata</i> [259]
<i>G. lactea</i> [302]	3,6-Dihydroxy-1,5-dimethoxyxanthone (61)
<i>Saponaria vaccaria</i> [192]	<i>Calophyllum austroindicum</i> [172]
<i>Swertia bimaculata</i> [113]	3,8-Dihydroxy-1,7-dimethoxyxanthone (62)
<i>S. chirata</i> [79, 112]	(Isogentiacalein)
<i>S. chirayita</i> [22]	<i>Gentiana kochiana</i> [136, 292]
<i>S. dilatata</i> [329]	<i>Haploclathra paniculata</i> [259]
<i>S. gracilescens</i> [329]	4,6-Dihydroxy-1,3-dimethoxyxanthone (63)
<i>S. japonica</i> [180–189]	<i>Alnus glutinosa</i> [197]
<i>S. milensis</i> [150]	5,6-Dihydroxy-1,3-dimethoxyxanthone (64) (Ferrxanthone)
<i>S. mussotii</i> [321]	<i>Haploclathra leiantha</i> [256]
<i>S. nervosa</i> [329]	<i>H. piniculata</i> [259]
<i>S. paniculata</i> [13]	<i>Mesua ferrea</i> [337]
<i>S. patens</i> [219]	1,2,3-Trihydroxy-5-methoxyxanthone (65)
<i>S. petiolata</i> [195]	<i>Centaurium erythraea</i> [162–243]
<i>S. racemosa</i> [329]	1,2,8-Trihydroxy-3-methoxyxanthone (66)^b
<i>S. speciosa</i> [238]	<i>Archytaea multiflora</i> [206]
<i>S. tetrapetala</i> [7]	1,3,5-Trihydroxy-2-methoxyxanthone (67)
1,8-Dihydroxy-3,6-dimethoxyxanthone (52)	(Tovopyrifolin-C)
<i>Diploschistes sp</i> [95]	<i>Bonnetia dinizii</i> [270]
1,8-Dihydroxy-3,7-dimethoxyxanthone (53)^a	(Haploxanthone)
(Methylswertianin or Swertiaperennin)	<i>Calophyllum apetalum</i> [165]
<i>Blackstonia perfoliata</i> [334]	<i>Calophyllum bracteatum</i> [312]
<i>Canscora decussata</i> [66]	<i>C. inophyllum</i> [171]
<i>C. cachanlahuen</i> [335]	<i>C. tomentosum</i> [28]
<i>C. pulchellum</i> [246]	<i>C. trapezifolium</i> [128]
<i>Gentiana ciliata</i> [239]	<i>Centaurium linarifolium</i> [114]
<i>G. karelinii</i> [50]	<i>Kayea stylosa</i> [131]
<i>G. tenella</i> [52]	<i>Monnina obtusifolia</i> [283]
<i>Schultesia lisianthoides</i> [328]	<i>Pentadesma butyracea</i> [81]
<i>Swertia chirata</i> [112]	<i>Tovomita pyrifolium</i> [245]
<i>S. chirayita</i> [22]	1,3,5-Trihydroxy-6-methoxyxanthone (68)
<i>S. dilatata</i> [329]	<i>Canscora decussata</i> [66–107]
<i>S. erythrosticta</i> [160]	<i>Haploclathra leiantha</i> [256]
<i>S. gracilescens</i> [329]	<i>Hoppea dichotoma</i> [110]
<i>S. iberica</i> [85]	
<i>S. japonica</i> [180–189]	
<i>S. lawii</i> [105]	
<i>S. milensis</i> [150]	
<i>S. mussotii</i> [321]	
<i>S. nervosa</i> [329]	
<i>S. paniculata</i> [13]	
<i>S. patens</i> [149]	
<i>S. perenis</i> [154, 292]	

Table 2 (continued)

1,3,6-Trihydroxy-5-methoxyxanthone (69) <i>Canscora decussata</i> [107, 108] <i>Hoppea dichotoma</i> [110]	(Gentiakochianin or Swertianin) <i>Chironia krebsii</i> [342] <i>G. lactea</i> [302] <i>G. ramosa</i> [186] <i>G. strictiflora</i> [187] <i>Swertia chirata</i> [112–161] <i>S. dilatata</i> [329] <i>S. erythrosticta</i> [160] <i>S. gracilescens</i> [329] <i>S. hookeri</i> [106] <i>S. japonica</i> [180–188] <i>S. nervosa</i> [329] <i>S. paniculata</i> [13] <i>S. perennis</i> [154] <i>S. perfoliata</i> [145] <i>S. purpurescens</i> [8–111] <i>S. racemosa</i> [329] <i>S. speciosa</i> [90]
1,3,6-Trihydroxy-7-methoxyxanthone (70) <i>Poeciloneuron pauciflorum</i> [330]	
1,3,7-Trihydroxy-6-methoxyxanthone (71) (Isoathyriol) <i>Athyrium mesosorum</i> [331,332]	
1,3,7-Trihydroxy-8-methoxyxanthone (72)^b <i>Hoppea fastigiata</i> [253] <i>Haploclathra leiantha</i> [259] <i>H. paniculata</i> [259]	
1,3,8-Trihydroxy-5-methoxyxanthone (73) (Isobellidifolin or Swertianol) <i>Gentiana algida</i> [326] <i>Gentiana bellidifolia</i> [52–234] <i>G. campestris</i> [52] <i>G. germanica</i> [52] <i>G. karelinii</i> [50] <i>G. ramosa</i> [52] <i>G. tenella</i> [52] <i>Swertia chirata</i> [112] <i>S. erythrosticta</i> [160] <i>S. hookeri</i> [106] <i>S. japonica</i> [19] <i>S. mussotii</i> [321] <i>S. paniculata</i> [13] <i>S. purpurascens</i> [111] <i>Schultesia lisianthoides</i> [328]	1,6,7-Trihydroxy-3-methoxyxanthone (82)^b (Athyriol) <i>Athyrium mesosorum</i> [331, 332]
1,3,8-Trihydroxy-7-methoxyxanthone (74) (Isogentiakochianin) <i>Calophyllum inophyllum</i> [171] <i>Canscora decussata</i> [66] <i>G. Cerastioides</i> [187] <i>G. Germanica</i> [186] <i>Kielmeyera speciosa</i> [120] <i>Swertia iberica</i> [85] <i>Schultesia lisianthoides</i> [328]	1,6,8-Trihydroxy-2-methoxyxanthone (83) <i>Iris nigricans</i> [11]
1,4,7-Trihydroxy-3-methoxyxanthone (75) <i>Garcinia eugenifolia</i> [171]	1,7,8-Trihydroxy-3-methoxyxanthone (84)
1,4,7-Trihydroxy-8-methoxyxanthone (76) <i>Cratoxylum formosanum</i> [166]	1,7,8-Trihydroxy-6-methoxyxanthone (85) <i>Archytaea multiflora</i> [206]
1,4,8-Trihydroxy-3-methoxyxanthone (77)^b <i>Gentiana bellidifolia</i> [235]	2,4,5-Trihydroxy-1-methoxyxanthone (86) <i>Gentiana bavarica</i> [156–158] <i>G. brachyphylla</i> [155, 156] <i>G. ciliata</i> [239] <i>G. favrati</i> [156] <i>G. karelinii</i> [50] <i>G. kochiana</i> [136–292] <i>G. nivalis</i> [155, 156] <i>G. rostani</i> [156] <i>G. verna</i> [153, 156] <i>Orphium frutescens</i> [297] <i>Swertia calycina</i> [295] <i>S. decussata</i> [292] <i>S. dilatata</i> [78] <i>S. erythrosticta</i> [160] <i>S. gracilescens</i> [329] <i>S. iberica</i> [85] <i>S. japonica</i> [21–33] <i>S. lawii</i> [105] <i>S. mussotii</i> [321] <i>S. nervosa</i> [329] <i>S. racemosa</i> [329] <i>S. speciosa</i> [238]
1,4,8-Trihydroxy-6-methoxyxanthone (78) <i>Swertia japonica</i> [33]	(BR-xanthone-B) <i>Garcinia mangostana</i> [26]
1,5,6-Trihydroxy-3-methoxyxanthone (79) <i>Canscora decussata</i> [109] <i>Hypericum androsaemum</i> [263] <i>Swertia chirata</i> [231] <i>Schultesia lisianthoides</i> [328]	3,5,6-Trihydroxy-1-methoxyxanthone (87) <i>Calophyllum sclerophyllum</i> [182]
1,5,7-Trihydroxy-3-methoxyxanthone (80)^b <i>Hoppea fastigiata</i> [251]	1,3,5,6-Tetrahydroxyxanthone (88) <i>Calophyllum brasiliense</i> [198] <i>C. sclerophyllum</i> [182] <i>Canscora decussata</i> [66, 107] <i>Cratoxylum cochinchinense</i> [310] <i>Hypericum androsaemum</i> [263] <i>Hypericum patulum</i> [178]
1,5,8-Trihydroxy-3-methoxyxanthone (81) (Bellidifolin) <i>Gentiana algida</i> [326] <i>G. bellidifolia</i> [233] <i>G. campestris</i> [188]	

Table 2 (continued)

<i>Mammea africana</i> [56]	<i>Symphonia globulifera</i> [220, 222]
<i>Morus tinctoria</i> [185]	1,3,7,8-Tetrahydroxyxanthone (92) (Norswertianin)
<i>Ochrocarpus odoratus</i> [227]	<i>Canscora decussata</i> [66]
<i>Psorospermum febrifugum</i> [4]	<i>Chironia krebsii</i> [342]
<i>Symphonia globulifera</i> [220–222]	<i>Gentiana bavarica</i> [158]
1,3,5,7-Tetrahydroxyxanthone (89)	<i>Orphium frutescens</i> [297]
<i>Garcinia pedunculata</i> [289]	<i>Swertia chirata</i> [112]
1,3,5,8-Tetrahydroxyxanthone (90) (Demethylbellidifolin)	<i>S. dilatata</i> [329]
<i>Gentiana bellidifolia</i> [52–233]	<i>S. erythrosticta</i> [160]
<i>G. lactea</i> [302]	<i>S. gracilescens</i> [329]
<i>G. ramosa</i> [52–186]	<i>S. hookeri</i> [106]
<i>G. strictiflora</i> [187]	<i>S. iberica</i> [85]
<i>Iris nigricans</i> [11]	<i>S. japonica</i> [21, 189]
<i>Swertia chirata</i> [112]	<i>S. lawii</i> [105]
<i>S. dilatata</i> [329]	<i>S. nervosa</i> [329]
<i>S. erythrosticta</i> [160]	<i>S. perennis</i> [154]
<i>S. gracilescens</i> [329]	<i>S. purpurascens</i> [111]
<i>S. hookeri</i> [106]	<i>S. racemosa</i> [329]
<i>S. japonica</i> [19, 21, 189]	1,7-Dimethoxy-2,3-methylenedioxyxanthone (93)
<i>S. lawii</i> [105]	<i>Polygala tenuifolia</i> [100]
<i>S. macrosperma</i> [350]	1,8-Dimethoxy-2,3-methylenedioxyxanthone (94)
<i>S. nervosa</i> [329]	<i>Polygala nyikensis</i> [236]
<i>S. purpurescens</i> [111]	1,2,3,7-Tetramethoxyxanthone (95)
<i>S. racemosa</i> [329]	<i>Frasera albicaulis</i> [314]
1,3,6,7-Tetrahydroxyxanthone (91) (Norathyriol)	<i>Polygala tenuifolia</i> [174–181]
<i>Allanblackia floribunda</i> [227]	1,2,6,8-Tetramethoxyxanthone (96)
<i>Athyrium mesosorum</i> [265, 332]	<i>Bredemeyera brevifolia</i> [268]
<i>Canscora decussata</i> [109]	1,3,4,5-Tetramethoxyxanthone (97)
<i>Chlorophora tinctoria</i> [122]	<i>Frasera albicaulis</i> [314]
<i>Cratoxylum pruniflorum</i> [199]	1,3,4,7-Tetramethoxyxanthone (98)
<i>Garcinia echinocarpa</i> [27]	<i>Frasera albicaulis</i> [314]
<i>G. mangostana</i> [152]	1,3,5,8-Tetramethoxyxanthone (99)
<i>G. multiflora</i> [70]	<i>Swertia hookeri</i> [106]
<i>G. pedunculata</i> [289]	1,3,6,7-Tetramethoxyxanthone (100)
<i>G. terpnophylla</i> [27]	<i>Allanblackia floribunda</i> [226]
<i>Hypericum androsaemum</i> [263]	<i>Polygala tenuifolia</i> [100]
<i>H. aucheri</i> [200]	2,3,4,5-Tetramethoxyxanthone (101)
<i>Iris nigricans</i> [11]	<i>Halenia campanulata</i> [161]
<i>Maclura pomifera</i> [343]	
<i>Mammea africana</i> [56]	
<i>Morus tinctoria</i> [185]	
<i>Ochrocarpus odoratus</i> [227]	
<i>Pentaphalangium solomonse</i> [271]	

^a The compounds 51/53, 51/54, 66/84, 72/82, 77/80, have the same structure, but they are cited under different names in the references.

^b The compounds 51/53, 51/54, 66/84, 72/82, 77/80, have the same structure, but they are cited under different names in the references.

Clusiaceae, Bennett and Lee (1989) listed 50 tetraoxygenated xanthenes from Clusiaceae species. A review by Mandal et al. (1992) 113 simple tetraoxygenated, prenylated and related xanthenes are listed. Between 1942 and mid 1995, approx. 115 tetraoxygenated naturally occurring xanthenes were presented in reviews. In the present review, 228 of these compounds found in the literature are listed (Tables 2–6).

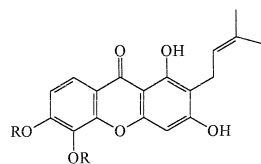
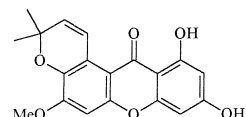
7. Synthesis and biosynthesis of xanthenes

Some authors have reported the preparation of hydroxyxanthenes (Atkinson and Heilbron, 1926; Grover

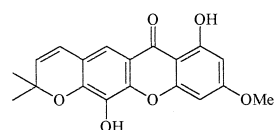
et al., 1955; Shah and Shah, 1956; Quillinan and Scheinmann, 1972, 1973; Simoneau and Brassard, 1984), but the first xanthone synthesis was proposed by Kostanecki (1892) and the last by Ravi et al. (1994) describing a new route to xanthone synthesis, and Vitale et al. (1994) also describing a novel route for the preparation of xanthenes and chromanones.

The preparation of nine 1,2,3,8-tetraoxygenated xanthenes was proposed by Gil et al. (1990) and 1,3,5,6-, 3,4,5,6-, 3,4,6,7- and 2,3,6,7-tetrahydroxyxanthone were synthesized from benzophenone precursors (Sundholm, 1978). The total synthesis of lichen xanthenes (Patel and Trivedi, 1983), synthesis of furanoxanthenes (Pinto and Polonia, 1974; Patel and Trivedi, 1991), synthesis of new

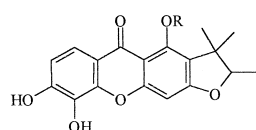
Table 3

Mono C₅ tetraoxygenated naturally occurring xanthenes**1,3,5,6-Tetrahydroxy-2-(3-methylbut-2-enyl)xanthone (102)***Calophyllum brasiliensis* [72]*C. austroindicum* [172]*C. canum* [57]*C. neo-ebudicum* [303]*C. sclerophyllum* [182]*C. scriblitfolium* [183]*C. fragrans* [224]*C. inophyllum* [10, 184](102 R = H) (103 R = CH₃)**1-Hydroxy-3,5,6-trimethoxy-2-(3-methylbut-2-enyl)xanthone (103)***Calophyllum ramiflorum* [39]**Paxanthone (104)***Hypericum paturum* [177]

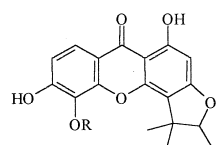
(104)

Forbexanthone (105)*Garcinia forbesii* [147]

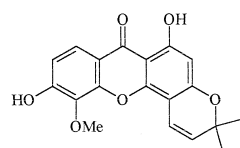
(105)

Toxyloxanthone C (106)*Calophyllum zeylanicum* [133]*Kielmeyera ferruginea* [121]*Maclura pomifera* [86]

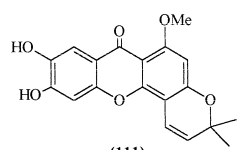
(106 R=H; 107 R=Me)

Geronthoxanthone J (107)*Cudrania cochinchinensis* [64]**2-Deprenylrheediaxanthone B (108)***Hypericum roeperanum* [290]

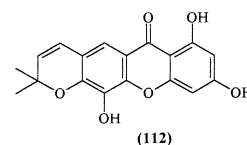
(108 R=H; 109 R=Me)

5-Methoxy-2-deprenylrheediaxanthone B (109)*Hypericum roeperanum* [290]**5-O-Methylisojacareubin (110)**

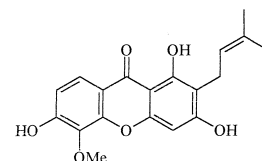
(110)

Lorostemin A (111)*Lorostemon coelhoi* [48]*L. negrensis* [48]

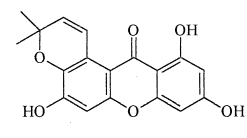
(111)

1,3,5-Trihydroxy-6',6'-dimethylpyrano(2',3':6,7)xanthone (112)*Rheedia brasiliensis* [82]

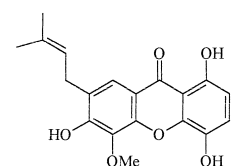
(112)

Morusignin D (113)*Morus insignis* [144]*Hypericum patulum* [179]

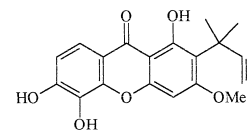
(113)

Toxyloxanthone-B (114)*Hypericum androsaemum* [263]*H. paturum* [177]*H. sampsonii* [71]*Maclura pomifera* [76–86]*Morus insignis* [144]

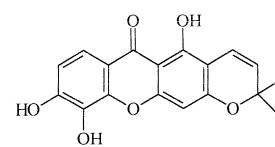
(114)

1,4,6-Trihydroxy-5-methoxy-7-(3-methylbut-2-enyl)xanthone (115)*Garcinia dulcis* [148]

(115)

Cudranixanthone (116)*Cudrania cochinchinensis* [62]*Cudrania javanensis* [255]

(116)

Jacareubin (117)*Calophyllum austroindicum* [172]*C. bracteatum* [312]*C. brasiliense* [72, 280]*C. calaba* [209, 312]*C. canum* [57]*C. cordato-oblongum* [134]*C. cuneifolium* [130]*C. fragrans* [224]*C. inophyllum* [10–184, 208]*C. neo-ebudicum* [303]*C. ramiflorum* [39]*C. sclerophyllum* [182]*C. scriblitfolium* [183]*C. thwaitesii* [77]*C. tomentosum* [191]*C. trapezifolium* [128]*C. walkerii* [77]*C. zeylanicum* [133]*Kielmeyera ferruginea* [121]*Pentadesma butyracea* [81]

(117)

Table 3 (continued)

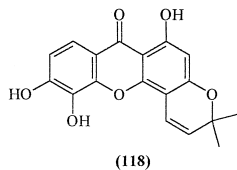
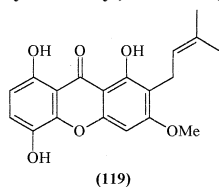
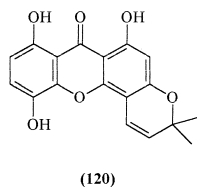
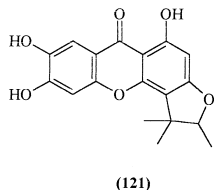
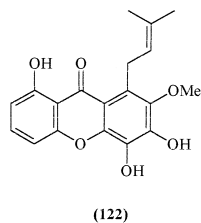
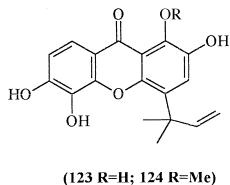
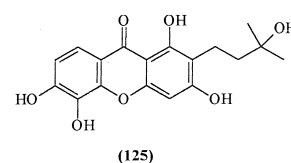
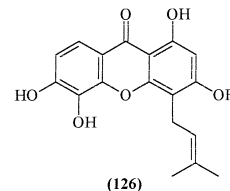
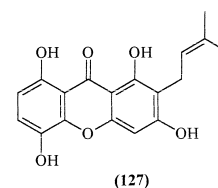
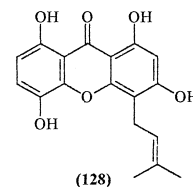
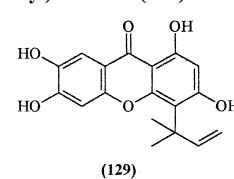
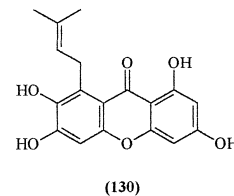
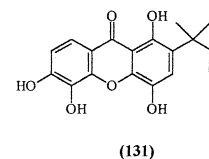
Isojacareubin (118)*Hypericum roeperanum* [290]**1,5,8-Trihydroxy-3-methoxy-2-(3-methylbut-2-enyl)xanthone (119)***Garcinia mangostana* [275, 276]**Morusignin C (120)***Morus insignis* [144]**1,6,7-Trihydroxy-4,4,5-trimethyldihydrofurano-(2,3:3,4) xanthone (121)***Allanblackia floribunda* [226]**Celebixanthone (122)***Cratoxylum celebicum* [317, 318]**Symphoxanthone (123)***Garcinia subelliptica* [248]*Symphonia globulifera* [223]**1-Methylsymphoxanthone (124)***Garcinia subelliptica* [248]**1,3,5,6-Tetrahydroxy-2-(3-hydroxy-3-methylbutyl)xanthone (125)***Calophyllum inophyllum* [119]**Ugaxanthone (126)***Symphonia globulifera* [221]**Morusignin B (127)***Morus insignis* [144]**Morusignin A (128)***Morus insignis* [144]**1,3,6,7-Tetrahydroxy-4-(1,1-dimethylallyl)xanthone (129)***Allanblackia floribunda* [226]**1,3,6,7-Tetrahydroxy-8-(3-methylbut-2-enyl)xanthone (130)***Hypericum androsaemum* [176–263]**Subelliptenone F (131)***Garcinia subelliptica* [168]*Garcinia dulcis* [166]

Table 4

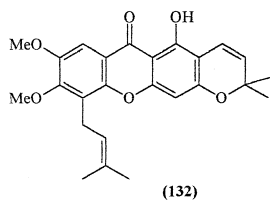
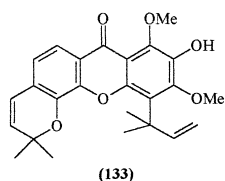
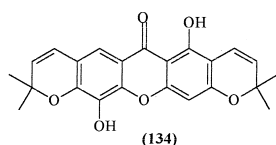
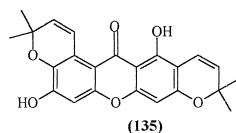
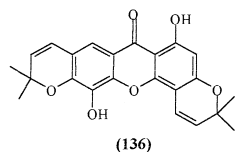
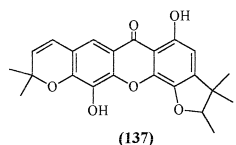
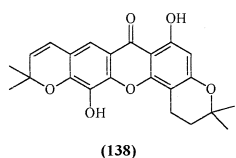
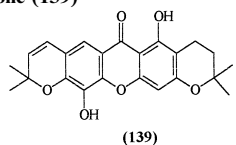
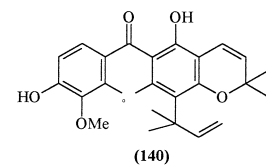
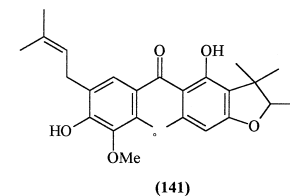
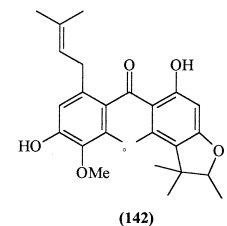
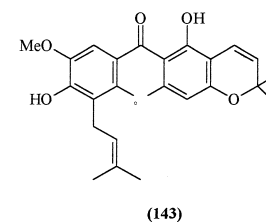
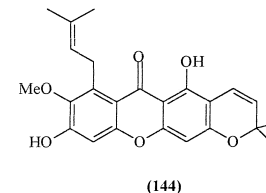
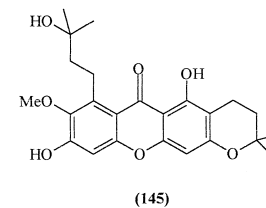
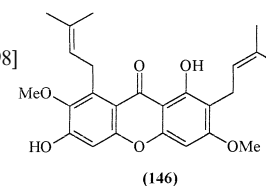
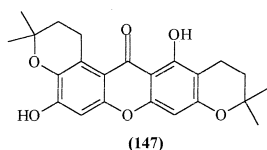
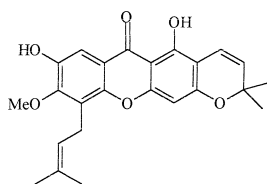
Di-C₅ tetraoxygenated naturally occurring xanthenes**Tovopyrifolin D (132)***Tovomita pyrifolium* [47]**Kayeaxanthone (133)***Kaya stylosa* [131]**Pyranojacareubin (134)***Garcinia densivenia* [339]*G. forbesii* [147]*Rheedia brasiliensis* [82]*R. gardneriana* [83, 84]**Padiaxanthone (135)***Hypericum patulum* [175]**Rheediaxanthone A (136)***Garcinia staudtii* [340]*Rheedia benthamiana* [80]*R. brasiliensis* [82]*R. gardneriana* [83]**Gerontoxanthone A (137)***Cudrania cochinchinensis* [64]*Rheedia brasiliensis* [82]**1,5-Dihydroxy-6,6-dimethylpyrano(2,3:6,7)-6'',6''-dimethyldihydropyrano(2'',3'':3,4)xanthone (138)***Rheedia brasiliensis* [82]**1,5-Dihydroxy-6,6-dimethylpyrano(2,3:6,7)-6'',6''-dimethyldihydropyrano(2'',3'':2,3)xanthone (139)***Rheedia brasiliensis* [82]**10-O-methylmacluraxanthone (140)***Kaya stylosa* [131]**Gerontoxanthone E (141)***Cudrania cochinchinensis* [62]**Caloxanthone B (142)***Carapia inophyllum* [173]**Tovopyrifolin A (143)***Tovomita pyrifolium* [47, 245]**3-Isomangostin (144)***Garcinia mangostana* [228, 305]**3-Isomangostin hydrate (145)***Garcinia mangostana* [228]**β-Mangostin (146)***Cratoxylum cochinchinense* [36]*Garcinia mangostana* [20, 126, 228, 298]

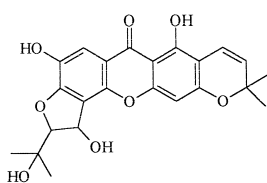
Table 4 (continued)

BR-xanthone A (147)*Garcinia mangostana* [26]

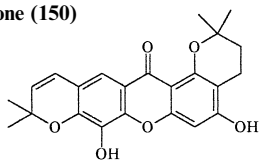
(147)

Manglexanthone (148)*Tovomita mangle* [237]

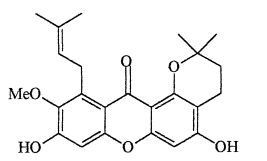
(148)

Caloxanthone D (149)*Calophyllum inophyllum* [171]

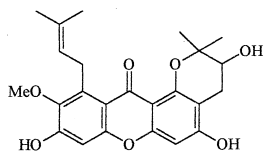
(149)

3,5-Dihydroxy-6,6-dimethylpyrano(2,3:6,7)-6''-dimethyldihydropyrano(2'',3'':1,2)xanthone (150)*Rheedia brasiliensis* [82]

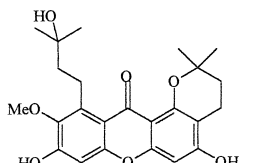
(150)

1-Isomangostin (151)*Garcinia mangostana* [228]

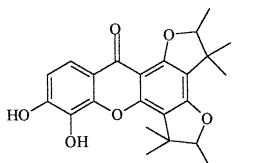
(151)

11-Hydroxy-1-isomangostin (152)*Cratoxylum cochinchinense* [310]

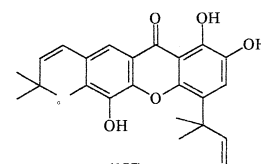
(152)

1-Isomangostin hydrate (153)*Garcinia mangostana* [228]

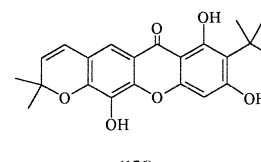
(153)

Rheediaxanthone C (154)*Rheedia brasiliensis* [82]*R. gardneriana* [83]*R. benthamiana* [80]

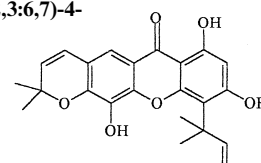
(154)

Subelliptenone H (155)*Garcinia subelliptica* [169]

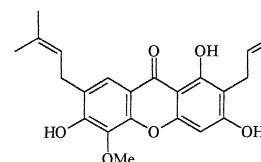
(155)

Gerontoxanthone B (156)*Cudrania cochinchinensis* [64]

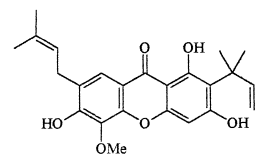
(156)

1,3,5-Trihydroxy-6,6-dimethylpyrano(2,3:6,7)-4-(1,1-dimethylallyl)xanthone (157)*Rheedia brasiliensis* [82]*Garcinia opaca* [118]

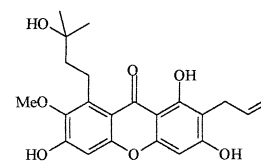
(157)

Cudraxanthone F (158)*Cudrania tricuspidata* [142]

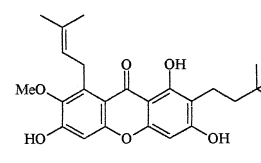
(158)

Cudraxanthone E (159)*Cudrania tricuspidata* [142]

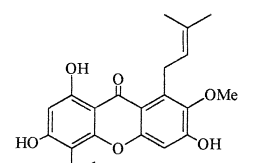
(159)

Garcinone D (160)*Cratoxylum cochinchinense* [36]*Garcinia mangostana* [307]

(160)

Cratoxylone (161)*Cratoxylum cochinchinense* [36]

(161)

Cudraxanthone C (162)*Cudrania tricuspidata* [141]

(162)

Table 4 (continued)

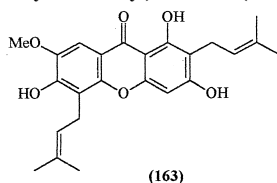
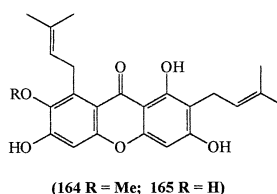
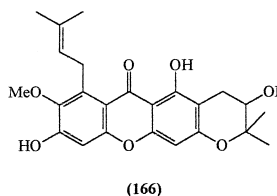
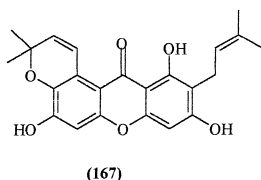
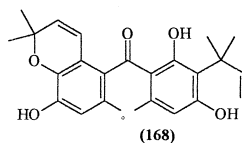
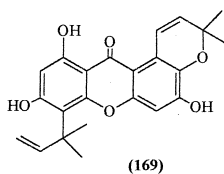
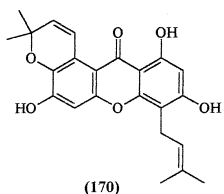
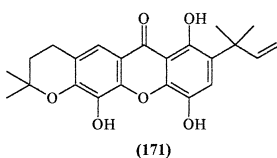
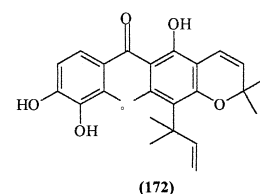
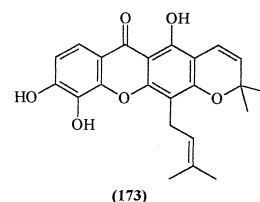
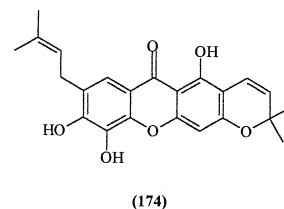
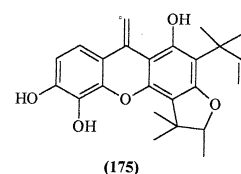
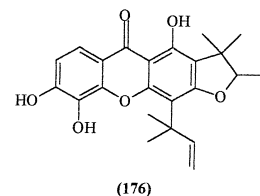
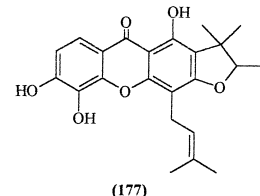
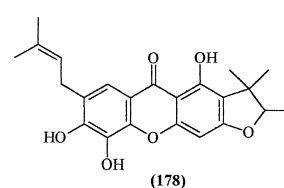
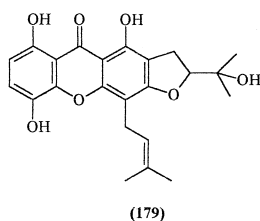
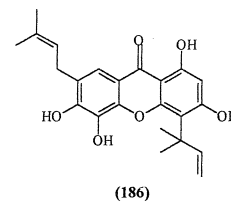
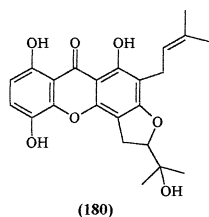
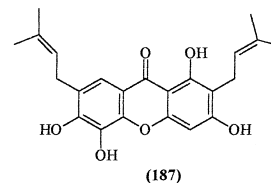
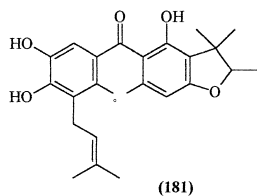
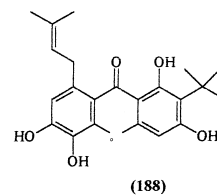
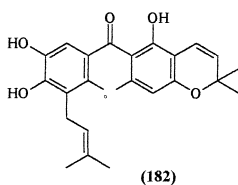
1,3,6-Trihydroxy-7-methoxy-2,5-bis(3-methyl-but-2-enyl)xanthone (163)
Garcinia cowa [280]**Mangostin (164)**
Cratoxylum cochinchinense [36]
Garcinia echinocarpa [27]
G. mangostana
[20, 92, 126–228, 298, 316]
G. terpnophylla [27]**γ-Mangostin or Normangostin (165)***Garcinia mangostana*
[20, 126, 228, 298]
Hypericum paturum [177]
Garcinia mangostana [260]**Mangostanol (166)**
Garcinia mangostana [260]**Garcinone B (167)**
Garcinia mangostana [298, 306, 308]
Hypericum patulu [176]
Morus insignis [144]**Cudraxanthone K (168)**
Cudrania tricuspidata [141]**Cudraxanthone B (169)**
Cudrania tricuspidata [264]**Paxanthone B (170)**
Hypericum patulum [176]**Subelliptenone I (171)**
Garcinia subelliptica [169]**Macluraxanthone (172)**
Calophyllum inophyllum [173]
Garcinia opaca [118]
G. ovalifolia [338]
Machura aurantica [17]
M. pomifera [344, 345]
Rheedia benthamiana [80]
R. brasiliensis [82]
R. gardneriana [83]**Xanthone V₁ (173)**
Vismia guineensis [45]**7-Prenyljacareubin (174)**
Rheedia gardneriana [83]**Rheediaxanthone B (175)**
Garcinia polyantha [12]
Rheedia benthamiana [80]
R. brasiliensis [82]
R. gardneriana [83]**Isorheediaxanthone B (176)**
Garcinia polyantha [12]
Rheedia brasiliensis [82]
R. gardneriana [83]**Gerontoxanthone C (177)**
Cudrania cochinchinensis [64]**Gerontoxanthone G (178)**
Cudrania cochinchinensis [62]

Table 4 (continued)

Morusignin E (179)*Morus insignis* [143]**1,3,5,6-Tetrahydroxy-4-(1,1-dimethylallyl)-7-(3-methylbut-2-enyl)xanthone (186)***Rheedia brasiliensis* [82]**Morusignin F (180)***Morus insignis* [143]**Toxyloxanthone-D (187)***Maclura pomifera* [86]**Cudraxanthone M (181)***Cudrania tricuspidata* [140]**Alvaxanthone (188)***Machura aurantica* [17]*M. pomifera* [344, 346]**Caloxanthone A (182)***Carapia inophyllum* [173]**Gartanin (189)***Garcinia mangostana*

[20, 126, 228, 260, 275, 298]

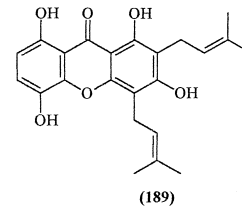
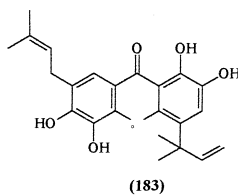
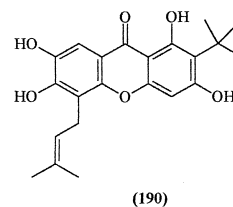
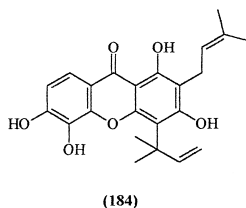
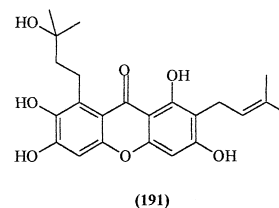
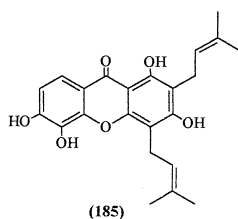
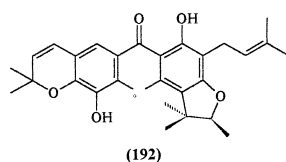
Morus insignis [144]**Subelliptenone B (183)***Garcinia subelliptica* [163]**Cudraxanthone L (190)***Cudrania tricuspidata* [140]**Gerontoxanthone I (184)***Cudrania cochinchinensis* [62]**Garcinone C (191)***Garcinia mangostana* [306]**Xanthone V_{1a} (185)***Vismia guineensis* [45]

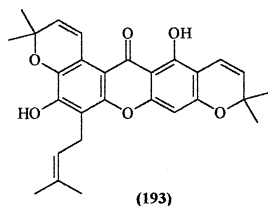
Table 5

Tri C₅ tetraoxygenated naturally occurring xanthenes

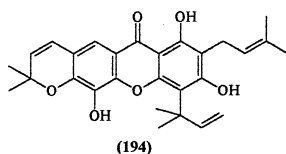
1,5-Dihydroxy-6,6-dimethylpyrano(2,3:6,7)-4'',4'',5''-trimethylfurano(2'',3'':3,4)-2-(3-methylbut-2-enyl)xanthone (192)
Garcinia opaca [118]



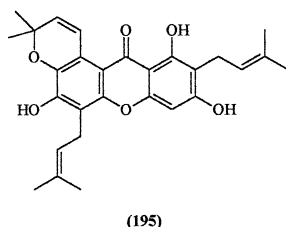
Tovophyllin B (193)
Tovomita macrophylla [269]
T. pyriformis [47, 245]



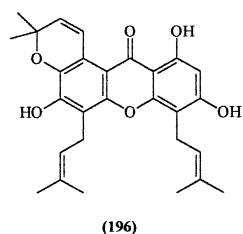
1,3,5-Trihydroxy-6,6-dimethylpyrano(2,3:6,7)-2-(3-methylbut-2-enyl)-4-(1,1-dimethylallyl)xanthone (194)
Garcinia opaca [118]



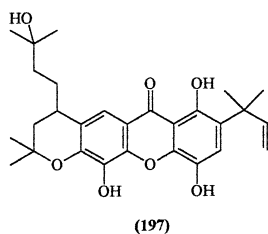
Tovophyllin A (195)
Cratoxylum cochinchinense [36]
Tovomita macrophylla [269]
T. pyriformis [47, 245]



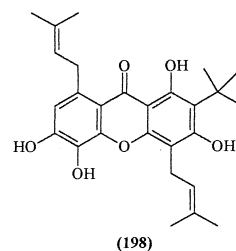
Pentadesmaxanthone (196)
Pentadesma butyracea [81]



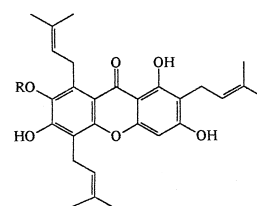
Subelliptenone E (197)
Garcinia subelliptica [168]



Nervosaxanthone (198)
Garcinia nervosa [12]



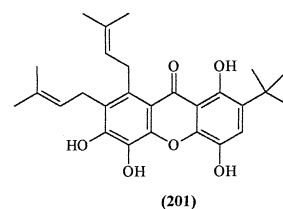
Garcinone E (199)
Garcinia mangostana
 [20, 92, 202, 260, 298]



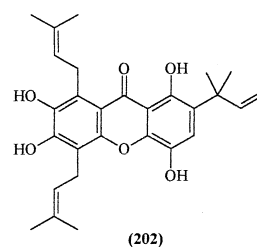
(199 R = H; 200 R = Me)

7-O-methylgarcinone (200)
Garcinia cowa [202]

Subelliptenone A (201)
Garcinia subelliptica [163, 248]



Dulciol B (202)
Garcinia dulcis [166]



Dulciol C (203)
Garcinia dulcis [166]

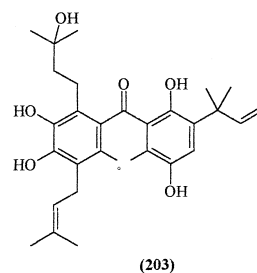
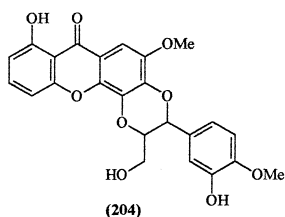


Table 6

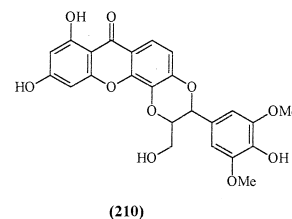
More complex tetraoxygenated naturally occurring xanthones

Cadensin A (204)

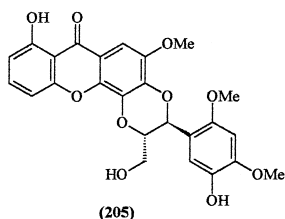
Caraipa densiflora [59]
C. grandifolia [104]
C. valloi [104]
Kielmeyera coriacea [59]
Vismia guaramirangae [132]

**Cadensin G (210)**

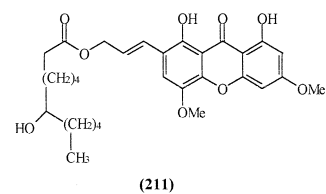
Psorospermum febrifugum [2]

**Cadensin-B (205)**

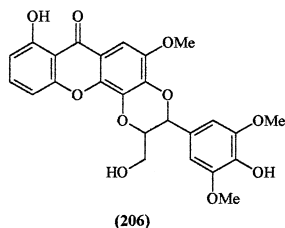
Caraipa densiflora [59]
Kielmeyera coriacea [59]
Vismia guaramirangae [132]

**Sapxanthone (211)**

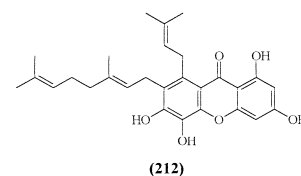
Saponaria vaccaria [193]

**Cadensin C (206)**

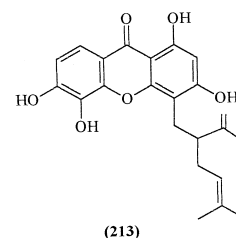
Vismia guaramirangae [132]

**Garciniaxanthone E (212)**

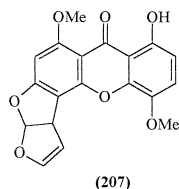
Garcinia subelliptica [248]

**Calycinoxanthone D (213)**

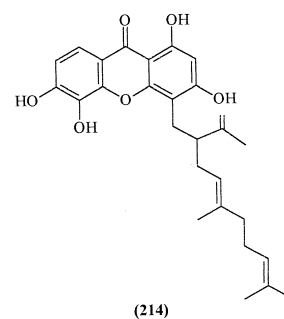
Hypericum roeperanum [290]

**5-Methoxysterigmatocystin (207)**

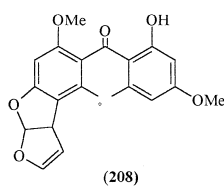
Aspergillus versicolor [151]

**Roeperanone (214)**

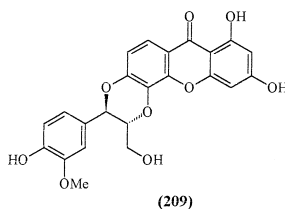
Hypericum roeperanum [290]

**6-Methoxysterigmatocystin (208)**

Aspergillus versicolor [49]

**5'-Demethoxycadensin G (209)**

Cratoxylum cochinchinense [310]

**5-O-Demethylpaxanthonin (215)**

Hypericum roeperanum [290]
H. patulum [175]

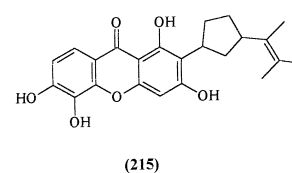


Table 6 (continued)

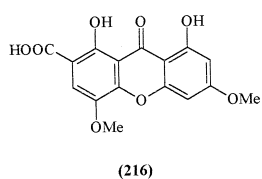
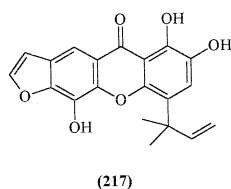
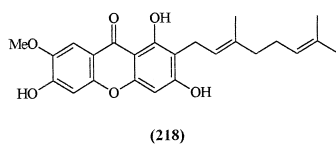
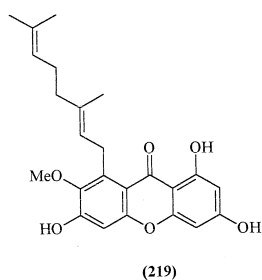
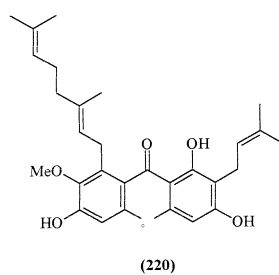
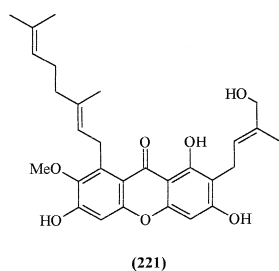
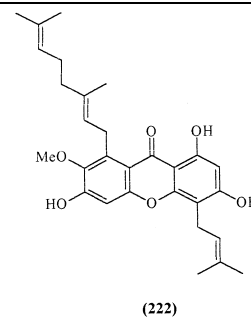
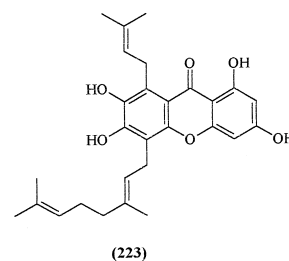
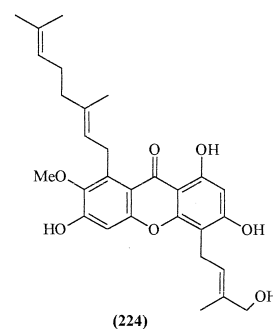
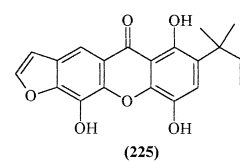
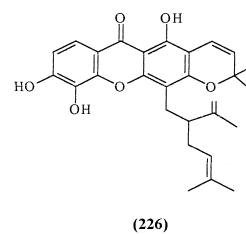
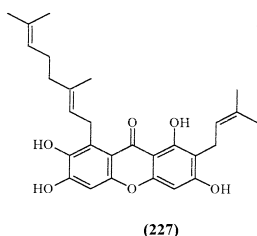
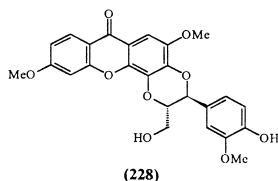
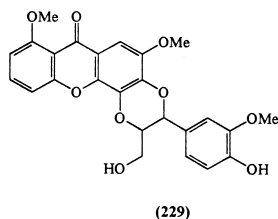
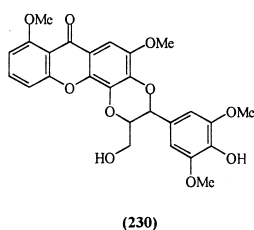
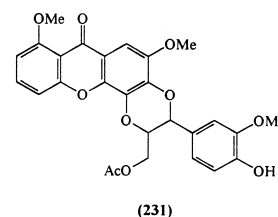
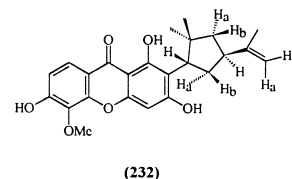
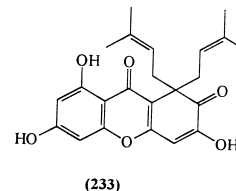
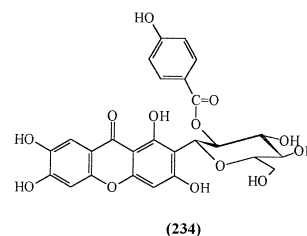
Vaccaxanthone (216)*Saponaria vaccaria* [192]**1,2,5-Trihydroxy-4-(1,1-dimethylallyl)-furano(2,3:6,7)xanthone (217)***Garcinia subelliptica* [162]**Cowaxanthone (218)***Garcinia cowa* [280]**Rubraxanthone (219)***Garcinia cowa* [211]*G. nervosa* [12]*G. pyrifera* [12]**Cowanin (220)***Garcinia cowa* [280]**Cowanol (221)***Garcinia cowa* [280]**Isocowanin (222)***Garcinia pyrifera* [12]**Dulciol A (223)***Garcinia dulcis* [166]**Isocowanol (224)***Garcinia pyrifera* [12]**Subelliptenone C (225)***Garcinia subelliptica* [162]*G. dulcis* [166]**Maculatoxanthone (226)***Hypericum maculatum* [14]

Table 6 (continued)

Norcowanin (227)*Garcinia cowa* [280]**6-Methoxykielcorin (228)***Hypericum reflexum* [53]**Isocadensin D (229)***Psorospermum febrifugum* [2]**Cadensin F (230)***Psorospermum febrifugum* [2]**Isocadensin D — monoacetate (231)***Psorospermum febrifugum* [2]**Paxanthonin (232)***Hypericum patulum* [176, 179]**1,2-Dihydro-3,6,8-trihydroxy-1,1-bis(3-methylbut-2-enyl)xanthen-2,9-dione (233)***Hypericum patulum* [178]**Muraxanthone (234)***Seneico mikanioides* [60]

xanthenes (Patolia and Trivedi, 1983), a new one-step method (Atkinson and Lewis, 1969) and a general study for synthesis of dioxygenated xanthenes are in a recent report by Lin et al. (1992).

The biosynthetic pathways to xanthenes have been discussed in recent years. Initially, these attempted to interrelate the observed oxygen pattern of natural xanthenes and correlate them with recognized oxygenation patterns. In general it seems that ring A and the attached CO group are provided by the shikimic acid pathway, whereas ring B arises via the acetate–malonate polyketide route (Locksley and Murray, 1970; Afzal and Al-Hassan, 1980; Sultanbawa, 1980). Therefore Locksley et al. (1967) reported the significance of maclurin in xanthone biosynthesis and the biogenetic-type synthesis of xanthenes from their benzophenone precursors (Locksley and Murray, 1970). Gottlieb (Gottlieb and Magalhães, 1966; Gottlieb, 1968; Gottlieb

et al., 1968) offered biogenetic proposals regarding xanthenes, and Bhanu et al. (1972) related the biogenetic implications in the conversion of 4-phenylcoumarins into xanthenes. More recently; biosynthetic studies on tajixanthone and shamixanthone (Ahmed et al., 1992) were reported.

Some xanthenes in lower plants have been proven to be totally acetate-derived, from seven acetate units (McMaster et al., 1960; Birch et al., 1976). However, the oxygenation patterns of all xanthenes in higher plants suggest that these are formed by a mixed shikimate–acetate pathway. This involves the condensation of shikimate and acetate-derived moieties to form benzophenones or benzophenone-like intermediates, which then react intramolecularly to form xanthenes. Mechanisms for this intramolecular reaction have been postulated involving either direct phenol oxidative coupling (Lewis, 1963), quinone addition (Ellis et al., 1967), dehydration

between hydroxyl groups on the acetate and shikimate-derived rings (Markham, 1965), or spirodienone formation and subsequent rearrangement to form the xanthone (Gottlieb, 1968; Carpenter et al., 1969).

Regarding lichen and fungi biosynthesis, it is important to say that many secondary metabolites found in lichen-forming fungi play a dominant role in the systematics of these organisms due to extensive morphological parallels and their clear ecological significance. Despite their common occurrence in a number of important genera, lichen xanthenes have not featured prominently in the repertoire of lichen taxonomists. Nevertheless, with the availability of more sensitive methods of detection and synthetic materials for comparison, these compounds have been effectively employed in recent systematic studies of lichens (Leuckert et al., 1990; Elix and Crook, 1992; Elix et al., 1992).

Elix and Crook (1992) reported the unambiguous total synthesis of 17 chlorine-containing derivatives of norlichexanthone, achieved using the condensation of an appropriately substituted methyl or ethyl orsellinate and phloroglucinol or 2-chlorophloroglucinol in the key step. Previously, Elix et al. (1992) reported the synthesis of several trioxxygenated lichen xanthenes (Elix et al., 1984).

8. Conclusion

The majority of xanthenes that have been isolated so far are of the tetraoxygenated-type. The main natural source of these xanthenes are plants from the Gentianaceae (14 genus, 72 species), Clusiaceae (23 genus, 84 species), Moraceae (4 genus, 8 species) and Polygalaceae (3 genus, 7 species) families. Other families of higher plants that produce tetraoxygenated xanthenes are Betulaceae, Caryophyllaceae, Gesneriaceae, Iridaceae, Loganiaceae, Lytracaceae and Polypodiaceae. Only three tetraoxygenated xanthenes have been identified as fungal and lichen metabolites: two in *Aspergillus versicolor* and one in *Diploschistes* sp. Therefore, tetraoxygenated xanthenes have no application in chemosystematics studies of these organisms.

Acknowledgements

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