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Review

Naturally Occurring Simple Oxygenated Benzophenones: Structural Diversity, Distribution, and Biological Properties

Teodor Marinov, Zlatina Kokanova-Nedialkova and Paraskev T. Nedialkov *

Pharmacognosy Department, Faculty of Pharmacy, Medical University of Sofia, 2 Dunav Str., 1000 Sofia, Bulgaria; 113625@students.mu-sofia.bg (T.M.); zlatina.kokanova@pharmfac.mu-sofia.bg (Z.K.-N.)
* Correspondence: pnedialkov@pharmfac.mu-sofia.bg; Tel.: +359-2-9236-529

Abstract: Naturally occurring benzophenones represent a relatively small group of plant metabolites with narrow distribution, mainly in members of Clusiaceae, Gentianaceae, Hypericaceae, Polygalaceae, Myrtaceae, etc.; however, there were reports of several compounds derived from microorganisms belonging to the Aspergillaceae and Valsaceae families and propolis. Benzophenones exhibit many biological activities, such as antioxidant, anti-inflammatory, cytotoxic, antimicrobial, etc. Few reviews on benzophenones that have appeared in the literature were focused on their prenylated derivatives. Summarized information on structural diversity, distribution, and biological activities of simple oxygenated naturally occurring benzophenones and their glycosides has not been found in the literature. Until 2000, only benzophenone C-glycosides were known to occur in nature. Since then, many O-glycosides have been isolated, structurally, and biologically characterized. This review covers the years from 1850 to 2023 and was compiled using databases such as Chemical Abstracts, Scopus, Google Scholar, PubMed, and ResearchGate. Based on their degree of oxidation, 210 chemical structures of benzophenone derivatives and glycosides were grouped into six categories. In addition, in one group of 40 miscellaneous benzophenones, where one or several protons are replaced by a methyl, alcohol, carboxyl, or acyl group, glycosidic forms with such an aglycone and dimeric compounds with xanthone was included. Simple oxygenated benzophenones and their glycosides were found in 77 plant genera belonging to 44 families. The allergy-associated bezophenone-1, benzophenone-2 and benzophenone-3 have limited distribution across natural sources. A wide range of biological activities (antioxidant, anti-inflammatory, cytotoxic, antitumor, cytoprotective, antimicrobial, MAO-A, antiarthritic, anticholinesterase, anti-atherosclerotic, laxative, etc.) of simple oxygenated benzophenones and their glycosides that appeared in the literature were discussed.

Keywords: simple oxygenated benzophenones; C-glycosides; O-glycosides; structural diversity; distribution; biological and pharmacological properties

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1. Introduction

Naturally occurring benzophenones are considered compounds derived from diphenylmethanone (Figure 1), in which one or several protons are replaced by hydroxyl, alkyl, alkyloxy groups, or halogen atoms. So far, unsubstituted benzophenone has been found in nature only in *Iris adriatica* [1] and *Hemidesmus indicus* [2].

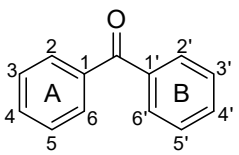

Figure 1. The structure of unsubstituted benzophenone.

Despite the large number of isolated compounds over the past 50 years, the few published reviews focused almost entirely on prenylated benzophenones [3–5]. Singh and

Bharate reviewed naturally occurring benzophenones with a phloroglucinol ring up to December 2005 [6]. Up to now, a systematic review of the existing naturally occurring simple oxygenated benzophenones and their glycosides has not been performed. This review compiles references from 1850 to 2023 using databases like Chemical Abstracts, Scopus, Google Scholar, PubMed, and ResearchGate. The main goal of this review is to summarize the available information on structural diversity of simple oxygenated benzophenones. A consensus classification of this group of compounds is also lacking. If the biogenesis of xanthones is considered, it can be seen that ring A and the attached CO group are produced by the shikimate pathway, while ring B is formed in the acetate–malonate pathway [7], yielding an oxygenated benzophenone intermediate, which subsequently undergoes molecular dehydration to give xanthone. Furthermore, it has been reported that the transformation can be accomplished from a benzophenone glycoside by elimination of the glycosidic moiety and subsequent dehydration [8]. Therefore, simple oxygenated benzophenones and their glycosides are precursors in the biogenesis of xanthones. Thus, the classification for the biosynthetically related xanthones provided by Mandal et al. [9] is used in this review. Special attention is given to benzophenone C- and O-glycosides. The second goal of this review is to summarize the published information on the distribution of simple oxygenated benzophenones and their glycosides. Some synthetic hydroxy and methoxy benzophenones are heavily used in sunscreens and in personal care cosmetic products and both associated with allergy and photoallergy [10]. This review tries to answer which of these compounds are found in natural sources. This review's third task is to summarize the biological properties of this class of naturally occurring compounds.

2. Structural Diversity of Simply Oxygenated Benzophenones

2.1. Monooxygenated Benzophenones

Only two naturally occurring benzophenones (Figure 2), which have a hydroxyl or methoxy group in *para* position to carbonyl function, were reported in the literature. *p*-Hydroxybenzophenone **1** was isolated from 1,2-dichloroethylene extract of *Talauma mexicana* (DC.) G.Don leaves [11] and *p*-methoxybenzophenone **2** was found as a component of the essential oil of *Costus speciosus* (J.Koenig) Sm. [12].

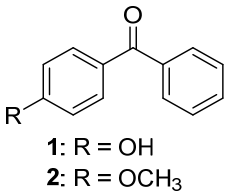

Figure 2. The structures of monooxygenated benzophenones.

2.2. Dioxygenated Bezophenones

The literature survey showed three compounds, **3**–**5** (Figure 3), isolated from the endophytic moss *Polytrichastrum formosum* (Hedw.) G.L. Smith [13], while **6** was found in *Pogonatum inflexum* (Lindb.) Sande Lac. [14]. The nitrogen-containing derivatives of 2,4-dihydrobenzophenone **7** and **8** were isolated from the ethanol extract of the moss *Polytrichum commune* Hedw. [15]. Compounds **9**–**11** were found in *Polytrichastrum formosum* [13,16] and compound **12** was detected in *Pogonatum inflexum* [14]. All of these compounds possess 2,4-dioxygenation pattern only in one of the phenyl rings. O-glycosidic forms of the deoxygenated benzophenones have not been discovered so far, but there was a report of a C-glycoside, namely hyperinone **13**, isolated from *Hypericum styphelioides* A.Rich. [17].

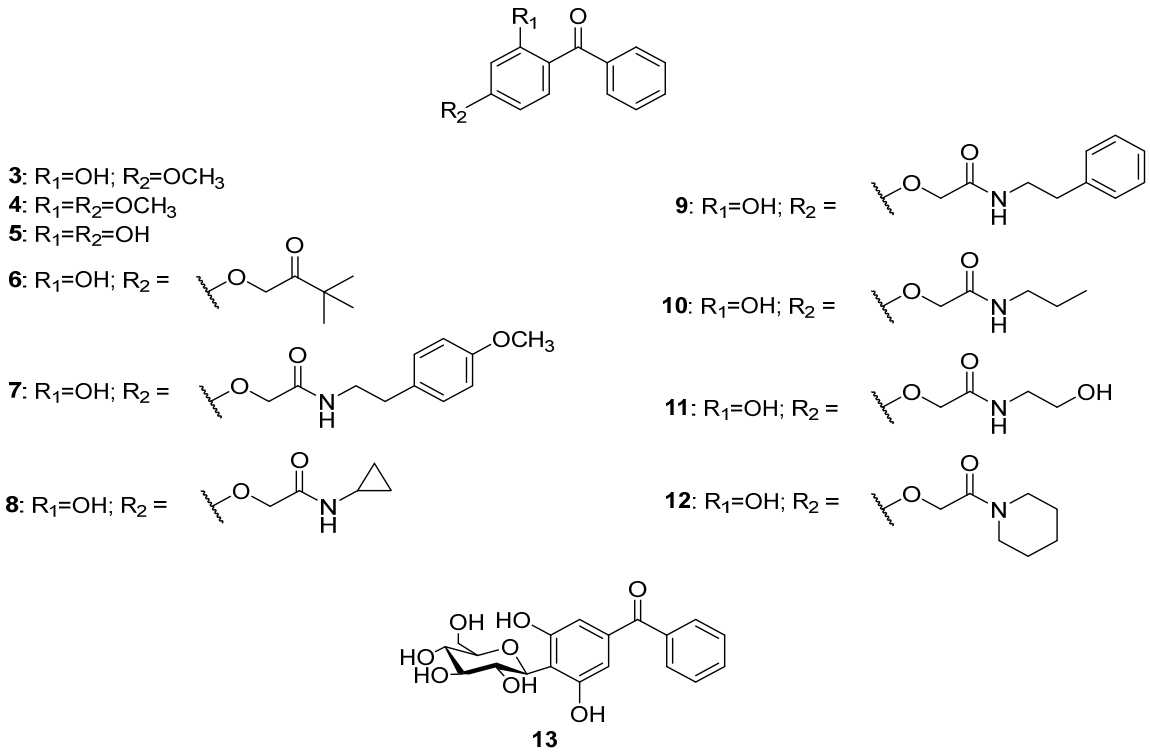

Figure 3. The structures of dioxygenated benzophenones.

2.3. Trioxygenated Bezophenones

The first reports of isolated trioxygenated simple benzophenones date from nearly a century and a half ago, when Jobst and Hesse began to study the composition of Coto and Paracoto barks. Although the origin of the two barks remains still unknown, it can be safely assumed that they belong to the Lauraceae family [18]. The first isolated compound was cotoin **14** (Figure 4), which was obtained from a diethyl ether extract of Coto bark [19,20]. Hydrocotoine **15** and methylhydrocotoine **16** were subsequently isolated from an alcoholic extract of Paracoto bark [20]. More than a decade later, thanks to the outstanding work of Ciamiciani and Silber, the structures of these compounds were finally established [21–24]. 2,4,6-Trihydroxybenzophenone **17** and 2,4-dihydroxy-6-methoxybenzophenone **18** were found to be major components in the methanol extract of leaves and stems of *Helichrysum triplinerve* DC. [25].

Most of the simply oxygenated naturally occurring benzophenones with 2,4,6-oxygenation patterns were alkyloxy derivatives. Sixteen compounds from this group have been reported to date, fourteen of which have been found in species of the genus *Hypericum*. The first alkyloxy benzophenone **19** was discovered in 1978 by Bohlmann and Suwita in the root of *Leontonyx squarrosus* DC and aerial parts of *L. spathulatus* Less. [26]. Eleven years later, four more compounds, **20**–**23**, belonging to this group were isolated from *Helichrysum asperum* (Thunb.) Hilliard and B.L.Burtt [27]. Phytochemical studies of the aerial parts of *Hypericum sampsonii* Hance led to the isolation of seven new compounds, **24**, **25** [28]; sampbenzophenones D-G (**26**–**29**) [29]; and **33** [30]. The compounds hyperinokone **30**, elegaphenone **31**, and hyperinagasone **32** were isolated from *H. nokoense* Ohwi [31], *H. elegans* Steph. ex Willd. [32] and *H. nagasawae* Hayata [33], respectively. In 1968, the isolation of a trioxygenated benzophenone cearoin **34** from extracts of *Dalbergia cearensis* Ducke and *D. miscolobium* Benth. was reported [34]. It was the first natural benzophenone with 2,4,5-trioxygenation pattern. In addition, two compounds with the same oxygenation pattern, **35** and **36**, were isolated from *D. odorifera* T. C. Chen [35] and *Securidaca longipedunculata* Fresen [36], respectively. Two benzophenones, **37** and **38**, possessing 2,3,4-trioxygenation patterns were isolated from *S. inappendiculata* Hassk [37]. In addition, compound **39** with

the same oxygenation was isolated from the dichloromethane extract of *S. diversifolia* (L.) Blake [38]. The only two trioxygenated benzophenones with oxygenation on both rings were **40** and **41** isolated from *Tolpis webbii* Sch. Bip. [39] and *Securidaca longepedunculata* Fresen. [36], respectively.

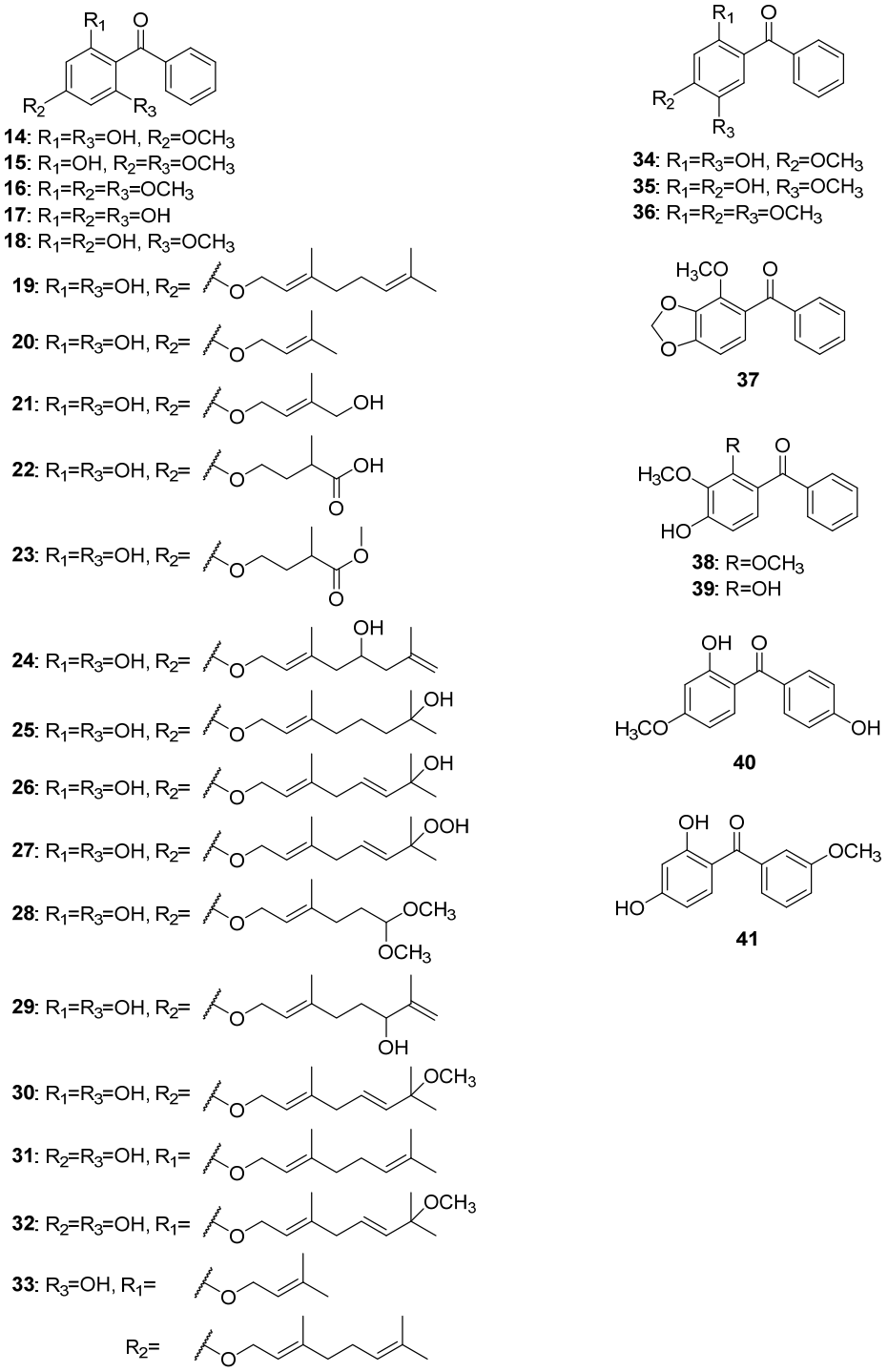

Figure 4. The structures of hydroxy, methoxy, and alkyloxy derivatives of trioxygenated benzophenones.

Fourteen glycosides of trioxygenated benzophenones (Figure 5) mostly sharing a common 2,4,6-trioxygenation pattern have been reported to date. The first tryoxygenated C-glycoside malaferin A **42** was isolated from an ethanolic extract of twigs and leaves of *Malania oleifera* Chun and S.K.Lee [40], while a di-C-glycoside arrilanin G **43** was obtained

from an ethanolic extract of the stem bark of *Polygala rillate* Buch.-Ham. ex D.Don [41]. 2,4,6-Trihydroxybenzophenone **17** was the most common aglycon of the O-glycosides of the of trioxygenated benzophenones. Garcimangosone D **44** was its first O-glycoside isolated from the ethanol extract of *Garcinia mangostana* L. fruits [42]. Furthermore, four 6-O-biosides of **17** including tricornoside A **46** (from *Polygala tricornis* Gagnep.) [43], pyrafortunoside B **47**, and C **48** (from *Pyracantha fortuneana* (Maxim.) H. Li) [44] as well as piperwallioside A **49** (from *Piper wallichii* (Miq.) Hand.-Mazz.) [45] were isolated from the respective species. Two 4-O-glycosides of **17** (**50** and **51**) were isolated from the ethanol extract of the *Psidium guajava* L. leaves [46,47]. The phytochemical investigations of *Polygala tenuifolia* Willd. led to the isolation of three O-glycosides of 2,4-dihydroxy-6-methoxybenzophenone **18**, namely tenuiside B **52** and C **45** [48] as well as the O-bioside tenuiphenone A **53** [49]. In addition, a O-bioside **54** of 4-hydroxy-2,6-dimethoxybenzophenone was found in *P. sibirica var. megalopha* Franch. [50]. An O-glycoside pruniflonone B **55** having an unusual aglycone (3,4,5-trihydroxybenzophenone) was isolated from the methanol extract of *Cratoxylum formosum* (Jack) Dyer roots [51].

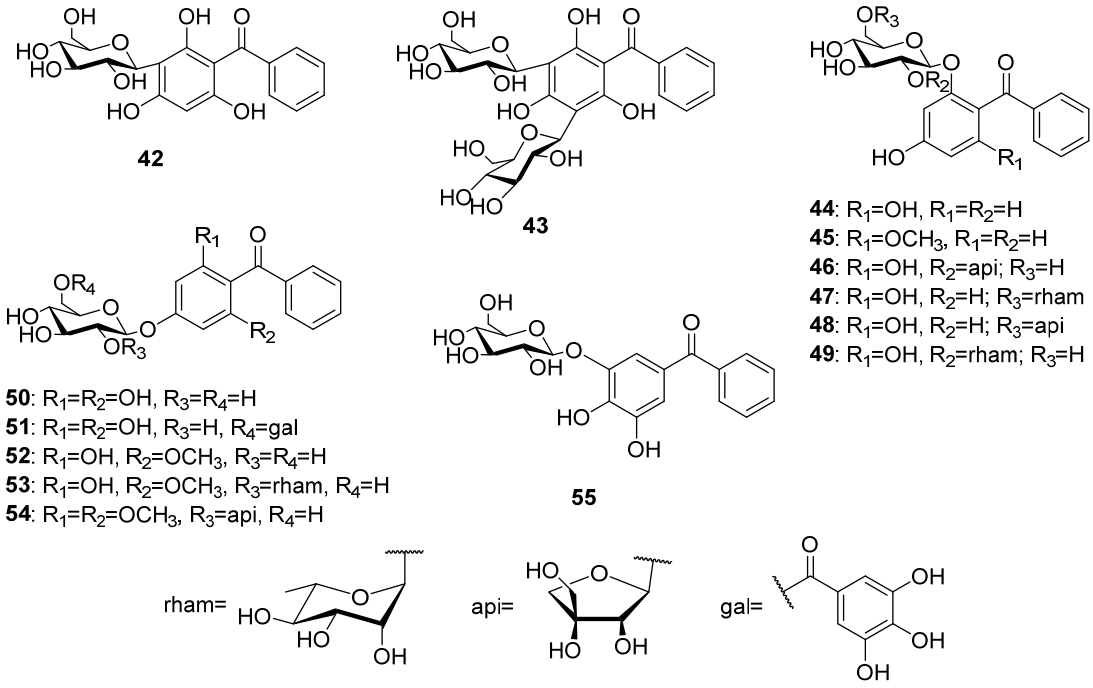

Figure 5. The structures of C- and O-glycosides of trioxygenated benzophenones.

2.4. Tetraoxygenated Bezophenones

This group includes eighteen hydroxy and methoxy tetraoxygenated benzophenones (Figure 6). Only three compounds (**56**–**58**) have substituents on ring A but not in B and share a common 2,3,4,5-tetraoxygenation pattern. Compounds **56** and **57** were isolated from the wood of *Machaerium scleroxylon* Tul. [52,53], while **58** was found in the roots of *Securidaca longipedunculata* [54]. Four compounds (**59**–**62**) share a common phloroglucinol oxygenation pattern in ring A and a monooxygenation in ring B. The first occurrence in nature of compounds **59**–**62** was reported for *Morus alba* L. [55], *Aniba duckei* Kosterm. [56], *Gentiana lutea* L. [57], and for *Allanblackia floribunda* Oliv. [58], respectively. Compounds **63**–**65** possess a rare 2,4,5-trioxynation pattern of ring A and structurally differ by the position of the hydroxyl group in ring B. The former two compounds, **64** and **65**, were isolated from the heartwood of *Dalbergia melanoxylon* Guill. and Perr. [59,60] while the latter **66** was found in *D. cochinchinensis* Pierre [61]. Compounds **66**–**69** shared a common pyrogallol-like ring A and monooxygenated ring B. These compounds were reported as the first to occur in biogenetically different plant species: **66** in *Securidaca diversifolia* [38]; **67** in *Anemarrhena asphodeloides* Bunge [62]; **68** in *Oroxylum indicum* (L.) (L.) Benth. ex Kurz [63];

and **69** in *Garcinia mangostana* [64]. Compounds **70**–**73** possess di-oxygenation on both rings and were found in *Garcinia cantleyana* Whit. var. *cantleyana* [65], *Hypericum lanceolatum* Lam. [66], *Garcinia eugenifolia* Wall. ex T. Anderson [67], and *Syzygium polyanthum* (Wight) Walp. [68], respectively.

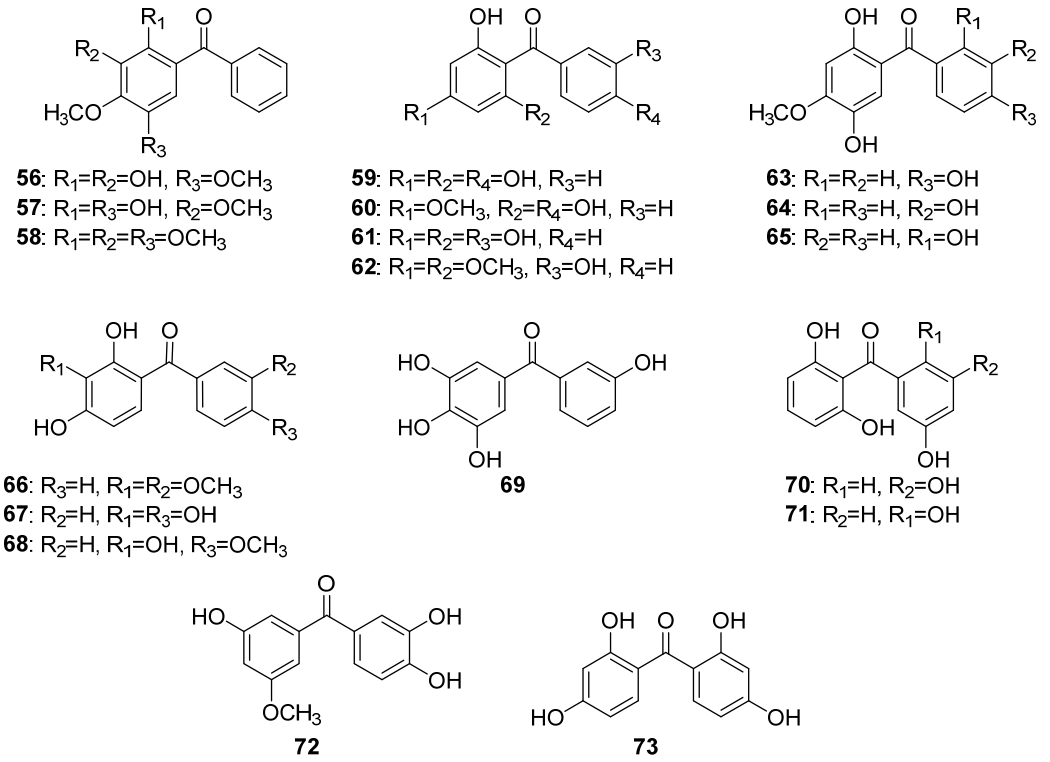

Figure 6. The structures of hydroxy and methoxy tetraoxygenated benzophenones.

To date, 24 C-glycosides of tetraoxygenated benzophenones (Figure 7) have been isolated from the plant sources. The aglycone of most of these compounds is iriflophenone **59**. The first occurrence of iriflofenone-3-C-β-D-glucoside **74** was reported for the leaf extracts of the ferns *Hypodematium fauriei* (Kodama) Tagawa and *H. crenatum* (Forssk.) Kuhn [69]. Two phytochemical studies on mango tree bark and leaves led to the isolation of the galloyl esters **75**–**77** [70,71] and one p-hydroxybenzoyl ester **78** [71] of **74**. Further galloyl and p-hydroxybenzoyl esters **79**–**84**, as well as an ester of 3,4-dihydroxy-5-methoxybenzoic acid **85**, were isolated from the ethanol extract of the leaves of *Mangifera indica* [72,73]. A mixed C,O-diglycoside **86** was isolated from water extract of aerial parts of *Cyclopia genistoides* (L.) R.Br. [74]. A di-C-glycoside **87** of iriflophenone **59** was isolated from the leaves extract of *Aquilaria sinensis* (Lour.) Spreng. [75]. Five C-glycosides **88**–**92** of 2,4′,6-trihydoxy-4-methoxybenzophenone **60** were found in leaves of *Mangifera indica* [72,73]. The only C-galactosyl benzophenone **93** known up to now was isolated from the leaves of the mango tree [76]. The only C-glycoside of 2,6,3′-trihydroxy-4-methoxybenzophenone rhodanthenone C **94** was isolated from a methanolic extract of the aerial parts of *Gentiana rhodantha* Franch. ex Hemsl. [77]. The di-C-glucosides **95** and **96** were isolated from *Polygala tenuifolia* [49] and *P. glomerata* Lour. (*P. chinensis* L.) [78], respectively. Di-C glucoside pseuduvarioside **97** was isolated from the leaves extract of *Pseuduvaria fragrans* Y.C.F.Su, Chaowasku and R.M.K.Saunders [79].

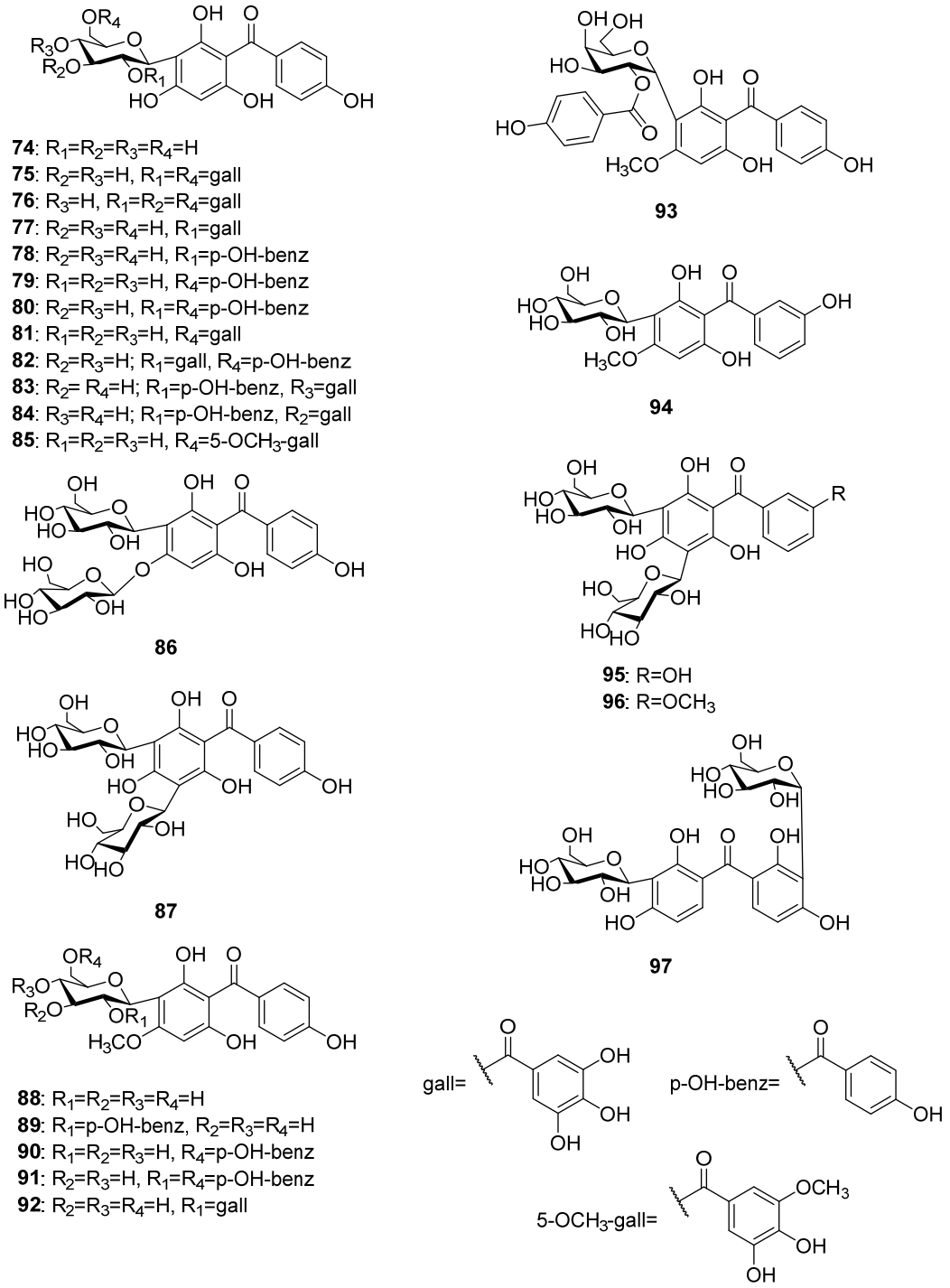

Figure 7. The structures of C-glycosides of tetraoxygenated benzophenones.

Some C-glycosyl tetraoxygenated benzophenones (Figure 8) form rare spirocyclic systems. The first compound from this group was aquilarinoside A **98**, which was isolated from hydroethanolic extract of *Aquilaria sinensis* leaves [80]. Compound **99**, similar to **98** but with β-configuration of fructofuranose, was isolated from hydroethanolic extract of mango tree leaves [76]. In addition, **100** and **101** were found in leaf extract from the later plant [81,82]. Compounds **102** and **103** were isolated from the later plant source differed from **99** and **101**, respectively, by the cyclization type of fructose unit [76].

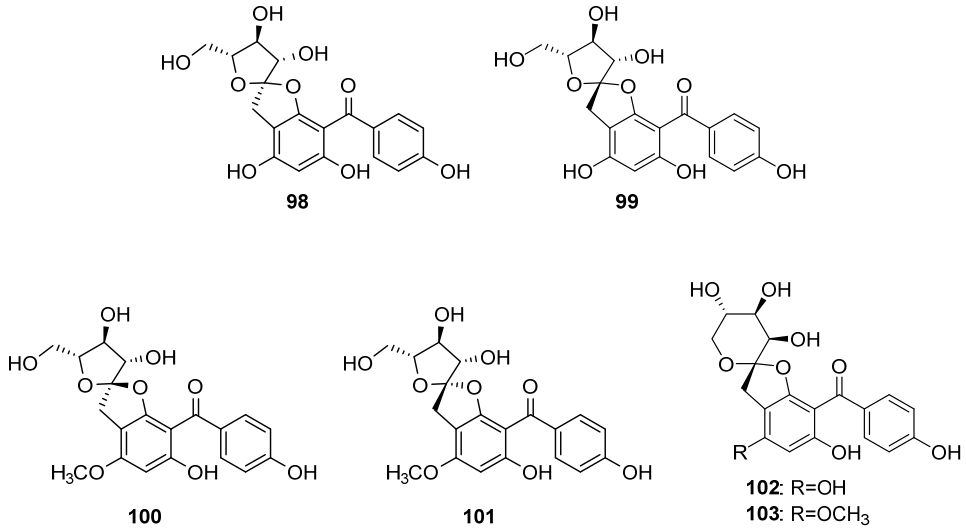

Figure 8. The structures of spirocyclic C-glycosides of tetraoxygenated benzophenones.

More than twenty O-glycosides of tetraoxygenated benzophenones (Figure 9) have been isolated, so far. Most of these compounds (**104**–**121**) share iriflophenone **59** as their aglycone. The first O-glycoside of iriflophenone **104** was isolated from *Coleogyne ramosissima* Torr. [83]. Three acylated derivatives, **105**–**107**, of **104** were found in the leaves of *Planchonella obovata* (R.Br.) Pierre [84]. Iriflophenone-2-O-α-L-rhamnoside **108** and its acylated derivatives **109**–**112** were reported for *Aquilaria sinensis* leaves and flower buds [75,85,86]. The methyl ester **113** of the later compound was isolated from the pericarps of *A. yunnanensis* S. C. Huang [87]. The presence of five biosides **114**–**118** of iriflophenone **59** in *A. sinensis* was established [85,88]. In addition, a 2-O-β-D-xylopyranoside **119** and a 2-O-α-L-arabinopyranoside **120** of **59** were reported for *A. sinensis* [86] and *Mangifera indica* [76], respectively. The only glycoside **121** with sugar connected to position 4 of iriflophenone was found in *Davallia solida* (G.Forst.) Sw. rhizomes [89]. Three compounds, **122**–**124**, possess 2,4′,6-trihydroxy-4-methoxybenzophenone **60** as aglycone. The former compound **122** was isolated from the aerial parts of *Gnidia involucrata* Steud. ex A.Rich. [90]. The latter two compounds **123** and **124** were reported for nut shell of *Phaleria macrocarpa* (Scheff.) Boerl. fruits [91] and for roots of *Vangueria agrestis* (Schweinf. ex Hiern) Lantz [92], respectively. Mahkoside A **125** was isolated from the ethanolic extract of *Phlaleria macrocarpa* pits [93]. The tetraoxygenated benzophenone **61** was an aglycone of three glycosides, **126**–**128**, that were isolated from *Gentiana rhodantha* Franch. ex Hemsl. [77], *G. verna* L. subsp. *pontica* (Soltok.) Hayek [94] and *Garcinia mangostana* fruit pericarp [95], respectively. The tetraoxygenated benzophenone O-glycosides **129**–**132** that possess unique aglycones were found in *Gentiana verna* subsp. *pontica* [94], *Tripterospermum japonicum* (Siebold and Zucc.) Maxim. [96], *Cratoxylum formosum* [97], and *Anemarrhena asphodeloides* [98], respectively.

2.5. Pentaoxygenated Benzophenones

More than 20 non-glycosylated (aglycones) naturally occurring pentaoxygenated benzophenones (Figure 10) representing seven oxygenation patterns have been reported, so far. Maclurin **133** was the firstly found pentaoxygenated benzophenone possessing 2,3′,4,4′,6-pentaoxygenation pattern. It was isolated in 1850 by Wagner from *Maclura tinctoria* (L.) Steud. [99,100] but its structure was finally established in 1895 by Ciamician and Silber [101]. Methoxy derivatives **134**–**138** of maclurin were found in *Garcinia subelliptica* Merr. [102], *G. multiflora* Champ. ex Benth. [103], *G. mangostana* [104], *G. livingstonei* T.Anderson [105], and *G. mangostana* [106], respectively. Compounds **139** and **140** were the only methylenedioxy-benzophenones with 2,3′,4,4′,6-pentaoxygenation pattern originally isolated from *Aniba pseudocoto* bark [20,22]. Compounds **141** and **142** were found in *Garcinia subelliptica* [107] and *G. smeathmannii* (Planch. and Triana) Oliv. [108], respectively, and

shared a common 2,2′,3′,4,6-pentaoxygenation pattern. Compounds **143**–**148**, possessing a common 2,3′,4,5′,6-pentaoxygenation pattern, were originally isolated from *G. pedunculata* Roxb. ex Buch.-Ham. [109], *G. mangostana* [106], *G. hombroniana* Pierre [110], *G. speciosa* Wall. [111], *Hypericum annulatum* Moris [8], and *H. sampsonii* [112], respectively. The rare compounds **149** and **150** share common ring A and differ in ring B; both were isolated from *Dalbergia melanoxylon* [59,113]. Compounds **151**–**153** possess a common 3,3′,4,5,5′-pentaoxygenation pattern. The former **151** and **152** were isolated from the twigs of *Garcinia cantleyana* var. *cantleyana* [65] while the later **153** was found in the pericarp of mangosteen (*G. mangostana*) [114]. The sole compound **154** with 2,3,3′,4,4′-pentaoxygenation pattern was isolated from the *Securidaca diversifolia* roots [38].

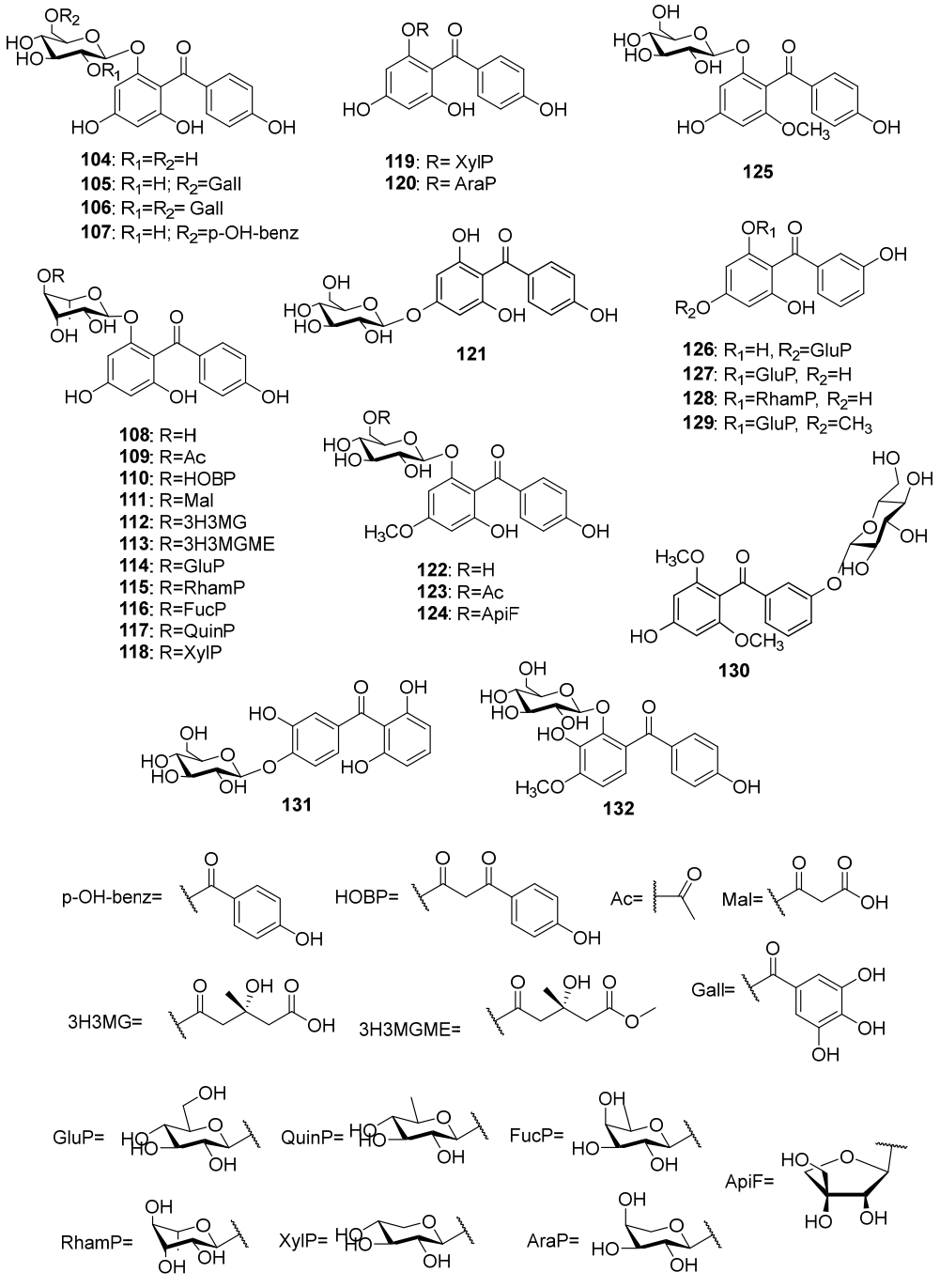

Figure 9. The structures of O-glycosides of tetraoxygenated benzophenones.

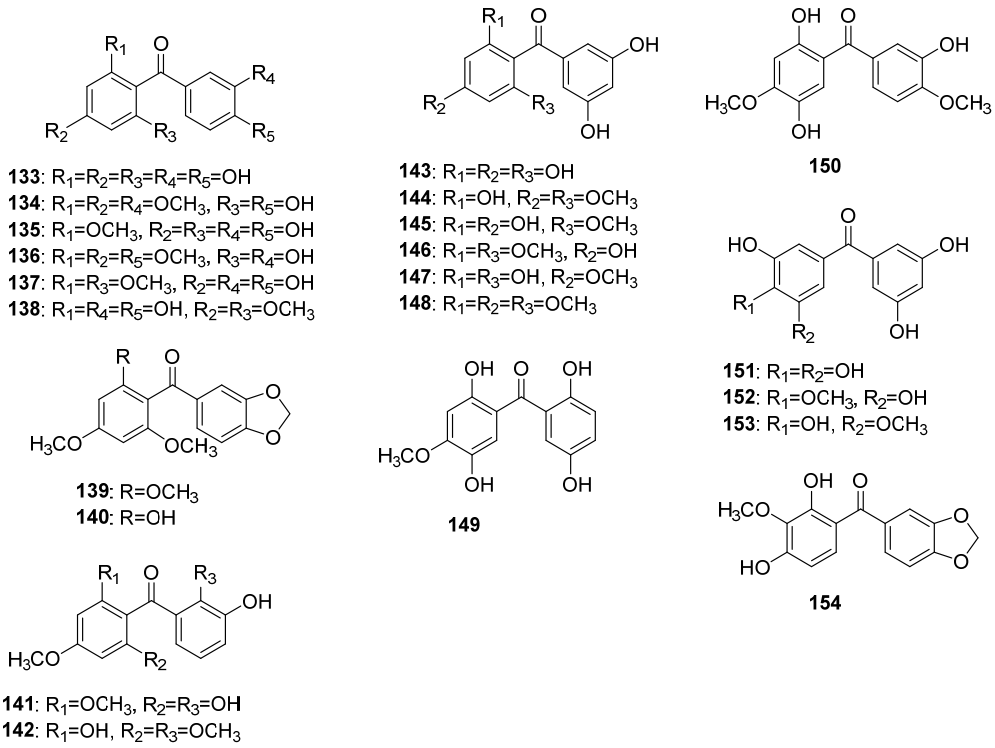

Figure 10. The structures of hydroxy and methoxy pentaoxygenated benzophenones.

More than fifteen C-glycosylated derivatives of the pentaoxygenated benzophenones (Figure 11) have been found in plants, so far. Most of these compounds possess a 2,3′,4,4′,6-pentaoxygenation pattern. The first report for naturally occurring C-glycosylated pentaoxygenated benzophenones dated from 1984 when Tanaka and coworkers isolated maclurin-3-C-β-D-glucoside **155** along with its galloyl and p-hydroxybenzoyl esters **156**–**159** from the *Mangifera indica* leaves [70]. Further galloyl esters **160** and **161** [71] as well as methoxy derivatives **162** [81] and **163** [72] of **155** were found in the same plant source. Additional methoxy derivatives **164**–**166** of **155** were isolated from the aerial parts of *Polygala telephioides* Willd. [115,116]. The only di-C-glycoside **167** and C,O-glycoside **168** of pentaoxygenated benzophenones were isolated from an ethanolic extract of *P. glomerata* [78]. Compound **169** is the only benzophenone C-glycoside with 2,3′,4′5′,6-pentaoxygenation pattern that was isolated from the aerial parts of *Hypericum humifusum* L. ssp. *austral* Rouy et Foue [117]. C-glycosyl benzophenones **170** and **171** share common ring A with 2,3,5,6-oxygenation patters and differ in the hydroxyl place in ring B. The former was isolated from *Gnidia involucrata* [90] while the later was found in *Polygala telephioides* [115].

Over 30 O-glycosides of pentaoxygenated benzophenones (Figure 12) have been reported to occur in plant species, so far. Contrary to C-glycosides, only six O-glycosides with 2,3′,4,4′,6-pentaoxygenation patterns **172**–**177** have been encountered. Maclurin-6-O-β-D-glucopyranoside **172** was simultaneously isolated from *Gentiana verna* subsp. *pontica* [94] and from *G. rhodantha* [77]. Compounds **173**, **174**, and **177** were isolated from *Dobinea delavayi* (Baill.) Baill. roots [118,119], while **175** and **176** were found in aerial parts of *Polygala tenuifolia* [48] and *Garcinia livingstonei* [105], respectively. The vast majority of O-glycosides (**178**–**205**) possess aglycones with 2,3′,4,5′,6-pentaoxygenation pattern and glycosylation at position 6(2), 4 or 3′(5′). The arabinofuranosides **178** and **179** were isolated from the aerial parts of *Hypericum annulatum* [120], while **180**–**183** were found in *H. thasium* Griseb. [121,122]. The 6(2)-O-rhamosides **187** and **188** were isolated from *H. elegans* [123] and *H. pseudopetiolatum* Keller, respectively. In addition, compounds **189**–**191** were also found in later species [124]. Further acylated rhamosides **192** and **193** of **143** were isolated from the aerial parts of *H. seniawinii* Maxim. [125]. The 6(2)-O-rhamnosides **194**–**196** of **145** were found in aerial parts of *H. wightianum* Wall. ex Wight et Arn. [126]. Only three

O-xylopyranosides **197**–**199** of penataoxygenated benzophenones were originally isolated from *H. thasium* [121], while only two O-arabinopyranosides **200** and **201** were found in *H. humifusum* [117]. Compounds **202** and **203** isolated from the later plant [117] possess glycosylation at position 4, while **204** and **205** were found in *H. sampsonii* [112] and *H. ellipticum* Hook. [127], respectively, the sugar was attached at position 5′(3′) position. The compounds **206** and **207** share rare 2,2′,4,5′,6-pentaoxygenation patterns that were isolated from *H. annulatum* [8] and *Garcinia mangostana* [128], respectively.

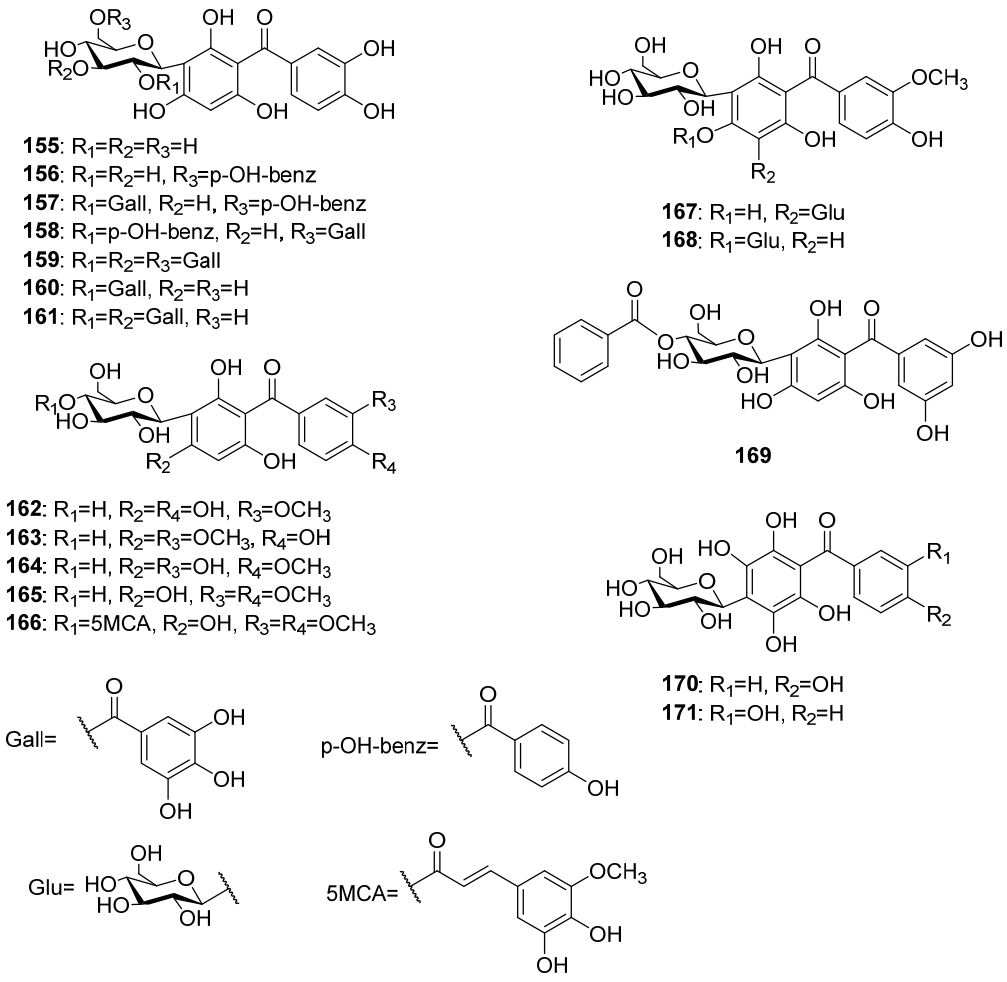

Figure 11. The structures of C-glycosides of pentaoxygenated benzophenones.

2.6. Hexaxygenated Benzophenones

Hexaxygenated benzophenones were rarely found in nature. To date, only three compounds, **208**–**210** (Figure 13), have been isolated from *Garcinia mangostana* [128,129].

2.7. Uncategorized and Miscellaneous Benzophenones

In addition to the compounds shown so far, there are data on benzophenone derivatives (Figure 14) in which one or several protons are replaced by a methyl, alcohol, carboxyl, or acyl group, and dimeric compounds with xanthone have also been found. Some glycosides of this class benzophenones have been detected, as well. The first records of this type of benzophenone appeared in 1963 when 6-hydroxy-2,4-dimethoxy-3-methylbenzophenone **211** and its isomer 2-hydroxy-4,6-dimethoxy-3-methylbenzophenone **212** were isolated from the essential oil of *Leptospermum luehmannii* F.M.Bailey [130]. Eighteen years later, bis(2-hydroxy-4,6-dimethoxy-3-methylphenyl)methanone **213** was found in a benzene extract of the wood of *Qualea lubouriauana* [131].

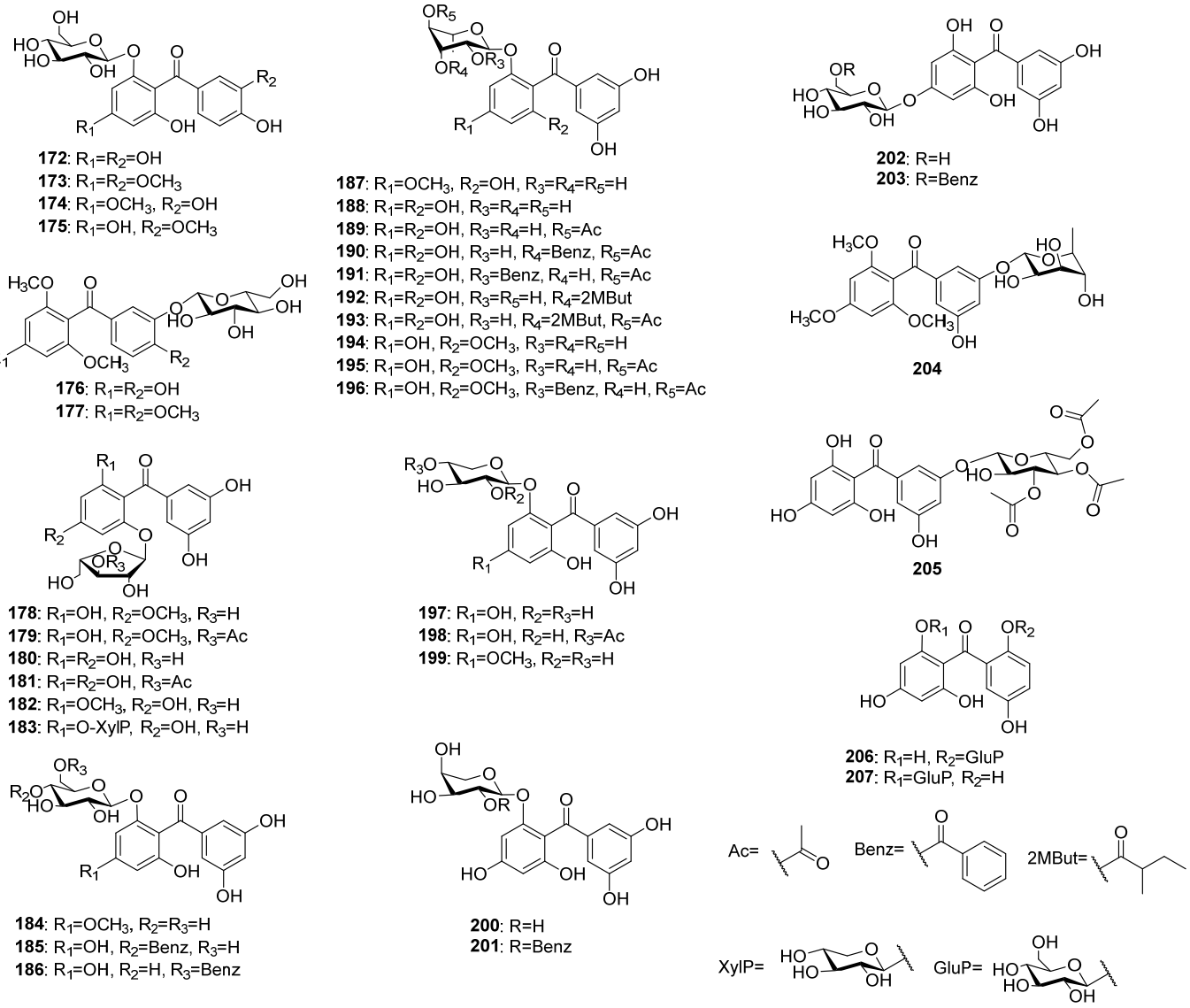

Figure 12. The structures of O-glycosides of pentaoxygenated benzophenones.

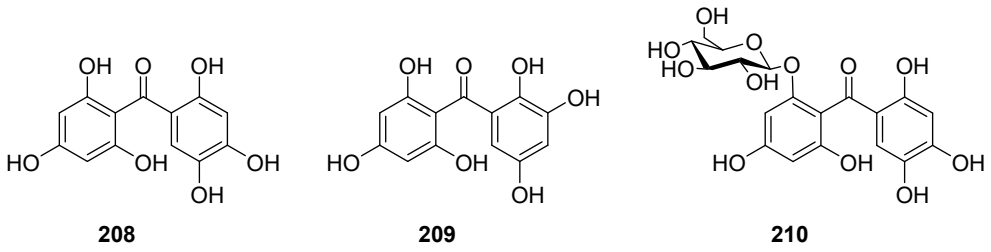

Figure 13. The structures of hexaoxygenated benzophenones.

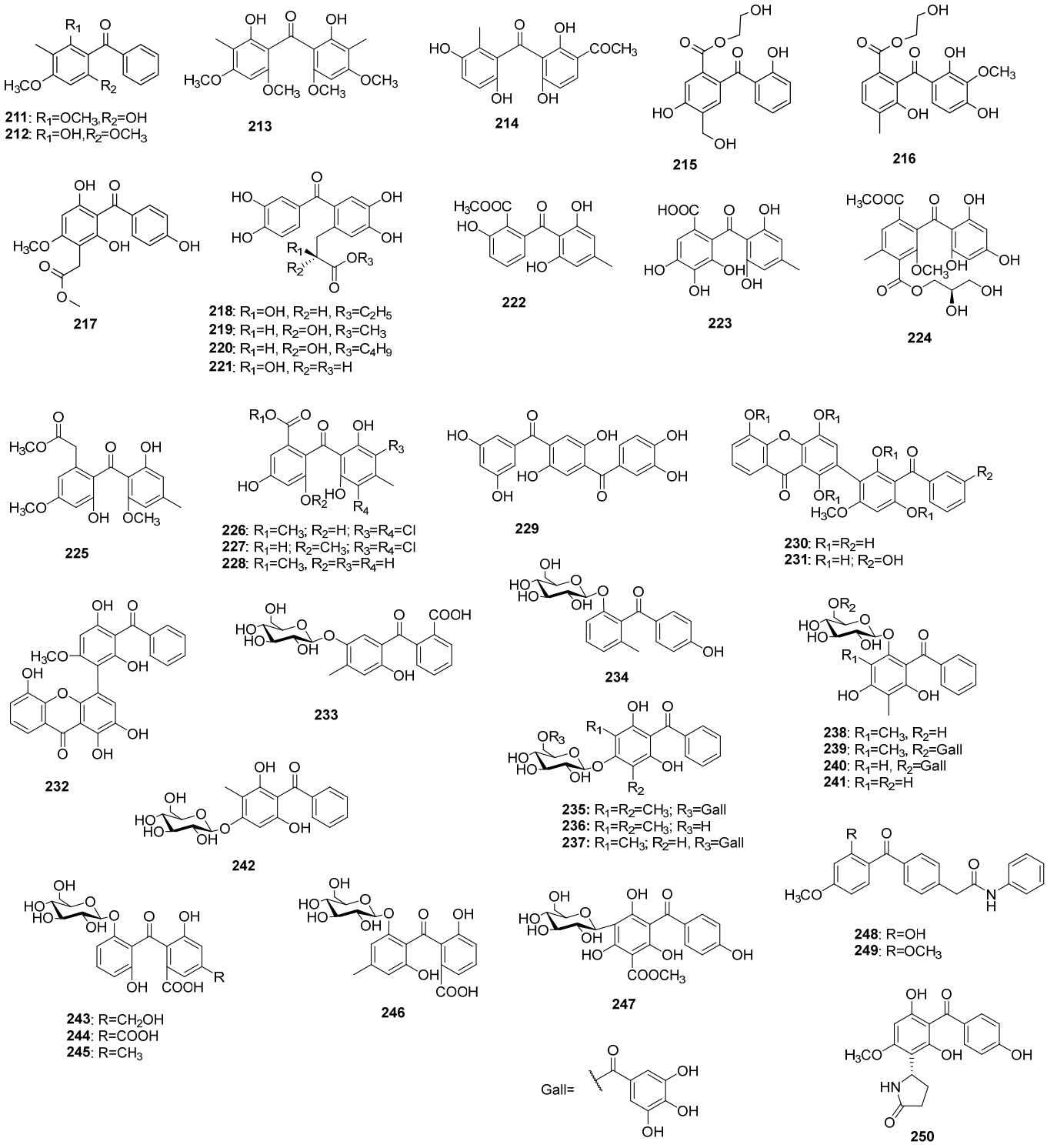

Figure 14. The structures of uncategorized and miscellaneous benzophenones.

For the first time, beishouwubenzophenone **214** was isolated from root tubers of *Cynanchum auriculatum* Royle ex Wight [132]. Morintrifolin A **215** and B **216** were obtained from hydromethanolic extract of *Morinda citrifolia* L. roots [133]. Compound **217** was found in an extract of the *Anemarrhena asphodeloides* roots [134]. The adducts of 3,3′,4,4′-trihydroxybenzophenone, and 2-hydroxypropionic acid **218**–**221** were isolated from *Ranunculus* ssp. The former three compounds were found in *R. ternatus* DC. [135,136], while the later was obtained from *R. muricatus* Moench [137]. The benzophenones **222**–**228**

have been isolated from fungi mostly belonging to *Ascomycota* group. Nidulalin B **222** was found in a dichloromethane extract of *Emericella nidulans* var. lata (Thom and Raper) Subram. [138], while cytosporaphenone A **223** was obtained from an ethyl acetate extract of *Cytospora rhizophorae* Kohlm. and E. Kohlm. [139]. Wentiphenone A **224** was discovered in the ethyl acetate extract of *Aspergillus wentii* Wehmer [140], while **225** was isolated from the fermentation broth of *A. fumigatus* Fresen. SWZ01 [141]. A halogenated benzophenone **226** was discovered in an extract of *A. flavipes* PJ03-11 [142], while **227** and **228** were found in *A. terreus* Thom [143] and *A. wentii* [144], respectively. Garcihombrianone **229**, which was found in the roots of *Garcinia hombroniana* Pierre [145], can be viewed as two benzophenone molecules sharing a common benzene nucleus. Three benzophenone-xanthone dimers **230**–**232** were isolated from roots of *G. dulcis* (Roxb.) Kurz [146]. Benzophenone O-glucosides **233** and **234** were found in *Mitracarpus villosus* (Sw.) DC. [147] and *Dobinea delavayi* [119]. Seven benzophenone O-glucosides **235**–**241**, some of which were galloyl esters, were isolated from the leaves or fruits of *Psidium guajava* [47,148–150], while **242** was found in *P. littorale* Raddi [151]. Compounds **243** and **244** were isolated from *Cassia senna* var. *angustifolia* L. [152], while **245** and **246** were found in *C. abbreviata* Oliv. [153]. The only C-glycoside **247** of this class of miscellaneous benzophenones was isolated from *Aquilaria sinensis* [154]. Two N-containing benzophenones **248** and **249** were found in the moss *Pogonatum spinulosum* Mitt. [155], while **250** was detected in *Anemarrhena asphodeloides* [62].

3. Distribution of Naturally Occurring Simply Oxygenated Benzophenones

The distribution of the benzophenones from Figures 2–14 is provided in Table 1. Up to now, simple oxygenated benzophenones and their glycosides have been established in 77 plant genera distributed in 44 families, from which the family Corallinaceae belong to the division Rhodophyta; the family Polytrichaceae to division Bryophyta; the families Davalliaceae, Dryopteridaceae, and Hypodematiaceae to the division Polypodiophyta; and 36 families from the division Magnoliophyta. The simply oxygenated benzophenones are isolated from various plant organs, mainly from aerial parts, leaves, roots, rhizomes, barks, and wood of angiosperms. They are less commonly found in stems, twigs, flowers, and fruits of angiosperms; the thallus of mosses and leaves; and rhizomes of ferns. There are only a few cases in which the compound from this group is obtained using essential oils or a thallus of algae. Of all 250 reported compounds, the largest number of representatives 51 were isolated from the Hypericaceae family, followed by 43 representatives from Anacardiaceae, 36 from Clusiaceae, 24 from Polygalaceae, 22 from Thymelaeaceae, and 18 from Fabaceae. In addition, there are data on the isolation of one compound from Nepalese propolis and seven from microorganisms belonging to the Aspergillaceae and Valsaceae families.

Table 1. Distribution of naturally occurring simply oxygenated benzophenones.

Family	Species	Compounds
	Division Rhodophyta	
Corallinaceae	*Jania rubens* (L.) J.V. Lamouroux	**159**^{T} [156]
	Division Bryophyta	
Polytrichaceae	*Polytrichum commune* Hedw.	**7**, **8**^{T} [15]
	Polytrichastrum formosum (Hedw.) G.L. Smith	**3**, **4**, **5**, **11**^{T} [13], **9**, **10**^{T} [16]
	Pogonatum inflexum (Lindb.) Sande Lac.	**6**, **12**^{T} [14]
	P. spinulosum Mitt.	**248**, **249**^{T} [155]
	Division Polypodiophyta	
Davalliaceae	*Davallia solida* (G. Forst.) Sw.	**121**^{RH} [89]
Dryopteridaceae	*Dryopteris ramosa* (C.Hope) C.Chr.	**74**^{L} [157]
Hypodematiaceae	*Hypodematium fauriei* (Kodama) Tagawa	**74**^{L} [69]
	Hypodematium crenatium (Forssk.) Kuhn.	**74**^{L} [69]

Table 1. *Cont.*

Family	Species	Compounds
	Division Magnoliophyta	
Anacardiaceae	*Dobinea delavayi* (Baill.) Baill.	**121**, **174**, **177**, **234**^{R} [119], **134**, **173**^{R} [118]
	Mangifera indica L.	**59**, **93**, **103**, **102**, **99**^{L} [76], **60**, **104**, **120**, **98**, **162**^{L} [81], **74**$^{P, B, L}$, **77**$^{B, L}$, **78**$^{B, L}$, **160**$^{P, B}$, **161**^{P} [71], **75**, **155**, **156**, **157**, **158**, **159**^{L} [70], **88**, **89**, **90**, **163**, **79**, **80**, **81**^{L} [72], **91**, **92**, **82**, **83**, **84**, **85**^{L} [73], **122**^{L} [158], **100** [81], **101**^{L} [82]
Annonaceae	*Huberantha jenkinsii* (Hook.f. and Thomson) Chaowasku	**74**, **87**^{L} [159]
	Polyalthia cerasoides (Roxb.) Bedd. (*Huberantha cerasoides* (Roxb.) Chaowasku)	**74**, **104**^{TW} [160]
	Pseuduvaria fragrans Y. C. F. Su, Chaowasku and R. M. K. Saunders	**97**^{L} [79]
Apocynaceae	*Cynanchum auriculatum* Royle ex Wight (*Vincetoxicum auriculatum* (Royle ex Wight) Kuntze)	**214**ND [132]
	Cynanchum bungee Decne.	**214**^{R} [161]
	C. otophyllum C. K. Schneid	**214**^{RH} [162]
Asparagaceae	*Anemarrhena asphodeloides* Bunge	**59**, **132**^{RH} [89], **60** ^{RH} [163], **67**, **250**^{RH} [62], **74**, **104**, **122**, **125**^{RH} [164], **217** ^{RH} [134]
Asphodelaceae	*Aloe vera* Burm. f.	**34**^{L} [165]
Asteraceae	*Helichrysum asperum* (Thunb.) Hilliard and B.L.Burtt	**20**, **21**, **22**, **23**^{AP} [27]
	H. triplinerve DC.	**17**, **18**, **19**^{AP} [25]
	Leontonyx spathulatus Less. (Thunb.) (*Helichrysum litorale* Bolus)	**19**^{R} [26]
	Tolpis webbii Sch. Bip	**40**^{AP} [39]
	Tolpis sp.	**40**^{AP} [39]
Bignoniaceae	*Oroxylum indicum* (L.) Benth. ex Kurz	**68**^{S} [63]
Campanulaceae	*Codonopsis pilosula* Franch.	**34**^{R} [166]
Cistaceae	*Fumana montana* Pomel. (*Fumana ericoides* subsp. *montana* (Pomel) Maire)	**104**^{WP} [167]
Clusiaceae	*Allanblackia floribunda* Oliv.	**15**, **62**^{W} [58]
	Garcinia assigu Lauterb.	**133**^{B} [168]
	G. cantleyana Whitm. var. *cantleyana* Whitm.	**69**, **70**, **151**, **152**^{TW} [65]
	G. dulcis (Roxb.) Kurz	**230**, **231**, **232**^{R} [146]
	G. eugenifolia Wall. ex T.Anderson	**69**, **72**^{R} [67]
	G. hombroniana Pierre	**61**, **135**^{B} [169], **145**^{B} [110], **229**^{R} [145]
	G. livingstonei T. Anderson	**135**, **137**, **176**$^{W, TW}$ [105]
	G. mackeaniana Craib	**137**^{L} [170]
	G. mangostana L.	**44**^{F} [42], **61**, **144**, **138**^{R} [106], **69**, **143**^{F} [64], **127**^{F} [171], **128**^{F} [95], **133**^{W} [172], **135**, **153**,^{F} [114], **136**^{B} [104], **145**^{B} [173], **172**^{F} [114,174], **207**, **209**^{F} [128], **208**, **210**^{F} [129]
	G. multiflora Champ. ex Benth.	**61**, **133**, **135**^{S} [103]
	G. pedunculata Roxb. ex Buch.-Ham.	**143**^{W} [109]
	G. porrecta Laness.	**146**^{B} [175]
	G. preussii Engl.	**44**^{L} [176]
	G. smeathmannii (Planch. and Triana) Oliv.	**142**^{B} [108]
	G. speciosa Wall.	**143**, **135**, **137**, **145**, **146**^{S} [111]
	G. subelliptica Merr.	**134**^{W} [102], **141**^{W} [107]
	G. virgata Vieill. ex Guillaumin	**14**^{B} [177]
	G. xanthochymus Hook. f. ex T. Anderson	**133**^{F} [178]
	Symphonia globulifera L. f.	**133**^{W} [179]
	Tovomita longifolia (Rich.) Hochr.	**19**^{L} [180]
Combretaceae	*Laguncularia racemosa* (L.) C. F. Gaertn.	**133**^{B} [181]

Table 1. *Cont.*

Family	Species	Compounds
Costaceae	*Costus speciosus* (J. Konig) Sm. (*Cheilocostus speciosus* (J. Konig) C. Specht = *Hellenia speciosa* (J. Koenig) S.R.Dutta)	**2**^{EO} [12]
Crassulaceae	*Sedum aizoon* L.	**59**, **104**ND [182]
Datiscaceae	*Datisca cannabina* L.	**34**^{WP} [183]
Diospyraceae (Ebenaceae)	*Diospyros kaki* Thunb.	**44**^{L} [184]
Fabaceae (Leguminosae)	*Acacia catechu* (L.) Willd. (*A. catechuoides* (Roxb.) Benth. = *Senegalia catechu* (L.f.) P. J. H. Hurter and Mabb.)	**133**^{W} [185]
	A. catechuoides (Roxb.) Benth. (*A. catechu* (L.) Willd. = *Senegalia catechu* (L.f.) P. J. H. Hurter and Mabb.)	**133**^{W} [185]
	A. sundra (Roxb.) DC. (*Senegalia chundra* (Roxb. ex Rottler) Maslin)	**133**^{W} [185]
	Calliandra umbellifera Benth.	**104**ND [186]
	Cassia abbreviata Oliv.	**245**, **246**^{B} [153]
	C. senna var. *angustifolia* L. (*Senna alexandrina* Mill. = *C. angustifolia* M. Vahl)	**243**, **244**^{F} [152]
	Cyclopia genistoides (L.) Vent.	**74**, **155**$^{S, L}$ [187], **86**$^{S, L}$ [65], **104**^{WP} [188]
	C. pubescens Eckl. and Zeyh.	**86**, **155**$^{S, L}$ [189]
	C. subternata Vogel (*Cyclopia falcata* (Harv.) Kies)	**74**^{WP} [190]
	Dalbergia cearensis Ducke	**34**^{W} [34], **57**^{W} [191]
	D. cochinchinensis Pierre ex Laness.	**65**^{S} [61]
	D. congesta Graham ex Wight. and Arn.	**34**^{R} [192]
	D. cultrata Graham ex Benth.	**34**^{B} [193]
	D. latifolia Roxb.	**34**^{W} [194]
	D. melanoxylon Guill. and Perr.	**34**, **63**, **150**^{W} [59], **64**, **149**^{W} [113]
	D. miscolobium Benth. (*D. violacea* (Vogel) Malme)	**34**^{W} [34], **57**^{W} [191]
	D. odorifera T. Chen	**34**^{W} [195], **35**^{W} [35], **65**^{W} [196]
	D. parviflora Roxb.	**34**^{W} [197]
	D. sissoo Roxb.	**34**^{W} [198]
	D. volubilis Roxb.	**34**^{W} [199]
	Machaerium scleroxylon Tul.	**56**^{W} [52], **57**^{W} [53]
	Pterocarpus santalinus L. f.	**34**^{W} [200], **150**^{W} [201]
Gentianaceae	*Centaurium erythraea* Rafin.	**61**^{CC} [202]
	Gentiana lutea L.	**61**^{RH} [57]
	G. rhodantha Franch. ex Hemsl.	**94**, **126**, **172**^{WP} [77]
	G. verna L. subsp. *pontica* (Soltok.) Hayek	**127**, **129**, **172**^{AP} [94]
	Swertia chirayita (Roxb. ex Fleming) H. Karst.	**59**, **133**^{WP} [203]
	Tripterospermum japonicum (Sieb. and Zucc.) Maxim. (*Tripterospermum trinervium* (Thunb.) H.Ohashi and H.Nakai)	**130**^{AP} [96]
Hypericaceae	*Cratoxylum formosum* Benth. and Hook. f. ex Dyer	**55**^{L} [44], **131**^{S} [97]
	Hypericum androsaemum L.	**17**, **61**^{CC} [204]
	H. annulatum Moris	**147**, **206**^{AP} [8], **178**, **179**^{AP} [120], **184**^{AP} [205]
	H. beanii N. Robson	**44**^{AP} [206]
	H. densiflorum Pursh	**31**^{AP} [207]
	H. elatoides R. Celler	**44**, **241**^{AP} [208]
	H. elegans Stephan ex Willd.	**184**, **187**, **206**^{AP} [123], **31**^{AP} [32]
	H. ellipticum Hook.	**205**^{AP} [127]
	H. humifusum L.	**169**, **202**, **203**, **200**, **201**^{AP} [117]
	H. pseudopetiolatum var. *kiusianum* (Y. Kimura) Y. Kimura (*H. kiusianum* Koidz.)	**188**, **189**, **190**, **191**^{AP} [124]

Table 1. *Cont.*

Family	Species	Compounds
	H. lanceolatum Lam.	**71**$^{L, B}$ [66]
	H. maculatum Crantz	**147**, **178**, **179**^{AP} [209]
	H. nagasawae Hayata	**32**^{AP} [33]
	H. nokoense Ohwi	**19**, **30**^{AP} [31]
	H. przewalskii Maxim.	**71**, **19**^{WP} [210], **185**, **186**^{AP} [211]
	H. sampsonii Hance	**44**^{WP} [212], **148**, **188**, **204**^{AP} [112], **19**, **26**, **27**, **28**, **29**^{AP} [29], **24**, **25**^{WP} [28], **33**^{AP} [30]
	H. seniawinii Maxim.	**192**, **193**$^{\mathbf{AP}}$ [125]
	H. styphelioides A. Rich	**13**^{L} [17]
	H. thasium Griseb.	**44**, **197**, **198**, **199**, **181**^{AP} [121], **180**, **182**, **183**^{AP} [122]
	H. wightianum Wall. ex Wight. and Arn.	**194**, **195**, **196**^{WP} [126]
Iridaceae	*Belamcanda chinensis* (L.) DC. (*Iris domestica* (L.) Goldblatt and Mabb.)	**59**^{RH} [213], **104**, **122**^{RH} [214]
	Iris adriatica Trin. ex Mitić	**60**^{RH} [1]
	I. dichotoma Pall.	**104**, **122**^{RH} [214]
	I. florentiana L.	**59**^{RH} [215]
	I. germanica L.	**59**ND [216]
	I. humilis Georgi	**59**, **60**^{RH} [217]
	I. lactea Pall.	**59**$^{RH, L}$, **60**^{RH} [218]
	I. pallida Lam.	**60**^{RH} [219]
	I. pumila L.	**59**, **60**$^{RH, AP}$ [217]
	I. potaninii Maxim.	**59**^{AP} [220]
	I. scariosa Willd. ex Link	**59**^{RH} [221]
	I. tectorum Maxim.	**104**, **122**^{RH} [214]
	I. variegata L.	**59**, **60**$^{RH, AP, FL}$ [217]
Lamiaceae	*Salvia miltiorrhiza* Bunge	**108**^{R} [222]
Lauraceae	*Aniba duckei* Kosterm. (*Aniba rosodora* Ducke)	**14**^{W} [223], **60**^{W} [56]
	Coto (unidentified sp.)	**14**^{B} [19,20]
	Lindera fruticosa Hemsl. (*L. neesiana* (Wall. ex Nees) Kurz)	**37**^{R} [224], **38**^{R} [225]
	Nectandra coto Rusby	**14**, **15**, **16**, **139**, **140**^{B} [226]
	Paracoto (unidentified sp.)	**15**, **16**, **139**^{B} [20], **140**^{B} [22]
Malvaceae	*Cola nitida* Schott and Endl.	**34**^{F} [227]
Magnoliaceae	*Talauma mexicana* (DC.) G. Don (*Magnolia mexicana* DC.)	**1**^{L} [11]
Moraceae	*Morus tinctoria* L. (*Maclura tinctoria* (L.) Steud. = *Chlorophora tinctoria* (L.) Benth.)	**133**^{W} [99]
	Morus alba L.	**59**, **133**^{W} [55]
Myrtaceae	*Eucalyptus hemiphloia* Roxb.	**133**ND [228]
	E. maideni F. Muell.	**44**^{BR} [229]
	Leptospermum luehmannii F. M. Bailey	**211**, **212**^{L} [130]
	Myrtus communis L.	**34**^{AP} [230]
	Psidium guajava L.	**44**^{L} [150], **50**^{L} [46], **51**, **235**^{L} [47], **104**^{L} [231], **236**, **237**^{F} [148], **238**, **239**, **240**^{L} [149], **241**^{L} [150,232]
	P. littorale Raddi (*P. cattleyanum* Sabine)	**50**, **237**, **242**^{L} [151]
	Syzygium polyanthum (Wight) Walp.	**34**, **73**, **133**^{L} [68]
Olacaceae	*Malania oleifera* Chun and S. K. Lee	**42**, **44**^{TW} [40]
Paeoniaceae	*Paeonia* x *suffruticosa* Andrews	**104**^{R} [233]
Passifloraceae	*Passiflora tripartita* (Juss.) Poir.	**237**^{F} [234]
Piperaceae	*Piper wallichii* (Miq.) Hand.-Mazz.	**49**^{S} [45]
Polygalaceae	*Polygala arillata* Bush.-Ham. ex D. Don	**43**^{B} [41]
	P. arvensis Willd.	**44**$^{S, L, R}$ [235]
	P. glomerata Lour. (*Polygala chinensis* L.)	**43**, **95**, **96**, **167**, **168**^{WP} [78]
	P. tricornis Gagnep. (*Polygala karensium* Kurz)	**44**, **46**^{R} [43]
	P. sibirica L.	**175**^{R} [236]
	P. sibirica L. var. *megalopha* Franch.	**54**^{WP} [50]

Table 1. *Cont.*

Family	Species	Compounds
	P. telephioides Willd.	**44**, **166**^{WP} [116], **164**, **165**, **171**^{WP} [115]
	P. tenuifolia Willd.	**45**, **52**, **175**^{AP} [48], **53**, **95**^{B} [49]
	Securidaca diversifolia (L.) S. F. Blake	**39**, **66**, **154**^{R} [38],
	S. inappendiculata Hassk.	**37**, **38**^{R} [37]
	S. longipedunculata Fresen.	**37**^{RB} [237], **36**, **38**, **39**, **41**^{R} [36], **58**^{R} [54]
Ranunculaceae	*Ranunculus muricatus* L.	**221**^{AP} [137]
	R. ternatus Thunb.	**218**^{R} [135], **219**, **220**^{R} [136]
Rhamnaceae	*Frangula purshiana* (DC.) A. Gray ex J. G. Cooper	**16**^{B} [238]
Rosaceae	*Coleogyne ramosissima* Torr	**104**^{AP} [83]
	Pyracantha fortuneana (Maxim.) H. L. Li	**44**, **47**, **48**^{F} [44]
Rubiaceae	*Coffea arabica* L.	**74**^{L} [239]
	Mitracarpus villosus (Sw.) DC. (*Mitracarpus hirtus* (L.) DC.)	**233**^{L} [147]
	Morinda citrifolia L.	**215**, **216**^{R} [133]
	Vangueria agrestis (Schweinf. ex Hiern) Lantz.	**122**, **124**^{R} [92]
Sapindaceae	*Litchi sinensis* Sonn.	**44**^{F} [240]
Sapotaceae	*Planchonella obovata* (R.Br.) Pierre.	**104**, **105**, **106**, **107**^{L} [84]
Theaceae	*Camellia sinensis* (L.) Kuntze (*Thea sinensis* L.)	**44**ND [241]
Thymelaeaceae	*Aquilaria crassna* Pierre ex Lecomte	**74**, **87**, **108**^{L} [242]
	A. sinensis (Lour.) Gilg	**59**, **98**^{L} [80], **74**, **114**^{L} [88], **87**, **108**^{L} [75], **104**, **247**^{S} [154], **115**, **116**, **117**, **118**, **109**^{L} [85], **110**, **111**, **112**, **119**^{FB} [86]
	A. malaccensis Lam.	**74**, **108**, **109**^{L} [243]
	A. yunnanensis S.C.Huang	**104**, **108**, **109**, **113**^{F} [87]
	Gnidia involucrata Steud. ex A.Rich.	**122**, **170**^{AP} [90]
	Phaleria macrocarpa (Scheff.) Boerl.	**60**^{L} [244], **122**$^{L, F}$ [245,246], **125**^{F} [247], **123**^{F} [91]
	P. nisidai Kanehira	**108**^{L} [248]
Vochysiaceae	*Qualea lubouriauana* Paula	**213**^{W} [131]
	Division Ascomycetes	
Aspergillaceae	*Aspergillus flavipes* (Bainier and Sartory) Thom and Church	**226**, **227**, **228** [142]
	Aspergillus fumigatus Fresen.	**225** [141]
	Thom	**227** [143]
	Aspergillus wentii Wehmer	**224** [140], **228** [144]
	Emericella nidulans var. *lata* (Thom and Raper) Subram. (*Aspergillus latus* (Thom and Raper) A.J.Chen, Frisvad and Samson)	**222** [138]
Valsaceae	*Cytospora rhizophorae* Kohlm. and E. Kohlm.	**223** [139]
	Other sources	
	Nepalese Propolis	**34** [249]

^{L} leaves; ^{EO} essential oil; ^{T} talus; ^{RH} rhizomes; ^{R} roots; ^{P} peels; ^{B} bark; ^{TW} twigs; ND not detected; ^{AP} aerial parts; ^{WP} whole plant; ^{S} stem; ^{W} wood; ^{F} fruit; ^{CC} cultured cells; ^{FL} flower; ^{RB} root bark; ^{BR} branches; ^{FB} flower buds

It should also be noted that the least numerous groups of simply oxygenated benzophenones are those with mono- and hexaoxygenation. The former group includes only two representatives isolated from *Talauma mexicana* (Magnoliaceae) and *Costus speciosus* (Costaceae), while the later consists of three representatives obtained from *Garcinia mangostana* (Clusiaceae). Dioxygenated benzophenones number 11 compounds, one of which was isolated from *Hypericum styphelioides* (Hypericaceae), while the remaining 10 were found in mosses from Polytrichaceae. Trioxygenated benzophenones comprise 42 compounds detected in species of Clusiaceae (1 compound), Olacaceae (1), Piperaceae (1), Fabaceae (2), Rosaceae (2), Myrtaceae (2), Lauraceae (3), Asteraceae (8), Hypericaceae (11), and Polygalaceae (11). The most numerous groups are those of pentaoxygenated and tetraoxygenated benzophenones. The former group consists of 75 representatives found in members of Gentianaceae (1), Moraceae (1), Thymelaeaceae (1), Lauraceae (2), Fabaceae

(2), Polygalaceae (8), Anacardiaceae (12), Clusiaceae (16), and Hypericaceae (32) while the latter include 77 compounds isolated from species of Annonaceae (1), Rosaceae (1), Davalliaceae (1), Rubiaceae (1), Myrtaceae (1), Bignoniaceae (1), Lauraceae (1), Moraceae (1), Hypodematiaceae (2), Asparagaceae (2), Hypericaceae (2), Sapotaceae (3), Polygalaceae (4), Clusiaceae (5), Gentianaceae (5), Fabaceae (6), Thymelaeaceae (17), and Anacardiaceae (23).

The allergy-associated benzophenones **3** (bezophenone-3 or BP-3), **5** (benzophenone-1 or BP-1), and **73** (benzophenone-2 or BP-2) [10] have limited distribution across natural sources. The former two compounds were found only in *Polytrichastrum formosum* while the later was detected only in *Syzygium polyanthum*. The origin of these compounds is uncertain: whether they are a result of biosynthesis or environmental pollution.

4. Biological Properties of Naturally Occurring Simply Oxygenated Benzophenones

Biological and pharmacological studies on simple oxidized benzophenones and their glycosides have established various activities, among which the most prominent are antioxidant, anti-inflammatory, cytotoxic, and antimicrobial. Additionally, their influence on α-glucosidase, fatty acid, and triglyceride metabolism has also been reported. Up to the beginning of 2023, 250 compounds have been isolated or detected, of which *ca* 150 have been pharmacologically tested, which is 60% of all.

4.1. Antioxidant Activities

4.1.1. DPPH Radical Scavenging Activity

The results of in vitro radical scavenging activity assays using 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical showed moderate to strong activity for **31** [205,209,250], **55** [51], **61** [169], **133** [103], **137** [51,105], **145** [169], **147**, **206** [205,209,250], **208**, and **210** [129]. Low or very low radical-scavenging activity was found for **44** [176], **59** [76], **78**, **79** [81], **87** [251], **93** [76], **98**, **120** [81], **142** [108], **162**, **163** [81], **176** [105], **178**, **179**, **184** [205,209,250], **225** [141], **238**, and **241** [232].

4.1.2. ABTS Radical Scavenging Activity

The radical scavenging activity of the benzophenones was confirmed in vitro using 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) ($ABTS^{\bullet+}$) radical cation-based assays. The tested compounds possessed moderate to strong radical scavenging activities. Compound **13** showed moderate activity (1.93 mM TE) compared to the activity of the reference antioxidant compounds quercetin (3.33 mM TE) and rutin (2.78 mM TE) [17]. Annulatophenone **147** (91.7%) and its O-glycosides annulatophenonoside **178** (93.35%) and acetylannulatophenonoside **179** (85.9%) possessed significantly strong ABTS radical scavenging activity, which is comparable to that of ascorbic acid (96.2%) [209]. The results of another study showed that neoannulatophenonoside **184** (IC_{50} = 0.25 μM) showed the highest ABTS activity, while hypericophenonoside **206** (IC_{50} = 41.52 μM), elegaphenonoside **187** (IC_{50} = 87.17 μM), and elegaphenone **31** (IC_{50} = 379.85 μM) possessed moderate to lower activity compared to hyperoside (IC_{50} = 6.61 μM) and BHT (IC_{50} = 0.08 μM) [250]. Moreover, compounds **145** (IC_{50} = 4.92 μM), **135** (IC_{50} = 4.60 μM), and **61** (IC_{50} = 9.9 μM) displayed higher inhibition of $ABTS^{\bullet+}$ than Trolox (IC_{50} = 10.9 μM) [169]. The results showed that iriflophenone-3-C-glucoside **74** (1.04 μM TE) scavenged $ABTS^{\bullet+}$ radicals [252], while **142** (IC_{50} > 100 μg/mL) possessed lower activity [108]. Additionally, guavinoside D **241** (IC_{50} = 29.27 μg/mL) and guavinoside E **238** (IC_{50} = 32.97 μg/mL) displayed moderate activity compared to vitamin C (IC_{50} = 8.53 μg/mL) [232].

4.1.3. FRAP (Ferric Reducing Antioxidant Power) Assay

FRAP activities of compounds annulatophenonoside **178**, acetylannulatophenonoside **179**, annulatophenone **147** (0.1 mM) were compared to BHT and Vit C at the same concentration. In contrast to both glycosides, only their aglycone **147** possessed moderate activity (6.9 mM TE) [209]. Furthermore, compound **31** displayed (942.16 μM TE) stronger FRAP activity compared to the control hyperoside (421.75 μM TE) [250]. Addi-

tionally, iriflophenone 3-C-β-D-glucoside **74** (1.2 mmol Fe^{2+}/g) and iriflophenone-3,5-C-β-D-diglucoside **87** (0.2 mmol Fe^{2+}/g) showed lower FRAP activity as compared to Trolox (8.0 mmol Fe^{2+}/g) [251].

4.1.4. Inhibition of Lipid Peroxidation

The inhibition of lipid peroxidation of compounds (0.1 mM) compounds **31**, **206**, **184**, and **187** were determined in a linoleic acid system using the ferric thiocyanate (FTC) method. Only neoannulatophenonoside **184** inhibited the oxidation of linoleic acid for five days. All tested benzophenones demonstrated lower antioxidant activity compared to BHT [250]. The antioxidant activity 4-geranyloxy-2,6-dihydroxybenzophenone **19** (70%) was assessed by monitoring the fluorescence decay of Fe^{2+}-induced oxidation of a model liposome system [207], while compound **205** exhibited 61% inhibition of Fe^{2+}-induced lipid peroxidation by using large unilamellar vesicles (LUVs) [127]. Additionally, **151** inhibited the copper-mediated oxidation of LDL (low-density lipoprotein) with IC_{50} = 3.6 μM, which was comparable to that of the positive control probucol (0.6 μM) [65].

4.2. Antiallergic Activity

In the mast cell degranulation experiment, cearoin **34** displayed significant inhibitory effects on the release of β-glucuronidase (IC_{50} = 17.9 μM) and histamine (IC_{50} = 16.3 μM) from rat mast cells compared to the positive control mepacrine (IC_{50} = 22.3 μM for β-glucuronidase and IC_{50} = 14.7 μM for histamine). The results suggested that **34** could be a promising antiallergic agent [253].

4.3. Immunosuppressive Activity

Compounds **100** and **101** estimated a good inhibition of concanavalin A-induced spleen cell proliferation in a concentration-dependent manner (10 to 40 μM). At a concentration of 40 μM, **100** (31.92% ± 3.84) and **101** (31.67% ± 3.43) had a similar immunosuppressive activity lower than the activity of positive control dexamethasone (56.99% ± 4.22) at the same concentration [82].

4.4. Anti-Inflammatory Activity

Rat neutrophil degranulation showed the significant inhibitory ability of cearoin **34** on the release of β-glucuronidase and lysozyme with IC_{50} values of 7.9 μM and 11.7 μM, respectively, compared to a positive control of trifluoperazine (IC_{50} = 16.9 μM for β-glucuronidase and 12.8 μM for lysozyme) [253]. Moreover, **34** showed significant concentration-dependent inhibition of NO (nitric oxide) production in lipopolysaccharide (LSP)-activated macrophage-like J774.1 cells with better IC_{50} = 15.4 μM value than the positive control NG- monomethyl-L-arginine (L-NMMA) (IC_{50} = 27.1 μM) [249]. The anti-inflammatory activities were also investigated by measuring NO production in LSP-induced RAW 264.7 cells. The results showed that **50** (10 μmol/L) [46], **34** (IC_{50} = 11.7 μM) [254], **148** (IC_{50} = 2.40 μM), **204** (IC_{50} = 2.29 μM), **188** (IC_{50} = 2.00 μM) compared to the positive control cadamonin (IC_{50} = 1.41 μM) [112], and **44** (IC_{50} = 17.23 μM, compared to indomethacin IC_{50} = 15.20 μM) [255] possessed significant inhibitory activity against NO production. Additionally, the results showed that iriflophenone-2-O-α-L-rhamnoside **108** were able to reduce significantly NO production in RAW 264.7 cells stimulated by LPS/IFN-ɣ at low concentration (6.25 μg/mL) [243] and possessed IC_{50} = 19.22 μM in LPS-treated RAW 264.7 cells [222]. Some of the tested benzophenones showed moderate NO inhibitory activities on LSP-induced RAW 264.7 macrophage cells such as hydrocotoin **15** with an inhibition rate of 38.12% [256] and compounds **60**, **78**, **79**, **88**, **98**, **120**, **122**, **162**, at concentrations of 50 and 100 μM [81]. Additionally, low NO inhibitory activities on LSP induced RAW 264.7 macrophage cells displayed benzophenones aquilarinenside E **109** (200 μg/mL), **74** (10, 25 and 200 μg/mL) [243,251], **19** (IC_{50} = 23.41 μM), **33** (IC_{50} = 6.23 μM) [30], **30** (IC_{50} = 30.05 μM) [31], **32** (IC_{50} = 26.14 μM) [33], **192**, **193** (IC_{50} > 20 μM) [125], **93** (IC_{50} > 100 μM), **59** (IC_{50} = 58.72 μM) [76], **95** (16.97%) [256], and

113 (IC_{50} = 95.4 μM) [87]. The anti-neuroinflammatory activity of **186** was evaluated by determining its ability to inhibit the production of NO in LPS-activated BV-2 microglial cells. The results showed that **186** displayed significant anti-neuroinflammatory activity (IC_{50} = 0.61 μM) [211]. Garcimangosone D **44** also exhibited high anti-inflammatory activities in LPS-stimulated BV-2 microglial cells (IC_{50} = 14.52 μM) and LPS-stimulated THP-1 macrophage cells (IC_{50} = 19.14 μM) compared to indomethacin (IC_{50} = 17.64 μM and IC_{50} = 19.37 μM), respectively [255]. Furthermore, iriflophenone **59** (IC_{50} = 52.59 μM) and aquilarinoside A **98** (IC_{50} = 89.92 μM) showed significant inhibitory activity against neutrophil respiratory burst stimulated by PMA [80], while hydrocotoin **15** (IC_{50} = 11.03 μM) showed strong inhibitory effects on PGE2 production in RAW 264.7 macrophage cells [256]. In addition, the cyclooxygenase assay of **31** estimated a 13% inhibition of the COX-1 enzyme and 48% for COX-2 at a concentration of 25 μg/mL [207].

4.5. Estrogenic Activity

Compounds **108** (IC_{50} = 630 μM) and 59 (IC_{50} = 700 μM) showed significant binding abilities to the estrogen receptor (ERα) at 1 mM concentration compared to positive control of 17β-estradiol (IC_{50} = 18 nM). Furthermore, **108** and **59** exhibited 80% and 68% inhibition, respectively, of labeled estradiol binding to Erα at 1 mM [248].

4.6. Cytotoxic and Antitumor Activities

4.6.1. Cytotoxicity on Human Cancer Cell Lines

Cytotoxicity assays performed on cell lines HD-MY-Z (Hodgkin's lymphoma), K-562 (chronic myeloid leukemia), KE-37 (T-cell leukemia), CCRF-CEM (acute lymphoblastic leukemia), HL-60 (myeloid leukemia), and Raji cells (non-Hodgkin's lymphoma) showed significant antiproliferative activity of elegaphenone **31** with IC_{50} values of 15.9 μM (HD-MY-Z), 13.9 μM (K-562), 16.9 μM (KE-37) [32], and **108** with IC_{50} = 8.9 μM (HL-60) [222]. Furthermore, hyperinagazone **32** exhibited IC_{50} = 29.05 μM on CCRF-CEM [33], hyperinokone **30** showed IC_{50} = 36.44, while **19** had IC_{50} = 27.04 [31]. In addition, a short-term in vitro assay with 12-O-tetradecanoylphorbol-13-acetate (TPA)-induced Epstein–Barr virus early antigen (EBV-EA) activation in Raji cells showed a significant inhibitory effect of maclurin **133**, compared to a positive control of the strong antitumor promoter glycyrrhetic acid (enoxolone) [168]. Assay performed on the MCF-7 cell line (breast adenocarcinoma) showed significant cytotoxicity of **19** with an IC_{50} value of 4.8 μg/mL [180]. Very low cytotoxicity on the MCF-7 cell line showed benzophenones **15** (IC_{50} > 200 μM) [119], **145** (inhibition < 10% at 20 μM) [169], **146** (IC_{50} = 119.3 μg/mL) [175], sampbenzophenones D–G **26**–**29** (IC_{50} > 40 μM) [29], **7** (IC_{50} > 100 μM), **8** (IC_{50} > 100 μM) [15], **172** (IC_{50} > 100 μM), **127** (IC_{50} > 100 μM), **143** (IC_{50} > 100 μM), and 44 (IC_{50} > 100 μM) [257]. Weak cytotoxicity against MDA-MB-231 cells was reported for garcimangosone D **44** (IC_{50} = 67.20 ± 1.19 μM) [255], hyperprzeone A **19** (IC_{50} = 123.87 μM), and **71** (IC_{50} > 200μM) [210]. Another study showed that **135** (ED_{50} = 2.56 μM) and **145** (ED50 = 6.91 μM) displayed significant cytotoxic activity against BCA-1 cell line (human breast cancer) [111]. Additionally, treatment of MCF-7 and T-47D (infiltrating ductal carcinoma of the breast) cell lines with **59** was reported to result in increased cell proliferation in a concentration-dependent manner with EqE_{10} values of 0.7 μM and 4.9 μM for MCF-7 and T-47D cell lines, respectively [213]. Melanoxoin **150** showed high cytotoxicity against Ca9-22 (gingival carcinoma), with an IC_{50} value of 0.46 μg/mL [201]. An analysis performed on the HCT-116 cell line (colon cancer with a mutation in codon 13 of the ras-protooncogene) showed a significant cytotoxicity of **31** (IC_{50} = 8.2 μg/mL) [207], **208** (IC_{50} = 1.9 μM), and **210** (IC_{50} = 1.8 μM) [129]. The results also showed that compounds **239** (IC_{50} = 60 μM) and **235** (IC_{50} = 80.3 μM) inhibited HCT-116 cells growth up to 81.4% and 66.2% at dose of 100 μM, respectively [258]. Low cytotoxicity on the HCT-116 cell line was reported for **248**, **249** (IC_{50} > 50 μM) [155], **7**, **8** [15], **9**, **10** [16], **44**, **172**, **127**, **143** with IC_{50} values > 100 μM [257]. Furthermore, very low cytotoxic activity against the HT-29 (colorectal adenocarcinoma with epithelial morphology) cell line possessed garcimangozone D **44** (IC_{50} > 150 μM) [176]. Moreover, moderate to low

activity against cellular Col-2 line (human colon cancer) was reported for compounds **135** (ED_{50} = 11.76 μM) and **145** (ED_{50} = 20.85 μM) compared to the positive control ellipticine (ED_{50} = 2.43 μM) [111]. Assays performed on HepG2 cell line (liver cancer) showed high cytotoxicity for **12** [15], **11** (IC_{50} = 38.14 μM) [13], **250** (IC_{50} = 153.1 nM), **217** (IC_{50} = 3161 nM), and **67** (IC_{50} = 1764 nM). Additionally, the last four compounds were compared to the positive control 5-fluorouracil (IC_{50} = 5659 nM) [62]. Moderate cytotoxicity against HepG2 cell line displayed **145** (IC_{50} = 9.81 μM) and **138** (IC_{50} = 19.41 μM) compared to the positive control sorafenib (IC_{50} = 2.66 μM) and doxorubicin (IC_{50} = 3.07 μM). [106]. Furthermore, very low cytotoxic activity possessed benzophenones **174**, **234**, **121** [119], **248** (IC_{50} > 50 μM), **249** (IC_{50} > 50 μM) [155], and **44**, **172**, **127**, **143** [257]. Furthermore, **250** (IC_{50} = 180.6 nM), **217** (IC_{50} = 6250 nM), **96** (IC_{50} = 1182 nM), and **67** (IC_{50} = 2274 nM) showed significant cytotoxicity against Hep3B (liver cancer with epithelial morphology) cells compared to the positive control 5-fluorouracil (IC_{50} = 51709 nM) [62]. Additionally, compound **71** showed moderate cytotoxic against SMMC-7721 cells, with IC_{50} values of 46.91 μM compared to the positive control cisplatin (IC_{50} = 12.49 μM) [210]. A significant and moderate cytotoxic effect against KB (human oral nasopharyngeal carcinoma) cells was reported for **135** (ED_{50} = 2.02 μM) and **145** (ED_{50} = 14.12 μM), respectively, compared to the positive control ellipticine (ED50 = 2.19 μM) [111]. Cytotoxicity assays performed on AGS (gastric adenocarcinoma) and SGC-7901 (human gastric carcinoma) cell lines showed an IC_{50} value for **31** was 12.4 μg/mL (AGS) [207], for **241** and **238** were >10 μg/mL (SGC-7901) [232] and **44** (IC_{50} = 107.73 μM) (SGC-7901) compared to cisplatin (IC_{50} = 15.74 μM) [255]. The cytotoxicity study of **145** on U2OS (human osteosarcoma with epithelial morphology) cell line demonstrated 27% cell death at 72 h [169]. Benzophenone **210** possessed a significant cytotoxic potential towards A549 (human alveolar basal epithelial cell adenocarcinoma) (IC_{50} = 1.4 μM), while **208** exhibited moderate activity with IC_{50} = 2.3 μM in comparison to doxorubicin (IC_{50} = 0.6 μM) [129]. Compounds **135** (ED_{50} = 5.68 μM) and **145** (ED_{50} = 12.34 μM) showed a significant and moderate cytotoxic potential, respectively, against Lu-1 (human lung cancer) cells compared to ellipticinec (ED_{50} = 2.11 μM) [111]. Benzophenone **19** (4.4 μg/mL) demonstrated significant cytotoxic activities towards H460 (non-small cell lung cancer) [180], while alternative study showed IC_{50} = 52.13 μM. In the later research compound **71** (IC_{50} = 97.13 μM) showed low cytotoxicity against the same cell line compared to cisplatin (IC_{50} = 8.78 μM) [210]. Garcimangosone D **44** displayed strong cytotoxic activity against A-375 cell line (human malignant melanoma) with an IC_{50} value of 24.67 μM compared the positive control cisplatin (IC_{50} = 6.61 μM) [255]. Additionally, **19** (IC_{50} = 100.21 μM) and **71** (IC_{50} = 63.67 μM) showed weak cytotoxic activity against A375 [210]. Cytotoxicity assays performed against cell lines SHSY-5Y (neuroblastoma), IMR-32 (neuroblastoma with rare areas of organoid differentiation) demonstrated IC_{50} values of 16.83 μM (IMR-32) for compound **32** compared to doxorubicin (IC_{50} = 0.037 μM) [33] and IC_{50} values of 25.54 μM and 69.36 μM (SHSY-5Y) for **19** and **71**, respectively, compared to cisplatin (IC_{50} = 4.00 μM) [210]. In addition, **44** was found to possess high and selective cytotoxicity (IC_{50} = 27.70 μM) against SHSY-5Y cells compared to cisplatin (IC_{50} = 5.14 μM) [255]. Benzophenone **145** (at 20 μM) was reported to cause 49% cell death after 72 h treatment in DBTRG (human glioblastoma) cell line [169], while **205** inhibited the proliferation of SF-268 (human brain glioblastoma/astrocytoma) cell line by 73% at a concentration of 25 μg/mL [127]. Cytotoxicity of **19** was reported to be high against SF-268 cells at a concentration of 2.0 μg/mL [180]. Garcimangosone D **44** was reported to exhibit cytotoxicity against the SiHa (human cervical squamous cell carcinoma) cell line with an IC_{50} value of 64.83 μM compared to a positive control cisplatin (IC_{50} = 9.87 μM) [255]. The cytotoxicity test against PANC-1 cell line (pancreatic carcinoma with epithelial morphology) showed that pogonatone C **248** possessed high activity with an IC_{50} value of 9.2 μM, while pogonatone D **249** had moderate activity with an IC_{50} of 28.3 μM compared to vinblastine (IC_{50} = 2.7 μM) [155].

4.6.2. Cytotoxicity on Animal Cell Lines and Models

The brine shrimp lethality test (BSL) showed high toxicity for maclurin **133** (LD_{50} = 43.1 µM) [103]. Benzophenone O-glucoside **122** demonstrated cytotoxicity in a dose-dependent manner with an IC_{50} value of 83 µg/mL against the NS-1 (mouse myeloma) cell line [245] and inhibitory ability with an IC_{50} of 5.1 µg/mL against L1210 (mouse leukemia) cell line [259]. Aquilaside B **111** and C **112** were found to show moderate cytotoxicity against SK-MEL (mammalian amelanotic cutaneous melanoma) cells with an IC_{50} value of 17.0 and 12.0 µg/mL, respectively, compared to doxorubicin (IC_{50} = 1.6 µg/mL) [86]. Furthermore, the assay against ASK (rat glioma cell) showed that **135** also possessed moderate cytotoxic activity with an ED_{50} value of 9.95 µM compared to ellipticine [111].

4.7. Cytoprotective Effects

The benzophenones **147**, **178**, **179**, **184**, and **206** were tested for hepatoprotective effect against carbon tetrachloride toxicity in isolated rat hepatocytes. The results indicated that **147**, **178**, and **179** showed weaker toxic effects compared to CCl_4 and in combination exhibited statistically significant protection against the toxic agent [260]. In addition, the benzophenone O-glycosides **178**, **179**, **184**, and **206** exhibited cytoprotective effects in a model of epirubicin-induced cellular toxicity in K-562 cells. The cytoprotective potential was concentration-dependent and more pronounced at the higher concentration of 25 µM with IC_{50} values of 1.45–3.51 µM. Furthermore, benzophenones **178**, **179**, and **184** showed an ability to ameliorate epirubicin-induced anti-clonogenic effects on bone marrow cell colony-forming units in vitro [205]. It was found that compounds **43**, **95**, **96**, **167**, and **168** at a concentration of 10^{-5} mol/mL showed hepatoprotective activity against D-galactosamine-induced toxicity in WB- F344 rat hepatic epithelial stem-like cells [78]. Furthermore, guavinoside B **235** was reported to exhibit significant activity on acetaminophen (APAP)-induced liver injury in vitro and in vivo. In vitro, at a concentration of 30 µM, **235** significantly reduced intracellular ROS levels in HepG2 cells. Additionally, in vivo pretreatment with compound **235** (100 mg/kg/day) significantly alleviated hepatocyte infiltration and necrosis in C57BL/6 mice, improved serum and liver biochemical parameters such as ALT, AST, SOD, GSH, ROS, MDA as well as TNF-α levels [261]. It was reported that iriflofenone-3,5-C-β-diglucoside **87** at a very low concentration (1 ng/mL) showed protective activity (81.77% cell viability) on cultured P19-derived neurons compared to the control condition (52.81% cell viability). The results also showed that compound **87** could significantly increase the number of neurites (3.77 branches) and stimulate the outgrowth of the cultured neurons (64.62 µm) compared with the control (number of neurites: 1.71 branches; length: 40.97 µm) [262]. The protective effects of hyperwightin E **196** and petiolin G **189** against corticosterone-induced PC12 cell injury were assessed. The tested benzophenones exhibited noticeable neuroprotection at 10 µM. They significantly increased the cell survival rate from 58.57% (for the model) to 67.89% and 66.23%, respectively, compared to positive control desipramine (cell viability of 72.33%) [126].

4.8. Antimicrobial Activity

4.8.1. Antibacterial Activity

The benzophenones **19** (MIC = 12.5 µg/mL) [180] and **31** (MIC = 5–12.5 µM) [263] were reported to have inhibitory activity against Gram-positive *Staphylococcus aureus*. Iriflofenone-3-C-β-D-glucoside **74** (MIC = 62.5 µg/mL) also exhibited strong antibacterial activity against *S. aureus* in comparison to cefixime, a well-known antibiotic (MIC = 62.5 µg/mL) [157]. Moderate antibacterial activities possessed mitraphenone A **14** (MIC = 50 µM) compared to moxifloxacin [147] and cearoin **34** (with 15 mm inhibitory zone) compared to a positive control imipenem (with 30 mm inhibitory zone) [230]. Weak antibacterial activity against *S. aureus* was reported for **142** (MIC = 128 µg/mL) [108], **44** (MIC = 250 µg/mL), **241** (MIC = 400 µg/mL) [150], **60** (MIC = 1800 µg/mL), **122** (MIC = 1800 µg/mL) [264], and melannoin **63** (MIC = 3.1 mg/mL) [60]. Weak antibacterial activity against *Bacillus subtilis* was also reported for **74** (MIC = 125 µg/mL) [157], **34** (with 12 mm inhibitory

zone) [230], **60** (MIC = 1800 µg/mL), and **122** (MIC = 1800 µg/mL) [264]. Elegaphenone **31** showed good antibacterial activity against *Enterococcus faecalis* (MIC = 7.5 µM) and *E. rivorum* (MIC = 12.5 µM) [263]. Mitraphenone A **233** [147] and garcimangosone **44** [176] showed moderate and weak antibacterial activity against *E. faecium* with MIC = 50 µM and MIC > 128 µg/mL, respectively. Significant antibacterial activity against *Mycobacterium tuberculosis* was found for **219** (MIC = 41.67 µg/mL) compared to rifampicin as a reference drug (MIC = 2.08 µg/mL). Additionally, the combination (1:1) of **219** and gallic acid (MIC = 20.83 µg/mL) was better than that of **219** alone [136]. Furthermore, the results also showed that **233** (MIC > 50 µM) [147] possessed moderate activity, while **220** (MIC = 266.67 µg/mL) exhibited weak antibacterial activity against *M. tuberculosis* [136]. Additionally, **19** was reported to exhibit significant activity at a concentration of 12.5 µg/mL against *M. smegmatis* [180]. Iriflofenone-3-C-β-D-glucoside **74** (MIC = 62.5 µg/mL) exhibited strong antibacterial activity against Gram-negative bacteria *Escherichia coli* in comparison to cefixime (MIC = 62.5 µg/mL) [157]. Weak and very weak antibacterial activity against *E. coli* was reported for garcimangosone D **44** (MIC = 650 µg/mL), guajaphenone A **241** (MIC = 900 µg/mL) [150], **60** (MIC = 900 µg/mL), and **122** (MIC = 900 µg/mL) [264]. A moderate antibacterial activity against *Pseudomonas aeruginosa* was determined for cearoin **34** (16 mm inhibitory zone) compared to a standard drug imipenem (with 24 mm inhibitory zone) [230]. In addition, it was found that elegaphenone **31** enhanced the elimination of intracellular *P. aeruginosa* in macrophages exposed to subinhibitory concentrations of the fluoroquinolone antibiotic norfloxacin [263]. Furthermore, **37** (4 mm inhibitory zone) showed weak antibacterial activity compared to gentamicin (15 mm inhibitory zone) [237]. In addition, very weak activity against *P. putida* was found for **60** and **122** with an MIC value of 900 µg/mL [264]. Cearoin **34** exhibited antibacterial activity against *Salmonella typhi* with an inhibitory zone of 18 mm compared to a standard drug imipenem (25 mm) [230]. To date, antibacterial activity against *Klebsiella pneumoniae* has been reported only for iriflofenone-3-C-β-D-glucoside **74**, which showed significant activity with an MIC value of 31.1 µg/mL comparable to the well-known antibiotic cefixime (MIC = 31.1 µg/mL) [157].

4.8.2. Antimycotic Activity

Significant antimycotic activity against *Aspergillus fumigatus* has been reported for **37** with an inhibitory zone of 11 mm compared to ketoconazole (inhibitory zone of 16 mm) [237]. Compounds **242** (MIC = 25 µg/mL) and **237** (MIC = 25 µg/mL) exhibited better antimycotic activity against *Candida glabrata* than the positive control fluconazole (MIC = 50 µg/mL). The results also showed that compound **50** (MIC = 50 µg/mL) showed the same antimycotic activity as the positive control. Furthermore, compound **242** (MIC = 25 µg/mL) showed better antimycotic activity against *C. krusei* than fluconazole (MIC = 50 µg/mL), while the other compounds, **50** and **237**, possessed the same activity as the positive control [151]. Additionally, compound **124** demonstrated a weak inhibitory activity (29%) on *Cryptococcus neoformans* [92].

4.8.3. Antiviral Activity

Benzophenone **66** showed selective and moderate inhibitory activity in vitro against the proliferation of *Herpes simplex* type 1 (HSV-1) with an IC_{50} value of 4 µg/mL compared to a positive control pirodavir (IC_{50} = 0.085 µg/mL) [38]. Compound **143** exhibited very high anti-HIV activity against syncytium formation in the syncytium inhibition assay (EC_{50} = 68.88 µM, SI > 1.59) and in the reverse transcriptase assay (IC_{50} = 271.75 µM) [111]. Furthermore, garcimangosone D **44** exhibited moderate anti-HIV-1 activity with EC_{50} values of 18.06 µg/mL and TI (therapy index) > 11.07, while malaferin A **42** showed weak bioactivity with EC_{50} = 131.70 µg/mL and TI > 1.52 [40]. In addition, foliamangiferoside A4 **92** showed a moderate inhibitory activity against influenza NA (neuraminidase) from pandemic A/RI/5+/1957 H2N2 influenza A virus (47.4%) and coxsackie B3 virus 3C protease (53.8%) at a concentration of 100 µM [265].

4.8.4. Antiparasitic Activity

It was found that compound **122** exhibited considerable growth-suppressing effect against *Trypanosoma brucei* with IC_{50} values of 22.3 μM [92], while cearoin **34** has very weak activity against *Leishmania major* (IC_{50} > 100 μM) [193]. In addition, **38** (IC_{50} = 18.6 μM) and **58** (IC_{50} = 28.8 μM) showed ex vivo antiplasmodial activities [54].

4.8.5. Antimalarial Activity

The antimalarial activity of **174** was assessed as weak with an inhibition value of 29.8%, relative to the positive control of chloroquine diphosphate (95.1%) [119].

4.9. Metabolic Syndrome

4.9.1. Antidiabetic Activity

1. α-Glucosidase inhibitory activity

It was found that compounds **227** (IC_{50} = 0.042 mM) and **228** (IC_{50} = 0.199 mM) showed stronger α-glucosidase inhibitory activity than positive control acarbose (IC_{50} = 0.685 mM) [142]. The results also showed that aquilarisinin **114** (IC_{50} = 151.6 μg/mL) exhibited a strong inhibitory effect against α-glucosidase, which was about twofold that of acarbose (IC_{50} = 372.6 μg/mL) [88]. The benzophenone **106** showed 91.4% inhibition activity at 10 μg/mL against the α-glucosidase from *Bacillus stearothermophilus* compared to acarbose (inhibition = 70.5% at 40 ng/mL) [84], while compounds **155** and **86** exhibited significant α-glucosidase inhibitory activity of 54% and 43%, respectively (at 200 μM), against an enzyme mixture extracted from rat intestinal acetone powder [74]. Furthermore, inhibitory effect against α-glucosidase of compounds iriflofenone-2-O-α-L-rhamnoside **108** (IC_{50} = 143.7 μg/mL) and iriflofenone-3-C-β-D-glucopyranoside **74** (IC_{50} = 165.1 μg/mL) was about twofold of that of acarbose (IC_{50} = 372.0 μg/mL), while iriflofenone-3,5-C-β-diglucoside **87** (273.6 μg/mL) showed inhibitory effect almost the same as the positive control [88]. In addition, strong to moderate α-glucosidase inhibitory activity compared to acarbose (IC_{50} = 185.25 μM) possessed benzophenones **162** (IC_{50} = 284.93 μM), **78** (IC_{50} = 415.79 μM), **120** (IC_{50} = 520.94 μM), **60** (IC_{50} = 657.23 μM), and **79** (IC_{50} = 834.66 μM) [81].

2. α-Amylase inhibitory activity

Garcimangophenone A **209** (IC_{50} = 12.2 μM) and B **207** (IC_{50} = 9.3 μM) showed significant α-amylase inhibitory activity compared with acarbose (IC_{50} = 6.4 μM) [128]. Additionally, the results also showed that garcimangophenone C **128** exhibited very strong α-amylase inhibition with IC_{50} of 12.9 μM compared to acarbose (IC_{50} = 6.7 μM) [95].

3. The efficiency of glucose uptake

The assay for glucose uptake stimulatory activity conducted in rat skeletal muscle L6 cells reported that iriflofenone-3-C-β-D-glucoside **74** (100 μg/mL) and iriflofenone-3,5-C-β-diglucoside **87** (100 μg/mL) showed a glucose uptake enhancement of 234.5% and 119.9%, respectively, when compared with the blank control (100% uptake). The positive control insulin (0.5 μM) showed 146.6% enhancement [159].

4.9.2. Antihyperlipidemic Activity

At a dose of 30 μM, compounds **74**, **78**–**81**, **88**, and **155** [72], as well as **84** (10 μM) and **85** (10 μM), significantly suppressed triglyceride (TG) and free fatty acid (FFA) accumulation in 3T3-L1 adipocytes [73]. Based on the AMP-activated protein kinase (AMPK) signaling pathway, several of the abovementioned benzophenones were found to increase the AMPK enzyme expression and downregulate lipogenic enzyme gene expression such as SREBP1c (sterol regulatory element-binding protein 1c), FAS (fatty acid synthase), and HSL (hormone-sensitive lipase). The results showed that compared with the control group, AMPK gene expression of compounds **58**, **74**, **78**, **88**, **122**, **155**, **163** [72], **82**–**85**, **91**, and **92** [73] were significantly increased. All of these compounds significantly suppressed the SREBP1c level [72,73]. Furthermore, compounds **52**, **56**–**59**, **84**, **85**, **135** [72], and **61**–**63** [73]

significantly downregulated HSL gene expression. It was found that **74**, **78**, **88**, **155** [72], **82–85,** and **92** [73] significantly reduced FAS gene expression. Additionally, compounds **69** and **143** exhibited better inhibitory activity against FAS than the known FAS inhibitor EGCG (epigallocatechin gallate) (IC_{50} = 51.97 μM), returning lower IC_{50} values of 14.76 μM and 8.59 μM, respectively [64].

4.9.3. Antihypertensive Activity

It was reported that maclurin-6-O-β-D-glucopyranoside **172** significantly alleviated the exaggerated vasoconstriction of metabolic syndrome (MetS) aortae and at the same time showed significant vasodilation of PE (phenylephrine) precontracted aortae. To further illustrate the mechanism of action, the observed vasodilation was completely blocked by the nitric oxide (NO) synthase inhibitor Nω-nitro-L-arginine methyl ester hydrochloride and inhibited by guanylate cyclase inhibitor methylene blue. The results showed that vasodilation was not affected by the potassium channel blocker, tetraethylammonium, or the cyclooxygenase inhibitor; indomethacin and **172** stimulated NO generation from isolated aortae to levels comparable with acetylcholine. Furthermore, **172** inhibited reactive oxygen species generation in MetS aortae. In conclusion, it could be said that maclurin-6-O-β-D-glucopyranoside (**172**) ameliorated the exaggerated vasoconstriction in MetS aortae through the vasodilatation-NO generation mechanism [171].

4.10. Inhibitory Activities on Platelet Aggregation

Until now, only three compounds possessed inhibitory potential against platelet aggregation induced by one, two, or three inducers such as arachidonic acid (AA), adenosine diphosphate (ADP), and collagen at 100 μg/mL in human whole blood in vitro. Among the tested compounds, only **152** exhibited strong inhibitory activity against platelet aggregation induced by AA (IC_{50} = 53.6 μM), ADP (IC_{50} = 125.7 μM), and collagen (IC_{50} = 178.6 μM). The results also showed that benzophenone **152** was the only compound effective against collagen-induced platelet aggregation. Compound **151** demonstrated the strongest inhibition on platelet aggregation induced by ADP with an IC_{50} value of 34.7 μM. Additionally, **70** showed selective inhibitory activity on platelet aggregation induced by AA and ADP with IC_{50} values of 91.1 μM and 69.5 μM, respectively [65].

4.11. MAO-A Inhibition Activity

It was found that compounds **129** and **172** exhibited significant inhibitory activity against MAO-A with an IC_{50} value of 31.3 μM and 41 μM, respectively, compared to the positive control clorgyline (IC_{50} = 0.08 μM) [266]. A weak MAO-A inhibitory effect was found for compounds **180** (IC_{50} = 111.2 μM), **182** (IC_{50} = 310.3 μM), and **183** (IC_{50} = 726.0 μM). Clorgyline was again used as positive control MAO-A inhibitor with an IC_{50} value of 0.5 μM [122].

4.12. Antiarthritic Activity

Studies on proapoptotic activity on TNF-α-stimulated synovial cells isolated from patients with rheumatoid arthritis demonstrated that iriflofenone 3-C-β-glucoside **74** possessed 71% efficacy, measured as the percent of apoptotic cells [187].

4.13. Anticholinesterase Activity

Elegaphenone **31** was found to possess moderate inhibitory activity against acetylcholinesterase with IC_{50} value of 192.19 μM, against a positive control of galantamine hydrobromide (IC_{50} = 0.43 μM) [250].

4.14. Anti-Atherosclerotic Activity

It was reported that compound **37** (0.40 mM) exhibited inhibitory activity of 54% against hACAT-1 (human acyl-CoA: cholesterol acyltransferase) compared to the positive control oleic acid anilide (57% inhibition at 0.3 μM concentration) [224].

4.15. Laxative Effect

The laxative effect of iriflofenone-2-O-α-L-rhamnoside **108** was estimated in vivo in male ddY mice (aged 7–10 weeks and 20–35 g body weight) after administration of an oral dose of 1000 mg/kg. The results showed that benzophenone **108** exhibited slow-acting laxative activity, as its effect appears 6–8 h after administration and does not cause subsequent diarrhea [75].

4.16. Negative Effects of Naturally Occurring Simply Oxygenated Benzophenones on Human and Animal Health and the Environment

However, of the variety and number of benzophenone products of natural and synthetic origin, only a small part of them, in particular those possessing a hydroxyl or methoxy group in the para position to the carbonyl function, a model of 2,4-dioxygenation and rarer model of 2,2′4,4′-tetraoxygenation, are among the most tested for negative effects on humans and the environment. This is due to the fact that these groups of compounds are among the most commonly used UV absorbing agents, mainly due to their large molar extinction coefficients in both the UVA and UVB ranges. 2-Hydroxy-4-methoxybenzophenone (benzophenone-3 or BP-3) **3** is known to have been used for many years as a UV filter in sunscreen cosmetics [267]. On the other hand, **3** has been shown to be metabolized to three intermediates in rats, including 2,4-dihydroxybenzophenone (benzophenone-1 or BP-1) **5**, which is formed by demethylation [268]. The latter is also used as a UV filter in sun protection products. Exposure to elevated levels of **5** may be associated with increased chances of endometriosis diagnosis in women [269], and it has also been reported to have significant uterotrophic effects to increase the growth of BG-1 human cancer cells on ovaries and to show high affinity in binding to hERα (human estrogen receptor α), while **3** showed only a slight estrogenic effect in the assay with MCF-7 human cancer cells and pS2 protein [270]. Compound **5** was also reported to exhibit greater inhibitory activity against human KGN 3β-HSD (3β-hydroxysteroid dehydrogenase) with an IC_{50} = 5.66 μM, than BP-3 (5.84 μM) [271]. In addition, in vitro yeast-based reporter assay found that compound **5** has strong estrogenic (EC_{50} = 1.29 μM), weak antiandrogenic (IC_{50} > 30 μM), and mushroom tyrosinase inhibitory activity (IC_{50} > 50 μM), while **3** has weak estrogenic (EC_{50} > 30 μM), antiandrogenic (IC_{50} > 30 μM), mushroom tyrosinase inhibitory (IC_{50} > 50 μM), and moderate antiprogestrogenic activity (IC_{50} = 11.81 μM). Furthermore, 2,2′,4,4′-tetrahydroxybenzophenone (benzophenone-2 or BP-2) **73** exhibits weak estrogenic activity (EC_{50} = 17.29 μM) and significant inhibitory activity against mushroom tyrosinase (IC_{50} = 19.7 μM) [272]. A number of studies have been conducted to evaluate the estrogenic and toxic effects of benzophenone UV filters in fish. It was established that compound **3** at a concentration of 2.4–312 μg/L affected genes involved in steroidogenesis and hormonal pathways in zebrafish at different developmental stages [273]. Furthermore, acute toxicity tests with medaka larvae showed that at 96 h exposure, compounds **3** (LC_{50} = 4.10 μM) and **5** (LC_{50} = 2.22 μM) exhibited significantly higher toxicity than **73** (LC_{50} = 18.43 μM). The latter at an ecologically relevant concentration (5–50 nM) did not alter locomotion and oxidative stress responses of larvae from 24 h to 7-day exposure, while **3** even at 5 nM induced hypoactivity or changed fish swimming angles [272]. In addition, adverse effects on algae (*Scenedesmus vacuolatus* and *Desmodesmus subspicatus*), freshwater flea (*Daphnia magna*), and planarian (*Dugesia japonica*) altered endocrine signaling gene expression, ultraspiracle in aquatic invertebrate (*Chironomus riparius*), and reduced reproductive performance in Japanese medaka (*Oryzias latipes*) after exposure to 620 μg/L for 21 days have been reported for compound **3** [270].

5. Biogenetic Significance of Simply Oxygenated Benzophenones

Simply oxygenated benzophenones are active secondary metabolites and are closely related to xanthones as their immediate biosynthetic precursors. Biogenetic relationship between benzophenones and xanthones were discussed in several reviews. The intermediate benzophenones were built by acetate and shikimate biosynthetic pathways. Further

intermolecular reaction led to formation of a xanthone. The mechanisms of last formation step could involve four possible pathways [7,274–276]. The literature data showed that maclurin **133** is an intermediate in the biosynthesis of macluraxanthone [277], 1,3,5,6- and 1,3,6,7-tetraoxyxanthones from the families Guttiferae and Moraceae [179]. Furthermore, after feeding *Anemarrhena asphodeloides* with radiolabeled 1,3,6,7-tetrahydroxyxanthone and **133**, only the latter was efficiently incorporated into mangiferin and isomangiferin, indicating that C-glucosylation of mangiferin and isomangiferin occurs prior to xanthone core formation [278]. Additionally, the study of xanthones from *Gentiana lutea* with the inclusion of ^{14}C- and ^{3}H-labeled compounds demonstrated that compound **61** (2,3′,4,6-tetrahydroxybenzophenone) is a precursor of gentisein [279]. A study on *Hypericum annulatum* showed that an acid and enzymatic hydrolysis of hypericophenonoside **206** led directly to the formation of 1,3,7-trihydroxyxanthone (gentisein). This finding favored the hypothesis that some xanthones could be formed in plants by dehydration of 2,2′-dihydroxybenzophenones, and the intermediate precursors might be benzophenone with O-glycosilation ortho to the carbonyl function [8]. In general, the formation of the benzophenone (C_{13}) skeleton is catalyzed by benzophenone synthase. In cell cultures of *Hypericum androsaemum*, this enzyme stepwise condenses one molecule of benzoyl-CoA with three molecules of malonyl-CoA to provide a tetraketide intermediate, which is cyclized by an intramolecular Claisen condensation to **17** (2,4,6-trihydroxybenzophenone). The subsequent 3′-hydroxylation is catalyzed by cytochrome P_{450} monooxygenase [280]. In cell cultures of *Centaurium erythraea*, the preferred starting substrate for benzophenone synthase is 3-hydroxybenzoyl-CoA, immediately producing compound **61** [202]. In addition, it should be noted that in fungi, biogenetic benzophenone can be formed from two separate units, each separately derived from acetate and malonate pathways, or by an anthrone and/or anthraquinone intermediate derived from a single C_{16} polyketide chain [281].

6. Conclusions

This review includes more than 280 references to naturally occurring simple oxygenated benzophenones covering the years from 1850 up to 2023 and was compiled using databases such as Chemical Abstracts, Scopus, Google Scholar, PubMed, and ResearchGate. This article discusses the structural diversity, distribution, and biological activities of natural simple oxidized benzophenones and their glycosides.

Two hundred and fifty chemical structures belonging to seven groups of benzophenone derivatives and their glycosides (mono-oxidized, di-oxidized, tri-oxidized, tetra-oxidized, penta-oxidized, hexa-oxidized, and others that cannot be classified into any of the first six) were established.

Naturally occurring benzophenones represent a relatively small group of plant metabolites with narrow distribution. Up to now, simple oxygenated benzophenones and their glycosides have been established in 77 plant genera distributed in 44 families. Of all 250 reported compounds, the largest number of representatives 51 was isolated from the Hypericaceae family, followed by 43 representatives from Anacardiaceae, 36 from Clusiaceae, 24 from Polygalaceae, 22 from Thymelaeaceae, and 18 from Fabaceae. The allergy associated bezophenone-1, benzophenone-2, and benzophenone-3 have limited distribution across natural sources.

A wide range of pharmacological activities of simple oxygenated benzophenones and their glycosides such as antioxidant activities; anti-inflammatory activity; cytotoxic, antitumor, and cytoprotective activities; antimicrobial activity; MAO-A inhibition activity; antiarthritic activity; anticholinesterase activity; anti-atherosclerotic activity; laxative effect; metabolic syndrome; etc., that appeared in the literature were discussed as well.

The authors hope that this review will draw the attention of scientists of simple oxygenated benzophenones and their glycosides and stimulate them to continue with phytochemical, pharmacological, and chemotaxonomical studies that could lead to the discovery of compounds that can serve as models for the synthesis of a new pharmacological agent as well as help to solve certain taxonomical issues.

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