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Chemical Profiles and Bioactive Molecules of Propolis: A Review

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ABSTRACT

Propolis is a dark sticky material that bees (indispensable actors in biosphere) harvest from exudates and buds of plants alongside pollinating them, promoting agriculture and protecting the ecosystem. Its chemical composition is highly variable and dependent on the local flora. In search for rapid chemical screening methods which are capable of characterizing propolis samples from various geographic origins, various hyphenated techniques such as HPLC-DAD, HPLC-MS/MS, LC–MS, LC–MS/MS, GC–MS etc., have been used and giving an insight on the regional variation in chemical composition. Various chromatographic techniques (CC, UPLC, HLPC, RP-HPLC, TLC….) are used in obtaining organic bioactive compounds from propolis. The structures of these compounds are characterised using state-of-the-art spectroscopic and spectrometric methods. There is no clear-cut distinction of propolis from different regions but the major chemical compounds can be classified in two main groups as those from temperate propolis and those from tropical propolis. Compounds isolated from propolis from temperate regions are mostly flavones, flavonols, flavanones, flavanonols, chalcones, aurones, pterocarpans, lignans, phenolic acids and their esters, etc. Compounds isolated from propolis from tropical and subtropical regions are mostly terpenoids, steroids and xanthones. Propolis is very rich in structurally diverse molecules which are capable of being isolated. These compounds/potential drugs are usually subjected directly to bioassays or used as starting material for synthesis in view of obtaining their derivatives or synthetic analogues with enhanced biological activities.

1. Introduction

As remedial measures to environmental protection and deforestation, alternative sources of natural products other plants are being encouraged. Propolis is a dark sticky material that honeybees harvest from plant secretions and buds and apply inside the hive to seal cracks om walls and embalm dead invaders [1]. Bees by harvesting the plants also act as pollinating agents and equally play a vital role in sustaining the ecosystem. A remarkable number of scientific publications dealing with propolis chemistry and pharmacology keep appearing and researchers begin to comprehend how the chemical constituents in propolis vary from one region to another depending on the plants that grow at the site and season of collection.

Due to the need for rapid chemical screening that is capable of detecting chemical profiles of propolis samples from different geo-ecological areas, various hyphenated techniques usually with methodological modifications such as HPLC-DAD, HPLC-MS/MS, LC–MS, LC–MS/MS, GC–MS etc., have been used giving an insight on the regional variation in chemical composition. Considering the fact that propolis contains relatively polar compounds in addition to the advent of softer ionization methods that are compatible with liquid chromatography makes methods such as HPLC-DAD and HPLC–MS preferable for propolis analysis. However, with improved resolving capacity of capillary GC and the important fragmentation patterns in EIMS that gives useful structural information makes a remarkable comeback for GC-MS.

Various chromatographic techniques (CC, UPLC, HLPC, RP-HPLC, TLC….) are used in obtaining organic bioactive compounds from propolis. The structures of these compounds are characterised using state-of-the-art spectroscopic and spectrometric methods such as ^{1}H NMR, ^{13}C NMR DEPT 135, DEPT 90, COSY (^{1}H-^{1}H), NOESY (^{1}H-^{1}H), HSQC, HMBC, UV, IR, EIMS, ESI-TOF-MS, HRMS, FAB-MS etc.,.

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2. Chemical Profiles of Propolis Samples of Some Countries

For propolis from some countries, various hyphenated techniques have been used to report variable chemical compositions as follows:

2.1 France

Benzyl caffeate, pinocembrin and trans-p-coumaric acid were described as main constituents of French propolis [2]. Detailed profiling of French poplar propolis by HPLC/UV/MS technique enabled the identification of 48 metabolites which mostly to phenolic compounds, benzoic acid and cinnamic acid derivatives. Examples include p-coumaric acid, isopent-3-enyl caffeate, pinobanksin-3-acetate, prenyl caffeate, 2-acetyl-1,3-dicoumaroylglycerol, cinnamyl isoferulate, cinnamyl p-coumarate, chrysin, benzyl p-coumarate, galangin, benzyl ferulate, cinnamyl benzoate, cinnamyl cinnamate, pinocembrin, benzyl caffeate and 3,4-dimethoxycinnamic acid [3].

2.2 Malta

Propolis from Malta analysed by gas GC-MS was shown to contain sugars and diterpenoids most abundantly diterpene acids: communic, pimaric, isocupressic and imbricatoloic acids together with totarol and 13-epitorulosal. Ferutinin, 2-acetoxy-6-p-methoxybenzoyl-jaeschkeanadiol, teferin and 2-acetoxy-6-p-hydroxy-benzoyl-jaeschkeanadiol were mono- and sesquiterpenyl esters also detected equally [4].

2.3 Italy

Propolis from Sicily (Italy) subjected to GC-MS contained mostly diterpenic acids, such as isocupressic acid, communic acid and acetylisocupressic acid while propolis from Italy central indicated a rich phenolic profile containing caffeic acid, caffeic acid phenyl ester, p-coumaric acid, ferulic acid, quercetin, pinocembrin, galangin, apigenin, kaempferol, chrysin, benzyl salicylate and benzyl cinnamate [5,6]. HPLC-MS/MS was used to detect the presence of caffeic acid, ferulic acid, p-coumaric acid, caffeic acid phenylethyl ester, apigenin, chrysin, pinobanksin, galangin, naringenin, quercetin, kaempferol, pinocembrin, pinostrobin, caffeic acid cinnamyl ester and pinobanksin-3-O-acetate in ethanolic extracts of propolis from the province of Bologna (Italy) [7].

HPLC-ESI-TQ MS profiling showed 21 compounds mostly phenolics. The most abundant compounds being chrysin, pinocembrin and galangin. Mediterranean and temperate area propolis contained notably high amounts of ferulic and isoferulic acids [8].

2.4 Portugal

LC-DAD-ESI-MS/MS detected 76 polyphenols and this enabled the propolis to be grouped into two: common temperate propolis containing mainly flavonoids and their methylated/esterified forms, phenylpropanoid acids and their esters which are typical poplar phenolic compounds and an unusual propolis type rich in quercetin and kampferol glycosides [9]. Furthermore, caffeic acid, 3,4 dihydroxy vinyl benzene, p-coumaric acid, ferulic acid, isoferulic acid and their esters together with dihydroflavonols, flavanones, flavones and flavonols were characterized. HPLC-UV profile suggested that Portuguese propolis was mostly rich in pinocembrin, chrysin and pinobanksin 3-O-acetate.

2.5 Greece

GC-MS of derivatized sample revealed the presence of anthraquinones and terpenes in important quantities and the low amounts of phenolic acids and their esters, hence similarity in chemical constituents with propolis of East Mediterranean rather than typical European propolis [10]. HPLC-UV showed phenolic acids such as ferulic acid, p-coumaric acid, caffeic acid, caffeic acid phenethylester and flavonoids precisely quercetin, galangin, luteolin, apigenin in samples from West Macedonia. HPLC-PDA-ESI of Greek propolis led to the identification and quantification 59 phenolic compounds in hydroalcoholic extracts out of which nine of them were reported for the first time here. GC-MS analysis was carried out to compliment this study and detected eight more newly reported compounds amongst which are hesperetin, acacetin, kaempferide, eriodictyol, isosakuranetin, luteolin, rhamnetin and pinostrobin. The following six compounds were most dominant and common for all the regions: pinocembrin, chrysin, galangin, apigenin, pinobanksin 3-O-acetate, and catechin [11].

2.6 Thailand

RP-TLC afforded phenylallylflavanone, pinocembrin and (E)-cinnamyl-(E)-cinnamylidenate from methanolic extract of propolis from Thailand was reported. 19 compounds were also isolated and identified to be phenolic esters and flavonoids. These isolated constituents were much similar structurally to the compounds common in the propolis of temperate regions in China, Uruguay, Europe and Mexico [12].

2.7 China

using UHPLC on 15 samples, pinobanksin, chrysin, pinocembrin, galangin, pinocembrin 3-acetate, p-coumaric, ferulic, isoferulic, caffeic and 3,4-dimethyl caffeic acids and caffeic acid phenyl ethyl ester was quantified [13]. Furthermore, 38 compounds were identified by Time of Flight mass spectrometry UHPLC/Q-TOF-MS mainly phenolic acids and flavonoids with chrysin, pinocembrin, galangin, and pinobanksin 3-acetate as the primary constituents.

2.8 Oman

GC-MS characterization showed over 50 compounds grouped into the following classes: fatty acids, cardanols and cardols, anacardic acids, flavan derivatives, triterpenes, sugars, polyols, hydroxyl acids, prenylated flavanones and chalcones. Omani propolis are void of the common phenolic acids and their esters found in poplar propolis [14]. The usual poplar-type flavonoids such as pinocembrin, pinobanksin 3-O-acetate, galangin, and chrysin were not detected. Further, the samples do not contain any diterpenes, which are characteristic for Mediterranean type propolis [4].

2.9 Argentina

HPLC-DAD and HPLC-ESI-MS/MS led to the identification of one methoxychalcone, one dihydroxychalcone, galangin, pinocembrin and 7-hydroxy-8-methoxy-flavanone [15]. RPHPTLC and RPHPLC of twenty-five samples of propolis led to the identification of ferulic acid, coumaric acid, cinnamic acid, quercetin, pinobanksin, kaempferol, pinocembrin, apigenin, 1,1-dimethylallylcaffeic acid, chrysin, galangin, kaempferide and tectochrysin [16].

2.10 Brazil

UPLC-ESI-MS/MS experiments classified propolis samples into three main groups and mass fragment ions marker characterizing each of these three groups were identified. The Brazilian samples of propolis from one state displayed a very abundant marker at 501.3 m/z which needs further studies to be characterized. In the second group ions specific for formononetin, pinocembrin and biochanin A were detected. For the third group a marker ion at 601.35 was possibly attributed to a benzophenonic molecule [17].

Liquiritigenin, biochanin A, medicarpin, Formononetin, neovestitol, vestitol, cis-asarone, elemicin, (2S)-7-hydroxyflavanone, Chrysin, Guttiferone and 7-O-Methylvestitol amongst other constituents where detected in Brazilian red propolis by HPLC-ESI-MS/MS [18] which is the most studied of propolis samples in the world.

2.11 Cuba

HPLC-DAD and HPLC-ESI-MS data and then a qualitative and quantitative GC-MS study was developed, especially for aliphatic compounds (triterpenoids) and the breakthrough of this work was that it was the first report of some triterpenes belonging to the class of ursane, lupane, lanostane and oleanane skeletons identified as major constituent compounds [19].

2.12 Cameroon

GC–MS analysis revealed alk(en)ylphenol and alk(en)ylresorcinols as major constituents and characteristic profiles of Cameroonian propolis [1] and those with mono-unsaturated and saturated side aliphatic chain lengths in the range of C11 to C15 to C19 and C19 respectively [20]. In addition, as contribution to the chemical profiling of selected samples of African propolis using dereplication (LC-HRMS), a sample of propolis from Cameroon was proven to be significantly rich in triterpenoids [21]. Another detailed study revealed three diprenyl-flavonoids, thirteen triterpenes, one fatty acid ester and two monoterpenic alcohols in Cameroonian propolis samples from Oku (North-west Region), Ngaoundal and Tekel (Adamawa region) [22].

2.13 South Africa

UPLC-ESI-MS analysis of 39 samples of South African propolis were undertaken in order to determine its chemical composition and regional variability. UPLC-PDA-qTOF-MS/MS analysis led to the identification of representative chemical markers from the various groups and 15 major flavonols and phenolic acids from propolis of South African were identified. Data of chemometric analysis of the UPLC-ESI-MS showed that there are two distinct clusters within the propolis samples of South African. Quercetin, chrysin, tectochrysin, galangin, galangin-5-methyl-ether, caffeic acid, p-coumaric acid, pinocembrin, pinobanksin and its derivatives were major compounds detected and characterised [23].

2.14 Kenya

GC-MS and TLC profiles differed from those of European poplar-type propolis as well as those of propolis from many other tropical regions such as green and red Brazilian and Pacific type propolis. The presence of sugars and triterpene alcohols were revealed in this study as well as some diterpenic acids. Two new aryl napthalene lignans tetrahydrojusticidin B and 6-methoxydiphyllin were isolated along with four known phenolic compounds phyllamyricin C, macarangin, schweinfurthin A and schweinfurthin B found for the first time in propolis [24].

2.15 Egypt

HPLC analysis of Egyptian was done and compared with Chinese propolis. This study indicated significant and variable contents in phenolic compounds between Chinese and Egyptian propolis samples. The concentrations of the following phenolic compounds chlorogenic acid, vanillic acid, benzoic acid, ferulic acid, caffeic acid, pinocembrin, chlorogenic acid, catechin, gallic acid, esculetin, tannic acid, catechol and ferulic acid were higher in Egyptian samples than in Chinese samples. On the other hand, the amounts of apigenin, cinnamic acid, pyrogallol, p-OH-cinnamic acid, acacetin and itaconic acid where greater in Chinese propolis than in Egyptian propolis. GC-MS profiles of Egyptian propolis enabled the identification of 25 compounds which were phenolic acids (1.1%), phenolic acid esters (72.7%), dihydrochalcones (6.5%), Chalcones (1.7 %), flavones (4.6%), flavanones (1.9%), aliphatic acids (2.4%), and tetrahydrofuran derivatives (0.7%) [25].

2.16 Morocco

LC-ESI-MS was used to identify quercetin-arabinoseglucoside, wogonoside, baicalin or wogonin glucoside, apigenin dihexoside, rhamnetin hexoside, rhamnetin or isorhamnetin, afzelechin-catechin dimmer, saphnin or daphnitin, alongside other flavonoids in Moroccan propolis [26].

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2.17 Tunisia

HPLC detected chrysin, pinobanksin, tectochrysin, pinocembrin, dimethyallyl caffeate, galangin, myricetin 3,7,4′,5′-tetramethyl ether, phenylethyl caffeate, and quercetin 3,7,3′-trimethyl ether making it to resemble European and North american propolis [27].

2.18 Algeria

HPLC-DAD enabled the classification of Algerian propolis into two main types of; the one that was rich in polyphenols and the other rich in diterpenes. Certain polyphenols including naringenin, pinostrombin chalcone, suberosin, galangin, methoxychrysin, tectochrysin, pectolinarigenin, pilosin, pinobanksin, caftaric acids, pinobanskin 3-O-acetate, pinobanksin 3-(E)-caffeate and their methyl esters were detected in of propolis from Algeria [28]. Diterpenes and diterpenic acids are also reported in propolis from Algeria [29].

2.19 Nigeria

HPLC-UV-ELSD indicated that the chemical composition of Nigerian propolis samples is characterized by a broad diversity. The propolis samples collected in the central area of Nigeria predominantly displayed an intense ELSD response with weak or absence of UV absorption peaks indicating that they could be very rich in terpenoids and/or fats and void of any compounds containing UV chromophore such as phenolic compounds, flavonoids or lignans etc. GC-MS profiling showed relatively similar chromatograms for these samples indicating intense peaks in the retention time range of 41–43 minutes. The corresponding mass fragmentation spectra of these peaks were detected and identified as long chain fatty acids, waxes and triterpenoids by searching each corresponding mass spectrum in the NIST library database. On the other hand, samples harvested from Southern part of Nigeria indicated strong UV-ELSD responses. Three triterpenes: mangiferonic acid, ambonic acid and a mixture of α-amyrin with mangiferonic acid alongside xanthones; 1,3,7-trihydroxy-4,8-di-(3-methylbut-2-enyl) xanthone, a previously undescribed xanthone and 1,3,7-trihydroxy-2,8-di-(3-methylbut-2-enyl) xanthone were isolated and their structures determined by NMR and LC-MS [30].

2.20 Canada

Propolis extracts showed polyphenol and flavonoid contents and ESI-MS fingerprints enabled the detection of the chemical composition of the propolis extracts. Chrysin, pinocembrin, clerodane diterpenoid, dehydrated ellagic acid, dihydrokaemferid, 3-prenyl-4-(2-methylproprionyloxy) cinnamic acid, palmitic acid, naringenin, isopentyl caffeate, acacetin, benzyl caffeate and caffeic acid phenethyl ester were amongst the identified compounds [31,32]. The HPLC analysis revealed the occurrence of quercetin and its methyl ethers such quercetin-3-methyl ether, quercetin-3'-m ethyl ether, quercetin-3,3 '-dimethyl ether, quercetin-7,3'-dim ethyl ether, quercetin-3,7-dimethyl ether and quercetin-3,7,3'-trimethyl ether. GC-MS revealed pinocembrin, pinobanksin, pinobanksin-3-acetate, chrysin, galangin, kaempferol, p-coumaric and cinnamic acids, acetophenones and dihydrochalcones with p-hydroxyacetophenone, benzyl hydroxybenzoate and cinnamic acid being most abundant [33, 31].

2.21 Guinea Bissau

LC/DAD/ESI-MS led to the identification of eight compounds, mostly isoflavonoids, resembling Nigerian and Brazilian red propolis. The compounds identified were isoflavone-C-glycoside, hydroxy-genistein-C-glycoside, genistein-C-glycoside, vesticarpan, vestitone, sativanone, mucronulatol, and trihydroxy-methoxyisoflavone. The total phenolics, flavone/flavonol, and flavanone/dihydroflavonol contents were measured by spectrophotometry method [34].

2.22 Turkey

LC-MS/MS of 11 raw propolis samples collected from different geographical areas in Turkey led to the detection and grouping of the following compounds. Flavones: apigenin, luteolin, emodin. Isoflavones: daidzein, biochanin. Phenolic acids: 3-4 dimethoxycinnamic acid, cafeic acid, p-coumaric acid, myristic acid, syringic acid, rosmarinic acid, chlorogenic acid, ferrulic acid, sinapic acid, protocatheuic acid, gallic acid, benzoic acid, trans-Cinnamic acid, ellagic, ferulic acid, trans-3-Hydroxy-cinamic, acid, caffeic acid phenethyl ester, protocatechuic acid. Flavanols: cathechin, kaempherol, quercetin. Flavanones: naringenin, pinobanksin, pinostrobin, hesperidin [35]. Comprehensive analysis of phenolic profiles of botanically different subtypes of Turkish 36 propolis samples were performed using UHPLC–LTQ/Orbitrap/MS/MS. Benzoic acid and its derivatives: p-Hydroxybenzoic acid, vanillin. Phenolic acids and their derivatives: protocatechuic acid, caffeic, p–coumaric acid, ferulic acid, cinnamic, 3,4-dimethyl-caffeic acid, p–coumaroylquinic acid, prenyl caffeate, caffeic acid phenethyl ester, caffeic acid cinnamylester, p–coumaric methyl butenyl ester, benzyl caffeate, methyl-O-caffeoylquinate. Flavonols: quercetin, rhamnetin, kaempferol, isorhamnetin, kaempferide, bis–methylated quercetin, galangin, hesperetin. Flavanonols: pinobanksin, pinobanksin–5–methyl-ether–3–O–acetate, pinobanksin–3–O–acetate, pinobanksin–5–methyl-ether, pinobanksin–3–O–propionate, pinobanksin–3–O–butyrate, pinobanksin–3–O–pentanoate. Flavones: luteolin, apigenin, acacetin, chrysin, dihydroxyflavone. Flavanones: sakuranetin, naringenin, liquiritigenin, pinostrobin, pinocembrin. Glycosides: rutin, apigetrin (Apigenin-7-O-glucoside), quercetin 3-O-galactoside. Phenolic glycerides: caffeoylglycerol, coumaroylferuoyl glycerol, dicoumaroyl acetyl glycerol, dicaffeoyl acetyl glycerol, acetyl-coumaroyl—feruloylglycerol, acetyl-diferuloylglycerol [36]. GC-MS analysis revealed some of the compounds above together with terpenoids, steroids, sugars and aliphatic acids [37].

2.23 USA

GC-MS chemical profiling the propolis samples was performed and the samples classified into several groups as follows: (1) rich in cinnamic acid derivatives, (2) rich in flavonoids, and (3) rich in triterpenes. Major compounds were: aromatic acids and esters such as benzoic, cinnamic, p-coumaric, and ferulic acids and benzyl-p-coumarate. flavonoids such as pinocembrin, pinobanksin, pinobanksin-3-O-acetate, chrysin, galangin, and pinocembrin chalcone. Triterpenes mainly oleanolic and oleanonic acids and 3-oxo-6β-hydroxy-lup-20(29)-en-28-oic acid isolated [38]. A comprehensive GC-MS analyses showed important amounts of fatty acids, benzoic acid and their derivatives while HPLC determination of flavonoids, aromatic acids, and esters revealed caffeic acid, p-Hydroxy benzoic acid, ferulic acid, p-Hydroxy acetophenone, p-Coumaric acid, cinnamic acid, 1,1-dimethylallyl caffeate, phenylethyl caffeate, isosakuranetin, pinocembrin, chrysin, galangin, cinnamyl cinnamate [39].

3. Bioactive Compounds of Propolis

However, no clear-cut distinction can be done between propolis composition from different zones, the compounds isolated can be classified into two mutually unexclusive groups: those from temperate and those from tropical zones.

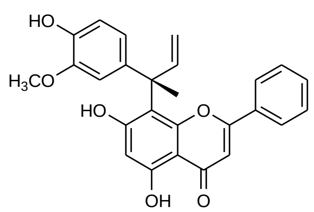
3.1 Compounds Isolated from Propolis from Temperate Regions

In the temperate zones all over the world, the main source of bee glue is poplar tree, mainly the black poplar *Populus nigra* [40]. For this reason, propolis from temperate regions contains the typical poplar bud phenolics such as flavonoid aglycones, phenolic acids and their esters [5]. The quantity of flavonoids is used as a criterion to evaluate the quality of temperate propolis [21]. The compounds found in propolis from temperate regions are mainly flavanones, flavones, flavanonols, flavonols, isoflavones, chalcones, isodihydro flavones, dihydrochalcones, flavans, neoflavonoids, isoflavans, aurones, pterocarpans, coumarins, lignans, phenolic acids and their derivatives [5,21].

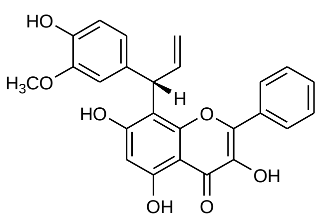
3.2 Compounds Isolated from propolis from Tropical and Subtropical Regions

The bee glue from different tropical regions is chemically diverse and devoid or containing only traces of poplar constituents [40]. They are rich mainly in terpenes and their derivatives but might equally contain other constituents including xanthones, steroids, lignans, prenylated derivatives of p-coumaric acids, different phenolics, flavonoids and benzophenones [1,40, 41]. However, data about the chemical composition and biological activity of propolis from the subtropical areas are limited.

3.3 Structures of Flavones and Flavonols Isolated from Temperate Propolis



(7″ R)-8-[1-(4′-hydroxy-3′-methoxyphenyl) prop-2-en-1-yl] chrysin [42]



(7″R)-8-[1-(4′-hydroxy-3′-methoxyphenyl) prop-2-en-1-yl] galangin [43]

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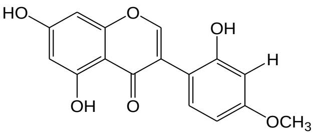
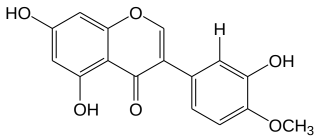
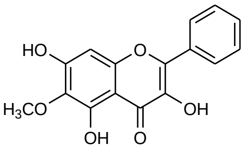
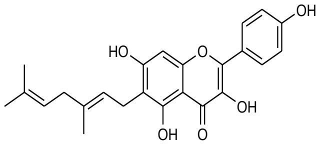
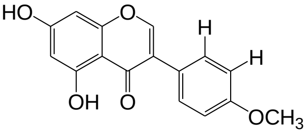
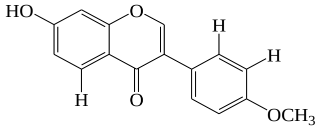

2'-hydroxybiochanin A [45]

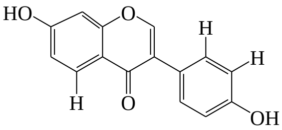

calycosin [46]

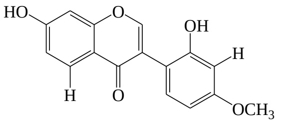

Alnusin [43]


Macarangin [24]

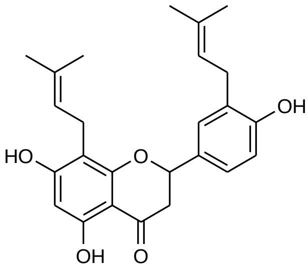

Biochanin A [45]

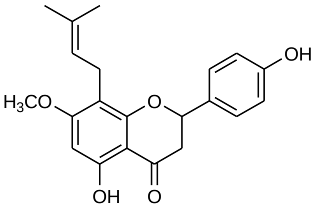

Formononetin [45]

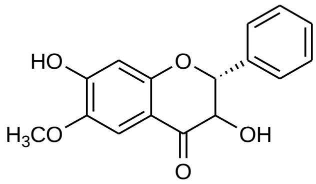

daidzein [45]

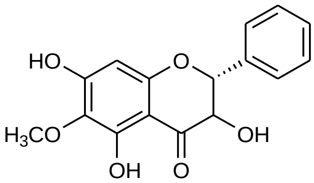

Xenognosin B [45]

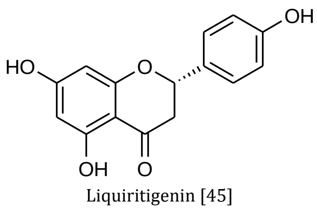
3.4 Some Flavanones and Flavanonols Isolated from Temperate Propolis

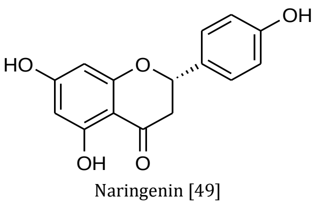

8-prenylnaringenin [43]

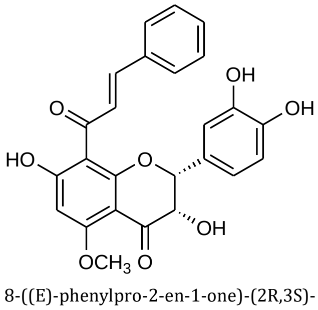

7-O-methyl-8-prenylnaringenin [45]

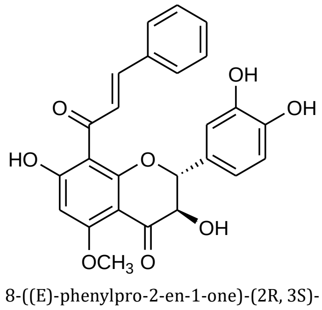

(2R,3R)-3,7-dihydroxy-6-methoxyflavone [47]

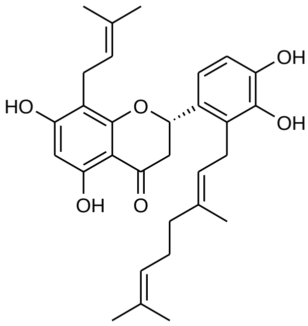

Alnustinol [48]

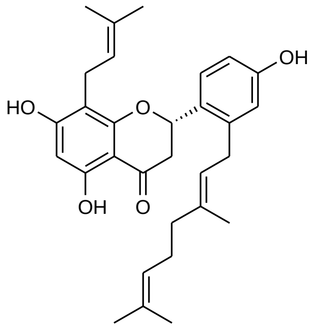

Liquiritigenin [45]

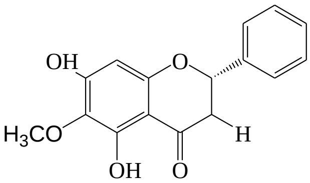

Naringenin [49]

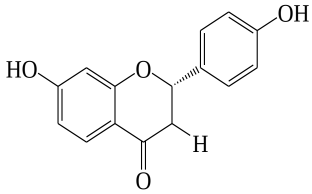

8-((E)-phenylpro-2-en-1-one)-(2R,3S)-5-methoxycatechin [3]

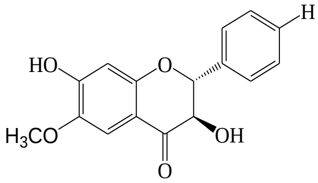

8-((E)-phenylpro-2-en-1-one)-(2R, 3S)-5-methoxycatechin [3]

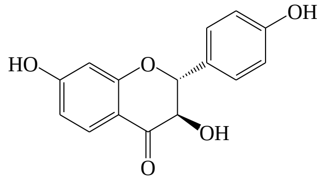

Solophenol A [43]


Sophoraflavanone A [43]

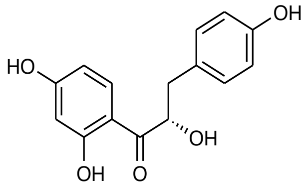

(2S)-dihydrooroxylin A [44]

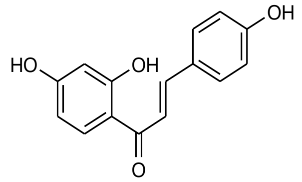

(2S)-liquiritigenin [48]

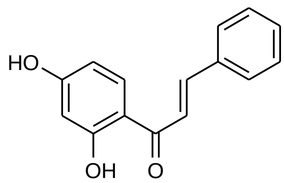

(2R,3R)-3,7-dihydroxy-6-methoxyflavanone [45]

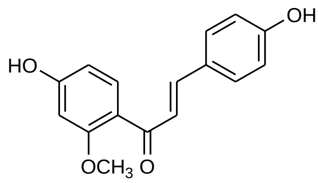

Garbanzol [49]

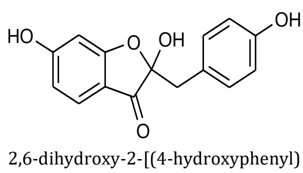
3.5 Some Chalcones and Aurones Isolated from Temperate Propolis

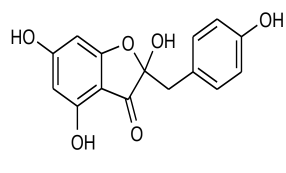

(αS)-α2′,4, 4′-tetrahydroxydihydrochalcone [43]


Isoliquiritigenin [49]

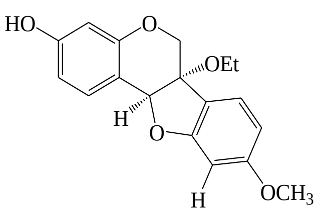

2′,4′-dihydroxychalcone [43]

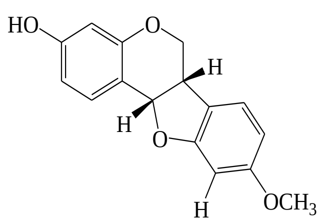

Isoquitigenin [46]


2,6-dihydroxy-2-[(4-hydroxyphenyl) methyl]-3-benzofuranone [45]


Maesopin [45]

3.6 Some Pterocarpans Isolated from Temperate Propolis


(6aS,11aS)-6a-ethoxymedicarpan [43]


(6aS,11aS)-medicarpan [48]

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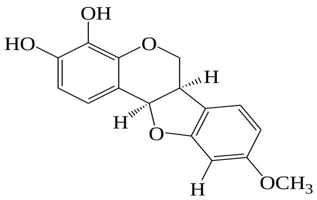
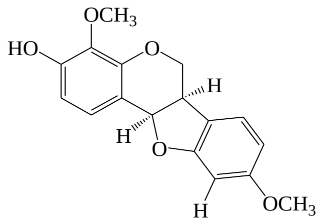
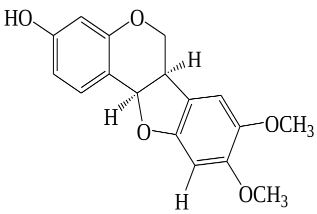
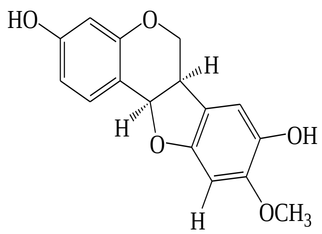
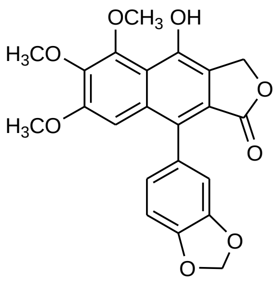

(6aR,11aR)-3,4-dihydroxy-9-methoxypterocarpan [48]

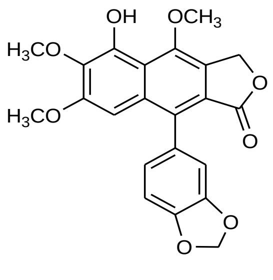

(6aR,11aR)-4-methoxymedicarpan [49]

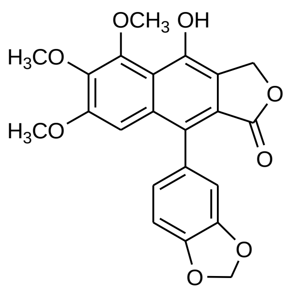

(6aR,11aR)-3-hydroxy-8,9-dimethoxypterocarpan [45]

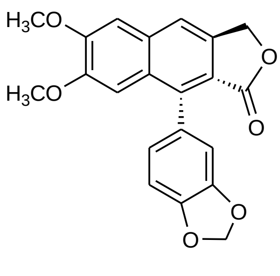

(6aR,11aR)-3,8-dihydroxy-9-methoxypterocarpan [45]

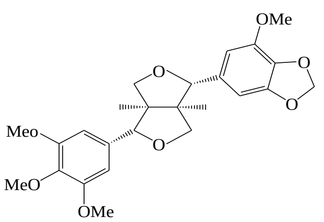
3.7 Some Lignans Isolated from Temperate Propolis

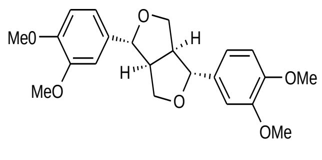

6-methoxydiphyllin [24]


6-hydroxyjustidin A [24]

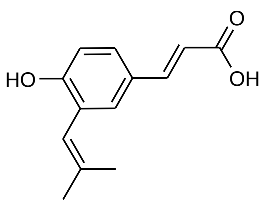

6-methoxydiphyllin [24]

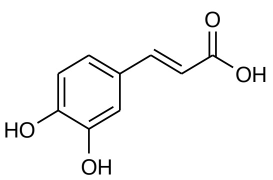

Tetrahydrojustidin B [24]

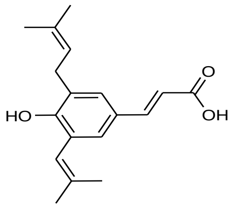

Sesartenin [45]

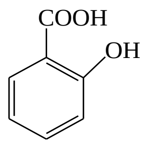

(+)-pinoresinol dimethyl ether [45]

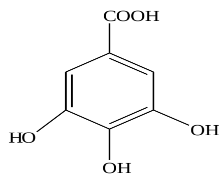
3.8 Some Phenolic Acids and Their Esters Isolated from Temperate Propolis

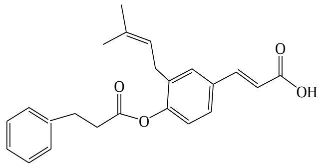

3-prenyl-4-hydroxylcinnamic acid [43]

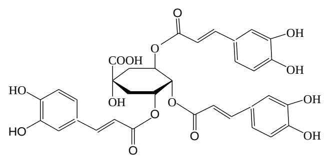

Caffeic acid [43]

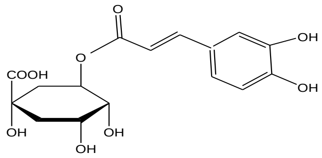

3,5-diprenyl-4-hydroxylcinnamic acid [43]

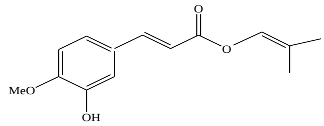

Salicylic acid [43]

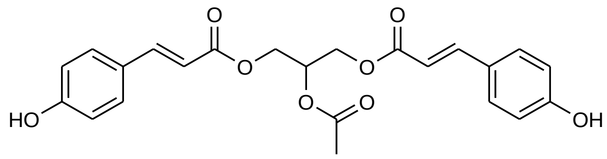

Gallic acid [43]

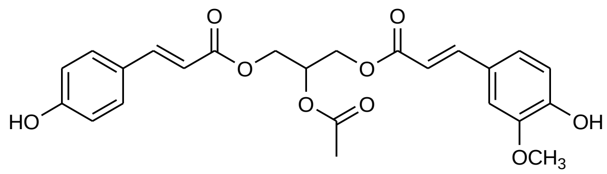

Baccharin [44]


3,4,5-Tricafeoylquinic acid [43]

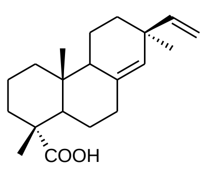

Chlorogenic acid [43]

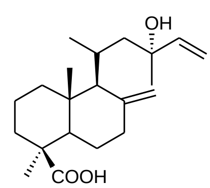

Prenyl ferulate [43]

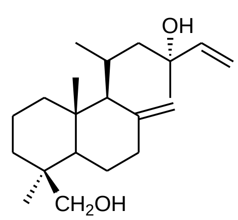

2-acetyl-1,3-dicoumaroylglycerol [50]

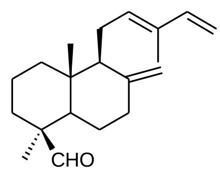

2-acetyl-1-coumaroyl-3-feruloylglycerol [50]

3.9 Some Terpenoids and Steroids Isolated from Tropical Propolis


Pimaric acid [51]


13-epi-isocupressic acid [51]


13-epi-torulosole [51]


Commurale [51]

https://doi.org/10.30799/jnpr.079.19050203

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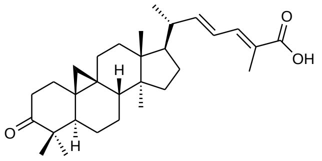
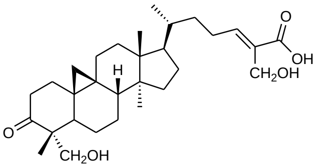
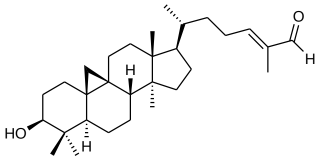


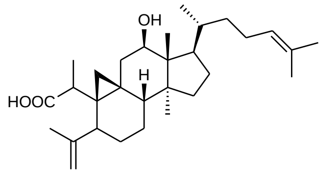
(22Z,24E)-3-oxocycloart-22,24-dien-26-oic acid [52]



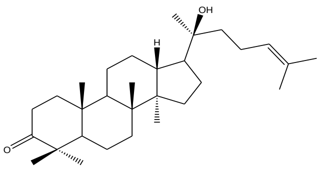
(24E)-3-oxo-27,28-dihydroxycycloart-24-ene-26-oic acid [52]



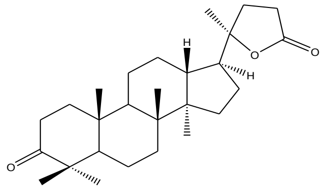
(24E)-3β-hydroxycycloart-24-en-26-al [52]



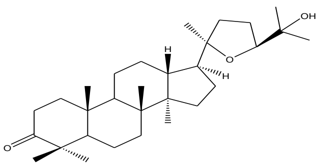
3,4-secocycloart-12-hydroxy-4(28)-24-dien-3-oic acid [52]



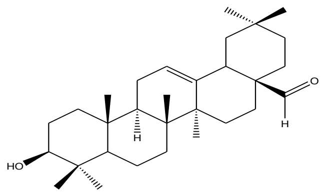
Dipterocarpol [41]



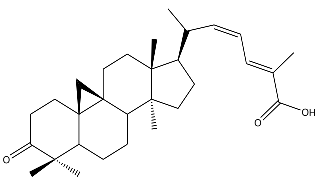
Cabralealactone [41]



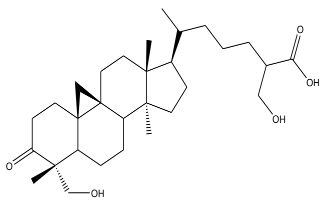
Ocotillone I [41]



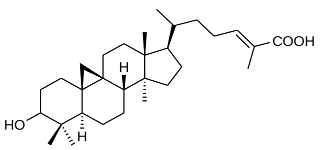
Oleanolic aldehyde [41]



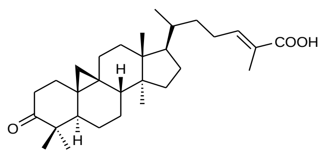
(22*Z*,24*E*)-3-oxocycloart-22,24-dien-26-oic acid [52]



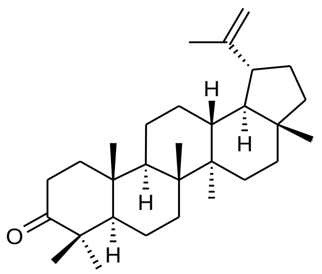
(24*E*)-3-oxo-27,28-dihydroxycycloart-24-en-26-oic acid [52]



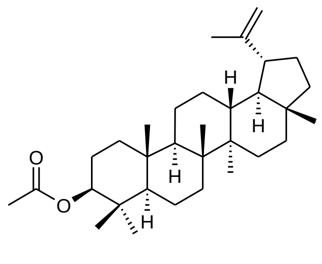
Isomangiferolic acid [52]



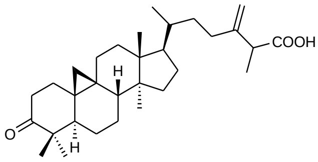
Mangiferonic acid [52]



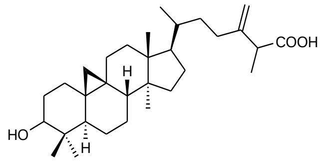
Lup-20(29)-3-one [53]



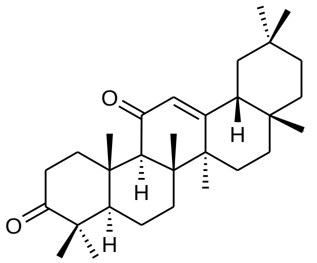
Lupeol acetate [53]



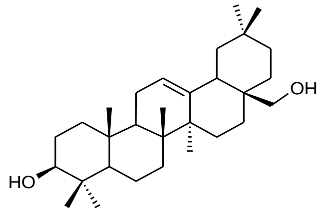
Ambonic acid [20]



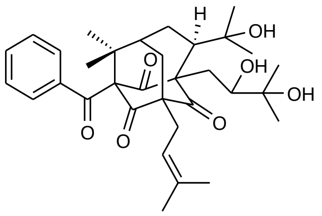
Ambolic acid [20]



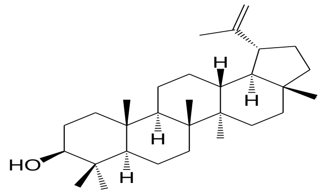
18-iso-olean-12-en-3,11-dione [53]



Olean-12-en-3β,28-diol [54]

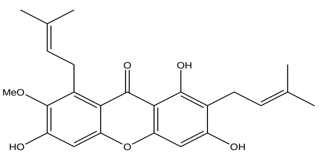


Phlogucinonone [55]

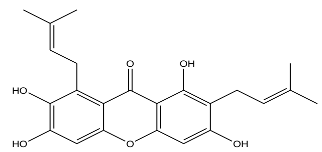


3β-hydroxylup-20(29)-ene [54]

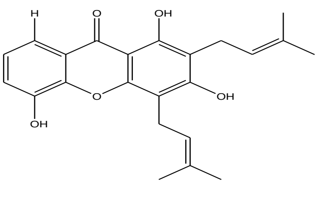
3.10 Some Xanthones Isolated from Tropical Propolis



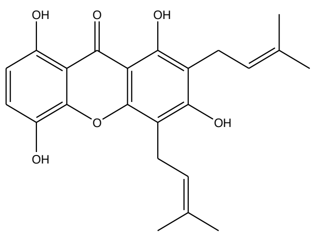
α-mangostin [41]



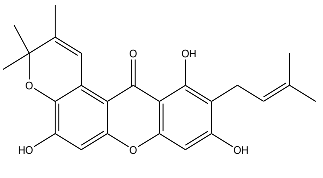
γ-mangostin [41]



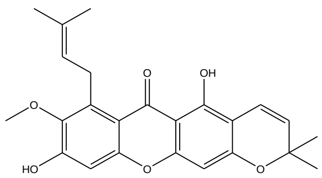
8-deoxygartanin [41]



Gartanin [41]



Garcinone B [41]



Mangostanin [41]

4. Conclusion

The compounds are usually subjected directly to bioassays or used as starting material for synthesis in view of obtaining their derivatives or synthetic analogues with enhanced biological activities. The pharmacological action of natural products has significant acceptance and their use is becoming more popular in the form of food supplements, complementary and alternative medicine. Currently, the World Health Organization (WHO) estimates that approximately 80% of the inhabitants of planet have recourse to traditional medicines, using natural products for primary health care.

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