

9.1. *PISTACIA* L.

The constituents of several *Pistacia* species, and in particular *Pistacia vera* (pistachio) have been extensively studied.

Proximate Composition

Anon (1917) reported the following composition of the kernels of the nuts of *Pistacia vera*: water, 7.4; crude proteins, 22.7; fat, 51.1, carbohydrates (by differences), 13.0; cellulose, 2.5; and ash, 3.3%. The fruits of *Pistacia vera* and *Pistacia terebinthus* contained an average of water 4, 5.9; fat 58.9, 42.0; protein 21.5, 9.7; N-free extract 10.8, 14.2; crude fiber 2.0, 23.7 and ash 2.4, 2.1% respectively (Yazicioglu, 1950).

The mineral composition of fruits of pistachio (*Pistacia vera* L.) selections from Turkey were: 3.04-4.20% N, 0.168-0.441% P, 0.348-1.084% K, 0.189-2.819% Ca, 0.762-2.445% Mg, 11, 14-330.36 ppm Fe, 2.36-4.82 ppm Mb, 4.23-31.49 ppm Zn and 0.43-22.71 ppm Cu. Their leaf nutrient contents were 1.12-2.18% N, 0.006-0.132% P, 0.44-2.47% K, 2.82-6.35% Ca, 2.97-4.67% Mg, 25.3-314.8 ppm Fe, 6-67 ppm Mn, 11.0-33.2 ppm Zn and 4.75-91.79 ppm Cu (Kazankaya *et al.*, 2008).

Lipids

The fatty acids of the oils of inner and outer parts of *Pistacia terebinthus* seeds were as follows: stearic 5.4, 4.2; palmitic 14.2, 21.5; oleic 41.5, 45.7; palmitoleic 14.3, 18.0 and linoleic 24.5, 8.6% respectively (Bilecan and Baykut, 1964). The fruits and seeds of *Pistacia terebinthus* and *Pistacia vera* contained saturated acids 29.06, 20.3; oleic acid 58.4, 62.8 and linoleic acid 21.1, 17.0% respectively (Yazicioglu, 1950). The fatty acid composition of oil of Ohadi variety of pistachio nuts (*Pistacia vera*) of Kerman, Iran, as compared with other varieties is very different e.g. oleic acid is less (49.5 vs. 69.6%) and palmitic and linoleic acids are more (13.4 vs. 8.27% and 31.8 vs. 19.8% respectively) (Shokraii, 1977). In pistachio grown in various areas of Southern Turkmenia farms with kernels containing 60-63 or 64-66.2% oil and in pistachio grown in Southern Tadjikistan farms with kernels having 59-61.4% oil were found. The oil contained six fatty acids: C_{16:0}, C_{16:1}, C_{18:0}, C_{18:1}, C_{18:2} and trace amounts of C_{18:3}. The oleic, linoleic and palmitic acid contents varied, depending on the site; they were 53.6-77.7, 12.6-35.5 and 8-12% of the oil respectively (Eramkov *et al.*, 1982). The fatty acid analyses of Iranian pistachio oils (*Pistacia vera*) showed a significant difference between varieties in their fatty acids composition. Palmitic acid ranged from 7.1 to 8.6%. Linolenic acid content was between 15.2 and 38.6%. Oleic acid ranged from 53.0 to 77.6%. The results showed that the major molecule species was triolein (OOO) with 14.8 - 46.7% of the total. Dioleoylacyl glycerols (OOO, LOO, and OLO) species were found in important amounts (9.1-11.7%), and the amount of triacyl glycerol with three saturated fatty acids was rare (Mohamadi, 2006). The yield of kernel oils of two varieties (Uzum and Siirt) of *Pistacia vera* grown in different regions of Turkey varied between 57.1-58.9 and 56.1-62.6% respectively. Fourteen fatty acids representing about 99% of the total oils were characterized. Oleic acid (55.4-62.6% and 60.7-65.5%, respectively) was the main fatty acid

component in both varieties. Pentadecanoic acid, (*Z*)-7-hexadecenoic acid, margaric acid, (*Z*)-7-octadecenoic acid, arachidic acid, 11-eicosenoic acid, and behenic acid were detected in both varieties (Satil *et al.*, 2003). Fat contents of 4 *Pistacia vera* samples ranged from 48.9 to 56.2%. Palmitic acid (10.95 to 16.26%) was the major fatty acid in the samples. The main monounsaturated and polyunsaturated fatty acids in the kernels of all varieties were found to be oleic acid (51.28 to 58.38%) and linolenic acid (28.34 to 37.76%), respectively (Roozban *et al.*, 2006). Two phytyglycolipids (PGI₁, PGI₂) were isolated from the seeds of *Pistachia vera*, which in equal composition of their long-chain bases, sugar components, and fatty acids showed a close similarity with the phytyglycolipids of other plant seeds. The saccharide chain contained inositol, glucuronic acid, glucosamine, mannose, galactose and arabinose. The major fatty acids were the saturated 2-hydroxy C₂₂, C₂₃ and C₂₄ acids; the major long-chain bases were dehydrophytyosphingosine and phytyosphingosine (Imre, 1974).

The fatty acids identified in the oil kernel of *Pistacia eurycarpa* are as follows: the major compounds were 18:2 (9, 12; 52.2%), oleic (17.7%), palmitic (16.7%), stearic (4.3%), palmitoleic (2.0%), 11-eicosenoic acid (1.4%), and heptadecene-8-oic (1.3%) acids. In addition, 13:0 (0.3%), 17:1 (9, 10; 0.2%), 17:0 (0.1%), 20:0 (0.4%), 22:1 (13, 0.1%), 22:0 (0.2%), ricinoleic, arachidic, myristic, 9,10-methylene hexadecanoic, behenic, erucic, 2-ethyl hexanoic acids were detected in amounts less than 1%, whereas octanoic, decanoic, lauric and pentadecanoic acids were detected in trace amounts (Kafkas *et al.*, 2007).

Essential Oils

Pistacia species are often infected by gall-forming insects. The resins (and in particular their volatile constituents) exuded from the galls and trunks of several species have been investigated. The following are examples of these species and their volatile constituents:

1. *Pistacia chinensis* Bunge: Thirty six components were identified from the plant cultivated in Egypt. The major fraction of the oil was monoterpenoid hydrocarbons (47.68%); of which α -pinene (13.95%), *p*-cymene (12.61%) and sabinene (11.22%), were the major components (Zaghloul and Abdel-Rahman, 2006). The leaf volatile oil of the Chinese medicinal herb (*Pistacia chinensis*) has been reported to contain 99 compounds, which mainly included many kinds of long-chain aliphatic hydrocarbons and aromatic alcohols (Yuan *et al.*, 2005). A total of 58 compounds was identified in the leaf oils of the plant collected from five locations in China, and a relatively high variation in their contents was found. The major compounds include β -phellandrene (0.54-53.86%), α -pinene (4.74-54.44%), β -pinene (0.49-42.90), caryophyllene (5.64-20.01%), *cis*-ocimene (tr-43.93%), eudesmadiene (0-15.06%) and camphene (tr-20.57%). Cluster analysis classified the leaf oils into two chemotypes; one rich in α -pinene and β -pinene, and the other rich in phellandrene (Zhu *et al.*, 2006a).
2. *Pistacia eurycarpa* Yalt.: Both α - and β -pinenes were the major constituents of the essential oil of the mastic (Demirci *et al.*, 2001).
3. *Pistacia integerrima* Stew. ex Brandis: The essential oil of the galls of the stem was rich in α -pinene (Karimullah *et al.*, 1945; Ansari *et al.*, 1991), β -pinene, β -phellandrene, γ -pinene, γ -terpinene, limonene, α - and β -terpineol and α - and β -ocimene (Ansari *et al.*, 1991, 1993a). The volatile constituents of the galls and stem bark of the plant contained 38 components of which 91% were found to be monoterpenes. The bark oil was found to contain 22 constituents of which 82.3% were monoterpenes. The major constituents of the gall oil were α -pinene (34.5%), sabinene (14.0%), β -pinene (12.6%), and limonene (9.1%). The main components of the bark oil were terpinen-4-ol (30.3%), α -terpineol (13.7%) and α -pinene (14.0%) (Ansari *et al.*, 1998).

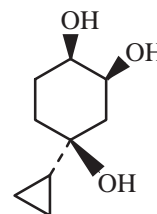
4. *Pistacia mutica*: Twenty-one compounds, accounting for 82.95% of the total oil (0.75% yield) were identified in the essential oil of leaves. The main constituents of the essential oil were α -pinene (25.25%), myrcene (9.99%), γ -cadinene (8.37%) and *trans*-caryophyllene (8.08%). Twenty-six compounds, accounting for 93.21% of the total oil (1.25% yield) were identified in the essential oil of the fruits. The main constituents of the fruit oil were α -pinene (21.47%), myrcene (15.90%), terpinolene (11.48%) and limonene (7.76%) (Moghtader, 2010).
5. *Pistacia palaestina* Boiss. (*Pistacia terebinthus* L. var. *palaestina* (Boiss.) Engl.): The analysis of the essential oils of leaves, galls produced by *Baizongia pistaciae* (gall forming insect) and ripe and unripe fruits of the plant, collected in Jordan are reported. Both qualitative and quantitative differences between different parts of the plant were observed. The oil was rich in sesquiterpenes, and the main constituents were α -pinene (63.1%) and myrcene (13.3%) in the leaves and α -pinene (49.4%), sabinene (22.8%), and limonene (8.1%) in the galls. (*E*)-Ocimene (33.8-41.3%), sabinene (20.3-24.1%), and (*Z*)-ocimene (3.8-13.0%) were the main ones in both unripe and ripe fruits. Sesquiterpenes have been detected in small quantities in leaves and fruits and in trace amounts in galls (Flamini *et al.*, 2004).
6. *Pistacia terebinthus* L.: Earlier investigation of the essential oil of the resin revealed that it consists chiefly of pinene, dipentene and borneol which occurs free and as acetate (Tsatse, 1937). Fernandez *et al.* (1998) identified 36 components (accounting for 34.7%) of the essential oil of the aerial parts. The dominant constituents were the monoterpene hydrocarbons *trans*-ocimene (15.0%), α -pinene (7.9%), and an unknown terpene (17.7%). Lesser amounts of T-muurolol (2.6%), *trans*-nerolidol (1.5%) and β -pinene (1.5%) were identified. The essential oil contents (dry weight basis) of young shoots, flowers, unripe and ripe fruits of the turpentine tree (*Pistacia terebinthus*) were determined as 0.74, 0.70, 0.54 and 0.73% respectively (Couladis *et al.*, 2003). The main components identified (the identified components represent 90.7, 96.1, 98.0 and 99.0% of the respective oils) were limonene (3.0, 9.4, 34.2 and 32.8%), α -pinene (5.3, 12.4, 15.6 and 5.3%), β -pinene (1.4, 8.0, 11.5 and 22.5%) and germacrene D (trace, 19.9, 3.5 and 4.6%) (Couladis *et al.*, 2003). The oil yields obtained from different aerial parts of *Pistacia terebinthus* range from 0.01-1.5%. α -Pinene was the main constituent of each of the oils with the twig oil containing the highest concentration of 66.6%. In fruitful twigs the α -pinene concentration was 54.8% while in the leaf oil it was 16.4%. The other major component was β -pinene, the level of which in the oils of fruitful twigs and leaves was 22.5% and 13.5% respectively (Usai *et al.*, 2006).
7. *Pistacia terebinthus* var. *chia* (Chios turpentine): The essential oil contained 101 components, 81 of which were identified. The main components were α -pinene (39.6%), β -pinene (19.5%), sabinene (6.5%), terpinen-4-ol (3.8%) and δ -3-carene (3.3%) (Papageorgiou *et al.*, 1999).
8. *Pistacia vera* L.: Fifty-four compounds were identified from the hulls of the fruits, with α -pinene (54.40%) being the major constituent (Kusmenoglu *et al.*, 1995). Chahed *et al.* (2008) studied the composition of hull essential oil during fruit formation and ripening. Monoterpene hydrocarbons, mainly represented by α -pinene (15.0-47.4%) and terpinolene (32.2-51.1%) were prominent during all fruit development, reach 90.3% of the oil at full ripeness (Chahed *et al.*, 2008). Twenty-six compounds, accounting for 98.1% of the essential oil obtained from the fruit husk were identified. The main class of compounds was hydrocarbon monoterpenes (96.0%). The major constituents were limonene (35.1%), α -pinene (28.7%) and α -terpinolene (21.1%) (Nickavar *et al.*, 2004). The essential oil of the gum of *Pistacia vera* contained about 89.67% monoterpenes, 8.1% oxygenated

monoterpenes and 1.2% diterpenes. α -Pinene (75.6%), β -pinene (9.5%), *trans*-verbenol (13.0%), camphene (1.4%), *trans*-pinocarveol (about 1.20%) and limonene (1.0%) were the major components (Alma *et al.*, 2004). Two *p*-menthane monoterpenes (**51**,**52**) with the unique feature of an extra C-9, C-10 linkage to give a cyclopropane ring have been found in the oleoresin of *Pistacia vera* (Mangoni *et al.*, 1982), *Trans*-verbenol, (-)-pinocarveol and terpinolene were also isolated from the resin (Monaco *et al.*, 1982). The possible defence role of monoterpenes against gall forming aphids (insects) has been discussed by Monaco *et al.* (1982). Since gall-free species of *Pistacia atlantica* as well as *Pistacia vera* have been found to contain monoterpenes, it is possible that these compounds play a specific repellent role against aphids and are responsible for the lack of galls (Monaco *et al.*, 1982).

9. *Pistacia weinmannifolia* J. Pisson ex Franch.: Thirty-four compounds were identified from the leaf oil (0.91%). The oil was dominated by an α -pinene (38.8%) and myrcene (17.4%). The oil also contained moderate amount of camphene (5.2%) and β -pinene (8.1%) (Dung *et al.*, 2000). Zhou (2008) reported the identification of 29 compounds (accounting for 99.54% of its total content) from the leaf oil.



51 (+)-9,10-Cyclopropylterpinen-4-ol



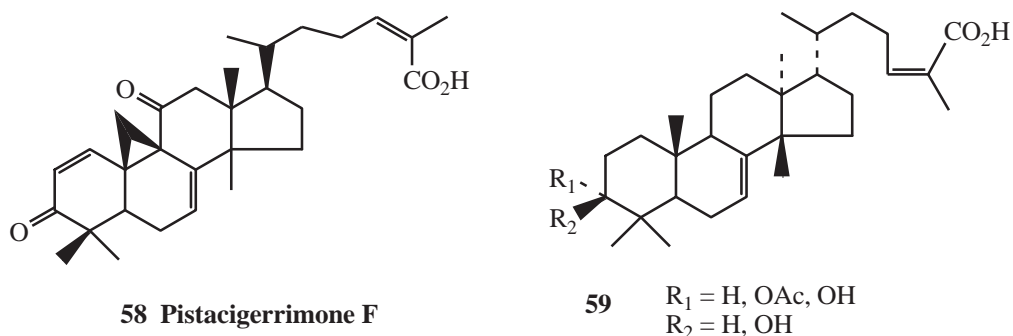
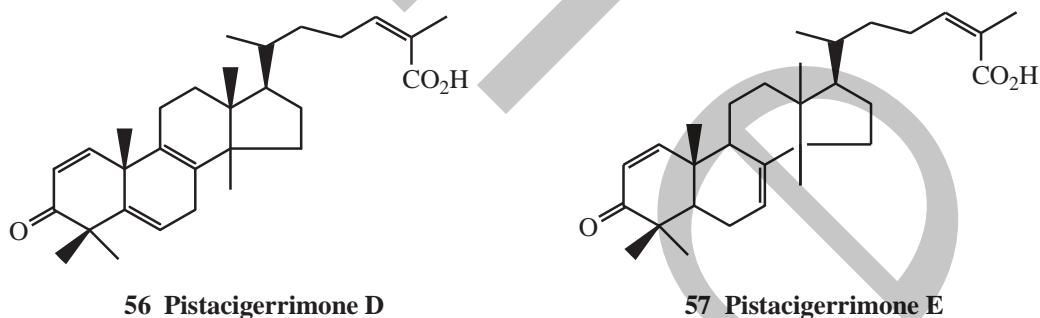
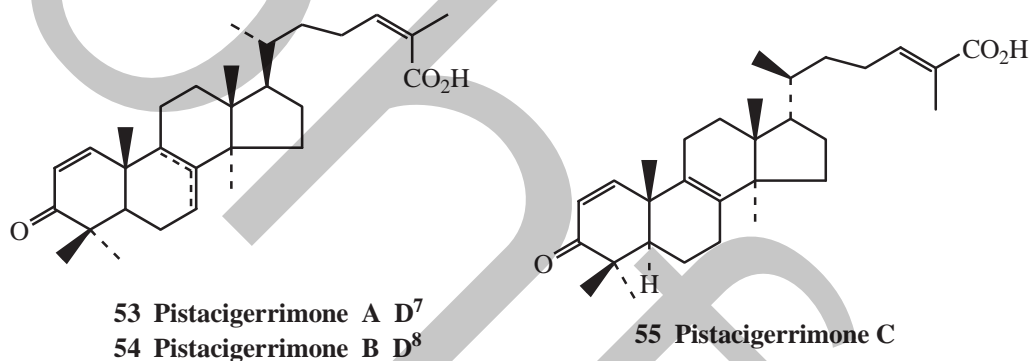
52 (+)-9,10-Cyclopropylterpin-2,4-diol

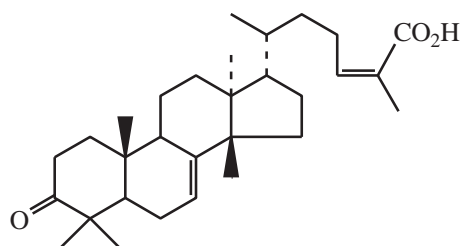
Triterpenes, Sterols and Related Substances

The following are examples of the triterpenes and sterols, isolated from some *Pistacia* species:

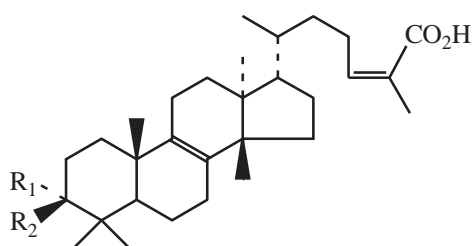
1. *Pistacia chinensis* Bunge: The seed oil contains the following compounds: β -sitosterol, stigmasterol, Δ^5 -avenasterol, α -spinasterol, campesterol, cholesterol, gramisterol, α -amyrin and lupeol (Li *et al.*, 1989).
2. *Pistacia integerrima* Stew.: The galls contain several triterpene acids *viz.* pistacienonic acid A, pistacienonic acid B, (Rao and Bose, 1956-1957), pistacigerrimone A (**53**), pistacigerrimone B (**54**), pistacigerrimone C (**55**) (Ansari *et al.*, 1992, 1993b), pistacigerrimone D (**56**), pistacigerrimone E (**57**) and pistacigerrimone F (**58**) (Ansari *et al.*, 1994). *n*-Decan-3'-ol-yl-*n*-eicosanoate, *n*-octadecan-9,11-diol-7-one and 3-oxo-9 β -lanost-1,20(22)-dien-26-oic acid along with β -sitosterol were also isolated from the galls (Ahmad *et al.*, 2010).
3. *Pistacia mexicana*: Masticadienoic acid, sitosterol and an aliphatic ketone were isolated from the bark (Dominguez *et al.*, 1974).
4. *Pistacia palaestina*: Nineteen triterpenes of structures (**59-70**) were isolated from galls produced by *Pemphigus cornicularius* on the plant (Caputo *et al.*, 1979).
5. *Pistacia terebinthus*: The plant is known to produce different galls depending on the insects *Pemphigus* species (Monaco *et al.*, 1974). The following neutral triterpenes and triterpene acids were isolated from the resinous exudates of the galls produced on the leaves by *Pemphigus corniculatus*: masticadienonic acid (**60**), isomasticadienonic acid (**62**), isomasticadienolic acid, masticadienolic acid (Caputo and Mangoni, 1970), tirucallol (**71**), oleanonic aldehyde (**67**), oleanolic aldehyde (**64**), dipterocarpol (**70**), dammarediol (**69**), 26-hydroxytirucallone (**72**), erythrodiol and isomasticadienol (**73**)

- (Monaco *et al.*, 1973a). In addition, the galls induced by *Pemphigus urticulatus* contained methyl dihydroisomasticadienonate (**74**), dihydromasticadienediol (**75**) and methyl dihydro-3-epidihydroiso-masticadienolate (**76**) (Caputo *et al.*, 1975). The resin of *Pistacia terebinthus* also contains a bicyclic triterpenoid (**77**) representing an apparent trapped intermediate of squalene 2,3-epoxide cyclization (Boar *et al.*, 1984). The galls which are produced on the young leaves by *Pemphigus semilunarius* have been found to contain some of the above triterpenoids (Monaco *et al.*, 1974). Lupeol, cycloartenol and β -sitosterol (free and esterified with polyhydroxy acids) were isolated from the leaves and small branches of the plant (Tabacik-Wlotzka *et al.*, 1967). Three polyisoprenoid alcohols have been also isolated from the plant (Tabacik-Wlotzka and Pistre, 1967).
6. *Pistacia vera*: Triterpenes (**78-80**) were isolated with several triterpene acids and C-3 β -equatorial neutral triterpenes from the oleoresin of the plant (Caputo *et al.*, 1978). A triterpene triol $3\beta,11\alpha,13\beta$ -trihydroxyoleanane (**81**) was identified in the oleoresin from trunks of uninfected *Pistacia vera* (Monaco *et al.*, 1982). The unsaponifiable fraction of pistachio seed oil contains C_{14-32} paraffins, squalene, some terpenic alcohol, β -sitosterol and stigmasterol (Curro and Calabro, 1968).

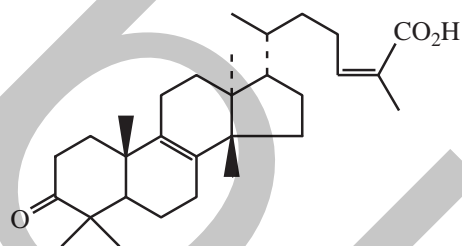




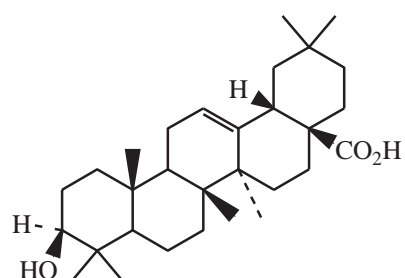
60 Masticadienonic acid



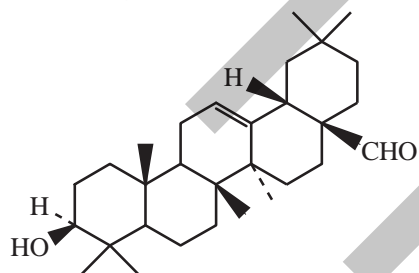
61
 $R_1 = \text{H, OAc, OH}$
 $R_2 = \text{H, OH}$



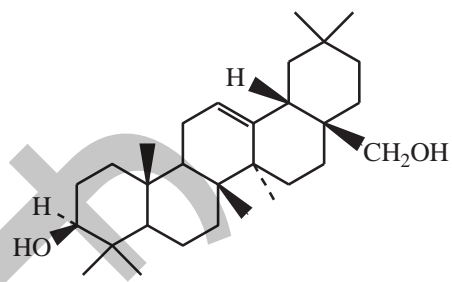
62 Isomasticadienonic acid



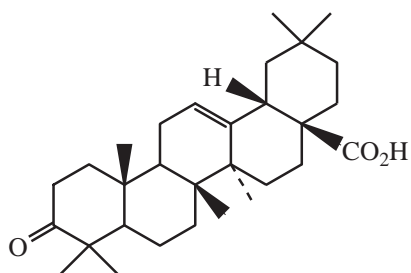
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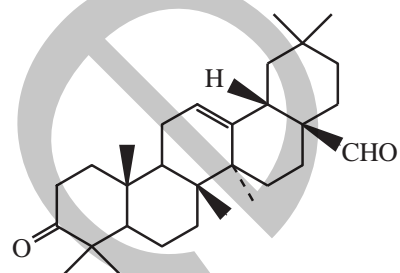
64 Oleanolic aldehyde



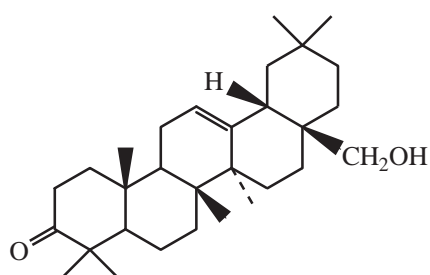
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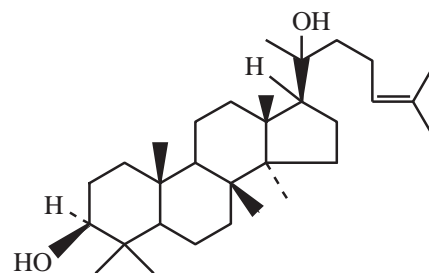
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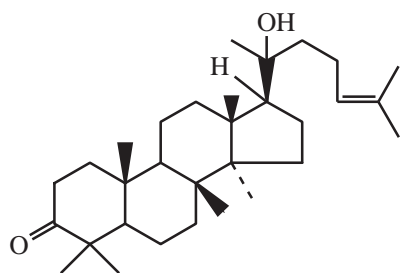
67 Oleanonic aldehyde



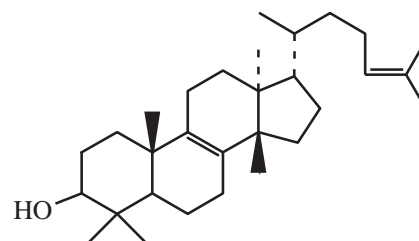
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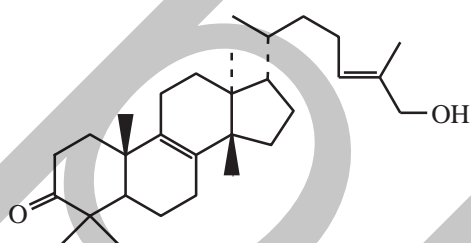
69 Dammarendiol



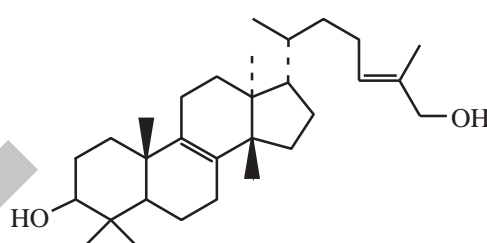
70 Diptercarpol



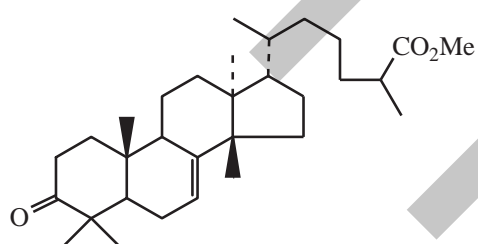
71 Tirucallol



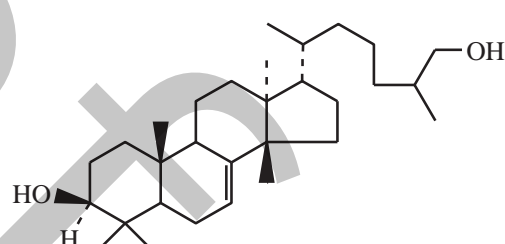
72 26-Hydroxytirucallone



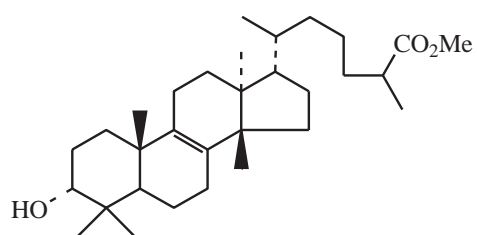
73 Isomasticadienediol



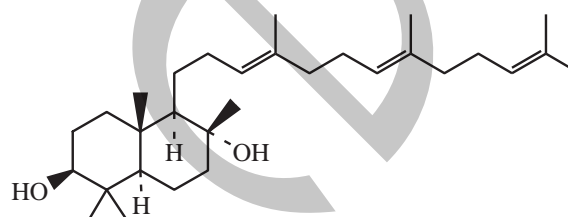
74 Methyl dihydroisomasticadienonate



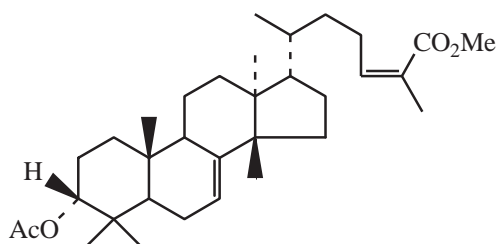
75 Dihydromasticadienediol



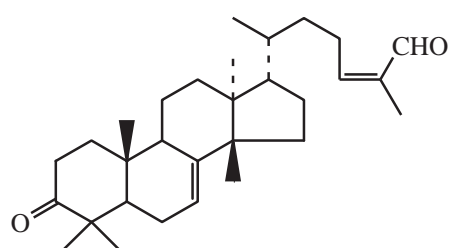
76 Methyl dihydro-3-epidihydroisomasticadienolat



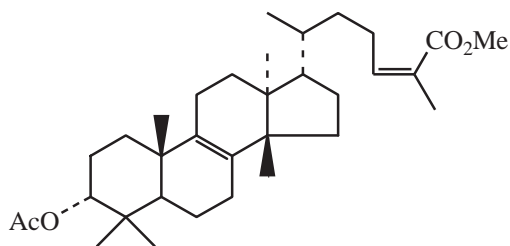
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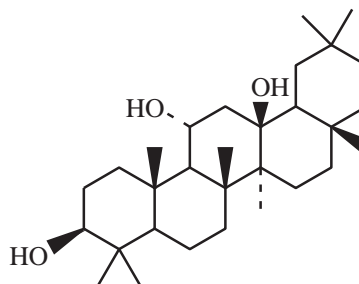
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79



80

81 3 β ,11 α ,13 β -Trihydroxyoleanane

Flavonoids and Other Phenolic Compounds

The following are examples of flavonoids and other phenolics (e.g. gallic acid) identified in some *Pistacia* species:

1. *Pistacia chinensis* Bunge.: The wood contains the flavonoids fisetin, fusetin, quercetin and taxifolin and gallic acid (Hiori *et al.*, 1966). The leaves contain quercetin, quercitrin,, quercetin 3-*O*-(6"-galloyl)- β -D-glucoside, gallic acid, *m*-digallic acid, and 6-*O*-galloyl arbutin (Shi and Zuo, 1992). Free and non-free gallic acid in leaf amounted totally to 29.20 % (Luo, 1996). Two 4-aryl-coumarin (neoflavone) dimers were isolated from twigs of the plant (**82**). Their structures were elucidated as 3,3"-dimers of 4-aryldihydrocoumarins (3,4-dihydro-4-(4'-hydroxyphenyl)-7-hydroxycoumarin) differing only in the stereochemistry disposition of the linkage between the two 4-arylcoumarin moieties (Nishimura *et al.*, 2000).
2. *Pistacia integerrima*: (-)-Eriodictyol, luteolin and dihydroquercetin were isolated from the plant (Kalidhar and Sharma, 1985).
3. *Pistacia mexicana*: The bark contains ethyl ester of gallic acid (Dominguez *et al.*, 1974).
4. *Pistacia mutica*: The leaves and fruit pericarp contain antimicrobial compound identified as being phenolic (Malekzadeh, 1974).
5. *Pistacia vera*: The main anthocyanin pigment in pistachio nut skin is cyaniding 3-*O*- β -galactoside (Miniati, 1981). The outer green shell of the nut was found to contain a mixture of phenolic acids identified as 6-alkyl and *cis*-6-alkenylsalicylic acids. The approximate composition was found to be: (13:0) 46%, (13:1) 17.4%, (15:0) 10.3%, (15:1) 7.3% and (17:1) 19.0% anacardic acids (Yalpani and Tyman, 1983).
6. *Pistacia weinmannifolia* J. Pisson ex. French.: The following compounds have been identified from the plant: gallotannins e.g. pistafolin A (**83**) and pistafolin B (**84**), catechin, gallo catechin (Hou *et al.*, 2000a,b), gallic acid, 3-*O*-galloylquinic acid, methyl gallate, ethyl gallate, penta-*O*-galloyl- β -D-glucopyranoside, myricetin 3-*O*- α -L-rhamnopyranoside and myricetin 3-*O*-(3"-*O*-galloyl)- α -L-rhamnopyranoside (Minami *et al.*, 2006).

Other Constituents

A pyrrolidine derivative, pistaciamide [4-hydroxy-5-(2-oxo-1-pyrrolidinyl)-benzoic acid] was isolated from *Pistacia chinensis* (Liu *et al.*, 2008c).