Pergamon

PII: S0031–9422(97)01020–0

Phytochemistry, Vol. 49, No. 4, pp. 901–951, 1998

Printed in Great Britain
0031–9422/98/$—see front matter

REVIEW ARTICLE NUMBER 134

PHARMACOLOGY AND CHEMOTAXONOMY OF *DIOSPYROS*

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(*Received in revised form* 20 *October* 1997)

Key Word Index—*Diospyros*; Ebenaceae; pharmacology; chemotaxonomy; pentacyclic triterpenes; juglone based naphthoquinones; naphthols; benzopyrones; chemical markers; biogenesis.

Abstract—*Diospyros* is numerically and economically the most important genus of Ebenaceae. The medicinal uses and chemical constituents of various *Diospyros* species are now reviewed. About 300 organic chemicals have been isolated and identified. The uniqueness of the genus is the elaboration of a large number of pentacyclic triterpenes and juglone based 1,4-naphthoquinone metabolites. These metabolites can be used as chemical markers for taxonomic studies. A common biogenetic pathway for their co-occurrence is now proposed. Various compounds are tabulated according to their classes and their structures are given in the Appendix.

INTRODUCTION

The family Ebenaceae with about 500 species is widespread chiefly in tropics and subtropics. According to Hegnauer [1], it consists of 7 genera namely *Diospyros*, *Euclea*, *Maba*, *Onotheca*, *Rhaphidanthe*, *Royena* and *Tetraclis*. However, taxonomists later modified and grouped them into 3 genera viz. *Diospyros*, *Euclea* and *Lassiocarpa*. The genera *Maba*, *Rhaphidanthe*, *Royena* and *Tetraclis* are included under *Diospyros* and *Onotheca* is included as a monotypic family [2].

The genus, *Diospyros* (Syn: Persimmon, ebony) with more than 350 species is the most important, both numerically and economically. *Diospyros* Linn. (an old Greek name used by Theophrastus, from dios-divine and pyros-wheat i.e. celestial food) consists of trees and shrubs chiefly tropical and widely distributed in both the hemispheres [3, 4]. About 41 species occur in India mostly in evergreen forests of Deccan, Assam and Bengal and a few are in North India [5, 6].

The characteristic features of the *Diospyros* species are: trees, rarely shrubs, leaves alternate; flowers green, white or yellow, few to many; axillary cymes or the pistillate solitary; corolla campanulate, urceolate or tubular, the lobes 3–7 (usually 4–5); stamens 4–many (commonly 16); mostly with 4–8 staminodia in pistillate flowers, ovary 4–16 celled, fruit is a large juicy 1–10 seeded berry; the sap wood is white and soft and heartwood is black and hard [3, 4]. The genus is of great economic importance with many species yielding edible fruits, ebony and valuable timbers. The best fruit yielding species is the kaki or Japanese persimmon, *D. kaki*. Although *D. kaki* has been cultivated in Japan for several centuries, it originated in China [7]. The kaki fruits, large orange-red berries, are very astringent until fully ripe, at which time the tannin content is completely transformed into insoluble crystals. The juice is then sweet and palatable. The other notable fruit yielding species are *D. virginiana* (U.S.A.), *D. ebenaster* (Mexico), *D. lotus* (Central Asia and Middle East), *D. mespiliformis* (Africa) and *D. melanoxylon* (India). The cultivated species are decorative, mostly ornamental trees with handsome, lustrous, foliage. Particularly the wood of *D. kaki* is of decorative class with an exceptionally smooth surface and with a marble like coldness to the touch. In Japan, *D. kaki* is highly valued for ornamental work in making boxes, desks and mosaics. Many species yield useful and valuable wood ebonies [9]. The true ebonies are obtained by stripping off the peripheral light coloured wood of falled trees. Fine ebonies are obtained from *D. dendo* and *D. mespiliformis* (Africa), *D. crassiflora* (Gabon and Cameroon). *D. ebenum* (Ceylon), *D. melanoxylon* (India), *D. perrieri* and *D. haplostylis* (Madagascar) and *D. celebica* (Celebes). The heartwoods of certain *Diospyros* species provide interesting colours, for example *D. chloroxylon* (India)—green; *D. rubra* (Mascarene Islands)—red,

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D. chryophyllos (Mascarene Islands)—white and *D. hirsuta* (variegated) [8].

In the entire *Diospyros* genus, only the leaves of *D. melanoxylon* are of commercial value. The leaves, are highly esteemed for wrapping bidis (cigarettes). Their flavour, flexibility and resistance to decay are the key factors in making their use valuable in the bidi industry. *D. melanoxylon* (ver: Kendu) leaf trade is one of the important tribal activities of India and is a good revenue earner for Government, besides providing gainful employment to several tribal peoples [5, 6]. *D. tomentosa* leaves are also reported to be useful in bidi wrapping but they are not widely used.

Many *Diospyros* species have been reported to exhibit interesting biological and pharmacological activities. Some of the significant biocidal reports are: (i) the wood of *D. virginiana*, from which 7-methyljuglone has been isolated as the chief constituent, was reported to exhibit termicidal activity [10]; (ii) the chief constituent of *D. kaki*, plumbagin is reported to exhibit antifeedant, insecticidal, insect growth regulator and sterilant activities [11]; (iii) in a major plant screening programme the leaves of *D. diepenhorstii* of Thailand were found to exhibit piscicidal and molluscicidal activities [12]; and (iv) the petrol, chloroform and methanol extracts of the root bark of *D. zombensis* [23, 24] and the alcohol extract of *D. usambarensis* [19] showed molluscicidal and fungicidal activities. The phytochemical research on *Diospyros* species was started almost a decade ago. The number of papers published on the phytochemical examination alone has now reached 150. The results of these studies indicate that the *Diospyros* genus elaborate a great diversity of compounds ranging from hydrocarbons, steroids, terpenoids, naphthoquinones to naphthalene based aromatics [13].

In the following pages the pharmacological activities and types of secondary metabolites produced by the members of *Diospyros* plants are reviewed.

PHARMACOLOGICAL ACTIVITY

This section includes the details of traditional medicinal uses followed by pharmacological screening of various extracts and some of the major metabolites of *Diospyros* species. These species are known for their medicinal uses since olden times. In many traditional medicinal systems of the world such as the Ayurveda, the African folklore and the Chinese, the role of *Diospyros* plants as medicinal agents is well documented [14–37]. It is very interesting that almost all parts of these plants have been used as medicines e.g. the leaves are good for lumbago, the fruits are carminative, astringent and cure biliousness and vata (Ayurveda), the seeds are sedative and the bark is bitter, astringent and febrifuge. The remedies of various *Diospyros* plants reported in different traditional systems of the world are presented in Table 1.

In Indian Ayurveda, Yunani and other traditional systems twelve *Diospyros* plants have been used extensively [14–16, 38–43] (Table 2) of which *D. melanoxylon* and *D. peregrina* are the two most potent and most widely used plants. The Charaka Samhita recommends the juice of the bark and leaves of *D. peregrina* together with the root juice of *Albizia lebek* for snake bite [41]. The dried flowers of *D. melanoxylon* are recorded in Yunani medicine for urinary discharges, inflammation of the spleen and enrichment of blood and its bark extract is used in Ayurveda as an astringent lotion for eyes [14–16, 42].

Reports on *in vivo* and *in vitro* bio-assay of various *Diospyros* extracts, though started in 1952, appeared mostly during 1970–80. Three species viz. *D. kaki*, *D. montana* and *D. peregrina* have been screened extensively and interesting pharmacological activities have been attributed to them [43]. It is interesting to note that the leaf extract of Japanese persimmon (*D. kaki*) in combination with jasmine has been used in Japan for making anti-tobacco smoking candies [44], since leaves of some of the *Diospyros* species (e.g. *D. melanoxylon*, *D. tomentosa*) have been used for wrapping bidis. Details of pharmacological screening of various extracts of 14 *Diospyros* species are available in literature and are given in Table 3.

The oral and topical anti-inflammatory activity of ten triterpenoids belonging to the lupane, oleanane and ursane series was evaluated by Rios *et al.* [56]. All the triterpenoids were remarkably active against the edema produced by TPA, while the basic carbon skeleton has no influence on the activity, the presence of a C-28 or C-30 carboxylic group and an alcoholic group at C-28 increases the activity in carrageenan and EPP induced edemas. Incidentally most of the tested triterpenoids were also isolated from various *Diospyros* species. Detailed pharmacological screening for some of the single and pure *Diospyros* metabolites has been done and the activities are given in Table 4.

CHEMOTAXONOMY

Out of 350 identified *Diospyros* species more than 130 species have so far been screened phytochemically (Table 5) and a variety of compounds have been isolated and identified.

Although, identification of tannins and their dependence on astringency were reported from *D. kaki* fruits [85] in early 1900, the first report on the identification of chemical constituents, was that of Iwata, who reported d-mannitol from the fruits of *D. kaki* in 1929 [86, 87]. Subsequently the carotenoid pigments, β-carotene, cryptoxanthin, lycopene and zeaxanthin were reported from the fruits of *D. kaki* [88] and *D. costata* [89]. Plumbagin (2-methyl-5-hydroxy-1,4-naphthoquinone), the first biologically active compound of *Diospyros* was isolated in 1952 from *D. hebecarpa* [90, 91]. The isolation of ursolic, oleanolic and betulinic acids from the ethanol extract of the

Table 1. Use of *Diospyros* species in traditional medicinal system of the world

SI. No.	Country	Species	Medicinal uses	Ref.
1.	America	*D. virginiana*	(i) Anthelmintic	25
			(ii) Antifungal	
			(iii) Astringent	
			(iv) For internal hemorrhage	26
2.	Bahamas	*D. crassinervis*	(i) For bedwetting in children	27
			(ii) Woman's medicine	
3.	Brazil	*D. paralea*	—	15
4.	Cambodia	*D. decandra*	(i) For insomnia	15
			(ii) Emmenagogue	
			(iii) Vermicide and vermifuge	
5.	China	*D. kaki*	Hiccough	15, 16, 28
		D. lotus	(i) Sedative	15, 16
			(ii) Antifebrile	
			(iii) To promote secretions	
		D. peregrina	Astringent	15, 16
6.	East Africa	*D. loureiriana*	Chewing stick	14
7.	Guinea	*D. mespiliformis*	Bactericidal	8, 15
8.	Japan	*D. kaki*	(i) Hiccough	28–30
			(ii) Antihypertentsive	31
			(iii) Dysponea	28–30
9.	Madagascar	*D. gracilipes*	Causing skin lesion	32
		D. megasepala	—	15
		D. perrieri	—	15
10.	Malaysia	*D. ebenum*	Astringent	26
		D. ismailii	For curing skin diseases	29
		D. kaki	For cough	28, 29
		D. lotus	For cough	28, 29
		D. rufa	For curing skin diseases	29
		D. siamang	For curing skin diseases	29
		D. toposoides	For curing skin diseases	29
		D. wallichi	For curing skin diseases	29
11.	Malawi	*D. usambarensis*	To cure schistosomiasis	19
		D. zombensis	To cure schistosomiasis	23, 24
12.	Maritius	*D. leucomelas*	—	15
		D. melanoxylon	—	15
		D. tesselaria	—	15
13.	Phillippines	*D. embryopteris*	Astringent	26
14.	Samoan Islands	*D. samoensis*	(i) Astringent	33
			(ii) To treat tetanus and apoplectic attack	
			(iii) Can blister the skin	
15.	Sierra Leone	*D. heudelotii*	Chewing stick	25
16.	South Africa	*D. hirsuta*	(i) Purgative	14
			(ii) To treat gonorrhoea	
		D. lucida	To relieve excessive menstrual pain	14
		D. loureiriana	Chewing stick	14, 25
		D. villosa	(i) Purgative	14
			(ii) For healing of fractures	
17.	Sri Lanka	*D. quaesita*	Antiasthmatic	17
18.	Taiwan	*D. morrisiana*	Antibiotic	34, 37
19.	Tanzania	*D. cornii*	—	21
		D. kirkii	—	21
		D. mespiliformis	Bactericidal	8, 21
		D. verrucosa	Antileprosy	21
20.	Thailand	*D. mollis*	Anthelmintic	35
		D. rhodocalyx	(i) Antidiarrhoeal	
			(ii) Antidiuretic	
			(iii) To control bleeding	
			(iv) For abdominal discomfort	
			(v) For symptomatic relief of leukorrhoea	
			(vi) To treat parasitic infestion, abscess and renal disease	
21.	West Africa	*D. barteri*	Chewing stick	25
		D. elliotii	Chewing stick	25
		D. tricolor	Chewing stick	25
22.	Zambia	*D. lycioides*	Chewing stick	25

Table 2. Use of various *Diospyros* species in Indian traditional systems

SI. No.	Species	Part used	Medicinal uses
1.	*D. candolleana*	Bark	For rheumatism and swellings
2.	*D. ebenum*	—	Astringent, attenuant and lithontriptic
3.	*D. embryopteris*	—	For chronic dysentry
4.	*D. exsculpta*	Bark	As haemostat for cuts and wounds
		Fruit	For diarrhoea and dysentry
		Root	For scorpion bite
5.	*D. lanceifolia*	Fruit	Fish poison
		Seed	For skin disease
6.	*D. lotus*	Fruit	Anti-febrile and used to promote secretions
		Seed	Sedative
7.	*D. malabarica*	Fruit	Anti-diarrhoeal, to cure blisters in mouth and as tonic
		Fruit & stem bark	Abortifacient and used to treat cholera and menorrhagia
8.	*D. melanoxylon*	Bark & leaf	Diuretic, carminative laxative, styptic and used as astringent lotion for eyes
		Flower	Used in skin disease, urinary discharge, inflammation of spleen and enrichment of blood
		Seed	As germicide and used in dysentry
9.	*D. montana*	Bark	For delirium in high fevers and to treat vomiting and jaundice
		Fruit	For cracks in sole of feet and as oral application for boils
		Gum	To cure tuberculosis
		Root	Abortifacient
		Part not specified	Used for diarrhoea, fever, menor, neural, pleuracy and pneumonia
10.	*D. paniculata*	Bark	For rheumatisim and ulcers
		Fruit	Used in biliousness and blood poisoning
		Leaf	Fish poison
11.	*D. peregrina*	Bark	Good for dysentry and intermittent fevers
		Flower	Good for lumbago and blindness
		Fruit (ripe)	Used in biliousness, urinary losses and to remove stones in the urinary tract
		Fruit (unripe)	As astringent for bowels and for healing of wounds
		Leaf	Useful in the treatment of snake-bite
		Seed	For dysentry and diarrhoea
		Wood	Cures biliousness
12.	*D. tomentosa*	Part not specified	For bleeding gums, bronchitis, carbuncle, cholera, colic, cough, cramps, diarrhoea, fevers, fistula, pleurisy, pneumonia, syphylis and tumors

calyx of a Japanese persimmon in 1955 marks the beginning of triterpenoid research in the *Diospyros* genus [92].

It is interesting to note that almost all parts of the *Diospyros* species have been exploited for chemical examination and a variety of compounds have been isolated (Table 6) of which the triterpenoids and the naphthoquinones are found widespread and present in almost all parts of the plant species.

The compounds isolated so far are grouped according to recognisable classes and subclasses and the uniqueness or otherwise of these compounds is noted in the discussion. A full listing of the compounds isolated and whose structures have been unambiguously established is given in the Appendix.

TERPENOIDS

The occurrence of mono-, di- and sesquiterpenes has not been reported so far in the *Diospyros* genus. In contrast the triterpenes are widely distributed and found in more than 90% of *Diospyros* plants screened so far. Although, these metabolites are detected in almost all parts of the plant, they are found abundant in leaves and heartwood. Interestingly, the triterpenes isolated so far are all with pentacyclic core and belong

Table 3. Details of pharmacological screening of various *Diospyros* extracts

SI. No.	Species	Part	Extract	Pharmacological activity	Ref.
1.	*D. chloroxylon*	PER	50% EtOH	Antiviral	45
2.	*D. cordifolia*	NS	Alcohol	Anti-inflammatory, anti-pyretic, analgesic, CNS depressant, spasmolytic, produces bradycardia and hypotension	46, 47
3.	*D. embryopteris*	Leaves	80% EtOH	Showed abolition of libido in 100% male rats	48
4.	*D. exsculpta*	PER	50% EtOH	Showed activity on cardiovascular system	49
		Seeds	Unsaponified matter	Produced fall in blood pressure and increase in respiration, also showed anorexia, CNA depressant and anti-bacterial activities	
5.	*D. insignis*	PER	50% EtOH	Antifertility	51
6.	*D. kaki*	Fruit	—	(i) Showed strong detoxyfying activity (8–32 times higher than tannic acid) on various snake venoms (ii) Inactivates bacterial toxins such as *Clostridium tetani* and *Diphtheria*, *Straphylococcus alpha* and *Bordetella pertussis*	52
		Leaves	Tannin	(i) Increases life span and decreases brain haemorrhage and infarction in stroke prone spontaneously hypertensive rats (SPSHR) (ii) Showed scavenging action towards active oxygen free radicals (iii) Inhibited lipid peroxidation similarly to (−)-epigallocatechin (20 times more than α-tocopherol in terms of 50% inhibitory concentration)	53
		Leaves	MeOH	Showed hypotensive activity against urethane anaesthatised rats	54
7.	*D. leucomelas*	Leaves	CH_2Cl_2 & MeOH	Showed anti-inflammatory activity in the carrageenan and serotonin paw edema tests and TPA and EPP ear edema tests	55, 56
8.	*D. melanoxylon*	Seed	Unsaponified matter	Antibacterial	57
9.	*D. mespiliformis*	Seed	—	Antibacterial	58
10.	*D. montana*	Leaves	Pet. ether, CCl_4, C_6H_6	Antibacterial and effective against most of the organisms tested. Pet. ether and CCl_4 extracts were especially active against *Bacillus subtilis* and *Corynebacterium pyrogenes*	59
		Bark	90% EtOH	Inhibited the growth of Ehrlich ascites carcinoma in mice	60
		—	—	Showed potent anti-inflammatory and anti-pyretic activities in rats and analgaesic activity in mice	61
		Bark	Alcohol	Showed CNS depressant activity, decreases locomotor activity and loss of righting reflux in mice and rats, also had spasmolytic activity on rabbit and guinea pig ileum and produced hypotension in anaesthetised dogs	62
11.	*D. morrisiana*	Stem	Hexane	Showed significant cytotoxicity against *in vitro* tissue culture cells of human KB and A-549 lung carcinoma, HCT-8 colon tumor and murine P-388 and L-1210 lymphocytic leukaemia	37
12.	*D. peregrina*	Fruit	Ether	Antibacterial	63
		NS	Alcohol	Anti-amoebic, anti-viral and hypoglycaemic activities	64

Table 3. Details of pharmacological screening of various *Diospyros* extracts

SI. No.	Species	Part	Extract	Pharmacological activity	Ref.
		PER	50% EtOH	Showed activity on human epidermoid carcinoma of nasopharynx in tissue culture and diuretic activity	65
		—	EtOAc	Significantly prevented rats from stress, gastric ulcers and hepatotoxicity	66
13.	*D. virginiana*	Fruit	—	Produced tumors at the injection site in 66% or more of the treated rats	67
		Fruit	—	Showed cholesterol lowering activity	68
14.	*D. zombensis*	Root bark	Petrol & $CHCl_3$	Showed cytotoxicity against human colon carcinoma cells	23, 24

PER: plant excluding root, NS: not specified.

to lupane (**A**), ursane (**B**), oleanane (**C**), taraxerane (**D**) and friedelane (**E**) skeletons (Chart 1).

Among the above skeletons the lupane, ursane and oleananes are more prevalent in the *Diospyros* genus and in most of the species the co-existence of any two or all the three has been reported. These pentacylic triterpenoids have long been thought of as pharmacologically inactive, but now assume significance in view of the recently established anti-cancer, anti-HIV and anti-inflammatory activities of some of the lupane, ursane and oleananes.

Lupanes

The most common triterpene skeleton found in *Diospyros* is that represented by lupane group of compounds. It is evident from the fact that out of 65 publications of *Diospyros* terpenoids more than 35 papers reported the exclusive isolation of the lupane group of triterpenes. Significantly, this class of compounds accumulate in bark and heartwood. The major metabolites of this class are lupeol (**1**), betulin (**2**) and betulinic acid (**3**) each of which has been reported from more than 25 *Diospyros* plants (Table 7). Betulinic acid is the first lupane derivative isolated from a *Diospyros* species in 1955 [89]. Since then it has been identified as a chief constituent in a number of *Diospyros* plants along with either betulin or lupeol.

It is very interesting to note that apart from lupeol (**1**), betulin (**2**) and betulinic acid (**3**) very few lupane derivatives have been isolated from *Diospyros* species. Allobetulin (**7**) and oxyallobetulin (**8**), the two interesting rearranged metabolites of betulin (**2**), have been reported from few *Diospyros* plants [95, 114, 131]. As the formation of allobetulin (**7**) could be mimicked chemically by acid catalysed rearrangement of betulin (**2**) [136] (Scheme 1), the natural occurrence of compounds **7** and **8** is doubtful and they may be isolated as artifacts.

Recent addition to this class is lup-20(29)-ene-3α,27-diol (peregrinol, **6**), isolated from the antibacterial extract of the fruits of *D. peregrina* [129].

Ursanes

Another class of pentacyclic triterpene metabolites which are widespread in the *Diospyros* are the ursanes. In all 9 ursane type triterpenoids with either urs-12-ene or urs-7-ene frameworks have so far been isolated (Chart 2).

α-Amyrin (**10**), bauerenol (**11**) and ursolic acid (**12**) are the three major metabolites of this class. It is interesting to note that, ursolic acid (**12**) accumulates in significant quantities in a number of *Diospyros* plants and co-exists mostly with α-amyrin (**10**). Few ursolic acid esters [acetate (**13**)—*D. lotus* [134, 135], *D. eriantha* [105], palmitate (**14**) and stearate (**15**)—*D. montana* [137] are also elaborated by *Diospyros* species. The natural occurrence of α-amyrenone (**16**) and 3α,28-dihydroxy-urs-12-ene (epi-uvaol, **17**) was reported for the first time from *D. ebenum* [101–104] and *D. montana* [138] respectively. Bauerenol (**11**) is the sole representative of urs-7-ene skeleton and its occurrence was reported from five *Diospyros* species [111, 112, 120, 121, 139, 140]. The variation in the double bond position from 12 (13) to 11 (12) was noted in compound **19a**, which was isolated only once from the bark of *D. eriantha* [105]. The isolation of marsformosanone (**19b**) with a homoannular diene system from the petrol extract of the fruits of *D. peregrina* [116] and 19α-hydroxyursolic acid (**19c**) from the calyx of *D. kaki* [30] are the other interesting examples of this class (Table 8).

Oleananes

In the entire *Diospyros* genus triterpene glycosides were isolated only with oleanane skeleton. The oleanolic acid glycosides (**20**–**23**) have been isolated from the alcoholic extracts of the barks of *D. peregrina* [143] and *D. zombensis* [23, 24]. The glycoside, 3-*O*-[α-L-rhamnopyranosyl-(1-3)-β-D-glucopyranosyl] oleanolic acid (**21**), isolated from *D. zombensis* is particularly interesting in view of its strong molluscicidal

Table 4. Pharmacological activities of single isolated metabolites of *Diospyros* species

SI. No.	Compound	Pharmacological activity	Ref.
1.	β-Amyrin	Moderately cytotoxic	37
2.	Betulin	(i) Anti-inflammatory activity	55, 56
		(ii) Active against the Walker-Carcinoma-256 (intramuscular) tumor system	69
3.	Betulinic acid	(i) Showed potent anti-inflammatory activity against TPA—induced edema	55, 56
		(ii) Active against the Walker-Carcinoma-256 tumor system	69
		(iii) Inhibited P-388 leukaemia growth	70
		(iv) Found to possess highly selective activity against human melanoma *in vitro* and *in vivo*. Its preclinical development is underway	71
4.	Lupeol	Active against the Walker-Carcinoma-256 tumor system	69
5.	Lupeol acetate	Inhibited stress induced ulcers in rats, also decreases incidence of gastric ulceration induced by pyloric ligation	72
6.	2α,3β-Dihydroxy-olean-12-ene-28-oic acid (maslinic acid)	(i) Showed anti-inflammatory effect on carrageenan-induced oedema and an inhibitory effect on histamine induced ileum contraction	73
		(ii) Showed potent inhibitory activity against HIV-1 protease	74
7.	Oleanolic acid	(i) Inhibited 12-*O*-tetradecanoyl-phorbal-13-acetate induced Epstein-Barr virus activation	75
		(ii) Showed potent antiarthritic and anti-inflammatory activities	76
8.	Taraxerol	Inhibited stress induced ulcers in rats, also decreases incidence of gastric ulceration induced by pyloric ligation	72
9.	Ursolic acid	(i) Anti-inflammatory activity	55, 56
		(ii) Inhibited 12-*O*-teradecanoyl-phorbal-13-acetate induced Epstein-Barr virus activation	75
		(iii) Suppressed tumor promoter induced inflammation of mouse ear	77
		(iv) Inhibited stress induced ulcers in rats, also decreases incidence of gastric ulceration induced by pyloric ligation	72
		(v) Increases blood sugar concentration, glycogen and ATP contents in muscles, heart and uterus on intragastric administration into rats	78
		(vi) Showed potent inhibitory activity against HIV-1 protease	76
10.	Plumbagin	(i) Stains the skin, produces blisters and effects mucous membrane	79
		(ii) Inhibits the growth of all gram +ve and −ve test bacteria	80
11.	7-Methyljuglone	Showed cytotoxic activity against human colon carcinoma cells	23, 24, 81
12.	Diospyrin	(i) Inhibited the *in vivo* growth of Ehrlich Ascites Carcinoma (EAC), in Swiss Albino mice	82
		(ii) Showed *in vitro* activity against the protozoan *L. donovani*	83
13.	Isodiospyrin	Showed cytotoxic activity against HCT-8 colon tumor and P-388 lymphocytic leukaemia	23, 24, 37
14.	Diospyrol	Showed anthelmintic activity in hamsters infected with human hookworm, *Necator americanus*. Also active against *Hymenolepis nana* and *Nematospiroides dubius* parasites in mice	52, 207
15.	Astragalin	Inhibited the angiotensin converting enzyme activity	84
16.	Kaempferol-3-*O*-(2″-*O*-galloyl)-glucoside	Inhibited the angiotensin converting enzyme activity	84
17.	Isoquercitrin	Inhibited the angiotensin converting enzyme activity	84
18.	Quercetin-3-*O*-(2″-*O*-galloyl)-glucoside	Inhibited the angiotensin converting enzyme activity	84

activity [23, 24]. In fact, the aglycone of these metabolites, oleanolic acid (**24**) is the most abundant oleanane skeleton of the *Diospyros* genus. Like ursolic acid this compound also occurs as a free acid and isolated as a bare unsubstituted moiety without further hydroxylation or unsaturation in any of the rings. The other oleanane metabolites isolated from *Diospyros* species are β-amyrin (**25a**), olean-12-ene-3-one (**25b**), acetyl and fatty acid esters (**26**–**28**) of oleanolic acid. Interesting addition to this class is 18(19)-olean-28-oic acid (**29**) isolated from *D. malanonilau* [141] (Table 9).

Table 5. List of *Diospyros* species chemically examined

D. abyssinica, *D. acuta*, *D. alboflavescena*, *D. argentea*, *D. austro-africana*, *D. batocana*, *D. bipindensis*, *D. blancoi*, *D. buxifolia*, *D. canaliculata*, *D. candolleana*, *D. castanea*, *D. cauliflora*, *D. celebica*, *D. chaetocarpa*, *D. chevalieri*, *D. chloroxylon*, *D. cinnabarina*, *D. consolatae*, *D. cordifolia*, *D. cornii*, *D. costata*, *D. crassiflora*, *D. curranii*, *D. dendo*, *D. diepenhorstii*, *D. digyna*, *D. discolor*, *D. ebenaster*, *D. ebenum*, *D. ehretioides*, *D. elliptifolia*, *D. embruyopteris*, *D. eriantha*, *D. evena*, *D. exsculpta*, *D. ferrea*, *D. fischeri*, *D. fragrans*, *D. gabunensis*, *D. gilleti*, *D. gracilescens*, *D. gracilipes*, *D. greeniway*, *D. guianensis*, *D. hebecarpa*, *D. heterotricha*, *D. hirsuta*, *D. hoyleana*, *D. indica*, *D. inhacaensis*, *D. insignis*, *D. ismailii*, *D. iturensis*, *D. japonica*, *D. kachiya*, *D. kaki*, *D. kaki* var. *sylvestris*, *D. kamerunensis*, *D. kirkii*, *D. kotida*, *D. lanceifolia*, *D. leucomelas*, *D. longiflora*, *D. lotus*, *D. lycioides*, *D. lycopersicon*, *D. mafiensis*, *D. maingayi*, *D. malabarica*, *D. malanonilau*, *D. mannii*, *D. maritima*, *D. maritinia*, *D. maritinone*, *D. mebola*, *D. melanoxylon*, *D. mespiliformis*, *D. microphylla*, *D. mollis*, *D. monobuttensis*, *D. montana*, *D. moonii*, *D. morrisiana*, *D. natalensis*, *D. nicaraguensis*, *D. obliquifolia*, *D. oblongifolia*, *D. oppositifolia*, *D. palmeri*, *D. peregrina*, *D. philippinesis*, *D. pilosantera*, *D. pseudo-malabarica*, *D. quaesita*, *D. quiloensis*, *D. ramulosa*, *D. rheophytica*, *D. rhodocalyx*, *D. rotundifolia*, *D. rubriflora*, *D. samoensis*, *D. sanarosa*, *D. sanza-minika*, *D. sapota*, *D. senensis*, *D. siamang*, *D. siamensis*, *D. siderophylla*, *D. singaporensis*, *D. spinescens*, *D. squarrosa*, *D. sumatrana*, *D. sylvatica*, *D. texana*, *D. thomasii*, *D. thwaitesii*, *D. tomentosa*, *D. toposia*, *D. tricolor*, *D. usambarensis*, *D. variegata*, *D. verrucosa*, *D. virginiana*, *D. wallichii*, *D. walkeri*, *D. whyteana*, *D. xanthoclamys*, *D. zenkeri*, *D. zombensis*

Synonyms:
D. buxifolia = *D. microphylla*; *D. cordifolia* = *D. montana*
D. discolor = *D. mebola* = *D. blancoi*; *D. ebenum* = *D. sapota* = *D. hebecarpa* = *D. assimilis*
D. ehretioides = *D. mollis*; *D. embryopteris* = *D. malabarica* = *D. peregrina*
D. exsculpta = *D. tomentosa*; *D. elliptifolia* = *D. siamang*; *D. melanoxylon* = *D. tupru*
D. racemosa = *D. toposia*; *D. marmorata* = *D. oocarpa*

Table 6. Distribution of chemial constituents in various parts of *Diospyros* species

SI. No.	Class of compounds	Part of the species
1.	Carotenoids	Fruit
2.	Tannins	Fruit, leaf
3.	Sugars	Fruit, seed, root
4.	Hydrocarbons	Fruit, seed, leaf
5.	Lipids	Fruit, seed, bark
6.	Aromatics	Fruit, root, bark
7.	Flavonoids/coumarins	Fruit, leaf, root, sapwood
8.	Terpenoids	Fruit, leaf, calyx, seed, root, bark, heartwood, ebony
9.	Steroids	leaf, root, bark, heartwood
10.	Naphthoquinones	Fruit, leaf, root, bark, heartwood

Taraxeranes

Taraxerol (**30**), its acetate (**31**) and taraxerone (**32**) are the only metabolites of this class so far to have been detected in *Diospyros* species (Table 10). Especially compounds **30** and **32** are found to be widespread and in most of the cases their co-existence with lupane or ursane or oleanane derivatives was reported. It is interesting to note that further hydroxylation or unsaturation did not take place in this class of compounds also and no significant biological activity has been reported for these metabolites.

Friedelanes & miscellaneous

These skeletons do not seem to be widely represented in the *Diospyros* genus. So far, there are only three reports on the isolation of friedelanes and related pentacyclic triterpenes. The hexane-soluble portion of the alcoholic extract of the leaves of *D. ferrea* [149] is reported to yield friedelin (**33**) and friedelin-3-ol (**34**). Waterman *et al.* reported the isolation of 2α-hydroxyfriedelin (cerin **35**) and glut-5(6)-ene-3β-ol (**36**) from the African plants, *D. iturensis* and *D. sanza-minika* respectively [93]. Very recently friedelin (**33**) was isolated along with some ursane and lupane derivatives from the ethyl alcohol extract of *D. eriantha* bark [105].

STEROIDS

The structural diversity of these compounds is limited and so far only six steroidal metabolites have been detected and isolated from *Diospyros* plants (Table 11). The most common steroidal skeleton found is β-sitosterol (**37a**) and it occurs, in both free and glycosidic (**38**) forms. β-Sitosterol was found to accumulate

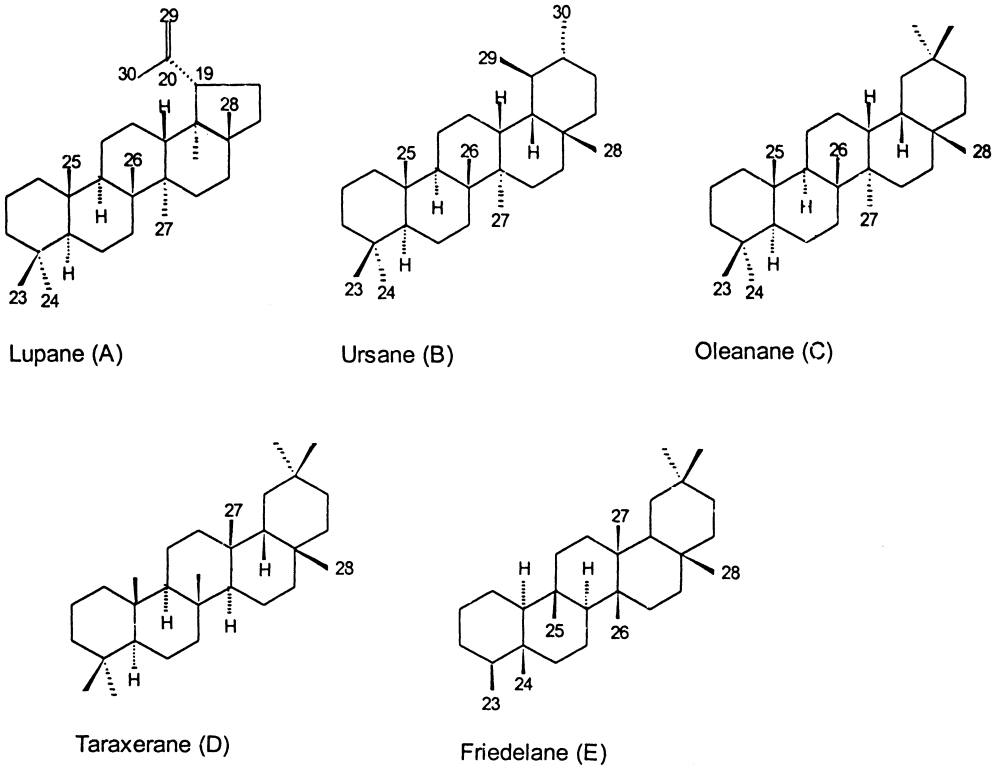


Chart 1.

in a number of species and so far it was detected in more than 30 *Diospyros* plants. Campesterol (**37b**), stigmasterol (**39**), stigmasta-4-ene-3-one (**40**) and stigmasta-5,6-dihydro-22-one-3β-ol (**41**) are the other steroidal molecules isolated in the *Diospyros* genus.

NAPHTHOQUINONES

The *Diospyros* genus elaborate a large number of 1,4-naphthoquinone metabolites belonging to the juglone class [158]. About 75% of the phytochemical reports of *Diospyros* are on the detection and isolation of 1,4-naphthoquinones, which include several monomers, dimers, a few trimers and tetramers. In fact, these species are characterised by their ability to produce 1,4-naphthoquinones, which in turn can be used as chemical markers for taxonomic studies. The orange red pigment plumbagin (**42**) is the first naphthoquinone isolated along with a colourless β-hydroproduct of 7-methyljuglone (**43**) from *D. hebecarpa* [88]. Plumbagin and 7-methyljuglone are the most widely distributed monomeric naphthoquinones and are found to accumulate in significant quantities in a number of *Diospyros* species (Table 12). It is interesting to note that plumbagin is found more in leaves and heartwood, while 7-methyljuglone is in the bark and wood.

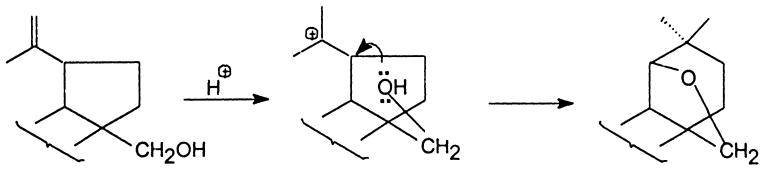
Although the 1,4-naphthoquinone metabolites are most common, three 1,2-naphthoquinones, viz. 8-hydroxy-1,2-naphthoquinone (**44**, *D. tricolor*) [166–168], 3-methyl-8-methoxy-1, 2-naphthoquinone (**45a**, *D. melanoxylon*) [151] and 6-methyl-8-methoxy-1,2-naphthoquinone (**45b**, *D. celebica*) [169] are also reported. The juglone based 1,4-naphthoquinones of *Diospyros* can be classified into two major groups viz. (1) substituted metabolites of plumbagin and 7-methyljuglone and (2) oligomeric metabolites of plumbagin and 7-methyljuglone.

Substituted metabolites of plumbagin and 7-methyljuglone

About 24 metabolites of this class have so far been isolated (Table 13). *D. melanoxylon*, also known as coromandel persimmon, is found to be the potential source for substituted plumbagins (**46–49**) [151–170]. Some *Diospyros* plants have been reported to produce useful orange red substituted plumbagins such as 3-halo (Br: **50**; Cl: **51**) [160], 3-hydroxy (droserone, **52**) [160] and 8-hydroxy (methyl naphthazarin, **53**) [161, 171]. While the partial quinone reduction products of 7-methljuglone (shinanolone, **54**) [10, 94, 107, 108, 150] and plumbagin (iso-shinanolone, **55**, epi-iso-shinanolone, **56**) [93, 94, 145, 172] have been isolated from few *Diospyros* plants, the completely reduced quinone skeletons have not yet been detected in the genus. The α- and γ-benzopyronyl substituted metabolites of 7-methyljuglone (ismailin, **57**, chromenone ester, **58** and chromenone acid, **59**) [131, 173, 174] and plumbagin (canaliculatin, **60** and cyclocanaliculatin,

Table 7. Distribution of lupane type triterpenes in *Diospyros* plants

SI. No.	Compound	Species [Ref.]
1.	Lupeol (**1**), Betulin (**2**) & Betulinic acid (**3**)	*D. abyssinica* [93], *D. argentea* [94], *D. bipindensis* [18], *D. buxifolia* [95], *D. canaliculata* [93], *D. candolleana* [97], *D. castanea* [98], *D. cauliflora* [98], *D. chevalieri* [93], *D. cinnabarina* [18, 93], *D. crassiflora* [93], *D. curranii* [98], *D. dendo* [93], *D. discolor* [94], *D. ebenum* [101, 102], *D. elliptifolia* [98], *D. embryopteris* [95], *D. eriantha* [105], *D. evena* [98], *D. exsculpta* [95], *D. fragrans* [93], *D. gabunensis* [93], *D. gracilescens* [18, 93], *D. guianensis* [106], *D. hirsuta* [17], *D. hoyleana* [93], *D. ismailii* [94], *D. iturensis* [93], *D. kaki* var. *sylvestris* [107], *D. kamerunensis* [93], *D. longiflora* [93], *D. lotus* [94, 114], *D. maingayi* [94, 98], *D. mannii* [96], *D. maritima* [145], *D. melanoxylon* [109–111], *D. mespiliformis* [93], *D. monobuttensis* [93], *D. montana* [98, 113], *D. moonii* [17], *D. morrisiana* [114], *D. obliquifolia* [18], *D. peregrina* [115], *D. pseudo-malabarica* [98], *D. quaesita* [17], *D. sanza-minika* [93, 98], *D. siamang* [94], *D. siamensis* [98], *D. siderophylla* [100], *D. singaporensis* [94], *D. spinescens* [17], *D. sumatrana* [94], *D. sylvatica* [111, 112], *D. thwaitesii* [17], *D. tomentosa* [95], *D. virginiana* [117], *D. walkeri* [17], *D. wallichii* [94], *D. zenkeri* [93]
2.	Lupeol (**1**) & Betulin (**2**)	*D. elliptfolia* [118], *D. kirkii* [119], *D. melanoxylon* [112], *D. microphylla* [95], *D. mollis* [13, 98], *D. oblongifolia* [17], *D. peregrina* [116], *D. rotundifolia* [112], *D. variegata* [98]
3.	Lupeol (**1**) & Betulinic acid (**3**)	*D. consolatae* [120], *D. cornii* [121], *D. diepenhorstii* [98], *D. ehretioides* [98], *D. greeniway* [123], *D. kaki* [107, 108], *D. mafiensis* [123], *D. montana* [153], *D. natalensis* [123]
4.	Betulin (**2**) & Betulinic acid (**3**)	*D. chloroxylon* [125], *D. consolatae* [21, 22, 121], *D. discolor* [109, 110], *D. ebenum* [103], *D. kaki* [125, 126], *D. leucomelas* [55, 56], *D. malanonilau* [141], *D. montana* [146], *D. peregrina* [109, 110, 143], *D. verrucosa* [20]
5.	Lupeol (**1**)	*D. acuta* [17], *D. cordifolia* [127], *D. cornii* [21, 22], *D. oppositifolia* [17], *D. rheophytica* [17], *D. rhodocalyx* [98], *D. toposia* [98]
6.	epi-Lupeol (**4**)	*D. ebenaster* [128], *D. palmeri* [128]
7.	Lupenone (**5**)	*D. mollis* [13]
8.	Peregrinol (**6**)	*D. peregrina* [129]
9.	Betulin (**2**)	*D. ebenaster* [128], *D. indica* [130], *D. kaki* [126], *D. peregrina* [144]
10.	Allobetulin (**7**)	*D. montana* [131]
11.	Oxyallobetulin (**8**)	*D. lotus* [95, 114], *D. montana* [131], *D. morrisiana* [114]
12.	Betulinic acid (**3**)	*D. alboflavescena* [132], *D. discolor* [133], *D. ebenum* [104], *D. ferrea* [95], *D. gilleti* [132], *D. holyeana* [132], *D. kaki* [92, 108], *D. lotus* [134, 135], *D. palmeri* [128], *D. verrucosa* [21, 22, 121]
13.	Betulinaldehyde (**9**)	*D. canaliculata* [93], *D. eriantha* [105]



Scheme 1.

61) [93, 173, 174] are the most interesting examples of this class of compounds. The dihydroxynaphthalene substituted 7-methyljuglone (celebaquinone, **62** and isocelebaquinone, **63**) [169] and plumbagin (ebenone, **64**) [175] have been isolated from the heartwood of *D. celebica* and stem bark of *D. ebenum* respectively. Yerrinquinone (**65**) isolated from the fungal infested stems of *D. montana* is the lone example of a 1,4-naphthoquinone metabolite without a methyl group at 2- or 7- position [176]. The monomeric 1,4-naphthoquinone metabolites isolated so far from *Diospyros* are presented in Table 13.

Oligomers of plumbagin and 7-methyljuglone

The majority of the *Diospyros* naphthoquinones are of this class and so far 33 oligomeric metabolites have

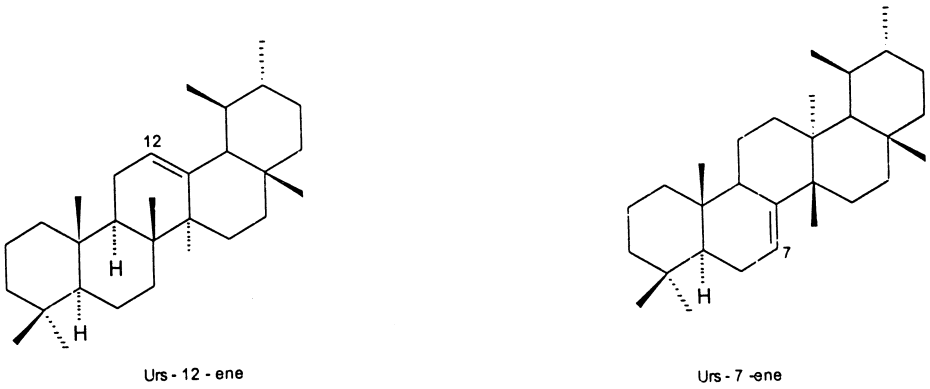


Chart 2.

Table 8. Distribution of ursane type triterpenoid metabolites in *Diospyros* species

SI. No	Compound	Species [Ref.]
1.	Ursolic acid (**12**)	*D. castanea* [98], *D. cauliflora* [98], *D. cordifolia* [127], *D. curranii* [98], *D. ebenum* [102, 103], *D. evena* [98], *D. ferrea* [95], *D. hirsuta* [17], *D. kaki* [30, 92, 108, 125], *D. leucomelas* [55, 56], *D. lotus* [94, 114], *D. malanonilau* [141], *D. melanoxylon* [110, 140], *D. montana* [98, 137], *D. morrisiana* [114], *D. quaesita* [17], *D. tomentosa* [95]
2.	Ursolic acid esters	
	a. acetate (**13**)	*D. eriantha* [105], *D. lotus* [134, 135]
	b. palimitate (**14**) & stearate (**15**)	*D. montana* [137]
	c. 3β-acetoxy-11-ene-28,13-olide (**19a**)	*D. eriantha* [105]
3.	α-Amyrenone (**16**)	*D. ebenum* [101, 103]
4.	epi-Uvaol (**17**)	*D. montana* [138]
5.	α-Amyrin (**10**)	*D. cordifolia* [127], *D. cornii* [23, 121], *D. ebenum* [101–104], *D. kaki* [126], *D. kirkii* [21, 22, 121], *D. mafiensis* [123], *D. maingayi* [94], *D. melanoxylon* [142], *D. mespiliformis* [21, 22, 121], *D. montana* [137], *D. natalensis* [123], *D. sylvatica* [139]
6.	Uvaol (**18**)	*D. kaki* [108], *D. lotus* [94], *D. maingayi* [94]
7.	Marsformosanone (**19b**)	*D. peregrina* [116]
8.	Bauerenol (**11**)	*D. ebenum* [101, 103], *D. kirkii* [120, 121], *D. melanoxylon* [140], *D. mespiliformis* [120, 121], *D. sylvatica* [139]
9.	19α-hydroxyursolic acid (**19c**)	*D. kaki* [30]

Table 9. Distribution of oleanane type triterpenes in *Diospyros* species

SI. No	Compound	Species [Ref.]
1.	Oleanolic acid (**24**)	*D. castanea* [98], *D. cauliflora* [98], *D. curranii* [98], *D. evena* [98], *D. kaki* [30, 92, 108, 125], *D. malanonilau* [141], *D. melanoxylon* [111, 139], *D. montana* [98, 137], *D. moonii* [17], *D. oblongifolia* [17], *D. peregrina* [144], *D. tomentosa* [95], *D. zombensis* [23, 24]
2.	Oleanolic acid glycosides (**20**–**23**)	*D. peregrina* [143], *D. zombensis* [23, 24]
3.	Oleanolic acid acetate (**26**)	*D. eriantha* [105], *D. lotus* [94]
4.	Oleanolic acid fatty esters (**27** & **28**)	*D. montana* [137]
5.	β-Amyrin (**25a**)	*D. cordifolia* [127], *D. lotus* [134, 135], *D. morrisiana* [37], *D. peregrina* [146]
6.	Olean-12-ene-3-one (**25b**)	*D. morrisiana* [37]

Table 10. Distribution of taraxeranes in various *Diospyros* species

SI. No.	Compound	Species [Ref.]
1.	Taraxerol (**30**)	*D. cordifolia* [127], *D. ferrea* [95], *D. hirsuta* [17], *D. kaki* [146, 147], *D. lotus* [94, 95, 114], *D. mollis* [13], *D. morrisiana* [114], *D. nicaraguensis* [148]
2.	Taraxeryl acetate (**31**)	*D. maingayi* [94], *D. singaporensis* [94]
3.	Taraxerone (**32**)	*D. acuta* [17], *D. ferrea* [95], *D. lotus* [94], *D. moonii* [17], *D. quaesita* [17], *D. thwaitesii* [17], *D. oblongifolia* [17], *D. oppositifolia* [17], *D. rheophytica* [17]

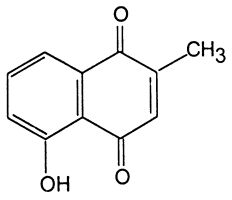
Table 11. Distribution of steroidal skeletons in *Diospyros* species

SI. No.	Compound	Species [Ref.]
1.	β-Sitosterol (**37a**)	*D. acuta* [17], *D. buxifolia* [95, 98], *D. chaetocarpa* [17], *D. chloroxylon* [109, 156], *D. cordifolia* [127], *D. discolor* [109, 130], *D. ebenaster* [128], *D. ebenum* [103], *D. eriantha* [105], *D. ferrea* [95], *D. hirsuta* [17], *D. indica* [130], *D. kaki* [30, 108, 109], *D. kirkii* [119], *D. lotus* [95], *D. malanonilau* [49, 50], *D. melanoxylon* [110, 112, 151], *D. moonii* [138], *D. montana* [137, 138, 152, 154], *D. morrisiana* [150, 155], *D. oblongifolia* [17], *D. oppositifolia* [17], *D. peregrina* [112, 115, 137, 144], *D. quaesita* [17], *D. rheophytica* [17], *D. spinescens* [17], *D. texana* [128], *D. tomentosa* [95], *D. thwaitesii* [17], *D. walkeri* [17]
2.	β-Sitosterol glucoside (**38**)	*D. kaki* [30], *D. montana* [137, 138], *D. morrisiana* [150], *D. peregrina* [115, 137]
3.	Stigmasterol (**39**)	*D. buxifolia* [98], *D. castanea* [98], *D. cauliflora* [98], *D. curranii* [98], *D. dipenhorstii* [98], *D. ebenum* [103], *D. evena* [98], *D. kaki* [108], *D. mollis* [98], *D. montana* [98, 138, 154], *D. morrisiana* [155], *D. sanza-minika* [98], *D. variegata* [98]
4.	Stigmasta-4-ene-3-ol (**40**)	*D. morrisiana* [155]
5.	Stigmasta-5,6-dihydro-22-ene-3-ol (**41**)	*D. discolor* [157]
6.	Campesterol (**37b**)	*D. kaki* [108]

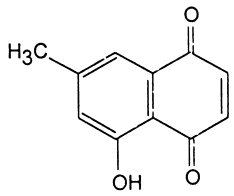
Table 12. Distribution of plumbagin and 7-methyljuglone in *Diospyros* species

SI. No.	Compound	Species [Ref.]
1.	Plumbagin (**42**)	*D. canaliculata* [93], *D. ebenum* [90], *D. elliptifolia* [118], *D. gracilipes* [159], *D. hebecarpa* [90, 91], *D. kaki* [107, 108], *D. maritima* [145, 160], *D. siamang* [94], *D. siderophylla* [100], *D. walkeri* [17], *D. wallichii* [94]
2.	7-Methyljuglone (**43**)	*D. alboflavescena* [132], *D. austro-africana* [161], *D. chloroxylon* [156], *D. ebenaster* [128], *D. ebenum* [90], *D. ferrea* [145], *D. fischeri* [123], *D. gilleti* [132], *D. guianensis* [106], *D. heterotricha* [162], *D. hoyleana* [132], *D. inhacaensis* [161], *D. ismailii* [94], *D. kaki* [107, 108], *D. kaki* var. *sylvestris* [147], *D. lotus* [114, 134], *D. mafiensis* [123], *D. mannii* [96], *D. melanoxylon* [163], *D. montana* [131], *D. moonii* [18], *D. natalensis* [161], *D. nicaragunesis* [148], *D. rotundifolia* [161], *D. squarrosa* [121], *D. sumatrana* [94], *D. usambarensis* [19, 164], *D. verrucosa* [20], *D. virginiana* [10], *D. whyteana* [165], *D. zombensis* [23, 24, 120]

been isolated (Table 14). These oligomers are formed by coupling between (i) 7-methyljuglone monomers (ii) plumbagin monomers and (iii) 7-methyljuglone and plumbagin monomers. The coupling patterns can be conveniently identified by ^{1}H NMR resonances [178]. It is very interesting to note that 32 out of 33 oligomers isolated so far belong to type 1 and type 2 coupling patterns. Oligomers of type 3 are rare and so far only one compound viz. ehretione (**70**) has been isolated [179]. Waterman *et al.* reported that the oligomeric synthesis in *Diospyros* sp. is under some type of control, probably by a photochemical process [18].



Plumbagin (42)



7 - Methyljuglone (43)

Table 13. Distribution of monomeric, 1,4-naphthoquinone metabolites in *Diospyros*

SI. No.	Species [Ref.]	Compound
1.	*D. celebica* [169]	2-methyl-5-methoxy-6-hydroxy-1,4-naphthoquinone (diomelquinone, **46**)
2.	*D. melanoxylon* [151, 166–168]	(i) 2-methyl-5-methoxy-6-hydroxy-1,4-naphthoquinone (diomelquinone, **46**) (ii) 2-methyl-5-methoxy-1,4-naphthoquinone (**47**) (iii) 2-methyl-3-hydroxy-5-methoxy-1,4-naphthoquinone (**48**) (iv) 2-methyl-5, 6-dimethoxy-1,4-naphthoquinone (**49**)
3.	*D. maritima* [160]	(i) 3-bromo plumbagin (**50**) (ii) 3-chloro plumbagin (**51**) (iii) 3-hydroxy plumbagin (droserone, **52**)
4.	*D. heterotricha* [161, 171]	methylnaphthazarin (**53**)
5.	*D. lycioides* [171]	methylnaphthazarin (**53**)
6.	*D. kaki* and *D. kaki* var. *sylvestris* [107, 108]	shinanolone (**54**)
7.	*D. maingayi* [94]	shinanolone (**54**)
8.	*D. morrisiana* [150]	shinanolone (**54**)
9.	*D. virginiana* [10]	shinanolone (**54**)
10.	*D. maritima* [145]	isoshinanolone (**55**)
11.	*D. samoensis* [172]	isoshinanolone (**55**)
12.	*D. siamang* [94]	isoshinanolone (**55**)
13.	*D. wallichii* [94]	isoshinanolone (**55**)
14.	*D. canaliculata* [93]	epi-isoshinanolone (**56**)
15.	*D. ismailii* [173, 174]	ismailin (**57**)
16.	*D. montana* [131]	(i) chromenone ester (**58**) (ii) chromenone acid (**59**)
17.	*D. canaliculata* [93, 173, 174]	(i) canaliculatin (**60**) (ii) cyclocanaliculatin (**61**)
18.	*D. celebica* [169]	(i) celebaquinone (**62**) (ii) isocelebaquinone (**63**)
19.	*D. ebenum* [175]	ebenone (**64**)
20.	*D. montana* [176]	yerrinquinone (**65**)
21.	*D. alboflavescena* [132]	plumbagone (**66**)
22.	*D. gilleti* [132]	plumbagone (**66**)
23.	*D. hoyleana* [132]	plumbagone (**66**)
24.	*D. samoensis* [172]	plumbagone (**66**)
25.	*D. morrisiana* [150]	3-methoxyjuglone (**67**)
26.	*D. kaki* [177]	3-methoxy-7-methyljuglone (**68**)
27.	*D. usambarensis* [19]	(i) 3-methoxy-7-methyljuglone (**68**) (ii) 2-methoxy-7-methyljuglone (**69**)

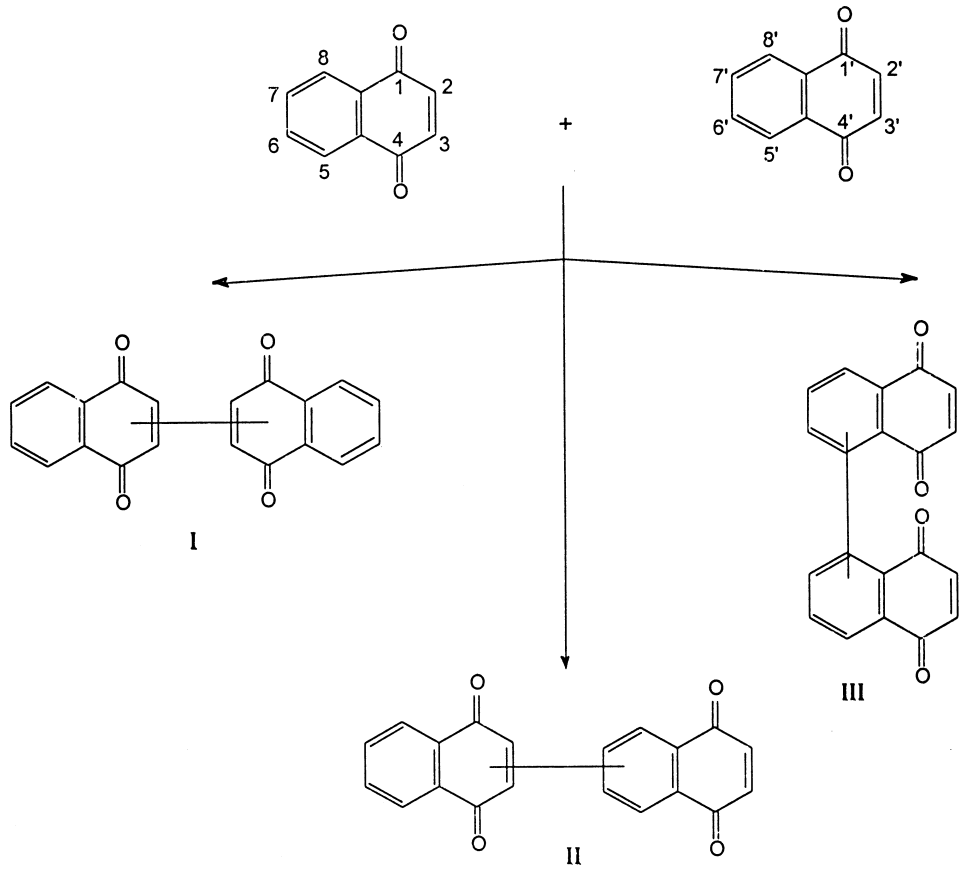
The oligomers differ in the points through which monomers are attached. The monomers can be linked in three ways viz. (i) quinoid–quinoid (**I**, 2-2′ or 2-3′), (ii) quinoid–benzenoid (**II**, 2-6′ or 2-8′) and (iii) benzenoid–benzenoid (**III**, 5-5′ or 6-6′ or 6-8′) (Scheme 2).

The site of linkage in various oligomers can be located by studying their respective NMR spectra, especially by the methyl and hydrogen bonded hydroxyl resonances [178]. The different oligomers formed by the above linkage patterns, showed marked biological and chemical properties. It has been

Table 14. The distribution of different oligomeric naphthoquinone metabolites in *Diospyros* species

Sl. No.	Compound	Coupling pattern*	Species [Ref.]
1.	Diospyrin (**71**)	7-Mej × 2 (q-ar, 2-6′)	*D. abyssinica* [93], *D. chloroxylon* [156], *D. cinnabarina* [18], *D. fragrans* [93], *D. gracilescens* [18], *D. kaki* [107, 108], *D. kamerunensis* [93], *D. longiflora* [93], *D. mannii* [96], *D. montana* [83, 131, 153], *D. obliquifolia* [156], *D. spinescens* [17], *D. virginiana* [118]
2.	Neodiospyrin (**81**)	7-Mej × 2 (q-ar, 2 or 3-8′)	*D. kaki* [107, 108, 177], *D. ismailii* [94]
3.	*β*′-Dihydrodiospyrin (**82**)	7-Mej × 2 (q-ar, 2-6′)	*D. montana* [186]
4.	3′-Methoxydiospyrin (**83**)	7-Mej × 2 (q-ar, 2-6′)	*D. mannii* [96]
5.	Tetrahydrodiospyrin (**84**)	7-Mej × 2 (q-ar, 2-6′)	*D. montana* [187]
6.	8-Hydroxydiospyrin (**85**)	7-Mej × 2 (q-ar, 2-6′)	*D. montana* [131]
7.	Cyclodiospyrin (**73**)	7-Mej × 2 (q-ar, 2-6′ & 3-5′)	*D. montana* [131]
8.	2′-Chlorodiospyrin (**86**) 3′-Chlorodiospyrin (**87**) 3′-Chloro-2′-hydroxydiospyrin (**88**)	7-Mej × 2 (q-ar, 2-6′)	*D. montana* [131]
9.	Isodiospyrin (**72**)	7-Mej × 2 (ar-ar, 6-8′)	*D. abyssinica* [9], *D. alboflavescena* [132], *D. bipindensis* [18], *D. chloroxylon* [156], *D. dendo* [93], *D. ebenaster* [128], *D. ferrea* [145], *D. gilleti* [132], *D. gracilescens* [18, 93], *D. hoyleana* [132], *D. kaki* & *D. kakisylvestris* [107, 108, 147], *D. lotus* [114, 135], *D. maingayi* [94], *D. mespiliformis* [118], *D. montana* [131], *D. morrisiana* [37, 114], *D. nicaraguensis* [48], *D. texana* [128], *D. usambarensis* [19], *D. verrucosa* [20], *D. virginiana* [118], *D. whyteana* [165], *D. zombensis* [23, 24, 166–168]
10.	3′-Methoxyisodiospyrin (**89**) 2′-Methoxyisodiospyrin (**90**) 3,3′-Dimethoxyisodiospyrin (**91**) 2,3′-Dimethoxyisodiospyrin (**92**) 2,2′-Dimethoxyisodiospyrin (**93**) 8′-Hydroxy-3-methoxy isodiospyrin (**94**)	7-Mej × 2 (ar-ar, 6-8′)	*D. morrisiana* [150]
11.	8-Hydroxyisodiospyrin (**95**)	7-Mej-methylnaphthazarine (q-ar, 3-8′)	*D. ferrea* [145], *D. heterotricha* [171, 188], *D. kaki* [177], *D. lycioides* [171, 188]
12.	Bisisodiospyrin (**80**)	7-Mej × 4 (ar, ar-q, q-ar, ar, 8-6′, 3′-3″, 6″-8″)	*D. japonica* [135], *D. lotus* [114, 135], *D. maingayi* [94], *D. morrisiana* [114, 135], *D. usambarensis* [164]
13.	Diosindigo A (**96**)	7-Mej × 2 (q-q, 3-3′)	*D. bipindensis* [18], *D. buxifolia* [98, 100], *D. cauliflora* [98–100], *D. consolatae* [120], *D. dendo* [93], *D. ehretioides* [98], *D. ferrea* [145], *D. fischeri* [123], *D. hirsuta* [17], *D. kirkii* [123], *D. mafiensis* [123], *D. maingayi* [98], *D. melanoxylon* [181], *D. moonii* [17], *D. squarrosa* [120], *D. sumatrana* [98], *D. usambarensis* [164], *D. variegata* [98], *D. verrucosa* [20], *D. zenkeri* [93], *D. zombensis* [120]
14.	Diosindigo B (**75**)	7-Mej × 2 (q-q, 2-2′)	*D. celebica* [98, 99, 169], *D. melanoxylon* [181], *D. usambarensis* [164]
15.	Rotundiquinone (**97**)	7-Mej × 2 (q-q, 2-3′)	*D. ismailii* [94], *D. rotundifolia* [99]
16.	Pentacyclic quinone (**74**)	—	*D. melanoxylon* [181]
17.	Biramentaceone (**98**)	7-Mej × 2 (q-q, 2-2′)	*D. melanoxylon* [181], *D. montana* [131]
18.	Diosquinone (**76**)	7-Mej × 2	*D. mafiensis* [123], *D. tricolor* [182], *D. zombensis* [120]
19.	Batocanone (**77**)	7-Mej × 2 (ar-ar, 6-8′)	*D. batocana* [183]
20.	Ethylidene-6,6′-biplumbagin (**78**)	—	*D. maritima* [184]
21.	Xylospyrin (**79**)	7-Mej × 3 (q-q-q, 3-3′, 2′-2″, 3″-2)	*D. chloroxylon* [185], *D. ebenaster* [128], *D. texana* [128]
22.	Mamegakinone (**99**)	7-Mej × 2 (q-q, 3-3′)	*D. kaki* & *D. kaki sylvestris* [107, 108], *D. lotus* [114, 135], *D. lycioides* [188], *D. mollis* [13], *D. montana* [114], *D. obliquifolia* [18], *D. usambarensis* [19, 164], *D. zombensis* [164]
23.	3,3′-Dimer of 6-hydroxy-5-methoxy-2-methyl-1,4-naphthoquinone (**100**)	Plmb × 2 (q-q, 3-3′)	*D. melanoxylon* [189]
24.	Elliptinone (**101**)	Plmb × 2 (ar-ar, 6-6′)	*D. elliptifolia* [118], *D. maritima* [145, 184], *D. mollis* [13], *D. samoensis* [172], *D. siamang* [94], *D. walkeri* [17], *D. wallichii* [94]
25.	Maritinone (**102**)	Plmb × 2 (ar-ar, 8-8′)	*D. kaki* [177], *D. maritima* [145, 184], *D. samoensis* [172]
26.	Ehretione (**70**)	7-Mej-Plmb (q-ar, 2-6′)	*D. ehretioides* [179]

* 7-Mej: 7-methyljuglone; Plmb: plumbagin; q: quinone; ar: aryl.



Scheme 2.

reported in literature that closely related sympatric species will tend to elaborate a diverse profile of secondary metabolites so as to face potential predators with the largest possible range of detoxification problems [180]. This may also hold good for the *Diospyros* genus, which elaborate a variety of naphthoquinones.

Further coupling in the naphthoquinone dimeric structures generates interesting pentacyclic systems and so far two such metabolites viz. cyclodiospyrin (**73**) with an additional 3–5′ coupling and a pentacyclic quinone (**74**) with an additional 1–3″ coupling have been isolated from *D. montana* [131] and *D. melanoxylon* [181] respectively. These pentacyclic metabolites may be isolated as artifacts, since exposure of diosindigo B (**75**), a dimer of 7-methyljuglone to sunlight resulted in the formation of traces of compound **73** [181]. Another variation in these skeletons is the isolation of dimeric naphthoquinone epoxides. So far only two such metabolites, diosquinone (**76**) [20, 120, 122, 182] and batocanone (**77**) [183] have been isolated. The isolation of ethylidene-6,6′-biplumbagin (**78**) from *D. maritinone* is the first example of naphthoquinone dimer connected through an ethylidene linkage [184]. So far only one triquinone, xylospyrin (**79**) [128, 185] and one tetraquinone, bisisodiospyrin (**80**) [94, 114, 134, 184] have been isolated in the *Diospyros* genus. Interestingly in both the cases the monomer is 7-methyljuglone.

Common biogenetic pathways for triterpene and naphthoquinone metabolites of Diospyros

The uniqueness of *Diospyros* genus is the elaboration of a large number of triterpenoid and napthhoquinone metabolites. It is very interesting to note that the triterpenes isolated so far are all with a pentacyclic core and the naphthoquinones are with a juglone framework. In view of the co-occurrence of these two classes in significant quantities in a number of *Diospyros* plants, their biosynthesis assumes significance. The biosynthesis of pentacyclic triterpenes has been examined in considerable detail and proceeds through three major steps viz. (i) the formation of a biological isopentane unit from acetate via mevalonic acid, (ii) transformation of mevalonic acid to 3(*S*)-squalene-2,3-epoxide and (iii) conversion of squalene epoxide to cyclic terpene moieties [190–193]. Experimental verification for the above hypothesis has been provided by Tomita *et al.* by studying the ^{13}C labelling patterns elucidated by NMR experiments in the oleanane and ursane type triterpenes isolated from *Isodon japonicus* tissue cultures fed with [4-^{13}C] mevalonic

acid [194, 195]. Four different biosynthetic pathways for the formation of naphthoquinones in higher plants have been described [158, 192, 193] and they are: (i) incorporation of shikimic acid into the benzenoid naphthoquinone ring with retention of the carboxyl group [196, 197], (ii) homogentisic acid pathway involving the condensation of mevalonic acid and toluhydroquinone [198], (iii) prenylation of *p*-hydroxybenzoic acid with geranyl pyrophosphate followed by decarboxylation and ring closure [199] and (iv) polyacetate-melonate pathway [200]. The structurally simple naphthoquinone metabolite juglone [162] is derived from the shikimic acid pathway. Floss *et al*. [201] have confirmed this hypothesis by feeding experiments on *Juglans regia* with 1,6-^{14}C or 3-^{3}H labelled shikimic acid. But interestingly this hypothesis has been proved wrong, with plumbagin (**42**) and 7-methyljuglone (**43**), the two key monomeric naphthoquinone metabolites of *Diospyros*, *Drosera* and *Plumbago*. Although, a polyacetate–melonate pathway has been confirmed for their presence in *Drosera* and *Plumbago* plants [200], their biosynthetic pathways in *Diospyros*, have not yet been established thoroughly. However, Tezuka *et al*. [145] have suggested an acetate–polymelonate pathway in view of the significant accumulation of naphthol and naphthoquinone metabolites. In view of the co-occurrence of pentacylic triterpenes and juglone-based naphthoquinone metabolites, a common biogenetic precursor, acetate is believed to be responsible for their unusual co-existence in *Diospyros*. The phenolic metabolite, 3-methyl-naphthalene-1,8-diol (**104**), isolated from the berries of *D. mollis* [202] is biogenetically significant and assumed to be the key precursor for all the phenolic and naphthoquinone constituents of *Diospyros* plants. A possible biogenetic pathway for the co-occurrence of pentacyclic triterpenes and naphthoquinones in the *Diospyros* genus is presented in Scheme 3.

The phenol **104** is assumed to undergo a variety of transformations to form biogenetically useful metabolites such as plumbagin (**42**), 7-methyljuglone (**43**) (by hydroxylation in either of the rings followed by oxidation) and diospyrol (**105**), an anthelmintic principle of *D. mollis* by aryl–aryl coupling. In fact, diospyrol is believed to be the precursor for a number of oligomeric naphthoquinones such as elliptinone (**101**) and mamegakinone (**99**). It is also believed that the actual dimersation step probably takes place before oxidation to the quinone level. The isolation of ebenone (**64**) from *D. ebenum* [175] provides evidence for this hypothesis.

NAPHTHALENE-BASED AROMATICS

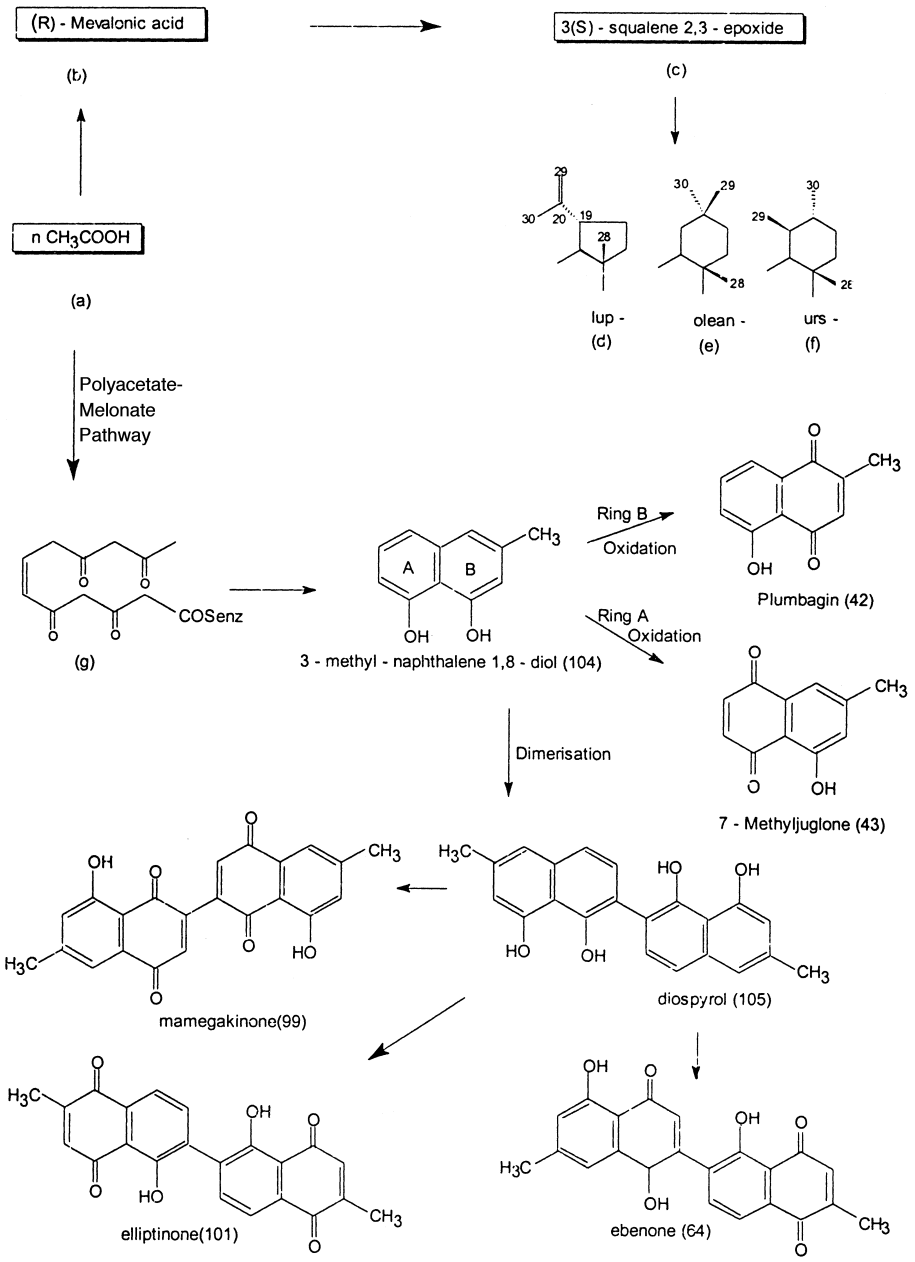
Some of these metabolites are assumed to be the precursors of naphthoquinones. Due to their tendency to transform further, these metabolites have been isolated from a limited number of *Diospyros* plants. Mostly these metabolites have been isolated with aldehydic, carboxylic and hydroxylic (phenolic) functionalities (Table 15). The isolation of 3-methyl-naphthalene-1,8-diol (**104**) and its 6,6′-coupled product (diospyrol, **105**) from the berries of *D. mollis* is very significant in view of their biogenetic importance.

BENZOPYRONES

A significant number of α- and γ-benzopyrone (coumarin & flavonoid) based metabolites mostly with glycosidic linkages accumulate in *Diospyros* plants. Among the coumarins, the 6-methyl ether of umbelliferone (scopoletin, **124**) [10, 17, 99, 128, 159, 210], ellagic acid (**125**) [110] and its glycosides (**126**–**128**) [211–213] are notable with the former being widespread. The flavonoids isolated so far all belong to the 3,5,7-trihydroxyflavone subclass with a glycosidic linkage at 3-position. The *D. kaki* leaves are the potential source for these metabolites and so far have yielded 14 flavonol glycosides (**132**–**145**) and some of them have been reported to inhibit angiotensin converting enzyme activity [84, 206, 218]. The glycosides (**147**–**149**) of *D. peregrina* [219–221] and the proanthocyanidin polymers, **150** (*D. virginiana*, [222]) and **151** (*D. diepenhorstii*, [12]) are the structural variants of this class. The metabolite, **151** with a 2,3-*cis* prodelphinidin polymeric unit is particularly interesting in view of its significant piscicidal and molluscicidal activities. Various benzopyrone metabolites of *Diospyros* are listed in Table 16.

HYDROCARBONS AND LIPIDS

Considerable work has been done on the lipid soluble fractions of *Diospyros* plants. Mostly, these fractions are found to accumulate as long chain hydrocarbons, fatty alcohols and acids. The majority of these compounds are saturated and the C_{31} alkane (hentriacontane, **154**) and its corresponding alcohol (hentriacontanol, **158**) are found to present in a maximum number of species. Notable compounds of this group are (i) nonadecan-7-ol-2-one (**160**) isolated from the ethanol extract of *D. peregrina* stem [223], (ii) 8-hydroxyoctadec-10(*Z*)-enoic acid (**161**) isolated from petrol extract of *D. montana* seeds [224], (iii) keto-*cis*-13-octadecenoic acid (**162**) and (iv) cyclopropenoid fatty acids viz; malvalic acid (**163**) and sterculic acid (**164**) in the seed oil of *D. melanoxylon* [225]. Certain *Diospyros* seed oils have been screened for fatty acid composition and for possible usage in foods [226] and drugs [227]. The fatty acid composition of *D. melanoxylon* [228], *D. montana* [154] and *D. peregrina* [146] is found to be: (compound No. and %): lauric (**165**; 4.8; nil; nil), myristic (**166**; 9.9; nil; 7.28), palmitic (**167**; 37.9; 27.9; 8.42), stearic (**168**; 16.1; 11.09; 10.36), arachidic (**169**; 5.3; nil; 4.84), behenic (**170**; 5.3; nil; nil), oleic (**171**; 19.7; 37.08; 46.89), linoleic (**172**; 1.2; 23.92; 15.02), linolenic (**173**; nil; nil; 9.02). Palmitic



Scheme 3.

(**167**) and stearic (**168**) acids were also detected in one of the species i.e. *D. kaki* [30].

AMINO ACIDS, CAROTENOIDS AND SUGARS

A significant number of primary metabolic substances (e.g. amino acids and sugars) and polyenes (e.g. carotenoids) are found to accumulate in *Diospyros* species. The genus has so far yielded 14 amino acids, 14 free sugars and more than 16 carotenoid pigments. Interestingly, the majority of these compounds were isolated from *D. kaki* fruits. The amino acids are mostly non-essential and found with a variety of functionalities. TLC, column chromatography and reverse phase HPLC techniques have been successfully employed to detect and quantify the carotenoid content of *Diospyros* fruits. The carotenoids are found to accumulate four times more in skin than in pulp of the fruit. The oxygenated pigments (xanthophylls) are more prevalent than the hydrocarbon derivatives. The presence of some neocarotenoids has also been noted in the Japanese varieties, *D. kaki* and *D. kachiya*. Among the sugars, monosaccharides are more abundant and d-mannitol is the first sugar detected in *Diospyros*. In 1922, Iwata and Tazaki first found that 'Kakishibu' (tannin like component of kaki

Table 15. Naphthalene-based aromatics of *Diospyros* species

SI. No.	Species [Ref.]	Compound
1.	*D. celebica* [203]	(i) 1,8-dimethoxy-6-methyl-2-naphthol (macassar II, **106**) (ii) 1,2,8-trimethoxy-6-methyl-naphthalene (macassar III, **107a**)
2.	*D. celebica* [169]	dihydrodiosindigo B (**107b**)
3.	*D. chloroxylon* [157]	(i) 2-methyl-3,6-dihydroxy-4,5-dimethoxy-naphthalene (**108**) (ii) 2-methyl-3,4,5,6-tetramethoxy-naphthalene (**109**)
4.	*D. ebenum* [103, 104, 204]	(i) 6-hydroxy-4,5-dimethoxy-2-naphthaldehyde (**110**) (ii) 4,5,6-trimethoxy-2-naphthalene (**111**) (iii) 6-hydroxy-4,5-dimethoxy-2-naphthoic acid (**112**) (iv) 2-carbomethoxy-4,5-dimethoxy-6-hydroxy-naphthalene (**113**)
5.	*D. melanoxylon* [151]	(i) 3-methyl-1,8-dimethoxynaphthalene (**114**) (ii) 3-methyl-2,8-dimethoxy-1-naphthol (**115**) (iii) 3-methyl-4,8-dimethoxy-1-naphthol (**116**) (iv) 3-methyl-8-methoxy-1-naphthol (**117**)
6.	*D. mollis* [13, 175, 205–208]	(i) 3-methylnaphthalene-1,8-diol (**104**) (ii) 6,6′-dimer of 3-methylnaphthalene-1,8-diol (diospyrol, **105**) (iii) diospyrol-8,8′-di-*O*-6-*β*-D-epiofuranosyl-*β*-D-glucopyranoside (**118**)
7.	*D. quiloensis* [209]	(i) 4,5,6,8-tetramethoxy naphthaldehyde (**119**) (ii) 5-hydroxy-4,6,8-trimethoxynaphthaldehyde (**120**) (iii) 4,5,6-trimethoxynaphthalehyde (**121**) (iv) 4,5-dimethoxynaphthaldehyde (**122**) (v) 5-hydroxy-4-methoxy-2-naphthaldehyde (**123**)

fruit) contained a white crystalline component of sweet taste. Later in 1929 Iwata identified the material as d-mannitol (**210**) and found that it is the notable factor in sweetening element of *D. kaki* [86, 87]. Initially it was reported that the white powder of dried persimmon contains mannitol, but it was later proved to be wrong by several groups. Haq and Hennan reported an elegant procedure for the extraction of free sugars from *D. discolor* fruits [248]. The pre-treated fruits were successively extracted with hot water and dilute acid. The acid soluble portion was purified by repeated dissolution in water, dialysis and precipitation with ethanol. The hot water and acid solubles on individual analysis found to contain D-galactose (**205**), D-galacturonic acid (**206**), D-glucose (**208**), L-arabinose (**203**), D-xylose (**217**) and L-rhamnose (**213**). Various compounds isolated so far in these groups are listed below:

Amino acids

Alanine (**174**; *D. kaki* [229], *D. peregrina* [230]); asparitic acid (**175**; *D. kaki* [229], *D. lotus* [231]); L-citrulline (**176**; *D. kaki* [232]); cystine (**177**; *D. lotus* [231], *D. peregrina* [230]); glutamic acid (**178**; *D. kaki* [229]); glycine (**179**; *D. kaki* [229], *D. peregrina* [230]); hydroxyproline (**180**; *D. peregrina* [230]); leucine (**181**; *D. lotus* [231], *D. kaki* [229]); methionine (**182**; *D. peregrina* [230]); norvaline (**183**; *D. peregrina* [230]); phenylalanine (**184**; *D. lotus* [231]); serine (**185**; *D. kaki* [229]); threonine (**186**; *D. lotus* [231], *D. kaki* [229]) and tyrosine (**187**; *D. lotus* [231], *D. kaki* [229]).

Carotenoids

Antheraxanthin (**188**; *D. kaki* [235, 240], persimmon [238]); α-carotene (**189**; *D. costata* [89]; persimmon [233, 236]; *D. kaki* [235, 240]; *D. kachiya* [239]); *β*-carotene (**190**; *D. costata* [89]; *D. kaki* [88, 235, 237, 240]; persimmon [233, 236, 238]); *ξ*-carotene (**191**; *D. kaki* [235]); *γ*-carotene (**192**; *D. kaki* [235]); cryptoxanthin (**193**; *D. costata* [89]; *D. kaki* [235, 237, 240]; *D. kachiya* [239]; persimmon [233, 234, 238]); leutein (**194**; *D. kaki* [235]); lutein epoxide (**195**; *D. kachiya* [239]); luteoxanthin (**196**; *D. kachiya* [239]); lycopene (**197**; *D. costata* [89]; *D. kaki* [235, 237]; persimmon [233, 234, 238]); *cis*-mutatoxanthin (**198**; *D. kaki* [240]); neo-carotenes (*D. kachiya* [239]); neo-lutein (**201**; *D. kaki* [240]); phytoene (**199**; *D. kaki* [235]); taraxanthin (=lutein epoxide, **195**; *D. kachiya* [239]); xanthophyll (=lutein, **194**; persimmon [233, 236]) and zeaxanthin (**202**; *D. kaki* [88, 235, 240], persimmon [233, 238]).

Sugars

Arabinose (**203**; *D. discolor* [243]); D-fructose (**204**; *D. kaki* [229, 240, 242–247], *D. peregrina* [249]); D-galacturonic acid (**206**; *D. discolor* [248]); α-D-glucose (**207**; *D. kaki* [247]); *β*-D-glucose (**208**; *D. discolor* [248], *D. kaki* [229, 240, 242–247], *D. peregrina* [249]); D-lactose (**209**; *D. peregrina* [249]); mannitol (**210**; *D. kaki* [69–81, 241], *D. virginiana* [117]); *β*-glucopyranose pentaacetate (**211**; *D. morrisiana* [150]); raffinose (**212**; *D. peregrina* [249]); L-rhamnose (**213**; *D. discolor* [248]); sequoyitol (**214**; *D. melanoxylon*

Table 16. Benzopyrone metabolites of *Diospyros* species

SI. No.	Compound	Species [Ref.]
1.	Scopoletin (**124**)	*D. ebenaster* [128], *D. gracilipes* [159], *D. kaki* [210], *D. quaesita* [17], *D. siderophylla* [100], *D. virginiana* [10], *D. walkeri* [17]
2.	Ellagic acid (**125**)	*D. ebenum* [103]
3.	3,3′-Di-*O*-methylellagic acid-4-*O*-*β*-D-galactopyranosyl (1-4)-*β*-D-glucopyranoside (**126**)	*D. discolor* [211]
4.	3,3′-Di-*O*-methylellagic acid-4-*O*-*β*-D-xylopyranosyl (1-4)-*β*-D-glucopyranoside (**127**)	*D. discolor* [212]
5.	3,3′-Di-*O*-methylellagic acid-4-*O*-*α*-L-rhamnopyranosyl (1-4)-*β*-D-glucopyranoside (**128**)	*D. mebola* [213]
6.	Diospyroside (**129**)	*D. sapota* [214]
7.	6-Hydroxy-7-methoxycoumarin (**130**)	*D. kaki* [210]
8.	4-Hydroxy-5-methylcoumarin (**131**)	*D. ismailii* [215]
9.	Kampferol (**132**)	*D. kaki* [30, 216]
10.	Kampferol 3-*O*-*α*-L-rhamnopyranoside (**133**)	*D. kaki* [216]
11.	Kampferol 3-*O*-*β*-D-xylopyranoside (**134**)	*D. kaki* [216]
12.	Kampferol 3-*O*-*β*-D-galactopyranoside (trifolin, **135**)	*D. kaki* [30, 216]
13.	Kampferol 3-*O*-*α*-L-arabinopyranoside (**136**)	*D. kaki* [216]
14.	Kampferol 3-*O*-*β*-D-glucopyranoside (astragalin, **137**)	*D. kaki* [216, 218]
15.	Kampferol 3-*O*-(2″-*O*-galloyl)-*β*-D-glucopyranoside (**138**)	*D. kaki* [70, 216, 218]
16.	Quercetin (**139**)	*D. kaki* [30, 216]
17.	Quercetin 3-*O*-*α*-L-arabinopyranoside (**140**)	*D. kaki* [216]
18.	Quercetin 3-*O*-*α*-L-rhamnopyranoside (quercetrin, **141**)	*D. zombensis* [23, 24]
19.	Quercetin 3-*O*-*β*-D-glucopyranoside (isoquerctrin, **142**)	*D. kaki* [70, 216, 218], *D. zombensis* [23, 24]
20.	Quercetin 3-*O*-*β*-D-galactopyranoside (hyperoside, **143**)	*D. kaki* [30, 216], *D. zombensis* [23, 24]
21.	Quercetin 3-*O*-(2″-*O*-galloyl)-*β*-D-glucopyranoside (**144**)	*D. kaki* [70, 216, 218]
22.	Myricetin 3-*O*-*β*-D-glucopyranoside (**145**)	*D. kaki* [216]
23.	Myricetin 3-*O*-*α*-L-rhamnopyranoside (myricetrin, **146**)	*D. lotus* [217]
24.	Leucopelargonidin-3-*O*-*α*-L-rhamnopyranoside (**147**)	*D. peregrina* [219]
25.	3,5,7,5′-Tetrahydroxy-3′-methoxyflavanone-4′-*O*-*α*-L-rhamnopyranoside (**148**)	*D. peregrina* [220]
26.	3,5,7,4′-Tetrahydroxyflavanone-3-*O*-*β*-D-glucopyranosyl(1-4)-*α*-L-rhamnopyranoside (**149**)	*D. peregrina* [221]
27.	Proanthocyanidin polymer (**150**)	*D. virginiana* [222]
28.	Proanthocyanidin polymer (**151**)	*D. diepenhorstii* [12]

Table 17. Hydrocarbons and lipid components of *Diospyros* species

SI. No.	Compound	Molecular formula	Species [Ref.]
1.	Hexacosane (**152**)	$C_{26}H_{54}$	*D. peregrina* [115, 137]
2.	Nonacosane (**153**)	$C_{29}H_{60}$	*D. discolor* [133], *D. malanonilau* [151]
3.	Hentriacontane (**154**)	$C_{31}H_{64}$	*D. austro-africana* [122], *D. cordifolia* [127], *D. discolor* [133], *D. melanoxylon* [142]
4.	Tritriacontane (**155**)	$C_{33}H_{68}$	*D. discolor* [133]
5.	Hexacosanol [cerylalcohol, **156**]	$C_{26}H_{54}O$	*D. ebenum* [101]
6.	Triacontanol (**157**)	$C_{30}H_{56}O$	*D. peregrina* [143]
7.	Hentriacontanol (**158**)	$C_{31}H_{64}O$	*D. cordifolia* [127], *D. melanoxylon* [142]
8.	Heptacosanoic acid (**159**)	$C_{27}H_{54}O_2$	*D. natalensis* [122]
9.	Long chain fatty acids	—	*D. morrisiana* [155]
10.	Nonadecan-7-ol-2-one (**160**)	$C_{19}H_{38}O_2$	*D. peregrina* [223]
11.	Saturated keto alcohol	—	*D. usambarensis* [121]
12.	8-Hydroxy-octadec-10(*Z*)-enoic acid (**161**)	$C_{18}H_{34}O_3$	*D. melanoxylon* [224]
13.	9-Keto-*cis*-13-octadecenoic acid (**162**)	$C_{18}H_{37}O$	*D. melanoxylon* [225]
14.	Malvalic acid (**163**)	$C_{18}H_{32}O_2$	*D. melanoxylon* [225]
15.	Sterculic acid (**164**)	$C_{18}H_{34}O_2$	*D. melanoxylon* [225]

[112]); L-sorbose (**215**; *D. peregrina* [249]); sucrose (**216**; *D. virginiana* [117]) and xylose (**217**; *D. discolor* [248]).

POLYPHENOLS AND TANNINS

These materials have been identified as the astringent principle of *Diospyros* species and found to accumulate significantly in fruit and leaf part of *D. kaki*. Large amounts of phenolic deposits have been found to occur in the leaves of *D. kaki* [250] and *D. ramulosa* [251]. The *D. kaki* leaves especially contain a maximum of 0.97–1.44% polyphenolics around full bloom in May. Delphinidin (**218**), cyanidin (**219**) and gallic acid (**220**) are detected as the major components of the polyphenolic fraction of persimmon fruits [252, 253]. Gallic acid was also detected in the fruits of *D. kaki* [240] and *D. peregrina* [115, 137]. Interestingly, the polyphenolic extracts of *D. kaki* leaves when tested on cotton seeds [254], stimulated germination and growth, prevented wilt and pathological increase of cellulolytic and pectolytic activity in the plant sap and increased lint yield by 51–90%. Procedures for extraction [253], detection by TLC [261] and quantification by UV (275 nm) spectroscopic methods [256] for persimmon tannins have been reported. High tannin levels are found between July and August in leaves and around October in fruits [257]. Matsuo *et al.* reported on persimmon tannin and proposed a repeating unit structure based on gel permeation chromatographic data of methylated tannin [258]. But in a subsequent paper [259] they have suggested that the kaki tannin obtained from fruit belongs to proanthocyanidin B group with C—C inter-flavone linkage from C-4 of one unit to C-6 or C-8 of another. The kaki tannin on acid hydrolysis yielded delphinidin and cyanidin along with catechin, catechin-3-gallate, gallocatechin, gallocatechin-3-gallate and an unknown terminal residue. Among the tannins, kaki tannins are interesting in view of their biological and commercial applications. The former applications have already been covered in the pharmacology section. The stable, non-irritating and astringent condensed persimmon tannins (0.001 $\sim$ 3.0% by wt) are found commercially useful in cosmetics, and a cream with the following composition was prepared by Japanese researchers [260]: squalene (25.0), cetyl alcohol (3.0), olive oil (5.0), glyceryl monostearate (2.0), stearic acid (3.0), xanthangum (0.2), triethanolamine (0.3), methyl-4-hydroxybenzoate (0.2), condensed persimmon tannins (0.001), water (61.2) and perfume (0.1) parts by weight.

MISCELLANEOUS COMPOUNDS

Numerous reports have appeared on the detection of vitamins (A, B_1, B_2 and C) in *Diospyros* and the most notable ones are: (i) detection of 54 IU of vitamin A (**221**) in 1 g of edible portion of *D. kaki* fruits [240] and (ii) isolation of vitamin C (ascorbic acid, **222**), in 2.4% from the fresh tissues of *D. costata* [261]. The lone report on the presence of indoleacetic acid (**223**) is that of Nakamura *et al.* who isolated the acid in 0.3% from the ether soluble portion of ethanol extract of *D. kaki* leaves by employing reverse phase TLC technique [262]. Significant work has been done on the volatile oily fractions of *Diospyros* plants and a variety of compounds have been identified by GC and GC-MS methods (Table 18). Interestingly, the two astringent cultivars of *D. kaki* (fujigaki and senboro) found to contain identical major components (**233**–**237**) [263] and the persimmon aroma has been attributed to the presence of large quantities of bornyl acetate (**204**) and *E*-2-hexenal (**231**) [264].

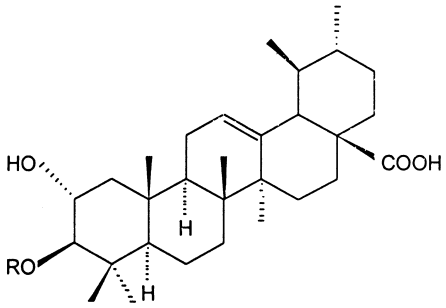
Free aliphatic and aromatic acids are found to accumulate mostly in *D. kaki* [30, 98–100, 240, 246], which so far yielded the following 11 carboxylic acids: malic (**286**), succinic (**269**), fumaric (**270**), isocitric (**271**) ascorbic (**222**), benzoic (**272**), salicylic (**273**), pyromucic (**274**), syringic (**275**), vanillic (**276**) and gallic acids (**220**). The only other carboxylic acid yielding species of the genus is the macassar ebony, *D. celebica* [267] whose bark chloroform extract gave a polar *cis*-cinnamic acid named macassaric acid (**277**). Macassaric acid was found to be a catabolic product of macassar II (dimethoxynaphthol, **106**) and its structure was confirmed by synthesising its corresponding methylester from *O*-naphthoquinone via a cyclic unsaturated anhydride.

A series of interesting guanidine derivatives have been detected in a *Diospyros* species by Kato *et al.* [268], by employing very efficient extraction and identification procedures. The lyophilised sample was extracted with 0.1 M KCl. The extract was treated with 0.1 M CCl_3COOH and eluted from a Dowex 50 W (H^+) column with 2 M NH_4OH. HPLC separation followed by fluorimetric determination with ninhydrin, the extract furnished the following guanidine compounds: guanidinosuccinic acid (**278**), creatine (**279**), guanidinoacetic acid (**280**), *N*-α-acetyl-L-arginine (**281**), γ-guanidinopropionic acid (**282**), γ-guanidinobutyric acid (**283**), L-arginine (**284**), γ-guanidinobutramide (**285**), guanidine (**286**), Me-guanidine (**287**) and about 20 unidentified guanidine derivatives.

The more interesting compounds of this class are anthraquinones and lignans. But these metabolites do not appear to accumulate to any significant extent. Although, naphthoquinone monomers and oligomers are more prevalent in this genus, only two anthraquinone pigments viz. 1,3,5,6-tetrahydroxy-2-methyl anthraquinone-8-*O*-β-D-glucopyranoside (**288**) and 1,3,5-trihydroxy-6-methoxy-2-methyl anthraquinone-8-*O*-β-D-glucopyranoside (**289**) have so far been isolated. Interestingly both the compounds have been isolated from the stem bark of *D. discolor* [269, 270]. So far there are only two reports on the isolation of lignans in *Diospyros* and they are (i) (−)-divanillyltetrahydrofuran ferulate (**290**) from the acetone extract of calyxes of *D. kaki* [271] and (ii) (+)-syr-

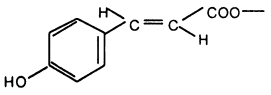
Table 18. Volatile constituents of various *Diospyros* species

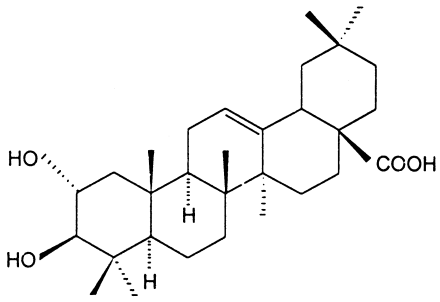
SI. No.	Species [Ref.] (Varieties analysed)	Compounds
1.	*D. kaki* [263]	eugenol (**224**), *p*-cresol (**225**)
	a. Commercial crude drug	dihydroactiniolide (**226**)
	b. Fuyugaki (sweet cultivar)	Me-4-pentenoate (**227**)
	c. Fujigaki (astringent cultivar)	hexanoic acid (**228**), 2-hexenal (**229**)
	d. Senboro (astringent cultivar)	3-hexen-1-ol (**230**), phenyl ethyl-alcohol (**231**), linalool (**232**), 2-butoxy ethanol (**233**), phenylacetaldehyde (**234**), 2,2′-6-trimethyl-6-vinyltetrahydro-2H-pyran-3-ol (**235**), cyclohexylbutyrate (**236**), glycerol triacetate (**237**)
2.	*D. kaki* [264]	(*E*)-2-hexenal (**229**), bornyl acetate (**238**)
	a. astringent	(*E*)-2-hexenol (**239**)
	b. non-astringent	phenylacetaldehyde (**234**), phenyl ethyl acetate (**240**), borneol (**241**), benzothiazole (**242**), neryl acetate (**243**), palmitic acid (**167**), *n*-tricosane (**244**), *n*-pentacosane (**245**)
3.	*D. virginiana* [264]	phenylacetaldehyde (**234**), phenyl ethyl acetate (**240**), borneol (**241**), benzothiazole (**242**), neryl acetate (**243**), palmitic acid (**167**), *n*-tricosane (**244**), *n*-pentacosane (**245**)
4.	*D. discolor* [264]	benzyl benzoate (**246**), benzyl salicylate (**247**), cinnamyl benxoate (**248**), benzyl butyrate (**249**), butyl benzoate (**250**)
5.	*D. blancoi* [266]	α-*trans*-*trans*-farnesene (**251**), methyl-*n*-butyrate (**252**), *n*-propyl-*n*-butyrate (**253**), *n*-butyl-*n*-butyrate (**254**), *n*-pentyl-*n*-butyrate (**255**), *n*-hexyl-*n*-butyrate (**256**), benzyl-*n*-butyrate (**249**), β-phenyl ethyl-*n*-butyrate (**257**), cinnamyl-*n*-butyrate (**258**), methyl-benzoate (**259**), ethyl benzoate (**260**), *n*-propyl benzoate (**261**), *n*-butyl benzoate (**250**), *n*-pentyl benzoate (**262**), *n*-hexyl benzoate (**263**), benzyl benzoate (**246**), β-phenylethyl benzoate (**264**), methyl-salicylate (**265**), benzyl salicylate (**247**), cinnamyl valerate (**266**), linalool (**232**), benzyl alcohol (**267**), β-phenylethyl alcohol (**231**)



(292) R = H

(293) R =





(294)

ingaresinol (**291**) from the ethanol extract of the dried bark of *D. eriantha* [105].

RECENT ADDITIONS TO *DIOSPYROS*

During our current search for alternative uses of kendu (*D. melanoxylon*) leaves, we have isolated hitherto unreported olean-and urs-12-enes (**19c**, **292**–**294**) along with large quantities of α-amyrin, β-amyrin, oleanolic acid and ursolic acid. Significantly, some of these metabolites are not only new to *D. melanoxylon*, but also to the entire *Diospyros* genus (unpublished results). The accumulation of large quantities of α-amyrin (0.70%) and ursolic acid (0.56%). in *D. melanoxylon* assumes significance in view of their recently attributed interesting pharmacological properties such as anti-cancer, anti-HIV and anti-inflammatory.

Acknowledgements—We are highly indebted to the Forest Department (kendu leaves), Govt. of Orissa, India, for their keen interest and generous financial assistance. We are also thankful to Prof. H. S. Ray, Director, Regional Research Laboratory, Bhubaneswar for his interest and encouragement.

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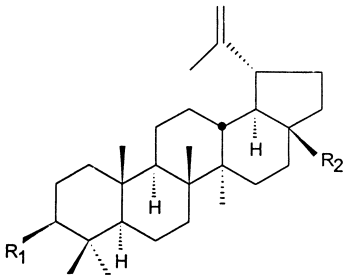
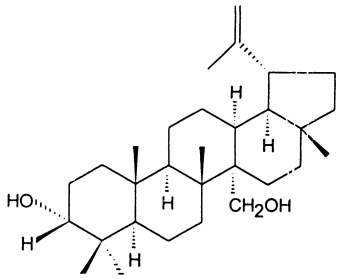
APPENDIX

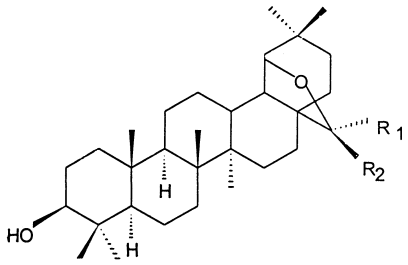
TRITERPENOIDS



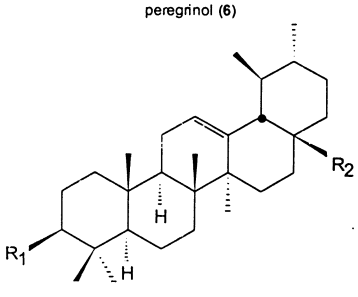
lupeol (1) R_1: β-OH ; R_2 : CH_3
betulin (2) R_1 : β-OH ; R_2 : CH_2OH
betulinicacid (3) R_1 : β-OH ; R_2 : COOH
epi - lupeol (4) R_1 : α-OH ; R_2 : CH_3
lupenone (5) R_1 : = 0 ; R_2 : CH_3
betulinaldehyde (9) R_1 : β-OH ; R_2 : CHO



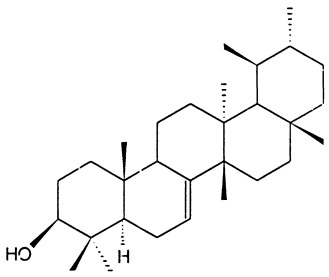
peregrinol (6)



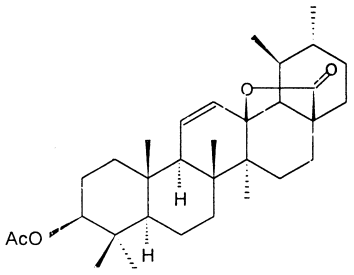
allobetulin (7) R_1 ; R_2 : H
oxyallobetulin (8) R_1 ; R_2 : =O



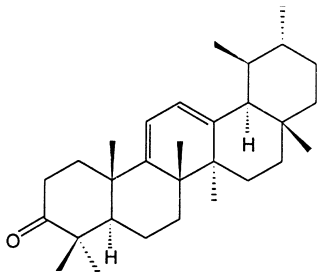
α-amyrin (10) R_1 : β-OH ; R_2 : CH_3
ursolic acid (12) R_1 : β-OH; R_2 : COOH
ursolic acid acetate (13) R_1 : β-$OCOCH_3$; R_2 : COOH
ursolic acid palmitate (14) R_1 : β-$OCO(CH_2)_{14}CH_3$; R_2 : COOH
ursolic acid stearate (15) R_1 : β-$OCO(CH_2)_{16}CH_3$; R_2 : COOH
α-amyrenone (16) R_1 : =O ; R_2 : $-CH_3$
epi-uvaol (17) R_1 : α-OH ; R_2 : CH_2OH
uvaol (18) R_1 : β-OH ; R_2 : CH_2OH



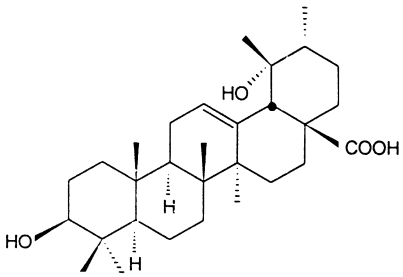
baurenol (11)



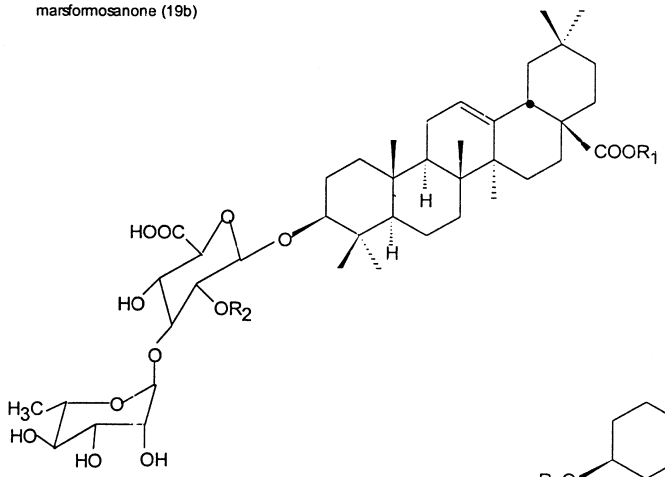
3β - acetoxy - urs-11 - ene - 28,13 - olide (19a)



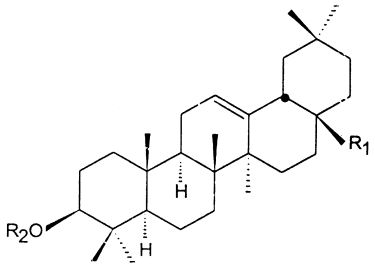
marsformosanone (19b)



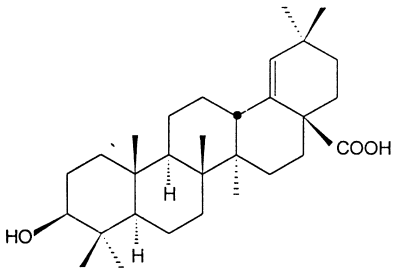
19 α - hydroxyursolic acid (19c)



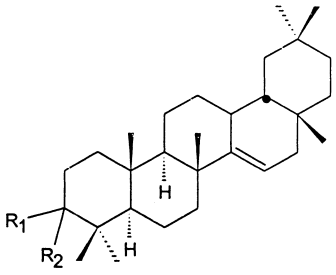
oleanolic acid gylcosides ; 20 : $R_1 = R_2 = H$
21 : R_1 = Glu ; $R_2 = H$
22 : R_1 = Glu ; R_2 = Xyl
23 : $R_1 = H$; R_2 = Xyl



oleanolic acid (24) ; R_1 = COOH ; $R_2 = H$
β-amyrin (25) ; $R_1 = CH_3$; $R_2 = H$
oleanolic acid acetate (26) ; R_1 = COOH ; $R_2 = COCH_3$
oleanolic acid palmitate (27) ; R_1 = COOH ; $R_2 = CO(CH_2)_{14}CH_3$
oleanolic acid stearate (28) ; R_1 = COOH ; $R_2 = CO(CH_2)_{16}CH_3$



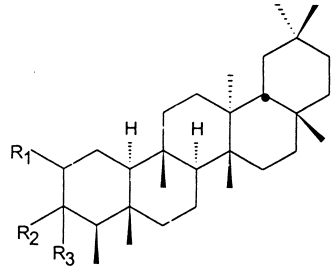
morolic acid (29)



taraxerol (**30**) : R_1 = α-H ; R_2 = β-OH

taraxeryl acetate (**31**) : R_1 = α-H ; R_2 = β-$OCOCH_3$

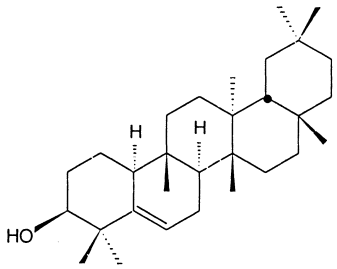
taraxerone (**32**) : R_1, R_2 : = O



friedelin (**33**) : R_1 = H ; R_2, R_3 = O

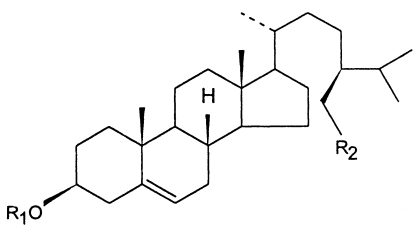
friedelin-3-ol (**34**) : R_1 = H, R_2 = β-H ; R_3 = α-OH

cerin (**35**) : R_1 = α-OH ; R_2, R_3 : =O



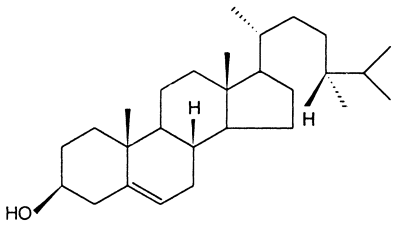
gult -5 (6) - en - 3β -ol (**36**)

STEROIDS

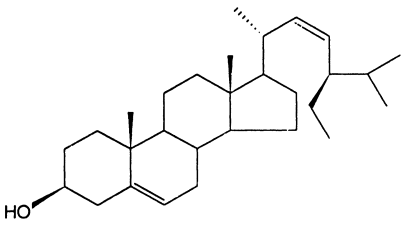


β-sitosterol (**37a**) : $R_1 = H$; $R_2 = CH_3$

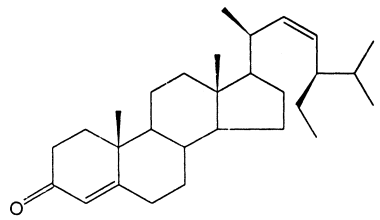
β-sitosterol glucoside (**38**) : R_1 = gluc. ; $R_2 = CH_3$



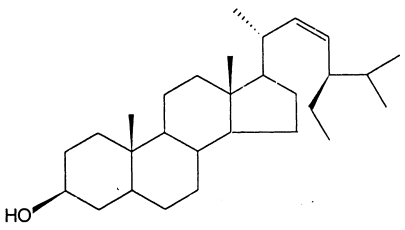
campesterol (**37b**) :



stigmasterol (**39**)

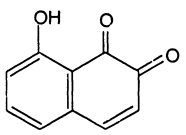


stigmasta - 4 - en - 3 - one (**40**)

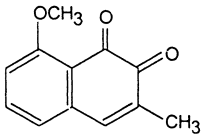


stigmasta - 5,6 - dihydro - 22 - en -3β -ol (**41**)

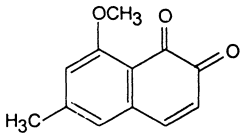
NAPHTHOQUINONES



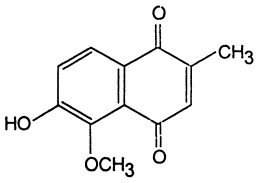
8-hydroxy - 1,2- naphthoquinone(44)



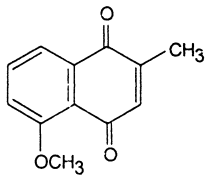
3 - methyl- 8 -methoxy - 1,2 - napthoquinone (45a)



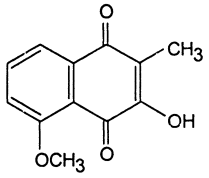
6 - methyl - 8 -methoxy - 1,2 - naphthoquinone (45b)



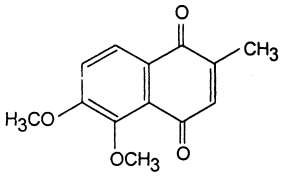
diomelquinone (46)



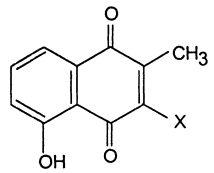
2- methyl - 5 -methoxy - 1,4 - naphthoquinone (47)



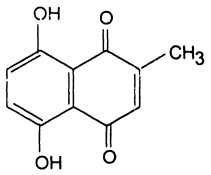
2 - methly - 3 -hydroxy - 5 - methoxy - 1,4 - naphthoquinone (48)



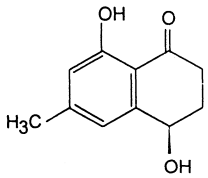
2 - methyl- 5,6 - dimethoxy - 1,4 - naphthoquinone (49)



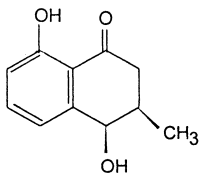
3 - bromo-plumbagin (50) : X = Br
3 - chloro-plumbagin (51) : X = Cl
3 - hydroxy-plumbagin (52) : X = OH
(droserone)



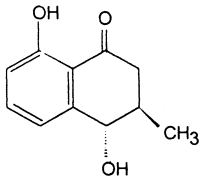
methyl naphthazarine (53)



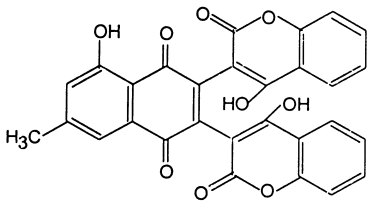
shinanolone (54)



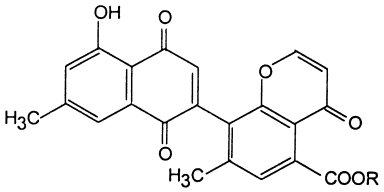
iso - shinanolone (55)



epi - isoshinanolone (56)

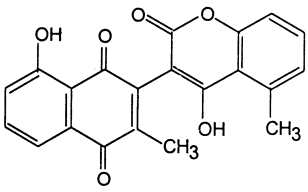


ismailin (**57**)

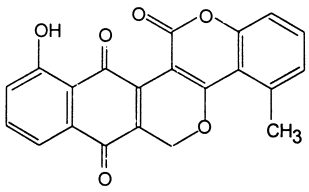


chromenone ester (**58**) R = C_2H_5

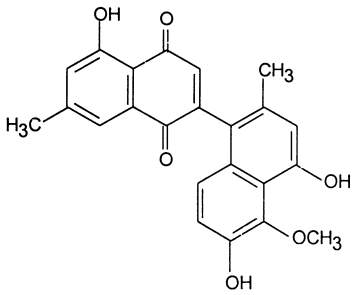
chromenone acid (**59**) R = H



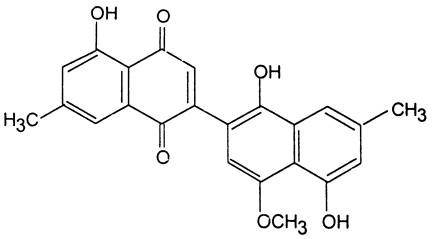
canaliculatin (**60**)



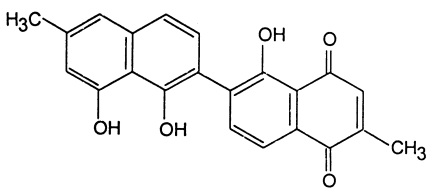
cyclo - canaliculatin (**61**)



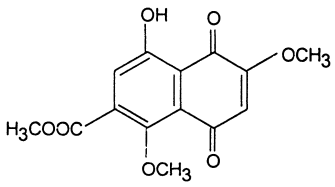
celebaquinone(**62**)



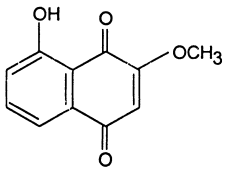
iso - celebaquinone (**63**)



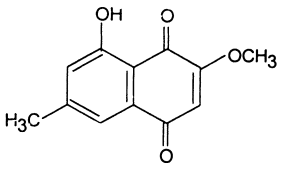
ebenone (64)



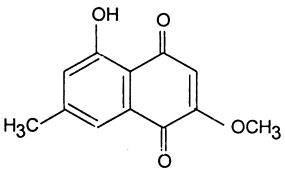
yenrinquinone (65)



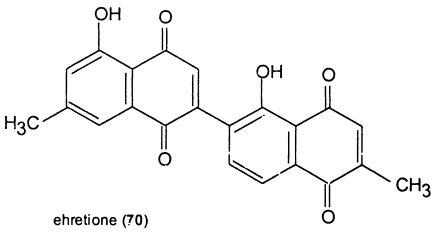
3 - methoxyjuglone (67)



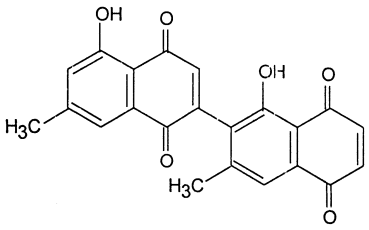
3 - methoxy - 7 - methyljuglone (68)



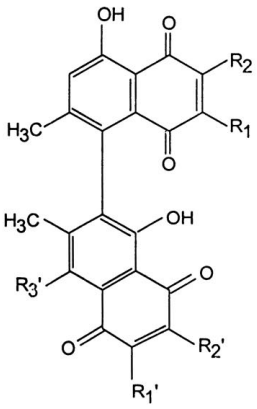
2 - methoxy - 7 - methyljuglone (69)



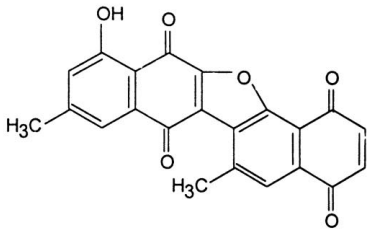
ehretione (70)



diospyrin (71)



isodiospyrin (**72**) $R_1 = R_2 = R_1' = R_2' = R_3' = H$



cyclodiospyrin (**73**)

3' - methoxy isodiospyrin (**89**) $R_1 = R_2 = R_1' = R_2' = R_3' = OCH_3$

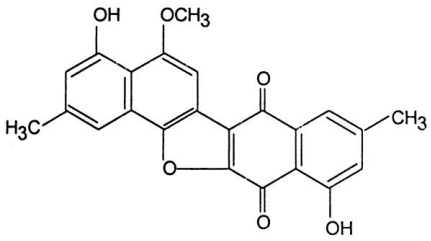
2' - methoxy isodiospyrin (**90**) $R_1 = R_2 = R_1' = R_2' = R_3' = OCH_3$

3,3' - dimethoxy isodiospyrin (**91**) $R_1 = R_2 = R_1' = R_2' = R_3' = OCH_3$

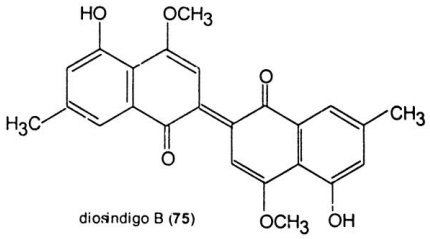
2,3' - dimethoxy isodiospyrin (**92**) $R_1 = R_2 = R_1' = R_2' = R_3' = OCH_3$

2,2' - dimethoxy isodiospyrin (**93**) $R_1 = R_2 = R_1' = R_2' = R_3' = OCH_3$

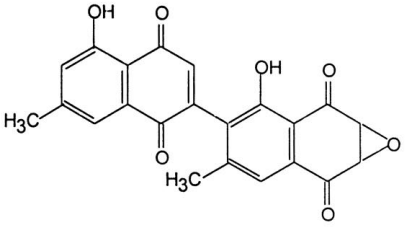
8' - hydroxy - 3 - methoxy isodiospyrin (**94**) $R_1 = R_1' = R_2' = H : R_2 = OCH_3 ; R_3' = OH$



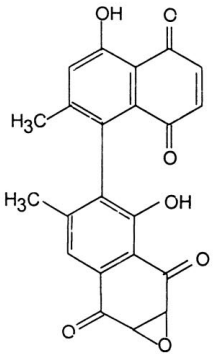
pentacyclic quinone (**74**)



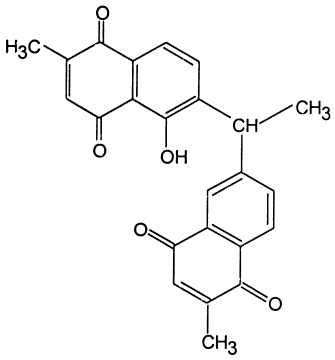
diosindigo B (**75**)



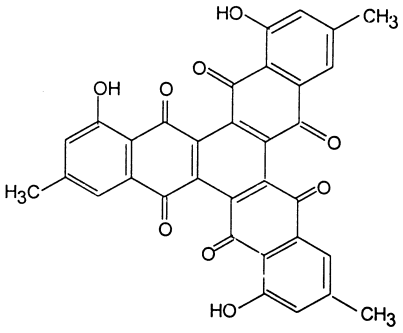
diosquinone(**76**)



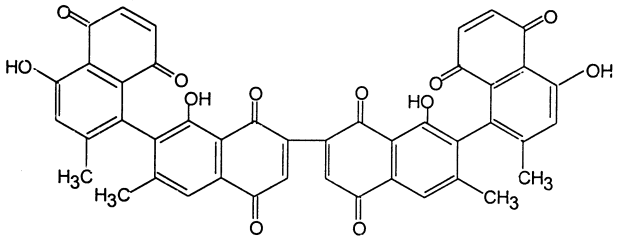
batacanone(**77**)



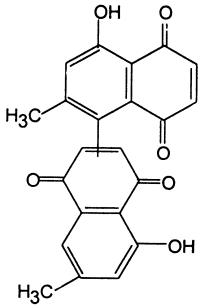
ethylidene - 6,6' biplumbagin(78)



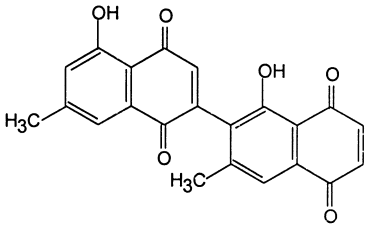
xylospyrin(79)



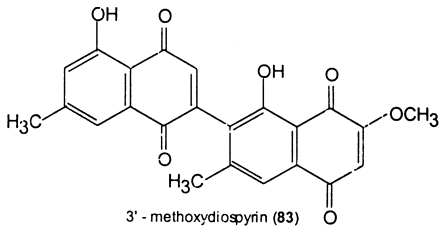
bis - isodiospyrin (80)



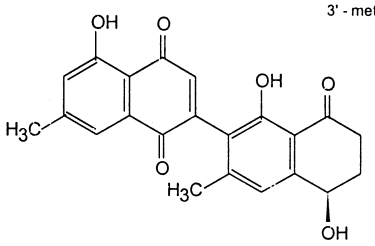
neodiospyrin (81)



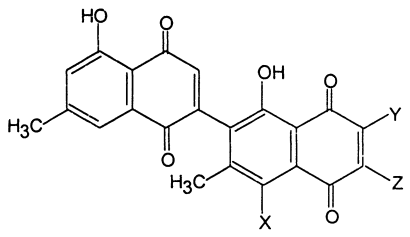
β' - dihydrodiospyrin (82)



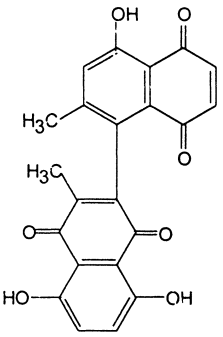
3' - methoxydiospyrin (83)



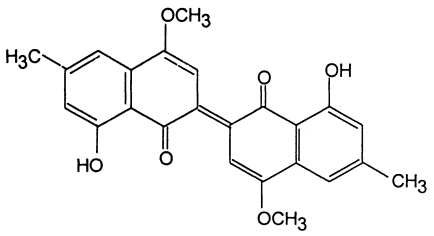
tetrahydrodiospyrin(84)



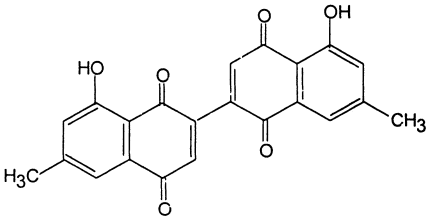
8-hydroxydiospyrin(**85**) ; X = OH ; Y = Z = H
2'-chlorodiospyrin(**86**) ; X = Y = H ; Z = Cl
3'-chlorodiospyrin(**87**) ; x = z = H ; y = Cl
3'-chloro-2'-hydroxydiospyrin(**88**) ; X = H ; Y = Cl ; Z = H



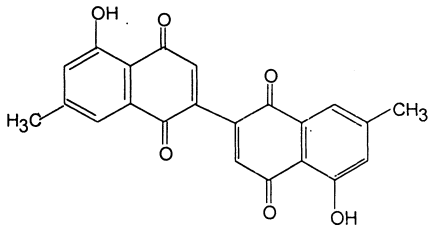
8'-hydroxyisodiospynn(**95**)



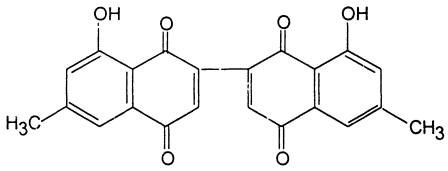
diosindigo A (**96**)



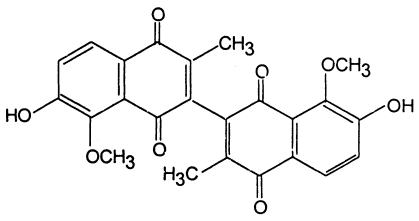
rotundiquinone (**97**)



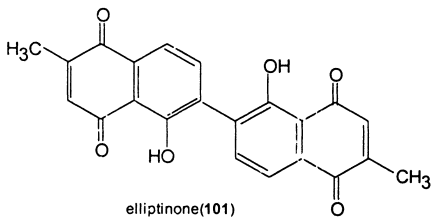
biramentaceone(**98**)



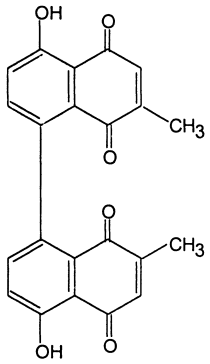
mamegakinone(**99**)



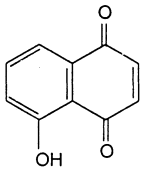
3.3'-dimer of 6-hydroxy-5-methoxy-2-methyl naphthoquinone (**100**)



elliptinone(**101**)

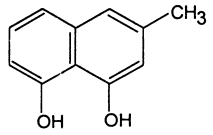


martinone(**102**)

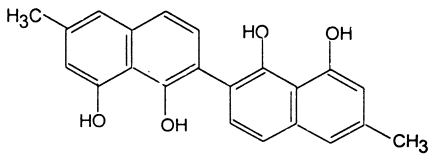


juglone (**103**)

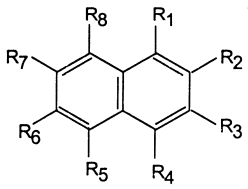
NAPHTHALENE BASED AROMATICS

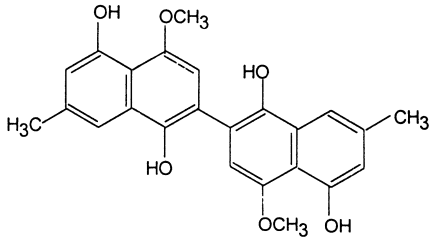


3 - methyl - naphthalene 1,8 - diol (**104**)



diospyrol (**105**)





dihydrodiosindigo B (**107b**)

106 : $R_1 = R_8 = OCH_3$; $R_2 = OH$; $R_3 = R_4 = R_5 = R_6 = R_7 = H$

107a : $R_1 = R_2 = R_8 = OCH_3$; $R_3 = R_4 = R_5 = R_6 = R_7 = H$

108 : $R_1 = R_7 = R_8 = H$; $R_2 = CH_3$; $R_3 = R_6 = OH$; $R_4 = R_5 = OCH_3$

109 : $R_1 = R_7 = R_8 = H$; $R_2 = CH_3$; $R_3 = R_4 = R_5 = R_6 = OCH_3$

110 : $R_1 = R_3 = R_7 = R_8 = H$; $R_2 = CHO$; $R_4 = R_5 = OCH_3$

111 : $R_1 = R_3 = R_7 = R_8 = H$; $R_2 = CHO$; $R_4 = R_5 = R_6 = OCH_3$

112 : $R_1 = R_3 = R_7 = R_8 = H$; $R_2 = COOH$; $R_4 = R_5 = OCH_3$; $R_6 = OH$

113 : $R_1 = R_3 = R_7 = R_8 = H$; $R_2 = COOCH_3$; $R_4 = R_5 = OCH_3$; $R_6 = OH$

114 : $R_1 = R_8 = OCH_3$; $R_2 = R_4 = R_5 = R_6 = R_7 = H$; $R_3 = CH_3$

115 : $R_1 = OH$; $R_2 = R_8 = OCH_3$; $R_3 = CH_3$; $R_4 = R_5 = R_6 = R_7 = H$

116 : $R_1 = OH$; $R_2 = R_5 = R_6 = R_7 = H$; $R_3 = CH_3$; $R_4 = R_8 = OCH_3$

117 : $R_1 = OH$; $R_2 = R_4 = R_5 = R_6 = R_7 = H$; $R_3 = CH_3$; $R_8 = OCH_3$

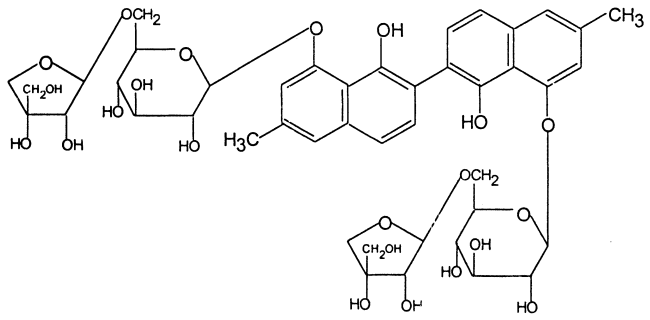
119 : $R_1 = R_2 = R_3 = R_7 = H$; $R_4 = R_5 = R_6 = R_8 = OCH_3$

120 : $R_1 = CHO$; $R_2 = R_3 = R_7 = H$; $R_4 = R_6 = R_8 = OCH_3$; $R_5 = OH$

121 : $R_1 = CHO$; $R_2 = R_3 = R_7 = R_8 = H$; $R_4 = R_5 = R_6 = OCH_3$

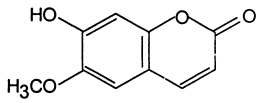
122 : $R_1 = CHO$; $R_2 = R_3 = R_7 = R_8 = H$; $R_4 = R_5 = OCH_3$

123 : $R_1 = R_3 = R_6 = R_7 = R_8 = H$; $R_2 = CHO$; $R_4 = OCH_3$; $R_5 = OH$

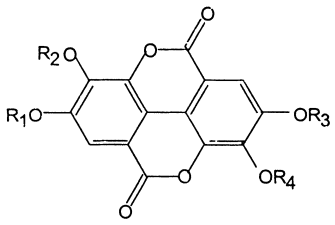


diospyrol - 8, 8' - di - o - 6 β - D - epiofuranosyl - β - D - glucopyranoside (**118**)

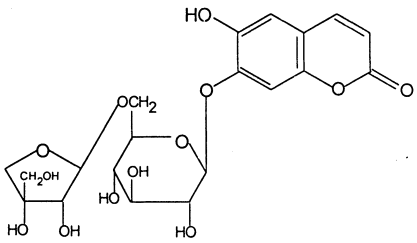
BENZOPYRONES



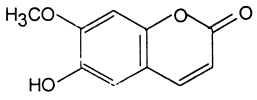
scopoletin (**124**)



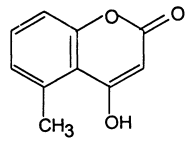
125 : $R_1 = R_2 = R_3 = R_4 = H$ (ellagic acid)
126 : $R_2 = R_4 = CH_3$; R_3 = β - D - galactopyranosyl - (1⟶4) - β - D - glucopyranoside
127 : $R_2 = R_4 = CH_3$; R_3 = β - D - xyiopyranosyl - (1⟶4) - β - D - glucopyranoside
128 : $R_2 = R_4 = CH_3$; R_3 = β - D - rhamnopyranosyl - (1⟶4) - β - D - glucopyranoside



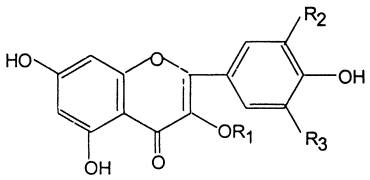
diospyroside(**129**)



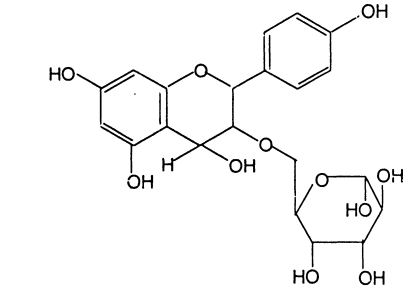
6 - hydroxy - 7 - methoxy - coumarin (**130**)



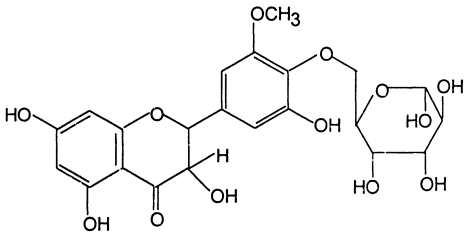
4 - hydroxy - 5 - methoxy-coumarin (131)



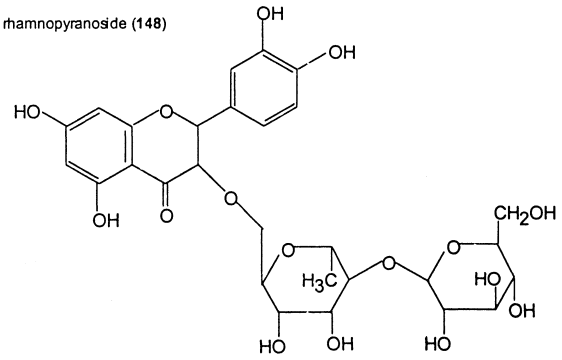
132 : $R_1 = R_2 = R_3 = H$ (kampferol)
133 : R_1 = α - L - rhamnopyranoside ; $R_2 = R_3 = H$
134 : R_1 = β - D - xylopyranoside; $R_2 = R_3 = H$
135 : R_1 = β - D - galactopyranoside; $R_2 = R_3 = H$ (Trifolin)
136 : R_1 = α - L - arabinopyranoside ; $R_2 = R_3 = H$
137 : R_1 = β - D - glucopyranoside , $R_2 = R_3 = H$
138 : R_1 = (2" - o - galloyl) - β – D - glucopyranoside ; $R_2 = R_3 = H$
139 : $R_1 = R_3 = H$; R_2 = OH (quercetin)
140 : R_1 = α - L - arabinopyranoside ; R_2 = OH ; $R_3 = H$
141 : R_1 = α - L - rhamnopyranoside ; R_2 = OH ; $R_3 = H$
142 : R_1 = β - D - glucopyranoside ; R_2 = OH ; $R_3 = H$
143 : R_1 = β - D - galactopyranoside; R_2 = OH ; $R_3 = H$ (Hyperin)
144 : R_1 = (2" - o - galloyl) - β - D - glucopyranoside ; R_2 = OH ; $R_3 = H$
145 : R_1 = β - D - glucopyranoside ; $R_2 = R_3$ = OH
146 : R_1 = α - L - rhamnopyranoside ; $R_2 = R_3 = H$



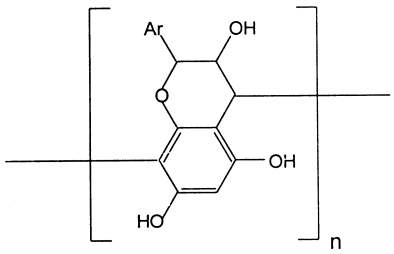
leucopelargonidin - 3 - o - α - L - rhamnopyranoside (147)



5,7,3,5' - tetrahydroxy - 3' - methoxy - flavanone - 4' - o - α - L - rhamnopyranoside (148)

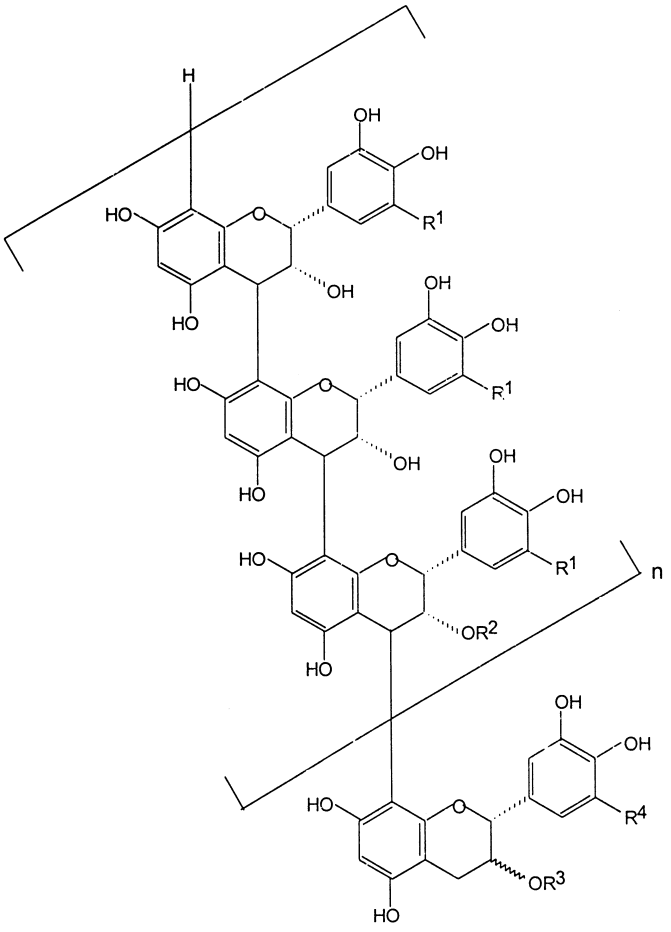


5,7,3',4' - tetrahydroxy flavanone - 3 - o - β - D - glucopyranosyl - (1 → 4) - α - L - rhamnopyranoside (149)



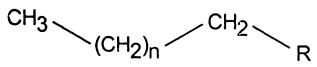
Ar = 3,4,5 - $(OH)_3C_6H_2$

proanthocyanidin(**150**)

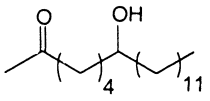


proanthocynidin polymer (**151**) : R^1 = OH ; R^2 = galloyl ; R^3 = R^4 = H

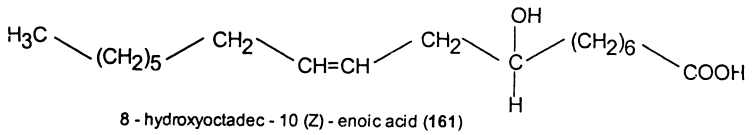
HYDROCARBONS AND LIPIDS



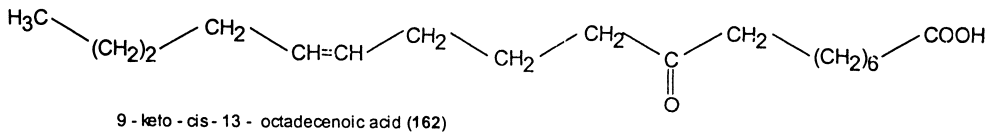
hexacosane (**152**) : n = 24 ; R = H
nonacosane (**153**) : n = 27 ; R = H
hentriacontane (**154**) : n = 29 ; R = H
tritriacontane (**155**) : n = 31 ; R = H
hexacosanol (**156**) : n = 24 ; R = OH
triacontanol (**157**) : n = 28 ; R = OH
hentriacontanol (**158**) : n = 29 ; R = OH
heptacosanonic acid (**159**) : n = 24 ; R = COOH
lauric acid (**165**) n = 9 ; R = COOH
myristic acid (**166**) n = 11 ; R = COOH
palmitic acid (**167**) n = 13 ; R = COOH
stearic acid (**168**) n = 15 ; R = COOH
arachidic acid (**169**) n = 17 ; R = COOH
behenic acid (**170**) n = 19 ; R = COOH
hexanoic acid (**228**) n = 3 ; R = COOH
n - triacosane (**244**) n = 21 ; R = H
n - pentacosane (**245**) n = 23 ; R = H



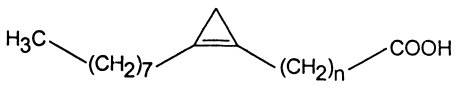
nonadecan - 7 - ol - 2 - one(**160**)



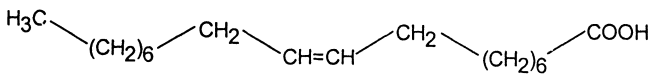
8 - hydroxyoctadec - 10 (Z) - enoic acid (**161**)



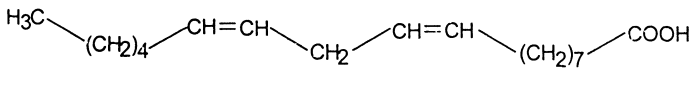
9 - keto - cis - 13 - octadecenoic acid (**162**)



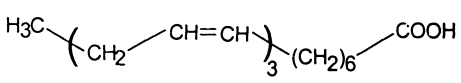
malvalic acid (**163**) n = 6
sterculic acid (**164**) n = 7



oleic acid (**171**)

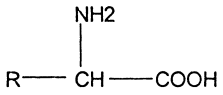


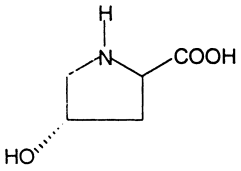
linoleic acid (**172**)



linolenic acid (**173**)

AMINO ACIDS





hydroxyproline (**180**)

alanine (**174**) R = CH_3

aspartic acid (**175**) R = HOOC - CH_2–

L - citrulline (**176**) R = $H_2NCONH(CH_2)_3$ –

cystine (**177**) R = HOOC - $\overset{NH_2}{\overset{|}{C}}HCH_2$ - S - S - CH_2 –

glutamic acid (**178**) R = HOOC - CH_2 - CH_2 –

glycine (**179**) R = H

lucine (**181**) R = $(CH_3)_2$ $CHCH_2$ –

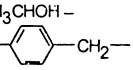
methionine (**182**) R = CH_3SCH_2 CH_2 –

norvaline (**183**) R = CH_3 CH_2 CH_2 –

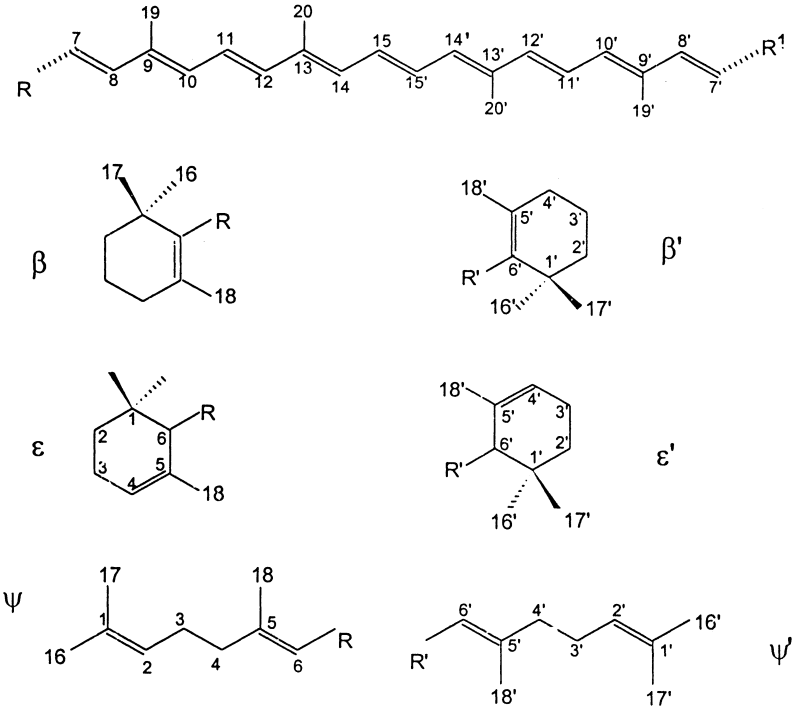
phenylalanine (**184**) R = C_6H_5 CH_2 –

serine (**185**) R = $HOCH_2$ –

threonine (**186**) R = CH_3CHOH –

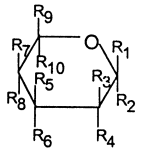
tyrosine (**187**) R = HO—  —CH_2—

CAROTENOIDS



antheraxanthin (**188**); 5,6 - epoxy - 5,6 - didehydro - β β' - carotene - 3,3' - diol
α - carotene (**189**): (6' R) - β, ε' - carotene
β - carotene (**190**): β, β' - carotene
ψ - carotene (**191**): 7,8,7',8' - tetrahydro - ψ, ψ' - carotene
γ - carotene (**192**): β, ψ' - carotene
cryptoxanthin (**193**): (3R) - β, β' - carotene - 3 - ol
lutein (= xanthophyll, **194**): (3R, 3'R, 6'R) - β, ε' - carotene - 3,3' - diol
lutein epoxide (= taraxanthin, **195**): (3S, 5R, 6S, 3'S, 6'R) - 5,6 - epoxy - 5,6 - dihydro - β, ε' - carotene - 3,3' - diol
luteoxanthin (**196**): 5, 6, 5', 8' - diepoxy - 5, 6, 5', 8' - tetrahydro - β, β' - carotene
licopene (**197**): ψ, ψ' - carotene
cis - mutatoxanthin (**198**): 5, 8, - epoxy - 5, 8 - dihydro - β, β' - carotene - 3,3' - diol
phytoene (**199**): 7, 8, 11, 12, 7', 8', 11', 12', - octahydro - ψ, ψ' - carotene
phytofluene (**200**): 7, 8, 11, 12, 7', 8' - hexahydro - ψ, ψ' - carotene
violaxanthin (**201**): (3S, 5R, 6S, 3'S, 5'R, 6'S) - 5, 6, 5', 6' - diepoxy - 5, 6, 5', 6' - tetrahydro - β, β' - carotene - 3,3' - diol
zeaxanthin (**202**): (3R, 3'R) - β, β' - carotene - 3,3' - diol

SUGARS



β - L - arabinose (**203**) : $R_1 = R_3 = R_6 = R_8 = R_9 = R_{10} = H$; $R_2 = R_4 = R_5 = R_7 = OH$

β - D - fructose (**204**) : $R_4 = R_5 = R_7 = R_9 = R_{10} = H$; $R_1 = R_3 = R_6 = R_8 = OH$; $R_2 = CH_2OH$

D - galactose (**205**) : $R_1 = R_3 = R_6 = R_8 = R_{10} = H$; $R_2 = R_4 = R_5 = R_7 = OH$; $R_9 = CH_2OH$

D - galacturonic acid (**206**) : $R_1 = R_3 = R_6 = R_8 = R_{10} = H$; $R_2 = R_4 = R_5 = R_7 = OH$; $R_9 = COOH$

α - D - glucose (**207**) : $R_1 = R_3 = R_6 = R_7 = R_{10} = H$; $R_2 = R_4 = R_5 = R_8 = OH$; $R_9 = CH_2OH$

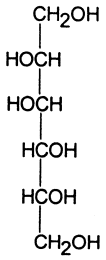
β - D - glucose (**208**) : $R_2 = R_3 = R_6 = R_7 = R_{10} = H$; $R_1 = R_4 = R_5 = R_8 = OH$; $R_9 = CH_2OH$

β - D - glucopyranose pentaacetate (**211**) : $R_2 = R_3 = R_6 = R_7 = R_{10} = H$; $R_1 = R_4 = R_5 = R_8 = OAC$; $R_9 = CH_2OAC$

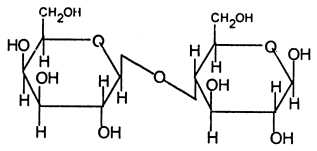
α - L - rhamnose (**213**) : $R_2 = R_3 = R_5 = R_8 = R_9 = H$; $R_1 = R_4 = R_6 = R_7 = OH$; $R_{10} = CH_3$

L - sorbose (**215**) : $R_4 = R_5 = R_8 = R_9 = R_{10} = H$; $R_1 = R_3 = R_6 = R_7 = OH$; $R_2 = CH_2OH$

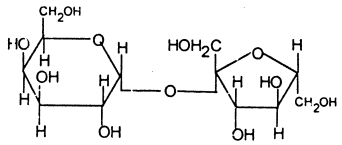
xylose (**217**) : $R_1 = R_3 = R_6 = R_7 = R_9 = R_{10} = H$; $R_2 = R_4 = R_5 = R_8 = OH$



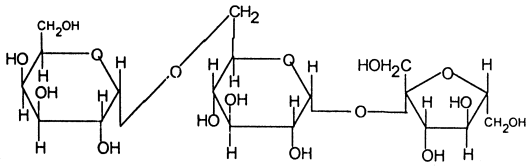
D - mannitol (**210**)



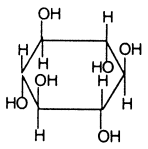
D - lactose (**209**)



sucrose (**216**)

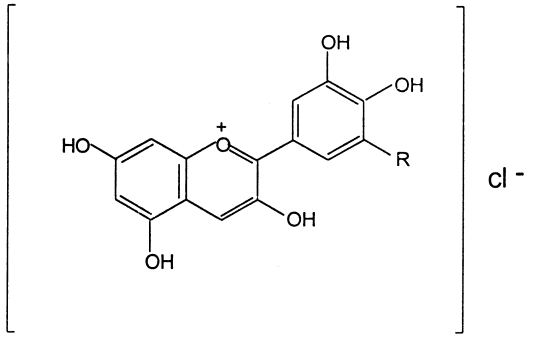


raffinose (**212**)

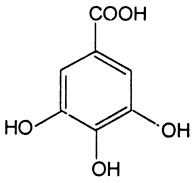


sequoyitol (**214**)

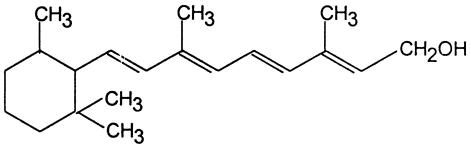
MISCELLANEOUS



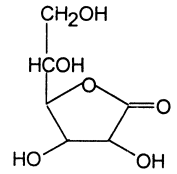
delphinidin (**218**) R = OH
cyanidin (**219**) R = H



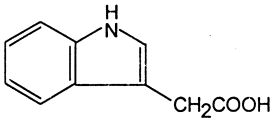
gallic acid (**220**)



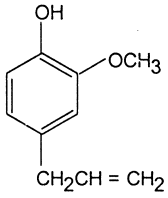
vitamin A (**221**)



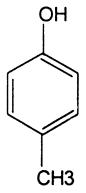
ascorbic acid (**222**)



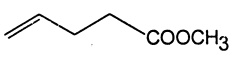
indole acetic acid (**223**)



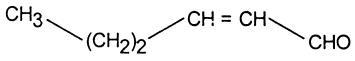
eugenol (**224**)



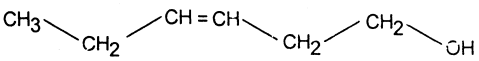
p - cresol (**225**)



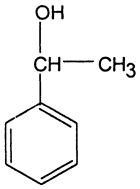
methyl - 4 - pentenoate (**227**)



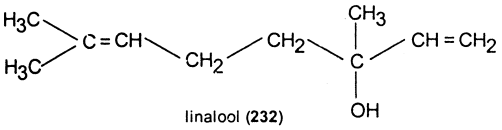
2 - hexenal (**229**)



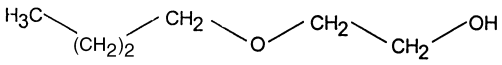
3 - hexen - 1 - ol (**230**)



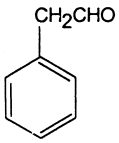
phenyl ethyl alcohol (**231**)



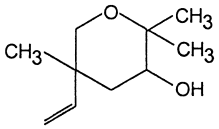
linalool (**232**)



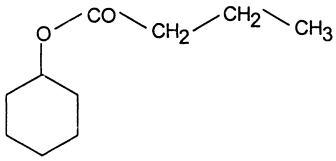
2 - butoxy ethanol (**233**)



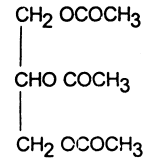
phenylacetaldehyde (**234**)



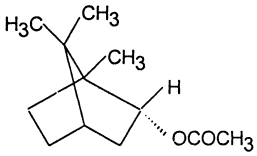
2, 2, 6 trimethyl - 6 - vinyl - tetrahydro - 2H - pyran - 3 - ol (**235**)



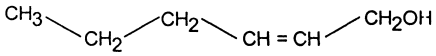
cyclohexyl butyrate (**236**)



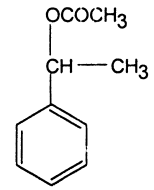
glycerol triacetate (**237**)



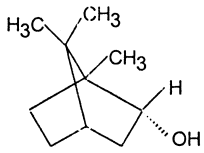
bornyl acetate (**238**)



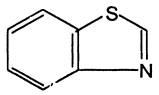
E - 2 - hexenol (**239**)



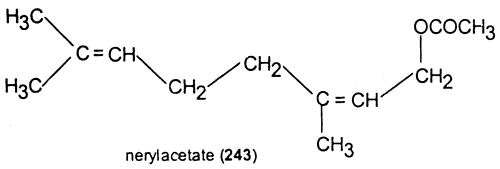
phenylethylacetate (**240**)



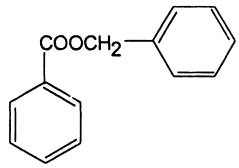
borneol (**241**)



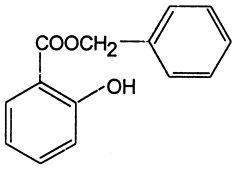
benzothiazole(**242**)



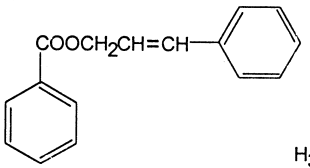
nerylacetate (**243**)



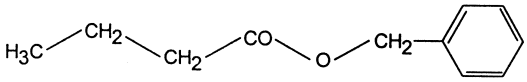
benzyl benzoate(**246**)



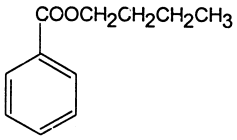
benzyl salicylate(**247**)



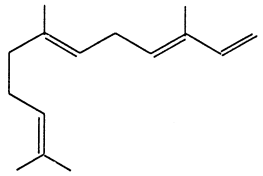
cinnamyl benzoate (**248**)



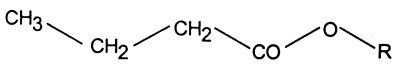
benzyl butyrate (**249**)



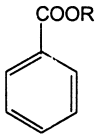
butyl benzoate (**250**)



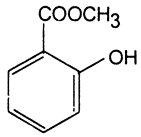
α -trans-trans-farnesene(**251**)



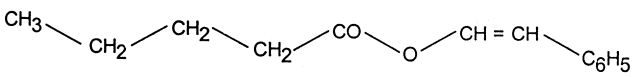
methyl n-butyrate(**252**) R=CH_3
n-propyl n-butyrate(**253**) R= -CH_2 CH_2 CH_3
n-butyl n-butyrate(**254**) R= -CH_2 $(CH_2)_2$ CH_3
n-pentyl n-butyrate(**255**) R= -CH_2 $(CH_2)_3$ CH_3
n-hexyl n-butyrate(**256**) R= -CH_2 $(CH_2)_4$ CH_3
β- phenyl ethyl n-butyrate(**257**) R= -CH_2 CH_2 C_6H_5
cinnamyl n-butyrate(**258**) R= -CH=CH C_6H_5



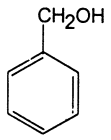
methyl benzoate(**259**) R= -CH_3
ethyl benzoate(**260**) R= -CH_2 CH_3
n-propyl benzoate(**261**) R= - CH_2 CH_2 CH_3
n-pentyl benzoate(**262**) R= - CH_2 $(CH_2)_3$ CH_3
n-hexyl benzoate(**263**) R= - CH_2 $(CH_2)_4$ CH_3
β-phenyl ethyl benzoate(**264**) R= - CH_2 CH_2 C_6H_5



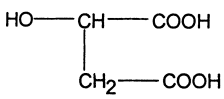
methyl salicylate(**265**)



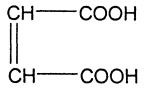
cinnamyl valerate(**266**)



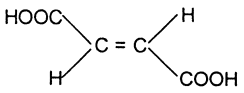
benzyl alcohol(**267**)



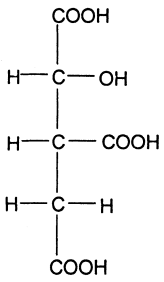
malic acid (**268**)



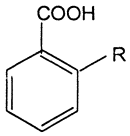
succinic acid (**269**)



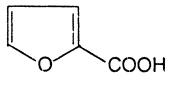
fumaric acid (**270**)



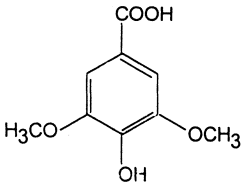
isocitric acid (**271**)



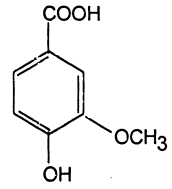
benzoic acid (**272**) R = H
salicylic acid (**273**) R = OH



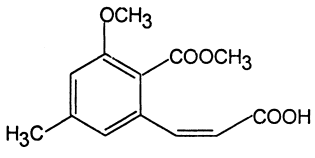
pyromucic acid (**274**)



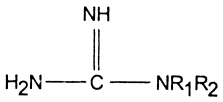
syringic acid (**275**)



vanilic acid(**276**)



macassaric acid (**277**)



guanidinosuccinic acid (**278**) : R_1 = H ; R_2 = C - COOH
HC - COOH

creatine (**279**) : $R_1 = CH_3$; $R_2 = CH_2COOH$

guanidinoacetic acid (**280**) : R_1 = H ; $R_2 = CH_2COOH$

N - α - acetyl - L - arginine (**281**) $R_1 = COCH_3$; $R_2 = (CH_2)_3\ CH(NH_2)COOH$

β - guanidinopropionic acid (**282**) R_1 = H ; $R_2 = CH_2CH_2COOH$

γ - guanidinobutyric acid (**283**) R_1 = H ; $R_2 = (CH_2)_3COOH$

L - arginine (**284**) R_1 = H ; $R_2 = (CH_2)_3CH(NH_2)COOH$

γ - guanidinobutramide (**285**) R_1 = H ; $R_2 = (CH_2)_3CONH_2$

guanidine (**286**) $R_1 = R_2$ = H

Me - guanidine (**287**) : R_1 = H ; $R_2 = CH_3$