CHAPTER II

HISTORICAL

1. Chemical Constituents of Plants in the Genus *Prismatomeris*

The chemical constituents of plants in the genus *Prismatomeris* can be classified into three groups, namely anthraquinones, steroids and triterpenoids, as shown in Table 1.

Table 1 Distribution of chemical constituents in the genus *Prismatomeris*

Plant and chemical compound	Category	Part	Reference
Prismatomeris tetrandra* subsp. *malayana*			
Rubiadin [**1**]	Anthraquinone	root	Lee, 1969: 501-503
Rubiadin-1-methy ether [**2**]	Anthraquinone	root	Lee, 1969: 501-503
P. tetrandra			
Rubiadin [**1**]	Anthraquinone	root	Tu, Pang, and Bi, 1981: 631-634
Rubiadin-1-methy ether [**2**]	Anthraquinone	root	Tu *et al.*, 1981: 631-634
2-Methylanthraquinone [**3**]	Anthraquinone	root	Tu *et al.*, 1981: 631-634
Damnacanthal [**4**]	Anthraquinone	root	Tu *et al.*, 1981: 631-634
β-Sitosterol [**5**]	Steroid	root	Tu *et al.*, 1981: 631-634
Unidentified compound	Anthraquinone	root	Tu *et al.*, 1981: 631-634
Unidentified compound	Triterpenoid	root	Tu *et al.*, 1981: 631-634

*Davies, 1991: 265.

2. Chemical Constituents of *Diospyros montana*

The chemicals found in *Diospyros montana* can be classified into six groups, namely naphthoquinones, triterpenoids, steroids, fatty acids, amino acids, and metals, as shown in Table 2.

Table 2 Chemical constituents of *Diospyros montana*

Plant part and chemical compound	Category	Reference
Bark		
Diospyrin [**6**]	Naphthoquinone	Kapil and Dhar, 1961: 498-500
β′-Dihydrodiospyrin [7]	Naphthoquinone	Pardhasaradhi and Sidhu, 1972: 4201-4204
7- Methyljuglone [**8**]	Naphthoquinone	Lillie, Musgrave, and Skoyles, 1976: 2155-2161
Mamegakinone [**9**]	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
Biramentacenone [**10**]	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
Isodiospyrin [**11**]	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
3,5′-O-cyclodiospyrin [**12**]	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
8′-Hydroxydiospyrin [**13**]	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
Diosquinone [**14**]	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
Tetrahydrodiospyrin [**15**]	Naphthoquinone	Pardhasaradhi and Krishnakumari, 1979: 684-685

Table 2 (continued)

Plant part and chemical compound	Category	Reference
Lupeol [**16**]	Triterpenoid	Lillie *et al.*, 1976: 2155-2161
Betulinic acid [**17**]	Triterpenoid	Lillie *et al.*, 1976: 2155-2161
Betulin [**18**]	Triterpenoid	Lillie *et al.*, 1976: 2155-2161
Allobetulin [**19**]	Triterpenoid	Lillie *et al.*, 1976: 2155-2161
Oxyallobetulin [**20**]	Triterpenoid	Lillie *et al.*, 1976: 2155-2161
2′-Chlorodiospyrin [**21**]**	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
3′-Chlorodiospyrin [**22**]**	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
3′-Chloro-2-hydroxy-diospyrin [**23**]**	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
Chromenone ester [**24**]**	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
Chromenone acid [**25**]**	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
Wood		
β′-Dihydrodiospyrin [**7**]	Naphthoquinone	Pardhasaradhi and Sidhu, 1972: 4201-4204
Diospyrin [**6**]	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
3,5′-O-cyclodiospyrin [**12**]	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161

Table 2 (continued)

Plant part and chemical compound	Category	Reference
8′-Hydroxydiospyrin [**13**]	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
2′-Chlorodiospyrin [**21**]**	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
3′-Chlorodiospyrin [**22**]**	Naphthoquinone	Lillie *et al.*, 1976: 2155-2161
Lupeol [**16**]	Triterpenoid	Lillie *et al.*, 1976: 2155-2161
Betulinic acid [**17**]	Triterpenoid	Lillie *et al.*, 1976: 2155-2161
Betulin [**18**]	Triterpenoid	Lillie *et al.*, 1976: 2155-2161
β-Sitosterol [**5**]	Steroid	Lillie *et al.*, 1976: 2155-2161
Stem		
2,6-Dimethoxy-7-methoxy-carbonyljuglone [**26**]	Naphthoquinone	Thomson, 1987: 226
Fungal-infested stem		
Yerrinquinone [**27**]	Naphthoquinone	Pardhasaradhi and Rao, 1990: 2355-2356
Leaf		
Diospyrin [**6**]	Naphthoquinone	Narayan, Row, and Satyanarayana, 1978: 345
β-Sitosterol [**5**]	Steroid	Dutta, Dutta, and Chakravarti, 1972: 1180-1181
Stigmasterol [**28**]	Steroid	Dutta *et al.*, 1972: 1180-1181

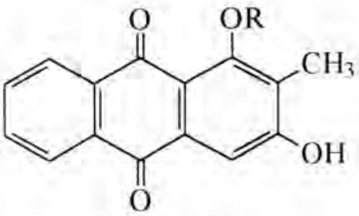
Table 2 (continued)

Plant part and chemical compound	Category	Reference
Epi-uvaol [**29**]	Triterpenoid	Dutta *et al.*, 1972: 1180-1181
Oleanolic acid [**30**]	Triterpenoid	Dutta *et al.*, 1972: 1180-1181
Betulin [**18**]	Triterpenoid	Dutta *et al.*, 1972: 1180-1181
Betulinic acid [**17**]	Triterpenoid	Narayan *et al.*, 1978: 345
Lupeol [**16**]	Triterpenoid	Narayan *et al.*, 1978: 345
Ursolic acid [**31**]	Triterpenoid	Zafar, Singh, and Khan, 1991: 432-433
Fruit		
α-amyrin [**32**]	Triterpenoid	Misra, Nigam, and Mitra 1972: 1508-1509
Betulinic acid [**17**]	Triterpenoid	Misra *et al.*, 1972: 1508-1509
Betulin [**18**]	Triterpenoid	Misra *et al.*, 1972: 1508-1509
Oleanolic acid [**30**]	Triterpenoid	Misra *et al.*, 1972: 1508-1509
Ursolic acid [**31**]	Triterpenoid	Misra *et al.*, 1972: 1508-1509
Lupeol [**16**]	Triterpenoid	Raj and Agrawal, 1979: 735-736
β-Sitosterol [**5**]	Steroid	Raj and Agrawal, 1979: 735-736
Palmitic acid [**33**]	Fatty acid	Misra *et al.*, 1972: 1508-1509

Table 2 (continued)

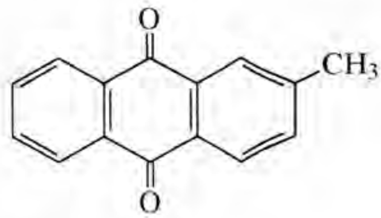
Plant part and chemical compound	Category	Reference
Stearic acid [**34**]	Fatty acid	Misra *et al.*, 1972: 1508-1509
Zn, Ni, Co, Cr, Fe, Ca, Mg, Cu, K, and Na	Metals	Raj and Agrawal, 1979: 735-736
Seed		
Betulinic acid [**17**]	Triterpenoid	Raj and Agrawal, 1979: 735-736
L-cystine [**35**]	Amino acid	Goutam and Purohit, 1974: 100-101
L-arginine [**36**]	Amino acid	Goutam and Purohit, 1974: 100-101
L-glutamic acid [**37**]	Amino acid	Goutam and Purohit, 1974: 100-101
Glycine [**38**]	Amino acid	Goutam and Purohit, 1974: 100-101
L-alanine [**39**]	Amino acid	Goutam and Purohit, 1974: 100-101
L-proline [**40**]	Amino acid	Goutam and Purohit, 1974: 100-101
L-leucine [**41**]	Amino acid	Goutam and Purohit, 1974: 100-101

**Artefacts from isolation procedure.

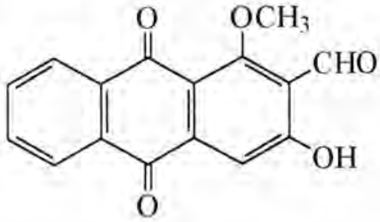


[**1**] Rubiadin; R=H

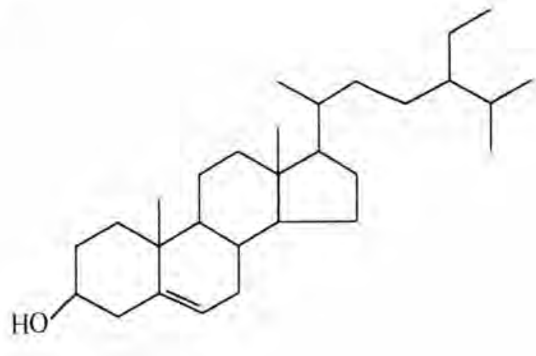
[**2**] Rubiadin-1-methyl ether; R=CH_3



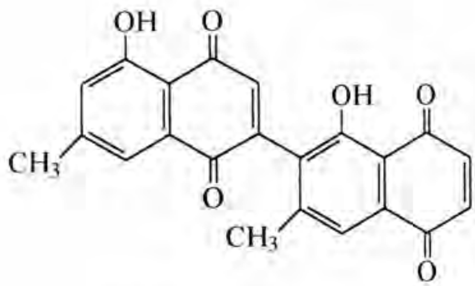
[**3**] 2-Methylanthraquinone



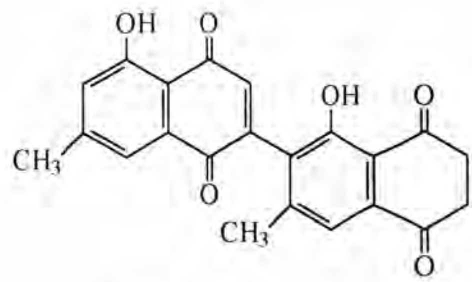
[**4**] Damnacanthal



[**5**] β-Sitosterol

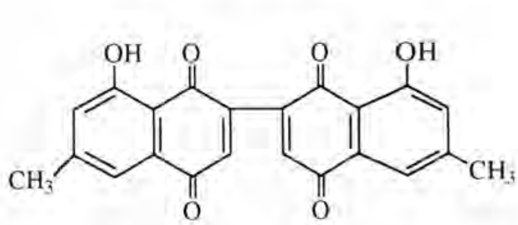


[**6**] Diospyrin

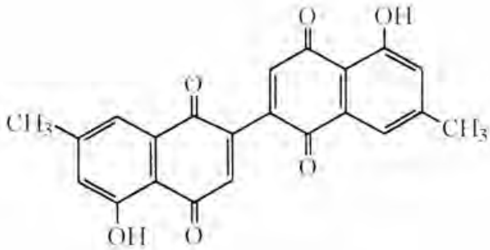


[7] β'-Dihydrodiospyrin

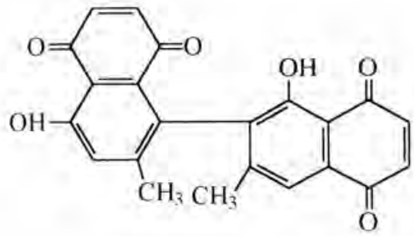
[**8**] 7-Methyljuglone



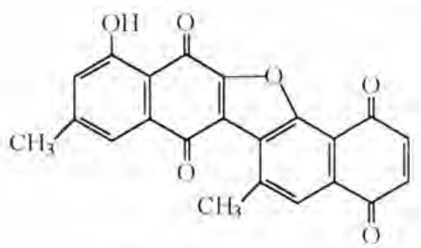
[**9**] Mamegakinone



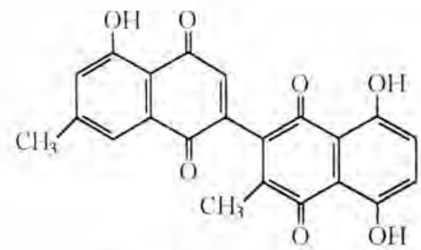
[**10**] Biramentacenone



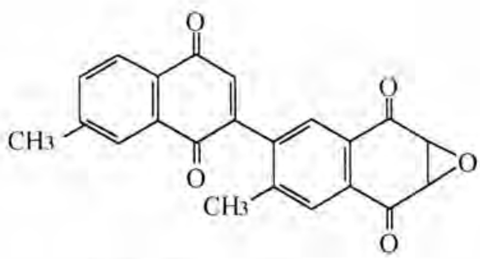
[**11**] Isodiospyrin



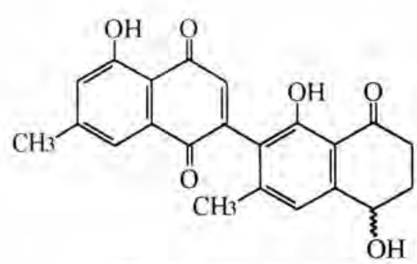
[**12**] 3,5′-O-cyclodiospyrin



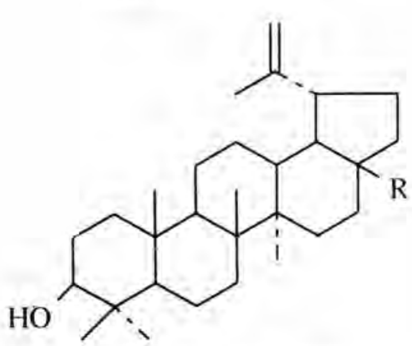
[**13**] 8′-Hydroxydiospyrin



[**14**] Diosquinone



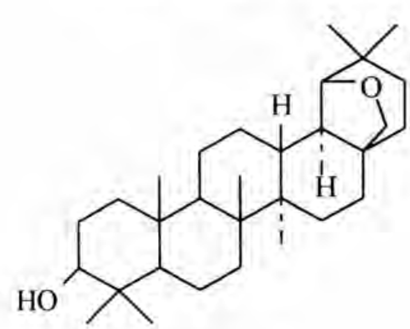
[**15**] Tetrahydrodiospyrin



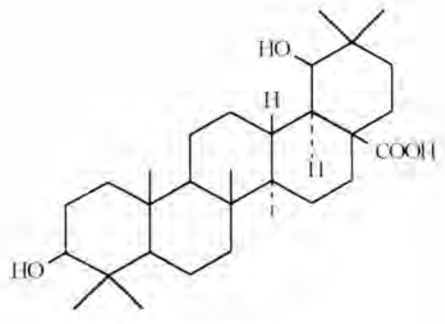
[**16**] Lupeol; R=CH_3

[**17**] Betulinic acid; R=COOH

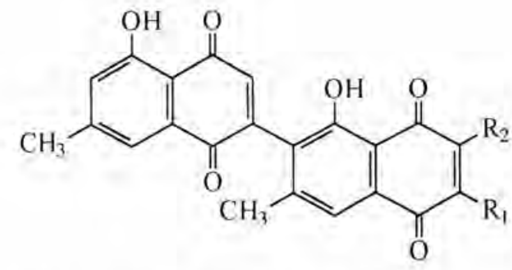
[**18**] Betulin; R=OH



[**19**] Allobetulin



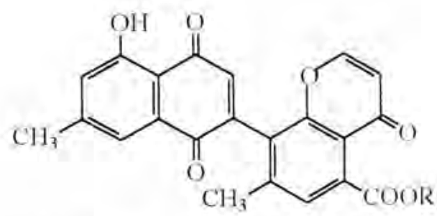
[**20**] Oxyallobetulin



[**21**] 2′-Chlorodiospyrin; R_1=Cl, R_2=H

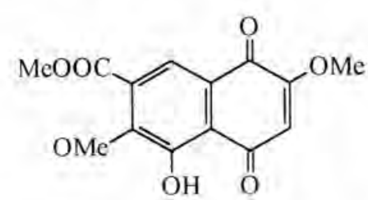
[**22**] 3′-Chlorodiospyrin; R_1=H, R_2=Cl

[**23**] 3′-Chloro-2′-hydroxydiospyrin; R_1=OH, R_2=Cl

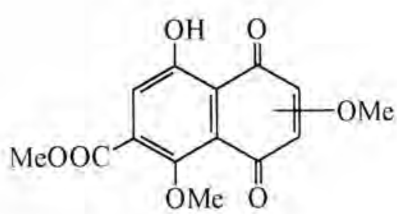


[**24**] Chromenone ester; R=Et

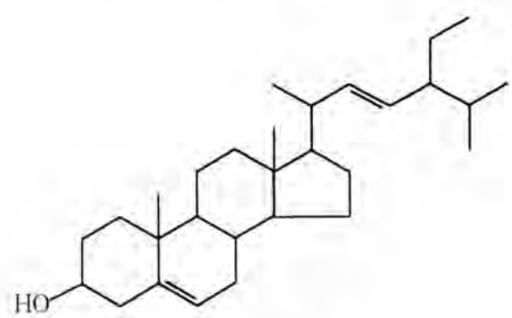
[**25**] Chromenone acid; R=H



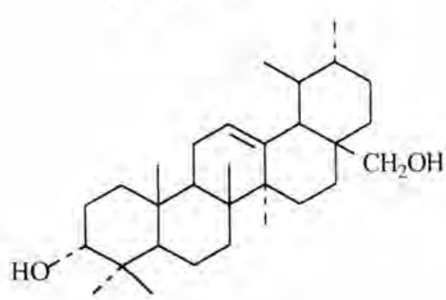
[**26**] 2,6-Dimethoxy-7-methoxycarbonyljuglone



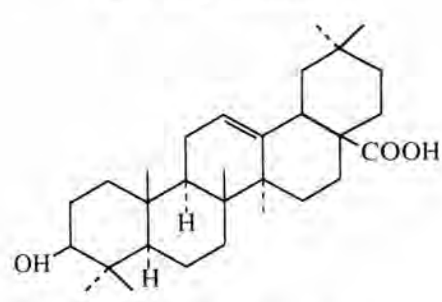
[**27**] Yerrinquinone



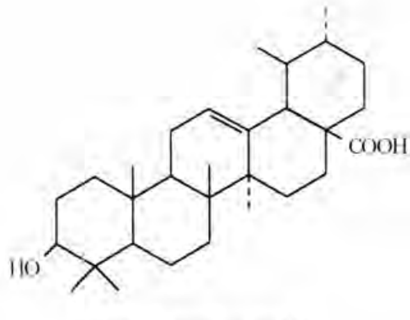
[**28**] Stigmasterol



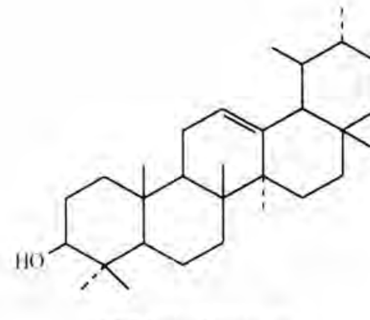
[**29**] Epi-uvaol



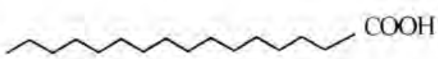
[**30**] Oleanolic acid



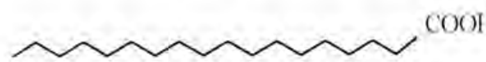
[**31**] Ursolic acid



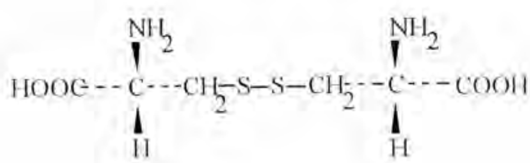
[**32**] α-Amyrin



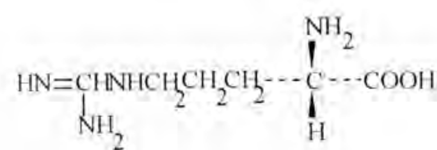
[**33**] Palmitic acid



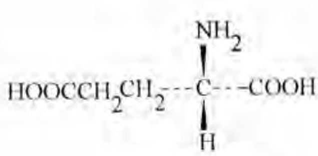
[**34**] Stearic acid



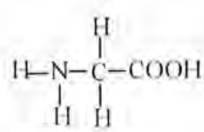
[**35**] L-cystine



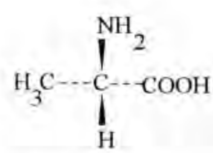
[**36**] L-arginine



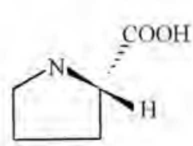
[**37**] L-glutamic acid



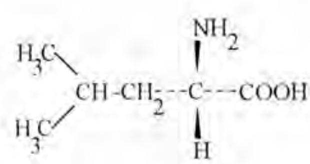
[**38**] Glycine



[**39**] L-alanine



[**40**] L-proline



[**41**] L-leucine

3. Biogenesis of Naturally Occurring Quinones

Like other secondary metobolites, the quinones are derived from a few key intermediates, principally acetate, shikimate and mevalonate, by a series of reactions which lead to the formation of benzenoid compounds. It is assumed that the last stages involve the oxidation of a phenol. Probably most quinone arise by the acetate-malonate pathway, particularly those elaborated by fungi, but the extent to which shikimate is involved is still a matter for conjecture. It does, however, appear to be an important intermediate in the formation of many quinones in higher plants. Wholly terpenoid quinones are relatively few but some quinones of mixed origin posses a side chain or ring derived from mevalonate (Thomson, 1971: 5).

3.1 Anthraquinones

In monocotyledons, anthraquinone derivatives are found only in the Liliaceae and Xyridaceae. Among dicotyledons they occur in the Rubiaceae, Leguminosae, Polygonaceae, Rhamnaceae, Ericaceae, Euphorbiaceae, Lythraceae, Saxifragaceae, Scrophulariaceae and Verbenaceae. They appear to be absent from the Bryophyta, Pteridophyta and Gymnosperms but occur in certain fungi and lichens (Evans, 1996: 232-233). In animals, a few occur in insects (Coccidae only) and in feather stars (Crinoidea) (Thomson, 1971:1).

Substances of the anthraquinone type were the first to be recognized, both in the free state and as glycosides. Further work showed that natural products also contained reduced derivatives of the anthraquinones (oxanthrones, anthranols, and anthrones) and compounds formed by the union of two anthrone molecules (i.e. the dianthrones) (Evans, 1996: 232).

Natural anthraquinones are either synthesized via the acetate-malonate pathway or derived from shikimate and mevalonate (Evans, 1996: 233). The majority of anthraquinones present in Rubiaceous plants are substituted in only one benzenoid ring and may be totally devoid of a carbon side chain or hydroxyl groups (Thomson, 1971: 9).

3.2 Naphthoquinones

The distribution of the naphthoquinones is sporadic. Nearly half of them occur in higher plants, scattered through some twenty families. They have been found in leaves, flowers, wood, bark, root, and fruit (Thomson, 1971: 2).

Natural naphthoquinones occur in a number of plants commonly in the reduced and glycosidic forms. In some heart-wood, e.g. *Diospyros spp.* (Ebenaceae) naphthoquinones occur as monomers, complex dimers and trimers (Evans, 1996: 248).

Naphthoquinones have been shown to be biosynthesized via a variety of pathways including acetate and malonate (plumbagin of *Plumbago spp.)*, shikimate / succinyl CoA combined pathway (lawsone) and shikimate / mevalonate combined pathway (alkannin) (Evans, 1996: 248).