

CHAPTER I

INTRODUCTION

The quinone pigments are the largest class of natural coloring matters. They range from pale yellow to almost black in color. They are found chiefly in higher plants, fungi and bacteria, and in the animal kingdom, in arthropods and echinoderms. About half the total number occur in higher plants. They are found mainly in the bark or roots and if present elsewhere are usually masked by other pigments. Moreover quinones sometimes exist in the plant in a reduced form, having little or no color (Thomson, 1971 : 1).

There have been a number of reports regarding biological activities of quinones: antiplatelet aggregation (Yun-Choi, Kim, and Takido, 1990: 630-633; Chung *et al.*, 1993: 929-934; Teng *et al.*, 1993: 1014-1018; Chung *et al.*, 1994: 313-316), laxative effect (Bruneton, 1995: 349-366; Evans, 1996: 232-247), xanthine oxidase inhibition (Noro *et al.*, 1987: 4314-4316), monoamine oxidase inhibition (Yamasaki *et al.*, 1988: 670-675), immunosuppressive effect (Lu and Chen, 1989: 223-226), antibacterial activity (Cai and Chen, 1988: 282-284; Mineo *et al.*, 1988: 249-251; Tanaka *et al.*, 1990: 688-692), antiviral activity (Schinazi *et al.*, 1990: 265-272; Evans, 1996: 454-455), antimalarial activity (Abu El Heiga *et al.*, 1990: 1620-1623; Koumglo *et al.*, 1992: 533-534), nucleoside transport inhibition (Su *et al.*, 1994 : 656-661), lipid peroxidation inhibition (Huang, Yeh, and Hong, 1995: 1365-1371), antitumor activity (Thomson, 1987: 506-511), and diuretic effect (Zhou and Chen, 1988: 17-20).

The plants selected for investigation in this study are *Prismatomeris sessiliflora* Pierre ex Pitard and *Diospyros montana* Roxb. They belong to the families Rubiaceae and Ebenaceae, respectively. Many members of these two families are known to be rich sources of quinone compounds.

Prismatomeris sessiliflora Pierre ex Pitard is an indigenous plant known in Thai as Phayaa Khrut. It was first found in Udawn and Nakawn Panom provinces (Craib, 1932: 184-185). The genus *Prismatomeris* belongs to the family Rubiaceae of the order Rubiales. It is the smallest genus in the family with 2-3 species distributed in the tropical India and Malayan (Hooker, 1973: 159).

The plants in the genus *Prismatomeris* are usually shrubs with compressed 4-gonous branches. Leaves opposite; stipules 1-2 cuspidate. Flowers bisexual, in axillary and terminal fascicles, white. Calyx tube of male small, turbinate; of female larger, cupular, persistent. Corolla tube cylindric, throat glabrous; lobes 4-5 spreading, valvate in bud. Stamens 4-5, in the corolla tube; filaments short; anthers linear, included. Ovary 2-celled; style filiform, branches 2 free or united; ovules 1 attached above the middle of the septum in each cell. Berry small, 1-2 celled, 1-2-seeded. Seeds subglobose, peltate, ventrally excavated, testa membranous; embryo small, cotyledon reniform, radicle inferior (Backer and Bakhuizen Van Den Brink, ed, vol. II, 1965: 278; Hooker, 1973: 159).

According to Tem Smitinand (1980: 274-275) the species of genus *Prismatomeris* found in Thailand are as follows.

<i>Prismatomeris filamentosa</i> Craib	พุดป่า Phut paa (Rayong)
<i>P. fragrans</i> Geddes	ข้าวสาร Khaao saan (Nakhon Phanom)
<i>P. griffithii</i> Ridley	ตุ๊กไก่ Duuk kai (Trang)
<i>P. memecyloides</i> Craib	พริกป่า Phrik paa (Trat)
<i>P. tetrandra</i> Schum.	ตะไทร Ta lai (Chiang Mai)
subsp. <i>malayana</i> (Ridley) Fohansson	กรัก Krak (Prachup Khiri Khan);
(<i>P. malayana</i> Ridley)	กรักผี Krak phae,
(Davies, 1991: 256)	ตุ๊กไต่ดำ Duuk kai dam (Peninsular);

ขอนแก่น Son paa (Nakhon
Ratchasima);
สระบุรี Son kra (Central)

Prismatomeris sessiliflora Pierre ex Pitard (Figure 1) : Petit arbre ou arbuste, haut de 2-4 m. Rameaux grêles, quadrangulaire, aplatis, rapidement arrondis, à écorce gris clair. Feuilles longues de 6-23 cm. sur 2-8 cm., elliptiques ou oblongues-lancéolées, acuminées au sommet, aiguës à la base, brun clair ou vert brunâtre et luisantes en dessus, brun clair et mates en dessous, coriaces; nervures 6-12 paires, étalées, fines, également saillantes sur les 2 faces, réticulées; pétiole long de 2-8 mm., aplati en dessus, épais; stipules longues de 3-5 mm, triangulaires, acuminées, bifides. Inflorescence terminale ou axillaire; fleurs fasciculées par 5-12, odorantes, branches; pédicelle long de 1 mm. ou nul. Sépales 4, excessivement courts, triangulaires, aigus; tube long de 2 mm., largement évasé, membraneux. Pétales 4, longs de 6 mm., linéaires; tube long de 14-17 mm., étroit, glabre. Élamines 4, insérées vers les 2 tiers supérieurs du tube; filet très court; anthère longue de 2.5 mm., linéaire, dorsifixe. Ovaire à 2 loges; style long de 15 mm., grêle et glabre; stigmates longs de 1.5 mm., sudés; ovule 1 par loge. Fruit charnu; baie haute et large de 8 mm., globuleuse, couronnée par les restes du calice; épicarpe noirâtre; graine 1 généralement, haute et large de 6 mm., à hile ventral étroit; testa noirâtre, mat; albumen semilunaire entourant une vaste cavité garnie des tissus mortifiés du placenta; embryon petit. Fl. d' avril en août; fr. en juillet et août (Lecomte, 1922: 429-430).

Diospyros montana Roxb. is an indigenous plant known in Thai as Maklua pa (มะเกลือป่า). The genus *Diospyros* belongs to the family Ebenaceae of the order Ebenales. It is the biggest genus in the family with 500 species (Evans, 1996: 46), mainly distributed in the tropics, and a few in the subtropics (Tem Smitinand and Larsen, ed., vol. 2, 1981: 281).

The plants in the genus *Diospyros* are usually trees or shrubs, dioecious, sometimes monoecious or polygamous; mostly unarmed; all parts often turning blackish when dry. Leaves distichous, and mostly reflexed, penninerved. Inflorescences cymose or fasciculate, axillary or ramiflorous, rarely cauliflorous, or flowers solitary. Flowers actinomorphic. Calyx more or less deeply lobed, persistent and usually accrescent in fruit; lobes valvate or imbricate in bud. Corolla gamopetalous, caducous; segments patent, contorted in bud. Stamens 6- α , free, or in pairs, on the base of corolla-tube, or in bundles on receptacle; anthers basifixed, 2-locular, longitudinally dehiscent. Rudimentary ovary usually present in male flowers. Staminodes usually present in female flowers. Ovary superior, (3-) 4 (-16)-locular; ovules 1(-2) in each locule, pendulous; styles 1-5. Fruit indehiscent, fleshy, dry or woody, 1-many-seeded, endosperm ruminant or smooth (Tem Smitinand and Larsen, ed., vol. 2, 1981: 281).

According to Tem Smitinand (1980: 122-126), the species of genus *Diospyros* found in Thailand are as follows.

<i>Diospyros apiculata</i> Hiern	มะพลับไชนก Maphlap khai nok (Central)
<i>D. areolata</i> King & Gamble	พลับ Phlap, มะพลับ Ma phlap (Central)
<i>D. bambuseti</i> Fletch	มะเกลืออรัญญ์ Ma Kluea aran (Prachin Buri)
<i>D. hejaudii</i> Lec.	พลับดง Phlap dong (Chon Buri);
(<i>D. retrofracta</i> Bakh.)	อีโต้ Ee do (Chaiyaphum)
<i>D. borneensis</i> Hiern	กานะบุรง Kaa-na buu-rong (Malay-Yala),
(<i>D. fecunda</i> Fletch.)	ขี้หนู Khee nuu (Northeastern)
<i>D. brandisiana</i> Kurz	ดำ Dam (Ranong, Nakhon Si Thammarat; พริก Phrik (Yala)
<i>D. buxifolia</i> Bl. ex Hiern	รีบู Ree buu, รีผา Ree phao, สังท่า Sang tham (Peninsular)

<i>D. castanea</i> Fletch.	กะละมັก Kalamak (Kanchanaburi, Ratchaburi); ตะโกพนม Tako phanom (General); มะด้ามหมุย Ma daam mui, มะด้า Ma dam (Northern); มะต๊ับหมาก Ma tap maak (Chiang Mai, Lamphun); หนังด้า Nang dam, หลังด้า Lang dam (Northeastern); หมากค้อน Maak khon (Nakhon Ratchasima)
<i>D. cauliflora</i> Bl. (<i>D. trunciflora</i> Ridl.)	กรอดคะเมา Krot-kha-mao (Khmer- Chanthaburi); ตุนอ Tuu-bo (Malay-Pattani); เท้แสนปม Thao saen pom (General); ไหม้ Mai (Yala, Narathiwat)
<i>D. coaetanea</i> Fletch.	ล่าตาคาย Lam taa khwaai (Phitsanulok); หอมหวาน Hom khwaan (Loei)
<i>D. confertiflora</i> Bakh.	ลูกหัวนุก Luuk hua nok (Peninsular)
<i>D. crumenata</i> Thw.	กรอดคะเมา Krot-kha-mao (Khmer- Chanthaburi)
<i>D. curranii</i> Merr.	กล้วย Klaai (Pattani); นังจ้อย Nang choi (Nakhon Ratchasima); รักด้า Rak dam (Ubon Ratchathani)
<i>D. dasyphylla</i> Kurz	จันเข่า Chan khao (Prachin Buri); จันตง Chan dong (Lampang)
<i>D. decandra</i> Lour. (<i>D. packmanni</i> Clarke)	จัน Chan (General); จันเข่า Chan khaao, จันอุกหอม Chan luuk hom (Central)

<i>D. dictyoneura</i> Hiern	ดงน้ำ Dong nam (Chon Buri);
(<i>D. brachiata</i> King & Gamble)	นางก้อ Naang ko (Trang)
<i>D. diepenhorstii</i> Miq.	เนียน Nian (Pattani)
(<i>D. pyrifer</i> Ridl.)	
<i>D. dumetorum</i> W.W. Smith	มะเกลือน้อย Ma Kluea noi (Northern)
<i>D. eburnum</i> Koen.	ด่าง Dam dong (Prachuap Khiri Khan)
<i>D. ehretoides</i> Wall.	ขึ้นขวาง Chin kwaang,
(<i>D. putii</i> Fletch.)	เรือนขวาง Ruean kwaang,
	ลินขวาง Lin kwaang (Prachin Buri);
	ดืบเต่าตัน Taptao ton,
	ดืบเต่าหลวง Taptao luang (Ratchaburi);
	มะโกป่า Ma ko paa (Phrae);
	มะมั่ง Ma mang (Nakhon Ratchasima);
	มะไฟผี Ma fai phee (Chiang Rai);
	มาเมียง Maa-miang (Khmer-Swrin);
	เขื่อนขวาง Huean kwaang (Northern,
	Northeastern);
	แฮดขวาง Haet kwaang (Northeastern)
<i>D. ferrea</i> Bakh.	โครมด Khrai mot (Chiang Mai);
	ทึงทวด Thing thwat (Chon Buri);
	ปู่สะแซ Puu-la-sae (Malay-Narathiwat);
	ลำบิต Lambit (Central);
	ลำบิตทะเล Lambit thale (Ranong);
	ลำอิต Lam it (Narathiwat);
	หมากน้อย Maak not (Chiyaphum)
<i>D. filipendula</i> Pierre ex Lecomte	จิ้งนัง Chang nang (Surin);
	ดำนิตดง Dambit dong,
	ลำนิตดง Lambit dong (Ranong)

<i>D. frutescens</i> Bl.	พลับกล้วย Phlap kluai (Nakhon Si Thammarat)
<i>D. fulvopilosa</i> Fletch.	เนียน Nian (Pattani)
<i>D. glandulosa</i> Lace	กล้วยฤาษี Kluai ruesee (Chiang Mai, Mae Hong Son); จันทป่า Chan paa (Chiang Mai); มะเขือเถื่อน Ma khuea thuean (Loei); เหลสกุ่มมอ Le-ko-mo (Karen-Chiang Mai); อาล่องยุ่ม Aa-long-yum (Lawa-Chaiang Mai)
<i>D. gracilis</i> Fletch.	กะลา Kaacha (Nakhon Ratchasima); น้ำจ้อน Nam chon, มะเกลือกา Ma kluea kaa (Prachin Buri); มะหวัด Ma weet (Saraburi)
<i>D. hasseltii</i> Zöll.	ตะโก Tako (Nakhon Ratchasima);
(<i>D. horsfieldii</i> Hiern)	ตะโกจัน Tako chan (Bangkok); บานง Baa-neng (Malay-Narathiwat)
<i>D. hermaphroditica</i> Bakh.	โกพนม Ko phanom (Prachin Buri); จันทดำ Chan dam, ตาดำ Taa dam (Trat); ตึง Dee ngu (Phthalung); นางดำ Naang dam (Saraburi); ย่างทราย Yaang saai (Chanthaburi)
<i>D. insidiosa</i> Bakh.	จันทเขาก Chan khao (Peninsular)
<i>D. kaki</i> Linn.	พลับจีน Phlap cheen (Central); Japanese Persimmon; Chinese Date Plum, Persimmon

<i>D. kerrii</i> Craib	มะพลับดง Ma phlap dong (Petchabun)
<i>D. latisejala</i> Ridl.	กลูแปบุรง Kluu-pae bu-rong (Malay-Pattani); เทพพนม Thep phanom (General)
<i>D. longipilosa</i> Phengklai	มะพลับขน Maphalap khon (Peninsular)
<i>D. malabarica</i> Kostel.	ตะโกไทย Tako Thai (Central); ตะโกสวน Tako suan, ปลาบ Plaap (Phetchaburi); มะเขือเถื่อน Ma khuea thuean (Sakon Nakhon); มะสุลัวะ Ma-su-lua (Karen-Lampang)
var. <i>siamensis</i> Bakh.	มะพลับ Ma phlap (General)
<i>D. martabanica</i> Clarke	ไข่เต่า Khai tao (General)
<i>D. mollis</i> Griff	ผีเผา Phee-phao (Shan-Northern); มะเกลือ Ma kluea (General); มักเกลือ Mak-kluea (Khmer-Trat); Ebony tree
<i>D. montana</i> Roxb.	ตานสั้น Taan saan (Central); ต้นไฟผี Thaanfai phee (Northern); มะเกลือป่า Ma kluea paa (Nakhon Sawan, Prachin Buei); มะตูมดำ Ma tuum dam (Saraburi)
<i>D. oblonga</i> Miq.	ทะยั้ง Tha ying (Nakhon Ratchasima); นางดำ Naang dam, โมรี Moree (Chantaburi); มันกล้วย Man kluai (Lampang); หลักดำ Lakdam (Maha Sarakham)
<i>D. pendula</i> Hasselt ex Hassk.	มะพลับดง Maplap dong (Chanthaburi);
(<i>D. schmidtii</i> Craib)	อินป่า In paa (Trat)

<i>D. philippensis</i> A. DC.	มะริด Ma rit (Peninsular);
(<i>D. discolor</i> Willd.)	Butter Fruit
<i>D. pilosanthera</i> Blanco	กะลิง Ka ling (Ubon Ratchathani);
(<i>D. helferi</i> Clarke)	ดินหมี Dan mee (Pattani)
<i>D. pilosula</i> Hiern	ทางทพุ Haang nuu (Phetchabun)
<i>D. pubicalyx</i> Bakh.	ด้าดง Dam dong (Prachuap Khiri Khan);
	อิน In (Kanchanaburi)
<i>D. rhodocalyx</i> Kurz	โก Ko (Northeastern);
	ตะโกนา Tako naa (General);
	นมจ้ว Nom ngua (Nakhon Ratchasima);
	มะโก Mako (Northern);
	มะถ่านไฟผี Ma thaanfai phee (Chiang Mai);
	Ebony
<i>D. rubra</i> Lec.	พญารากดำ Phayaa raak dam (General)
<i>D. saxosa</i> Fletch.	ขล่าย Khlaai (Nakhon Sawan);
	ตีหมี Dee mee (Prechuap Khri Khan);
	ไฟ Fai (Nakhon Ratchasima);
	มวยด้าเซา Muai dam khao (Chumphon);
	สะล่างตัวผู้ Salaang tuaphuu (Chanthaburi)
<i>D. scortechinii</i> King & Gamble	ไขนุก Khai nok (Peninsular)
<i>D. sumatrana</i> Miq	ลักเคยลักเกลือ Lak khoi lak kluea (Krabi)
<i>D. tahanensis</i> Bakh.	ไหม้ Mai (Krabi)
(<i>D. trimera</i> Fletch.)	
<i>D. thaiensis</i> Phengklai	มะพลับเสี้ยนาง Maphlap lep naang (Peninsular)
<i>D. toposia</i> Ham.	ข้าวเม่าเหล็ก Khaao mao lek (Peninsular)
var. <i>toposioides</i> King & Gamble	เม่าเหล็ก Mao lek (Krabi)
<i>D. transitoria</i> Bakh.	ตานด้า Taan dam,

	มะขามโคก Ma khaam khok (Chanthaburi);
	น้ำผึ้ง Nam phueng (Prachin Buri);
	ลำบิตใบใหญ่ Lambit bai yai (Chon Buri);
	สาวดำ Saa dam,
	อีสาวดำ Ee saao dam (Nakhon Si Thammarat);
	หมาเล็ก Maa lek (Surat Thani)
<i>D. trianthos</i> Phengklai	สามเกลอ Saam kloe (General)
<i>D. undulata</i> Wall.	จะเพลิง Chaphloing (Chong-Chanthaburi);
<i>(D. cratericalyx</i> Craib)	ตุ๊กค้าง Duuk khaang,
	ตุ๊กช้าง Duuk chaang (Peninsular);
	ตาโกดำ Taako dam (Trat);
	พลับเขา Phlap khao (Surat Thani);
	สร้าง Salaang)Prachin Buri)
<i>D. variegata</i> Kurz	น้ำจ้อย Nam choi (Prachin Buri);
	พญารากดำ Phayaa raak dam (Sukhothai);
	พลับดำ Phlap dam (Kanchanaburi);
	มะเขือเถื่อน Ma khuea thuean,
	อีดำ Ee dam (Kamphaeng Phet)
<i>D. wallichii</i> King & Gamble	กุ่มง Ku-mung (Malay-Pattani);
	กุ่ม Kuu-muu (Malay-Songkhla);
	ข้าวไหม้ Khaao mai,
	ดำเขา Dam khao,
	ดำตะโก Dam tako (Songkhla, Narathiwat);
	เจียด Chiat (Surat Thani);
	ตะกราย Ta kraai (Yala);
	เนียนป่า Nian paa (Songkhla)

D. winitii Fletch.

มะพลับเจ้าคุณ Maphlap chaokhun (General);

ท่าพาน Ham faan (Lampang)

Diospyros montana Roxb. (Figure 2) is an evergreen tree, up to 15 m high; twigs armed. Leaves elliptic, oblong, ovate or obovate, 1.5-12 by 1-5 cm, base acute, rounded, truncate or cordate, apex acute or obtuse, chartaceous, subcoriaceous rarely coriaceous, pubescent, glabrescent on both surfaces; secondary nerves 3-7 pairs, faint, \pm impressed on upper surface, prominent on lower surface; tertiary veins impressed on upper surface, inconspicuous on lower surface; petiole 2-10 mm long, pilose. Male flowers cymose, 4-merous; pedicle \pm 2 mm long, pubescent, glabrescent. Calyx broadly campanulate, 1-2 mm long, divided \pm to the base, globrous or sparsely pubescent on both sides. Corolla urceolate, 8-10 mm long, divided to half of two thirds, glabrous on both sides. Stamens 14-20, glabrous. Rudimentary ovary hirsute. Female flowers solitary, 4-merous; pedicel \pm 5 mm long, \pm glabrous. Calyx and Corolla as in male flowers. Ovary globose, glabrous, 8-locular; styles 4, glabrous. Staminodes 4-12, glabrous. Fruit globose or ellipsoid, 1-3 by 1-3 cm, dry at maturity, base rounded, apex rounded with short cusp; fruiting calyx divided to the base, pubescent then glabrescent on both sides; lobes spreading horizontally or reflexed, undulate, not plicate, with inconspicuous nerves; fruit-stalk 5-7 mm long; endosperm smooth.

It is widely distributed in Thailand and also found in India, Burma, Laos, Cambodia, Vietnam, Malay Peninsula, Indonesia, Philippines. Its wood is used in the furniture industry, and its fruit is used as a fish poison (Tem Smitinand and Larsen, ed., vol. 2, 1981: 308-310).

Up to the present, no phytochemical investigation of *P. sessiliflora* has been reported. As for *D. montana*, except for the root, several studies on the other parts have been published (Kapil and Dhar, 1961: 498-500; Dutta, Dutta, and Chakravarti, 1972: 1180-1181; Misra, Nigam, and Mitra, 1972: 1508-1509; Pardhasaradhi and

Sidhu, 1972: 4201-4204; Goutam and Purohit, 1974: 100-101; Lillie, Musgrave, and Skoyles, 1976: 2155-2161; Narayan, Row, and Satyanarayana, 1978: 345; Pardhasaradhi and Krishnakumari, 1979: 684-685; Ray and Agrawal, 1979: 735-736; Thomson, 1987: 226; Pardhasaradhi and Rao, 1990: 2355-2356; Zafar, Singh, and Khan, 1991: 432-433). These prompted the author to investigate the constituents of these plants in the hope of obtaining additional information which may lead to the better understanding of the occurrence and distribution of quinone compounds. This study was concerned with the isolation, purification and structure determination of chemical compounds from the roots of *P. sessiliflora* and *D. montana*.

The main objectives in this investigation are as follows:

1. to isolate and purify quinone compounds from the roots of *P. sessiliflora* and the roots of *D. montana*.
2. to determine the chemical structure and physical properties of each isolated compound.



Figure 1 *Prismatomeris sessiliflora* Pierre ex Pitard

(Photographed by Assistant Professor Vichien Jongboonprasert,
the Phuwua Wild Life Sanctuary, Nongkhai province, Thailand, March, 1996)



Figure 2 *Diospyros montana* Roxb.

A Habit; *B* Male inflorescence; *C* Male flowers;
D Female flowers; *E* Fruit; *F* Seeds; *G* Leaf base.

(Tem Smitinand and Larsen, ed., vol. 2, 1981: 309)