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Naphthoquinone Derivatives from the Ebenaceae. I. Diospyrol and the Related Naphthoquinones from *Diospyros mollis* Griff.[1]

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The structure of diospyrol, the anthelmintic principle of fresh fruits of *Diospyros mollis* Griff., was revised to I by the preparation of the derivatives shown in Chart 1 and by their spectral examinations especially by nuclear magnetic resonance (NMR) shown in Table I. The dried fruits, bark, and fresh roots were also examined and the presence of elliptinone (VI), mamegakinone (VII), and 4,5,8-trimethoxy-2-naphthaldehyde (XIII) besides triterpenoids, lupeol, lupenone, betulin, and taraxerol, was revealed.

The Ebenaceae is a family with about 500 species and is widespread chiefly in tropics and subtropics. The constituents of the family, especially of the genus *Diospyros*, the largest genus of the family, have been rather extensively studied[3] and the plants have been proved to be rich sources of naphthalene and naphthoquinone derivatives.[4–16] We have so far studied the constituents of *Diospyros japonica, D. kaki, D. kaki* var. *sylvestris, D. lotus, D. maritima, D. morrisiana,* and *Maba buxifolia,* which are all species of the genera growing in Japan, and of *D. mollis* growing in Thailand. Some of the results so far obtained have already been reported in the preliminary communications.[1,17] This paper and the forthcoming papers will report the experimental details of the works.

Diospyros mollis Griff. is a shrub growing in South-East Asian countries and bears the fruits of 2—2.5 cm in diameter in summer. The extracts of the fresh fruits are used in Thailand as an anthelmintic and as a black dye and a readily oxidizable phenolic constituent, named diospyrol, was obtained by extraction with ether,[18] acetone,[19] or ethanol followed

1) A part of the work was reported in the preliminary communication (*Tetrahedron Letters*, **1967**, 4857). This paper also constitutes Part VI of "Studies on Thai Medicinal Plants" (Part V: V. Podimuang, S. Mongkolsuk, K. Yoshihira, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **19**, 207 (1971)).

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3) R. Hegnauer, "Chemotaxonomie der Pflanzen," Band 4, Birkhäuser Verlag, Basel und Stuttgart, 1966, p. 45.

4) Th.M. Meijer, *Rec. Trav. Chim.*, **66**, 193 (1947).

5) R.G. Cooke, H. Dowd, and L.J. Webb, *Nature*, **169**, 974 (1952).

6) A.G. Brown, L.C. Lovie, and R.H. Thomson, *J. Chem. Soc.*, **1965**, 2355.

7) A.G. Brown and R.H. Thomson, *J. Chem. Soc.*, **1965**, 4292.

8) A.L. Fallas and R.H. Thomson, *J. Chem. Soc.* (*C*), **1968**, 2279.

9) A.K. Ganguly and T.R. Govindachari, *Tetrahedron Letters*, **1966**, 3373.

10) G.S. Sidhu and M. Pardhasaradhi, *Tetrahedron Letters*, **1967**, 1313.

11) G.S. Sidhu and K.K. Prasad, *Tetrahedron Letters*, **1967**, 2905.

12) G.S. Sidhu, A.V.B. Sankaram, and S.M. Ali, *Indian J. Chem.*, **6**, 681 (1968).

13) G.S. Sidhu and K.K. Prasad, *Tetrahedron Letters*, **1970**, 1739.

14) P.K. Gupta and M.M. Dhur, *Phytochemistry*, **8**, 789 (1969).

15) S.H. Harper, A.D. Kemp, and J. Tannock, *J. Chem. Soc.* (*C*), **1970**, 626.

16) S. Mongkolsuk and C. Sdarwonvivat, *J. Chem. Soc.*, **1965**, 1533.

17) K. Yoshihira, M. Tezuka, and S. Natori, *Tetrahedron Letters*, **1970**, 7; K. Yoshihira, M. Tezuka, C. Takahashi, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **19**, 851 (1971).

18) J.W. Loder, S. Mongolsuk, A. Robertson, and W.B. Whalley, *J. Chem. Soc.*, **1957**, 2233.

19) T. Nilanidhi and P. Prachankadee, *Proc. IXth Pacific Sci. Congr.* **1962**, p. 52.

by precipitation with aqueous acetic acid.[20,21] The phenol is assumed to be the main constituent for anthelmintic action and dying.[19,20] The chemical work by Loder, *et al.*[18] revealed the presence of dinaphthyl nucleus with two C-methyl and four hydroxyl groups in diospyrol and they proposed the structure (X) as a most probable one chiefly from the comparison of the ultraviolet (UV) spectra with those of the model compounds, though there existed no decisive evidence for the positions of the substituents and the linkage of the two naphthyl units. Since we obtained an enough amount of the material for further examination, we have carried out the preparation of the derivatives and the examination by spectral methods as follows.

Since diospyrol (I) itself is very sensitive to aerial oxidation, it was derived to tetraacetate[18] (II) and tetramethyl ether[18] (III). Methylation of I with diazomethane in dioxane gave dimethyl ether (IV), mp 183—184°, suggesting the presence of two hydrogen bonds between the four hydroxyl groups. Further methylation of IV with dimethyl sulfate gave tetramethyl ether (III). The molecular formula of I was confirmed by analyses and mass spectra (M^+ of III, *m/e* 402). The UV and infrared (IR) spectra of these derivatives suggested the presence of naphthalene nucleus. Symmetrical disposition of the hydroxyls and the methyls on the nucleus was clearly demonstrated by nuclear magnetic resonance (NMR) (Table I). In the mass spectrum of III double charged ions appear in *m/e* less than 201.5 ($(M+1)^{++}$). The NMR spectrum of dimethyl ether (IV) revealed that the methylation with diazomethane took place unsymmetrically and the presence of hydrogen bonds between hydroxyls and methoxyls was confirmed by IR (ν_{OH} 3420 cm^{-1} (CCl_4) (unaffected by dilution))[6,22] and NMR spectra (δ 9.71, 9.60 ($CDCl_3$)).[6] These observations were in good accord

Table I. NMR Spectra of Diospyrol Derivatives
(δ Values in ppm from the Internal Standard TMS)

compound	solvent	1- and 1′-OH, OMe or OAc	3- and 3′-H	4- and 4′-H	5- and 5′-H	6- and 6′-CH_3	7- and 7′-H	8- and 8′-OH, OMe or OAc
II	$CDCl_3$+CF_3COOH	1.96	7.33	7.71	7.57	2.50	6.98	2.34
			(d, J=8 cps)		(d, J=1.5 cps)			
III	$CDCl_3$	3.58	7.36	7.54	7.24(br)	2.45	6.72(br)	3.89
			(d, J=8 cps)					
IV	$CDCl_3$	3.49	7.22	7.34	7.05(br)	2.43	6.68(br)	9.71
			(d, J=8 sps)		[a]			
		9.60	7.36	7.43	7.28(br)	2.39	6.58(br)	3.97
			(d, J=9 cps)		[a]			
V	$CDCl_3$+CF_3COOH	3.58	7.62	7.94	—	2.16(d)	6.74(q)	—
			(d, J=10cps)			(J=1.5 cps)		
VI	$CDCl_3$+CF_3COOH	—[b]	7.84	7.84	—	2.28(d)	7.02(q)	—
						(J=1.5 cps)		
VII	$CDCl_3$+CF_3COOH	—	7.05	—	7.54(br)	2.48	7.18(br)	—[b]
VIII	$CDCl_3$	—	6.87	—	7.56(br)	2.49	7.05(br)	3.94
IX	$CDCl_3$+CF_3COOH	3.79	7.72	8.09	—	2.25(d)	6.98(q)	—
			(d, J=8 cps)			(J=1.5 cps)[a]		
		—	7.10	—	7.73(br)	2.57	7.29(br)	3.99

a) The coupling was confirmed by spin-decoupling. b) Not observed by the addition of CF_3COOH.

20) M. Mokkhasmit, *Bull. Dept. Med. Sci.*, Thailand, 3, 153 (1960).
21) Diospyrosquinone, colorless compound, mp 250—251°, obtained by Nguyen-Ba-Tuoc (*Thèse (Pharm.) Univ. Paris*(1953)) from the same source, is assumed to be identical with diospyrol.
22) H. Hoyer, *Chem. Ber.*, **86**, 507 (1953).

with the previous work[18] and suggested that diospyrol (I) must be a symmetrical dimer of 1,8-dihydroxymethylnaphthalene. However NMR spectra of these derivatives showed the presence of eight aromatic ring protons in two pairs each of *o*-coupled one and *m*-coupled one. Thus the structure (X) was proved to be untenable.

Hydrogen peroxide oxidation of III gave di-O-methyldiospyroquinone[18] (V), the spectral data of which showed the similarity with those of methyljuglone methyl ethers. The comparison of NMR spectrum of V with that of III (Table I) showed that one of the two methoxyl signals and the *m*-coupled proton signals disappeared and the *o*-coupled proton signals shifted to lower fields. Now the methyl signal shifted to higher field and showed a vinylic coupling with the adjacent ring proton,[23] indicating the presence of the methyl on the quinonoid ring in V and the presence of the methyl group in *m*-position to a hydroxyl group in I.

Oxidation of I with Fremy's salt gave two naphthoquinones; a quinone (VI), dark orange needles of mp 310° (decomp.), $C_{22}H_{14}O_6$, showed UV and IR absorption typical of a juglone and NMR signals (Table I) analogous to that of V except the methoxyl signal. Methylation of VI with methyl iodide and silver oxide gave V. After our preliminary communication[1] a quinone designated as elliptinone was isolated from *D. elliptifolia* by Fallas and Thomson[8] and the structure (VI) was put forward after comparison with our spectral data. The other quinone (VII), orange needles of mp 253°, $C_{22}H_{14}O_6$, also exhibited the typical UV ($\lambda_{max}^{dioxane}$ mμ (log ε): 253, 275, 434 (4.34, 4.28, 3.96)) and IR absorptions (ν_{max}^{KBr} cm^{-1}: 1652, 1625) of a methyljuglone. The quinone was later isolated from *D. lotus* L. (Japanese name: mamegaki) by us and designated as mamegakinone.[24] The quinone gave dimethyl ether (VIII). NMR

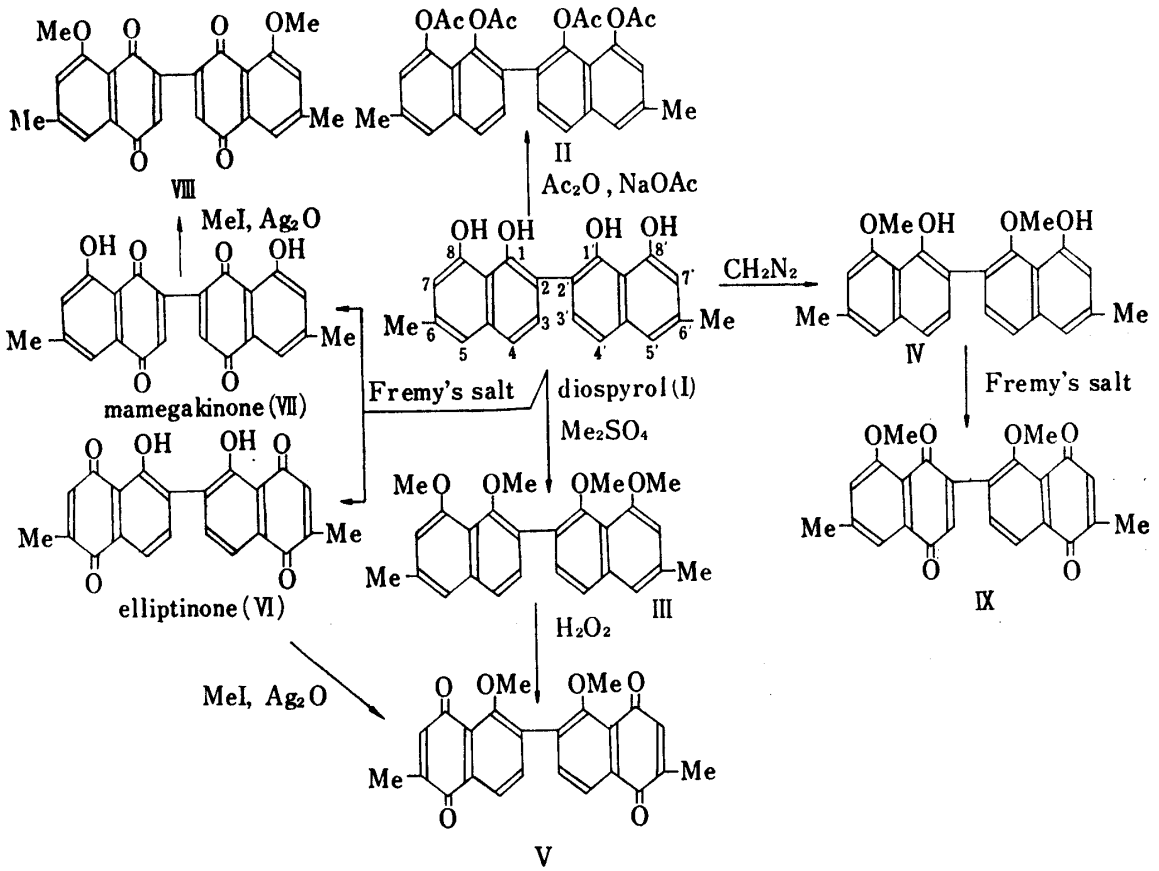
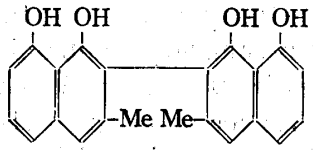


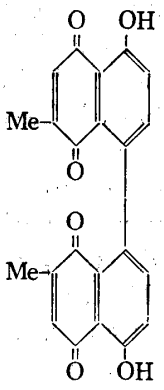
Chart 1

23) R.E. Moore and P.J. Scheuer, *J. Org. Chem.*, **31**, 3272 (1966).
24) K. Yoshihira, M. Tezuka, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), to be published. *cf.* the preliminary communication.[17]

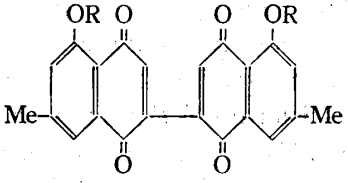
spectra of VII and VIII (Table I) showed the retention of the pair of *m*-coupled protons in II—IV and the disappearance of the pair of *o*-coupled protons. The methyl and the other ring proton signals now appear in singlets. In the IR spectra of VI and VII, ν_{O-H} absorption was not observed due to hydrogen bonds. These observations led to the conclusion that the two quinones (VI and VII) must be either VI or XI and VII or XII respectively, in which VI and VII suffice the conditions for both. Thus diospyrol must be expressed by the formula (I) (Chart 1). In the NMR spectra of V—VIII one of the two aromatic protons showing *o*- or *m*- coupling appears in low field, suggesting the location of the proton in *peri*-position.



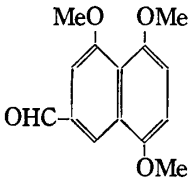
X



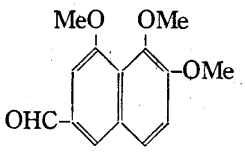
XI



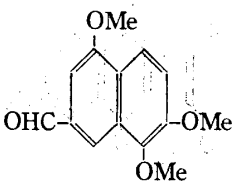
XII



XIII



XIV



XV

The oxidation of IV with Fremy's salt gave another dimeric naphthoquinone (IX), mp 269°. NMR spectrum of IX shows an unsymmetrical pattern similar to the summation of those of V and VIII.

All these reactions and spectral data are in good accord with the correlation shown in Chart 1 and the structure I of diospyrol was unequivocally established. The structure I and the correlation also lead to the formulation of elliptinone and mamegakinone as VI and VII.[25] Although all the derivatives do not show optical rotation, UV absorptions and the high field chemical shifts of methoxyl and acetoxyl methyls at 1- and 1'-positions indicate the presence of the two naphthyl nuclei in non-coplanarity.

Mamegakinone dimethyl ether (VIII) is sensitive to day light especially in protic solvents and changes into a dark red compound of high melting point and less solubility in organic solvents. This reaction is assumed to occur as shown in Chart 2.[26,27]

Diospyrol (I) is very sensitive to air and turns black. Chloroform extract of the black substance, after chromatography, afforded VI, VII and a dark red substance. Due to the less solubility the red substance was not characterized. The process of the formation of

25) A symmetrical dimer of 7-methyljuglone designated biramentacenone, was isolated from *Drosere ramentacea* and was assigned either VII or XII from the spectral observation. Direct comparison with our specimen of VII showed non-identity and hence the structure XII was put forward for the quinone (V. Krishnamoorthy and R.H. Thomson, *Phytochemistry*, **8**, 1591 (1969)).

26) A.J. Shand and R.H. Thomson, *Tetrahedron*, **19**, 1919 (1963).

27) R.G. Cooke and L.G. Sparrow, *Australian J. Chem.*, **18**, 218 (1965).

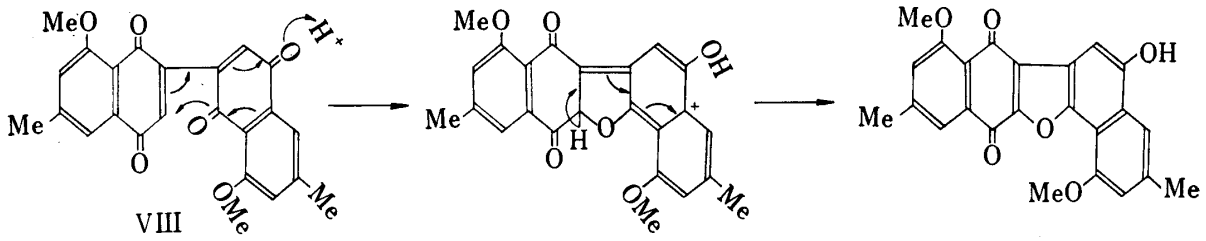


Chart 2

black pigments is assumed to be rather complicated,[28] including polymerization due to phenol radical coupling, quinone–phenol rearrangement,[26,27] and formation of charge-transfer complex between phenols and quinones.

For comparison dried fruits of *D. mollis*, which had turned black, were examined. Chloroform extract afforded VI and VII besides triterpenoids, lupeol and taraxerol. Thus, as far as the fruits concern, VI and VII are assumed to be 'natural artefact' formed in the course of drying. In the same manner chloroform extracts of the dried bark afforded VI and VII along with lupeol, lupenone, and betulin.

The constituents of fresh roots of *D. mollis* were also examined. The chloroform extract afforded, after chromatography, pale yellow needles (XIII) of mp 110—111°, along with betulin. The molecular formula $C_{14}H_{14}O_4$ (by mass spectrometry), UV, IR and NMR spectra suggested that the compound might be a naphthalene derivative bearing three methoxyl groups and one formyl group. Furthermore the existence of the four aromatic protons in two pairs showing *o*- and *m*-couplings, the latter of which are adjacent to the deshielding group (δ 7.28, 8.31), was revealed by NMR. The formulae (XIII—XV) sufficed the conditions, in which XIV was excluded by the nonidentity by direct comparison with the sample isolated from *D. ebenum*[7] and XV was assumed to be less probable from biogenetical grounds. At this stage of our work Harper, *et al.*[15] isolated 4,5,8-trimethoxy-2-naphthaldehyde (XIII) from *D. quiloensis* and established the structure by synthesis. The direct comparison of our compound (XIII) with the authentic sample from *D. quiloensis* showed the identity.

Mongkolsuk and Sdarwonvivat[16] claimed the isolation of 1,8-dihydroxy-3-methylnaphthalene from the fresh berries of *D. mollis*. Although the naphthol or the biogenetical equivalent is assumed to be the precursor of all the constituents of the plant, we have not encountered the naphthol in the materials so far studied.

Experimental[29]

Diospyrol (I), Tetraacetate (II), and Tetramethyl Ether (III)[30]——The sample of I, prepared by extraction of the fresh fruits with EtOH followed by precipitation with 10% HOAc under cooling and kept in a vacuum ampule,[20] was used throughout the work, mp 205—210° (decomp.) (lit.[18] 251—257° (decomp.)). Tetraacetate (II) and tetramethyl ether (III) were prepared by essentially the same methods as shown in the literature.[18] II, mp 240—241° (from EtOH) (lit.[18] 233°), UV λ_{max}^{EtOH} mμ (log ε): 221(4.77), 237(4.98), 250(4.83), 290(4.26); IR ν_{max}^{Nujol} cm^{-1}: 1770; NMR (Table I). III, mp 243° (from EtOH) (lit.[18] 232°), UV λ_{max}^{EtOH} mμ

28) R.H. Thomson, "Chemistry of Natural and Synthetic Colouring Matters and Related Fields," ed. by T.S. Gore, B.S. Joshi, S.V. Sunthankar, and B.D. Tilak, Academic Press, New York-London, 1962, p. 99.

29) Melting points were determined in a Yanagimoto melting point apparatus and are not corrected; for thin-layer chromatography Silica gel G with or without the treatment by oxalic acid solution was used and, unless otherwise specified, silica gel (Mallinckrodt) or the one washed with 3% CH_3COOH was used for column chromatography.

30) Although the direct comparison of our specimens with those of the British workers[18] has not been carried out due to the exhaustion of the samples (Professor W.B. Whalley, London School of Pharmacy, private communication), the comparison of the physical data showed the identity.

(log ε): 224(4.72), 243(4.80), 258(4.70), 312(4.30), 326(4.39), 339(4.43); IR ν_{max}^{Nujol} cm^{-1}: 1625, 1105; NMR (Table I); Mass Spectrum *m/e* (%): 402(M^+, 100), 388(10), 356(69), 341(17), 201.5(5), 201(13), 178(12), 170.5(6).

Diospyrol 1,8′-Dimethyl Ether (IV)——I(2.0 g) was treated with diazomethane in dioxane and, after removal of the solvent, the product was chromatographed on a column of silica gel (250 g) with benzene–chloroform (1:1). Recrystallization from EtOH gave colorless plates of IV(0.60 g), mp 183—184°, UV λ_{max}^{EtOH} mμ (log ε): 224(4.52), 243(4.54), 258(4.46), 315(3.96), 327(3.97), 340(4.01); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3420, 1635, 1350; NMR (Table I). *Anal.* Calcd. for $C_{24}H_{22}O_4$: C, 76.98; H, 5.92. Found: C, 76.32; H, 5.57.

A mixture of IV (0.05 g), KOH (0.2 g), dimethyl sulfate (0.3 g), and water (8 ml) was refluxed under N_2 stream for 10 hr. The reaction mixture was extracted with ether, the solvent was evaporated and the residue was recrystallized from EtOH to give colorless plates of mp 243° (0.03 g), which showed identity with III by IR and a mixed fusion.

Elliptinone Dimethyl Ether (Di-*o*-methyldiospyroquinone) (V)——Hydrogen peroxide oxidation of III[18] gave the quinone (V), mp 275—276° (decomp.) (from toluene) (lit.[18] 250° (decomp.)), UV λ_{max}^{EtOH} mμ (log ε): 219(4.48), 254(4.48), 360(3.82); IR ν_{max}^{KBr} cm^{-1}: 1655, 1625; NMR (Table I).

Elliptinone (VI), Mamegakinone (VII), and Mamegakinone Dimethyl Ether (VIII)——Fremy's salt solution (20 ml), prepared by the saturation of potassium nitrosodisulfonate in M/6 KH_4PO_4, was added to I (0.2 g) in acetone (200 ml) and the mixture was stirred for 24 hr at 20°. After removal of the solvent, the product was extracted with chloroform and chromatographed on acid-washed silica gel (50 g). Elution with benzene gave a mixture of the products, which was further purified by preparative layer chromatography on acid-treated silica gel using benzene–chloroform–AcOEt as the developer (95:2.5:2.5). The upper zone was collected to afford dark orange needles (VI) (5 mg) of mp 310° (decomp.) (from benzene) (lit.[8] mp>310° (decomp.)), UV $\lambda_{max}^{CHCl_3}$ cm^{-1}: 265 (4.48), 442 (4.09); IR ν_{max}^{KBr} cm^{-1}; 1669, 1643, 1602; NMR (Table I). *Anal.* Calcd. for $C_{22}H_{14}O_6$: C, 70.58; H, 3.77. Found: C, 70.41; H, 3.73.

VI was methylated with silver oxide-methyl iodide in chloroform treated with alkali[27] to give the dimethyl ether, orange needles of mp 273—275°, which showed the identity with V by IR, thin-layer chromatography (TLC), and NMR.

The lower zone of the preparative layer chromatography was collected, extracted, and recrystallized from benzene to give orange needles (VII) (48 mg) of mp 253°, UV $\lambda_{max}^{dioxane}$ mμ (log ε): 253(4.34), 275(4.28), 434(3.96); IR ν_{max}^{KBr} cm^{-1}: 1652, 1625; NMR (Table I). *Anal.* Calcd. for $C_{22}H_{14}O_6$: C, 70.58; H, 3.77. Found: C, 70.84; H, 4.11.

A mixture of VII (38 mg), silver oxide (from 1 g $AgNO_3$), methyl iodide (1 ml), and chloroform (50 ml) was refluxed for 20 hr. After filtration the solvent was evaporated and the residue was recrystallized from EtOH–benzene to give orange needles (VIII) (24 mg) of mp around 250° (decomp.), UV $\lambda_{max}^{CHCl_3}$ mμ (log ε); 253 (4.32), 414(3.70); IR ν_{max}^{KBr} cm^{-1}: 1655. *Anal.* Calcd. for $C_{24}H_{18}O_6$: C, 71.63; H, 4.51. Found: C, 71.72; H, 4.65.

The Binaphthoquinone (IX) from IV——To IV (0.5 g) in acetone (200 ml) was added Fremy's salt solution (30 ml) and the mixture was stirred for 24 hr at a room temperature. After removal of acetone, the reaction mixture was extracted with chloroform and was chromatographed on a column of acid-washed silica gel. Elution with chloroform–benzene–ethyl acetate (6:3:1) and recrystallization from benzene gave orage needles of IX (0.10 g) of mp 269°, UV $\lambda_{max}^{dioxane}$ mμ (log ε): 252 (4.37), 380 (3.79); IR ν_{max}^{KBr} cm^{-1}: 1655. *Anal.* Calcd. for $C_{24}H_{18}O_6$: C, 71.63; H, 4.51. Found: C, 71.78; H, 4.47.

Aerial Oxidation of I——I turns black immediately by exposure to air. After one month the black pigment (0.1 g) was extracted with chloroform and the chloroform soluble part was chromatographed through a column of acid-washed silica gel. Elution with benzene gave an orange band, which was further purified by preparative layer chromatography on acid-treated silica gel using benzene–chloroform–AcOEt (95:2.5:2.5) as the developer. Orange crystals (0.07 g) thus obtained were methylated with methyl iodide–silver oxide in chloroform and the products were separated again by TLC to give two orange crystals, which were respectively identified with elliptinone dimethyl ether (V) and mamegakinone dimethyl ether (VIII) by IR, NMR, and TLC.

Extraction of Dried Fruits of *Diospyros mollis*——The finely milled dried fruits (72 g, excepting seeds) was extracted with chloroform in a Soxhlet apparatus for 25 hr and the extract was chromatographed on a column of silica gel (1 kg). The elution with benzene gave three fractions, the first gave colorless needles (65 mg) of mp 221—223° (from EtOH), IR ν_{max}^{KBr} cm^{-1}: 3420, 1640, 882, and identified with lupeol by IR, NMR, and a mixed fusion. The second fraction gave orange needles (5 mg) of mp around 275° (decomp.), which showed practically identical IR, NMR, and TLC with VI, but the contamination of a little amount of VII was revealed by NMR. The third fraction gave colorless plates (30 mg) of mp 283° (from EtOH) (acetate, mp 310° (from EtOH)), IR ν_{max}^{KBr} cm^{-1}: 3520, 1640, 811, and identified with taraxerol.

Extraction of Dried Bark of *Diospyros mollis*——The finely milled bark (70 g) was extracted in a Soxhlet apparatas with chloroform and the extract was chromatographed on a column of acid-washed silica gel (300 g). Elution with chloroform gave three fractions; the first yielded lupenone as colorless needlles (11 mg) of mp 170—175° (from hexane), IR ν_{max}^{KBr} cm^{-1}: 1700, 885, identified with the authentic sample by IR, NMR TLC and a mixed fusion. The second fraction afforded colorlees needles (93 mg) of mp 221—223° (from EtOH), identified with lupeol. The acetate, mp 223°, was prepared and was also identified. The third

fraction was further separated into two bands by preparative layer chromatography on acid-treated silica gel. The upper zone was collected and recrystallized from benzene to give orange needles (6 mg) of mp 310° (decomp.), showing practically identical IR and NMR with those of VI. The lower zone gave orange needles (5 mg) of mp about 250° (decomp.), showing practically identical IR and NMR with those of VII. Further elution of the column with benzene–EtOAc gave a mixture, which, after treatment with charcoal and recrystallization from EtOH, afforded colorless needles (33 mg) of mp 252° (from EtOH), IR ν_{max}^{KBr} cm^{-1}: 3340, 879. The acetate, mp 223° (from EtOH), was prepared and identified with the sample of betulin acetate.

Extraction of Fresh Roots of *Diospyros mollis*——The fresh roots (450 g), collected at Chantaburi Botanic Garden, Department of Medical Sciences, Thailand, at August 1969, were extracted, after a week without drying, with chloroform and the extract was chromatographed on a silica gel column. The benzene eluate was further purified by preparative TLC and the upper zone gave betulin, colorless needles (0.8 g) of mp 252° (from EtOH), identified by the ordinary methods. The lower band gave pale yellow needles (20 mg) of mp 110—111° (from EtOH); M^+ 246.092 *m/e*; calcd. for $C_{14}H_{14}O_4$, 246.089; UV λ_{max}^{EtOH} mμ (log ε): 260 (4.71), 315 (3.96), 390 (4.20); IR ν_{max}^{KBr} cm^{-1}: 1690, 1600 1265, 1245, 1180; NMR δ (in $CDCl_3$): 3.89 (3H, s), 3.96 (3H, s), 4.00 (3H, s), 6.78 (1H, d, J=9.0 cps), 6.93 (1H, d, J=9.0 cps), 7.28 (1H, d, J=1.5 cps), 8.31 (1H, d, J=1.5 cps), 10.26 (1H, s). Comparisons with the authentic sample[15] of 4,5,8-trimethoxy-2-naphthaldehyde (XIII) by IR, NMR, TLC and a mixed fusion showed the identity.

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