

## Ebenaceae Extractives. Part V.<sup>1</sup> New Diospyrin Derivatives from *Diospyros montana* Roxb.

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The new extractives are the dinaphthofuran 3,5'-*O*-cyclodiospyrin (XVI), 8'-hydroxydiospyrin, 2'- and 3'-chlorodiospyrin, 3'-chloro-2'-hydroxydiospyrin, and the chromenone ester (XIX; R = Et) and acid (XIX; R = H). The last five of these appear to be artefacts formed from diosquinone (XXI), which is also present.

ALTHOUGH *Diospyros montana* Roxb. is a rich source of diospyrin (I; X = Y = Z = H),<sup>2,3</sup> only one other quinone, namely 2',3'-dihydrodiospyrin,<sup>4</sup> has been obtained from it. We have now re-examined the wood

<sup>1</sup> Part IV, O. C. Musgrave and D. Skoyles, *J.C.S. Perkin I*, 1974, 1128.

<sup>2</sup> R. S. Kapil and M. M. Dhar, *J. Sci. Ind. Res., India*, 1961, 20B, 498.

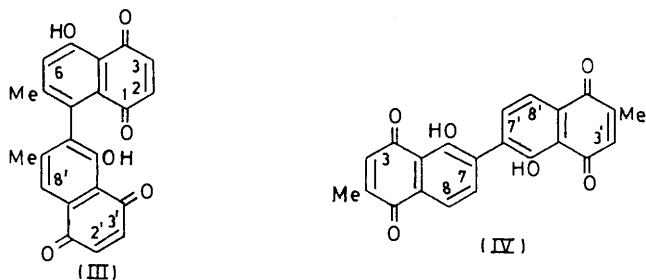
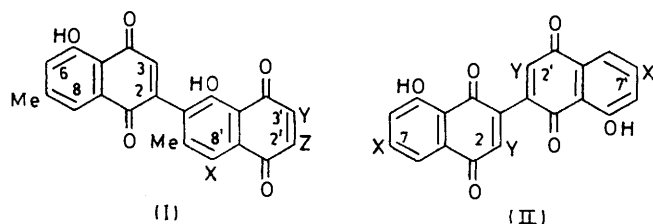
and the bark of this species and have isolated small amounts of several new derivatives of diospyrin, the mass spectra of which greatly facilitated the recognition of their main structural features. As only limited

<sup>3</sup> G. S. Sidhu and M. Pardhasaradhi, *Tetrahedron Letters*, 1967, 1313.

<sup>4</sup> M. Pardhasaradhi and G. S. Sidhu, *Tetrahedron Letters*, 1972, 4201.

information is available<sup>4-7</sup> concerning the routes by which natural bisnaphthoquinones break down in the mass spectrometer we start by discussing the mass spectra of some representative compounds.

Mamegakinone (II; X = Me, Y = H)<sup>8</sup> and 3,3'-biplumbagin (II; X = H, Y = Me),<sup>5</sup> diospyrin (I; X = Y = Z = H),<sup>2,3</sup> and isidiospyrin (III)<sup>6</sup> and elliptinone (IV)<sup>6</sup> exemplify the three ways in which the naphthoquinone units can be linked together, namely quinone-to-quinone, arene-to-quinone, and arene-to-arene. Their molecular ions, *m/e* 374, appear to undergo fragmentation mainly *via* (a) cyclisation reactions, (b) repeated extrusion of carbon monoxide, and (c) scission of the quinonoid rings, the proportions of these processes depending on the structures of the parent compounds.<sup>9</sup> The cyclisations usually involve the substituents *ortho* to the internuclear link and result in the expulsion of a hydrogen atom, or a methyl or



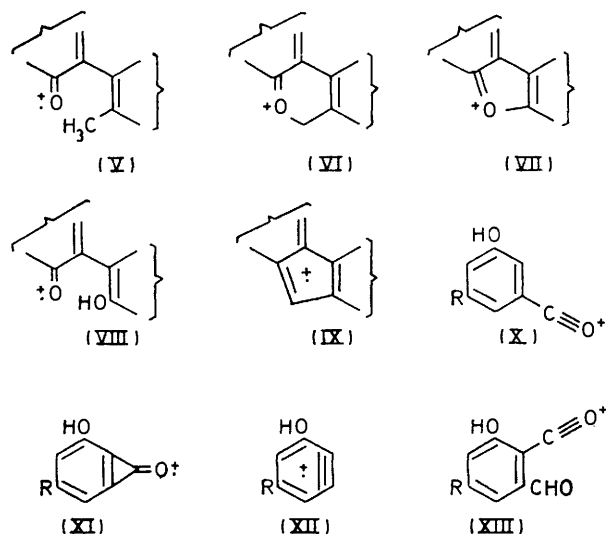
hydroxyl radical, or a water molecule, to give the ions *m/e* 373, 359, 357, and 356. For mamegakinone, 3,3'-biplumbagin, and diospyrin, these reactions can be represented by the partial structures (V) → (VI), (V) → (VII), (VIII) → (VII), and (V) → (IX), respectively. In the case of isidiospyrin the cyclisations presumably involve the carbonyl group at C-1, while elliptinone can undergo loss of hydroxyl or water by related reactions between the two hydroxy groups.<sup>6</sup> The ions produced by the scission of the quinone rings provide an indication of the mode of linkage of the two naphthoquinone systems. Both mamegakinone and diospyrin undergo cleavage of an internal quinone ring to form the expected<sup>10</sup> ions *m/e* 135 (X; R = Me), 134 (XI; R = H), and 106 (XII; R = Me). In addition diospyrin forms the ion *m/e* 163 (XIII; R = Me), presumably by the mode of cleavage shown in the part

<sup>5</sup> G. S. Sidhu and A. V. B. Sankaram, *Tetrahedron Letters*, 1971, 2385.

<sup>6</sup> A. L. Fallas and R. H. Thomson, *J. Chem. Soc. (C)*, 1968, 2279.

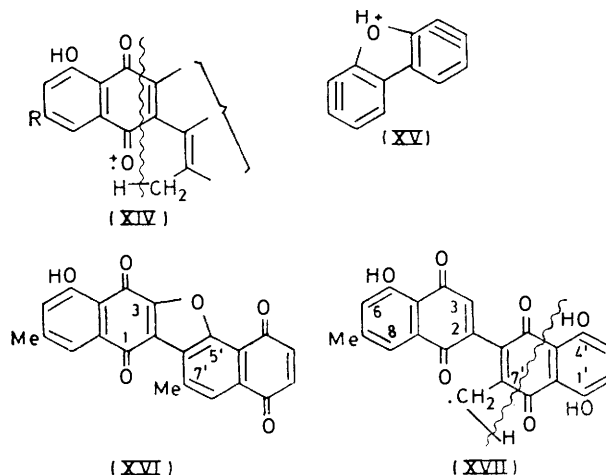
<sup>7</sup> V. Krishnamoorthy and R. H. Thomson, *Phytochemistry*, 1969, 8, 1591.

structure (XIV; R = Me). This last type of fragmentation is also shown by 3,3'-biplumbagin which, like



diospyrin, possesses a methyl group *ortho* to the internuclear linkage. In this case the ions obtained are *m/e* 149 (XIII; R = H) [from (XIV; R = H)], 121 (X; R = H), 120 (XI; R = H), and 92 (XII; R = H). Whereas isidiospyrin undergoes little cleavage of its terminal quinone rings, elliptinone shows abundant ions at *m/e* 278 and 165 (XV). These result, respectively, from the loss of one of the quinone rings of the molecular ion, and of both quinone rings of the ion (*M* - OH)<sup>+</sup>.

The light petroleum and chloroform extracts of the wood of Indian *D. montana* contained diospyrin and an orange quinone, C<sub>22</sub>H<sub>12</sub>O<sub>8</sub>, which we have shown to be the cyclodiospyrin (XVI). Its i.r. absorption bands in



the carbonyl region resemble closely those of 1,4-naphthoquinone (at 1675 cm<sup>-1</sup>) and 7-methyljuglone (at 1669 and 1640 cm<sup>-1</sup>) suggesting that only one of

<sup>8</sup> K. Yoshihira, M. Tezuka, and S. Natori, *Chem. and Pharm. Bull. (Japan)*, 1971, 19, 2308.

<sup>9</sup> D. Skoyles, Ph.D. Thesis, University of Aberdeen, 1971.

<sup>10</sup> J. H. Bowie, D. W. Cameron, and D. H. Williams, *J. Amer. Chem. Soc.*, 1965, 87, 5094.

its naphthoquinone units carries a hydroxy group, and it forms a leucopenta-acetate indicating the ethereal nature of one of the oxygen atoms. In the mass spectrometer it behaves as a 2,3-unsubstituted naphthoquinone, undergoing loss of two molecules of carbon monoxide and one of acetylene; the absence of appreciable further fragmentation indicates that the ion  $m/e$  290 so formed has a fused polycyclic structure. The mass spectrum of the leucopenta-acetate shows the loss from the molecular ion either of five molecules of keten or of four molecules of keten and one of acetone, the last-named presumably originating from a cyclisation reaction between the acetoxy group at C-1 and the methyl group at C-7'. Neither sequence shows the loss of a molecule of water which is typical of ions containing two hydroxy groups in positions *ortho* to the inter-nuclear linkage, and it follows that in the parent compound the oxygen atom at C-5' is not part of a hydroxy group. Accordingly if the compound is related to diospyrin it must be the dinaphthofuran (XVI), *i.e.* 3,5'-*O*-cyclodiospyrin. We confirmed this by treating diospyrin with potassium hydrogen carbonate in the presence of air, which yielded a small amount (2%) of the cyclodiospyrin.

Extraction of the bark of the Indian *D. montana* afforded 7-methyljuglone, mamegakinone, biramentaceone, diospyrin, isodiospyrin, 3,5'-*O*-cyclodiospyrin, and four other coloured compounds, quinones A—D. Quinone A,  $C_{22}H_{14}O_7$ , shows i.r. and u.v.-visible absorption which resemble those<sup>11</sup> of 7-methyljuglone and 2-methylnaphthazarin, suggesting that, like 8'-hydroxyisodiospyrin,<sup>12</sup> it contains two such units. The mass spectrum of quinone A is consistent with its being 8'-hydroxydiospyrin, (I; X = OH, Y = Z = H)  $\rightleftharpoons$  (XVII). As with diospyrin, cyclisation of the molecular ion leads to the expulsion of a hydrogen atom, a methyl and a hydroxyl radical, and a water molecule. Cleavage as shown in (XIV) of the internal quinone ring of the tautomer (I; X = OH, Y = Z = H) leads to the formation of the ions  $m/e$  163, 135, 134, and 106; the other tautomer can undergo cleavage as shown in structure (XVII) to give the related ions,  $m/e$  137 and 108. The n.m.r. spectrum of quinone A shows that in chloroform solution the predominant tautomeric form is (XVII), in which the quinone ring of the methylnaphthazarin unit is fully substituted. Thus the signal at  $\delta$  7.25 shown by the protons at C-2' and C-3' is typical of the aryl proton signals of a 2,3-disubstituted naphthazarin,<sup>13</sup> and is different from the quinonoid proton signal at  $\delta$  6.94 shown by the corresponding protons at C-2' and C-3' in diospyrin. We confirmed that quinone A is 8'-hydroxydiospyrin by making it from diospyrin by using hydrogen peroxide in acetic acid.<sup>12</sup> Since our

preliminary note,<sup>14</sup> 8'-hydroxydiospyrin has also been isolated from *Euclea lanceolata*.<sup>15</sup>

The molecular formula of quinone B,  $C_{22}H_{13}ClO_7$ , is that of a chlorohydroxydiospyrin and the compound undergoes fragmentation in the mass spectrometer in a similar manner to diospyrin. Except for the absence of signals for the quinone protons at C-2' and C-3' its n.m.r. spectrum resembles that of diospyrin and accordingly the extra substituents must be at C-2' and C-3'. The shift of its C-8' proton establishes that the compound is 3'-chloro-2'-hydroxydiospyrin (I; X = H, Y = Cl, Z = OH). The introduction of 2-hydroxy- and 3-chloro-substituents into 7-methyljuglone shifts its C-8 proton signal by +0.07 and +0.01 p.p.m., respectively.<sup>16</sup> The addition of these shift contributions to the shift ( $\delta$  7.53) of the C-8' proton of diospyrin gives a value ( $\delta$  7.61) in good agreement with that ( $\delta$  7.57) observed for quinone B. The corresponding shift calculated for the 2'-chloro-3'-hydroxy-isomer is  $\delta$  7.68.

Quinone C,  $C_{24}H_{18}O_7$ , contains two carbon atoms more than does diospyrin and, because it forms a leucotriacetate, must possess only one hydroxy group and one quinone system. Its i.r. spectrum shows the carbonyl band of an aromatic ester in addition to the expected quinone carbonyl absorption. Much of its n.m.r. spectrum bears a marked resemblance to that of diospyrin, and the two compounds appear to have the partial structure (XVIII) in common. The signal from the remaining quinonoid protons of diospyrin is replaced in quinone C by an AB quartet (centred at  $\delta$  6.30 and 7.66,  $J$  6 Hz) similar to that (at  $\delta$  6.34 and 7.88,  $J$  6.05 Hz) produced by the olefinic protons of chromen-4-one.<sup>17</sup> In addition quinone C gives signals characteristic of the ethyl ester of an aromatic acid. The incorporation of a chromenone system and an ethoxycarbonyl group into the partial structure (XVIII) leads to the complete structure (XIX; R = Et) and the fragmentation of quinone C in the mass spectrometer is fully compatible with this. The molecular ion initially loses an ethoxyl radical or a molecule of ethylene and a molecule of carbon dioxide; the expected cyclisation and fragmentation reactions follow. The spectra of the leucotriacetate are consistent with its being derived from structure (XIX; R = Et). Thus the i.r. spectrum shows carbonyl bands typical of an aromatic ester, an aryl acetate, and chromen-4-one.<sup>18</sup> Its mass spectrum shows the loss of three molecules of keten and of an ethoxyl radical from the molecular ion. Although cyclisation occurs between the acetate group at C-1' and the methyl group at C-7, with the expulsion of a molecule of acetone, no loss of water appears to take place from the ion  $(M - 3CH_2CO)^+$ , confirming that only one acetoxy group occupies a position *ortho* to the inter-nuclear linkage.

<sup>15</sup> M. A. Ferreira, M. H. Lopes, M. A. Cruz Costa, and A. Correia Alves, *Phytochemistry*, 1974, **13**, 499.

<sup>16</sup> T. J. Lillie and O. C. Musgrave, *J.C.S. Perkin I*, in the press.  
<sup>17</sup> C. T. Mathis and J. H. Goldstein, *Spectrochim. Acta*, 1964, **20**, 871.

<sup>18</sup> J. H. Looker and W. W. Hanneman, *J. Org. Chem.*, 1962, **27**, 381.

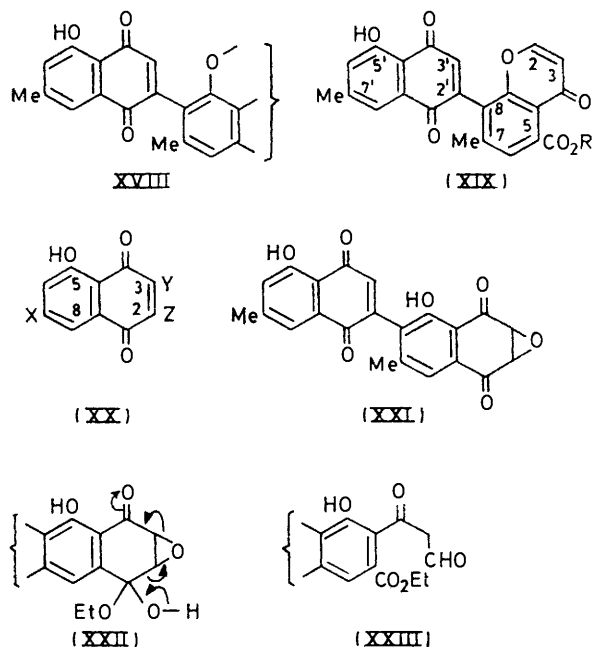
<sup>11</sup> R. H. Thomson, 'Naturally Occurring Quinones,' Academic Press, London, 2nd edn., 1971.

<sup>12</sup> M. Tezuka, C. Takahashi, M. Kuroyanagi, M. Satake, K. Yoshihira, and S. Natori, *Phytochemistry*, 1973, **12**, 175.

<sup>13</sup> R. E. Moore and P. J. Scheuer, *J. Org. Chem.*, 1966, **31**, 3272.

<sup>14</sup> D. Skoyles and O. C. Musgrave, *Phytochemistry*, 1972, **11**, 874.

The spectra of quinone D,  $C_{22}H_{14}O_7$ , establish that it is the chromenone acid (XIX; R = H). Thus its u.v.-visible light absorption resembles that of quinone C and, apart from the absence of ethyl proton signals from quinone D, the n.m.r. spectra of the two compounds are almost identical. Its i.r. spectrum shows, in addition to quinone and chromenone carbonyl absorption, a carbonyl band typical of an aromatic carboxylic acid. Like other aromatic acids containing *ortho*-acyl groups, such as anthraquinone-1-carboxylic acid and 2-hydroxy-6-methoxy-8-methyl-9-oxoxanthen-1-carboxylic acid,<sup>19</sup> quinone D undergoes decarboxylation readily in the mass



spectrometer giving the ion  $(M - CO_2)^+$ ,  $m/e$  346, as the base peak. The subsequent fragmentation of this ion closely resembles the behaviour of the ion  $(M - C_2H_4 - CO_2)^+$ ,  $m/e$  346, obtained from quinone C.

We had not expected to isolate a chlorine-containing quinone from *D. montana* and therefore examined another sample of the same species, from Thailand. The light petroleum extract afforded only diospyrin, but the chloroform extract gave diospyrin, 8'-hydroxydiospyrin, and two isomeric chloro-compounds,  $C_{22}H_{13}ClO_6$ , which we formulate as 2'- and 3'-chlorodiospyrin (I; X = Y = H, Z = Cl) and (I; X = Z = H, Y = Cl). The carbonyl bands in their i.r. spectra, and their u.v. and visible light absorption resemble those of diospyrin, and in the mass spectrometer the three compounds exhibit the same modes of fragmentation. The chlorodiospyrins show n.m.r. spectra which differ significantly from that of diospyrin itself only in the shifts of the signals associated with the protons at C-2', C-3', and C-8', and the hydroxy proton at C-5'. Each of the chloro-compounds shows a one-proton singlet at  $\delta$  7.20 in place of the two-proton singlet at  $\delta$  6.94 observed for

the C-2' and C-3' protons of diospyrin. The downfield shift (+0.26 p.p.m.) of the former signal confirms that the chlorine atom is located at C-2' or C-3'. The C-5' hydroxy proton signals of the chlorodiospyrins (at  $\delta$  12.00 and 11.88) show shifts of -0.11 and -0.23 p.p.m. in comparison with the corresponding signal ( $\delta$  12.11) of diospyrin. Now the introduction of a substituent into juglone (XX; X = Y = Z = H) or a juglone derivative results in a shift of the proton signal of the C-5 hydroxy group, the magnitude of which depends on the nature and the position of the substituent and is essentially independent of the structure of the original juglone.<sup>16</sup> The conversion of 7-methyljuglone (XX; X = Me, Y = Z = H) into its 2-chloro- and 3-chloro-derivatives is accompanied by shifts in the C-5 hydroxy proton signals from  $\delta$  11.82 to 11.71 (*i.e.* -0.11 p.p.m.) and from  $\delta$  11.82 to 11.59 (*i.e.* -0.23 p.p.m.), respectively. These decrements are in excellent agreement with those observed for the two chlorodiospyrins and it follows that the isomer having the hydroxy proton signal at  $\delta$  12.00 is 2'-chlorodiospyrin (I; X = Y = H, Z = Cl). The shifts of the C-8' proton signals of the chlorodiospyrins relative to the corresponding signal of diospyrin support this assignment. Here the 2'-chloro- and 3'-chloro-substituents produce shifts of +0.11 and +0.03 p.p.m., respectively; the corresponding shifts for the C-8 proton signals of 2-chloro- and 3-chloro-7-methyljuglone are +0.10 and +0.01 p.p.m. Finally, we synthesised authentic 3'-chlorodiospyrin (I; X = Z = H, Y = Cl) by adding chlorine to diospyrin and dehydrochlorinating the product by boiling it with ethanol, a preparation analogous to that of 3-chlorojuglone from juglone.<sup>20</sup>

The presence of the three closely related chloro-compounds in the *D. montana* extracts suggested that these were artefacts produced from a common precursor. During the isolation procedure the crude mixtures had been in contact with both chloroform and any residual hydrochloric acid present in the 'acid-washed' silica gel and either of these could have supplied the necessary chloride ion. As expected, diospyrin itself did not form chlorinated products under these conditions. The corresponding (-)-epoxide, diosquinone (XXI),<sup>21</sup> which behaves chromatographically like diospyrin, appeared to be a more likely precursor. Unlike pure diospyrin the crude diospyrin fractions from *D. montana* proved to be weakly optically active and from them we eventually isolated some diosquinone. The normal acid-catalysed cleavage of the oxiran ring of diosquinone, in the presence of chloride ion, can clearly lead to the formation of the three chlorodiospyrins. An alternative sequence of reactions involving the oxiran ring accounts for the formation of the chromenone derivatives (XIX; R = Et) and (XIX; R = H). We suggest that, during the extraction of the *D. montana* bark, ethanol, which is present in the chloroform as stabiliser, reacts with diosquinone to give the adduct (XXII) which

<sup>20</sup> R. H. Thomson, *J. Org. Chem.*, 1948, **13**, 377.

<sup>19</sup> Boon Wai Au-Yeung, Tze-Lock Chan, and Shang Wai Tam, *Austral. J. Chem.*, 1975, **28**, 657.

<sup>21</sup> T. J. Lillie, O. C. Musgrave, and R. H. Thomson, *J.C.S. Chem. Comm.*, 1973, 463.

isomerises as shown forming the ethyl ester (XXIII). This then cyclises giving the chromenone ester. A similar reaction between diosquinone and water would give the corresponding carboxylic acid. It seems likely that the only other chloronaphthoquinone to have been obtained from a higher plant, namely 3-chloroplumbagin (XX; X = H, Y = Cl, Z = Me),<sup>5,22</sup> is also an artefact and is formed by reaction of plumbagin 2,3-epoxide with chloroform.

The i.r. absorption (measured in potassium bromide) of our pure diospyrin was significantly different to that of two authentic samples from Indian laboratories. We attribute this to differences in crystal structure because after dissolution in chloroform and evaporation of the solvent the Indian samples gave i.r. spectra identical with that of our specimen. The substance 'euclein' recently isolated<sup>23</sup> from *Euclea pseudebenus* is indistinguishable from diospyrin in most of its properties but its i.r. absorption in the solid state is different from that of the authentic Indian specimens. The spectrum is however identical with that of our sample and 'euclein' is therefore simply one of the crystalline forms of diospyrin.<sup>24</sup>

In addition to the expected<sup>2</sup> triterpenoids lupeol, betulin, and betulinic acid the extract from the *D. montana* bark also afforded a mixture of the related compounds allobetulin and oxyallobetulin which, after acetylation, we separated by t.l.c. Oxyallobetulin occurs in *D. lotus* L.<sup>8</sup> but there is no previous report of the presence of allobetulin in *Diospyros* spp.

#### EXPERIMENTAL

General instructions are given in Part IV.<sup>1</sup> For t.l.c. the silica gel was treated before use with aqueous 3% oxalic acid; for column chromatography it was washed with 2M-hydrochloric acid. 'Light petroleum' refers to the fraction b.p. 60–80 °C. C.d. data were obtained with a Jouan Dichrographe, model 2.

*Extraction of Wood of Indian Diospyros montana Roxb.*—The finely ground heartwood and sapwood (1 kg) was extracted (Soxhlet) successively with light petroleum and with chloroform for 24 h. Evaporation of the combined extracts gave a brown solid (4.5 g) which was triturated with dichloromethane. The insoluble residue sublimed at 295 °C and 0.5 mmHg and was then crystallised from ethanol to give betulinic acid (630 mg). The soluble material was separated by t.l.c. into four colourless fractions which after crystallisation from ethanol gave lupeol (190 mg),  $\beta$ -sitosterol (153 mg), betulin (300 mg), and betulinic acid (315 mg), respectively, and two orange fractions. After further t.l.c. [light petroleum–dichloromethane (4 : 1)] one of the latter afforded crude diospyrin (208 mg).

*3,5'-O-Cyclodiospyrin (7-Hydroxy-9,12-dimethyldinaphtho-[1,2-b : 2',3'-d]furan-1,4 : 6,11-diquinone)* (XVI).—(a) The other orange fraction, after further t.l.c. crystallised from light petroleum (b.p. 80–100 °C), giving the *cyclodiospyrin* as orange needles (9 mg), m.p. 269–271° (Found: *M*, 372.063 2.  $C_{22}H_{12}O_6$  requires *M*, 372.063 4),  $\nu_{\max}$  1 675

<sup>22</sup> G. Bendz and G. Lindberg, *Acta Chem. Scand.*, 1968, **22**, 2722.

<sup>23</sup> M. A. Ferreira, M. A. Cruz Costa, A. Correia Alves, and M. H. Lopes, *Phytochemistry*, 1973, **12**, 433.

and 1 664 (quinone C=O), 1 642 (hydrogen-bonded quinone C=O), and 1 600  $cm^{-1}$  (quinone C=C),  $\lambda_{\max}$  (CHCl<sub>3</sub>) 271 (log  $\epsilon$  4.61), 322 (3.92), and 448 nm (3.92),  $\lambda_{\text{inf}}$ . 265 (log  $\epsilon$  4.58), 314 (3.90), 370 (3.86), and 405 nm (3.87), *m/e* 374 [16%, (*M* + 2 H)<sup>+</sup>], 372 [100%, (*M*)<sup>+</sup>], 290 [3%, (*M* – 2CO – C<sub>2</sub>H<sub>2</sub>)<sup>+</sup>], 186 [2%, (*M*)<sup>2+</sup>], and 145 [2%, (*M* – 2CO – C<sub>2</sub>H<sub>2</sub>)<sup>2+</sup>].

(b) A mixture of diospyrin (50 mg), potassium hydrogen carbonate (5 g), and acetone (50 ml) was stirred for 15 min under nitrogen, then for 15 min in air, and acidified. Extraction with chloroform and separation of the resulting mixture by t.l.c. gave the cyclodiospyrin (2 mg), m.p. 270–271°.

*3,5'-O-Cyclodiospyrin Leucopenta-acetate.*—A mixture of the cyclodiospyrin (3 mg), acetic anhydride (1 ml), zinc dust (50 mg), and anhydrous sodium acetate (50 mg) was boiled under reflux for 30 min, and poured into water. Extraction with chloroform and crystallisation of the product from ethanol afforded the *leucopenta-acetate*, m.p. 251–253° (Found: *M*, 586.146 4.  $C_{32}H_{26}O_{11}$  requires *M*, 586.147 5),  $\nu_{\max}$  1 770  $cm^{-1}$  (aryl acetate C=O),  $\lambda_{\max}$  277 (log  $\epsilon$  4.52) and 384 nm (3.59),  $\lambda_{\text{inf}}$ . 269 (log  $\epsilon$  4.44), 300 (3.93), 308 (3.83), 321 (3.74), 338 (3.72), and 362 nm (3.58).

*Extraction of Bark of Indian Diospyros montana Roxb.*—The finely ground bark (950 g) was extracted as described above. The light petroleum extract was kept for 24 h, and filtered to remove betulinic acid (4.5 g). Evaporation of the combined light petroleum and chloroform extracts gave a solid (23 g) which was separated by column chromatography [elution successively with (i) light petroleum, (ii) light petroleum–benzene, (iii) benzene, and (iv) chloroform] into the corresponding fractions (i)–(iv). Fraction (i) was unidentified aliphatic material. Fraction (iii) was crystallised from chloroform and then from light petroleum–dichloromethane to give crude diospyrin (2.8 g); concentration of the mother liquors afforded lupeol (3.2 g).

*8'-Hydroxydiospyrin* (XVII). (a) Fraction (ii) was separated by t.l.c. [light petroleum–dichloromethane (1 : 1)] into 7-methyljuglone (9 mg), m.p. 125–126° [lit.,<sup>25</sup> 125.5–126.5°], mamegakinone (2 mg), m.p. 253–254° [lit.,<sup>8</sup> 256° (decomp.)], and a red solid. After further t.l.c. [tetrachloromethane–benzene (9 : 1)] the last-named gave biramentaceone (3 mg), m.p. 265–272° (decomp.) [lit.,<sup>7</sup> 235°; lit.,<sup>26</sup> 272° (decomp.)] and *8'-hydroxydiospyrin*, which crystallised from light petroleum (b.p. 80–100 °C) as red needles (1 mg), m.p. 266–268° (Found: *M*, 390.073 5.  $C_{22}H_{14}O_7$  requires *M*, 390.073 9),  $\nu_{\max}$  1 667 (quinone C=O), 1 642 and 1 621 (hydrogen-bonded quinone C=O), and 1 605  $cm^{-1}$  (quinone C=C),  $\lambda_{\max}$  255 (log  $\epsilon$  4.24), 483 (3.93), and 514 nm (3.91),  $\lambda_{\text{inf}}$ . 277 (log  $\epsilon$  4.17), 462 (3.91), and 548 nm (3.70),  $\delta$  2.16 (3 H, s, 7'-CH<sub>3</sub>), 2.46 (3 H, s, 7-CH<sub>3</sub>), 6.85 (1 H, s, H-3), 7.13br (1 H, s, H-6), 7.25 (2 H, s, H-2' and -3'), 7.49br (1 H, s, H-8), 11.80 (1 H, s, 5-OH), 12.28 (1 H, s, 4'-OH), and 12.57 (1 H, s, 1'-OH), *m/e* 390 [100%, (*M*)<sup>+</sup>], 389 [10%, (*M* – H)<sup>+</sup>], 375 [16%, (*M* – CH<sub>3</sub>)<sup>+</sup>], 373 [23%, (*M* – OH)<sup>+</sup>], 372 [11%, (*M* – H<sub>2</sub>O)<sup>+</sup>], 163 (8%), 137 (6%), 135 (12%), 134 (8%), 108 (9%), and 106 (13%).

(b) A mixture of diospyrin (200 mg), aqueous hydrogen peroxide (30%, 1.2 ml), and glacial acetic acid (8 ml) was boiled under reflux for 25 min. Water (8 ml) was added

<sup>24</sup> Cf. M. A. Ferreira, M. A. Cruz Costa, A. Correia Alves, and M. H. Lopes, *Phytochemistry*, 1974, **13**, 1587.

<sup>25</sup> R. G. Cooke and H. Dowd, *Austral. J. Chem.*, 1953, **6**, 53.

<sup>26</sup> B. C. Maiti, Ph.D. Thesis, Aberdeen, 1975.

and the mixture was boiled for 10 min and poured into water (100 ml). Extraction with chloroform gave a red solid (175 mg) from which 8'-hydroxydiospyrin (1 mg) was obtained by t.l.c. (dichloromethane).

*Compounds from fraction (iv).* A solution of fraction (iv) in hot light petroleum deposited betulinic acid (10.1 g) on being cooled. The soluble material was separated by repeated t.l.c. (dichloromethane and chloroform) into crude diospyrin (123 mg), 3,5'-O-cyclodiospyrin (4 mg), isodiospyrin (4 mg), m.p. 227—228° (lit.,<sup>6</sup> 226—228°), an inseparable mixture of allobetulin and oxyallobetulin (283 mg), betulin (185 mg), two red solids, and an orange solid.

*Allobetulin acetate and oxyallobetulin acetate.* Treatment of the mixture of allobetulin and oxyallobetulin with acetic anhydride and pyridine and separation of the products by t.l.c. (chloroform) gave allobetulin acetate as plates (from ethanol), m.p. 284—286° (lit.,<sup>27</sup> 288—290°) (Found: *M*, 484.392 4.  $C_{32}H_{52}O_3$  requires *M*, 484.391 6),  $\delta$  0.81, 0.85, 0.85, 0.87, 0.93, 0.93, 0.98 (each 3 H, s,  $CH_3C\equiv$ ), 1.10—1.90 (24 H, m,  $-CH_2-$  and  $-CH=$ ), 2.05 (3 H, s,  $CH_3CO_2R$ ), 3.45 and 3.78 (2 H, ABq, *J* 7.5 Hz,  $-CH_2OCH=$ ), 3.55 (1 H, s,  $=CHOCH_2-$ ), and 4.50 (1 H, m, H-3 $\alpha$ ), and oxyallobetulin acetate as plates (from ethanol), m.p. >340° (lit.,<sup>8</sup> >310°).

*3'-Chloro-2'-hydroxydiospyrin (I; X=H, Y=Cl, Z=OH).* The first red solid from fraction (iv) separated from light petroleum to give the *chlorohydroxydiospyrin* as red crystals (4 mg), m.p. 260—263° (decomp.) (Found: *M*, 424.035 1.  $C_{22}H_{13}^{35}ClO_7$  requires *M*, 424.035 0),  $\nu_{max}$ . 3 210 (hydrogen-bonded OH), 1 663 (quinone C=O), 1 643 and 1 623  $cm^{-1}$  (hydrogen-bonded quinone C=O),  $\lambda_{max}$ . 254 (log  $\epsilon$  4.10) and 438 nm (3.78),  $\lambda_{inf}$ . 234 (log  $\epsilon$  4.13), 274 (4.01), 296 (3.90), and 556 nm (2.97),  $\delta$  [ $CDCl_3-(CD_3)_2SO$ ] 2.31 (3 H, s, 7'- $CH_3$ ), 2.46 (3 H, s, 7- $CH_3$ ), 6.97 (1 H, s, H-3), 7.14br (1 H, s, H-6), 7.44br (1 H, s, H-8), and 7.57 (1 H, s, H-8'), *m/e* 424 [100%, (*M*)<sup>+</sup>], 423 [6%, (*M* - H)<sup>+</sup>], 409 [17%, (*M* -  $CH_3$ )<sup>+</sup>], 407 [8%, (*M* - OH)<sup>+</sup>], 406 [9%, (*M* -  $H_2O$ )<sup>+</sup>], 163 (11%), 135 (16%), 134 (11%), and 106 (21%).

*Ethyl 8-(5-hydroxy-7-methyl-1,4-naphthoquinon-2-yl)-7-methyl-4-oxochromen-5-carboxylate (XIX; R = Et).* The orange solid from fraction (iv) crystallised from tetrachloromethane to give the *chromenone ester* as orange needles (9 mg), m.p. 234—236° (Found: *M*, 418.104 5.  $C_{24}H_{18}O_7$  requires *M*, 418.105 2),  $\nu_{max}$ . 1 730 (aromatic ester C=O), 1 658 and 1 642 (quinone and chromone C=O), and 1 598  $cm^{-1}$  (C=C),  $\lambda_{max}$ . 296 (log  $\epsilon$  3.95) and 440 nm (3.66),  $\lambda_{inf}$ . 248 (log  $\epsilon$  4.28) and 304 nm (3.93),  $\delta$  1.43 (3 H, t, *J* 7 Hz,  $CH_3CH_2O_2CAR$ ), 2.34 (3 H, s, 7- $CH_3$ ), 2.47 (3 H, s, 7'- $CH_3$ ), 4.51 (2 H, q, *J* 7 Hz,  $CH_3CH_2O_2CAR$ ), 6.30 (1 H, d, *J* 6 Hz,  $-COCH=CHO-$ ), 6.91 (1 H, s, H-3'), 7.16br (1 H, s, H-6'), 7.29 (1 H, s, H-6), 7.51br (1 H, s, H-8'), 7.66 (1 H, d, *J* 6 Hz,  $-COCH=CHO-$ ), and 11.86 (1 H, s, 5'-OH),  $\delta$  [ $CDCl_3-(CD_3)_2SO$ ] (assignments as before), 1.40 (3 H, t), 2.37 (3 H, s), 2.49 (3 H, s), 4.45 (2 H, q), 6.29 (1 H, d), 7.01 (1 H, s), 7.17br (1 H, s), 7.31 (1 H, s), 7.50br (1 H, s), and 7.84 (1 H, d), *m/e* 418 [100%, (*M*)<sup>+</sup>], 373 [65%, (*M* -  $C_2H_5O$ )<sup>+</sup>], 355 (8%, 373 -  $H_2O$ ), 346 [39%, (*M* -  $C_2H_4$  -  $CO_2$ )<sup>+</sup>], 331 (13%, 346 -  $CH_3$ ), 329 (10%, 346 - HO), 328 (8%, 346 -  $H_2O$ ), 163 (7%), 135 (11%), 134 (5%), and 106 (10%).

Reductive acetylation of the chromenone, as described earlier for cyclodiospyrin, and purification of the product by t.l.c. (chloroform) gave *ethyl 7-methyl-4-oxo-8-(1,4,5-triacetoxy-7-methyl-2-naphthyl)chromen-5-carboxylate* as a glass (Found: *M*, 546.153 7.  $C_{30}H_{26}O_{10}$  requires *M*, 546.152 6),

$\nu_{max}$ . ( $CHCl_3$ ), 1 768 (aryl acetate C=O), 1 724 (aromatic ester C=O), and 1 655  $cm^{-1}$  (chromone C=O),  $\lambda_{max}$ . 234 (log  $\epsilon$  4.48) and 301 nm (3.84),  $\lambda_{inf}$ . 266 (log  $\epsilon$  3.76) and 331 nm (3.12).

*8-(5-Hydroxy-7-methyl-1,4-naphthoquinon-2-yl)-7-methyl-4-oxochromen-5-carboxylic acid (XIX; R = H).* The second red solid from fraction (iv) crystallised from light petroleum (b.p. 80—100 °C) to give the *chromenone acid* as red crystals (6 mg), m.p. 262—264° (Found: *M*, 390; (*M* -  $CO_2$ ), 346.083 9.  $C_{22}H_{14}O_7$  requires *M*, 390.  $C_{21}H_{14}O_5$  requires *M*, 346.084 1],  $\nu_{max}$ . 1 703 (carboxy C=O), 1 668, 1 645, and 1 626  $cm^{-1}$  (quinone and chromone C=O),  $\lambda_{max}$ . 306 (log  $\epsilon$  3.74), and 444 nm (3.50),  $\lambda_{inf}$ . 250 nm (log  $\epsilon$  4.14),  $\delta$  [ $CDCl_3-(CD_3)_2SO$ ] 2.36 (3 H, s, 7- $CH_3$ ), 2.47 (3 H, s, 7'- $CH_3$ ), 6.30 (1 H, d, *J* 6 Hz,  $-COCH=CHO-$ ), 7.01 (1 H, s, H-3'), 7.16br (1 H, s, H-6'), 7.38 (1 H, s, H-6), 7.47br (1 H, s, H-8'), and 7.86 (1 H, d, *J* 6 Hz,  $-COCH=CHO-$ ), *m/e* 390 [2%, (*M*)<sup>+</sup>], 346 [100%, (*M* -  $CO_2$ )<sup>+</sup>], 345 [14%, (*M* -  $CO_2$  - H)<sup>+</sup>], 331 (25%, 346 -  $CH_3$ ), 329 (20%, 346 - HO), 328 (7%, 346 -  $H_2O$ ), 163 (7%), 135 (16%), 134 (10%), and 106 (19%).

*Anthraquinone-1-carboxylic acid.* This showed *m/e* 252 [0.8%, (*M*)<sup>+</sup>], 208 [100%, (*M* -  $CO_2$ )<sup>+</sup>], 207 [7%, (*M* -  $CO_2H$ )<sup>+</sup>], 180 (79%, 208 - CO), 152 (40%, 180 - CO), 151 (25%, 152 - H), and 150 (11%, 151 - H).

*Extraction of Wood and Bark of Thai Diospyros montana Roxb.*—The wood (2.8 kg) and bark (1.65 kg) were extracted as described earlier. The combined light petroleum extracts and the combined chloroform extracts were evaporated and the residues (4.2 and 7.2 g, respectively) were subjected to column chromatography (light petroleum—benzene). The former gave crude diospyrin (460 mg) as the only coloured product. The latter gave crude diospyrin (3.56 g) and a red solid which, after t.l.c. (light petroleum—dichloromethane) afforded 8'-hydroxydiospyrin (1 mg) and a mixture of chlorodiospyrins.

*2'- and 3'-Chlorodiospyrin (I; X = H, Y and Z = H and Cl).* (a) Crystallisation of the mixture of chlorodiospyrins from light petroleum—dichloromethane gave the less-soluble component, *3'-chlorodiospyrin*, as orange-red needles (27 mg), m.p. 266—268° (Found: *M*, 408.040 1.  $C_{22}H_{13}^{35}ClO_6$  requires *M*, 408.040 1),  $\nu_{max}$ . 1 668, 1 647, 1 613 (quinone C=O), and 1 598  $cm^{-1}$  (quinone C=C),  $\lambda_{max}$ . 255 (log  $\epsilon$  4.27) and 441 nm (3.91),  $\lambda_{inf}$ . 276 nm (log  $\epsilon$  4.14),  $\delta$  2.32 (3 H, s, 7'- $CH_3$ ), 2.46 (3 H, s, 7- $CH_3$ ), 6.89 (1 H, s, H-3), 7.13br (1 H, s, H-6), 7.20 (1 H, s, H-2'), 7.50br (1 H, s, H-8), 7.58 (1 H, s, H-8'), 11.83 (1 H, s, 5-OH), and 11.88 (1 H, s, 5'-OH), *m/e* 408 [100%, (*M*)<sup>+</sup>], 393 [14%, (*M* -  $CH_3$ )<sup>+</sup>], 391 [7%, (*M* - OH)<sup>+</sup>], 390 [10%, (*M* -  $H_2O$ )<sup>+</sup>], 163 (9%), 135 (18%), 134 (22%), and 106 (28%). The mother liquor was evaporated and the residue, after t.l.c. (light petroleum—dichloromethane) to remove some 3'-chlorodiospyrin, separated from light petroleum—dichloromethane to give *2'-chlorodiospyrin* as red crystals (4 mg), m.p. 269—271° (Found: *M*, 408.039 7.  $C_{22}H_{13}^{35}ClO_6$  requires *M*, 408.040 1),  $\nu_{max}$ . 1 678, 1 638, 1 615 (quinone C=O), and 1 592  $cm^{-1}$  (C=C),  $\lambda_{max}$ . 252 (log  $\epsilon$  4.26) and 439 nm (3.85),  $\lambda_{inf}$ . 288 nm (log  $\epsilon$  4.02),  $\delta$  2.32 (3 H, s, 7'- $CH_3$ ), 2.46 (3 H, s, 7- $CH_3$ ), 6.89 (1 H, s, H-3), 7.13br (1 H, s, H-6), 7.20 (1 H, s, H-3'), 7.50br (1 H, s, H-8), 7.66 (1 H, s, H-8'), 11.83 (1 H, s, 5-OH), and 12.00 (1 H, s, 5'-OH). The mass spectrum was similar to that of the 3'-chloro-compound.

(b) A mixture of diospyrin (200 mg), chlorine (40 mg),  
<sup>27</sup> W. Lawrie, J. McLean, and G. R. Taylor, *J. Chem. Soc.*, 1960, 4303.

and glacial acetic acid (10 ml) was shaken for 14 h and then poured into water (100 ml). Extraction with chloroform gave an orange solid which was boiled under reflux with ethanol for 20 min. The solvent was evaporated off and after t.l.c. (dichloromethane) the residue afforded 3'-chlorodiospyrin, which separated from ethanol in orange needles (108 mg), m.p. 266—269°.

*Diospyrin* (I; X = Y = Z = H) and *Diosquinone* (XXI).—Crude diospyrin from Indian *Diospyros montana* had m.p. 257—258°, c.d. (CHCl<sub>3</sub>)  $\lambda_{\max}$  326 ( $\Delta\epsilon$  + 0.37) and 375 nm (−0.32). After five crystallisations from chloroform this (1 g) gave pure optically inactive diospyrin (430 mg), m.p. 257—258° (lit.,<sup>2</sup> 258°),  $\delta$  2.31 (3 H, s, 7'-CH<sub>3</sub>), 2.45 (3 H, s, 7-CH<sub>3</sub>), 6.89 (1 H, s, H-3), 6.94 (2 H, s, H-2' and -3'), 7.12br (1 H, s, H-6), 7.50br (1 H, s, H-8), 7.55 (1 H, s, H-8'), 11.85 (1 H, s, 5-OH), and 12.11 (1 H, s, 5'-OH),  $\delta$  [CDCl<sub>3</sub>-(CD<sub>3</sub>)<sub>2</sub>SO] 2.34 (3 H, s, 7-CH<sub>3</sub>), 2.48 (3 H, s, 7'-CH<sub>3</sub>), 7.00 (1 H, s, H-3), 7.04 (2 H, s, H-2' and -3'), 7.16br

(1 H, s, H-6), 7.46br (1 H, s, H-8), and 7.53 (1 H, s, H-8'). The mother liquor was evaporated and the residue was extracted (Soxhlet) with light petroleum (b.p. 30—40 °C) for 1 h. Evaporation gave a solid (83 mg) which on being subjected to repeated t.l.c. (light petroleum-dichloromethane) and crystallisation from light petroleum gave diosquinone (6 mg), m.p. 198—199°,  $[\alpha]_D^{20}$  −100° (c 0.5 in CHCl<sub>3</sub>) {lit.,<sup>16,21</sup> m.p. 200—200.5°,  $[\alpha]_D^{22}$  −106°, c.d. (CHCl<sub>3</sub>)  $\lambda_{\max}$  323 ( $\Delta\epsilon$  + 4.26) and 372 nm (−3.76)}.

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