#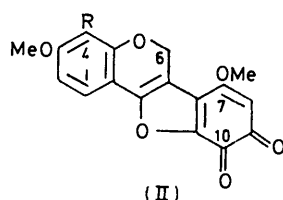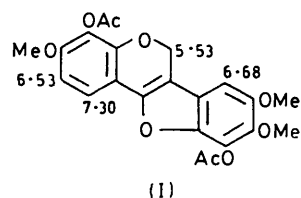 Naturally Occurring Quinones. Part XXV.[1] Pterocarpenequinones (6H-Benzofuro[3,2-c][1]benzopyranquinones) from Brya ebenus

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Bryaquinone. the principal purple pigment in the heartwood of Brya ebenus. is 4-hydroxy-3.7-dimethoxyptero-carpene-9.10-quinone; the corresponding 4-deoxyquinone is also present. Bryebinal. a minor yellow component. is probably a 2-arylbenzofuran-3-carbaldehyde.

SOME of the main colourless compounds in the heartwood of Brya ebenus DC (Leguminosae), a group of five pterocarpenes and an isoflavan, were described recently.[2] Yellow, orange, and purple pigments can also be extracted in very small amounts, some of which may be artefacts. We report here on four of these pigments.

The principal purple compound, bryaquinone, could only be separated from the main colourless compound,
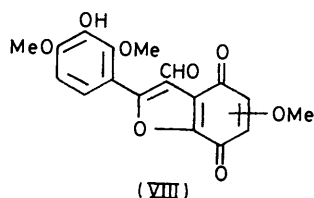

(I)

(II)

(III)

(IV)

(V)

(VI)

(VII)

(VIII)

bryacarpene-1 (I; OH in place of OAc) by acetylation and separation of the two acetates by chromatography. Bryaquinone acetate is a red compound, $C_{15}H_5O_4$-$(OMe)_2(OAc)$ ($\lambda_{max.}$ 520 nm), which we regard as (II; R = OAc) on the following grounds. Reductive acetylation gave a leucotriacetate (III) whose u.v. spectrum ($\lambda_{max.}$ 323, 337, and 355 nm) is very similar to that of
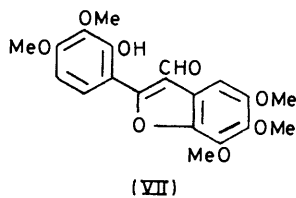
bryacarpene-1 diacetate (I) ($\lambda_{max.}$ 315, 333, and 350 nm).[2] The chemical shifts of the ring protons are also in close agreement [see (I) and (III)], and the 2H singlet at δ 5·54 disappears when the leucoacetate is oxidised with DDQ [2] to the lactone (IV). It is clear that bryaquinone leucotriacetate is a pterocarpene. On hydrogenolysis it afforded an isoflavan (V) readily identified by its characteristic [3] n.m.r. and mass spectra. Following losses of keten, the molecule fragments giving major peaks in the mass spectrum at m/e 182 (90%)(a), 169 (94)(b), and 153 (100)(c), indicating that ring B of the isoflavan carries

(a)

(b)

(c)
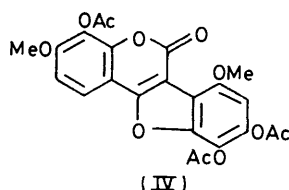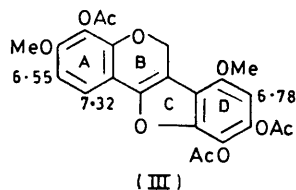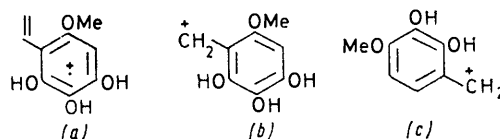
a hydroxy-, a methoxy-, and two acetoxy-groups, the other substituents being in ring A. These substituents can now be allocated to the corresponding rings (D and A) of the leucoacetate (III). The orientation of the substituents in ring A of (III) follows from the virtual identity of the chemical shifts of H-1 and H-2 in (III) and in bryacarpene-1 diacetate (I), and also in the derived lactones (IV) and bryacarpenone-1 diacetate.[2] On converting (III) into (IV) the chemical shift of the aromatic singlet remains unchanged. The proton in ring D is therefore not at C-7,[2] which must be occupied by a methoxy- or acetoxy-group. However this proton must be adjacent to the methoxy-group as irradiation at the frequency of the methoxy-signal (δ 3·87) of bryaquinone acetate produced a significant nuclear Overhauser effect, the intensity of the quinone ring proton signal increasing by ca. 40% (the 2-H signal was also affected to a smaller extent, more so by irradiation at δ 3·84).
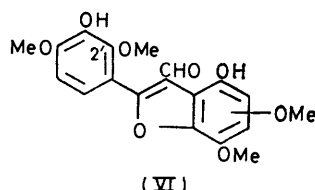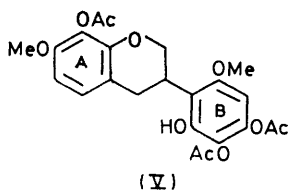
If the pigment is a p-quinone, the carbonyl groups at C-7 should deshield the protons at C-6 so that on conversion into the leucoacetate the 2H singlet should undergo a marked upfield shift. In fact the displacement is insignificant (0·03 p.p.m.) and in any case, the chemical shift for H-6 (δ 5·57) is normal for a pterocarpene.[2] We conclude therefore that there is a methoxy-group at C-7, and consequently bryaquinone acetate is the o-quinone (II; R = OAc) and the leucoacetate has structure (III). The mass spectrum of (II; R = OAc), while consistent with the proposed structure, is not very informative and does not distinguish between ortho- and para-quinone

1 Part XXIV, P. M. Brown, R. H. Thomson, B. M. Hausen, and M. H. Simatupang, Annalen, 1974, 1295.

2 M. A. Ferreira, M. Moir, and R. H. Thomson, J.C.S. Perkin I, 1974, 2429.

3 A. Pelter and P. I. Amenechi, J. Chem. Soc. (C), 1969, 887.

structures. The quinone also failed to react with *o*-phenylenediamine (virtually unchanged after refluxing for 6 h in acetic acid) which merely indicates that the compound is relatively unreactive since both methoxy-*o*- and -*p*-quinones normally condense with *o*-phenylenediamine.

Careful hydrolysis of bryaquinone acetate with sodium carbonate in methanol gave the free quinone (II; R = OH) as a purple solid, m.p. > 350°, λ_{max} 540 nm. During purification (t.l.c.) it was necessary to avoid complete evaporation of solvents as once in the solid state the quinone became practically insoluble, and gave poor n.m.r. spectra although very dilute solutions were quite intensely violet-red. It could not be crystallised but on acetylation it re-formed bryaquinone acetate.

A second purple quinone, $C_{17}H_{12}O_6$, isolated in very small amount (*ca.* 1 mg), is much more soluble. Its u.v. and i.r. spectra were very similar (where relevant) to those of bryaquinone acetate, as was its mass spectral fragmentation pattern. The difference lies in the absence of an acetoxy-group, which is most clearly evident in the n.m.r. spectrum; this is very like that of bryaquinone acetate with an additional signal at δ 6·49 which we attribute to H-4. We regard this quinone as 4-deoxy-bryaquinone (II; R = H), consistent with all the evidence.

One of the yellow pigments, bryebinal, isolated from the heartwood in very small amounts, is a phenolic aldehyde which we regard tentatively as having structure (VI). Bryebinal, $C_{19}H_{18}O_8$, contains four methoxy- and two hydroxy-groups, one of the latter being chelated (δ 9·87) to an aldehyde function (δ 9·79, ν_{max} 1645 cm⁻¹). The remaining n.m.r. signals comprise a singlet at δ 6·49 and an AB system centred at δ 7·16 and 6·79 [*cf.* δ 7·32 and 6·64 for the synthetic aldehyde (VII)[2]]. All the protons in bryebinal are thus accounted for, and all but one of the oxygens which must be in an ether bridge. Phytochemical analogy suggests a 2-arylbenzofuran structure of type (VI) derived from a pterocarpene by oxidative ring cleavage. The mass spectrum was consistent with structure (VI) but the peaks were too weak to be of diagnostic value. Reduction with borohydride gave an alcohol and as this failed to cyclise on heating in diglyme[4] it implies that there is a methoxy- rather than a hydroxy-group at C-2'.

On storage bryebinal partly changed into an orange quinone which was also isolated from the wood, possibly as an artefact. The quinone, $C_{18}H_{14}O_8$, which gave a positive Craven test, is formed at the expense of one hydroxy- and one methoxy-group, the aromatic singlet shifting upfield to δ 5·94 while the aldehyde proton signal moves downfield to δ 10·28. A possible structure is (VIII), but further evidence is obviously desirable.

EXPERIMENTAL

Spectra were measured for solutions in EtOH (u.v.) and $CDCl_3$ (n.m.r.), and for KBr discs (i.r.) unless otherwise stated.

Extraction of Brya ebenus.—Ground heartwood (700 g) was extracted (Soxhlet) successively with light petroleum

(3 l) and chloroform (3 l). Evaporation of the chloroform extract left a dark red solid (75 g). A portion (20 g) of this was chromatographed on a column of silica gel, first with chloroform (fraction A) and then with chloroform–ethanol (5%) as eluant to remove a major purple zone. This fraction (7·3 g) was re-run on a second column, and the purple band eluted with benzene–chloroform (10—60%), and transferred to a third column. The material obtained by elution with benzene–chloroform (10%) was further separated by preparative layer chromatography (p.l.c.) on silica gel in chloroform–ethyl acetate (3:1) to give *inter alia* a major purple band, and a minor orange band which yielded the quinone-aldehyde (VIII) (5 mg). The purple band, essentially a mixture (0·8 g) of bryaquinone and bryacarpene-1, was dissolved in pyridine (15 ml) and acetic anhydride (8 ml). Next day the red solution was poured into ice-water, and the dried precipitate was chromatographed (p.l.c.) on silica gel in benzene–ethyl acetate (4:1). The red band yielded bryaquinone acetate (15 mg).

Fraction A (above) was transferred to a column of silica gel and eluted with benzene–chloroform (10–50%). The main component was further purified by repeated t.l.c. on silica gel in chloroform, chloroform–benzene (4:1), and chloroform–ethyl acetate (99:1); the final yellow band afforded bryebinal (8 mg). A minor purple component was purified by repeated t.l.c. on silica gel in chloroform–ethyl acetate (5:1), and chloroform alone, to give 4-deoxybryaquinone (1 mg).

Bryaquinone Acetate (4-*Acetoxy*-3,7-*dimethoxy*-6H-*benzofuro*[3,2-c][1]*benzopyran*-9,10-*quinone*) (II; R = OAc).—This was crystallised from dichloromethane–light petroleum and then from ether to give red *needles*, m.p. 258—260° (Found: C, 61·2; H, 4·1%; M^+, 370·0682. $C_{19}H_{17}O_6$ requires C, 61·6; H, 3·8%; M, 370·0688), λ_{max} 288, 318, 340sh, and 520 nm (log ε 3·93, 3·98, 3·92, and 3·48), λ_{max} ($CHCl_3$) 243, 288, 316, and 538 nm (log ε 4·20, 4·19, 4·20, and 3·84), ν_{max} 1778, 1680, 1653, 1635, and 1593 cm⁻¹, δ 7·45 and 6·63 (each 1H, d, *J* 9 Hz, H-1 and -2), 5·79 (1H, s, quinone H), 5·57 (2H, s, 6-H), 3·87 and 3·84 (each 3H, s, OMe), and 2·34 (3H, s, OAc), *m/e* 370(25%), 329(14), 328(100), 327(40), 313(7), 299(10), 298(5), 285(5), and 229(6). Reduction with zinc–acetic anhydride–sodium acetate gave the *leucoacetate* (III), needles, m.p. 205° (from ether) (Found: M^+, 456·1056. $C_{23}H_{20}O_{10}$ requires M, 456·1055), λ_{max} 246, 255, 323sh, 337, and 355 nm (log ε 4·27, 4·26, 4·29, 4·35, and 4·34), ν_{max} 1765, 1655w, 1618w, and 1510 cm⁻¹, δ 7·32 and 6·55 (each 1H, d, *J* 9 Hz, H-1 and -2), 6·78 (1H, s, ArH), 5·54 (2H, s, H-6), 3·84 and 3·82 (each 3H, s, OMe), and 2·43, 2·32, and 2·30 (each 3H, s, OAc).

The leucoacetate (10 mg) in ethyl acetate (10 ml) was shaken with hydrogen and palladised charcoal (10%; 10 mg) for 2 h. After removal of catalyst and solvent, the residual 4',5',8-*triacetoxy*-2',7-*dimethoxyisoflavan*-6'-*ol* (V) crystallised from ether as needles (Found: M^+, 460·1366. $C_{23}H_{24}O_{10}$ requires M, 460·1368), λ_{max} 230sh and 279 nm, ν_{max} 3420, 1765, 1630, and 1505 cm⁻¹, δ 6·87 and 6·51 (each 1H, d, *J* 9 Hz, H-1 and -2), 6·19 (1H, s, ArH), 5·53br (1H, s, OH, exchangeable with D_2O), 4·55 (1H, d, *J* 10 Hz, H-2), 4·24 (1H, m, H-2), 3·43br (1H, m, H-3), 2·78 (2H, m, H-4), 3·82 and 3·78 (each 3H, s, OMe), 2·33 (6H, s, OAc), and 2·24 (3H, s, OAc), *m/e* 460(3%), 418(22), 377(8), 376(90), 335(14), 334(100), 182(90), 181(96), 180(14), 170(13), 169(94), 168(16), 165(8), 154(13), 153(100), and 149(16).

The leucoacetate (10 mg) was left overnight in benzene

[4] W. J. Bowyer, J. N. Chatterjea, S. P. Dhoubhadel, B. O. Handford, and W. B. Whalley, *J. Chem. Soc.*, 1964, 4212.

(10 ml) and dioxan (10 ml) with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (100 mg). After removal of solvents, the residue was chromatographed in chloroform on a column of alumina to give 4,9,10-*triacetoxy*-3,7-*dimethoxy*-6H-*benzofuro*[3,2-c][1]*benzopyran*-6-*one* (IV), needles, m.p. 247—248° (from ether) (Found: M^+, 470·0848. $C_{23}H_{18}O_{11}$ requires M, 370·0848), $\lambda_{max.}$ 252, 264sh, 306sh, 343, and 362sh nm (log ε 4·36, 4·25, 3·93, 4·41, and 4·25), $\nu_{max.}$ 1770, 1742, 1630, and 1515 cm⁻¹, δ 7·84 and 7·01 (each 1H, d, J 9 Hz, H-1 and -2), 6·78 (1H, s, ArH), 3·94 and 3·90 (each 3H, s, OMe), 2·46 (6H, s, OAc), and 2·41 (3H, s, OAc).

Bryaquinone (4-*Hydroxy*-3,7-*dimethoxy*-6H-*benzofuro*-[3,2-c][1]*benzopyran*-9,10-*quinone*) (II; R = OH).—Brya-quinone acetate (10 mg) in methanol (30 ml) was stirred with sodium carbonate (10 mg) at room temperature for 4 h. The purple solution was filtered and evaporated to 10 ml; then chloroform (20 ml), water (40 ml), and dilute hydrochloric acid (few drops) were added. The chloroform layer was dried (MgSO₄) and evaporated to small volume. [²H]-Chloroform was then added and the solution again evaporated to low volume. This was repeated twice more, and the solution so obtained was used for n.m.r. spectroscopy. Finally evaporation to dryness gave *bryaquinone* as a purple-brown solid (7 mg), m.p. >350° (Found: M^+, 328·0581. $C_{17}H_{12}O_7$ requires M, 328·0582), $\lambda_{max.}$ 230, 295, 420, and 540 nm (log ε 4·56, 4·36, 4·12, and 3·77), $\nu_{max.}$ 3480, 3330, 1665, 1645, 1630, and 1617 cm⁻¹, δ 7·15 and 6·58 (each 1H, d, J 9 Hz, H-1 and -2), 5·99 (1H, s, OH, exchangeable with D₂O), 5·80 (1H, s, quinone H), 5·62 (2H, s, H-6), and 3·94 and 3·88 (each 3H, s, OMe), m/e 328(100%), 327(94), 314(20), 313(13), 312(6), 299(10), 298(5), and 229(11).

4-*Deoxybryaquinone* (3,7-*Dimethoxy*-6H-*benzofuro*[3,2-c]-[1]*benzopyran*-9,10-*quinone*) (II; R = H) crystallised from chloroform–light petroleum in purple needles, subl. 200° (Found: M^+, 312·0634. $C_{17}H_{12}O_6$ requires M, 312·0633), $\lambda_{max.}$ 275, 310, and 528 nm, $\lambda_{max.}$ (CHCl₃) 242, 280, 310, and 540 nm, $\nu_{max.}$ 1685, 1650, 1622, and 1595 cm⁻¹, δ 7·49 (1H, d, J 9 Hz, H-1), 6·58 (1H, dd, J 2 and 9 Hz, H-2), 6·49 (1H, d, J 2 Hz, H-4), 5·78 (1H, s, quinone H), 5·55 (2H, s, 6-H), and 3·85 and 3·79 (each 3H, s, OMe), m/e 313(14%), 312(100),

311(87), 297(6), 283(18), 282(8), 269(9), 268(5), 227(5), and 201(20).

Bryebinal (VI).—This formed yellow needles, m.p. 182—183° (from ether–benzene) (Found: M^+, 374·0992. $C_{19}H_{18}O_8$ requires M, 374·1001), $\lambda_{max.}$ 223, 268, 288, and 348—350 nm (log ε 4·33, 4·21, 4·18, and 3·85), $\lambda_{max.}$ (EtOH–HO⁻) 227, 256, 286, and 384 nm (log ε 4·33, 4·32, 4·21, and 3·82), $\nu_{max.}$ 3300, 1645, 1625, and 1605 cm⁻¹, δ 9·87 (1H, s, OH, exchangeable with D₂O), 9·79 (1H, s, CHO), 7·16 and 6·79 (each 1H, d, J 9 Hz, ArH), 6·49 (1H, s, ArH), 5·80 (1H, s, OH, exchangeable with D₂O), 4·00 (6H, s, OMe), and 3·90 and 3·84 (each 3H, s, OMe), m/e 375(16%), 374(100), 359(71), 343(4·5), 331(5), 329(5), 187(2), 181(1·5), and 153(2). The aldehyde (10 mg) in ether (20 ml) was treated with an excess of sodium borohydride (20 mg). After 10 min water was added and the product was extracted into chloroform. The dried extract was diluted with light petroleum to precipitate the alcohol, δ 7·03 and 6·75 (each 1H, d, J 9 Hz, ArH), 6·49 (1H, s, ArH), 5·70br (2H, OH), 4·86 (2H, s, CH_2OH), and 4·00, 3·94, 3·88, and 3·70 (each 3H, s, OMe).

Bryebinalquinone (VIII).—This formed orange needles, subl. 220°, m.p. 235—237° (from chloroform–ether) (Found: M^+, 358·0689. $C_{18}H_{14}O_8$ requires M, 358·0688), $\lambda_{max.}$ 220, 260, and 329sh nm, $\nu_{max.}$ 3380, 1685, 1645w, and 1610 cm⁻¹, δ 10·28 (1H, s, CHO), 7·21 and 6·73 (each 1H, d, J 9 Hz), 5·94 (1H, s, quinone H), 5·70br (1H, s, OH, exchangeable with D₂O), 3·98 (3H, s, OMe), and 3·90 (6H, s, OMe), m/e 361 (16%), 360(89) (M + 2, probably quinol), 359(25), 358(100), 357(13), 345(10), 344(10), 343(40), 329(28), 327(18), 314(28), 313(13), 312(11), 300(16), 287(11), 181(20), 173(11), 167(11), 164(35), and 149(13).