Naturally Occurring Quinones. Part 27.[1] Sesquiterpenoid Quinones and Related Compounds from *Hibiscus elatus*: Crystal Structure of Hibiscone C (Gmelofuran)

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The blue-grey or pink-grey heartwood of *Hibiscus elatus* (Blue Mahoe), which turns to light yellow or buff-grey on exposure to light, contains a group of colourless sesquiterpenoid ketones (hibiscones A—D) and *o*-naphthoquinones (hibiscoquinones A—D) based on a cadinane skeleton. The structure of the furanodiketone, hibiscone C (gmelofuran) (3) was determined by *X*-ray crystallography, to which hibiscones A, B, and D were related by spectroscopic and chemical methods.

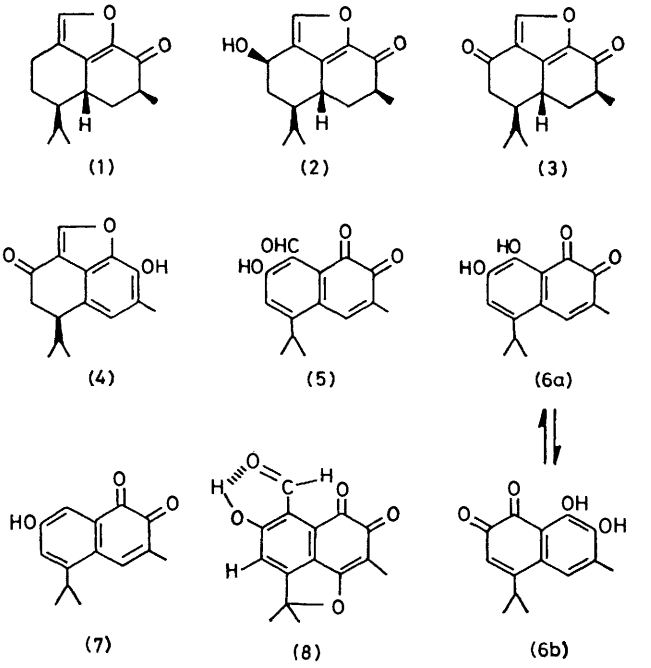
Hibiscoquinones B and C fade slowly in light but hibiscoquinone A, 8-formyl-7-hydroxy-5-isopropyl-3-methyl-1,2-naphthoquinone, is very photolabile and rearranges quickly in daylight to a colourless lactone. The model compound 8-formyl-7-hydroxy-1,2-naphthoquinone behaves in the same way while 8-formyl-7-hydroxy-1,4-naphthoquinone rearranges much more slowly in daylight to an isomeric lactone.

MANY timbers change colour on exposure to daylight,[2] and a striking example is provided by the wood of Blue Mahoe (*Hibiscus elatus*, Malvaceae), the national tree of Jamaica. Artefacts made of Blue Mahoe are a light yellow to buff-grey in colour whereas the freshly cut heartwood is a dark bluish grey, sometimes streaked with pink, and may be an intense blue-black. This colour change led us to examine the extractives of *H. elatus*. Extraction with chloroform gave a series of coloured and colourless compounds which we have named hibiscoquinones and hibiscones, respectively.

Hibiscones.—The most abundant compound was hibiscone C, $C_{15}H_{18}O_3$. Spectroscopic evidence (see Experimental section) showed this to be an aromatic diketone possessing an isopropyl and a secondary methyl group. As overlapping n.m.r. signals (100 MHz, δ 3.2—1.7) from eight protons, representing a substantial part of the molecule, were not readily interpretable the structural problem was solved by *X*-ray crystallographic analysis.

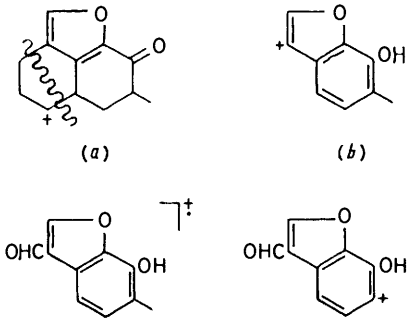
The structure thus revealed is shown in (3) (arbitrary absolute configuration). The methyl group is axial and the isopropyl group equatorial. The geometry shows no very remarkable features. The furan ring is nearly planar and its α-carbonyl substituent is very nearly in the plane of the aromatic ring. The β-carbonyl substituent, however, is twisted by *ca.* 5° from this plane. The geometry is quantitatively described in the list of torsion angles (Table 4). Thus hibiscone C is the same as gmelofuran found recently in the heartwood of *Gmelina arborea*.[3]

Hibiscone B, $C_{15}H_{20}O_3$, has two more hydrogen atoms than hibiscone C and contains a ketonic group (ν_{CO} 1 640 cm^{-1}), and a secondary alcohol function [$\nu_{max.}$ 3 450 cm^{-1}; δ 5.01 (1 H, br, $W_{\frac{1}{2}}$ 7 Hz)]. On oxidation with DDQ it gave hibiscone C. As the n.m.r. signal for the furan α-proton moves upfield from δ 8.10 in hibiscone C to 7.68 in hibiscone B, and decoupling experiments showed that the >C*H*OH proton is not coupled to the >C*H*Me proton, the ketone must have structure (2) with an axial hydroxy-group. Hibiscone A, $C_{15}H_{20}O_2$, has one oxygen atom less than hibiscone B, and although lacking the alcohol function is in all other respects very similar. As the furan α-proton signal has again shifted upfield to δ 7.34 and spin decoupling revealed that the >C*H*Me proton resonates at δ 2.73, *i.e.* α to carbonyl, structure (1) is indicated for hibiscone A. This is supported by the mass spectrum; the base peak at *m/e*



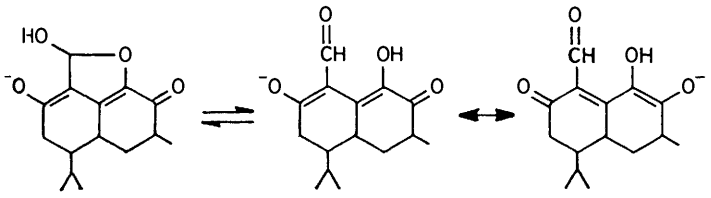
147 ($C_9H_7O_2$) corresponds to the benzofuran cation (*b*) formed by initial loss of $Me_2CH\cdot$ to give (*a*) and then fragmentation, as indicated, with hydrogen transfer. The mass spectrum of hibiscone C suggests a similar mode of decomposition to give ions (*c*) (or isomer) (*m/e* 176, 100%) and (*d*) (*m/e* 161, 80%); hibiscone B fragments in the same way to give major ions at *m/e* 178 (32%) and 163 (100%).

A striking change is observed on addition of sodium hydroxide to hibiscone C in alcohol; a bright yellow solution is obtained, $\lambda_{max.}$ shifting from 267 to 414 nm with increased intensity whereas hibiscones A and B give no alkali shift. It is unlikely that such a change would result merely from formation of an anion of (3), and moreover the furan proton signal shifts downfield



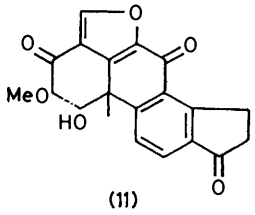
from δ 8.34 (in CD_3OD) to 9.11 (in CD_3OD–DO^-). The new chromophore is probably the mesomeric anion (10) which arises by nucleophilic attack on the furan ring of hibiscone C (3), activated by the two carbonyl groups, to give (9) followed by opening of the lactol ring to form the aldehyde function which accounts for the n.m.r. singlet at δ 9.11. The whole process is reversed if the solution is acidified after a short time. The diketofuran structure in hibiscone C is rare; another example is seen in viridin (11) [4] which forms an orange-yellow solution instantly on addition of alkali, $\lambda_{max.}$ (MeOH) shifting from 310 (log ε 4.00) to 454 nm (log ε 3.9). Further reactions then ensue as the spectrum does not return to the original on acidification.

Hibiscone D, $C_{15}H_{16}O_3$, contains two hydrogen atoms less than hibiscone C, and is a phenolic ketone (i.r., u.v.). The n.m.r. spectrum shows that the isopropyl

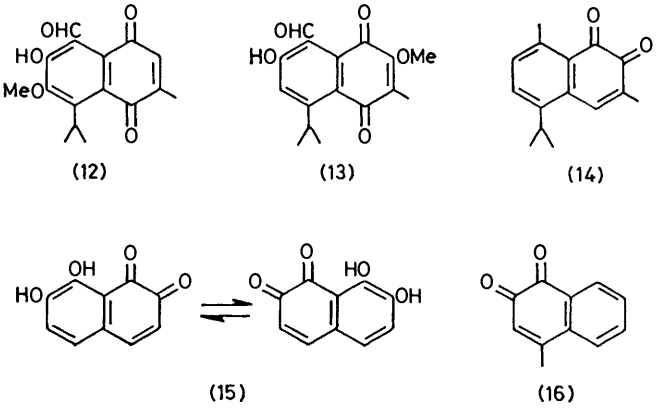


group is retained, the methyl group is aromatic (δ 2.42), and at low field there is a signal from a benzenoid proton (δ 6.94) in addition to the furan proton (δ 7.96). Spin decoupling established that a methylene doublet at δ 2.82 (J 5 Hz) was adjacent to a benzylic proton (δ 3.26) which was also coupled to the isopropyl methine proton at δ 2.05. Hibiscone D is therefore (4); inspection of a Dreiding model shows that the methylene group can only be symmetrical if it lies below the plane of the furan ring with the benzylic proton equatorial. Oxidation of both (3) and (4) to the quinone (6) provides further evidence.[5]

Hibiscoquinones.—Hibiscoquinone A, $C_{15}H_{14}O_4$, is a purple crystalline solid forming red solutions in organic solvents, and reduced instantly by dithionite. The structure (5) of hibiscoquinone A is defined by the ^1H n.m.r. spectrum which comprises signals for an aldehyde function (δ 10.56), a chelated hydroxy-group (12.17), an aromatic proton (7.17), an *o*-quinone ring proton (7.52, q) coupled to a quinone methyl (2.07, d), and an



aromatic isopropyl group (3.35, 1 H, septet; 1.31, 6 H, d). Where relevant the spectrum is in good agreement with those of *p*-hemigossypolone 7-methyl ether [6] (12), bombaxquinone B (13),[6,7] and the mansonone family of *o*-quinones, *e.g.* mansonone C (14).[8] However, unlike the *p*-quinones (12) and (13) hibiscoquinone A



shows visible absorption at $\lambda_{max.}$ 484 nm, shifting to 670 nm in alkaline solution, whereas (12) has $\lambda_{max.}$ (HO^-) 528 nm and no maximum in the visible region in neutral solution. Like many *o*-naphthoquinoes, hibiscoquinone A (5) shows a significant (28%) $M^+ + 2$ peak in its mass spectrum.[9] The *p*-hemigossypolones [*e.g.* (12)] are found in cotton (*Gossypium* spp., Malvaceae); analogous *o*-quinones have not been reported but isohemigossypol, a phytoalexin produced by *Gossypium* in response to infection by *Verticillium dahliae* [10] is the quinol of hibiscoquinone A.

Hibiscoquinone C, $C_{14}H_{14}O_3$, has only fourteen carbon atoms. The n.m.r. spectrum closely resembles that of hibiscoquinone A except that the aldehyde proton singlet has been replaced by an aromatic proton doublet (δ 7.27, J 2 Hz) which is coupled to another at δ 6.99. This suggests structure (7) which is supported by the u.v.–visible spectrum showing $\lambda_{max.}$ 500 nm, shifting to 655 nm in alkali, similar to that of 7-hydroxy-1,2-naphthoquinone. In the mass spectrum the weak molecular ion at *m/e* 230 (4%) is actually weaker than

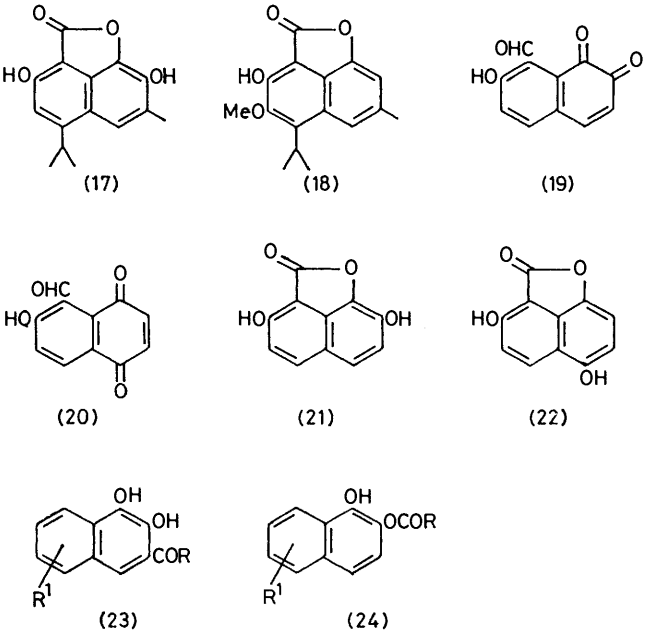
the $M^+ + 2$ ion (11%), the base peak falling at 202 ($M^+ - CO$); the mass spectrum of 7-hydroxy-1,2-naphthoquinone is similar.

Hibiscoquinone B, $C_{14}H_{14}O_4$, has one more oxygen atom than hibiscoquinone C. The n.m.r. spectrum comprises signals for an isopropyl group, a methyl singlet, two broadened one-proton singlets at δ 6.96 and 6.26, and broad signals from two hydroxy-protons at δ 12.65 and 6.20. Relative to the spectrum of hibiscoquinone C (7) it is apparent that the lower field aromatic proton has been replaced by a signal from a strongly chelated hydroxy-proton, suggesting structure (6). In alkaline methanol the anion shows $\lambda_{max.}$ 498 and 670 nm which compares with $\lambda_{max.}$ * 476 and 650 nm for the parent compound (15).[11] The mass spectrum of hibiscoquinone B does not show a significant $M^+ + 2$ peak. The tautomeric nature of hibiscoquinone B is evident from its n.m.r. spectrum. In (5), (7), and (14) the quinone methyl protons resonate as a fine doublet at δ *ca.* 2—2.1 but in hibiscoquinone B the corresponding singlet is downfield at δ 2.33 in the aromatic methyl region and coupled to a ring-proton signal at δ 6.96 which is devoid of fine structure [*cf.* 7.69 (q) for H-4 in (7)]. The other ring proton resonates at δ 6.26 compared to 6.99 for H-6 in (7). This large upfield shift cannot be accounted for merely by the introduction of a *meta*-hydroxy-group at C-8 and the resonance position is more profitably compared with that of the quinonoid proton in (16), whose chemical shift is δ 6.38.[12] The n.m.r. evidence seems to favour (6b) rather than (6a) in [^{2}H]-chloroform solution; unfortunately comparison with the parent compound (15) was not possible.

Hibiscoquinone D, $C_{15}H_{12}O_5$, is generally similar to hibiscoquinone A ($C_{15}H_{14}O_4$). The n.m.r. spectrum reveals the presence of a quinone methyl group (singlet), an aromatic proton, an aldehyde function (δ 11.05), and a chelated hydroxy-group (δ 12.39). However there is no signal from a quinone-ring proton and the usual isopropyl group is replaced by a *gem*-dimethyl group resonating as a singlet at δ 1.76. Accordingly hibiscoquinone D has structure (8). Long-range coupling was observed between the formyl proton (d, J 1 Hz) and the H-6 proton showing that the aldehyde function is held in the configuration shown (8).

Photochemistry.—On exposure to daylight hibiscoquinones B and C fade very slowly but dilute solutions of hibiscoquinone A (5) in chloroform or benzene are rapidly decolourised (*ca.* 20 min). Even in the solid state the crystals slowly become colourless as they transform into the isomeric photo-product, the lactone (17). Hibiscolactone A (17) shows $\lambda_{max.}$ 356 nm shifting in alkali to 398 nm, $\nu_{max.}$ 3 510 and 1 720 cm^{-1}, and the n.m.r. spectrum includes singlets for two aromatic protons at δ 7.61 and 7.04 in addition to signals for aromatic methyl and isopropyl groups. The lactone was also isolated from the wood of *H. elatus* in very small amount, and was probably an artefact.

The presence of the hibiscoquinones, especially A, is obviously a major factor in the colour change which the heartwood of *H. elatus* undergoes on exposure to light. Probably simple photoreduction is mainly responsible as the content of hibiscoquinone A is usually small. In addition to the free quinones, part of the wood colour derives from the turquoise anion of hibiscoquinone B. After extracting the wood with chloroform the sawdust has a green tinge, and if it is then soaked in chloroform containing acetic acid it turns red, and more hibiscoquinone can be recovered from the solution. When a chloroform extract of some wood batches was chromatographed on silica gel in chloroform, a green band ran at the solvent front. This gave hibiscoquinone B on acidification. Apparently some hibiscoquinone B anion is 'complexed' in some way with lipid, making it effectively non-polar.



Despite the photolability of the *o*-quinone-*peri*-aldehyde (5) the analogous *p*-quinone-*peri*-aldehydes (12) and (13) appear to be stable, and no difficulty has been reported in handling these compounds. In order to make a closer comparison we prepared the *o*-(19) and *p*-(20)-quinone-aldehydes by oxidising 2,7- and 2,8-dihydroxy-1-naphthaldehydes, respectively, with Fremy's salt. The *o*-quinone (19) is a purple-brown compound like (5) and equally photo-labile; in solution, when exposed to daylight, it rearranges rapidly and quantitatively to the lactone (21). Figure 1 shows the change in the visible spectrum with time for a solution in benzene (*ca.* 0.001M). The orange-brown *p*-quinone isomer (20) is relatively stable, rearranging slowly in daylight to the lactone (22), and rapidly on irradiation using a medium-pressure mercury lamp. A lactone for which structure (18) was suggested,[13] co-occurs with the quinone (13) in the root bark of *Bombax malabaricum* (Malvaceae). Spectroscopically it is similar to hibiscolactone A and probably has the isomeric structure

* No solvent mentioned.

(18; MeO at C-2 instead of C-6),[6] in which case it may well be a photo-artefact of (13).

Intermolecular photochemical reactions between quinones and aldehydes are well-known, and usually require long irradiation times.[14] The products from simple quinones are *C*-acyl and/or *O*-acyl quinols. 1,4-Quinones[14] give predominantly 2-acylquinols; 1,2-naphthoquinones[15] and aliphatic aldehydes (RCHO) yield both (23) and (24, or isomer) but with aromatic aldehydes *O*-acylation occurs exclusively to give the

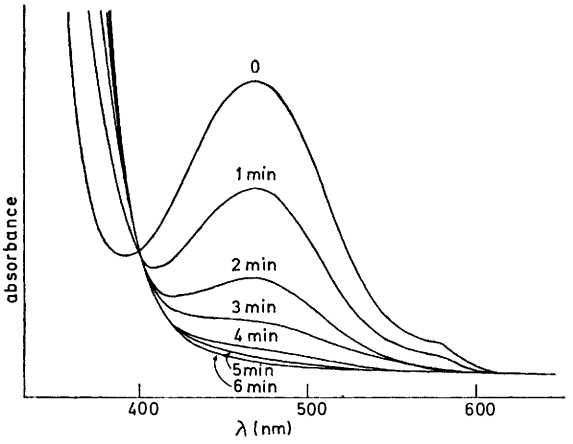


FIGURE 1 Change in the visible spectrum with time for a 0.001M-solution of the quinone (19) in benzene upon exposure to daylight

mono-esters (24, or isomer). The formation of the lactones (17) and (21) from the corresponding 1,2-naphthoquinone-*peri*-aldehydes is an intramolecular version of the latter reaction, and intramolecular *O*-acylation is also preferred by the 1,4-naphthoquinone-*peri*-aldehyde (20) in forming the lactone (22). Analo-

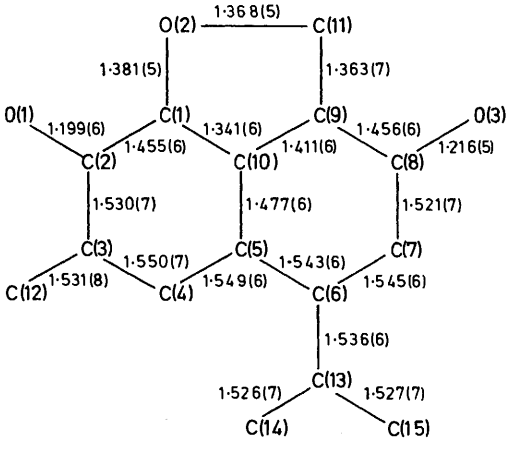


FIGURE 2 Crystallographic numbering and bond lengths for hibiscone C

gous intramolecular *C*-acylation is obviously not possible, and in that respect quinones (19) and (20) can be compared with 9,10-phenanthrenequinone which reacts photochemically with aldehydes to form hydroxydiketones [1,2-adducts (25)] and mono-esters [1,4-adducts (26)].

A CIDNP study of the photochemical reaction between 9,10-phenanthrenequinone and acetaldehyde is summarised in Scheme 1 (R = Me).[16] After initial hydrogen

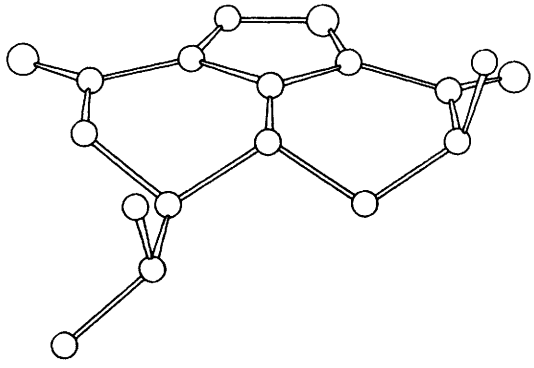
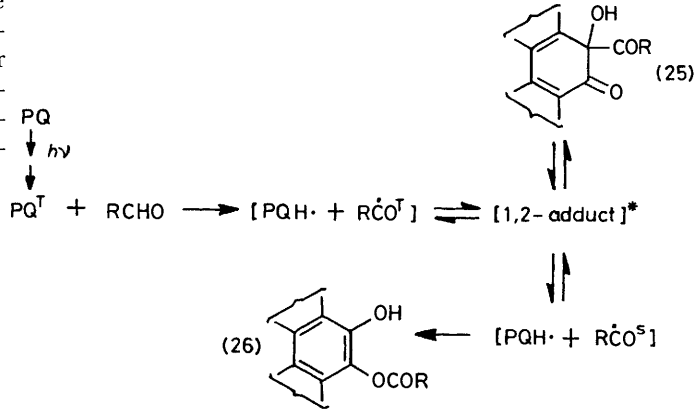


FIGURE 3 Perspective drawing of hibiscone C

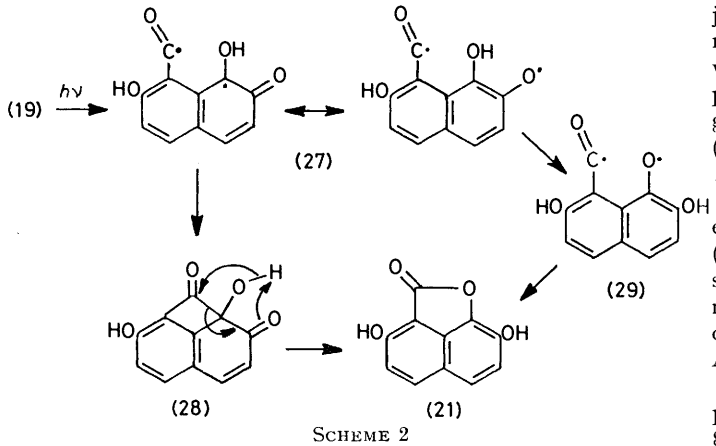
abstraction from the formyl group by the quinone triplet, in-cage combination of the radical pair leads to formation of a vibrationally excited 1,2-adduct which either decays to the ground state (25) or dissociates to another radical pair (singlet) which then recombines to give the 1,4-adduct (26). For the quinone (19), intramolecular hydrogen abstraction will produce the species (27) which can then couple to form the tricyclic molecule (28). This could not lead to the final product by an



SCHEME 1

analogous dissociation–recombination process as in Scheme 1 but the lactone (27) could be formed by rearrangement of (28) in the ground state as indicated (Scheme 2). An alternative to the formation of the strained diketone (28) would be the hydrogen-atom transfer (27) → (29) and radical combination to give (21). At present we cannot distinguish between these pathways. Similar mechanisms (Scheme 3) can be envisaged for the transformation of the *p*-quinone (20) into the lactone (22) but the postulated hydrogen-transfer step (30) → (31) would be a less favourable intermolecular

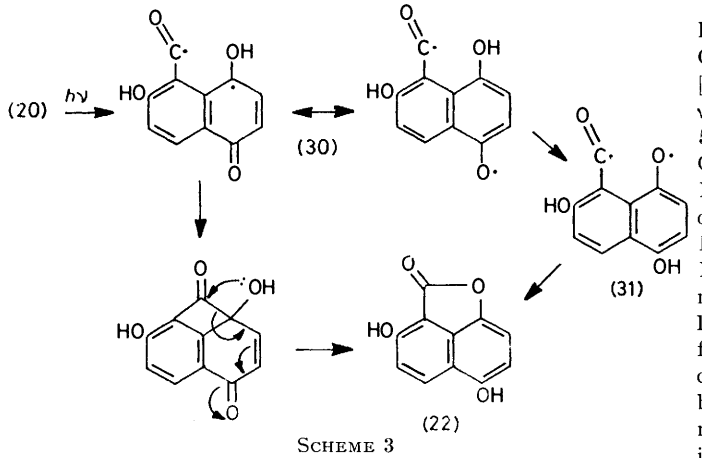
process, and by-products would be expected. A CIDNP examination of the photolytic (u.v.) rearrangements (19) ⟶ (21) and (20) ⟶ (22), under conditions [16] where the reactions are very fast, revealed no emission



SCHEME 2

signals, which indicates that the reactions are entirely intramolecular.

Hibiscoquinone D (8) behaved differently to A (5). It rearranged in daylight more slowly to give a coloured photo-product, not yet identified owing to lack of material. Possibly the additional five-membered ring in



SCHEME 3

(8) prevents the formation of an intermediate analogous to (28).

EXPERIMENTAL

Spectroscopic measurements were made for KBr discs (i.r.) and for solutions in ethanol (u.v.) and $CDCl_3$ (n.m.r.) unless stated otherwise. All operations involving hibiscoquinones were conducted as far as possible in the absence of light.

Extraction of Hibiscus elatus.—(*a*) Ground heartwood (500 g) was extracted (Soxhlet) with chloroform. The dark brown semi-solid extract was chromatographed on a column of silica gel in chloroform. Some batches gave an initial brown or green fore-run (I) followed by a red eluate (II). When elution of the red zone was complete the upper greenish zone was stripped off using methanol–acetic acid (9 : 1), the colour changing to pink (III). Fraction (II) was separated by repeated preparative t.l.c. on silica gel in chloroform to give hibiscones A (40 mg), B (34 mg), and C (910 mg), and hibiscoquinones A (16 mg) and C (90 mg). Fraction (III) was diluted with water, extracted with chloroform, and shaken with portions of aqueous sodium hydrogen carbonate (10% w/v) until the aqueous phase just turned green-blue. The last portion was acidified to return the quinone to the chloroform phase which was then washed with water, dried, evaporated, and purified by preparative t.l.c. in chloroform–methanol (19 : 1) on silica gel plates (prepared in 0.5M-HCl) to give hibiscoquinone B (92 mg). More of the latter was obtained by acidification of fraction (I).

(*b*) (With Dr. P. Singh) Ground heartwood (200 g) was extracted with cold chloroform for 24 h. Work-up as in (*a*) and elution of the red zone gave a mixture which was separated by preparative t.l.c. on silica gel in chloroform–methanol (50 : 1) to give, in addition to the above, hibiscoquinone D (3 mg), hibiscone D (5 mg), and hibiscolactone A (2 mg).

Hibiscone A (1) crystallised from chloroform–light petroleum as needles, m.p. 94—95° (Found: C, 77.6; H, 8.8%; M^+, 232.146 0. $C_{15}H_{20}O_2$ requires C, 77.6; H, 8.6; *M*, 232.146 3); $[\alpha]_D^{25}$ +40° (*c* 0.74 in $CHCl_3$); $\lambda_{max.}$ 280 nm (log ε 4.09); $\nu_{max.}$ 3 100 and 1 650 cm^{-1}; δ 7.34br (1 H, s, furan-H), 3.0—2.3, 2.3—1.6, and 1.5—1.2 (total 10 H, m, CH_2 and CH), 1.29 (3 H, d, *J* 7 Hz, CH*Me*), and 1.02 and 0.88 (each 3 H, d, *J* 7 Hz, CH*Me*$_2$); *m/e* 232 (M^+, 71%), 217 (9), 189 (35), 161 (11), 147.044 8 (100; $C_9H_7O_2$ requires 147.044 8), 91 (20), and 83 (18).

Hibiscone B (2) formed needles, m.p. 123° (from ether–light petroleum) (Found: C, 72.6; H, 7.8%; M^+, 248.141 2. $C_{15}H_{20}O_3$ requires C, 72.6; H, 8.1%; *M*, 248.141 2); $[\alpha]_D^{23.5}$ +3° (*c* 1.12 in $CHCl_3$); $\lambda_{max.}$ 276 nm (log ε 4.18); $\nu_{max.}$ 3 450, 3 100, and 1 640 cm^{-1}; δ 7.68 (1 H, s, furan-H), 5.01br (1 H, s, $W_{\frac{1}{2}}$ 7 Hz, C*H*OH), 2.34br (1 H, s, D_2O exch., OH), 2.9—2.5 and 2.3—1.5 (total 8 H, m, CH_2 and CH), 1.29 (3 H, d, *J* 7 Hz, CH*Me*), and 1.03 and 0.89 (each 3 H, d, *J* 7 Hz, CH*Me*$_2$); *m/e* 248 (M^+, 84%), 215 (5), 205 (18), 187 (6), 178.062 6 (32; $C_{10}H_{10}O_3$ requires 178.062 9), and 163 (100). To hibiscone B (50.7 mg) in chloroform (20 ml) was added DDQ (45.6 mg) and a few drops of 2M-hydrochloric acid. The mixture was heated under reflux for 30 h, the solvent removed *in vacuo*, and the residue chromatographed on silica gel in chloroform. The first band, after further preparative t.l.c., gave hibiscone C (3), m.p. 124° (from chloroform–light petroleum) (40 mg), identical (mixed m.p., i.r., n.m.r.) with that described below.

Hibiscone C (gmelofuran) (3) crystallised from chloroform–light petroleum as needles, m.p. 124—125° (Found: C, 73.2; H, 7.0%; M^+, 246.125 4. $C_{15}H_{18}O_3$ requires C, 73.2; H, 7.3%; *M*, 246.125 5); $[\alpha]_D^{27}$ −23° (*c* 1.49 in $CHCl_3$); $\lambda_{max.}$ 232 and 267 nm (log ε 4.10 and 4.09); $\lambda_{max.}$ (EtOH–OH^-) 258 and 414 nm (log ε 3.71 and 4.59); $\nu_{max.}$ 3 115, 1 693, 1 668, 1 602, and 1 525 cm^{-1}; δ 8.10 (1 H, s, furan-H), 3.2—1.7 (8 H, m, CH_2 and CH), 1.35 (3 H, d, *J* 7 Hz, CH*Me*), and 1.03 and 0.97 (each 3 H, d, *J* 6 Hz, CH*Me*$_2$), the CH*Me*$_2$ doublets overlapping to give a 'triplet' signal which was resolved into two clear doublets in CD_3OD or C_5D_5N; *m/e* 246 (M^+, 80%), 203 (40), 176.046 9 (100; $C_{10}H_8O_3$ requires 176.047 3), 161.024 1 (80; $C_9H_5O_3$ requires 161.023 8), and 163.0398 (100; $C_9H_7O_3$ requires 163.039 5), and 77 (14).

Hibiscone D (4), needles, had m.p. 140° (from chloroform) (Found: C, 73.6; H, 6.5%; M^+, 244.110 1. $C_{15}H_{16}O_3$

requires C, 73.8; H, 6.6%; *M*, 244.109 9); $[\alpha]_D^{26}$ +37° (*c* 0.97 in $CHCl_3$); $\lambda_{max.}$ 229sh, 243sh, and 330 nm (log ε 3.98, 3.93, and 3.12); $\lambda_{max.}$ (EtOH–OH^-), 230sh, 268, and 405 nm; $\nu_{max.}$ ($CHCl_3$) 3 570, 3 210br, 1 680, and 1 633 cm^{-1}; δ 7.96 (1 H, s, furan-H), 6.94 (1 H, s, ArH), 5.7br (1 H, D_2O exch., OH), 3.26 (H, m, $CH_2CHCHMe_2$), 2.82 (2 H, d, *J* 5 Hz), 2.42 (3 H, s, $ArCH_3$), 2.05 (1 H, m, $CHMe_2$), and 0.89 and 0.83 (each 3 H, d, *J* 6 Hz, $CHMe_2$); *m/e* 244 (M^+, 10%), 201 (100), 173 (2), and 145 (5). It gave an oily acetate, δ 7.97 (1 H, s, furan-H), 7.04 (1 H, s, ArH), 3.30 (1 H, m, $CH_2CHCHMe_2$), 2.80 (2 H, d, *J* 5 Hz), 2.40 (3 H, s, ArMe), 2.33 (3 H, s, $MeCO_2$), 2.04 (1 H, m, $CHMe_2$), and 0.90 and 0.83 (each 3 H, d, *J* 6 Hz, $CHMe_2$).

Hibiscoquinone A (5), purple brown needles, had m.p. 145° (from ether) (Found: C, 69.6; H, 5.4%; M^+, 258.089 3. $C_{15}H_{14}O_4$ requires C, 69.8; H, 5.5%; *M*, 258.089 2); $\lambda_{max.}$ 229, 262, 309, 342sh, and 484 nm (log ε 4.12, 3.93, 3.86, 3.54, and 3.01); $\lambda_{max.}$ (EtOH–OH^-) 252sh, 314, 380sh, 490sh, and 670 nm; $\nu_{max.}$ 1 680w, 1 660, 1 642, and 1 615 cm^{-1}; δ 12.17br (1 H, s, D_2O exch., OH), 10.56 (1 H, s, CHO), 7.52 (1 H, q, *J* 2 Hz, QH), 7.17 (1 H, s, ArH), 3.35 (1 H, septet, *J* 6 Hz, $CHMe_2$), 2.07 (3 H, d, *J* 2 Hz, QMe), and 1.31 (6 H, d, *J*, 6 Hz, $CHMe_2$); *m/e* 260 (28%), 258 (M^+, 100), 243 (11), 230 (50), 215 (16), 212 (6), 187 (45), and 115 (8).

Hibiscoquinone B (6), purple brown leaflets, had m.p. 169° (from benzene) (Found: C, 68.3; H, 5.8%; M^+, 246.089 5. $C_{14}H_{14}O_4$ requires C, 68.3; H, 5.7%; *M*, 246.089 2); $\lambda_{max.}$ (MeOH) 228, 276, 317sh, 415, and 534 nm (log ε 4.12, 435, 3.51, 3.33, and 3.40); $\lambda_{max.}$ (MeOH–HO^-) 256, 338, 498, and 670 nm; $\nu_{max.}$ (KBr) 3 560, 3 450, 1 663, 1 641s, and 1 621 cm^{-1}; δ 12.65br (1 H, D_2O exch., 8-OH), 6.96br (1 H, s, 4-H), 6.26br (1 H, s, 6-H), 6.20br (1 H, s, D_2O exch., 7-OH), 3.17 (1 H, m, $CHMe_2$), 2.33 (3 H, s, Me), and 1.27 (6 H, d, *J* 6 Hz, $CHMe_2$); *m/e* 246 (M^+, 16%), 218 (50), 203 (100), and 175 (5).

Hibiscoquinone C (7) crystallised from methanol as brown red leaflets, decomp. >225° (Found: C, 72.8; H, 5.8%; M^+, 230.094 4. $C_{14}H_{14}O_3$ requires C, 73.0; H, 6.1%; *M*, 230.094 2); $\lambda_{max.}$ 284, 362, and 500 nm (log ε 4.23, 3.20, and 3.34); $\lambda_{max.}$ (EtOH–HO^-) 319, 392, and 680 nm; $\nu_{max.}$ ($CHCl_3$) 3 510, 3 200br, 1 685w, and 1 654 cm^{-1}; δ(CD_3OD) 7.69 (1 H, q, *J* 1 Hz), 7.27 (1 H, d, *J* 2 Hz, 8-H), 6.99 (1 H, d, *J* 2 Hz, 6-H), 3.3 (1 H, m, overlapped by solvent peak, $CHMe_2$), 1.98 (3 H, d, *J* 1 Hz, QMe), and 1.27 (6 H, d, *J* 6 Hz, $CHMe_2$); *m/e* 232 (11%), 230 (M^+, 4), 202 (100), 187 (75), 159 (4), 144 (5), and 115 (6).

Hibiscoquinone D (8), dark brown needles, decomp. >350° (from chloroform) (Found: M^+, 272.068 8. $C_{15}H_{12}O_5$ requires *M*, 272.068 4); $\lambda_{max.}$ (MeOH) 233, 282, 295sh, 337, and 520 nm (log ε 4.28, 4.02, 4.00, 3.93, and 3.12); $\lambda_{max.}$ (MeOH–HO^-) 296, 357, and 596 nm; $\nu_{max.}$ 3 400, 1 690, 1 645, and 1 619 cm^{-1}; δ 12.39br (1 H, s, D_2O exch., OH), 11.05 (1 H, d, *J* 1 Hz, CHO), 7.19 (1 H, s, 6-H), 1.93 (3 H, s, QMe), and 1.76 (6 H, s, Me_2C); *m/e* 274 (3%), 272 (M^+, 100) 257 (3), 244 (7), 229 (8), 216 (20), 201 (35), 188 (5), 187 (6), 173 (11), 145 (6), 115 (6), and 93 (13).

In the following oxidations a freshly made solution of Fremy's salt (10 g) in water (570 ml) and 0.17M-potassium dihydrogen phosphate (170 ml) was used.

8-Formyl-7-hydroxy-1,2-naphthoquinone (19).—This preparation was carried out with the exclusion of light. To 2,7-dihydroxy-1-naphthaldehyde [17] (2.75 g) in methanol (150 ml) was added Fremy's salt solution (640 ml) giving an immediate purple precipitate which was collected and dissolved in acetone (20 ml). On addition of light petroleum, with cooling, the *o*-quinone separated as purple-brown needles, m.p. 149—150° (2.1 g, 71%) (Found: C, 65.1; H, 3.2%; M^+, 202.026 4. $C_{11}H_6O_4$ requires C, 65.3; H, 3.0%; *M*, 202.026 6); $\lambda_{max.}$ ($CHCl_3$) 250, 296, 340sh, and 478 nm (log ε 3.93, 4.16, 3,52, and 3.27); $\nu_{max.}$ 1 655 and 1 642 cm^{-1}; δ($CDCl_3$) 12.33 (1 H, s, D_2O exch., OH), 10.82 (1 H, s, CHO), 7.50, 7.42, and 7.26 (each 1 H, d, *J* 8 Hz, 3-, 4-, and 5-H), and 6.25 (1 H, d, *J* 8 Hz, 6-H); *m/e* 204 (32%), 202 (M^+, 89), 174 (94), and 146 (100).

8-Formyl-7-hydroxy-1,4-naphthoquinone (20).—2,8-Dihydroxy-1-naphthaldehyde [18] (2 g) (prepared according to ref. 17) in methanol (110 ml) was treated with Fremy's salt solution (470 ml). After 15 min the mixture was extracted with chloroform (2 × 100 ml) and the extract dried ($MgSO_4$) and evaporated. The residual gum was chromatographed on silica gel in chloroform to give the desired p-*quinone* as orange-brown needles (0.88 g, 41%), m.p. 135° (from chloroform) (Found: C, 65.6; H, 3.2%; M^+, 202.026 0. $C_{11}H_6O_4$ requires C, 65.3; H, 3.0%; *M*, 202.026 6); $\lambda_{max.}$ 248, 278sh, 315sh, and 379 nm (log ε 4.22, 3.93, 3.51, and 3.39); $\lambda_{max.}$ (EtOH–HO^-) 234, 314, and 528 nm; $\nu_{max.}$ 1 654 and 1 649 cm^{-1}; δ 12.77 (1 H, s, D_2O exch., OH), 10.89 (1 H, s, CHO), 8.25 (1 H, d, *J* 8 Hz, 5-H), 7.31 (1 H, d, *J* 8 Hz, 6-H), and 6.95 (2 H, s, 2- and 3-H); *m/e* 202 (M^+, 100%), 174 (6), 146 (45), 118 (63), 92 (32), and 89 (16).

Hibiscolactone A (17).—A solution of hibiscoquinone A (6 mg) in chloroform (or toluene-free benzene) (15 ml) was left exposed to daylight until it became colourless (<30 min). Evaporation left the *lactone* (100% conversion, t.l.c.) which recrystallised from methanol or benzene as needles, m.p. 225—226° (5 mg, 82%) (Found: M^+, 258.089 3. $C_{15}H_{14}O_4$ requires *M*, 258.089 2); $\lambda_{max.}$ (MeOH) 234, 263, and 356 nm (log ε 4.28, 4.32, and 4.03); $\lambda_{max.}$ (MeOH–HO^-) 271 and 398 nm; $\nu_{max.}$ ($CHCl_3$) 3 510 and 1 720 cm^{-1}; $\nu_{max.}$ (KBr) 3 290, 1 701, 1 641, and 1 625 cm^{-1}; δ($[^2H_6]Me_2CO$) 9.29br (1 H, D_2O exch., OH), 7.26br (1 H, s, 4-H), 7.05 (1 H, s, 6-H), 3.7 (1 H, sept., *J* 6 Hz, $CHMe_2$), 2.44br (3 H, s, ArMe), and 1.37 (6 H, d, *J* 6 Hz, $CHMe_2$), 1 OH not observed; *m/e* 258 (M^+, 100%), 243 (18), 229 (6), 225 (4), and 115 (4). The identical (i.r., t.l.c., mixed m.p.) compound was isolated from the cold chloroform extract of *H. elatus*.

Lactone of 1,2,7-Trihydroxy-8-naphthoic Acid (21).—A solution of 8-formyl-7-hydroxy-1,2-naphthoquinone (100 mg) in chloroform (100 ml) was left exposed to daylight until it became colourless. After evaporation the residue crystallised from chloroform–methanol (4 : 1) to give the *lactone* as needles, m.p. 228—230° (0.76 g, 76%) (Found: C, 65.2; H, 3.2%; M^+, 202.026 4. $C_{11}H_6O_4$ requires C, 65.3; H, 3.0%; *M*, 202.026 6); $\lambda_{max.}$ (MeOH) 256 and 357 nm (log ε 4.00 and 3.61); $\lambda_{max.}$ (MeOH–HO^-) 270 and 394 nm; $\nu_{max.}$ 3 504, 3 360, 3 210, 1 710, and 1 656 cm^{-1}; δ($[^2H_6]$DMSO) 11.88 and 10.59 (each 1 H, br s, OH), 8.08 (1 H, d, *J* 8 Hz, 5-H), 7.57 (1 H, d, *J* 8 Hz, 6-H), 7.16 (1 H, d, *J* 7 Hz, 3- or 4-H), and 7.02 (1 H, d, *J* 7 Hz, 4- or 3-H).

Lactone of 1,4,7-Trihydroxy-8-naphthoic Acid (22).—(*a*) A solution of 8-formyl-7-hydroxy-1,4-naphthoquinone (72 mg) in chloroform (25 ml) was exposed to daylight. After 2 h crystals of the *lactone* began to separate, and after *ca.* 15 h conversion was complete (100%, t.l.c.). After removal of solvent the lactone was recrystallised from acetic acid as yellow or yellow-brown rods, decomp. 280—290° (Found: C, 64.9; H, 3.2%; M^+, 202.026 4. $C_{11}H_6O_4$ requires C,

65.3; H, 3.0%; *M*, 202.026 6); $\lambda_{max.}$ (MeOH) 230, 279, 342, and 390 nm (log ε 4.04, 4.15, 3.64, and 3.61); $\nu_{max.}$ 3 300br, 1 725, 1 641, and 1 625 cm^{-1}; δ([$^2H_6$]DMSO) 10.12br (1 H, HO), 8.23 (1 H, d, *J* 8 Hz, 5-H), 7.29 (1 H, d, *J* 8 Hz, 7-H), and 7.04 and 6.68 (each 1 H, d, *J* 7 Hz, 2- and 3-H), 1 OH not observed; *m/e* 202 (M^+, 100%), 174 (7), 146 (3), 118 (32), and 89 (10).

(*b*) A solution of 8-formyl-7-hydroxy-1,4-naphthoquinone (64 mg) in toluene-free benzene (90 ml) was irradiated, under nitrogen, with a medium-pressure mercury lamp for 15 min. The lactone, which deposited, was recrystallised from acetic acid, decomp. 280—290° (44 mg), identical with that obtained in (*a*).

X-*Ray Structure Determination*.—Cell parameters were first found from oscillation and Weissenberg photographs and later from least-squares from the setting angles of 20 reflections on a Hilger–Watt four-circle diffractometer.

Crystal Data.—$C_{15}H_{18}O_3$, *M* = 246.3. Orthorhombic, *a* = 7.253(2), *b* = 16.854(3), *c* = 10.794(2) Å, *U* = 1 319.5 Å^3, D_c = 1.24 g cm^{-3}, D_m = 1.24 g cm^{-3}, *Z* = 4, *F*(000) = 528. Space group $P2_12_12_1$ from systematic absences. Mo-K_α radiation (graphite monochromator) λ = 0.710 69 Å, μ = 0.92 cm^{-1}.

Reflections were scanned (ω — 2θ mode) out to θ = 25°. There were 1 365 observable reflections in this range and 888 had a net count >3σ and were deemed observed and used in the subsequent calculations. Lorentz and polarisation, but not absorption, corrections were applied.

The structure was solved routinely using MULTAN.[19] Refinement was by full-matrix least-squares with hydrogen atoms, all located from a difference map, included with *U* = 0.05 but not refined. At convergence the maximum shift was 0.07σ and the conventional *R* was 4.48%.

Table 1 shows the fractional coordinates of the atoms, Table 2 gives the bond angles, and Table 3 the torsion angles. Figure 2 shows the bond lengths and the crystallographic numbering, and Figure 3 is a perspective drawing [20] of the molecule. Apart from MULTAN all computations were done using the Oxford ' CRYSTALS ' [21] system. Thermal parameters and observed and calculated structure factors are available in Supplementary Publication No. SUP 22648 (13 pp.).*

TABLE 1

Fractional co-ordinates (×10^4) with standard deviations in parentheses

Atom	*x*	*y*	*z*
C(1)	−625(7)	9 953(3)	8 447(4)
C(2)	−873(8)	10 669(3)	7 713(5)
C(3)	721(9)	10 801(3)	6 808(5)
C(4)	1 597(8)	10 020(3)	6 326(5)
C(5)	2 250(7)	9 471(3)	7 389(4)
C(6)	2 753(7)	8 618(3)	6 994(4)
C(7)	3 079(7)	8 094(3)	8 149(5)
C(8)	1 465(7)	8 054(3)	9 046(4)
C(9)	343(7)	8 770(3)	9 080(4)
C(10)	728(7)	9 419(3)	8 295(4)
C(11)	−1 246(8)	8 957(3)	9 687(5)
C(12)	2 140(10)	11 346(3)	7 419(6)
C(13)	4 358(7)	8 576(3)	6 068(4)
C(14)	4 600(7)	7 747(3)	5 524(5)
C(15)	6 187(8)	8 867(4)	6 603(6)
O(3)	1 161(5)	7 475(2)	9 685(3)
O(2)	−1 871(5)	9 686(2)	9 320(3)
O(1)	−2 163(6)	11 110(2)	7 799(4)

TABLE 2

Bond angles (°), with standard deviations in parentheses

O(2)–C(1)–C(2)	124.1(5)	C(6)–C(7)–C(8)	114.9(4)
O(2)–C(1)–C(10)	110.1(4)	C(7)–C(8)–C(9)	114.1(4)
C(2)–C(1)–C(10)	125.5(5)	C(7)–C(8)–O(3)	122.5(5)
C(1)–C(2)–O(1)	124.7(6)	O(3)–C(8)–C(9)	123.4(5)
C(1)–C(2)–C(3)	123.3(5)	C(8)–C(9)–C(10)	121.1(4)
O(1)–C(2)–C(3)	112.0(3)	C(8)–C(9)–C(11)	132.6(5)
C(2)–C(3)–C(4)	113.6(4)	C(10)–C(9)–C(11)	106.1(4)
C(2)–C(3)–C(12)	108.7(5)	C(1)–C(10)–C(9)	107.6(4)
C(12)–C(3)–C(4)	112.2(5)	C(1)–C(10)–C(5)	126.0(4)
C(3)–C(4)–C(5)	112.6(4)	C(5)–C(10)–C(9)	126.3(4)
C(4)–C(5)–C(6)	115.1(4)	C(9)–C(11)–O(2)	110.4(4)
C(4)–C(5)–C(10)	107.3(4)	C(1)–O(2)–C(11)	105.8(4)
C(10)–C(5)–C(6)	107.7(4)	C(6)–C(13)–C(14)	112.4(4)
C(5)–C(6)–C(7)	110.2(4)	C(6)–C(13)–C(15)	113.4(4)
C(5)–C(6)–C(13)	113.7(4)	C(14)–C(13)–C(15)	109.9(5)
C(13)–C(6)–C(7)	112.5(4)		

TABLE 3

Torsion angles (°)

O(1)–C(8)–C(9)–C(10)	−178.4	O(1)–C(8)–C(9)–C(11)	−5.1	C(7)–C(8)–C(9)–C(10)	2.4
C(7)–C(8)–C(9)–C(11)	175.7	O(1)–C(8)–C(7)–C(6)	150.0	C(9)–C(8)–C(7)–C(6)	−30.8
C(11)–O(2)–C(1)–C(10)	−1.0	C(11)–O(2)–C(1)–C(2)	172.9	C(1)–O(2)–C(11)–C(9)	0.5
O(2)–C(1)–C(10)–C(5)	176.1	O(2)–C(1)–C(10)–C(9)	1.1	C(2)–C(1)–C(10)–C(5)	2.3
C(2)–C(1)–C(10)–C(9)	−172.7	O(2)–C(1)–C(2)–O(3)	1.3	O(2)–C(1)–C(2)–C(3)	−178.9
C(10)–C(1)–C(2)–C(3)	174.2	C(10)–C(1)–C(2)–C(3)	−6.0	C(6)–C(5)–C(10)–C(1)	−147.9
C(6)–C(5)–C(10)–C(9)	26.2	C(4)–C(5)–C(10)–C(1)	−23.4	C(4)–C(5)–C(10)–C(9)	150.7
C(10)–C(5)–C(6)–C(7)	−51.3	C(10)–C(5)–C(6)–C(13)	−178.7	C(4)–C(5)–C(6)–C(7)	−171.0
C(4)–C(5)–C(6)–C(13)	61.7	C(10)–C(5)–C(4)–C(3)	47.8	C(6)–C(5)–C(4)–C(3)	167.7
C(8)–C(9)–C(10)–C(1)	174.1	C(8)–C(9)–C(10)–C(5)	−0.9	C(11)–C(9)–C(10)–C(1)	−0.7
C(11)–C(9)–C(10)–C(5)	−175.7	C(8)–C(9)–C(11)–O(2)	−173.9	C(10)–C(9)–C(11)–O(2)	0.1
C(5)–C(6)–C(7)–C(8)	57.1	C(13)–C(6)–C(7)–C(8)	−174.9	C(5)–C(6)–C(13)–C(14)	−169.9
C(5)–C(6)–C(13)–C(15)	64.8	C(7)–C(6)–C(13)–C(14)	63.9	C(7)–C(6)–C(13)–C(15)	−61.4
C(1)–C(2)–C(3)–C(4)	31.8	C(1)–C(2)–C(3)–C(12)	−93.9	O(3)–C(2)–C(3)–C(4)	−148.4
O(3)–C(2)–C(3)–C(12)	85.9	C(5)–C(4)–C(3)–C(2)	−55.2	C(5)–C(4)–C(3)–C(12)	68.6

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