

A NEW BISJUGLONE FROM *JUGLANS REGIA* ROOT BARK

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Key Word Index—*Juglans regia*; Juglandaceae; 3,3'-bisjuglone.

The isolation and structure elucidation of cyclo-*tris*-juglone [1] has been reported earlier from the chloroform extracts of *Juglans regia* root bark. Column chromatography of the chloroform extract yielded yet another quinonoid pigment mp 270°; sparingly soluble in organic solvents and giving a violet colour with NaOH. That it is a quinonoid pigment is indicated by its reversible oxidation and reduction with sodium dithionite.

Its IR spectrum indicated bonded and nonbonded carbonyl groups but no hydroxylic absorption. Its UV spectrum in dioxane 272(4.06) and 425(3.66) nm indicated the presence of a *peri* hydroxy-1,4-naphthoquinone system in the molecule. Its mass spectrum shows the molecular ion at 346 and successive losses of four CO units. Hence, the natural product is a bimer of juglone. It yielded a hexaleucoacetate (2) on reductive acetylation indicating the presence of two naphthoquinone moieties with two hydroxy substituents in the molecule. It gave a dimethyl ether (3) and a monomethyl ether (4) on methylation. The PMR (100 MHz, CDCl₃) of the hexaleucoacetate showed three different acetoxy signals at δ 2.02(6H, s), 2.34(6H, s) and 2.44(6H, s). The signal at 2.02 is ascribed to C-4, C'-4 acetoxy groups shielded due to aromatic ring currents. The aromatic protons are seen at δ 7.14(2H, q, $J_{BC} = 8$ Hz, $J_{AC} = 2$ Hz, C-6 and C'-6), 7.52 (2H, t, $J_{BC} = J_{AB} = 8$ Hz, C-7 and C'-7) and 7.8(2H, q, $J_{AB} = 8$ Hz, $J_{AC} = 2$ Hz, C-8 and C'-8). The two aromatic protons *ortho* to the binaphthyl linkage are seen merged with the chloroform signal in CDCl₃ at 7.32. Hence, the natural product (1) is a symmetrical bimer with quinone-quinone linkage (3,3' or 2,2').

The natural product and its two methyl ethers are not soluble enough to record PMR spectra. The dimethyl ether (3) when exposed to sunlight in chloroform-ethanol, underwent a photo-rearrangement [2] to yield a deep purple compound *iso*-bisjuglone dimethyl ether (5). Its IR spectrum showed a broad hydroxylic stretching absorption at 3325 cm⁻¹ and non-bonded carbonyl

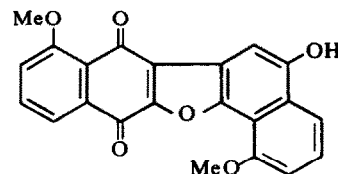
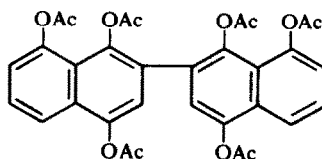
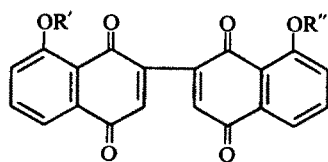
at 1650 cm⁻¹ (cf. broad hydroxylic stretching in dimethyl isodianellinone [3] at 3300 cm⁻¹). The PMR spectrum of (5) also could not be recorded due to its insolubility. As the bisjuglone (1) itself is stable to sunlight, it is obvious that the rearrangement is inhibited by hydrogen bonding of the carbonyls involved in cyclization. Removal of the hydrogen bonding by methylation permits this photo-rearrangement, indicating that the two carbonyl groups *ortho* to the linkage are hydrogen bonded with *peri*-hydroxyl group. Hence, the natural product has been assigned structure (1) with 3,3'-linkage.

Mass spectrum of (1) shows peaks characteristic of juglone while successive loss of four CO units is characteristic of bimeric naphthoquinones. The co-occurrence of 3,3'-bisjuglone and cyclo-*tris*-juglone [1] in *J. regia* is of interest because analogous compounds derived from 7-methyljuglone viz. mamegakinone [4] and xylopyrin [5] have been reported earlier from *Diospyros* species. Although this is the first report of the natural occurrence of 3,3'-bisjuglone, the compound has recently been synthesized in the laboratory [6].

EXPERIMENTAL

3,3'-bisjuglone (1). The residue of the CHCl₃ extract of *J. regia* root bark was chromatographed on a Si gel column and eluted with C₆H₆. Collection of the fractions and concn gave 3 compounds JR-3, JR-4 and JR-5 in the order of increasing polarity. JR-3 and JR-5 were found to be juglone and cyclo-*tris*-juglone, respectively. JR-4 was crystallized from C₆H₆ as orange crystals, mp 270° (decomp), 0.012%. (Found: C, 69.00; H, 2.97. C₂₀H₁₀O₆ requires: C, 69.37; H, 2.91%). $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3030, 1660, 1625, 1600, 1565; MS *m/e*: 346 (62), 329 (19), 318 (10), 290 (24), 289 (31), 262 (38), 234 (32), 120 (100) and 92 (81).

3,3'-bisjuglone dimethyl ether (3). 3,3'-Bisjuglone (30 mg) dissolved in CHCl₃ (50 ml) was shaken with MeI (4 ml) and Ag₂O (200 mg) at room temp. for 6 hr. The product was purified by chromatography and crystallized from CHCl₃-petrol (1:3) as light yellow crystals, mp 250°, yield 23 mg. $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 250 (4.70), 400 (4.68); $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3070, 1650, 1590.



1 R' = R'' = H
3 R' = R'' = Me
4 R' = H, R'' = Me

3,3'-bisjuglone monomethyl ether (4). 3,3'-Bisjuglone (25 mg) in CHCl_3 (35 ml) was shaken with MeI (2 ml) and Ag_2O (150 mg) at room temp. Formation of the monomethyl ether of 3,3'-bisjuglone was followed by TLC. The monomethyl ether was isolated after chromatography and crystallized from C_6H_6 in yellow crystals (10 mg), mp 270° ; $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3060, 1660, 1630 and 1610, $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 255 (4.44), 412 (3.93).

Dimethyl isobisjuglone (5). 3,3'-Bisjuglone dimethyl ether (20 mg) in CHCl_3 (15 ml) and a little EtOH , was exposed to sunlight for 3 hr. Dimethyl *iso*-bisjuglone separated as deep purple coloured crystals (19 mg), mp 324° . (Found: C, 69.61; H, 3.59, $\text{C}_{22}\text{H}_{14}\text{O}_6$ requires: C, 70.59; H, 3.77%). $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3325, 2900, 2820, 1650; $\lambda_{\text{max}}^{\text{Dioxane}}$ nm: 265(2.47), 295(1.83), 370(1.29) and 490(1.53).

3,3'-bisjuglone hexaleucoacetate (2). 3,3'-Bisjuglone (50 mg), dry NaOAc (100 mg), Zn dust (240 mg) and Ac_2O (9 ml) were refluxed for 2 hr. The product, after chromatography and crystallization from CH_2Cl_2 - MeOH , was colourless (45 mg),

mp 275° . (Found: C, 63.80; H, 4.51. $\text{C}_{32}\text{H}_{26}\text{O}_{12}$ requires: C, 63.87; H, 4.35%). $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2920, 1745, 1600, 1490, 1415; $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 235(4.80), 253 sh (4.60), 280(4.07) and 292(4.07).

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2-METHYLANTHRAQUINONE FROM *CLAUSENA HEPTAPHYLLA*

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In the previous communication [1], we reported several carbazole alkaloids including 3-methylcarbazole [2] (1), the progenitor of the carbazole alkaloids, from *Clausena heptaphylla* Wt. & Arn. We now report the isolation of 2-methylantraquinone from a petrol extract of the stem bark of the same plant. It had mp 178° , M^+ 222 ($\text{C}_{15}\text{H}_{10}\text{O}_2$) and NMR signals δ 7.7–8.6 (m, 7, ArH) and 2.65 (s, ArCH_3). It was identical by mmp, UV, IR and TLC with authentic material.

The co-occurrence of 2-methylantraquinone and 3-methylcarbazole in *Clausena heptaphylla* suggests that the ring C of carbazole alkaloids is of mevalonoid origin, as is ring C of 2-methylantraquinone [3]. Proof of the mevalonoid origin of ring C of carbazole alkaloids however awaits biosynthetic investigation.

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