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TECOMAQUINONE-III: A NEW QUINONE FROM *TABEBUIA PENTAPHYLLA*

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Key Word Index—*Tabebuia pentaphylla*; Bignoniaceae; tecomaquinone; 1,4-naphthoquinone.

Abstract—Tecomaquinone-III, isolated from the heartwood of *Tabebuia pentaphylla*, has been identified as 6,10,15-trihydro-9(2-hydroxy-2-methylpropyl)-6,6-dimethyldibenzo[a,i]pyrano[2′,3′-c]xanthen-10,15-quinone by spectroscopic methods.

The heartwood of *Tabebuia pentaphylla* (Bignoniaceae) contains [1] several C_{15} naphthoquinones related to lapachol, and two dimeric C_{30} quinones, tecomaquinone-I (**1**) [1, 2] and tecomaquinone-II (**2**) [1, 3]. We now describe a third C_{30} quinone, tecomaquinone-III (**3**) from the same source.

The violet pigment, tecomaquinone-III, is reversibly reduced with dithionite, and there is IR, ^1H and ^{13}C NMR evidence for two quinone carbonyls and a tertiary hydroxyl group (see Experimental). As the molecular formula is $C_{30}H_{26}O_5$ the two remaining oxygens must be in ether bridges. One of these is a pyran ring like that in **1** as the ^1H NMR spectrum contains methyl singlets at $\delta 1.49$ and 1.52, coupled vinyl doublets at 5.80 and 6.71 ($J = 10.0$ Hz), and the ^{13}C NMR spectrum includes a singlet at $\delta 76.11$. The remainder of the ^1H NMR spectrum comprises signals for eight aromatic protons, two further methyl singlets ($\delta 1.08$ and 1.39), and a methine double doublet at $\delta 4.73$ coupled to a 2H methylene multiplet at 1.87. These aliphatic signals we ascribe to a $-CH-CH_2-C(OH)Me_2$ side chain located at C-9 in **3** to account for (i) the base peak in the MS at $[M - C_4H_9O]^+$ (accurately measured), (ii) a singlet in the ^{13}C NMR spectrum at $\delta 70.25$ and (iii) the optical activity of the pigment (measured on the leucotriacetate). Further, heteronuclear decoupling established that the methine proton resonating at $\delta 4.73$ is attached to a carbon at $\delta 25.85$, i.e. the side chain is attached to carbon and is not linked to oxygen (cf. **1**).

The combined evidence shows that tecomaquinone-III has structure **3** which is isomeric with **1** $(+H_2O)$. As tecomaquinone-III does not react with *o*-phenylenediamine in boiling methanol (3 hr) the alternative *o*-quinone structure can be excluded.

EXPERIMENTAL

Tecomaquinone-III (6,10,15-*trihydro*-9(2-*hydroxy*-2-*methylpropyl*)-6,6-*dimethyldibenzo*[*a,i*]*pyrano* [2′,3′-*c*]*xanthen*-10,15-*quinone*) (**3**). *Tabebuia pentaphylla* heartwood was extracted and the residue chromatographed on silica gel as before [1]. Elution with C_6H_6 afforded a violet fraction which was purified by PLC in C_6H_6–Me_2CO (4:1) to give **3** as dark violet crystals, mp 219–222° (Me_2CO–petrol). Found: C, 77.4; H, 5.5%; $[M]^+$, 466.1785. ($C_{30}H_{26}O_5$ requires C, 77.3; H, 5.6%; M, 466.1779); UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 252, 269, 278, 341, 354sh, 524 (4.56, 4.49, 4.48, 3.81, 3.78, 3.20; λ_{max}^{MeOH} nm 484; IR ν_{max}^{KBr} cm^{-1}: 3530, 3450 *br*, 1672, 1655, 1632, 1592, 1344, 1255, 1200; ^1H NMR (360 MHz, $CDCl_3$): $\delta 1.08$, 1.39 [each 3H, *s*, $Me_2C(OH)$], 1.49 1.52 (each 3H, *s*, Me_2C), 1.87 (2H, *ddd*, $J = 14.6, 9.4, 3.4$ Hz, CH_2), 2.26 (1H, *br s*, OH), 4.73 (1H, *dd*, $J = 9.4, 3.4$ Hz, $\underline{CH}CH_2$), 5.80, 6.71 (each 1H, *d*, $J = 10.0$ Hz, CH=CH), 7.48 (1H, *dt*, $J = 6.9, 1.3$ Hz, ArH), 7.55 (1H, *dt*, $J = 6.9$, 1.3, Hz, ArH), 7.72 (2H, *m*, ArH), 8.16 (3H, *m*, ArH), 8.39 (1H, *d*, $J = 8.1$ Hz); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta 25.85$ (*d*), 27.26 (*q*), 27.48 (*q*), 29.45 (*q*), 30.72 (*q*), 51.46 (*t*), 70.25 (*s*), 76.11 (*s*), 111.73 (*s*), 116.59 (*s*), 118.00 (*d*), 121.18 (*d*),121.82 (*d*), 124.22 (*s*), 124.48 (*s*), 125.28 (*s*), 125.96 (*d*), 126.35 (*d*), 126.50 (*d*), 127.03 (*d*),130.73 (*d*), 130.90 (*s*), 132.19 (*s*), 133.49 (*d*), 134.02 (*d*), 139.80 (*s*), 146.36 (*s*), 152.97 (*s*), 178.12 (*s*), 185.70 (*s*); EIMS (probe) 70 eV, *m/z* (rel. int.) 466 (21, M^+), 451 (10), 394 (32), 393.1147 ($C_{26}H_{17}O_4$ requires 393.1127, 100) $[M^+-C_4H_9O]$, 378 (9), 364 (13), 189 (13).

The leucotriacetate (Ac_2O–NaOAc–Zn) crystallized from aq. MeOH in small plates, mp 215–217°. Found: $[M]^+$, 594.2249 ($C_{36}H_{34}O_8$ requires M, 594.2253); $[\alpha]_D^{20}$ $-1.01°$ ($CHCl_3$; *c* 0.4); UV λ_{max}^{MeOH} nm: 232, 268, 277, 349 (w); IR ν_{max}^{KBr} cm^{-1}: 1770, 1731, 1650 (w), ^1H NMR (220 MHz, $CDCl_3$): $\delta 1.32$ [6H, *s*, $Me_2C(OAc)$], 1.43, 1.45 (each 3H, *s*, Me_2C), 1.50, 2.57, 2.64 (each 3H, *s*, 3 × OAc), 2.19, 2.30 (each 2H, *dd*, $J = 6.5$ and 16 Hz, CH_2), 4.76 (1H, *t*, $J = 6.5$ Hz, $\underline{CH}CH_2$), 5.77, 6.67 (each 1H, *d*, $J = 11$ Hz, CH=CH), 7.48 (4H, *m*, ArH), 7.71, 7.88 (each 1H, *dd*, $J = 2$ and 9 Hz, ArH), 8.16 (2H, *dd*, $J = 2$ and 9 Hz); EIMS (probe) 70 eV, *m/z* (rel. int.): 594 (M^+, 40), 479.1475 ($C_{30}H_{23}O_6$ requires 479.1494, 80) $[M^+ - C_6H_{11}O]$, 437.1366 ($C_{28}H_{21}O_5$ requires 437.1386, 100) $[M^+ - C_6H_{11}O - C_2H_2O]$, 395 (10), 394 (35), 393 (52), 379 (28), 208 (20).

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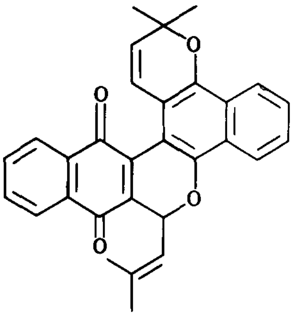

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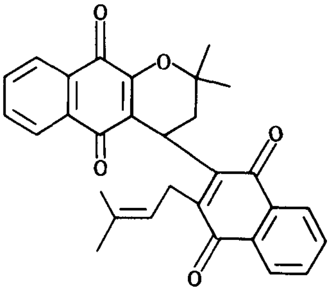

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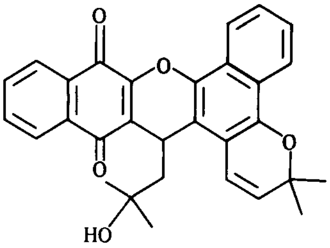

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