# Balanocarpol, a New Polyphenol from *Balanocarpus zeylanicus* (Trimen) and *Hopea jucunda* (Thw.) (Dipterocarpaceae)

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Balanocarpol, a new polyphenol, has been isolated from two endemic dipterocarp species and has been shown to have a similar biogenetic origin to that of hopeaphenol.

*Balanocarpus zeylanicus* and *Hopea jucunda* are two endemic dipterocarpaceae species. In our continuing studies[1-3] of the polyphenols of the Dipterocarpaceae, we have now examined the polyphenols of *B. zeylanicus* and *H. jucunda* and herein we report the isolation of a new polyphenol, balanocarpol (**2**), from the bark acetone extracts of both species.

## Results and Discussion

The bark acetone extracts of *Balanocarpus zeylanicus* gave a brown powder which on chromatographic separation gave a pure polyphenol which we have named balanocarpol, m.p. 240 °C; $[\alpha]_D$ −17° (MeOH). Balanocarpol was assigned structure (**2**) on the basis of the following data. Its molecular formula is $C_{28}H_{22}O_7$ ($M^+$, 470.1348). The i.r. spectrum showed the presence of OH (3 250 $cm^{-1}$), –C=C– (1 600 $cm^{-1}$), and 1,4-disubstituted benzene nuclei (830 $cm^{-1}$). The u.v. spectrum indicated that balanocarpol was similar to the other polyphenols isolated by us,[1-3] with its main absorption at $\lambda_{max.}$ 290 nm. The mass spectrum gave several fragment ions at *m/z* 94 (100%, $PhO\overset{+}{H}H$), 452 (35, $M^+ - H_2O$), and 376 ($M^+$ − PhOH), indicating the compound to be a (poly)phenol. Dimethyl sulphate methylation even under forced conditions gave only a pentamethyl derivative. Acetylation with pyridine–acetic anhydride resulted in the formation of a hexa-acetate. This observation, coupled with the prominent mass fragment at *m/z* 452 ($M^+ - H_2O$), shows that balanocarpol contains five phenolic hydroxy groups and probably one aliphatic hydroxy group. This accounts for six of the seven oxygen atoms in the molecular formula. The remaining oxygen atom may be present as an ether linkage as in the other polyphenols isolated[1,2] from Dipterocarpaceae.

Balanocarpol pentamethyl ether, m.p. 105 °C, $[\alpha]_D$ +2.0° ($CHCl_3$), was subjected to high-resolution $^1$H n.m.r. (250 MHz) studies. It showed the presence of (i) four sets of *ortho*-coupled protons at $\delta_H$ 6.57 (2 H, d, *J* 8.7 Hz), 6.77 (2 H, d, *J* 8.7 Hz), 7.02 (2 H, d, *J* 8.7 Hz), and 7.59 (2 H, d, *J* 8.7 Hz); (ii) four *meta*-coupled protons at $\delta_H$ 6.03 (1 H, d, *J* 2.2 Hz), 6.21 (1 H, d, *J* 2.2 Hz), 6.22 (1 H, d, *J* 2.4 Hz), and 6.28 (1 H, d, *J* 2.4 Hz); (iii) two *trans*-coupled protons at $\delta_H$ 5.28 (1 H, d, *J* 9.9 Hz) and 5.79 (1 H, d, *J* 9.9 Hz) and two *cis*-coupled protons at $\delta_H$ 4.88 (1 H, d, *J* 1.8 Hz) and 5.40 (1 H, d, *J* 1.8 Hz).

$D_2O$ exchange showed that the hydroxyl proton is coupled with the proton at $\delta_H$ 5.40. This signal underwent a low-field shift in the $^1$H n.m.r. spectrum of balanocarpol hexa-acetate. The *meta*-coupled proton signal at $\delta_H$ 6.03 is broadened by long-range coupling with the aliphatic proton at $\delta_H$ 5.40 as shown by homodecoupling experiments. Irradiation at $\delta_H$ 5.40 results also in collapse of the signal at $\delta_H$ 4.88 to a singlet, thus indicating vicinal coupling. The aromatic proton at $\delta_H$ 6.03 can be seen in a nuclear Overhauser enhancement (n.O.e.) difference experiment by saturation of the signal at $\delta_H$ 5.40 which leads also to an enhancement of the signals at $\delta_H$ 4.88 and $\delta_H$ 5.28. From this n.O.e. experiment the relative configuration of the protons at $\delta_H$ 5.40 and $\delta_H$ 5.28, the latter being attached to the five-membered ring, is established as *cis*.

Irradiation at $\delta_H$ 5.28 results in the signal at $\delta_H$ 5.79 collapsing to a singlet. The coupling constant ($^3J$ 9.9 Hz) shows the orientation of these protons to be *trans*. Saturation of the proton at $\delta_H$ 5.79 showed n.O.e.s of the proton signals at $\delta_H$ 7.59 and 6.77 (protons of the freely rotating *para*-substituted aromatic rings), and of the aromatic proton signal at $\delta_H$ 6.22 which is *meta*-coupled to the proton at $\delta_H$ 6.28. By these n.O.e. experiments the relative configurations of all asymmetric centres in the molecule and the conformation of the seven-membered ring were established. The assigned structure and the complete $^1$H n.m.r. data for balanocarpol pentamethyl ether are given in the Figure.

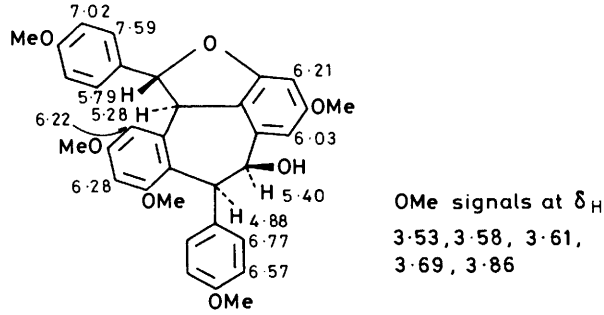
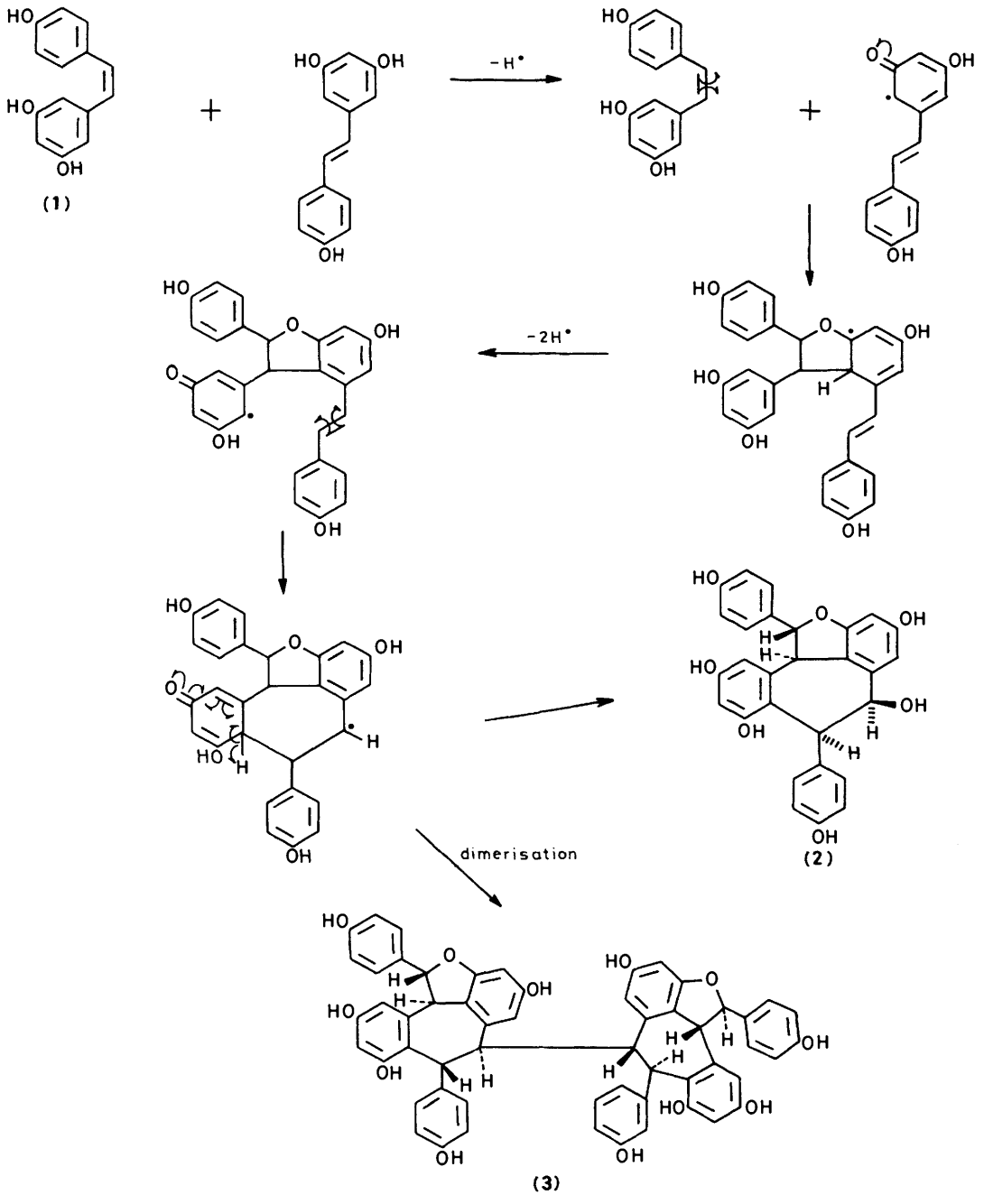



**Figure.** $^1$H Chemical shifts of balanocarpol pentamethyl ether in $CDCl_3$ (250 MHz)

The $^{13}$C n.m.r. spectrum of balanocarpol pentamethyl ether showed the presence of (i) four aliphatic carbon atoms of the CH type at $\delta_C$ 49.50, 52.15, 72.72, and 93.00 p.p.m.; (ii) eight aromatic carbon atoms of the CH type at $\delta_C$ 94.23, 97.71, 101.71, 103.54, 112.71, 114.52, 128.58, and 130.32 p.p.m. The signals at $\delta_C$ 112.71, 114.52, 128.58, and 130.32 p.p.m. integrated for two carbon atoms each, because of the $C_2$ symmetry of the *para*-substituted aromatic ring; (iii) twelve aromatic quarternary aromatic carbon atoms at $\delta_C$ 113.81, 121.84, 132.04, 133.14, 138.54, 140.83, 157.83, 158.68, 159.03, 159.16, 160.13, and 161.39 p.p.m. These data show that balanocarpol pentamethyl ether contains twenty-four aromatic and four aliphatic carbon atoms. It is probable that balanocarpol ($C_{28}H_{22}O_7$) is derived from two resveratrol ($C_{14}H_{12}O_3$) units, thus accounting for all the

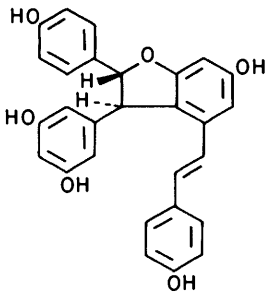



**Scheme.** Postulated biosynthesis route to balanocarpol (**2**) and hopeaphenol (**3**)

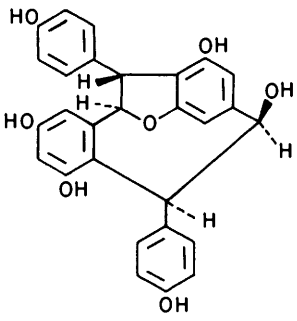
aromatic and aliphatic carbon atoms. Two of the possible twenty-four hydrogen atoms seem to be lost during the dimerisation of resveratrol units which leads to balanocarpol. The additional oxygen atom is probably inserted during biosynthesis as shown in the Scheme. The proposed structure (**2**) for balanocarpol can thus be accommodated by the biosynthetic Scheme. Other biosynthetic pathways for the dimerisation of two resveratrol (**1**) units by the phenol oxidative coupling mechanism are of course possible.

One such dimerisation results in the formation of ε-viniferin (**4**) which was isolated by us[3] in another study of a Dipterocarp species, *Vatica affinis*. Though compound (**4**) could be easily hydrogenated in the presence of a catalyst, resulting in the reduction of the C=C bond, balanocarpol was resistant to hydrogenation. This observation ruled out an ε-viniferin (**4**)-type skeleton for balanocarpol. The resveratrol dimer (**5**) can also accommodate most of the observed $^1$H n.m.r. and $^{13}$C n.m.r. data for balanocarpol. However, structure (**5**) requires balanocarpol to possess a highly strained nine-membered ring as opposed to the proposed structure (**2**) which possesses a seven-membered ring. Besides, King and co-workers[4] characterised the first polyphenol, hopeaphenol, from *Hopea odorata* and *Balanocarpus heimii* and assigned the structure (**3**) from *X*-ray crystallographic studies.[5]

Balanocarpol was also isolated by us from another dipterocarp species, *Hopea jucunda* (see above), and *Balanocarpus zeylanicus* was once reclassified by Ashton on taxonomic evidence[6] as a *Hopea* species, *viz. Hopea brevipetiolaris*. The



(4)



(5)

isolation of balanocarpol (**2**) and hopeaphenol (**3**) from *Hopea* species points to a common biosynthetic origin for these two polyphenols as shown in the Scheme, and favours structure (**2**) for balanocarpol.

Although Ashton[6] reclassified *Balanocarpus zeylanicus* as *Hopea brevipetiolaris*, Kostermans has more recently reinstated the earlier classification and maintained that this species is distinct from the *Hopea* species and should be described as *Balanocarpus brevipetiolaris* (Thw.) Alston. Our present results justify the amalgamation of the genus *Balanocarpus* into *Hopea* as proposed by Ashton.[6]

## Experimental

The bark of *Balanocarpus zeylanicus* (= *Hopea brevipetiolaris* Thw. Alston) was collected in the Central Hill Country of Sri Lanka, whereas *Hopea jucunda* was collected from the Kanneliya rain forest reserve in the south of Sri Lanka. The powdered bark was, in each case, extracted with cold acetone for 7 days. The solvent evaporated off to give a pale brown solid which, on column chromatographic separation (silica gel) and elution with acetone–benzene (3:7), gave the crude phenol which was further purified by preparative t.l.c. (p.l.c.) (silica gel) with acetone–benzene (2:3) as developer. M.p.s were obtained using a Kofler melting-point apparatus. I.r. spectra were obtained using a Perkin-Elmer model 257 spectrophotometer. U.v. spectra were obtained using a Pye Unicam SP 3000 spectrophotometer. The high-resolution $^1H$ n.m.r. and $^{13}C$ n.m.r. spectra were obtained using a Brucker WM 250 (250 MHz) instrument and the mass spectra were obtained using a Varian MAT 311A instrument. Optical rotations were measured on a Perkin-Elmer (Model 241) instrument.

*Balanocarpol* (**2**).—Balanocarpol was obtained as an *amorphous solid*, m.p. 240 °C; $[\alpha]_D$ −17° [*c* 5 mg in MeOH (10 ml)]); (Found: $M^+$, 470.1348. $C_{28}H_{22}O_7$ requires *M*, 470.1696); $\lambda_{max.}$(MeOH) 290 nm (log ε 4.02); $\nu_{max.}$(KBr) 3 000—3 600, 1 600, 1 500, 1 440, 1 340, 1 225, 1 170, 1 130, 1 030, 985, and 830 $cm^{-1}$; $\delta_H$ ($CD_3OD$ + $CDCl_3$; 250 MHz) 5.14 (1 H, d, *J* 9.2 Hz), 5.39 (1 H, d, *J* 2.0 Hz), 5.72 (1 H, d, *J* 9.2 Hz), 5.98 (2 H, s), 6.17 (2 H, s), 6.41 (2 H, d, *J* 8.5 Hz), 6.69 (2 H, d, *J* 8.5 Hz), 6.92 (2 H, d, *J* 8.4 Hz), and 7.46 (2 H, d, *J* 8.4 Hz); *m/z* 470 (25%), 452 (35), 376 (7), 348 (70), 254 (15), 107 (20), and 94 (100).

*Balanocarpol Pentamethyl Ether.*—A solution of balanocarpol (**2**) (230 mg) in acetone (5 ml) was heated under reflux for 24 h with $Me_2SO_4$ (1 ml) and $K_2CO_3$ (500 mg). The product was isolated in the usual way and was purified by p.l.c. [silica gel; MeOH–$CH_2Cl_2$ (1:100)] to give the pure product (110 mg). This was recrystallised from $CH_2Cl_2$–light petroleum (b.p. 40—60 °C) to give an amorphous solid, m.p. 105 °C; $[\alpha]_D$ +2.0° [*c* 5 mg in MeOH (10 ml)]; (Found: $M^+$, 540); $\lambda_{max.}$(MeOH) 283 nm (log ε 4.00); $\nu_{max.}$(KBr) 3 450, 2 950, 1 600, 1 450, 1 250, 1 130, 1 030, and 830 $cm^{-1}$; $\delta_H$ ($CDCl_3$; 250 MHz) see Figure.

*Balanocarpol hexa-acetate.*—A solution of Balanocarpol (100 mg) in pyridine (1.5 ml) and acetic anhydride was left at room temperature for 2 days. The product was purified by p.l.c. [silica gel; MeOH–$CH_2Cl_2$ (1:100)] to yield the hexa-acetate as a white amorphous powder, m.p. 180—181 °C; $[\alpha]_D$ −16° [*c* 5 mg in $CHCl_3$(10 ml)]; $\delta_H$ ($CDCL_3$; 250 MHz) 4.78 (1 H, d, *J* 1.3 Hz), 5.40 (1 H, d, *J* 8.7 Hz), 5.92 (1 H, d, *J* 8.7 Hz), 6.03 (1 H, d, *J* 1.3 Hz), 6.43 (1 H, d, *J* 1.9 Hz), 6.52 (1 H, d, *J* 1.9 Hz), 6.70 (2 H, d, *J* 8.7 Hz), 6.78 (1 H, d, *J* 2.2 Hz), 6.83 (2 H, d, *J* 8.7 Hz), 6.87 (1 H, d, *J* 2.2 Hz), 7.24 (2 H, d, *J* 8.8 Hz), and 7.65 (2 H, d, *J* 8.8 Hz); *m/z* 722 ($M^+$, 5%), 662 (50), 620 (75), 578 (100), 536 (90), and 485 (60).

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