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ANODIC OXIDATION OF 2-PROPENYLPHENOLS

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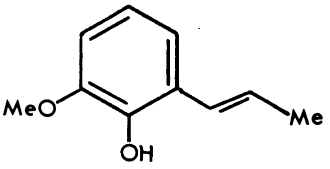
Anodic oxidation of 2-propenylphenols in MeOH was carried out under various conditions, using an undivided cell, to afford several oxidation products including the corresponding asatone-, carpanone-, arylpropanoid-, and austrobailignan-type compounds. Among them, the carpanone-type neolignans can be produced *via* the corresponding bis-*o*-quinonemethides.

From view points of physiological and biological activities (antitumor substances, plant germination inhibitors, and growth inhibitors against insects), structural and synthetic studies on both lignans and neolignans have been attracting increasing attention. In connection with these neolignans, we wish to describe anodic oxidation of 2-propenylphenols giving some new results remarkably different from those of 4-propenylphenols,[1] as demonstrated in the case of two conjugated ones (1 and 2).

A 200 ml glassy carbon beaker (GC-20, geometrical surface area: 120 cm^2) and a GC disk (0.2 cm^2) were used as an anode and an auxiliary electrode, respectively, without separation, unless otherwise stated. A solution of 1 (2 mmol) in MeOH (200 ml) containing $LiClO_4$ (40 mmol) was electrolyzed at a controlled potential (+900 mV *vs*. SCE) and quenched at 1.2 F/mole to afford an asatone-type dimer (3) and two arylpropanoids (4a and 4b) in 25, 1.4, and 1.4% yields,[2] respectively, the structures of which were supported by their physical data.[3] In the case of higher controlled potential (+1600 mV *vs*. SCE),[4] the dimer (3) was obtained in 44% yield, in addition to small amounts of new dienones (5 and 6),[5] both of which are -4e products and must be produced by further oxidative methoxylation at the double bond centered in a plausible *o*-quinonemethide intermediate. On addition of AcOH (200 mmol),[6] the compounds (5 and 6) were produced in 6.8 and 6.6% yields, respectively, although the yield of 3 was reduced to 26%. On the other hand, when electrolyzed in MeOH containing NaOH (5 mmol) at a controlled current density (0.083 mA/cm^2) and quenched at 1.1 F/mole, the phenol (1) was converted into a carpanone-type compound (7),[7] in 16% yield, *via* a plausible bis-*o*-quinonemethide (8), as described later.



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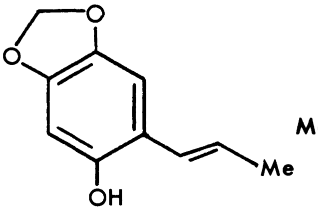

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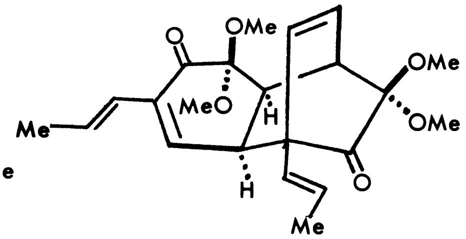

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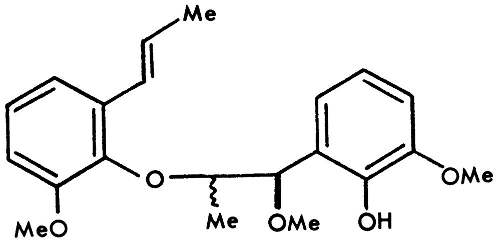
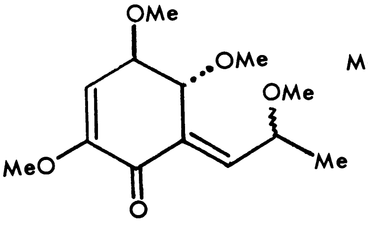


4a (threo); 4b (erythro)



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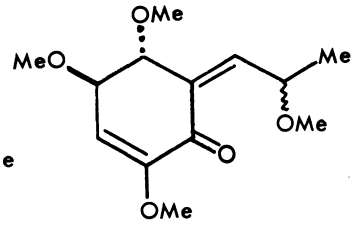

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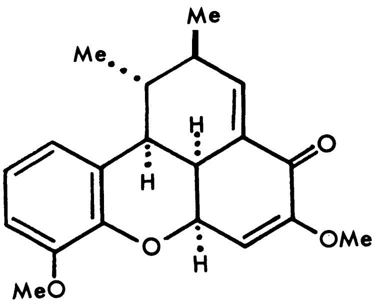

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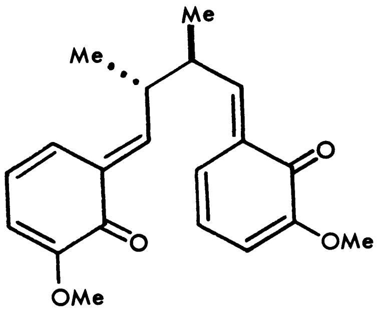

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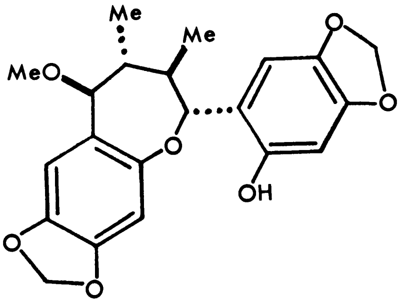

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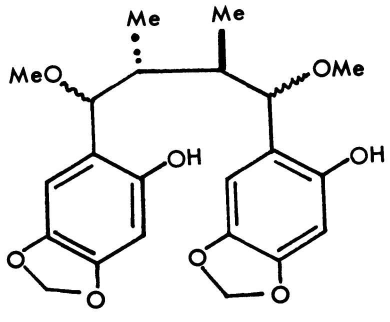

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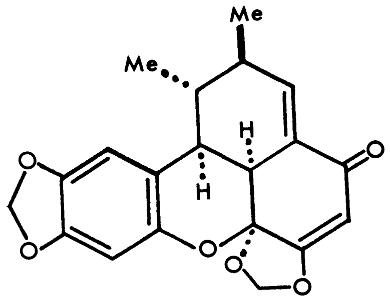

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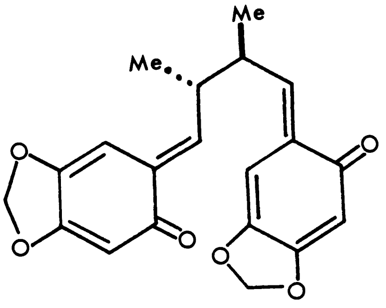

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Anodic oxidation of the conjugated phenol (2) (2 mmol) in MeOH (200 ml) containing $LiClO_4$ (40 mmol) was also carried out at a controlled potential (+600 mV *vs*. SCE) and quenched at 1.0 F/mole to give several oxidation products, from which three radical-coupling dimers (9, 10, and 11) and 2-hydroxy-4,5-methylenedioxybenzaldehyde (12) were obtained in 44, 15, 11, and *ca*. 1% yields, respectively. Among them, the spectral data of the compound (11) were completely identical with those of carpanone.[8] The structures of the remaining compounds were determined by their spectral data.[9] Presumably, these three dimeric compounds (**9**, **10**, and **11**) seem to be derived from the common intermediate of the plausible bis-*o*-quinonemethide (**13**), as suggested by Chapman *et al.*[10] Further studies on such highly reactive species as *o*- and *p*-quinonemethides are in progress.

References and Notes

1. M. Iguchi, A. Nishiyama, Y. Terada, and S. Yamamura, Analytical Lett., **12 (A10)**, 1079 (1979) and references cited therein.
2. The yields indicate the isolated ones, unless otherwise stated.
3. **3**: mp 122-125 °C; $C_{22}H_{28}O_6$ [m/e 388(M^+)]; ν_{max}(KBr) 1740, 1710, and 1650 cm^{-1}; δ($CDCl_3$) 1.78 (3H, d, J= 6.5Hz), 1.86(3H, d, J= 6.5Hz), 3.05(3H, s), 3.19(3H, s), 3.39(3H, s), 3.44(3H, s), 2.9-3.4(3H, superimposed on MeO signals), and 5.6-6.4(7H, complex). **4a** (threo): mp 208-210 °C; $C_{21}H_{26}O_5$ [m/e 358(M^+)]; ν_{max}(KBr) 3430br., 1600, 1580, and 1480br.cm^{-1}; δ(CCl_4) 1.02(3H, d, J= 6Hz), 1.87(3H, dd, J= 6.5, 2Hz), 3.21(3H, s), 3.72(3H, s), 3.84(3H, s), 4.45(1H, quintet, J= 6Hz), 4.68(1H, d, J= 6Hz), 5.98(1H, dq, J= 15.5, 6.5Hz), 6.14(1H, s), and 6.5-6.9(7H, complex). **4b** (erythro): mp 204-206 °C; $C_{21}H_{26}O_5$ [m/e 358(M^+)]; ν_{max}(KBr) 3530br., 1600, 1580, and 1480br.cm^{-1}; δ(CCl_4) 1.13(3H, d, J= 6Hz), 1.90(3H, dd, J= 6.5, 2Hz), 3.29(3H, s), 3.74 (3H, s), 3.80(3H, s), 4.22(1H, m), 4.65(1H, d, J= 3Hz), 5.80(1H, s), 6.05(1H, dq, J= 16, 6.5Hz), and 6.5-7.0(7H, complex).
4. The reaction was quenched at 1.9 F/mole.
5. **5**: mp 76-78 °C; $C_{13}H_{20}O_5$ [m/e 256(M^+)]; ν_{max}(KBr) 1690 and 1635 cm^{-1}; δ(CCl_4) 1.23(3H, d, J= 6Hz), 3.24(3H, s), 3.26(3H, s), 3.33(3H, s), 3.60(3H, s), 3.7-4.6(3H, complex), 5.59(1H, d, J= 6Hz), and 6.63(1H, d, J= 8Hz). **6**: mp 73-77 °C; $C_{13}H_{20}O_5$ [m/e 256(M^+)]; ν_{max}(KBr) 1680 and 1630 cm^{-1}; δ(CCl_4) 1.20(3H, d, J= 6Hz), 3.21(3H, s), 3.38(6H, s), 3.59(3H, s), 3.99-4.12 (2H, m), 4.61(1H, m), 5.56(1H, d, J= 6Hz), and 5.94(1H, d, J= 8Hz). Particularly, each geometry of the exocyclic double bonds in both **5** and **6** is based on their NMR signals (δ6.63 in **5**; δ5.94 in **6**).
6. Electrolysis was carried out at a controlled potential (+1600 mV *vs.* SCE) and stopped at 3.1 F/mole.
7. **7**: mp 181-184 °C; $C_{20}H_{22}O_4$ [m/e 326(M^+)]; ν_{max}(KBr) 1680, 1630, and 1585 cm^{-1}; δ($CDCl_3$) 0.57 (3H, d, J= 7Hz), 1.16(3H, d, J= 7Hz), 2.19(1H, m), 2.54(1H, m), 3.02-3.40(2H, complex), 3.73 (3H, s), 3.80(3H, s), 4.62(1H, dd, J= 6, 2Hz), 6.17(1H, d, J= 6Hz), 6.56-7.04(3H, complex), and 7.14(1H, br.d, J= 5Hz).
8. G. C. Brophy, T. Mohandas, M. Slaytor, S. Sternhell, T. R. Warson, and L. A. Wilson, Tetrahedron Lett., **1969**, 5159.

9. **9**: mp 169-172 °C; $C_{21}H_{22}O_7$ [m/e 386(M^+)]; ν_{max}(KBr) 3370br., 1635, and 1580 cm^{-1}; δ(DMSO-d_6) 0.72(3H, d, J= 6Hz), 1.10(3H, d, J= 6Hz), 1.40-2.20(2H, complex), 2.96(3H, s), 3.41(1H, d, J= 12Hz), 3.60(1H, d, J= 8Hz), 5.02(1H, s), 5.61(1H, s), 5.72(2H, s), 5.76(2H, s), 6.18(1H, s), 6.23(1H, s), and 8.73(1H, s). **10**: mp 87-89 °C; $C_{22}H_{26}O_8$ [m/e 418(M^+)]; ν_{max}(KBr) 3350br. and 1620 cm^{-1}; δ($CDCl_3$) 0.77(3H, d, J= 6Hz), 0.80(3H, d, J= 6Hz), 1.70-2.04(1H, m), 2.40-2.88(1H, m), 3.26(3H, s), 3.33(3H, s), 4.14(2H, d, J= 10Hz), 5.75(2H, m), 5.80(2H, br.s), 6.28(1H, s), 6.30(1H, s), 6.67(1H, s), and 6.72(1H, s). **12**: mp 85-87 °C; $C_8H_6O_4$ [m/e 166(M^+)]; ν_{max}(KBr) 1640 and 1605 cm^{-1}; δ($CDCl_3$) 5.99(2H, s), 6.45(1H, s), 6.84(1H, s), and 9.59(1H, s).
10. O. L. Chapman, M. R. Engel, J. P. Springer, and J. C. Clardy, J. Am. Chem. Soc., 93, 6696 (1971).

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