hydroxy-4-methoxyphenyl)butanedione as yellow needles, mp 200–202°; MS m/z 330 $[M]^+$, 179, 151; ^1H NMR ($CDCl_3$): δ 3.36 (4H, *s*, 2 × CH_2), 3.83 (6H, *s*, 2 × OMe), 6.4 (4H, *m*, H-3, H-3′, H-5 and H-5′), 7.79 (2H, *d*, $J = 9$ Hz, H-6 and H-6′), 12.45 (2H, *s*, 2 × OH).

Acknowledgements—The authors thank Hakim Abdul Hameed for his kind interest in these studies and for awarding a fellowship to one of the authors (M.H.K.). They also thank Prof. M. R. Parthasarathy and Prof. M. Ilyas for useful discussion during the course of this work. Thanks are also due to Prof. R. P. Gandhi and Dr Jagdev Singh for their kind help in recording the NMR and mass spectra.

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Phytochemistry, Vol. 30, No. 3, pp. 1034–1036, 1991
Printed in Great Britain.

0031-9422/91 $3.00+0.00

METASEOL, A SYMMETRICAL DIPHENYLMETHANE FROM *METASEQUOIA GLYPTOSTROBOIDES*

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(*Received in revised form* 4 *September* 1990)

Key Word Index—*Metasequoia glyptostroboides*; Taxodiaceae; root bark; metaseol; diphenylmethane; antibacterial activity.

Abstract—A unique symmetrical diphenylmethane derivative, 1,1-bis-(3′,5′-dimethyl-2′-hydroxyphenyl)-2-methylpropane, was isolated from the root bark of *Metasequoia glyptostroboides*; it inhibited the growth of some bacteria.

INTRODUCTION

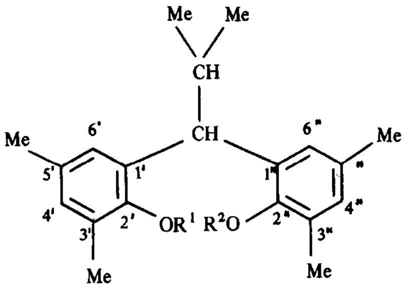
Metasequoia glyptostroboides Hu et Cheng is often considered to be a living fossil plant. Bisflavones [1], antibacterial diterpenoids [2], lignans [3], and sterols [4] have been reported from the leaves and twigs and sugars [5], waxes [6], and carotenoids [7] have been also detected. However, no study has been reported on the root and thus we examined the constituents of the root bark. We report the isolation of a unique symmetrical diphenylmethane derivative, metaseol (**1**), which was active at 5 μg/disk against *Bacillus subtilis* and *Escherischia coli*.

RESULTS AND DISCUSSION

The molecular formula of metaseol (**1**) was deduced as $C_{20}H_{26}O_2$ from elemental analysis and EIMS ($[M]^+$, m/z 298). The IR spectrum showed the presence of an hydroxyl group (3400 cm^{-1}) and a 1,2,3,5-tetrasubstituted phenyl ring (1600 and 856 cm^{-1}). The UV absorptions at 230 and 288 nm revealed **1** to be phenolic.

The symmetrical diphenylmethane structure of **1** was deduced by spectrometry (see Experimental and Table 1). The EI mass fragmentation supported this. Acetylation of **1** also afforded a symmetrical diacetate **2** and the slight downfield shifts (*ca* 0.1 ppm) of the aromatic proton signals by acetylation suggested their 1,3-relationship to the hydroxyl groups in **1**.

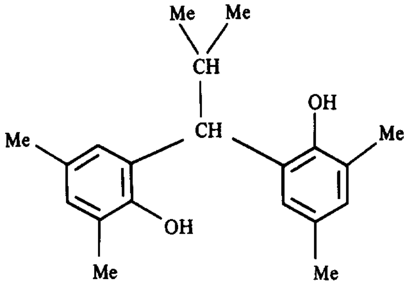
On the other hand, methylation of **1** with diazomethane afforded an asymmetrical monomethyl ether (**3**), which provided significant information regarding substitution on both phenyl rings. The ^{13}C NMR spectrum revealed 12 distinguishable carbon signals assignable to each aromatic carbon (Table 1), in which observed aromatic carbon data gave excellent agreement for those calculated [8] except for the α-carbon signals to the phenolic carbon. Thus, the structure of metaseol is 1,1-bis(3′,5′-dimethyl-2′-hydroxyphenyl)-2-methylpropane (**1**). The proposed structure was confirmed by synthesis. The acid catalysed reaction [9] of xylenol and isobutyraldehyde in 8 M HCl under nitrogen gave **1** in 19% yield.



1 R^1 = R^2 = H

2 R^1 = R^2 = Ac

3 R^1 = H, R^2 = Me



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As the ^{1}H NMR spectrum gave no sign of hydrogen-bonding interaction between the two hydroxyl groups (δ5.82), it may take an anti-conformation as shown in 4.

Metaseol (1) has a novel structure in that the two same aromatic rings are connected by a methylene bridge. Although some diphenylmethane derivatives have been reported [10], this is the first isolation of such a symmetrical structure.

EXPERIMENTAL

Mps: uncorr. ^{1}H NMR: 400 MHz; ^{13}C NMR: 100 MHz, TMS as int. standard. HPLC: column, Partisil M9.

Plant material. Root bark of *M. glyptostroboides* was collected at the garden of Suntory Institute, Osaka.

Extraction and isolation. The ground root bark (1 kg) was extracted with *n*-hexane and Et_2O. The ether extract (25 g) was chromatographed over silica gel. Elution with 1:1 mixt. of *n*-hexane and CH_2Cl_2 gave a powder (80 mg), which was purified by HPLC using CH_2Cl_2 as solvent to obtain 58 mg **1**.

Metaseol (**1**). Needles from hexane, mp 165–167°; EIMS *m/z* (rel. int.): 298 ($[M]^+$, 21), 255 (100), 239 (4), 225 (2.5), 209 (2.5), 134 (2.5), 179 (3.5), 175 (2.5), 135 (4), 121 (2.5), 115 (2.5), 105 (3), 91 (5), 77 (3.5); UV $\lambda_{max}^{CH_2Cl_2}$ nm: 230 (ε 6400) and 288 (ε 4500); IR ν_{max}^{Nujol} cm^{-1}: 3550–3400(sh), 3400, 1600, 856; ^{1}H NMR ($CDCl_3$): δ0.90 (6H, *d*, $J = 8$ Hz, –$CHMe_2$), 2.17 (6H, *s*, Me-5′ and Me-5″), 2.23 (6H, *s*, Me-3′ and Me-3″), 2.58 (1H, *m*, H-2), 3.97 (1H, *d*, $J = 12$ Hz, H-1), 5.82 (2H, *s*, –OH), 6.72 (2H, *br s*, H-6′ and H-6″), 6.91 (2H, *br d*, $J = 1.7$ Hz, H-4′ and H-4″). [Found: C, 80.45; H, 8.80%. $C_{20}H_{26}O_2$ requires: C, 80.49; H, 8.78%].

Table 1. ^{13}C NMR spectral data of compounds **1** and **3** (in $CDCl_3$, 100 MHz, δ ppm. TMS as int. standard)

C	1	3	(calculated)
1	44.0	44.3	
2	30.9	30.4	
3a	16.5	16.6	
3b	16.5	16.9	
1′	130.3	136.2	(135.8)
2′	149.3	150.2	(150.9)
3′	124.0	128.6	(125.1)
4′	129.3	129.6	(128.4)
5′	130.2	130.1	(130.5)
6′	125.7	125.3	(125.9)
1″	130.3	134.5	(133.8)
2″	149.3	152.2	(154.2)
3″	124.0	125.2	(123.1)
4″	129.3	128.9	(128.1)
5″	130.2	129.2	(129.7)
6″	125.7	123.8	(125.0)
Me	21.1	21.2	
	21.9	21.4	

*Calculated using the equation $\delta_C = 128.5 + \Sigma z_i$ [8].

Diacetylmetaseol (**2**). $C_{24}H_{30}O_4$, EIMS *m/z* (rel. int.): 382 ($[M]^+$, 14.5), 340 (59), 297 (100), 255 (91), 237 (13), 175 (9), 135 (4); UV λ_{max} nm (CH_2Cl_2): 236 (ε 6700) and 276 (ε 2900); IR ν_{max} cm^{-1} (liq. film): 1760, 1730(sh), 1600, 1220–1180, 1140, 910, 860; ^{1}H NMR ($CDCl_3$): δ0.85 (6H, *d*, $J = 9$ Hz), 2.04 (6H, *s*), 2.28 (6H, *s*), 2.35 (6H, *s*), 2.4 (1H, *m*), 3.75 (1H, *d*, $J = 12$ Hz), 6.85 (2H, *br s*), 7.02 (2H, *br s*).

Monomethylmetaseol (**3**). $C_{21}H_{28}O_2$, EIMS *m/z* (rel. int.): 312 ($[M]^+$, 24), 269 (42), 239 (2.5), 237 (7), 135 (100), 91 (3), 77 (1.5); UV $\lambda_{max}^{CH_2Cl_2}$ nm: 234 (ε 6100) and 286 (ε 2900); IR ν_{max} cm^{-1} (liq. film): 3400, 1220, 1005, 860; ^{1}H NMR ($CDCl_3$): δ0.93 (3H, *d*, $J = 9$ Hz), 0.98 (3H, *d*, $J = 9$ Hz), 2.18 (3H, *s*), 2.19 (3H, *s*), 2.23 (3H, *s*), 2.24 (3H, *s*), 2.68 (1H, *m*), 3.80 (1H, *d*, $J = 12$ Hz), 3.90 (3H, *s*), 6.72 (1H, *s*), 6.77 (1H, *br s*), 6.95 (2H, *br s*), 7.55 (1H, *s*).

Synthesis of metaseol. A mixt. of 2,4-xylenol (12.2 g; 0.1 mol), isobutyraldehyde (3.6 g; 0.05 mol) and 8 M HCl (32 ml) was stirred at room temp. for 24 hr in N_2. The mixt. was extracted with Et_2O. The ether extract was washed with aq. $NaHCO_3$ and H_2O. The Et_2O soln was removed *in vacuo* and the residue recrystallized from hexane to give 2.9 g (19%) of **1** as needles, mp 167–168°.

Acknowledgement—The authors thank Prof. M. Abe (Department of Biology, Kagoshima University) for the antimicrobial test.

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Phytochemistry, Vol. 30, No. 3, pp. 1036–1037, 1991
Printed in Great Britain.

0031-9422/91 $3.00+0.00

1,5,7-TRIHYDROXY-3-METHOXYXANTHONE FROM *HOPPEA FASTIGIATA*[*]

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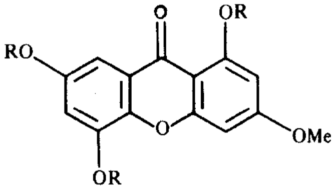
(*Received in revised form* 12 *July* 1990)

Key Word Index—*Hoppea fastigiata*; Gentianaceae; 1,5,7-trihydroxy-3-methoxyxanthone.

Abstract—The benzene whole plant extract of *Hoppea fastigiata* yielded a new xanthone, 1,5,7-trihydroxy-3-methoxyxanthone.

In continuation of our search for plant pigments, a phytochemical investigation of *Hoppea fastigiata* Clarke (Gentianaceae) [1] was undertaken as no previous chemical data have been reported for this plant. We report the isolation and structural elucidation of a new tetraoxygenated xanthone, 1,5,7-trihydroxy-3-methoxyxanthone (**1**) from the benzene extract of whole plants of *H. fastigiata*.



1 R = H
2 R = Me

The xanthone (**1**), $C_{14}H_{10}O_6$ ($[M]^+$ at m/z 274), exhibited UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε), 250 (4.50), 280 (4.15), 320 (3.90), 345 (3.70) and its IR spectrum showed absorption bands at $\nu_{\max}^{\mathrm{KBr}}$ 3360 (br chelated hydroxyl), 1660, 1625, 1605 and 1570 cm^{-1} (chelated, α,β-unsaturated carbonyl) suggesting the presence of a xanthone skeleton. The ^{1}H NMR spectrum (100 MHz, $CDCl_3$) of **1** showed four *meta* coupled doublets for four aromatic protons at δ6.45 ($J = 3$ Hz), 6.65 ($J = 3$ Hz), 7.30 ($J = 3$ Hz) and 7.80 ($J = 4$ Hz) beside a singlet for three protons at δ3.92 due to a methoxyl group. On complete methylation with dimethyl sulphate, **1** yielded a trimethyl derivative (**2**). Thus **1** must be a trihydroxy-monomethoxyxanthone. The appearance of four aromatic protons as four different *meta* split doublets suggests that two oxygen functions (one methoxy and three hydroxyls) are present in each ring and they are located in a 1,3-relationship. The appearance of an aromatic proton at δ7.80 as a *meta* split doublet is consistent with a proton at C-8 having an oxygen substituent at C-7 [2], hence two oxygen functions in ring B are at the C-5 and C-7 positions. The presence of a chelated hydroxyl necessitates the location of one of the hydroxyls at C-1. Further support for the presence of a hydroxyl group at C-1 was obtained from UV spectral measurements. Thus, in the presence of aluminium chloride, there was a bathochromic shift of the longer wavelength maximum by 22 nm (348→367 nm) which remained unchanged on addition of hydrochloric acid. The parent xanthone was found to be insoluble in 5% Na_2CO_3

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[*] Presented at Natural Products Symposium, pre-IUPAC Symposium 17, Calcutta, India, January 31–February 2 1990.