dried. Evaporation of the solvent yielded a thick liquid (2.2 g, 86%). ($C_{14}H_{20}O_3$ requires: C, 71.15; H, 8.53; Found C, 71,17; H, 8.51%). IR $\nu_{\max}^{\mathrm{CHCl}_3}$ cm^{-1}: 1680, 1460, 1380, 1360, 1310, 1290, 1060. ^{1}H NMR: δ1.15 (*d*, $J = 6.5$ Hz, 6H), 1.36 (*s*, 12H), 3.52 (*m*, 1H), 7.28 (*d*, $J = 1$ Hz, 1H).

Conversion of alkylidene **5** *to dienol* **6**. The alkylidene (2 g) was dissolved in benzene (50 ml) and refluxed under N_2 for 1 hr. Evaporation of the C_6H_6 under red. pres. on a rotavapor under N_2 yielded a white solid (2 g), mp 71°. ($C_{14}H_{20}O_3$ requires C, 71.15; H, 8.53. Found C, 71.10; H, 8.55%). IR $\nu_{\max}^{\mathrm{CHCl}_3}$ cm^{-1}: 3450, 1680, 1640, 1590, 1460, 1380, 1360, 1320, 1230, 1210, 1080, 1010. ^{1}H NMR: δ1.48 (*s*, 12H), 1.68 (*br s*, 3H), 1.96 (*br s*, 3H), 5.72 (*m*, 1H).

Reaction of dienol (**6**) *with diazomethane*. The dienol (1 g) was treated with an excess of an ethereal soln of CH_2N_2 and, after 30 min at 0°, the evaporation of solvent yielded a thick yellow liquid (1 g). ($C_{15}H_{22}O_3$ requires C, 71.97; H, 8.86. Found C, 71.95; H, 8.88%). IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 1680, 1646, 1585, 1455. ^{1}H NMR: δ1.44 (*s*, 3H), 1.93 (*s*, 3H), 1.56 (*br s*, 3H), 1.92 (*br s*, 3H), 3.8 (*s*, 3H), 5.84 (*m*, 1H).

Reaction of dienol (**6**) *with oxygen*. A soln of dienol (2 g) in C_6H_6 (50 ml) was stirred under an atmosphere of O_2. After 30 min, the evapn of solvent gave a white crystalline solid which showed IR, NMR and mass spectra superimposable with those of an authentic sample of G_3 ($R_1 = R_2 = Me$). By this method were also obtained G_1 ($R_1 = Me$, $R_2 = Et$) and G_2 ($R_1 = Et$, $R_2 = Me$).

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Phytochemistry, Vol. 26, No. 12, pp. 3369–3371, 1987.
Printed in Great Britain.

0031-9422/87 \$3.00+0.00

ACYLRESORCINOLS FROM SEED KERNELS OF *MYRISTICA DACTYLOIDES*

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(*Revised received* 18 *May* 1987)

Key Word Index—*Myristica dactyloides*; Myristicaceae; seeds; polyketides; ^{13}C NMR.

Abstract—A new polyketide 1-(2,6-dihydroxyphenyl)-9-(4-hydroxy-3-methoxyphenyl)nonan-1-one and five other polyketides 1-(2,6-dihydroxyphenyl)tetradecan-1-one and malabaricones A–D have been isolated from *Myristica dactyloides* seeds. ^{13}C NMR of the first and the second mentioned compounds are also reported for the first time.

INTRODUCTION

Myristica dactyloides is used in native medicine [1] in Sri Lanka and its seeds and aril are used as adulterants to *M. fragrans* (nutmeg). Previously only myoinositol [2], malabaricone A (**2**) and 1-(2,6-dihydroxyphenyl)tetradecan-1-one (**1**) [3] have been isolated from the bark of *M. dactyloides*. We now report the isolation of six acylresorcinols (**1**–**6**) from seeds of *M. dactyloides*.

RESULTS AND DISCUSSION

Column chromatography of an acetone seed extract of *M. dactyloides* yielded six phenols. All six compounds had similar UV spectra, showed bathochromic shifts with alkali and gave a violet colouration with fast blue B salt, thus confirming their phenolic nature.

The peak around 3360 cm^{-1} in the IR spectrum confirmed the presence of a hydrogen-bonded hydroxyl.

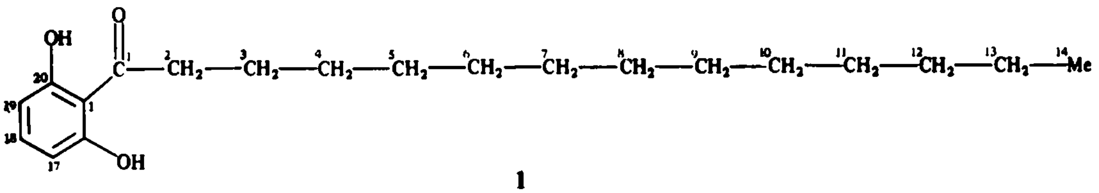
A base peak at (m/z) 137 and a less intense peak at 109 in the mass spectrum and a sharp band around 1640 cm^{-1} in the IR spectrum confirmed the presence of a 2,6-dihydroxyacetophenone moiety in all the compounds isolated.

The molecular formula of **1** was confirmed to be $C_{20}H_{32}O_3$ [M^+ (m/z) 320.2356; found, C, 74.89%; H, 9.96%]. ^1H NMR showed the presence of three aromatic protons [δ7.22 (1H, *t*, $J = 8$ Hz) and 6.38 (2H, *d*, $J = 8$ Hz)] and hence the presence of one benzene ring. Further $J = 8$ Hz showed *ortho* coupling of the hydrogens. The triplet at δ3.12 indicated that a $-CH_2-CH_2$ group is attached to a carbonyl group. The distorted triplet at δ0.88 indicated the presence of a -Me group connected to an *n*-alkyl group and other signals δ1.69 (2H, *m*, $-CH_2-$) and 1.27 (2OH, *m*, $-CH_2-$) account for 22H. The ^{13}C NMR spectrum of this compound was in agreement with the structure 1-(2,6-dihydroxyphenyl)tetradecan-1-one (**1**).

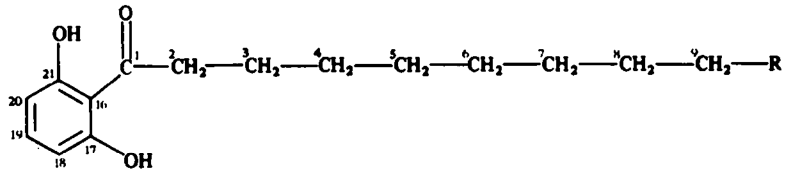
Compounds **2**, **3**, **5** and **6** were identified as malabaricones A, D, B and C, respectively from their UV, IR, ^1H NMR, MS data, mmps and co-TLC.

Compound **4** which is a new acylresorcinol had a molecular formula $C_{22}H_{28}O_5$ [M^+ (m/z) 372.1947; found: C, 71.03%; H, 7.48%] IR(KBr) supporting the presence of one free and one hydrogen bonded hydroxyl (3450 and 3340 cm^{-1}) and hydrogen bonded carbonyl group. ^1H NMR revealed two benzene rings one 1,2,3-trisubstituted [δ7.20 (1H, *t*, $J = 8$ Hz), 6.37 (2H, *d*, $J = 8$ Hz)] and the other 1',3,4 trisubstituted δ6.98 (1H, *d*, $J = 8$ Hz), 6.73 (1H, *d*, $J = 2$ Hz), 6.65 (1H, *dd*, $J = 8$ and 2 Hz), singlets at δ3.80, 5.60 and 9.50 correspond to a methoxy group, a free hydroxyl and two hydrogen bonded hydroxyl groups.

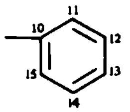
The base peak in the HRMS at m/z 137.0605 ($C_8H_9O_2$) and acetylvanillic acid (mmp and co-TLC) in the oxidative products of acetylated **4** indicated the presence of a 4-hydroxy-3-methoxybenzylic moiety in [3] the second ring. The ^{13}C NMR of **4** was similar to that



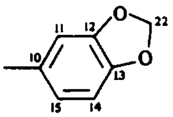
1



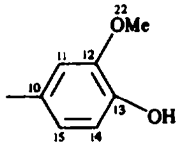
2 R



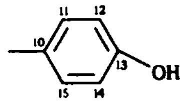
3 R



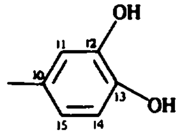
4 R



5 R



6 R



of **6** except for a (−) signal at δ5.60 due to a methoxy group.

EXPERIMENTAL

Mps: uncorr. ^{1}H NMR was run at (CD_2Cl_2) 100 MHZ and 400 MHz and ^{13}C NMR spectra (CD_2Cl_2) at 74.2 MHz. HRMS, ^{13}C NMR and micro-analysis were performed at the Department of Chemistry, University of British Columbia, Canada.

Isolation and identification of phenolics. The dried powdered seeds (500 g) of *M. dactyloides* Gaertn., from Hanguranketa, Sri Lanka, were extracted with Me_2CO. The concd Me_2CO extract was defatted with petrol giving a viscous brown solid (165 g), which after CC on silica gel using petrol: EtOAc mixtures of increasing proportions yielded compounds **1–6**, which were purified by prep. TLC.

1-(2,6-*Dihydroxyphenyl)tetradecan*-1-*one* (**1**). Needles mp, 91–91.5° (petrol, lit [3] 91–92); Found: C, 74.89%; H, 9.96%; $C_{20}H_{32}O_3$ requires: C, 74.96%; H, 10.06%, UV λ_{max}^{EtOH} nm, 223, 268, 339, $\lambda_{max}^{EtOH/OH^-}$ nm 239, 283, 390; IR ν_{max}^{KBr} 3360 (*br*), 1640 (*s*) ^{1}H NMR (400 MHz, CD_2Cl_2) δ9.37 (2H, *br s*, OH-16, 20 D_2O exchangeable), 7.22 (1H, *t*, $J = 8$ Hz, H-18), 6.38 (2H, *d*, $J = 8$ Hz, H-17, 19), 3.12 (2H, *t*, $J = 7$ Hz, H-2), 1.69 (2H, *m*, H-3), 1.27 (20H, *m*, H-4-13), 0.88 (3H, *t*, $J = 7$ Hz, H-14); HRMS, *m/z* (rel. int.%) 320.2356 ($C_{20}H_{32}O_3$, 10), 302.2246 ($C_{20}H_{30}O_0$, 17), 189.0920 ($C_{12}H_{13}O_2$, 17), 165.0553 ($C_9H_9O_3$, 26), 152.0473 ($C_8H_8O_3$, 31), 137.0247 ($C_7H_5O_3$, 100) ^{13}C NMR assignments are given in Table 1.

Malabaricone A (**2**). Crystals (petrol) mp, 80–82° (lit. [4] 81–82°).

Malabaricone D (**3**). Pale yellow crystals (toluene) mp, 89–91° (lit [4] 90–91°).

1-(2,6-*Dihydroxyphenyl*)-9-(4-*hydroxy*-3-*methoxyphenyl*) *nonan*-1-*one* (**4**). White needles (toluene) mp 109–111°; found: C, 71.03%; H, 7.48%, $C_{22}H_{28}O_5$ requires: C, 70.95%; H, 7.58%; UV λ_{max}^{EtOH} nm 340, 272, 269, 220 $\lambda_{max}^{EtOH/OH^-}$ nm 386, 283, 238; IR ν_{max}^{KBr} cm^{-1} 3450 (*s*), 3340 (*br*), 1635 (*s*), ^{1}H NMR (CD_2Cl_2 run at 400 MHz) δ9.50 (2H, *s*, OH-17, 21, D_2O exchangeable), 7.20 (1H, *t*, $J = 8$ Hz, H-19), 6.98 (1H, *d*, $J = 8$ Hz, H-15), 6.73 (1H, *d*, $J = 2$ Hz, H-11), 6.65 (1H, *dd*, $J = 2$ and 8 Hz, H-14), 6.37 (2H, *d*, $J = 8$ Hz, H-20, 18), 5.60 (1H, *s*, D_2O exchangeable, OH-13), 3.80 (3H, *s*, H-22), 3.00 (2H, *t*, $J = 7$ Hz, H-2), 2.44 (2H, *t*, $J = 7$ Hz, H-9), 1.64 (4H, *m*, H-3, 8), 1.32 (8H, *m*, H-4-7); HRMS *m/z* (rel. int.%) 372.1947 ($C_{22}H_{28}O_5$, 52), 262.1568 ($C_{16}H_{22}O_3$, 21), 234.1618 ($C_{15}H_{22}O_2$, 15), 165.0548 ($C_9H_9O_3$, 22), 137.0605 ($C_8H_9O_2$, 100), 137.0244 ($C_7H_5O_3$, 79); ^{13}C NMR assignments are given in Table 2.

Table 1. ^{13}C NMR assignment (attached proton test) of compound **1**

Carbon no.	δ(ppm)	Intensity
1	207.79	6
2	44.82	32
3	24.41	48
4–11	29.66	90
	29.55	75
	29.40	52
	29.37	48
12	31.93	17
13	22.70	23
14	14.13	−14
15	110.03	v. weak
16, 20	161.03	15
17, 19	108.52	−100
18	135.57	−52

Table 2. ^{13}C NMR assignment (attached proton test) of compound **4**

Carbon no.	δ(ppm)	Intensity
1	207.95	6
2	44.71	41
3	24.37	46
4	29.12	47
5, 6	29.02	69
7	28.75	45
8	31.25	45
9	35.08	61
10	136.35	12
11	110.58	−48
12	145.05	8
13	144.52	5
14	114.57	−41
15	119.93	−39
16	110.05	6
17, 21	161.18	15
18, 20	108.42	−101
19	135.62	−50
22	56.01	−19

Oxidation of **4**. Compound **4** (75 mg) was heated in HOAc (0.3 ml) with one drop of concd H_2SO_4 at 60° for 15 min. Acetylated **4** (30 mg) in Me_2CO was stirred with a soln of $KMnO_4$ (0.2 g) in H_2O (0.5 ml) and Me_2CO (2 ml), decolourized with $NaHSO_3$ in dil. H_2SO_4 and extracted with Et_2O. Prep. TLC of the extract on silica gel with the upper layer of toluene–HOAc–H_2O (2:3:1) [5] gave acetylvanillic acid which was characterized by mmp and co-TLC with an authentic sample.

Malabaricone B (**5**). Pale yellow crystals (toluene) mp 100–102° (lit. [4] 102°).

Malabaricone C (**6**). Yellow crystals (toluene) mp 122–124° (lit. [4] 123–124°).

Acknowledgements—We thank International Seminar, Uppsala, Sweden for financial assistance to obtain the spectral data; Professor David Dolphin, Department of Chemistry, University of British Columbia, Canada, for ^{13}C NMR, HRMS, ^{1}H NMR and micro-analysis; Dr K K Purushothaman, Captain Sirinivasamurthi Drug Research Institute for Avyurveda, for providing the authentic samples. Dr M H Jayasuriya, Royal Botanical Garden Peradeniya, Sri Lanka, for identification of plant materials and Mrs S D Tennekoon for secretarial assistance.

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