Four New Sesquiterpenoid Derivatives from the Heartwood of *Mansonia gagei*

Pattara Tiew,[†,‡] Jean-Robert Ioset,[†] Udom Kokpol,[‡] Kurt Schenk,[§] Nongnuj Jaiboon,[‡] Narongsak Chaichit,[⊥] Warinthorn Chavasiri,[‡] and Kurt Hostettmann*[,†]

Institut de Pharmacognosie et Phytochimie, Université de Lausanne, BEP, CH-1015 Lausanne, Switzerland, Institut de Cristallographie, Université de Lausanne, BSP, CH-1015 Lausanne, Switzerland, Natural Products Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand, and Department of Physics, Faculty of Science and Technology, Thammasart University, Patumtani 12121, Thailand

Received January 31, 2002

Four new sesquiterpenoid derivatives named mansonones N (**1**), O (**2**), P (**3**), and Q (**4**) were isolated from a dichloromethane extract of the heartwood of *Mansonia gagei*, a plant used in folk medicine in Thailand. Their structures were resolved on the basis of spectrometric data interpretation and the single-crystal X-ray analysis of **1** and **2**.

Mansonia gagei Drumm is the only species of the family Sterculiaceae found in Thailand. This large tree is generally scattered in dry evergreen forests and is known locally as "chan-chamod", "chan-hom", "chan-khao", or "chan-phama". According to folkloric practice, the heartwood of the plant is locally utilized as a cardiac stimulant, antiemetic, and antidepressant agent.[1] In a previous study,[2] we reported the isolation and the structure characterization of three coumarin derivatives and mansonones C, G, and H from the heartwood of *M. gagei*. The aim of the present work was to complete the chemical investigation of the heartwood constituents of this traditional herbal medicine.

A molecular ion at *m/z* 278 in the EIMS, ^{1}H NMR, and ^{13}C NMR spectra of compound **1** suggested a molecular formula of $C_{16}H_{22}O_4$. Two different kinds of chemical shifts were noticed in the ^{13}C NMR spectrum: six resonances between 120 and 145 ppm, typical of an aromatic moiety, and eight signals from 15 to 80 ppm, characteristic of the presence of an aliphatic unit. A ketone carbonyl was also identified in the low-field region of the ^{13}C NMR spectrum by a resonance at δ 212.1 (C-6). This signal was positioned on the aliphatic unit from the HMBC correlations with ^{1}H NMR signals at δ 3.79 (H-8), 2.49 (H-7), 3.21 (H-7), and 2.15 (H-9). An isopropyl group was identified from the ^{1}H NMR spectrum by the presence of two methyl groups at δ 0.79 (d, J = 6.9 Hz, CH_3-9) and 0.99 (d, J = 6.7 Hz, CH_3-9) that correlated in the COSY spectrum with a methine resonance centered at δ 2.15 (sept, J = 6.9 Hz, H-9). This isopropyl unit also showed long-range heteronuclear correlations to the aliphatic group between the protons of the methyl units located at δ 0.79 (CH_3-9) and 0.99 (CH_3-9) in the ^{1}H NMR spectrum with the ^{13}C NMR resonance at δ 80.6 (C-5). The chemical shift of C-5 was typical of a quaternary oxygenated carbon. Two other methyl signals were also detected in the ^{1}H NMR spectrum. The doublet at δ 1.16 (d, J = 6.9 Hz, CH_3-8) was correlated in the COSY spectrum with the aliphatic proton at δ 3.79 (m, H-8). Further analysis of the aliphatic area of the same spectrum gave evidence for the presence of a $CH_3-CH-CH_2$ unit. The second methyl group was a singlet located at δ 2.30 (s, CH_3-3), suggesting an attachment to the aromatic system of the molecule. This hypothesis was supported by HMBC correlations between the signal at δ 2.30 and the ^{13}C NMR resonances at δ 120.1 (C-4), 128.8 (C-3), and 144.4 (C-2).

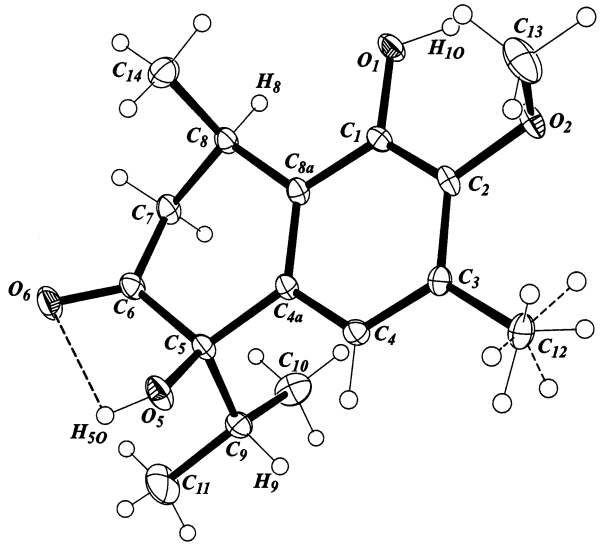


Figure 1. ORTEP (40% level) representation and atomic numbering scheme of mansonone N (**1**).

The only proton in the aromatic region of the ^{1}H NMR spectrum was positioned on C-4 as a result of the long-range heteronuclear correlations observed between the ^{1}H NMR signal at δ 6.86 (H-4) and the ^{13}C NMR resonances located at δ 80.6 (C-5), 16.0 (CH_3-3), 124.6 (C-8a), and 144.4 (C-2). This assignment was supported by the NOE effects observed between the proton at δ 6.86 (H-4) and the ^{1}H NMR signals at δ 2.15 (H-9), 2.30 (CH_3-3), and 0.99 (CH_3-9). Substitution of a methoxyl group (δ 3.79) at the C-2 position of the aromatic moiety was also confirmed through NOE correlations with the methyl group at δ 2.30 (CH_3-3). Spectrometric data permitted us to establish the structure of compound **1** as a new sesquiterpenoid derivative named mansonone N. Definitive evidence for this structure was obtained from a single-crystal X-ray analysis. The molecular structure and crystallographic numbering scheme are illustrated in Figure 1. The relative chiralities of carbons C-5 and C-8 are *R** and *R**, respectively, but, unfortunately, the measured crystal was an inversion twin and, therefore, the absolute configuration could not be determined. For ease of comparison with related compounds, the isolated products were given the same num-

* To whom correspondence should be addressed. Tel: 41 021 6924561. Fax: 41 021 6924565. E-mail: kurt.hostettmann@ipp.unil.ch.
† Institut de Pharmacognosie et Phytochimie, Université de Lausanne.
§ Institut de Cristallographie, Université de Lausanne.
‡ Natural Products Research Unit, Chulalongkorn University.
⊥ Department of Physics, Thammasart University.

10.1021/np020024e CCC: $22.00
Published on Web 07/20/2002

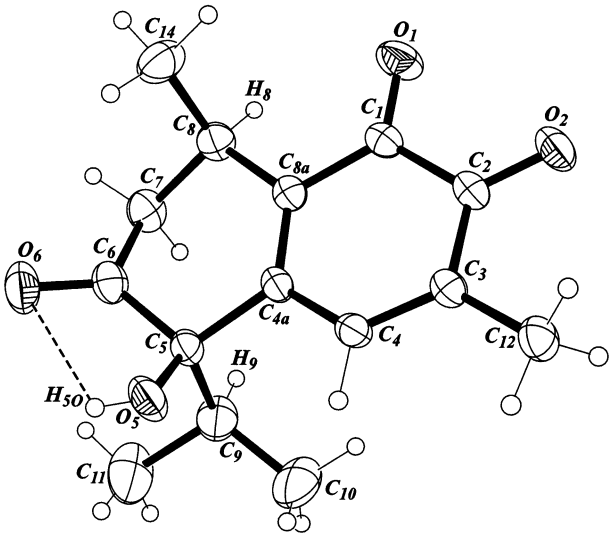
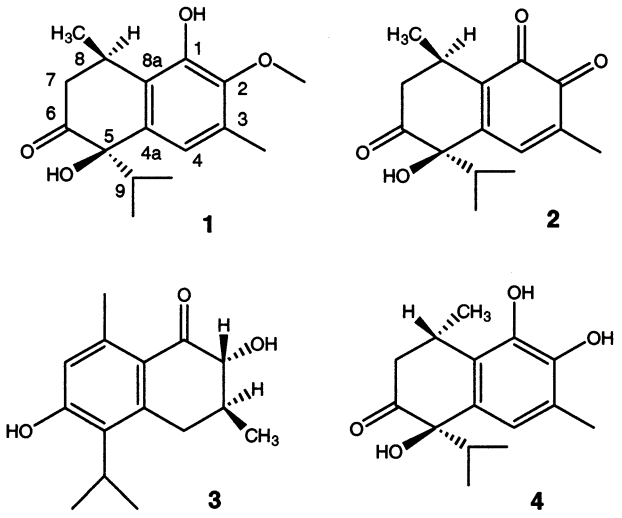


Figure 2. ORTEP (30% level) representation and atomic numbering scheme of mansonone O (**2**).

bering scheme as previously used in the literature, whereas the IUPAC denomination is given in the Experimental Section.[2,3]

A molecular ion at *m*/*z* 262 in the EIMS, ^{1}H NMR, and ^{13}C NMR spectra of compound **2** suggested a molecular formula of $C_{15}H_{18}O_4$. Comparison of the ^{1}H NMR and ^{13}C NMR spectra of compound **2** with those of **1** showed that the nonaromatic moieties of these two molecules were identical. The ^{1}H NMR singlet at δ 7.06 was positioned at C-4 after the observation of a long-range heteronuclear correlation between this signal and the ^{13}C NMR resonance at δ 79.3 (C-5). Measurement of a NOE effect between the same ^{1}H NMR singlet at δ 7.06 and the signal at δ 2.00 (3H) permitted the location of this methyl group at C-3. This result was confirmed by an HMBC correlation observed between the ^{13}C NMR resonance at δ 15.5 (CH_3-3) and the ^{1}H NMR singlet at δ 7.06 (H-4). Finally, two ketone carbonyl carbon signals seen in the ^{13}C NMR spectrum at δ 179.3 and 180.1 were located at C-1 and C-2, respectively, in agreement with the HMBC correlation observed between the ^{13}C NMR signal at δ 180.1 (C-2) and the ^{1}H NMR singlet at δ 7.06 (H-4). Compound **2** was identified as a new natural product named mansonone O. Definitive evidence of this structure was obtained from a single-crystal X-ray analysis. The relative chiralities of carbons C-5 and C-8 are *R** and *R**. The molecular structure and crystallographic numbering scheme are illustrated in Figure 2.

A molecular formula of $C_{15}H_{20}O_3$ was deduced for compound **3** from the ^{1}H NMR and ^{13}C NMR spectra, the EIMS (*m*/*z* 248 $[M]^+$), and the DCIMS (*m*/*z* 266 $[M + NH_4]^+$). As in the case of compound **1**, the ^{13}C NMR spectrum of **3** suggested the presence of an aromatic moiety with six signals located between 120 and 160 ppm as well as an aliphatic portion of the molecule represented by resonances found from 15 to 40 ppm. An isopropyl group was identified from the ^{1}H NMR spectral data by the presence of two methyl groups at δ 1.36 (d, J = 6.7 Hz, $(CH_3)_2$-9) and a methine resonance centered at δ 3.32 (sept, J = 6.7 Hz, H-9). This unit was assigned to C-5 from HMBC correlations observed between the septet at δ 3.32 and ^{13}C NMR signals observed at δ 143.8 (C-5), 158.5 (C-4a), and 129.2 (C-6). Other long-range heteronuclear correlations between the ^{1}H NMR signals of the methyl unit at δ 1.31 (CH_3-3) and the ^{13}C NMR resonances found at δ 77.9 (C-2), 36.9 (C-3), and 35.1 (C-4) allowed the placement of the latter methyl unit at C-3. A fourth methyl unit was positioned on the aromatic ring by HMBC correlations between its ^{1}H NMR signals at δ 2.57 (CH_3-8) and the ^{13}C NMR resonances at δ 118.8 (C-7), 122.4, (C-8a), and 141.8 (C-8). A ketone carbonyl was also identified in the low-field region of the ^{13}C NMR spectrum at δ 199.5 (C-1). This signal was shown to be linked to the aliphatic part of the molecule by HMBC correlations with ^{1}H NMR signals at δ 3.89 (H-2), 4.29 (OH-2), and 2.00 (H-3). The structure was finally confirmed by comparison of ^{1}H and ^{13}C NMR data with desacetylcalaminthone[4] and mansonone G.[5] Desacetylcalaminthone is a monoterpene derivative isolated from *Calamintha ashei* (Lamiaceae), with an aliphatic moiety closely related to that of **3**, while mansonone G, isolated for the first time from the heartwood of *Mansonia altissima*,[6] shares a common aromatic pattern with **3**. The relative chiralities of carbons C-2 and C-3 were determined as *R** and *S** on the basis of the *trans* pseudo-diaxial coupling constants calculated between the ^{1}H NMR signals H-2 and H-3 (J = 12.5 Hz) as well as between H-3 and H-4 (J = 11.8 Hz). The relative stereochemistry of **3** was confirmed by a NOE correlation observed between ^{1}H NMR resonances at δ 3.89 (H-2) and 2.61 (H-4). Compound **3** was characterized as a new natural product, named mansonone P.



The ^{1}H and ^{13}C NMR spectra of compound **4** were very similar to those of **1**. The two compounds differed by the absence of signals for the methoxyl group of δ 3.79 in the ^{1}H NMR spectrum and δ 60.6 in the ^{13}C NMR spectrum. This methoxyl group was replaced by a hydroxyl group characterized by the appearance of a ^{1}H NMR singlet at δ 4.65 ppm. The position of the hydroxyl unit was confirmed by long-range heteronuclear correlations, with the ^{13}C NMR resonances at δ 141.2 (C-1), 140.1 (C-2), and 122.1 (C-3). The EIMS (*m*/*z* 264 $[M]^+$) of compound **4** confirmed the substitution. NMR experimental data were in agreement with those of alangicadinosides H and I,[7] two sesquiterpene diastereomers isolated from *Alangium premnifolium* (Alangiaceae) that showed a related aromatic moiety substitution. Compound **4** was identified as a new natural product named mansonone Q. The relative chiralities of carbons C-5 and C-8 were determined as *R** and *S**, respectively. They were attributed on the basis of differences observed in the coupling constants of protons H-7 (2H) and H-8 (J = 10.1 and 4.6 Hz) of mansonone Q when compared with those of the structurally related mansonones N (J = 1.7 and 7.8 Hz) and O (J = 1.2 and 7.9 Hz) as well as after

Table 1. ^{1}H NMR Data of Compounds **1**−**4** ($CDCl_3$)

position	1	2	3	4
1				
2			3.89 dd (2.4, 12.5)	
3			2.00 m (11.7, 12.5)	
4	6.86 s	7.06 dd (1.5, 3.4)	3.16 dd (4.9, 17.1)	6.88 s
			2.61 dd (11.9, 17.4)	
4a				
5				
6				
7	2.49 dd (12.5, 1.7)	2.47 dd (1.2, 12.8)	6.49 s	2.50 dd (4.6, 16.8)
	3.21 dd (12.6, 7.8)	3.10 (7.9, 13.1)		3.04 dd (10.1, 16.8)
8	3.79 m	3.54 m		3.60 m (10.1, 7.3)
8a				
9	2.15 sept. (6.9)	2.21 sept. (6.9)	3.32 sept. (6.7)	2.10 sept. (6.9)
OH-1	5.84 s			5.46 s
OH-2			4.29 d (2.2)	4.65 s
OCH_3-2	3.79 s			
CH_3-3	2.30 s	2.00 d (1.5)	1.31 d (6.4)	2.25 s
OH-5	4.05 s	3.95 s		3.88 s
OH-6			5.67 s	
CH_3-8	1.16 d (6.9)	1.06 d (6.7)	2.57 s	1.52 d (7.3)
$(CH_3)_2$-9	0.79 d (6.9)	0.89 d (7.0)	1.36 d (6.7)	0.86 d (6.7)
	0.99 d (6.7)	1.08 d (7.0)	1.36 d (6.7)	0.93 d (6.7)

observation of a lower-field chemical shift of the CH_3-8 group at δ 1.52 for mansonone Q, which was at δ 1.16 and 1.06 for mansonones N and O, respectively. This attribution is in agreement with the NOE effects noticed between the CH_3-8 group at δ 1.52 and the signal at δ 0.93 belonging to one of the methyl groups of the isopropyl moiety (CH_3-9) and the NOE effects between the H-7α signal at δ 2.50 and the CH_3-8 and CH_3-9 groups positioned at δ 1.52 and 0.86, respectively. The relatively large coupling constant obtained between ^{1}H NMR signals at δ 3.04 and 3.60 (J = 10.1 Hz) was attributed to a *cis* arrangement of these two protons, due to the ring tension resulting from the steric hindrance between the isopropyl moiety and the CH_3-8 group. Further studies are planned for the determination the absolute configuration of the isolated compounds by LC/NMR analysis of small amounts of derivatives obtained by Mosher esterification.

Table 2. ^{13}C NMR Data of Compounds **1**−**4** ($CDCl_3$)

carbon	1	2	3	4
1	145.1	179.3	199.5	141.2
2	144.4	180.1	77.9	140.1
3	128.8	137.2	36.9	122.1
4	120.1	136.0	35.1	119.9
4a	136.5	148.8	158.5	133.0
5	80.6	79.3	143.8	80.4
6	212.1	208.8	129.2	212.5
7	43.8	42.6	118.8	40.5
8	32.4	32.0	141.8	29.3
8a	124.6	137.0	122.4	123.7
9	39.6	38.4	27.2	38.0
OCH_3-2	60.6			
CH_3-3	16.0	15.5	18.8	15.6
CH_3-8	22.0	21.7	22.8	23.4
$(CH_3)_2$-9	18.2	17.7	20.1	16.7
	16.3	16.9	20.1	15.6

Experimental Section

General Experimental Procedures. Melting points were measured on a Mettler-FP-80/82 hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova NMR instrument in $CDCl_3$ at 500.00 and 125 MHz, respectively, with TMS as internal standard. UV spectra were measured on a Varian DMS 100S UV−vis spectrophotometer. Optical rotations were obtained using a Perkin-Elmer-241 polarimeter. Thin-layer chromatography was performed on silica gel 60 F_{254} Al sheets (Merck) using petroleum ether−EtOAc, 1:1, and RP-18 HPTLC F_{254} plates (Merck) with MeOH−H_2O in different proportions. EIMS and DCIMS were recorded on a Finnigan MAT TSQ-700 triple-stage quadrupole instrument. Column chromatography was performed on a silica gel column (63−200 μm; 650 × 65 mm i.d., Merck). The purity control of the isolated compounds was performed by LC/UV-DAD (Hewlett-Packard 1090 Series II) with a Nova-Pak RP-18 column (4 μm; 250 × 3.9 mm i.d.; Waters). Separation of the constituents was achieved using an acetonitrile (0.5% TFA)−H_2O (0.5% TFA) gradient (20:80 → 100:0) in 30 min followed by acetonitrile (0.5% TFA)−H_2O (0.5% TFA), 100:0, for 10 min. The detection was set at 210, 254, 280, and 366 nm.

Plant Material. The dried heartwood of *Mansonia gagei* was collected from Saraburi Province, Thailand, in 1997. The identity of this plant was confirmed by comparison with a voucher specimen no. 43281 at the herbarium of the Royal Forestry Department of Thailand, Bangkok.

Extraction and Isolation. The dried heartwood of *M. gagei* (14 kg) was milled and extracted with CH_2Cl_2 three times at room temperature. Evaporation of the solvent under vacuum yielded 427.6 g of crude CH_2Cl_2 extract. Following the same procedure, this residue of extraction was successively extracted with EtOAc and MeOH to give the 309.7 g of EtOAc extract and 620.1 g of MeOH extract. A part of the CH_2Cl_2 crude extract (102.2 g) was subjected to silica gel column chromatography using a step gradient of hexane−CH_2Cl_2 (1:1 → 0:1), CH_2Cl_2−EtOAc (9:1 → 0:1), and EtOAc−MeOH (9.5:0.5 → 4:6) as solvent system. The fractions were collected and combined according to TLC analysis in order to obtain 10 fractions (1−10). Each fraction was further subjected to silica gel column chromatography using mixtures of hexane−EtOAc of increasing polarity (7:3 → 2:8) as eluents. Fraction 4 afforded compounds **1** (13.3 mg) and **2** (23.5 mg). Fraction 5 afforded compound **3** (39.7 mg). Fraction 6 afforded compound **4** (37.3 mg).

Mansonone N (1), 1-hydroxy-1-isopropyl-6-methoxy-4,7-dimethyl-3,4-dihydronaphthalen-2(1*H*)-one: white crystals (hexane−EtOAc); mp 144.8−145.5 °C; $[\alpha]^{20}_D$ +30° (*c* 0.2, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 204 (4.25), 281 (2.35) nm; ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 1; EIMS *m*/*z* 278 $[M]^+$ (10), 235 (100), 207 (34), 165 (18), 149 (22), 109 (18), 97 (34), 71 (51); DCIMS *m*/*z* 296 $[M + NH_4]^+$ (50), 278 $[M]^+$ (8), 261 (100); HRESIMS *m*/*z* 301.1410 $[M + Na]^+$ (calcd for $C_{16}H_{22}O_4Na$, 301.1410).

X-ray Crystal Structure Analysis of Mansonone N (1). A hemisphere of Bragg intensities was measured, at 293 K, on a Stoe IPDS instrument equipped with graphite-monochro-

matized Mo Kα radiation ($\lambda = 0.71073$ Å). Altogether, 13 375 reflections were integrated up to sin $\theta/\lambda = 0.66$ Å^{-1}, of which 3389 were unique ($R_{int} = 0.034$). The intensities were corrected for Lorentz and polarization effects, but no absorption correction was deemed necessary. The space group was $P2_12_12_1$, and the lattice constants were $a = 8.905(2)$ Å, $b = 11.963(2)$ Å, and $c = 13.595(3)$ Å. The structure was solved and refined, using SHELXTL,[8] to $R_1 = 0.036$. The structure owes its cohesion to rather strong hydrogen bonds between the alcohol groups O-1 and O-5 and the ether group O-2 and the keto groups O-6. There are two intermolecular (O-1−H-1···O-6 2.08(2) Å, 152.5(2)° and O-5−H-5···O-6 2.03(2) Å, 151.4(2)°) and two intramolecular hydrogen bonds per molecule. These hydrogen bonds result in endless chains of molecules along the *a* lattice vector.[9]

Mansonone O, 5-hydroxy-5-isopropyl-3,8-dimethyl-7,8-dihydronaphthalene-1,2,6(5*H*)-trione (2): violet orthorhombic crystals (hexane−EtOAc); mp 125−128 °C; $[\alpha]^{20}_D$ −76° (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 200 (3.96), 420 (2.79) nm; ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 1; EIMS *m*/*z* 262 $[M]^+$ (8), 244 (11), 234 (25), 192 (31), 177 (52), 164 (57), 149 (100); DCIMS *m*/*z* 280 $[M + NH_4]^+$ (100), 247 (9); HRESIMS *m*/*z* 285.1095 $[M + Na]^+$ (calcd for $C_{15}H_{18}O_4Na$, 285.1097).

X-ray crystal structure analysis of mansonone O (2): space group $P2_12_12_1$, $a = 6.420(0)$ Å, $b = 7.791(2)$ Å, $c = 27.127(3)$ Å, $V = 1356.9(4)$, D_x 1.284 g/cm^3, $Z = 4$. X-ray diffraction data of an approximate 0.25 × 0.47 × 0.23 mm crystal were collected at room temperature on a Bruker SMART CCD area detector. The collected data was reduced using SAINT, and empirical absorption correction was performed using SADABS. A total of 10 067 reflections were measured, of which 3899 ($R_{int} = 0.0313$) reflections were unique. The structure was solved by direct methods using SHELXS. The non-hydrogen atoms were refined by full-matrix least-squares method with anisotropic displacement parameters using SHELX97.[8] Hydrogen atoms were found from difference Fourier maps and included in the refinement with isotropic displacement parameters. The final refinement gave $R_1 = 0.0782$ and $wR_2 = 0.1969$ [$I > 2\sigma(I)$].[9]

Mansonone P (3), 2,6-dihydroxy-5-isopropyl-3,8-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one: pale yellow powder, mp 175.2−176.1 °C; $[\alpha]^{20}_D$ −13.5° (*c* 0.2, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 212 (4.18), 234 (4.10), 282 (4.08) nm; ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 1; EIMS *m*/*z* 248 $[M]^+$ (48), 175 (47), 149 (62), 111 (44), 97 (68), 85 (85), 83 (87); DCIMS *m*/*z* 266 $[M + NH_4]^+$ (7), 249 $[M + H]^+$ (100); HRESIMS *m*/*z* 271.1305 $[M + Na]^+$ (calcd for $C_{15}H_{20}O_3Na$, 271.1304).

Mansonone Q (4), 1,5,6-trihydroxy-1-isopropyl-4,7-dimethyl-3,4-dihydronaphthalen-2(1*H*)-one: pale yellow powder, mp 105−106 °C; $[\alpha]^{20}_D$ +9.5° (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 200 (3.98), 275 (2.40) nm; ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 1; EIMS *m*/*z* 264 $[M]^+$ (15), 246 (24), 221 (100); HRESIMS *m*/*z* 287.1252 $[M + Na]^+$ (calcd for $C_{15}H_{20}O_4Na$, 287.1253).

Acknowledgment. The authors would like to thank the Swiss National Science Foundation for financial support of this work (grant No. 063670.00 to K.H.). One of us (P.T.) is grateful to the Thailand Research Fund for a 1998 Royal Golden Jubilee Ph.D. research assistant fellowship.

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(9) Crystallographic data of compounds **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre, Cambridge, U.K., under the reference numbers CCDC-167488 and -170714. These data may be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

NP020024E