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NEOLIGNANS AND A SESQUITERPENE FROM *CARYODAPHNOSIS TONKINENSIS*

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Key Word Index—*Caryodaphnosis tonkinensis*; Lauraceae; bark; leaves; neolignans; benzofurans; sesquiterpene.

Abstract—In addition to various eupomatenoids 2-(4-hydroxyphenyl)-5-(2-oxopropyl)-3-methylbenzo[*b*]furan and (2*R*,3*R*)-2,3-dihydro-2-(4-hydroxyphenyl)-3-methyl-5-[(*E*)-1-propenyl]benzo[*b*]furan, three hitherto unknown constituents have been isolated from *Caryodaphnosis tonkinensis*. Their structures were elucidated by spectral methods as *erythro*-1-(3,4-methylenedioxyphenyl)-2-{4-[(*E*)-1-propenyl]phenoxy}propan-1-ol, 2-(4-hydroxyphenyl)-3-methylbenzo[*b*]furan-5-carbaldehyde and 1,2,3,3a,4,5,6,7,8,8a-decahydro-7-(1-hydroxy-1-methylethyl)-1,4-dimethylazulene-3a,8a-diol.

INTRODUCTION

The eupomatenoids **3–6** and **13** as well as three polar eupomatenoids have been isolated from the bark of *Caryodaphnosis tonkinensis* (Lec.) A.-Shaw., an endemic tree of Vietnam [1, 2]. In further studies on this plant, we isolated eupomatenoid 1 [3] (yield 0.001% from leaves), the eupomatenoids 3–6 [1] (yields 0.16, 0.016, 0.041 and 0.32%, respectively, from leaves), 2-(4-hydroxyphenyl)-5-(2-oxopropyl)-3-methyl-benzo-[*b*]furan [4] (yield 0.001% from bark), (2*R*, 3*R*)-2,3-dihydro-2-(4-hydroxyphenyl)-3-methyl-5-[(*E*)-1-propenyl]benzo[*b*]furan [5] (yield 0.009% from bark, 0.008% from leaves) and three unknown compounds (**1–3**), the structures of which have been elucidated as *erythro*-1-(3,4-methylenedioxyphenyl)-2-{4-[(*E*)-1-propenyl]phenoxy}propan-1-ol (**1**) (yield 0.004% from bark, 0.012% from leaves), 2-(4-hydroxyphenyl)-3-methylbenzo[*b*]furan-5-carbaldehyde (**2**) (yield 0.007% from bark) and 1,2,3,3a,4,5,6,7,8,8a-decahydro-7-(1-hydroxy-1-methylethyl)-1,4-dimethylazulene-3a,8a-diol (**3**) (yield 0.002% from bark).

RESULTS AND DISCUSSION

The elemental composition of compound **1** was $C_{19}H_{20}O_4$ based on high-resolution mass spectrometry. Diagnostic peaks were found at m/z 151 $[C_8H_7O_3]^+$ and 161 $[C_{11}H_{13}O]^+$ due to cleavage of the molecule into two parts as a result of fission of the 1,2-bond (α-splitting of alcohols and ethers). The details of the structure, especially the substitution pattern of the aromatic rings and the *trans*-configuration of the propenyl side chain, followed from the ^{1}H NMR spectrum. The coupling constant $J_{1,2} = 4.6$ Hz (in acetone-d_6) indicated the *erythro*-configuration, when compared with similar compounds [5].

High-resolution mass spectrometry indicated the elemental composition of compound **2** to be $C_{16}H_{12}O_3$. Comparison of its NMR spectra with those of eupomatenoids [1] proved the benzo[*b*]furan structure and the positions of the substituents.

The elemental composition of **3** was shown by mass spectrometry to be $C_{15}H_{28}O_3$ (high-resolution mass spectrometry of the $[M - H_2O]^+$ peak). The DQF-COSY spectrum showed two ^{1}H-spin systems: 1-Me, H-1, H-2, H-2′, H-3 and H-3′, and 4-Me, H-4, H-5, H-5′, H-6, H-6′, H-7, H-8 and H-8′. Geminal protons were detected and the corresponding ^{13}C-signals were assigned using the HMQC spectrum. The HMBC spectrum indicated couplings between C-8a and the protons of the 1-Me group, between C-3a and the protons of the 4-Me group and also between C-7 and the protons of the 1-hydroxy-1-methylethyl group. Structure **3** is in accordance with these data and takes into account the tertiary nature of all three hydroxyl groups which followed from the ^{1}H NMR spectrum. The relative and absolute configuration of **3** were not determined. A stereoisomer with the constitution of **3** has been synthesized previously [6]. Comparison of the methyl signals in the ^{1}H NMR spectrum displayed that both compounds were not identical.

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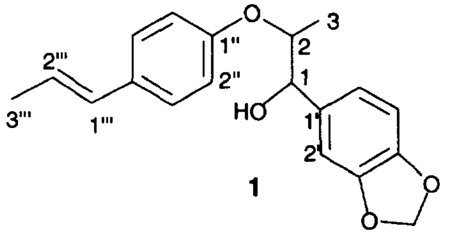

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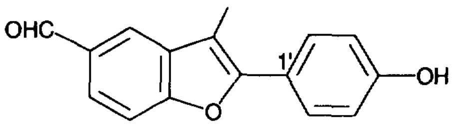

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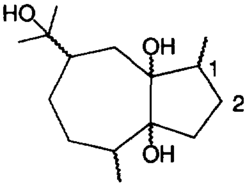

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EXPERIMENTAL

Plant material. Bark and leaves of *Caryodaphnosis tonkinensis* were collected in the National Park Cuc Phuong, Province of Ninh Binh, Vietnam, in January 1993. The species was identified by Dr Tran Dinh Dai, Hanoi. A voucher specimen is deposited in the Herbarium of the Institute of Ecology and Natural Resources of the National Centre for Scientific Research, Hanoi.

Extraction. The dried bark or leaves (at 40°) were extracted with petrol followed by MeOH at room temp. Evapn of the petrol and MeOH *in vacuo* gave two residues, respectively, the latter of which was partioned between H_2O and $CHCl_3$–EtOH (2:1). The organic phase was evapd *in vacuo*.

erythro-1-(3,4-*Methylenedioxyphenyl*)-2-{4-[(E)-1-*propenyl*]*phenoxy*}*propan*-1-*ol* (**1**). Chromatography of the petrol residue from bark or leaves over silica gel with $CHCl_3$–n-hexane (3:2) followed by prep. TLC (silica gel) with the same solvent furnished **1** as an oil, yield 0.004% from bark, 0.012% from leaves. $[\alpha]_D^{20}$ −36.1° ($CHCl_3$; c 0.66). ^1H NMR (500 MHz, $CDCl_3$): δ 1.18 (d, $J = 6.1$ Hz, H-3), 1.85 (d, $J = 6.6$ Hz, H-3'''), 2.44 (d, $J = 3.0$ Hz, OH), 4.50 (dq, $J = 3.9$ and 6.3 Hz, H-2), 4.92 (dd, $J = 3.0$ and 3.0 Hz, H-1), 5.95 (s, OCH_2O), 6.10 (dq, $J = 15.7$ and 6.5 Hz, H-2'''), 6.34 (dq, $J = 15.9$ and 1.5 Hz, H-1'''), 6.79 (d, $J = 8.0$ Hz, H-5'), 6.85 (d, $J = 8.8$ Hz, H-2'', H-6''), *ca* 6.85 (m, H-6'), 6.95 (d, $J = 1.5$ Hz, H-2'), 7.25 (d, $J = 8.5$ Hz, H-3'', H-5''); ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.2 (C-3), 18.5 (C-3'''), 75.0 (C-1), 78.1 (C-2), 101.0 (OCH_2O), 107.0 (C-2'), 108.1 (C-5'), 116.3 (C-2'', C-6''), 119.8 (C-6'), 124.0 (C-2'''), 127.0 (C-3'', C-5''), 130.2 (C-1'''), 131.5 (C-1'), 134.1 (C-4''), 147.0 (C-4'), 147.6 (C-3'), 156.3 (C-1''); EI-MS (70 eV) m/z (rel. int.): 312.1392 $[M]^+$ ($C_{19}H_{20}O_4$, calcd 312.1362) (20), 161.0983 ($C_{11}H_{13}O$, calcd 161.0966) (24), 151.0402 ($C_8H_7O_3$, calcd 151.0395) (100).

2-(4-*Hydroxyphenyl*)-3-*methylbenzo*[*b*]*furan*-5-*carbaldehyde* (**2**). Chromatography of the $CHCl_3$–EtOH extract from bark over silica gel with $CHCl_3$ followed by prep. TLC (silica gel) with the same solvent gave **2**; amorphous; yield 0.007%. ^1H NMR (500 MHz, $CDCl_3$-some drops of MeOH): δ 2.47 (s, 3-Me), 6.96 (d, $J = 8.7$ Hz, H-3', H-5'), 7.56 (d, $J = 8.4$ Hz, H-7), 7.68 (d, $J = 8.7$ Hz, H-2', H-6'), 7.82 (dd, $J = 8.4$ and 1.7 Hz, H-6), 8.06 (d, $J = 1.4$ Hz, H-4), 10.1 (s, CHO); ^{13}C NMR (126 MHz, $CDCl_3$): δ 9.3 (3-Me), 110.1 (C-3), 111.4 (C-7), 115.8 (C-3', C-5'), 121.9 (C-4), 123.5 (C-1'), 126.1 (C-6), 128.6 (C-2', C-6'), 131.8 (C-3a), 132.1 (C-5), 152.8 (C-7a), 155.9 (C-4'), 157.2 (C-2), 192.0 (CHO); EI-MS (70 eV) m/z (rel. int.): 252.0782 $[M]^+$ ($C_{16}H_{12}O_3$, calcd 252.0786) (100), 223.0821 $[M - CHO]^+$ ($C_{15}H_{11}O_2$, calcd 223.0759) (23).

1,2,3,3*a*,4,5,6,7,8,8*a*-*Decahydro*-7-(1-*hydroxy*-1-*methylethyl*)-1,4-*dimethylazulene*-3*a*,8*a*-*diol* (**3**). Chromatography of the petrol residue from bark over silica gel with $CHCl_3$–n-hexane (4:1) provided **3**; amorphous; yield 0.002%. $[\alpha]_D^{20}$ +3.6° ($CHCl_3$; c 0.10). ^1H NMR (500 MHz, $CDCl_3$, in part derived from DQF-COSY): δ 0.92 (d, $J = 7.1$ Hz, 1-Me), 1.00 (H-6), 1.07 (d, $J = 7.0$ Hz, 4-Me), 1.08 (H-3), 1.17, 1.20 (both s, Me_2COH), 1.50 (H-5), 1.54 (H-7), 1.64 (H-3'), 1.66 (H-2, H-8), 1.69 (H-6'), 1.72 (H-5'), 1.98 (H-2'), 2.14 (H-1), 2.32 (H-8'), 2.37 (H-4'); ^{13}C NMR (126 MHz, $CDCl_3$); δ 16.2 (4-Me), 17.0 (1-Me), 24.9 (C-6), 26.7, 27.6 (Me_2COH), 27.2 (C-3), 29.3 (C-8), 29.4 (C-2), 31.3 (C-5), 32.3 (C-4), 40.4 (C-1), 47.2 (C-7), 72.6 (C-8a), 73.3 (Me_2COH), 73.7 (C-3a); EI-MS (70 eV) m/z (rel. int.): 256 $[M]^+$ (1), 238.1972 $[M - H_2O]^+$ ($C_{15}H_{26}O_2$, calcd 238.1933) (1), 220.1825 $[M - 2H_2O]^+$ ($C_{15}H_{24}O$, calcd 220.1827 (9), 205.1595 $[220 - Me]^+$ ($C_{14}H_{21}O$, calcd 205.1592) (25), 59 $[Me_2COH]^+$ (100).

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