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Wasabidienone-E, a New Cyclohexadienone Derivative Containing Hydroxyethylamino Group, from Potato Culture Solution of Phoma wasabiae Yokogi[#]

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Wasabidienone-E, a new cyclohexadienone derivative containing hydroxyethylamino group, has been isolated from the potato culture solution, and its structure was determined to be 5-(2-hydroxyethylamino)-3-methoxy-2,6-dimethyl-(6R*)-[(2R*)-2-methylbutyryloxy]-2,4-cyclohexadien-1-one by spectroscopic analysis and chemical transformation.

In the previous studies,[1] we have reported the isolation and the structural elucidation of a novel natural cyclohexadienone derivative, wasabidienone-A (WA) as tautomeric mixture **1a** and **1b**, from the potato culture solution of Phoma wasabiae Yokogi.[2] WA is sensitive to oxygen and easily converted into some oxidized compounds containing 2-hydroxy-6-methoxy-3,4-dimethyl-1,4-benzoquinone.[3] Further investigation on the yellow pigments from the same culture solution has now led to the isolation of a new cyclohexadienone derivative containing hydroxyethylamino group named wasabidienone-E (WE) (**2**). This communication deals with the structure determination of **2**.

The blackish culture solution was treated with the same manner as described in the previous paper.[1] The yellowish-orange band on TLC [R_f value: 0.12 (C_6H_6-CH_3OH, 9:1)] was eluted with Et_2O and after further purification on TLC, the precipitates obtained from the elute were crystallized from hexane-Et_2O(1:2) to give yellowish-orange prisms, WE (**2**), yield 0.3-1.8 mg/l, mp 132-134 °C, $[\alpha]_D$ $+50.5\,^{\circ}$(c 1.1, $CHCl_3$), $C_{16}H_{25}NO_5$ [Found: m/z 311.1739 (Calcd: M^+ 311.1731) and Anal. C, H, N]. Other spectral data were as follows: IR (KBr) 3270, 1730, and 1620 cm^{-1}; UV (95% EtOH) 237 nm (log ε 4.41), 260$_{sh}$(3.71), 416 (4.02); ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.93 (3H, t, J=7.0 Hz), 1.19 (3H, d, J=7.0 Hz), 1.52 (3H, s), 1.59 (2H, m, J=7.0 Hz), 1.75 (3H, s), 2.48 (1H, m, J=7.0 HZ)), 3.19 (1H, t, J=5.0 Hz),[4] 3.25 (2H, t, J=5.0 Hz), 3.80 (2H, t, J=5.0 Hz), 3.88 (3H, s), 5.08 (1H, s), 5.15 (1H, t, J=5.0 Hz)[4] and ^{13}C NMR.[5] Comparison of these data with those[1] of WA (**1**) and its methyl ether (**3** and **4**) indicated the compound to be a butyryloxy-cyclohexadienone derivative. In particular, the ^{13}C NMR signals of **2**, except for those of δ 79.3, 59.4, and 44.8 of **2** and 55.9 of **3**,[1] were in good agreement with

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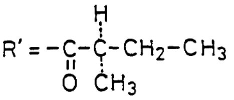
[#] This paper is dedicated to the late Professor Ryozo Goto, Kyoto university.

those of **3**. The acetylation of **2** with Ac_2O-C_5H_5N gave a monoacetate **5**, oily substance, m/z 353.1847 (Calcd for $C_{18}H_{27}NO_6$: M^+ 353.1839); IR ($CHCl_3$) 3420, 1740, 1680, and 1637 cm^{-1}; δ_H 2.08 (3H, s). Moreover, the reduction of **2** with Zn in AcOH gave a phenol derivative **6**, mp 125-127 °C (colorless prisms), m/z 211 (M^+); IR ($CHCl_3$) 3600, 3430, and 1620 cm^{-1}; δ_H 2.01, 2.08 (each 3H, s), 3.27 (2H, t, J=6.0 Hz), 3.48 (2H, bd),[4] 3.79 (3H, s), 3.90 (2H, t, J=6.0 Hz), and 5.99 (1H, s). The acetylation of **6** with Ac_2O-C_5H_5N at room temperature easily afforded a triacetate **7**, colorless oil, molecular formula $C_{17}H_{23}NO_6$ (Found: m/z 337.1543); IR ($CHCl_3$) 1770, 1740, 1660, and 1620 cm^{-1}.[6]

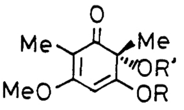
The existence of 2-hydroxyethylamino group in **2** was deduced from the presence of vicinal two methylene groups [δ_H 3.25, 3.80 (each 2H, t, J=5.0 Hz)] in the ^1H NMR spectrum of **2** and from the easy formation of the corresponding triacetate **7** from the phenolic derivative **6**. In the ^1H NMR spectrum of **7**,[6] in addition to the three acetoxyl signals, the spectrum also revealed as set of peaks [δ_H 3.56 (1H, m), 4.16 (1H, m), and 4.21 (2H, m)] suggesting the presence N-acetyl-2-acetoxyethylamino group[7] and one low-field singlet δ_H 6.58 (1H, s). The aromatic proton due to H-4 shifted considerably down field ($\Delta\delta$0.59) in **7** indicating that the proton is ortho position to the acetylated side chain. The NOE experiment (30% enhancement) of **7** also revealed then correlation between H-4 and methoxyl protons. Therefore, the structure of **7** was determined as 1-acetoxy-3-(N-acetyl-2-acetoxyethylamino)-5-methoxy-2,6-dimethylbenzene.

Thus based on chemical and spectral considerations, 5-(2-hydroxyethylamino)-3-methoxy-2,6-dimethyl-(6R*)-[(2R*)-2-methylbutyryloxy]-2,4-cyclohexadien-1-one structure (**2**) was assigned to wasabidienone-E.

1~**5**: R' =

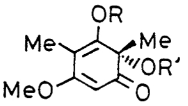


$-\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-CH_2-CH_3$



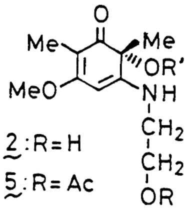
1a: R=H

3: R=Me



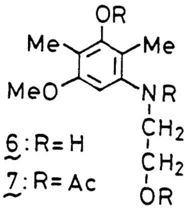
1b: R=H

4: R=Me



2: R=H

5: R=Ac



6: R=H

7: R=Ac

References

1) O. Soga, H. Iwamoto, S. Date, T. Watanabe, K. Tanaka, K. Hata, A. Takuwa, and M. Nakayama, Chem. Lett., 1984, 339; O. Soga, H. Iwamoto, A. Takuwa, H. Nozaki, J. Kuramoto, and M. Nakayama, Agric. Biol. Chem., 51, 283 (1987).

2) O. Soga, Z. Naturforsch., B, 31, 124 (1976); O. Soga, Agric. Biol. Chem., 46, 1061 (1982); H. Haraguchi, O. Soga, and M. Taniguchi, ibid., 50, 1905 (1986).

3) O. Soga and H. Iwamoto, Z. Naturforsch., B, 36, 277 (1981).

4) These signals disappeared by addition of deuterium oxide.

5) ^{13}C NMR δ s: 192.7, 174.7, 172.4, 161.7, 101.2, 78.4; d: 79.3, 40.3; t: 59.4, 44.8, 26.4; q: 55.7, 27.8, 16.4, 11.6, and 7.3.

6) ^1H NMR 1.79, 1.95, 1.98, 2.02, 2.33, 3.81 (each 3H, s), 3.56 (1H, m), 4.16 (1H, m), 4.21 (2H, m), and 6.58 (1H, s); ^{13}C NMR δ s: 171.1, 170.7, 168.3, 156.7, 149.4, 139.8, 120.6, 120.0; d: 108.3; t: 61.8, 47.3; q: 55.8, 22.1, 20.4, 11.0, and 9.4.

7) These abnormal chemical shifts were also observed clearly in those of a diacetyl compound [δ_H 3.41, 4.24 (each 1H, m), and 4.27 (2H, m)] derived from N-2-hydroxyethyl-o-toluidine.

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