BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (3), 943—944 (1978)

A Quinone and a Phenol from a Myrsinaceae Plant

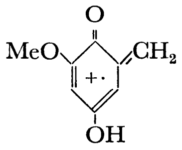
Takenori KUSUMI, Hiroshi KAKISAWA,* Yuh-Pan CHEN,* Jing-Ing LYN,* and Hong-Yen HSU*
Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 300-31
**Brion Research Institute of Taiwan, 116, Chung-Ching South Rd., Sec. 3, Taipei, Taiwan*

(Received June 18, 1977)

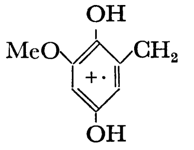
Synopsis. Ardisianone and ardisianol isolated from *Ardisia quinquegona* Blume were determined to be 2-(2-acetoxypentadecyl)-6-methoxy-1,4-benzoquinone and 4-acetoxy-2-(2-acetoxypentadecyl)-6-methoxyphenol, respectively.

In the course of our studies on constituents of Chinese herbal drugs, a yellow pigment and a phenol, designated as ardisianone and ardisianol, respectively, were found from *Ardisia quinquegona* Blume. The plants of Myrsinaceae species are known to contain many benzoquinoid pigments.[1–4] All of these quinones have been proved to possess 2-alkyl-3,6-dihydroxy(or methoxy)-1,4-benzoquinone chromophores. In contrast to these pigments, the present new pigment has been found to have 2-alkyl-6-methoxy-1,4-benzoquinone group.

The UV absorption maxima (268 and 363 nm) of ardisianone, $C_{24}H_{38}O_5$, appeared in shorter wave length than those of 2-hydroxy-5-methoxy-,[1] 2-hydroxy-6-methoxy-,[5] and 5-alkyl-3-hydroxy-2-methoxy-1,4-benzoquinones,[5] and coincided with those of 3-,[5] 5-,[5] and 6-methoxy-2-alkyl-1,4-benzoquinones.[5] The presence of the methoxybenzoquinone group was supported by the appearance of characteristic fragments[6] **a** and **b** in the mass spectrum. The PMR spectrum showed a pair of doublets at δ 5.84 (J=2 Hz) and 6.83 (J=2 Hz) assignable to 5- and 3-protons of 2-alkyl-6-methoxy-1,4-benzoquinone from the coupling constant. The latter doublet was broadened by coupling with methylene protons (δ 2.63) at 2-position. The PMR spectrum showed the signals of methoxyl (δ 3.80) and acetoxyl (δ 1.98) groups, in addition to a broad singlet (24 H) at δ 1.28 and a deformed triplet (3 H) at δ 0.88, which could be assigned to methylene and methyl protons of tridecyl group, respectively. Decoupling experiments revealed that two nonequivalent protons observed at δ 2.63 is coupled to a proton at δ 4.95 with J=8 and 4 Hz, and also to a quinoid proton at δ 6.83 with J=0.5 Hz, showing the presence of Ar–CH_2–CH(OAc)– moiety. Irradiation at δ 2.63 changed the multiplet at δ 4.95 into a broad triplet and the broad doublet at δ 6.83 into a sharp doublet. From these facts the structure of ardisianone was assigned to **1**.



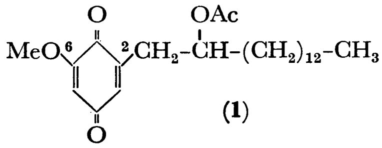
a



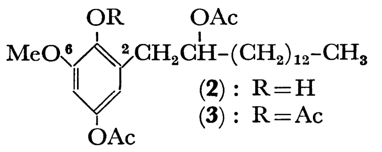
b

Ardisianol, $C_{26}H_{42}O_6$, showed UV maxima at 230 and 283 nm, which shifted to 258 and 298 nm by addition of aqueous potassium hydroxide. Its IR spectrum exhibited the absorption bands at 3400 (OH) and 1770 cm^{-1} (phenyl acetate). These spectral properties indicated that ardisianol is a phenol possessing an acetoxyl group on the aromatic ring. The intense absorptions at 2925 and 1720 cm^{-1} suggested the presence of an alkyl chain bearing another acetoxyl group. The PMR spectrum of ardisianol partly resembled that of **1**, and the presence of methoxyl and 2-acetoxypentadecyl groups was easily deduced from the signals at δ 3.81 (3H, s), 1.90 (3H, s), 2.80 (2H, $\underline{AB}$X), 5.05 (1H, m), 1.26 (24H, bs), and 0.90 (3H, t). A sharp singlet (3H) at δ 2.20 was assignable to an acetoxyl group of phenyl acetate. The aromatic protons of ardisianol appeared as a broad singlet at δ 6.41 (2H). These facts indicated that ardisianol was tetrasubstituted (OMe, OH, OAc, and 2-acetoxypentadecyl)benzene, but the positions of these substituents were not clarified from the spectral data.

Hydrogenation of **1** over platinum catalyst in acetic anhydride followed by addition of sodium acetate afforded a colorless monoacetyl product without formation of the diacetate. The monoacetylated product was found to be identical with ardisianol. The monoacetate was further converted into the diacetate (**3**) under rather forced reaction conditions. The monoacetyl group was first incorporated at C_4–OH group by steric effect, and hence the structure of ardisianol was represented by 4-acetyldihydroardisianone (**2**). The PMR spectrum of the diacetate (**3**) showed an AB quartet centered at δ 6.54 due to aromatic protons. The coupling constant (J=2 Hz) is well consistent with the 2,6-disubstituted hydroquinone of the structure (**3**).



(**1**)



(**2**) : R=H
(**3**) : R=Ac

Experimental

The melting points are uncorrected. PMR spectra were recorded on a Hitachi H-60 instrument, TMS being used as an internal standard (δ, ppm). IR spectra were taken on a Hitachi EPS-3T spectrometer. Mass spectra were obtained with a Hitachi RMU-6M spectrometer.

Isolation of Ardisianol (2). The dried and pulverized stems and leaves (720 g) of *Ardisia quinquegona* Blume (Myrsinaceae) were extracted with hot hexane three times. The combined hexane extracts were concentrated under vacuum, and the dark brown solid residue (20 g) was chromatographed on a column of silica gel (Merck, Kieselgel 60, Art, 7734, 1 Kg). Elution of the column with hexane–ethyl acetate (8 : 1) yielded a white solid, which on crystallization from hexane gave ardisianol (260 mg) as colorless needles; mp 82—84 °C. Found: C, 68.44; H, 9.39%. Calcd for $C_{26}H_{42}O_6 \cdot 1/3H_2O$: C, 68.38; H, 9.42%. UV (EtOH): 230sh (logε, 3.74) and 283 nm (3.52). IR (KBr): 3400, 2925, 2850, 1770, 1720, 1630, 1600, 1500, 1470, 1440, 1380, 1265, and 1230 cm^{-1}. MS *m/e* (rel intensity): 450 (M$^+$, 0.5), 422 (4), 408 (0.5), 390 (3), 380 (4), 362 (13), 348 (19), 320 (100), 154 (19), and 153 (18).

Isolation of Ardisianone (1). Further elution with hexane–ethyl acetate (8 : 1) furnished a yellow solid, which on crystallization from ethanol yielded ardisianone (350 mg) as yellow needles; mp 49—54 °C. Found: C, 70.82; H, 9.69%. Calcd for $C_{24}H_{38}O_5$: C, 70.90; H, 9.42%. UV (EtOH); 268 (logε, 4.12) and 363 nm (3.01). IR (KBr): 2925, 2850, 1730, 1690, 1655, 1625, 1605, 1470, 1380, 1330, 1240, and 1050 cm^{-1}. MS *m/e* (rel intensity): 408 (0.5), 407 (0.5), 406 (M$^+$, 0.5), 364 (7), 346 (27), 194 (21), 153 (20), and 152 (18).

Ardisianol from Ardisianone. A mixture of ardisianone (1; 17 mg) and platinum oxide (7 mg) in acetic anhydride (0.2 ml) was stirred under hydrogen atmosphere at room temperature. After 5 min, yellow color of the mixture disappeared. Sodium acetate (20 mg) was then added, and the mixture was stirred under hydrogen overnight. The product was taken up into ether. The ethereal solution was washed with water and brine, and dried over sodium sulfate. Evaporation of the ether yielded pale yellow crystals (17 mg). Recrystallization from hexane gave rise to white crystalline powder (mp 84—86 °C), the IR spectrum (KBr) of which was superimposable over that of ardisianol.

1,4-Diacetoxy-3-methoxy-5-(2-acetoxypentadecyl)benzene (3). A solution of ardisianol (14 mg) in pyridine (0.1 ml) and acetic anhydride (0.1 ml) was warmed at 45 °C in a sealed tube overnight. The reaction mixture was poured into water, and extracted with ether. After being washed with water, the ethereal layer was evaporated, affording colorless crystals. Recrystallization from hexane yielded ardisianol acetate (**3**); mp 60.5—62 °C. Found: C, 67.63; H, 8.94%. Calcd for $C_{22}H_{44}O_5 \cdot 1/3H_2O$: C, 67.46; H, 9.03. IR(KBr): 1750 and 1730 cm^{-1}. PMR (δ, CCl_4): 0.91 (3H, t), 1.28 (24H, bs), 1.98 (3H, s), 2.24 (3H, s), 2.30 (3H, s), 2.70 (2H, ABX, $J_{AB}=13$, $J_{AX}=6$, $J_{BX}=7$ Hz), 3.79 (3H, s), 4.75 (1H, m), and 6.55 (2H, AB, $J_{AB}=2$ Hz).

References

1) H. Ogawa and S. Natori, *Phytochemistry*, **7**, 773 (1968).

2) C. B. Rao and V. Venkateswarlu, *J. Org. Chem.*, **26**, 4529 (1942).

3) M. Hiramoto, *Yakugaku Zasshi*, **59**, 671 (1937), **62**, 460, 464 (1942).

4) H. Ogawa, S. Sakaki, K. Yoshihira, and S. Natori, *Tetrahedron Lett.*, **1968**, 1387.

5) R. H. Thomson, "Naturally Occuring Quinones," Academic Press, New York (1971), Chap. 3.

6) H. Ogawa and S. Natori, *Chem. Pharm. Bull.*, **16**, 1709 (1968).