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STRUCTURE OF ARNEBIFURANONE, NEW MONOTERPENYLBENZOQUINONE FROM ARNEBIA EUCHROMA

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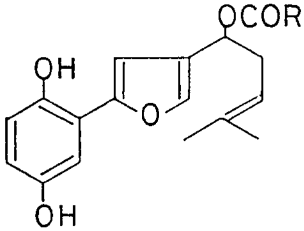
Summary: A new monoterpenylbenzoquinone named arnebifuranone (**5**) was isolated from Arnebia euchroma (Royle) Johnst. and its structure was elucidated to be a 2,3-dimethoxy-1,4-benzoquinone having a monoterpene side chain containing a furan ring. The monoterpene moiety is bonded to the benzoquinone ring with its head carbon.

During the course of our studies on biologically active compounds contained in medicinal plants, we have elucidated the structures of four inhibitors of prostaglandin (PG) biosynthesis, shikonofuran (**1**), arnebinol (**2**), des-O-methyllasiodiplodin (**3**) and arnebinone (**4**), which were isolated from the root of Arnebia euchroma (Royle) Johnst., an oriental medicinal drug called "Nanshikon" in Japan.3,4) As a continuing study on the constituents of A. euchroma, another new monoterpenylbenzoquinone has been isolated and this paper reports structural elucidation of the new benzoquinone. Repeated fractionation and separation of methanolic extracts of the title plant yielded the new benzoquinone as an orange oil, which was named arnebifuranone. It showed 18.7% inhibition of PG biosynthesis at a concentration of 20 µg/ml in our bioassay system and gave following spectral data. UV λ_{max}^{EtOH} nm: 212, 266, 404. IR ν_{max}^{nujol} cm^{-1}: 1655, 1600, 1500, 1450, 1380, 1005, 870. High MS m/z: 235.0951; Calcd for $C_{18}H_{20}O_5$ 235.0971. The UV spectrum was very similar to that of arnebinone (**4**) and the presence of 2,3-dimethoxy-1,4-benzoquinone chromophore was confirmed by the comparison with UV absorption data of benzoquinones having two methoxy groups.5) The ^1H- and ^{13}C-NMR spectra revealed the presence of three methylene groups in the side chain moiety.6) Upon irradiation of a methylene signal at δ 3.10(d, J=2.0 Hz) in ^1H-NMR a triplet at δ 6.24 (J=2.0 Hz) collapsed to a singlet, indicating that the side chain is bonded to the benzoquinone ring with the methylene group. Successive decoupling experiments revealed the sequence of methyl, olefinic methine and two methylene



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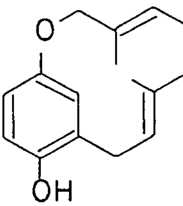

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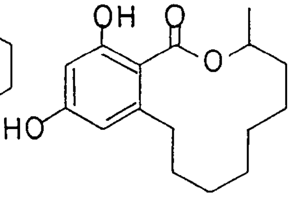

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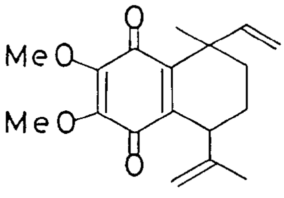

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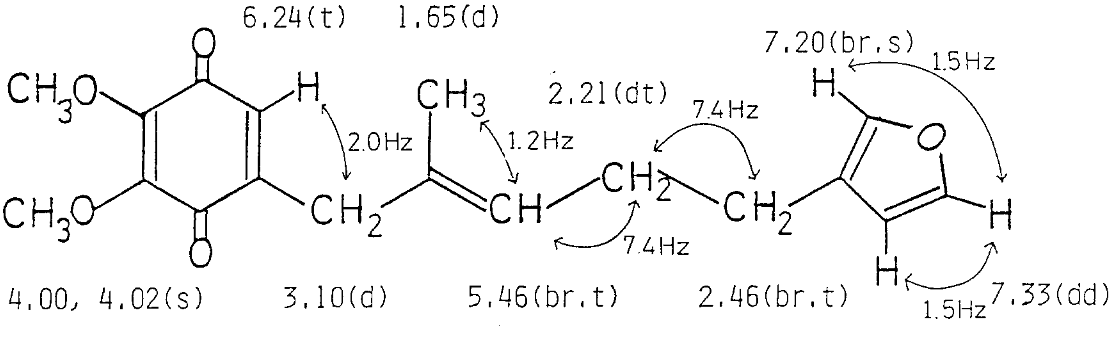
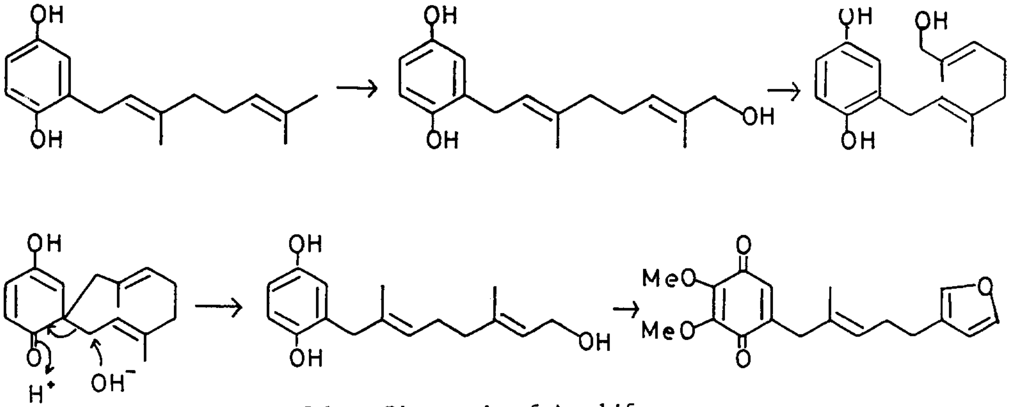


arnebifuranone (5)

groups as shown in structure **5**. Since the methylene signal at δ 3.10 showed clear coupling only with the quinone proton at δ 6.24, it should be bonded to quarternary carbon. Remained C_4H_3O moiety gave three proton signals at δ 6.25 (br.d), 7.20 (br.s) and 7.33 (dd, J=1.5, 1.5 Hz) and they were assigned to the protons of a furan ring. A signal of methylene group at δ 2.46 showed long range couplings with furan protons (δ 7.20 and 6.25), indicating that the furan ring is bonded to the methylene group. Thus emerged structure **5** has a monoterpenyl side chain bonded to the benzoquinone ring in a reverse way, i.e. the carbon corresponding to the head of geranyl chain is bonded to the benzoquinone ring. The biogenesis of arnebifuranone (**5**) may be rationally accounted for by starting from geranylhydroquinone which is a presumed intermediate in the biosynthesis of shikonofuran (**1**), arnebinol (**2**) and arnebinone (**4**).



Scheme Biogenesis of Arnebifuranone

References and Note

1) Visiting investigator from Shenyang College of Pharmacy, People's Republic of China.
2) Institute of Applied Microbiology, University of Tokyo.
3) Yao Xin-Sheng, Y.Ebizuka, H.Noguchi, F.Kiuchi, Y.Iitaka, U.Sankawa and H.Seto, Tetrahedron Lett., **24** 2407 (1983).
4) Yao Xin-Sheng, Y.Ebizuka, H.Noguchi, F.Kiuchi, Y.Iitaka, U.Sankawa and H.Seto, Tetrahedron Lett., **24** 3247 (1983).
5) R.A.Morton, in "Biochemistry of Quinone", Ed. by R.A.Morton, Chapt. 2, Academic Press, London, pp 23-65 (1965).
6) ^{13}C-NMR (100 MHz) ppm: 23.4(q), 24.7(t), 28.6(t), 30.7(t), 61.0(q), 61.1(q), 110.8(d), 124.3(s), 128.8 (d), 130.0(s), 130.3(s), 130.3(d), 130.8(s), 138.8(d), 142.6(d), 145.0(s), 184.0(s), 184.2(s).

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