Communications to the Editor

[Chem. Pharm. Bull.
36(8)3234—3236(1988)]

A NEW BINAPHTHOQUINONE FROM *DIOSPYROS MARITIMA* BLUME

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From the fresh fruit of *Diospyros maritima* Blume a new binaphthoquinone, ethylidene-6,6'-biplumbagin (1), was isolated, besides two known binaphthoquinones, elliptinone (2) and maritinone (3). The structure of the new compound was established by chemical and spectroscopic means.

KEYWORDS —— ethylidene-6,6'-biplumbagin; elliptinone; maritinone; binaphthoquinone; *Diospyros maritima*; Ebenaceae

In a previous paper,[1] we reported the isolation of 3-bromoplumbagin (4) from the fruit of *Diospyros maritima* Blume (Japanese name: ryukyugaki) (Ebenaceae). Here we describe the isolation and structure of a new binaphthoquinone from the same source.

The ethanol extract of the fresh fruit afforded, after column chromatographic separation (Wakogel C-300, Wako Pure Chemical), three naphthoquinones 1, 2, and 3.

The quinone (2), orange needles with mp of 290-300°C (dec.) from benzene, is elliptinone,[2-4] which formed dimethyl ether,[2,3] orange-yellow needles with mp of 266-268°C from benzene, when treated with methyl iodide and silver oxide in chloroform. The quinone (3), orange-red needles with mp of 199-200°C from hexane, is maritinone,[5] which formed dimethyl ether,[5] orange plates with mp of 269-271°C from benzene, in the same way as the quinone (2). These compounds were identified by comparing their spectral data with those described in the literature.

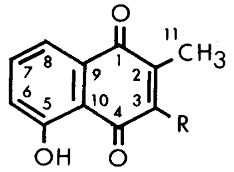
The quinone (1), orange-yellow needles with mp of 193-195°C from hexane, has a molecular formula $C_{24}H_{18}O_6$ (M^+ 402. Anal. Calcd: C, 71.64; H, 4.51. Found: C, 71.43; H, 4.49). The IR (ν_{max}^{KBr} cm^{-1}: 1660, 1638, 1602) and UV [$\lambda_{max}^{CHCl_3}$ nm(log ε): 247sh(4.35), 263(4.41), 437(4.04)] spectra had the characteristics of juglone derivatives. The ^1H-NMR spectrum (in $CDCl_3$) showed one singlet (2H) at δ 12.43 arising from two hydrogen bonded hydroxyls, one doublet (6H, J=1.5 Hz) at δ 2.14 from two quinonoid methyls, one quartet (2H, J=1.5 Hz) at δ 6.73 from two quinonoid protons, and two doublets (2H, J=8.0 Hz each) at δ 7.49 and 7.57 from two pairs of *ortho*-coupled aromatic protons. In addition, a doublet (3H, J=6.5 Hz) at δ 1.64 coupled to a quartet (1H, J=6.5 Hz) at δ 4.97 can be assigned to an ethylidene group, $CH_3CH<$, linking two benzene rings. This ^1H-NMR spectrum indicates that the quinone (1) is a symmetrical dimer of plumbagin (5) linked by an ethylidene bridge between the two benzene rings. The alternative 3-methyljuglone structure is eliminated by reduction of the quinone (1) with sodium dithionite,[6] which afforded plumbagin (5) in a low yield. Since the low field chemical shifts of the *ortho*-

coupled aromatic protons indicate that the protons are in the 7- and 8-posotions of the naphthoquinone ring, the new quinone (**1**) must be ethylidene-6,6'-biplumbagin. The position of the dimeric linkage can be established by the downfield shift of the signals of the carbons involved, with a reduction in intensity in the ^{13}C-NMR spectrum.$^{7)}$ The symmetrical dimeric linkage of the quinone (**1**) is reflected in its ^{13}C-NMR spectrum (Table I) which exhibits eleven lines for the 22 carbons, except for ethylidene carbons. Ten of these lines correspond closely to those of plumbagin (**5**) in both chemical shift and intensity. The eleventh line corresponding to C-6 (δ 124.1) in the ^{13}C-NMR spectrum of plumbagin (**5**) is replaced by a line at δ 140.5 with reduced intensity due to substitution.$^{7)}$ Structure **1** appears to be supported from the M^+-18 peak (rel. int. 41%) in the MS spectrum, which is attributable to a six-member stable oxonium ion formed by the intramolecular elimination of H_2O from the molecular ion. Thus, a 6-6' dimeric linkage through an ethylidene bridge is obvious, and structure **1** is established. The linkage by an ethylidene bridge between two naphthoquinone rings is quite rare in naturally occurring quinones.$^{4)}$ So far, only two compounds have been isolated from the pigments of *Spatangus purpureus* (sea urchin).$^{6)}$ This quinone (**1**) is the first example isolated as a plant constituent.

Table I. ^{13}C-NMR Chemical Shifts of **1** and **5** in $CDCl_3$ $^{a)}$

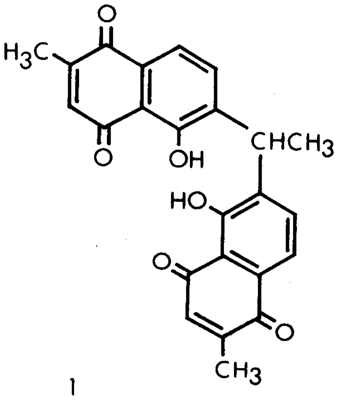
Carbon	1	5
1, 1'	184.8	184.5
2, 2'	149.8	149.5
3, 3'	135.6	135.3
4, 4'	190.7	190.1
5, 5'	159.3	161.0
6, 6'	140.5	124.1
7, 7'	134.2	136.0
8, 8'	119.2	119.1
9, 9'	130.6	131.9
10,10'	114.9	115.0
11,11'	16.7	16.5
$\underline{CH_3}CH<$	18.7	----
$CH_3\underline{CH}<$	32.6	----

a) Measured at 25 MHz with a JEOL FX-100 NMR spectrometer (pulse width: 7 μs, repetition time: 2.5 s, data points: 8 K).

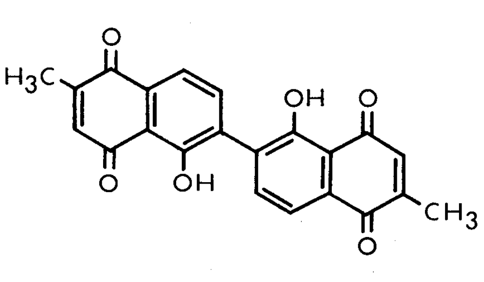


4 R = Br

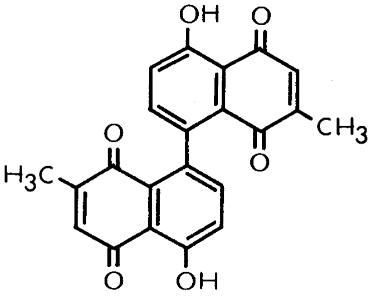
5 R = H



1



2



3

The formation of the dimers of plumbagin and 7-methyljuglone present in the genus *Diospyros* apparently involves the oxidative dimerization of 4,5-dihydroxy-2-methylnaphthalene.[4,5,8] The quinone (1) has an extra alkyl group compared to these dimers. Possibly the quinone (1) is an artefact caused by the reaction of ethanol (extraction solvent) with one of the quinonoid constituents of this fruit. But this was ruled out because the quinone (1) was isolated from the chloroform extract of the fruit. Recently, G. M. K. B. Gunaherath *et al.* isolated methylene-3,3'-biplumbagin from *Plumbago zeylanica*, and suggested that the biosynthesis of the quinone in the plant may involve the participation of formaldehyde.[9]

ACKNOWLEDGEMENT The author thanks Dr. Norio Koine, Ehime University, for his helpful suggestions and for ^{13}C-NMR measurement.

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(Received June 25, 1988)