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BENZOQUINONE PIGMENTS IN KENYAN MYRSINACEAE: NEW 2,5-DIHYDROXYALKYL DERIVATIVES FROM *MAESA LANCEOLATA*

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ABSTRACT. Chromatographic analysis of *Maesa lanceolata* (Forsk) fruit and bark chloroform extracts has led to the isolation of related new natural benzoquinones, 2,5-dihydroxy-3-pentadecyl-1,4-benzoquinone (**1**) and 2,5-dihydroxy-3-(pentadec-10'z-enyl)-1,4-benzoquinone (**2**).

INTRODUCTION

The fruit and bark of *Maesa lanceolata* (Forsk) are applied in Eastern Africa for anthelmintic, antibacterial and other purposes (1). The major benzoquinones in this plant (2) are reported to be maesaquinone (**3**, 11% in fruit) and acetyl maesaquinone (**4**, 5% in fruit). Maesanin or 2-hydroxy-5-methoxy-3-(pentadec-10'z-enyl)-1,4-benzoquinone (**5**) also constitutes a reasonable portion of the benzoquinone content (0.05% in fruit). This compound was first characterised and synthesised by Kubo and co-workers. The group had isolated it from *M. lanceolata* and showed that it was a non-specific mice defence stimulant against *Escherichia coli* (3). Our interest in *M. lanceolata* at present revolves around the desire to optimise a male anti-fertility drug from Myrsinaceae benzoquinones. During the separation of the plant extract to retrieve compounds for the anti-fertility tests, we have met two new dihydroxylated benzoquinones which are related to maesanin: 2,5-dihydroxy-3-pentadecyl-1,4-benzoquinone (**1**) and 2,5-dihydroxy-3-(pentadec-10'z-enyl)-1,4-benzoquinone (**2**).

RESULTS AND DISCUSSION

Compound **1** forms orange-red crystals from methanol with a m.p. of 130-132°C. An EI mass spectrum shows M^+ m/z peak at 350. The base peak at 154 is due to a fragmentation through a thermal retro-ene reaction (4) and shows that the benzoquinone ring is dihydroxylated (5). Peaks at m/z 43, 69 and 83 are caused by the linear pentadecyl side chain. The ^1H NMR spectrum shows a sharp singlet for benzoquinone proton at 6.0 ppm and therefore the substitution pattern may be similar to that of embelin (**6**) (6). The alternative 2,3-dihydroxy substitution is precluded with this information since the peak would not be a sharp singlet as long range coupling is expected as observed for 2,3-dihydroxy-6-methylbenzoquinone (7). Further confirmation that the benzoquinone substitution pattern is identical with that of embelin is obtained from two pieces of spectroscopic evidence. The UV λ_{max} positions are at 290 and 426 as is the case with embelin 292, 425 but different from the 2,6-dihydroxylated pattern which has peaks at 297 and 426 (8). There is also only one peak for the two carbonyl bonds at 1620 cm^{-1} (KBr) just like for embelin; 2,6-dihydroxylated-1,4-benzoquinone systems are known to show two carbonyl absorption frequencies, 1660 and 1641 cm^{-1} in KBr matrix (8).

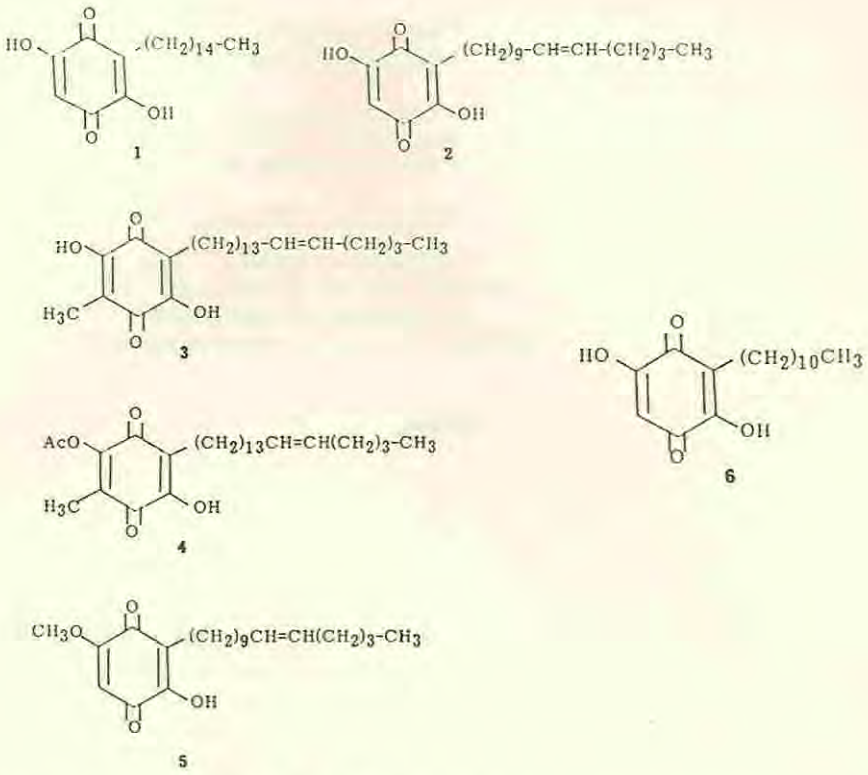

Fig. 1. Some bezoquinones of the Myrsinaceae.

The mass spectrum for compound **2** resembles closely that of **1** except that the molecular ion is at 348 with the base peak also at 154. The ^{1}H NMR spectrum is more complicated than in the case of **1** with two methine protons showing as a multiplet at 5.3 ppm which implicated the presence of a double bond and therefore led to the suspicion that it is related to compound **5**. In fact compound **2** was generated from maesanin (**5**) using boron trifluoride instead of boron tribromide in the demethylation reaction (9). Therefore maesanin is the 5-methyl ether of **2** while **1** is the side chain double bond dihydro derivative of **2**.

EXPERIMENTAL

Isolation. Each sample (collected and handled as in ref (2)) was extracted with hot solvent according to the procedure in reference (2) and also by cold extraction of fruit or bark by dichloromethane followed by solvent removal *in vacuo* in either case leading to brownish gummy solid. This solid was subjected to chromatographic separation on silica gel de-activated with 3% aqueous oxalic acid solution using solvents, hexane, dichloromethane and methanol. Both **1** and **2** elute from the column with dichloromethane. Preparative thin layer chromatography, for further purification of fractions, was performed on 2 mm thick plates prepared with silica gel slurried in 3% oxalic acid. The solvent system for tlc separation, both preparative and analytical, was n-hexane/ethyl acetate/acetic acid (17:2:1) as previously reported (2).

2,5-Dihydroxy-3-pentadecyl-1,4-benzoquinone (1). Orange red crystals (methanol) m.p. 130-132; IR ν_{max} (KBr) cm^{-1} 3300 (O-H), 1620 (chelated C=O); UV λ_{max} (MeOH) 420 (log ε, 2.42) and 290 (log ε, 4.19) nm; MS (70eV) m/z M^+350 (11), 155 (36), 154 (100), 153 (21) 142 (23), 125 (8), 83 (7), 69 (24), 55 (33), 43 (67). ^1H NMR($CDCl_3$) δ 7.66 (s 2H), 1.25 (m, 26H) and 0.88 (t, 3H) ppm.

2,5-Dihydroxy-3-(pentadec-10'z-enyl)-1,4-benzoquinone (2). Orange red crystals (methanol), m.p. 104-106; IR λ_{max} (KBr) cm^{-1} 3350(O-H), 3000 (Olefinic C-H), 1622 (chelated C=O); UV λ_{max} (MeOH) 440(2.70) and 385(4.20) nm; MS (70ev): m/z M^+ 348 (6), 155 (54), 154 (100), 153 (30), 142 (15), 125 (18), 95 (18), 81 (21), 69 (52), 55 (98), 41 (94); ^1H NMR ($CDCl_3$) δ7.65 (s, 2H), 6.00 (s, 1H), 5.3 (m, 2H), 2.44 (t, 2H), 1.26 (m, 18H) and 0.87 (t, 3H) ppm.

Generation of 2 from maesanin (5). To a solution of 10 mg of **5** in 5 ml dry dichloromethane in a 25 ml round bottom flask cooled in ice-salt water bath (-5°C) was added dropwise 1 ml of boron trifluoride etherate. After complete addition, the reaction was allowed to warm to room temperature in 30 min. Subsequent water hydrolysis was followed by partition into dichloromethane giving 3 mg of orange-red crystals from methanol which matched **2** in all respects.

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REFERENCES

1. J.O. Kokwaro, "Medicinal Plants of East Africa", East Africa Literature Bureau, Nairobi (1976).
2. J.O. Midiwo, L.M. Arot and C.L. Mbakaya, Bull. Chem. Soc. Ethiop., **2**(2), 83 (1988).
3. I. Kubo, K. Tadoa and M. Iwao, Tetrahedron Lett., **24**, 3825 (1983).
4. W.D. Huntsman, U.C. Solomon and D. Evos, J. Am. Chem. Soc., **80**, 5455 (1958).
5. H. Ogawa and S. Natori, Phytochemistry, **7**, 773 (1968).
6. S. Gupta, S.N. Sanyal and H. Kanuar, Contraception, **39**(3), 307 (1989).
7. Y. Yamamoto, H. Toshiyuki, O. Keiko, S. Kayoko, K. Shinji, M. Kimiduro, Chem. Pharm. Bull., **22**(1), 83 (1974).
8. H. Nakata, K. Sasaki, I. Marimoto and Y. Hirata, Tetrahedron, **20**, 2319 (1964).
9. F.L. Benton and T.E. Dillon, J. Am. Chem. Soc., **62**, 1257 (1940).