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BENZOQUINONES FROM *COSTUS SPECIOSUS* SEEDS

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Key Word Index—*Costus speciosus*; Costaceae; seeds; 6-methyl dihydrophytylplastoquinone; dihydrophytylplastoquinone; α-tocopherolquinone; 5α-stigmast-9(11)-en-3β-ol.

Abstract—In addition to α-tocopherolquinone and 5α-stigmast-9(11)-en-3β-ol, two new quinones have been isolated from the seeds of *Costus speciosus* and characterized as 6-methyl dihydrophytylplastoquinone (2,5,6-trimethyl-3-(3,7,11,15-tetramethylhexadecyl)-1,4-benzoquinone) and dihydrophytylplastoquinone (5,6-dimethyl-3-(3,7,11,15-tetramethylhexadecyl)-1-4-benzoquinone) respectively by physical data and chemical studies.

INTRODUCTION

As part of a programme to find new sources of diosgenin work was initiated on the seeds [1] of *Costus speciosus* Sm. This work has resulted in the isolation of several saponins [2, 3] and, as reported in this communication, two new benzoquinones.

RESULTS AND DISCUSSION

The two new benzoquinones, 6-methyl dihydrophytylplastoquinone and dihydrophytylplastoquinone, as well as α-tocopherolquinone and 5α-stigmast-9(11)-en-3β-ol, were isolated by silica gel CC and prep. TLC of the non-saponifiable *n*-hexane extract of the seeds of *C. speciosus*.

6-Methyl dihydrophytylplastoquinone (**1**) was obtained as an orange oil which showed IR absorption bands at 1650 (quinone CO), 1372, 1362, 1160 (isopropyl moiety) [4], 2905, 2870, 1460 and 730 cm^{-1} (long chain). Its UV spectrum had absorption bands at 254 and 264 nm which were similar to those of plastoquinones [5] and phytylplastoquinones [6]. Addition of sodium borohydride shifted the UV maximum to 288 nm [6]. The mass spectrum of **1** displayed an $[M]^+$ ion at *m/z* 430 which, together with elemental analysis, established the molecular formula as $C_{29}H_{50}O_2$. Formation of an ion at *m/z* 149 due to the loss of $C_{20}H_{41}$ (281 amu) indicated the presence of four C_5 units as the side chain of the quinone. Loss of CO and 2CO from the *m/z* 149 ion was seen at *m/z* 121 and 93 respectively. Significant ions at *m/z* 205 and 177 were obtained by the cleavage on both side of the tertiary C atom at C-3 of the side chain. An analagous ion to that at *m/z* 205 is formed by other plastoquinones [7, 8]. The base peak at *m/z* 178 was obtained by the partial loss of side chain with transfer of one hydrogen. These ions are depicted in Scheme 1. Absence of quinonoid proton signals in the ^{1}H NMR spectrum indicated that the quinone was fully substituted. Three methyl groups attached to the ring were seen as singlets at δ1.95, 2.08 and 2.18. Of the 41 protons of the saturated side chain, two protons adjacent to the quinone ring were obtained as a multiplet at δ2.50, five methyl groups as a doublet (J = 6 Hz) at δ0.80, four methine protons as a multiplet at δ1.81 and twenty methylene protons as a broad singlet at δ1.18. These data were fully consistent with structure **1**.

Dihydrophytylplastoquinone (**2**) was obtained as a red oil which had an IR spectrum similar to that of **1**. Its UV absorption band at 269 nm was also shifted to 286 nm by the addition of sodium borohydride. The mass spectrum of **2** showed an $[M]^+$ ion at *m/z* 416 which, along with elemental analysis, suggested the molecular formula as $C_{28}H_{48}O_2$. The fragmentation pattern of **2** was similar to that of **1**. The ^{1}H NMR spectrum of **2** displayed a triplet at δ6.12 for a single quinonoid proton [5] due to long range coupling with the adjacent methylene group of the $C_{20}H_{41}$ chain. Thus the side chain and the quinonoid proton were on the same side of the quinone ring. Two sharp singlets at δ1.95 and 2.12 showed the presence of only two methyl groups on the quinone ring. This fact in conjunction with a significant ion at *m/z* 191 indicated that **2** had one quinone methyl group less than **1**. Other features of the spectrum were similar to that of **1**. These data led to structure **2**. On treatment with acetic anhydride, fused sodium acetate and zinc dust **2** formed a leucodiacetate which on purification showed IR bands at 1757 and 1210 cm^{-1}.

α-Tocopherolquinone was analysed for $C_{29}H_{50}O_3$ by mass spectrometry (M^+ 446) and it was identified by comparison of lit. data (IR, UV [9, 10]). 5α-Stigmast-9(11)-en-3β-ol, mp 133°, was identified by comparison with an authentic sample (mmp, IR, Co-TLC). This report constitutes the second isolation of this sterol which was previously isolated from the roots of this plant [11].

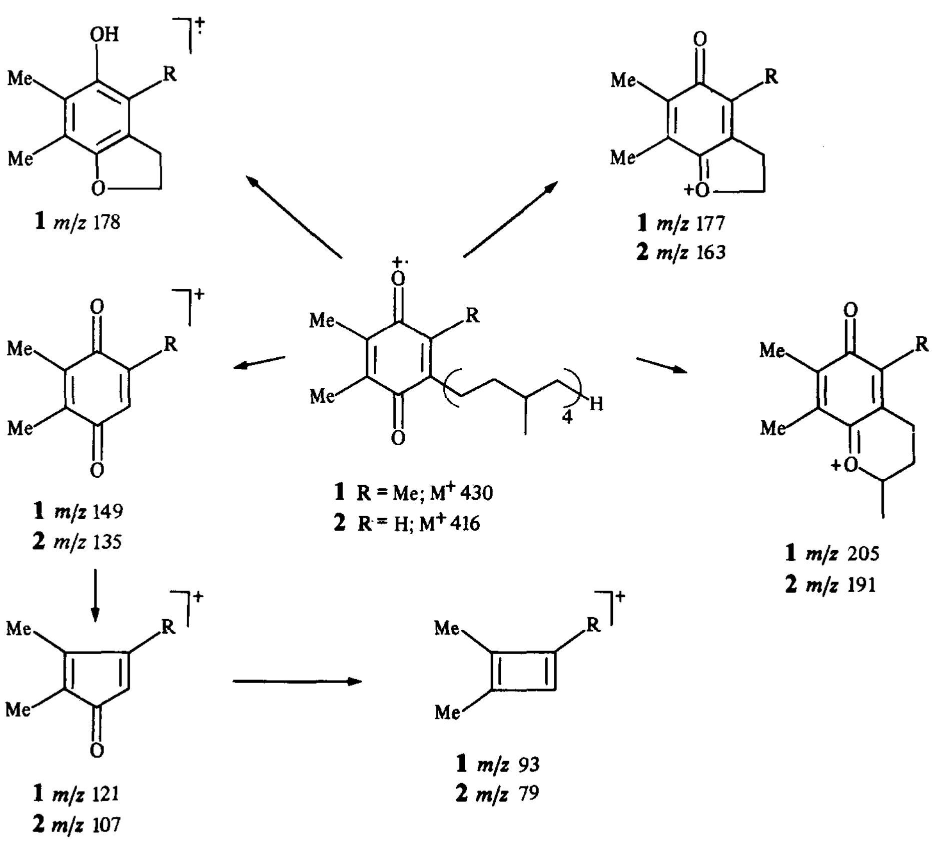
Identification of three additional compounds including a tocopherol from the hexane extract of the seeds of this plant is currently in progress.

EXPERIMENTAL

Mps: uncorr; IR: KBr or neat; ^{1}H NMR: 90 MHz, $CDCl_3$, TMS as int. standard; UV: MeOH unless stated otherwise; TLC: silica gel G, the spots were either self visible or visualized by exposure to I_2 vapour.

Plant material was cultivated at the Experimental farm of this Institute and a voucher specimen has been deposited in the Botany Department.

Extraction and isolation of compounds. Dried and powdered seeds (2.5 kg) of *C. speciosus* were extracted with MeOH (5 × 5 l.) and the extract concentrated to 500 ml. It was then diluted with H_2O (500 ml), extracted with *n*-hexane (6 × 1 l.) and dried



Scheme 1. Fragmentation ions of **1** and **2**.

(Na_2SO_4). Removal of solvent furnished an oily residue (190 g) which was saponified with 5% alcoholic KOH (500 ml) overnight at room temp. The solvent was then concentrated to 100 ml, diluted with H_2O (100 ml), extracted with *n*-hexane (2 × 200 ml) and the extract dried (Na_2SO_4). Removal of solvent provided a viscous residue (6.5 g), which was chromatographed over silica gel (210 g, 60–120 mesh, BDH) eluted with hexane, hexane–C_6H_6 (3:1), hexane–C_6H_6 (1:1), hexane–C_6H_6 (1:3) and C_6H_6. Fractions of 100 ml each were collected and monitored by TLC. Removal of solvent from the hexane–C_6H_6 (1:1) fractions yielded a coloured residue (80 mg) which was subjected to prep. TLC in hexane–C_6H_6–Me_2CO (80:17:3) to give, in increasing order of polarity, the three quinones **1**, **2** and α-tocopherolquinone.

6-Methyl dihydrophytylplastoquinone (**1**). Orange oil, 17 mg. (Found: C, 80.70; H, 11.40%. $C_{29}H_{50}O_2$ requires: C, 80.93; H, 11.62%.) UV λ_{max} nm: 254, 264; IR ν_{max} cm^{-1}: 2905, 2870, 1650, 1615, 1460, 1372, 1362, 1160, 730; ^{1}H NMR: δ0.80 (15H, *d*, *J* = 6 Hz, 5 × $C\underline{H}_3$–CH), 1.18 (20 H, *s* (*br*), 10 × CH_2), 1.95, 2.08, 2.18 (3H each, *s*, Me), 1.81 (4H, *m*, 4 × –CH), 2.50 (2H, *m*, quin-CH_2); MS *m/z* (rel. int.): 430 $[M]^+$ ($C_{29}H_{50}O_2$, 33), 415 (5), 205 (22), 178 (100), 177 (38), 151 (21), 150 (20), 149 (18), 121 (10), 93 (10), 71 (36), 69 (55), 57 (64), 43 (77).

Dihydrophytylplastoquinone (**2**). Red oil, 52 mg. (Found: C, 80.65; H, 11.50%. $C_{28}H_{48}O_2$ requires: C, 80.76; H, 11.53%.) UV λ_{max} nm: 269; IR ν_{max} cm^{-1}: 2905, 2865, 1652, 1612, 1460, 1370, 1360, 1160, 720; ^{1}H NMR: δ0.80 (15H, *d*, *J* = 6 Hz, 5 × $C\underline{H}_3$–CH), 1.20 (20H, *s* (*br*), 10 × CH_2), 1.95, 2.12 (3H each, *s*, Me), 1.85 (4H, *m*, 4 × –CH), 2.50 (2H, *m*, quin-CH_2), 6.12 (1H, *t*, *J* = 1.2 Hz, H-6); MS *m/z* (rel. int.): 416 $[M]^+$ ($C_{28}H_{48}O_2$, 100), 191 (18), 163 (5), 151 (64), 150 (32), 135 (10), 107 (8), 79 (5), 71 (22), 69 (52), 57 (41), 43 (51).

Reductive acetylation of **2**. A mixture of **2** (30 mg), Ac_2O (2 ml), fused NaOAc (50 mg) and Zn dust (20 mg, added gradually to the refluxing mixture) was refluxed for 3 hr. It was then diluted with cold H_2O (50 ml), extracted with Et_2O (5 × 50 ml), washed with H_2O (2 × 50 ml) and dried (Na_2SO_4). Removal of solvent provided a viscous mass which was purified by prep. TLC. IR ν_{max} cm^{-1}: 2905, 2840, 1757, 1460, 1370, 1360, 1210, 1180, 910, 860, 725.

α-Tocopherolquinone. Yellow oil, 4 mg. UV λ_{max}^{EtOH} nm: 261, 269. IR ν_{max} cm^{-1}: 3550, 2905, 2840, 1640, 1610, 1450, 1370, 1360, 1160, 710.

5α-Stigmast-9(11)-en-3β-ol. Removal of solvent from the hexane–C_6H_6 (1:3) fractions (52–61) afforded a residue, 4 mg, mp 133° (Me_2CO) which was identified by comparison with an authentic specimen (mmp, IR, MS, CO TLC).

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