

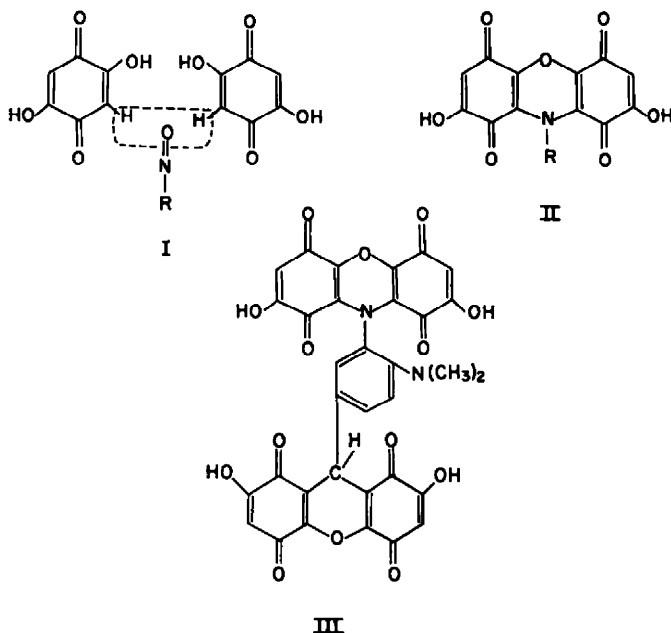
## CHEMICAL EXAMINATION OF *EMBELIA RIBES*—VII SYNTHESIS OF SOME NEW N-BIS(ANHYDROBENZOQUINONES)

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**Abstract**—By the condensation of 2,5-dihydroxy-1,4-benzoquinone (I) with various nitroso compounds, the corresponding N-bis(anhydro-2,5-dihydroxy-3,6-benzoquinones) (II) were obtained and their properties recorded.

AN EARLIER publication<sup>1</sup> deals with the synthesis of some N-bis(anhydrobenzoquinones) obtained by the condensation of embelin with various nitroso compounds. The study is now extended to 2,5-dihydroxy-1,4-benzoquinone (I) which readily undergoes condensation to give the corresponding N-bis(anhydro-2,5-dihydroxy-3,6-benzoquinone) (II). With *p*-dimethylamino-*m*-nitrosobenzaldehyde<sup>2</sup> III was readily formed.



### EXPERIMENTAL

**General procedure.** Compound I (2 moles) was condensed with the nitroso compound (1 mole) in glacial acetic acid or 50% ethanolic H<sub>2</sub>SO<sub>4</sub> by boiling for 1 hr on a waterbath. The cooled reaction mixture was decomposed using ice-water and the product crystallized from dioxan. In all cases, the corresponding anhydro compounds were obtained.

4'-Dimethylaminophenyl-1'-N-bis(anhydro-5-hydroxy-3,6-benzoquinone), (IIa, R = *p*-dimethylaminophenyl). Compound I (2 moles) was condensed with *p*-nitrosodimethylaniline (1 mole) yielding IIa as dark brown short prisms, melting above 320° from dioxan, showing a brown ferric

<sup>1</sup> T. V. Padmanabha Rao and V. Venkateswarlu, *Tetrahedron* 20, 2963 (1964).

<sup>2</sup> E. Jeney and Z. Sohnaï, *Acta Microbiol. Acad. Sci., Hungary* 2, 249 (1955).

reaction. (Found: C, 70.20; H, 3.72; N, 7.34;  $C_{20}H_{14}O_7N_2$  requires: C, 60.91; H, 3.55; N, 7.10%).

The hexaacetate of reduced IIa prepared using acetic anhydride and zinc dust in presence of a trace of triethylamine, crystallized as colourless rectangular plates, m.p. 294–295°d. from ethyl acetate-pet ether, b.p. 40–60°, giving a negative ferric reaction. (Found: C, 59.24; H, 4.81;  $-\text{COCH}_3$ , 40.01;  $C_{22}H_{20}O_{13}N_2$  requires: C, 59.07; H, 4.62;  $-\text{COCH}_3$ , 39.69%).

*4'-Diethylaminophenyl-1'-N-bis(anhydro-5-hydroxy-3,6-benzoquinone)*, (IIb, R = *p*-diethylamino-phenyl-). Compound I was condensed with *p*-nitrosodiethylaniline yielding IIb as dark brown square prisms melting above 320° from excess dioxan showing a brown ferric colour in dioxan solution. (Found: C, 62.71; H, 4.34; N, 6.77;  $C_{22}H_{18}O_7N_2$  requires: C, 66.56; H, 4.27; N, 6.64%).

The hexaacetate of reduced IIb, crystallized as colourless short needles, m.p. 287–290°d. from ethyl acetate-pet ether, giving a negative ferric reaction. (Found: C, 60.14; H, 5.21;  $-\text{COCH}_3$ , 38.26;  $C_{24}H_{24}O_{13}N_2$  requires: C, 60.19; H, 5.02;  $-\text{COCH}_3$ , 38.06%).

*1'-Hydroxynaphthyl-2'-N-bis(anhydro-5-hydroxy-3,6-benzoquinone)*, (IIc, R = 1-hydroxynaphthyl-). Compound I was condensed with 2-nitroso-1-naphthol to give IIc as brown rectangular plates and prisms melting above 290°d. from methanol showing a deep brown ferric colour in alcoholic solution. (Found: C, 63.56; H, 2.92; N, 2.64;  $C_{22}H_{11}O_8N$  requires: C, 63.31; H, 2.64; N, 3.37%).

The heptaacetate of reduced IIc, crystallized as colourless rectangular plates, m.p. 290–292°d. from ethyl acetate-pet ether, giving a negative ferric reaction. (Found: C, 60.74; H, 4.23;  $-\text{COCH}_3$ , 42.40;  $C_{28}H_{25}O_{13}N$  requires: C, 60.42; H, 4.06;  $-\text{COCH}_3$ , 42.10%).

*4'-Hydroxynaphthyl-1'-N-bis(anhydro-5-hydroxy-3,6-benzoquinone)*, (IId, R = *p*-hydroxynaphthyl-). Compound I was condensed with 4-nitroso-1-naphthol yielding IId which crystallized as deep brown short prisms, m.p. 304–306°d. from methanol showing a brown ferric colour in alcoholic solution. (Found: C, 63.47; H, 2.92; N, 3.47;  $C_{22}H_{11}O_8N$  requires: C, 63.31; H, 2.64; N, 3.37%).

The heptaacetate of reduced IId crystallized as colourless rectangular plates, m.p. 272–274°d. from ethyl acetate-pet ether, giving a negative ferric reaction. (Found: C, 60.74; H, 4.37;  $-\text{COCH}_3$ , 42.47;  $C_{28}H_{25}O_{13}N$  requires: C, 60.42; H, 4.06;  $-\text{COCH}_3$ , 42.10%).

*2'-Hydroxynaphthyl-1'-N-bis(anhydro-5-hydroxy-3,6-benzoquinone)*, (IIf, R = 2-hydroxynaphthyl-). Compound I was condensed with 1-nitroso-2-naphthol to give IIf which crystallized as short deep brown needles and prisms, m.p. 308–310°d. from methanol showing a brown ferric colour in alcoholic solution. (Found: C, 63.42; H, 2.82; N, 3.62;  $C_{22}H_{11}O_8N$  requires: C, 63.31; H, 2.64; N, 3.37%).

The heptaacetate of reduced IIf crystallized as colourless short needles, m.p. 320–322°d. from ethyl acetate-pet ether, giving a negative ferric reaction. (Found: C, 60.56; H, 4.36;  $-\text{COCH}_3$ , 42.41;  $C_{28}H_{25}O_{13}N$  requires: C, 60.42; H, 4.06;  $-\text{COCH}_3$ , 42.01%).

*4'-Hydroxyphenyl-1'-N-bis(anhydro-5-hydroxy-3,6-benzoquinone)*, (IIIf, R = *p*-hydroxyphenyl-). Compound I was condensed with *p*-nitrosophenol yielding IIIf which crystallized as deep brown rectangular plates, m.p. 335–337°d. from ethanol, showing a brown ferric reaction in alcoholic solution. (Found: C, 59.04; H, 2.67; N, 3.27;  $C_{18}H_9O_8N$  requires: C, 58.86; H, 2.45; N, 3.82%).

The heptaacetate of reduced IIIf crystallized as colourless short prisms, m.p. 264–266°d. from ethyl acetate-pet ether, giving a negative ferric reaction. (Found: C, 58.03; H, 4.24;  $-\text{COCH}_3$ , 45.37;  $C_{23}H_{17}O_{13}N$  requires: C, 57.75; H, 4.06;  $-\text{COCH}_3$ , 45.27%).

*4'-Hydroxy-3'-methylphenyl-1'-N-bis(anhydro-5-hydroxy-3,6-benzoquinone)*, IIg, R = 4-hydroxy-3-methylphenyl-. Compound I was condensed with *p*-nitroso-*o*-cresol to yield IIg, which crystallized as deep brown irregular prisms, m.p. 308–310°d. from ethyl acetate showing a brown ferric colour in alcoholic solution. (Found: C, 60.18; H, 3.14; N, 3.92;  $C_{19}H_{11}O_8N$  requires: C, 59.84; H, 2.89; N, 3.68%).

The heptaacetate of reduced IIg crystallized as colourless rectangular prisms, m.p. 288–290°d. from ethyl acetate-pet ether, giving a negative ferric reaction. (Found: C, 58.47; H, 4.52;  $-\text{COCH}_3$ , 44.67;  $C_{23}H_{23}O_{13}N$  requires: C, 58.32; H, 4.27;  $-\text{COCH}_3$ , 44.33%).

*2'-Dimethylamino-5' : 9'-(bisdesundecylanhydrovilanga)phenyl-1'-bis(anhydro-5-hydroxy-3,6-benzoquinone)* (III). Condensation of I (4 moles) with *p*-dimethylamino-*m*-nitrosobenzaldehyde (1 mole) resulted in the formation of III as deep pink brown prisms, m.p. 204–206°d. from dioxan showing a brown ferric colour in dioxan solution. (Found: C, 59.07; H, 2.25; N, 4.21;  $C_{23}H_{18}O_{11}N_2$  requires: C, 59.46; H, 2.74; N, 4.21%).

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