

CHEMICAL EXAMINATION OF *EMBELIA RIBES*—V SYNTHESIS OF SOME N-BIS(ANHYDROBENZOQUINONES)

T. V. PADMANABHA RAO and V. VENKATESWARLU
Department of Chemistry, Andhra University, Waltair

(Received in revised form 31 March 1964)

Abstract—By the condensation of embelin (I) with various nitroso compounds, the corresponding N-bis-anhydrobenzoquinones (II) have been synthesized and their properties recorded.

It has been reported¹ that embelin (I), a constituent of *Embelia ribes* and *E. robusta*, condenses with various aldehydes in acid solution to give analogues of vilangin and anhydrovilangin.² Kaul *et al.* have reported that in the presence of acids one molecule of embelin condenses with two molecules of nitroso compounds, yielding crystalline products. Similar to the condensation of embelin with various aldehydes, it has now been found that embelin (2 moles) condenses with various nitroso compounds (one mole) to give the corresponding N-bis(anhydrobenzoquinones) (II) which were characterized by the acetates of their reduction products. In the condensation with *p*-dimethylamino-*m*-nitrosobenzaldehyde,⁴ a more complicated reaction takes place with formation of III.

EXPERIMENTAL

General procedure. Embelin (2 moles) was condensed with the nitroso compound in glacial acetic acid or 50% ethanolic H₂SO₄ by boiling for 3 hr on a water bath. The reaction mixture was cooled and poured into ice water and the product crystallized from ethyl acetate. In all cases the corresponding anhydro compounds were obtained.

4'-Dimethylaminophenyl-1'-N-bis(anhydro-5-hydroxy-4-undecyl-3,6-benzoquinone), (IIa, R = *p*-dimethylaminophenyl). Embelin (2 moles) was condensed with *p*-nitrosodimethylaniline (1 mole), yielding IIa as brown irregular prisms from ethyl acetate, m.p. 202–204°d., giving a brown ferric reaction in alcoholic solution. (Found: C, 71.93; H, 8.43; N, 4.12. C₄₂H₅₈O₇N₂ requires: C, 71.80; H, 8.26; N, 3.99%). Kaul *et al.*³ reported a m.p. of 290° for the same compound.

The *tetra-2,4-dinitrophenylhydrazone* of IIa (green needles from ethanol) had m.p. 243–245°. (Found: C, 55.73; H, 5.42; N, 17.43. C₈₈H₇₄O₁₉N₁₈ requires: C, 55.69; H, 5.20; N, 17.22%).

The *hexaacetate of reduced* IIa was obtained, using acetic anhydride and zinc dust in presence of triethylamine, as colourless rectangular plates, m.p. 246–248°d. giving a negative ferric reaction. (Found: C, 67.62; H, 7.94; —COCH₃, 27.13. C₆₄H₇₄O₁₃N₂ requires: C, 67.48; H, 7.72; —COCH₃, 26.93%).

4'-Diethylaminophenyl-1'-N-bis(anhydro-5-hydroxy-4-undecyl-3,6-benzoquinone), (IIb, R = *p*-diethylaminophenyl). Embelin (2 moles) was condensed with *p*-nitrosodiethylaniline (1 mole), yielding IIb as orange brown rectangular plates, m.p. 146–147° from petrol, b.p. 40–60° giving a brown ferric colour in alcoholic solution. (Found: C, 72.54; H, 8.62; N, 3.97. C₄₄H₆₂O₇N₂ requires: C, 72.33; H, 8.49; N, 3.83%).

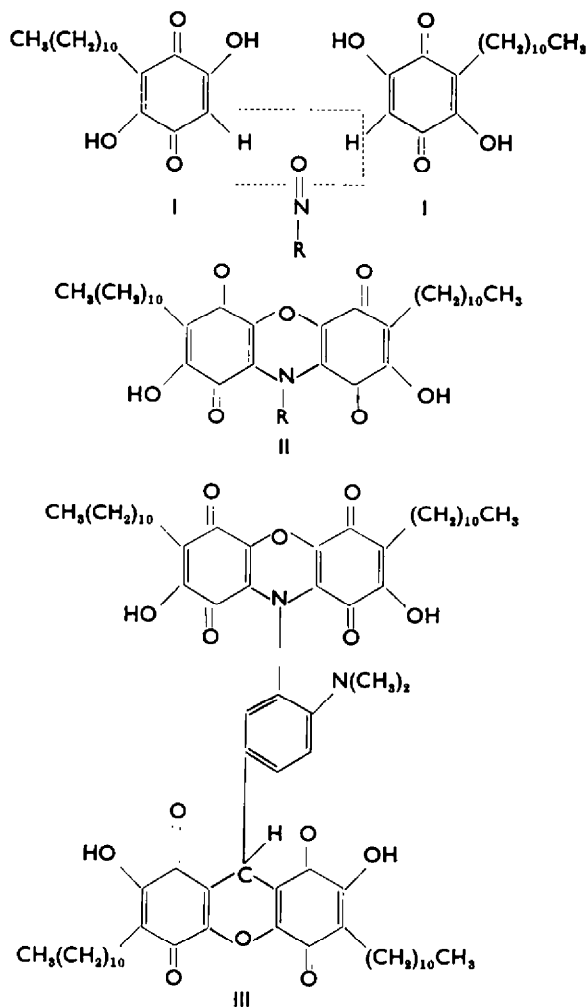
The *hexaacetate* of reduced IIb was prepared as described yielding colourless rectangular plates, m.p. 117–118° from petrol, b.p. 40–60° showing a negative ferric reaction. (Found: C, 68.32; H, 8.07; —COCH₃, 26.26. C₆₈H₇₈O₁₃N₂ requires: C, 68.16; H, 7.91; —COCH₃, 26.16%).

¹ Ch. Bheemasankara Rao and V. Venkateswarlu, *J. Org. Chem.* 4529 (1961).

² Ch. B. Rao and V. Venkateswarlu, *Tetrahedron* 18, 361, 951 (1962).

³ R. Kaul, A. C. Ray and S. Dutt, *J. Indian. Chem. Soc.* 6, 231 (1931).

⁴ E. Jeney and Z. Sohna, *Acta Microbiol. Acad. Sci., Hungary* 2, 249 (1955).



4'-Hydroxynaphthyl-1'-N-bis(anhydro-5-hydroxy-4-undecyl-3,6-benzoquinone), (IIc, R = *p*-hydroxynaphthyl-). Embelin was condensed with 4-nitroso-1-naphthol to yield IIc as brown prisms, m.p. 198–200°d. from benzene giving a brown ferric reaction in alcoholic solution. (Found: C, 73.01; H, 7.72; N, 2.11. C₄₄H₅₈O₈N requires: C, 72.83; H, 7.59; N, 1.93%.)

The *heptaacetate* of reduced IIc crystallized as colourless short prisms, m.p. 85–87° from petrol, b.p. 40–60° and showing a negative ferric reaction. (Found: C, 68.32; H, 7.31; —COCH₃, 29.61. C₆₈H₇₈O₁₅N requires: C, 68.05; H, 7.14; —COCH₃, 29.43%.)

1'-Hydroxynaphthyl-2'-N-bis(anhydro-5-hydroxy-4-undecyl-3,6-benzoquinone), (IId, R = 1-hydroxynaphthyl-). Embelin was condensed with 2-nitroso-1-naphthol yielding IId as orange brown prisms, m.p. 159–160° from benzene and showing a dark red-brown ferric reaction in alcoholic solution. (Found: C, 72.97; H, 7.67; N, 2.13. C₄₄H₅₈O₈N requires: C, 72.83; H, 7.59; N, 1.93%.)

The *heptaacetate* of reduced IId crystallized as colourless needles, m.p. 120–122° from petrol b.p. 40–60° and showing a negative ferric reaction. (Found: C, 68.27; H, 7.24; COCH₃, 29.13. C₆₈H₇₈O₁₅N requires: C, 68.05; H, 7.14; —COCH₃, 29.43%.)

2'-Hydroxynaphthyl-1'-N-bis(anhydro-5-hydroxy-4-undecyl-3,6-benzoquinone), (IIe, R = 2-hydroxynaphthyl-). Embelin was condensed with 1-nitroso-2-naphthol yielding IIe as brown square plates, mp. 182–184° from benzene and showing a dark brown ferric reaction. (Found: C, 73.01; H, 7.67; N, 2.04. C₄₄H₅₈O₈N requires: C, 72.83; H, 7.59; N, 1.93%.)

The *heptaacetate* of reduced IIe crystallized as colourless rectangular plates, m.p. 115–116° from pet. ether (b.p. 40–60°) and showing a negative ferric reaction. (Found: C, 68.17; H, 7.27; —COCH₃, 29.84. C₆₈H₇₃O₁₃N requires: C, 68.05; H, 7.14; —COCH₃, 29.43%).

4'-Hydroxyphenyl-1'-N-bis(anhydro-5-hydroxy-4-undecyl-3,6-benzoquinone), (IIf, R = *p*-hydroxyphenyl-). Embelin was condensed with *p*-nitrosophenol yielding IIf, m.p. 183–185° from pet. ether (b.p. 40–60°) and showing a dark brown ferric reaction. Kaul *et al.*³ reported a m.p. of 290° for the same compound. (Found: C, 56.64; H, 7.92; N, 2.27. C₄₀H₅₃O₈N requires: 56.48; H, 7.83; N, 2.07%).

The *heptaacetate* of reduced IIf crystallized as colourless rectangular plates, m.p. 75–77° from pet. ether (b.p. 40–60°) and showing a negative ferric reaction. (Found: C, 66.84; H, 7.42; —COCH₃, 31.31. C₆₄H₇₁O₁₃N requires: C, 66.61; H, 7.30; —COCH₃, 30.94%).

4'-Hydroxy-3'-methylphenyl-1'-N-bis(anhydro-5-hydroxy-4-undecyl-3,6-benzoquinone), (IIg, R = 4-hydroxy-3-methylphenyl-). Embelin was condensed with *p*-nitroso-*o*-cresol yielding IIg as deep greenish brown prisms, m.p. 156–158° from ethyl acetate–pet. ether (b.p. 40–60°) and showing a positive ferric reaction. (Found: C, 70.04; H, 7.94; N, 2.07. C₄₁H₅₅O₈N requires: C, 69.98; H, 7.82; N, 1.99%).

The *heptaacetate* of reduced IIg crystallized as colourless long needles m.p. 118–119° from pet. ether and showing a negative ferric reaction. (Found: C, 66.92; H, 7.54; —COCH₃, 30.92. C₆₆H₇₃O₁₃N requires: C, 66.86; H, 7.39; —COCH₃, 30.50%).

2'-Dimethylamino-5'(anhydrovilanga)phenyl-1'-N-bis(anhydro-5-hydroxy-4-undecyl-3,6-benzoquinone), (III). Condensation of embelin with *p*-dimethylamino-*m*-nitrosobenzaldehyde resulted in the formation of III as brown square prisms and pyramids, m.p. 131–133° from ethyl acetate–pet. ether (b.p. 40–60°) and showing a positive ferric reaction. (Found: C, 72.41; H, 8.20; N, 2.43. C₇₇H₁₀₃O₁₄N₂ requires: C, 72.14; H, 8.20; N, 2.19%).

Acknowledgement—One of the authors (T. V. P.) thanks the Council of Scientific and Industrial Research (India) for a maintenance grant.