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CHEMICAL EXAMINATION OF *EMBELIA RIBES*—III

A NEW SYNTHESIS OF VILANGIN

CH. BHEEMASANKARA RAO and V. VENKATESWARLU
Department of Chemistry, Andhra University, Waltair, India

Abstract—A new total synthesis of vilangin is effected.

AN earlier publication[1] deals with the synthesis of vilangin (I) using embelin and formaldehyde. In a new synthesis of vilangin, 2,5-dihydroxy-1,4-benzoquinone (II)[2] was condensed with formaldehyde to give methylene-bis (2,5-dihydroxy-3,6-benzoquinone) (III) which was subsequently alkylated using dilauroyl peroxide in dioxan solution with the formation of vilangin.

EXPERIMENTAL

Methylene-bis(2,5-*dihydroxy*-3,6-*benzoquinone*) (III). 2,5-Dihydroxy-1,4-benzoquinone[2] (1 g) in warm acetic acid (75 ml) was treated with formaldehyde (2·5 ml, 40%), when a copious yellow ppt formed almost immediately. Recrystallized from a large volume of dioxan, it appeared as yellow prisms, m.p. 293–95° (d), having a brown ferric reaction in dioxan solution. (Found: C, 53·7; H, 3·2; $C_{13}H_8O_8$ requires: C, 53·4; H, 2·8%).

Its *acetate*, prepared by the acetic anhydride–pyridine method appeared as pale yellow plates and prisms, m.p. 218–20° having a negative ferric reaction. (Found: C, 54·5; H, 3·8; -$COCH_3$, 36·8. $C_{13}H_4O_4(OCOCH_3)_4$ requires: C, 54·8; H, 3·5; -$COCH_3$, 37·4%).

Reductive acetylation of III using boiling acetic anhydride and zinc dust in presence of a trace of triethylamine during 2 hr gave methylene-bis(2,3,5,6-tetraacetoxybenzene), as colourless prisms from acetic acid, m.p. 246–48°, having a negative ferric reaction. (Found: C, 55·3; H, 4·9; -$COCH_3$, 54·0. $C_{13}H_4(OCOCH_3)_8$ requires: C, 55·1; H, 4·5; -$COCH_3$, 54·5%). Hydrolysis of the leuco-acetate using absolute alcoholic sulphuric acid (5%) in presence of a small quantity of zinc dust, gave methylene-bis(2,3,5,6-tetrahydroxybenzene)[3] as colourless prisms (dioxan) m.p. 310°(d). (Found: C, 52·8; H, 4·5. Calc. for $C_{13}H_{12}O_8$; C, 52·7; H, 4·1%).

Vilangin (I). A suspension of finely powdered methylene-bis(2,5-dihydroxy-3,6-benzoquinone) (2·9 g) and dilauroyl peroxide (4·2 g) in a mixture of acetic acid (100 ml) and dioxan (100 ml) was heated on a steam bath for 30 min while being stirred mechanically. Stirring was continued overnight and the precipitated solids fractionally crystallized using dioxan. The dioxan soluble fraction mainly contained vilangin which appeared as orange yellow prisms, m.p. 264–65°(d). A mixed m.p. with natural vilangin was undepressed. (Found: C, 70·1; H, 8·7. Calc. for $C_{35}H_{52}O_8$: C, 69·9; H, 8·7%).

[1] Ch. Bheemasankara Rao and V. Venkateswarlu, *J. Org. Chem.* **26**, 4529 (1961).
[2] R. G. Jones and H. A. Shonle, *J. Amer. Chem. Soc.* **67**, 1034 (1944).
[3] D. N. Mukerjee, *J. Chem. Soc.* 549 (1922).