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CHEMICAL EXAMINATION OF *EMBELIA RIBES*—IV

SOME CONDENSATION REACTIONS OF EMBELIN WITH PRIMARY AMINES

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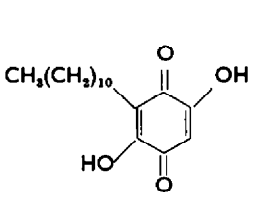
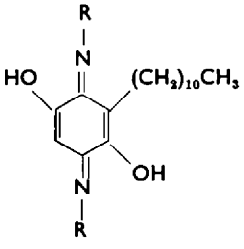
Abstract—By the condensation of embelin (I) with various primary amines the corresponding quinone di-imines (II) have been obtained and their properties recorded.

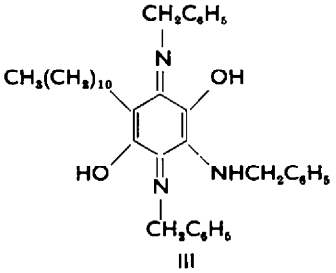
EMBELIN[1] and vilangin[2] are the two important constituents isolated from *Embelia ribes* and *robusta*, whose constitution and synthesis have been reported earlier. It has now been found that embelin (I) condenses with primary amines forming the corresponding quinone di-imines (II) which undergo decomposition on boiling with water or with concentrated hydrochloric acid forming mainly dark polymeric products and giving only traces of embelin. In the case of benzylamine, two products were obtained: (1) the normal quinone di-imine and (2) 3-benzylamino(bis-desoxy-bis(benzylimino)-embelin (III). These condensation reactions of embelin with primary amines explain the anamolous results reported by Kaul *et al.*[3]



I



II



III

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TABLE 1

Product	Method of prepn.	Appearance	M.P.	Ferric colour	Colour in alcoholic Alkali	Colour in alcoholic Acid	Formula	Analyses (theoretical in brackets)
Bisdesoxy-bis(methylimino)-embelin	a	Orange red prisms (Ethyl acetate)	167–168°*	Light green	Yellow	Red	$C_{19}H_{32}O_2N_2$	C, 71·32 (71.25); H, 10·34 (10·00); N, 8·94 (8·75).
Bisdesoxy-bis(phenyl-imino)embelin	a	Green prisms (Ethyl acetate -petrol)	203–204°†	Light green	Yellowish green	Bluish red	$C_{29}H_{36}O_2N_2$	C, 78·36(78·38); H, 8·04(8·11); N, 6·52(6·29).
Bisdesoxy-bis(2′-methyl-phenylimino)embelin	a	Violet rect. prisms (Ethyl acetate)	140–141°	Light green	Yellow	Red	$C_{31}H_{40}O_2N_2$	C, 78·92(78·81); H, 8·62(8·48); N, 6·12(5·93).
Bisdesoxy-bis(4′-methyl-phenylimino)embelin	a	Light green rect. prisms (Ethyl acetate)	214–215°	Faint green	Orange red	Bluish green	$C_{31}H_{40}O_2N_2$	C, 78·84(78·81); H, 8·72(8·48); N, 6·21(5·93).
Bisdesoxy-bis(4′-methoxy-phenylimino)embelin	a	Bottle green long rect. plates (acetone-petrol)	196–198°	Green	Orange red	Bluish green	$C_{31}H_{40}O_4N_2$	C, 73·74(73·81); H, 8·21(7·94); N, 5·69(5·56).
Bisdesoxy-bis(3′-methyl-phenylimino)embelin	a	Green prisms (acetone-petrol)	166–168°	Pale green	Yellowish green	Red	$C_{31}H_{40}O_2N_2$	C, 78·96(78·81); H, 8·70(8·48); N, 6·17(5·93).
Bisdesoxy-bis(2′-iodo-phenylimino)embelin	b	Red-brown rect. prisms (Ethyl acetate-petrol)	102–104°	Dark green	Yellow	Pink	$C_{29}H_{34}O_2N_2I_2$	C, 50·39(50·07); H, 4·97(4·89); N, 4·34(4·02).
Bisdesoxy-bis(4′acetyl-phenylimino)embelin	b	Violet irregular prisms (acetone-petrol)	190–192°	Light green	Greenish yellow	Red	$C_{33}H_{40}O_4N_2$	C, 75·27(75·01); H, 7·78(7·58); N, 5·57(5·30).
Bisdesoxy-bis(2′-napthyl-imino)embelin	a	Violet prisms (acetone-petrol)	196–198°	Light green	Yellow	Pink	$C_{37}H_{40}O_2N_2$	C, 81·92(81·62); H, 7·73(7·35); N, 5·42(5·15);
Bisdesoxy-bis(3′-carboxy-phenylimino)embelin	b	Crimson rect. prisms (Ethyl acetate)	246–248°	Light green	Light yellow	Pink	$C_{31}H_{38}O_6N_2$	C, 70·02(69·92); H, 6·84(6·77); N, 5·43(5·26).
Bisdesoxy-bis(benzyl-imino)embelin	b	Square red prisms (acetone)	156–157°	Light green	Yellow	Pink	$C_{31}H_{40}O_2N_2$	C, 79·02(78·81); H, 8·62(8·48); N, 6·07(5·93).
3-Benzylamino-bisdesoxy-bis(benzylimino)embelin	b	Orange brown prisms (acetone)	245–248°	Nil	Nil	Nil	$C_{38}H_{46}O_2N_3$	C, 80·24(80·19); H, 7·27(7·02); N, 7·56(7·37).
Bisdesoxy-bis(4′-phenoxy-phenylimino)embelin	a	Green rect. plates (Ethyl acetate-petrol)	168–170°	Green	Yellow	Red	$C_{41}H_{44}O_4N_2$	C, 78·52(78·34); H, 7·17(7·00); N, 4·92(4·46).
Bisdesoxy-bis(2′-carbo-methoxy phenylimino)-embelin	b	Long red needles (Ethyl acetate-petrol)	112–114°	Light green	Yellow	Pink	$C_{33}H_{40}O_6N_2$	C, 70·44(70·38); H, 7·40(7·14); N, 5·40(5·00).

* Kaul *et al.*[3] report, m.p. 216°. † Kaul *et al.*[3] report, m.p. 167–168°.

EXPERIMENTAL

Method of preparation

(a). Embelin (1 mole) and the primary amine (2 moles) were boiled under reflux on a metal bath during ½hr (where the amine is a liquid). The cooled reaction mixture was decomposed using excess ice cold dil. HCl and the product obtained, crystallized from ethyl acetate or acetone.

(b). The condensations were carried out in the same molar proportions as above except that acetic acid was used as a solvent, particularly in case of solid primary amines and the reaction mixture heated on a water bath at 100° for 3 hr.

The quinone di-imines are coloured deep red, reddish brown or violet and give a faint green ferric reaction in alcoholic solution. In benzene, they dissolve forming a red or dark red solution, while in alcohol, they give a yellow or yellowish-green solution. The colour changes in alcoholic alkali and acid media are also prominent. Table 1 gives a summary of the condensations effected and the properties of the products obtained.

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