

CHEMICAL EXAMINATION OF *EMBELIA* *RIBES*—VI

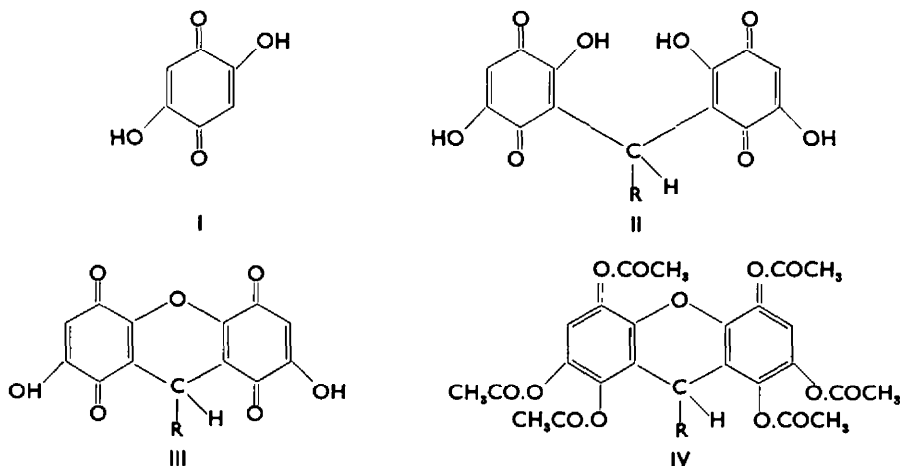
SYNTHESIS OF SOME NEW METHYLENE-BISBENZOQUINONES

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Abstract—By the condensation of 2,5-dihydroxybenzoquinone (I) with various aldehydes (bis-desundecyl)vilangins and anhydrovilangins (II and III), have been synthesized and their properties recorded.

OUR studies on the synthesis of vilangin and analogues of vilangin and anhydrovilangin,¹ have been extended to the synthesis of some lower homologues of vilangin and anhydrovilangin devoid of the undecyl groups. Similar to the condensation of embelin with various aldehydes, 2,5-dihydroxybenzoquinone (I) condenses with acetic, propionic and benzaldehydes to give both the products (bisdesundecyl)vilangins and anhydrovilangins (II and III). Only (bisdesundecyl)anhydrovilangins are obtained in the case of other aromatic aldehydes.



EXPERIMENTAL

9-Methyl(bisdesundecyl)vilangin (IIa, R = CH₃) and *9-Methyl(bisdesundecyl)anhydrovilangin* (IIIa, R = CH₃). 2,5-Dihydroxybenzoquinone (5 g) was condensed with acetaldehyde (1.25 ml) in alcoholic acetic acid solution (50%, 50 ml) by boiling during 3 hr which resulted in the formation of a mixture of IIa and IIIa, separated into a dioxan-soluble, containing IIa and a dioxan insoluble IIIa. IIa crystallized from dioxan as red brown prisms, m.p. 221–223°, giving a red ferric reaction. (Found: C, 55.02; H, 3.36. C₁₄H₁₀O₈ requires: C, 54.91; H, 3.27%). The *tetra-2,4-dinitrophenylhydrazone* of IIa crystallized as red brown prisms, m.p. 246–248°d. from methanol. (Found: C, 44.72; H, 2.74; N, 22.14. C₃₈H₁₆O₁₀N₁₄ requires: C, 44.45; H, 2.53; N, 21.83%).

IIIa crystallized as dark brown short prisms, m.p. 242–244° from excess dioxan giving a red ferric reaction. The same was also obtained by different methods: (1) By the conversion of IIa to

¹ Ch. B. Rao and V. Venkateswarlu, *Tetrahedron* **18**, 361, 951 (1962).

IIIa using alcoholic H_2SO_4 (4%), (2) by the condensation of I with acetaldehyde in alcoholic H_2SO_4 (4%). (Found: C, 58.61; H, 3.01. $C_{14}H_8O$, requires: C, 58.33; H, 2.78%).

The hexaacetate of IIa or IIIa, viz. 9-methyl(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin (IVa, R = CH_3) was obtained by the reductive acetylation of IIa or IIIa using acetic anhydride and Zn dust in presence of a trace of triethylamine. The product crystallized as colourless prisms, m.p. 225–226° from benzene showing a negative ferric reaction. (Found: C, 57.49; H, 4.63; $-COCH_3$, 47.67. $C_{36}H_{24}O_{18}$, requires: C, 57.36; H, 4.41; $-COCH_3$, 47.42%).

9-Ethyl(bisdesundecyl)vilangin (IIb, R = C_2H_5). Condensation of I (5 g) with propionic aldehyde (1.2 ml) in glacial acetic acid (15 ml) by warming on a steam bath during 2½ hr, resulted in the formation of IIb as orange red irregular prisms, m.p. 260–261° from methanol, giving a dark red ferric reaction. (Found: C, 56.37; H, 3.91. $C_{18}H_{12}O_8$, requires: C, 56.26; H, 3.75%).

The tetra-2,4-dinitrophenylhydrazone of IIb crystallized as red brown short prisms, m.p. 272–274°d. (Found: C, 45.27; H, 2.83; N, 21.86. $C_{30}H_{28}O_{20}N_{16}$, requires: C, 45.00; H, 2.69; N, 21.54%).

9-Ethyl(bisdesundecyl)anhydrovilangin (IIIb, R = C_2H_5). The cyclization of IIb using alcoholic anhydrous HCl by boiling during 2 hr on a water bath gave IIIb as red brown short prisms, m.p. 284–286° from methanol showing a purple ferric reaction in alcoholic solution. (Found: C, 59.74; H, 3.53. $C_{16}H_{10}O_7$, requires: C, 59.61; H, 3.31%).

The hexaacetate of reduced IIb or IIIb, viz. 9-ethyl(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin (IVb, R = C_2H_5), was obtained by the reductive acetylation of IIb or IIIb following the general procedure. The product crystallized as colourless square plates, m.p. 244–246° from benzene, giving a negative ferric reaction. (Found: C, 58.24; H, 4.82; $-COCH_3$, 46.47. $C_{27}H_{28}O_{18}$, requires: C, 58.06; H, 4.66; $-COCH_3$, 46.24%).

9-Phenyl(bisdesundecyl)vilangin (IIc, R = C_6H_5). Condensation of I (5 g) with benzaldehyde in alcoholic acetic acid (4%, 20 ml) by boiling during 2 hr, followed by removal of excess benzaldehyde by steam distillation, resulted in the formation of IIc which crystallized as short deep orange yellow prisms, m.p. 286–288°d. from benzene, showing a deep brown ferric reaction. (Found: C, 62.03; H, 3.37. $C_{19}H_{14}O_8$, requires: C, 61.95; H, 3.26%).

The tetra-2,4-dinitrophenylhydrazone of IIc crystallized as scarlet red short prisms, m.p. 222–224°d. from methanol. (Found: C, 47.61; H, 2.83; N, 20.64. $C_{48}H_{28}O_{30}N_{16}$, requires: C, 47.42; H, 2.57; N, 20.58%).

9-Phenyl(bisdesundecyl)anhydrovilangin (IIIc, R = C_6H_5). IIc was cyclized using alcoholic H_2SO_4 (4%) to give IIIc. The same was also obtained by the condensation of I with benzaldehyde in presence of conc. H_2SO_4 by warming on a water bath during 2½ hr. The excess benzaldehyde was removed by steam distillation and the product obtained crystallized as dark brown prisms, m.p. 320°d. from ethyl acetate showing a purple ferric reaction in alcoholic solution. (Found: C, 65.27; H, 3.04. $C_{19}H_{10}O_7$, requires: C, 65.13; H, 2.86%).

The hexaacetate of reduced IIc or IIIc, viz. 9-phenyl(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin (IVc, R = C_6H_5) obtained by the reductive acetylation of either IIc or IIIc following the normal procedure, crystallized as colourless rectangular plates, m.p. 306–308°d. from benzene giving a negative ferric reaction. (Found: C, 61.51; H, 4.37; $-COCH_3$, 42.81. $C_{31}H_{28}O_{18}$, requires: C, 61.38; H, 4.29; $-COCH_3$, 42.57%).

9-(4'-Methoxyphenyl)-(bisdesundecyl)anhydrovilangin (IIIId, R = p-methoxyphenyl). 2,5-Dihydroxybenzoquinone (5 g) was condensed with anisaldehyde (3.3 ml) in presence of ethanolic H_2SO_4 (50 ml, 2%) by boiling under reflux during 2 hr. IIIId crystallized as red brown square plates, m.p. 250–252°d. from ethyl acetate showing a brown ferric reaction in alcoholic solution. (Found: C, 63.31; H, 3.37. $C_{20}H_{12}O_8$, requires: C, 63.16; H, 3.16%).

The tetra-2,4-dinitrophenylhydrazone of IIIId crystallized as red brown short prisms, m.p. 236–238°d from methanol. (Found: C, 48.14; H, 2.72; N, 20.54; $C_{44}H_{28}O_{30}N_{16}$, requires: C, 47.99; H, 2.55; N, 20.36%).

The hexaacetate of reduced IIIId, viz. 9-(4'-methoxyphenyl)-(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin (IVd, R = p-methoxyphenyl) obtained following the normal procedure, crystallized as colourless square plates, m.p. 296–298°d. from ethyl acetate pet. ether, b.p. 40–60°, giving a negative ferric reaction. (Found: C, 60.54; H, 4.72; $-COCH_3$, 40.72. $C_{32}H_{28}O_{14}$, requires: C, 60.37; H, 4.55; $-COCH_3$, 40.56%).

9-(2'-Methoxyphenyl)-(bisdesundecyl)anhydrovilangin (IIIe, R = o-methoxyphenyl). The condensation of 2,5-dihydroxybenzoquinone (5 g) with o-methoxybenzaldehyde (3.3 g) using alcoholic

H₂SO₄ (50 ml, 4%) gave IIIe as red brown prisms, m.p. 238–240° from methanol, showing a purple ferric reaction in alcoholic solution. (Found: C, 63.24; H, 3.34. C₂₀H₁₁O₄ requires: C, 63.16; H, 3.16%).

The *tetra-2,4-dinitrophenylhydrazone* of IIIe crystallized as deep red brown prisms, m.p. 219–222° from methanol. (Found: C, 48.08; H, 2.76; N, 20.61. C₄₄H₂₅O₂₀N₁₆ requires: C, 47.99; H, 2.57; N, 20.36%).

The hexaacetate of reduced IIIe, viz. 9(2'-methoxyphenyl)-(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin (IVe, R = *o*-methoxyphenyl-) crystallized as colourless square plates, m.p. 284–286° from benzene, giving a negative ferric reaction. (Found: C, 60.61; H, 4.74; —COCH₃, 40.84. C₃₂H₂₅O₁₄ requires: C, 60.37; H, 4.55; —COCH₃, 40.56%).

9(3',4'-Dimethoxyphenyl)-(bisdesundecyl)anhydrovilangin (III f, R = 3,4-dimethoxyphenyl-). The condensation of I (5 g) with veratric aldehyde (4 g) in alcoholic H₂SO₄ (50 ml, 4%) by boiling during 3 hr gave III f which crystallized as deep red brown prisms, m.p. 256–258° from ethyl acetate, showing a purple ferric reaction. (Found: C, 61.72; H, 3.62. C₃₁H₁₄O₉ requires: C, 61.46; H, 3.41%).

The *tetra-2,4-dinitrophenylhydrazone* of III f crystallized as red brown prisms, m.p. 248–250° from ethanol. (Found: C, 47.87; H, 3.14; N, 20.04. C₄₆H₂₃O₂₁N₁₆ requires: C, 47.66; H, 2.91; N, 19.77%).

The hexaacetate of reduced III f, viz. 9(3',4'-dimethoxyphenyl)-(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin (IV f, R = 3,4-dimethoxyphenyl-) crystallized as colourless rectangular plates, m.p. 210–212° from benzene, giving a negative ferric reaction. (Found: C, 59.71; H, 4.72; —COCH₃, 39.01. C₃₂H₂₀O₁₅ requires: C, 59.46; H, 4.50; —COCH₃, 38.74%).

9(2',6'-Dimethoxyphenyl)-(bisdesundecyl)anhydrovilangin (III g, R = 2,6-dimethoxyphenyl-). Condensation of I (5 g) with 2,6-dimethoxybenzaldehyde (4 g) in alcoholic H₂SO₄ (25 ml, 2%) by boiling during 3 hr gave III g which crystallized as red brown prisms, m.p. 230–232° from ethyl acetate, showing a brown ferric reaction in alcoholic solution. (Found: C, 61.32; H, 3.67. C₃₁H₁₄O₉ requires: C, 61.46; H, 3.41%).

The *tetra-2,4-dinitrophenylhydrazone* of III g crystallized as bright red square plates, m.p. 226–228° from methanol. (Found: C, 47.52; H, 3.14; N, 20.03. C₄₆H₂₃O₂₁N₁₆ requires: C, 47.66; H, 2.91; N, 19.77%).

The hexaacetate of reduced III g viz. 9(2',6'-dimethoxyphenyl)-(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin (IV g, R = 2,6-dimethoxyphenyl-) crystallized as colourless prisms, m.p. 260–262° from benzene giving a negative ferric reaction. (Found: C, 59.62; H, 4.57; —COCH₃, 39.07. C₃₂H₂₀O₁₅ requires: C, 59.46; H, 4.50; —COCH₃, 38.74%).

9(3',4'-Methylenedioxyphenyl)-(bisdesundecyl)anhydrovilangin (III h, R = 3,4-methylenedioxyphenyl-). 2,5-Dihydroxybenzoquinone (5 g) was condensed with 3,4-methylenedioxybenzaldehyde (3.7 g) using alcoholic H₂SO₄ (50 ml, 4%) by boiling during 3 hr to give III h which crystallized as deep reddish brown prisms, m.p. 266–268° d. from methanol showing a purple ferric reaction in alcoholic solution. (Found: C, 60.72; H, 2.67. C₂₀H₁₀O₉ requires: C, 60.91; H, 2.54%).

The *tetra-2,4-dinitrophenylhydrazone* of III h crystallized as red brown prisms, m.p. 230–232° d. from methanol. (Found: C, 47.61; H, 2.64; N, 20.46. C₄₄H₂₃O₂₁N₁₆ requires: C, 47.41; H, 2.33; N, 20.11%).

The hexaacetate of reduced III h, viz. 9(3',4'-methylenedioxyphenyl)-(bisdesundecyl)hexa-O-tetrahydroanhydrovilangin, (IV h, R = 3,4-methylenedioxyphenyl-) crystallized as colourless square pyramids, m.p. 250–251° from benzene giving a negative ferric reaction. (Found: C, 59.24; H, 4.31; —COCH₃, 39.77; C₃₂H₁₆O₁₆ requires: C, 59.07; H, 4.00; —COCH₃, 39.69%).

9(4'-Dimethylaminophenyl)-(bisdesundecyl)anhydrovilangin (III i, R = *p*-dimethylaminophenyl-). Condensation of I (5 g) with *p*-dimethylaminobenzaldehyde (3.5 g) in alcoholic H₂SO₄ (50 ml, 4%) by boiling during 3 hr gave III i which crystallized as deep brown rectangular plates, m.p. above 320° d. from ethyl acetate, showing a purple ferric reaction in alcoholic solution. (Found: C, 64.34; H, 4.01; N, 3.74. C₂₁H₁₅O₇N requires: C, 64.12; H, 3.82; N, 3.56%).

The hexaacetate of reduced III i, viz. 9(4'-dimethylaminophenyl)-(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin (IV i, R = *p*-dimethylaminophenyl-) crystallized as colourless square prisms, m.p. 288–290° d. from benzene giving a negative ferric reaction. (Found: C, 61.32; H, 5.03; —COCH₃, 40.01. C₃₃H₂₁O₁₃N requires: C, 61.02; H, 4.78; —COCH₃, 39.76%).

9(3'-Nitrophenyl)-(bisdesundecyl)anhydrovilangin, III j, R = 3-nitrophenyl-. Condensation of I (5 g) with *m*-nitrobenzaldehyde (3.5 g) using alcoholic H₂SO₄ (50 ml, 4%) by boiling during 3 hr

gave IIIj which crystallized as deep brown prisms, m.p. 252–254°d. from ethyl acetate, showing a purple ferric reaction in alcoholic solution. (Found: C, 57.91; H, 2.43; N, 3.74. $C_{19}H_{10}O_8N$ requires: C, 57.72; H, 2.28; N, 3.54%.)

The *tetra-2,4-dinitrophenylhydrazone* of IIIj crystallized as deep red brown prisms, m.p. 240–242°d. from methanol. (Found: C, 46.43; H, 2.47; N, 21.72. $C_{43}H_{28}O_{21}N_{17}$ requires: C, 46.28; H, 2.24; N, 21.35%.)

The hexaacetate of reduced IIIj, viz. 9(3'-nitrophenyl)-(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin (IVj, R = 3-nitrophenyl-) crystallized as colourless square pyramids, m.p. 239–241° from benzene, giving a negative ferric reaction. (Found: C, 57.03; H, 4.14; $-\text{COCH}_3$, 40.14. $C_{81}H_{52}O_{16}N$ requires: C, 57.14; H, 3.84; $-\text{COCH}_3$, 39.63%.)

9(4'-Hydroxyphenyl)-(bisdesundecyl)anhydrovilangin, (IIIk, R = *p*-hydroxyphenyl-). Condensation of I (5 g) with *p*-hydroxybenzaldehyde (3.2 g) by boiling in ethanolic H_2SO_4 (50 ml, 4%) during 2 hr gave IIIk which crystallized as orange yellow rectangular plates, m.p. 131–132° from benzene, showing a purple ferric reaction. (Found: C, 62.41; H, 2.92. $C_{19}H_{10}O_8$ requires: C, 62.29; H, 2.73%.)

The heptaacetate of reduced IIIk, viz. 9(4'-acetoxyphenyl)-(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin (IVk, R = *p*-acetoxyphenyl-) crystallized as colourless prisms, m.p. 92–93° from benzene, giving a negative ferric reaction. (Found: C, 59.72; H, 4.43; $-\text{COCH}_3$, 45.27. $C_{88}H_{58}O_{16}$ requires: C, 59.64; H, 4.22; $-\text{COCH}_3$, 45.33%.)

9(2'-Hydroxyphenyl)-(bisdesundecyl)anhydrovilangin, (III l, R = *o*-hydroxyphenyl-). Condensation of I (5 g) with salicylaldehyde (3.5 ml) using alcoholic H_2SO_4 (50 ml, 4%) by boiling during 3 hr or using piperidine (5 drops) in the cold during 48 hr gave III l which crystallized as orange brown prisms, m.p. 232–234°d. from methanol, showing a brown ferric colour in alcoholic solution. (Found: C, 62.41; H, 3.03. $C_{19}H_{10}O_8$ requires: C, 62.29; H, 2.73%.)

The heptaacetate of reduced III l, viz. 9(2'-acetoxyphenyl)-(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin, (IVl, R = 2-acetoxyphenyl-) crystallized as colourless square plates, m.p. 190–192° from benzene, giving a negative ferric reaction. (Found: C, 59.42; H, 4.43; $-\text{COCH}_3$, 45.71. $C_{88}H_{58}O_{16}$ requires: C, 59.64; H, 4.22; $-\text{COCH}_3$, 45.33%.)

9(3'-Methoxy-4'-hydroxyphenyl)-(bisdesundecyl)anhydrovilangin, (III m, R = 3-methoxy-4-hydroxyphenyl-). I (5 g) was condensed with vanillin (4 g) using alcoholic H_2SO_4 (50 ml, 4%) by boiling during 2 hr to give III m which crystallized as violet brown short prisms, m.p. 246–248°d. from methanol, showing a brown ferric colour in alcoholic solution. (Found: C, 60.27; H, 3.41. $C_{20}H_{12}O_9$ requires: C, 60.60; H, 3.03%.)

The heptaacetate of reduced III m, viz. 9(3'-methoxy-4'-acetoxyphenyl)-(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin, (IV m, R = 3-methoxy-4-acetoxyphenyl-) crystallized as colourless rhombs, m.p. 242–244°d. from ethyl acetate–pet. ether, b.p. 40–60°, giving a negative ferric reaction. (Found: C, 59.04; H, 4.64; $-\text{COCH}_3$, 43.64. $C_{84}H_{50}O_{16}$ requires: C, 58.79; H, 4.32; $-\text{COCH}_3$, 43.37%.)

9(2'-Hydroxy-3'-methoxyphenyl)-(bisdesundecyl)anhydrovilangin, (III n, R = 2-hydroxy-3-methoxyphenyl-). I (5 g) was condensed with *o*-vanillin (4 g) using alcoholic H_2SO_4 (50 ml, 4%) by boiling during 2 hr to give III n which crystallized as orange red short prisms, m.p. 250–252°d. from ethanol, showing a purple ferric reaction. (Found: C, 60.64; H, 3.14. $C_{20}H_{12}O_9$ requires: C, 60.60; H, 3.03%.)

The heptaacetate of reduced III n, viz. 9(2'-acetoxy-3'-methoxyphenyl)-(bisdesundecyl)hexa-O-acetyltetrahydroanhydrovilangin, (IV n, R = 2-acetoxy-3-methoxyphenyl-) crystallized as colourless square plates, m.p. 262–264°d. from benzene, giving a negative ferric reaction. (Found: C, 59.13; H, 4.47; $-\text{COCH}_3$, 43.51. $C_{84}H_{50}O_{16}$ requires: C, 58.79; H, 4.32; $-\text{COCH}_3$, 43.37%.)

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