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CHEMICAL EXAMINATION OF *EMBELIA RIBES*—II

ANALOGUES OF VILANGIN AND ANHYDROVILANGIN

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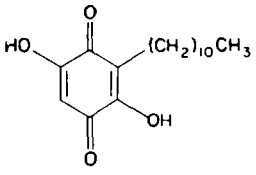
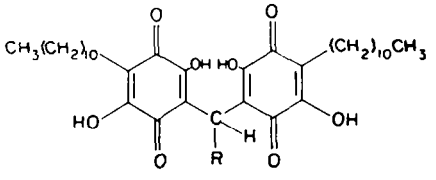
Abstract—By the condensation of embelin (I) with various aldehydes, analogues of vilangin (II) and anhydrovilangin (III) have been synthesized and their properties recorded.

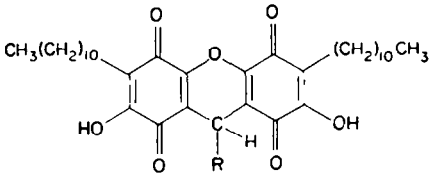
THE isolation, constitution and synthesis of vilangin has been reported earlier.[1] Further study reveals that embelin (I) reacts with various aldehydes to give analogues of vilangin (II) and anhydro-vilangin (III). With acetic, propionic and benzaldehydes, embelin condenses to give both the products; only the anhydro (III) is obtained in



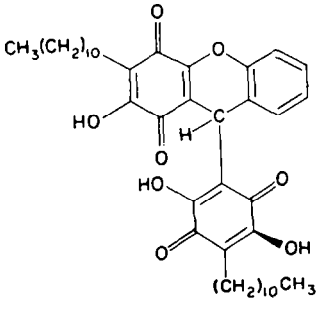
I



II



III



IV

[1] Ch. Bheemasankara Rao and V. Venkateswarlu, *J. Org. Chem.* in press.

TABLE 1

Product	Method of prepn.	Appearance	M.p.	Ferric colour	Formula	*Analysis* (theoretical in brackets)
Methylvilangin	a	Pale orange plates (methanol)	133–134°	Brown	$C_{36}H_{54}O_8$	C, 70·52 (70·31) H, 9·19 (8·85)
Tetra-O-methyl-methylvilangin	- -	Bright yellow prisms (petrol)	82–83°	nil	$C_{40}H_{62}O_8$	C, 71·53 (71·58) H, 9·50 (9·32) —OCH_3, 18·9 (18·5)
9-Methylanhydrovilangin	b	Orange red prisms (acetic acid)	182–83°	Purple brown	$C_{36}H_{52}O_7$	C, 72·21 (72·44) H, 9·03 (8·79)
2,7-Di-O-acetyl-9-methyl-anhydrovilangin	—	Pale yellow rhombs (petrol)	75–76°	nil	$C_{40}H_{56}O_9$	C, 70·82 (70·53) H, 8·53 (8·21) —$COCH_3$ 12·37 (12·64)
Ethylvilangin	a	Pale grey prisms (petrol).	107–108°	Deep brown	$C_{37}H_{56}O_8$	C, 71·00 (70·65) H, 9·32 (8·97)
9-Ethylanhydrovilangin	a	Orange red prisms (benzene)	144–145°	Purple	$C_{37}H_{54}O_7$	C, 72·57 (72·73) H, 9·23 (8·91)
Phenylvilangin	a	Orange yellow rhombs (petrol.)	112–113°	Purple brown	$C_{41}H_{56}O_8$	C, 72·44 (72·74) H, 8·52 (8·34)
9-Phenylanhydrovilangin	b	Orange rect. prisms (benzene)	150–152°	Intense purple	$C_{41}H_{54}O_7$	C, 74·23 (74·73) H, 8·71 (8·26)
9-Benzylanhydrovilangin	c	Orange rect. prisms (benzene-petrol.)	150–151°	Purple	$C_{42}H_{56}O_7$	C, 75·14 (74·94) H, 8·70 (8·39)
9(β-Phenylvinyl) anhydro-vilangin	b	Golden yellow rect. prisms (benzene)	170–172°	Purple	$C_{43}H_{56}O_7$	C, 75·78 (75·37) H, 8·52 (8·24)

Table 1(cont'd.)

Product	Method of prepn.	Appearance	M.p.	Ferric colour	Formula	*Analysis* (theoretical in brackets)
9(4′-Dimethylamino phenyl)-anhydrovilangin	c	Short scarlet red prisms (benzene)	99–100°	Deep brown	$C_{43}H_{59}O_7N$	N, 2·21 (2·00)
9(4′-Methoxyphenyl)-anhydrovilangin	b or c	Orange red rect. prisms (methanol)	132–133°	Intense purple	$C_{42}H_{56}O_8$	C, 73·41 (73·18) H, 8·51 (8·19)
9(3′,5′-Dinitrophenyl) anhy-hydrovilangin	b	Deep purple rhombs (methanol)	129–130°	Intense brown	$C_{41}H_{52}O_{11}N_2$	N, 4·00 (3·74)
9(2′-Methoxyphenyl) anhydro-vilangin	b or c	Deep orange prisms (Petrol.)	129–130°	Wine red turning brown	$C_{42}H_{56}O_8$	C, 73·38 (73·18) H, 8·55 (8·19)
9(3′,4′-methylene-dioxy-phenyl)-anhydrovilangin	b	orange red rect. prisms (petrol.)	111–112°	Brown	$C_{42}H_{54}O_9$	C, 71·92 (71·76) H, 7·83 (7·75)
9(3′,4′-Dimethoxyphenyl)-anhydrovilangin	b	Pale orange yellow short prisms (benzene)	157–158°	Reddish brown	$C_{43}H_{58}O_9$	C, 72·00 (71·81) H, 8·46 (8·15)
9(4′-Hydroxyphenyl)-anhydrovilangin	b	Orange plates and prisms (benzene)	168–169°	Brown turning black	$C_{41}H_{54}O_8$	C, 73·04 (72·95) H, 8·43 (8·07)
9(4′-Hydroxy-3′-methoxy-phenyl) anhydrovilangin	b	Orange red plates and prisms (benzene)	229–230°	Brown	$C_{43}H_{56}O_9$	C, 71·42 (71·55) H, 8·46 (8·01)
9(2′-Hydroxyphenyl)-anhydrovilangin or (IV)	b	Scarlet irregular prisms (benzene)	154–155°	Purple	$C_{41}H_{54}O_8$	C, 73·22 (72·95) H, 8·41 (8·07)
	c	Orange yellow rect. prisms (benzene)	161–162°	Purple brown	$C_{41}H_{54}O_8$	C, 73·00 (72·95) H, 8·41 (8·07)

the case of other aromatic aldehydes. While, in the case of salicylaldehyde, a product of type IV is also produced, more complicated reactions take place with *p*-hydroxy benzaldehyde and vanillin, possibly involving oxidation leading to resinification. There is no reaction between embelin and ketones. These condensation reactions explain the anomalous results reported by Kaul *et al.*[2]

EXPERIMENTAL

Method of preparation

(a) Embelin (2 moles) was condensed with (1 mole) of aldehyde in acetic acid or 25% ethanolic acetic acid solutions by boiling for 3 hr. The products were purified as indicated.

(b) The condensations were carried out using 10% alcoholic sulphuric acid or with saturated hydrogen chloride and boiling for 2 hr. The products were purified by short column chromatography.

(c) The reaction was carried out using piperidine in the cold during 24–36 hr and the products purified by chromatography.

The following Table gives a summary of the condensation reactions effected and the properties of the products obtained.

[2] R. Kaul, A. C. Ray and S. Dutt, *J. Ind. Chem. Soc.* **8**, 231 (1931).