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COMPOSITION OF BHILAWANOL FROM *SEMECARPUS ANACARDIUM*

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Key Word Index—*Semecarpus anacardium*; Anacardiaceae; bhilawan nut tree; bhilawanol; 1,2-dihydroxy-3-pentadecenylbenzene; 1,2-dihydroxy-3-pentadecadienylbenzene.

Abstract—Bhilawanol, isolated from bhilawan nut shell liquid, was shown by chromatography, NMR and IR to comprise 30–32% 1,2-dihydroxy-3-pentadecenylbenzene and 68–70% of the corresponding diene analogue.

INTRODUCTION

BHILAWAN nut shell liquid (BNSL) is a black corrosive liquid, forming about 30–40% by weight of the nut of the bhilawan nut tree (*Semecarpus anacardium* L.), whose habitat is the sub-Himalayan tract and the hotter parts of India. Considerable work has been carried out on the composition and substitution pattern in the aromatic ring of bhilawanol, the major component of BNSL, but there is no agreement between the results obtained by the various investigators.[1–5] The present work describes a re-examination of the constitution of bhilawanol.

RESULTS AND DISCUSSION

TLC of the dimethyl ether and diacetate derivatives of bhilawanol on $AgNO_3$–silica gel revealed the presence of two components. Examination of the two dimethyl ether components by NMR, showed that they are the monoene and diene respectively, with reference to the unsaturation of the side chain. This was achieved by integration of the protons in two regions of the NMR spectra, 1·2–3·0 ppm (methylenic protons) and 4·8–5·6 ppm (olefinic protons), and a comparison of their spectra in these regions with the NMR spectrum of the hydrogenated dimethyl ether of bhilawanol following the procedure used for identification of the components of cardanol.[6] The chemical shifts of the various protons in bhilawanol and its derivatives are given in Table 1. For the study of the substitution pattern in the aromatic ring of bhilawanol, the monomethyl ether–monoacetate derivative was found to be most suitable as one of its aromatic protons is deshielded enabling the assignment of the substitution pattern. Considering the two possible substitution patterns, 1,2,3 and 1,2,4 in the benzene nucleus of bhilawanol, four possible structures (1–4) can be

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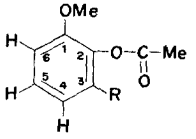
written for the monomethyl ether–monoacetate derivatives, two for each type of substitution.

TABLE 1. NMR DATA OF BHILAWANOL AND ITS DERIVATIVES
(Proton chemical shifts are given in δ ppm)

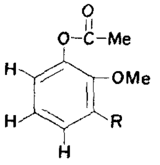
Compounds	H·Ar	O R_1 O R_2	Olefinic protons CH=CH	Methylenic protons				Methyl protons
				$-CH=CH-\underline{CH_2}-CH=CH-$	$-\underline{CH_2}-Ar$	$-\underline{CH_2}-CH=CH-$	$-(\underline{CH_2})n-$	$\underline{CH_3}-CH_2-$
Bhilawanol ($R_1 = R_2 = H$)	6·50 (*s*)	5·70 (*bs*)	5·00–5·43 (*t*)	2·23–2·83 (*m*)	2·23–2·88 (*m*)	1·66–2·23 (*dt*)	1·20 (*bs*)	0·66–1·01 (*dt*)
Dimethyl ether of bhilawanol ($R_1 = R_2 = Me$)	6·36–6·81 (*m*)	3·68 (*s*)	5·00–5·55 (*t*)	2·88–2·78 (*m*)	2·28–2·78 (*m*)	1·66–2·10 (*dt*)	1·20 (*bs*)	0·50–1·00 (*dt*)
Monomethyl ether of bhilawanol ($R_1 = H$; $R_2 = Me$)	6·51 (*s*)	5·40 (*s*) 3·66 (*s*)	5·00–5·33 (*m*)	2·33–2·80 (*t*)	2·33–2·80 (*m*)	1·66–2·10 (*dt*)	1·23 (*bs*)	0·66–0·96 (*dt*)
Hydrogenated dimethyl ether of bhilawanol ($R_1 = R_2 = Me$)	6·36–6·81 (*m*)	3·68 (*s*)	–	–	2·30–2·66 (*t*)		1·20 (*bs*)	0·56–1·01 (*dt*)
Monoene of dimethyl ether of bhilawanol ($R_1 = R_2 = Me$)	6·30–6·81 (*m*)	3·70 (*m*) 3·73 (*s*)	5·05–5·46 (*t*)	–	2·30–2·63 (*dt*)	1·66–2·28 (*dt*)	1·28 (*bs*)	0·50–1·00 (*dt*)
Diene of dimethyl ether of bhilawanol ($R_1 = R_2 = Me$)	6·30–6·83 (*m*)	3·63 (*s*) 3·66 (*s*)	5·00–5·46 (*t*)	2·28–2·81 (*m*)	2·28–2·81 (*m*)	1·63–2·21 (*dt*)	1·20 (*bs*)	0·50–1·00 (*dt*)
Diacetate of bhilawanol ($R_1 = R_2 = CO.Me$)	6·95 (*s*)	2·06 (*s*)	5·06–5·43 (*t*)	2·23–2·83 (*m*)	2·22–2·83 (*m*)	1·66–2·20 (*m*)	1·25 (*bs*)	0·58–1·00 (*dt*)
Monoene of diacetate of bhilawanol ($R_1 = R_2 = CO.Me$)	6·88 (*s*)	2·05 (*s*) 2·11 (*s*)	4·83–5·50 (*t*)	–	2·22–2·56 (*m*)	1·66–2·16 (*m*)	1·25 (*bs*)	0·66–1·00 (*dt*)
Diene of diacetate of bhilawanol ($R_1 = R_2 = CO.Me$)	6·88 (*s*)	2·05 (*s*) 2·10 (*s*)	4·83–5·50 (*t*)	2·23–2·83 (*m*)	2·23–2·83 (*m*)	1·66–2·23 (*m*)	1·23 (*bs*)	0·50–1·00 (*dt*)

Abbreviations: *s*—singlet; *t*—triplet; *m*—multiplet; *bs*—broad singlet; *dt*—distorted triplet.

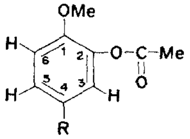
The splitting pattern of the proton signal with two *ortho* couplings (δ 6·88 ppm, J 7,8 Hz) favours structure (**1**) which is a 1,2,3 substitution pattern. In (**1**) the proton at C_5, which is *para* to the acetoxy group and has two *ortho* protons at C_4 and C_6, is deshielded by the acetoxy group. The remaining aromatic protons at C_4 and C_6 appear as a distorted multiplet in the region of 6·35–6·70 ppm. Had the compound shown a 1,2,4 substitution pattern, there would be only one *ortho* coupling (**3**). It is of interest that the elucidation of the structure has been possible because in the preparation of the monomethyl ether–monoacetate derivative, the bhilawanol was first converted into its monomethyl ether, the methylation being expected at the C_1 position which is the least hindered. In the subsequent acetylation the acetoxy group could then be expected to occupy the C_2 position. Had acetylation been done prior to methylation the elucidation of the structure would have been more difficult.



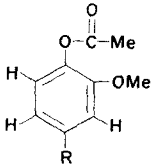
(1)



(2)



(3)



(4)

R is a 15-carbon alkyl side chain

The 1,2,3 substitution pattern was further confirmed by the aromatic C–H out-of-plane deformation bands found in the IR of the monomethyl ether–monoacetate derivative of bhilawanol at 740 and 770 cm^{-1} and the complete absence of a strong band between 800 and 860 cm^{-1} and a medium band between 860 and 900 cm^{-1} which are characteristic of a 1,2,4 type of aromatic substitution.

For quantitation, the diacetate derivatives were found to be the most suitable, and by using $AgNO_3$–silica gel column chromatography and densitometry, it was shown that the monoene and diene components of bhilawanol are present to the extent of 30–32% and 68–70% by weight respectively. The average unsaturation per mole calculated from these results (1·68) agrees well with that determined by the addition–substitution method[7] (1·69) and by NMR (1·61). These values however, differ from those obtained by Rao and Row[4,8] and Govindachari *et al.*[5]

EXPERIMENTAL

BNSL was cold-extracted with Et_2O from freshly picked bhilawan nut shells. Bhilawanol was isolated from BNSL by column chromatography on silica gel using C_6H_6 as eluant, and was found to comprise 85% BNSL. Bhilawanol had an average MW of 318 and refractive index, $[\mu_{\mathrm{D}_1}^{28^\circ}]$ 1·512435.

Mono- and di-methyl ethers of bhilawanol were prepared according to the method of Symes.[9] Diacetates were prepared by reaction with pyridine–AcO_2 (3:1) at 30° for 24 hr. The monomethyl ether–monoacetate was obtained by treating the pure monomethyl ether with pyridine–Ac_2O mixture as before. The dimethyl ether derivative of bhilawanol was hydrogenated in a Parr hydrogenator using EtOH and Pd–C catalyst at 2 atm. and 30°. All the products were purified by silica gel column chromatography. IR spectra were obtained using liquid films or solutions in CCl_4; NMR spectra were taken in CCl_4 using a Varian 60 MHz NMR spectrophotometer.

The quantitative estimation of the components of bhilawanol as their diacetate derivatives was done using $AgNO_3$–silica gel column chromatography, the monoene being eluted with C_6H_6 and the diene with C_6H_6–EtOAc (7:3), For quantitative estimation by densitometry, the diacetate derivatives are separated by TLC on 15% (w/w) $AgNO_3$–silica gel G layers using C_6H_6–EtOAc (19:1), followed by spraying with conc. H_2SO_4, charring and scanning in a Chromoscan double beam recording and integrating densitometer.

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