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δ-CUPARENOL, A NEW SESQUITERPENE PHENOL FROM THE LIVERWORT, BAZZANIA POMPEANA

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During the course of the investigation on the chemical constituents of the liverwort, Bazzania pompeana, a new sesquiterpene phenol, δ-cuparenol, was isolated as a minor component. The evidence for the proposed structure (I) is described.

In previous papers,[1,2] two new sesquiterpenoids, bazzanene and bazzanenol, have been isolated from Bazzania pompeana (Lac.) Mitt. which is a leafy liverwort belonging to the Lepidoziaceae family of Jungermaniales (Hepaticae). We now wish to report that another new sesquiterpene phenol, which was named as δ-cuparenol in relation to cuparenols,[3] was elucidated as 2-methyl-5-(1,2,2-trimethylcyclopentanyl)phenol (formula I).

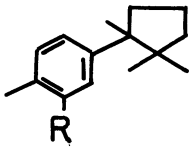
δ-Cuparenol (I), $C_{15}H_{22}O$ (obsd, 218.1660; calcd, 218.1668), $[\alpha]_D$ -73.5° ($CHCl_3$), was isolated in colorless oily state by means of combination of fractional distillation and elution chromatography. The IR (ν_{max}^{liq} 3350, 1620, 1580, 1505, 1455, 1410, 1385, 1375, 1365, 1240, 1180, 1110, 880 and 805 cm^{-1}) and UV spectra (λ_{max}^{EtOH} 274 and 281 nm; ε 2115 and 1890) suggested the compound to have a partial structure of 2,5-disubstituted phenol (1,2,4-trisubstituted benzenoid).[4] In fact, the compound afforded 3,5-DNB, m.p. 171.5-172.5°, and produced an oily acetate (II), $C_{17}H_{24}O_2$ (M^+ 260), ν_{max}^{liq} 1770, 1215 and 1015 cm^{-1}, on treatment with acetic anhydride in pyridine at room temperature.

The NMR spectrum, together with a phenolic hydroxyl proton ($\delta_{ppm}^{CCl_4}$ 5.35, 1H, exchangeable with D_2O), an aromatic methyl (δ 2.12, 3H, s) and three aromatic protons (δ 6.65, 1H, d, J=5.5 Hz; 6.68, 1H, br. d, J=5.5 Hz; 6.80, 1H, br. s), exhibited the existence of three aliphatic methylenes (δ 1.58, 6H, br. s) and three quarternary methyls (δ 0.53, 1.00 and 1.17, each 3H, s): the aromatic proton signals were similar to those of carvacrol, and one of the three quarternary methyls appeared in the upfield side due to the anisotropic effect of the aromatic nucleus. This NMR spectrum resembled closely those of cuparene (III),[5] which has been isolated from the same liverwort,[6] except the phenolic hydroxyl proton and the aromatic proton region.

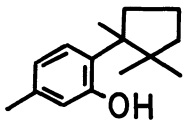
From the UV, IR and NMR spectra, the structure of this compound was deduced to be represented by formula (I) or (IV).

In order to determine the position of the hydroxyl group, the chemical shift of the aromatic methyl group of δ-cuparenyl acetate (II) was compared with that of

cuparene (III), and the remarkable upfield shift (0.24 ppm in CCl_4) was recognized. This upfield shift was assumed to be the anisotropic effect of the acetyl group. Furthermore, the chemical shifts of the aromatic methyls were examined about p-cymene (VII) and its acetoxy derivatives as shown in TABLE: carvacryl acetate (V) showed upfield shift in the same degree as that of δ-cuparenyl acetate (II), but thymyl acetate (VI) did not. As to the solvent effect, the similarity was also recognized between δ-cuparenyl acetate (II) and carvacryl acetate (V).



(I) R = OH
(II) R = OAc
(III) R = H



(IV)

TABLE Chemical Shifts of Aromatic Methyls of δ-Cuparenyl Acetate and Related Compounds (δ_{ppm})

Compounds	Chemical Shifts of Aromatic Methyls		
	in CCl_4	in C_6D_6	Δ value
δ-Cuparenyl acetate (II)	2.07	2.04	0.03
Cuparene (III)	2.31	2.18	0.13
Carvacryl acetate (V)	2.08	2.06	0.02
Thymyl acetate (VI)	2.28	2.06	0.22
p-Cymene (VII)	2.27	2.15	0.12

$\Delta = CCl_4 - C_6D_6$

Accordingly, δ-cuparenol, isolated from Bazzania pompeana, should be represented by the formula (I). This structure was further supported by the appearance of characteristic ions of $C_9H_{12}O$; 

, base ion, obsd m/e 136.0892, and of $C_{10}H_{12}O$; 

, 82 %, obsd m/e 148.0900, under electron impact.

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