The Products of the Reactions of Isohydrocoriamyrtin and Isocoriamyrtin with Phenylhydrazine Analogues

By TAKUO OKUDA,* TAKASHI YOSHIDA, and KUNIHIRO KONISHI

(*Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto, Japan*)

THE reaction of isohydrocoriamyrtin (I)[1] with excess α-methylphenylhydrazine in acetic acid yields a derivative whose analysis shows the presence of two moles of methylphenylhydrazine.[2] The structure of this derivative has now been shown to be (II).

The infrared spectrum which shows retention of γ-lactone by the peak at 1760 cm.$^{-1}$, the molecular formula, $C_{29}H_{36}O_3N_4$, which contains two atoms less of oxygen than (I), and the n.m.r. bands (in $CDCl_3$, τ 6·00 (d, $J = 3$ c./sec., 11-H), 5·40 (m, 3-H), 4·12 (d, $J = 3$ c./sec., 12-H) are indicative of the substitution of either 11-OH or 6-OH by the second methylphenylhydrazine molecule, in addition to the formation of methylphenylhydrazone at C-14. This is also supported by the n.m.r. spectrum measured in perdeuteriodimethyl sulphoxide, in which disappearance of the peaks

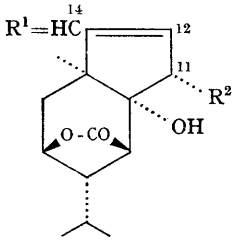
TABLE

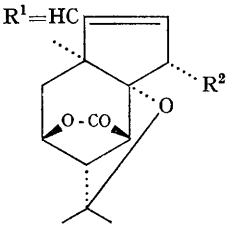
Compound	Absorption (log ε) 226 mμ	248 mμ	305 mμ (sh.)	328 mμ
(II)	(4·23)†	4·27	4·30	4·49
Methylphenylhydrazine	(3·65)	4·04	(3·27)	(2·08)
(II)–Methylphenylhydrazine	(4·10)	3·88	4·25	4·49
(III)	4·12	3·89	4·24	4·43

† No peak is shown where the data are written in the parentheses.

at τ 4·88s and at τ 5·10 (diffused doublet), and transformation of the multiplet at τ 6·25 (11-H) into a doublet (J = 3 c./sec.) are observed on the addition of D_2O, and also by the comparison of the ultraviolet spectra (see Table) which indicate that the difference of the intensities of the absorption peaks between (II) and the mono-methylphenylhydrazone (III), $C_{22}H_{28}O_4N_2$, corresponds to one mole of methylphenylhydrazine.

The reaction of isocoriamyrtin (VI)[1] with excess αα-diphenylhydrazine produced an analogous derivative (V), $C_{39}H_{38}O_3N_4$, whose structure is in accord with the following spectral data: λ_{max} (EtOH) 246 mμ (log ε 4·19), 306 (4·31), and 334 (4·34); ν_{max} (KBr) 3400 (NH) and 1772 (γ-lactone) cm.$^{-1}$; n.m.r., τ 6·17 (d, J = 3 c./sec., 11-H), 4·28 (d, J = 3 c./sec., 12-H), and 3·3 ~2·4 (m, aromatic H). The analogy of the formation of (V) to that of (II) settles the hydroxyl group in (I), substituted by the second molecule of methylphenylhydrazine, to be the allylic 11-OH.

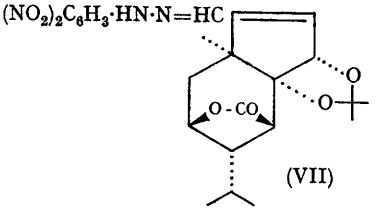




(I) R^1=O, R^2=OH
(II) R^1=NNMePh, R^2=NH·NMePh
(III) R^1=NNMePh, R^2=OH
(VI) R^1=NNMePh, R^2=OMe
(VIII) R^1=N·NH·$C_6H_3(NO_2)_2$, R^2=OH

(IV) R^1=O, R^2=OH
(V) R^1=$NNPh_2$, R^2=NH·NPh_2

The reaction of (I) with excess 2,4-dinitrophenylhydrazine in acetic acid yielded the mono-2,4-dinitrophenylhydrazone (VIII) only. Analogous treatment of (VIII) with methylphenylhydrazine resulted in recovery of (VIII). These results suggest that the effect of the substituent in the phenylhydrazine moiety in (III) could be one of the factors inducing the formation of (II).



(VII)

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[3] T. Okuda and T. Yoshida, *Tetrahedron Letters*, 1965, 4191; *Chem. and Pharm. Bull.* (*Japan*), in the press.