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INSECT ANTIFEEDANTS FROM PARABENZOIN TRILOBUM (II)

THE ABSOLUTE CONFIGURATION OF SHIROMODIOL-DIACETATE

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The structure of shiromodiol-diacetate has been derived from chemical and spectroscopic evidence[1)]. This paper presents evidence which let us assign the absolute configuration (I) for shiromodiol-diacetate.

Partial acetylation of shiromodiol (II) gave mainly the 6-monoacetate (III), $C_{17}H_{28}O_4$, m.p. 131°C, $(\alpha)_D^{25}$ +36.4, ν_{max}^{KBr} 3480, 1730 and 1240 cm^{-1}. The p-nitrobenzoate of III (IV), $C_{24}H_{31}O_7N$ has m.p. 199°C and $(\alpha)_D^{25}$ -33.3. On treatment with boron trifluoride etherate, the monoacetate (III) readily rearranged to a cyclized product[2)](V), $C_{17}H_{28}O_4$, m.p. 181°C, ν_{max}^{KBr} 3500, 3430, 1720 and 1270 cm^{-1}, nmr; 0.9(3H, d., j=6.3) and 1.0(3H, d., j=6.3) ($C\underline{H}_3$-CH-$C\underline{H}_3$), 1.2(3H, s., O-C-CH_3), 1.7(3H, s.,C=C-CH_3), 2.0(3H, s., O-CO-CH_3), 3.9(1H, dt.,j=10, 2.5, 2.5 $\underline{H}$-C-OH) and 5.1(1H, s., $\underline{H}$-C-OAc). Oxidation of V with chromic trioxide-pyridine gave the ketone (VI), $C_{17}H_{26}O_4$, m.p. 119°C, ν_{max}^{KBr} 3440, 1735, 1705 and 1240 cm^{-1}. These data indicate the presence of a tertiary alcohol group in V. That V is a cyclized product which is formed by the cleavage of the epoxy ring followed by trans-annular cyclization, is indicated from the nmr spectrum of V, which have no vinylic proton signal.

Both the double bond and epoxy ring in I must have trans configuration since biogenetic consideration suggests that germacrane sesquiterpenes are formed from all-trans farnesol and recently, X-ray analysis of germacranolides, elephantin[7)], elephantopin[7)] and heliangine[8)] have established that these compounds have the trans-substituted epoxy ring and double bond.

Thus, 6-monoacetate (III) having α-epoxy group would give the cyclized product which has 5α-hydrogen and 4α-hydroxy group as shown in the structure (V) by trans-annular cyclization, which is stereospecific in acidic media[3)].

The relative configuration of I was established by the detailed analysis of the nmr spectrum of V. The cycloheptene system has two energetically favoured conformers analogous to chair and boat form of the cyclohexane ring[4], so that the relative configuration of V could be depicted as the structure (A) or (B).

TABLE I. Dihedral Angles of Molecular Models A and B

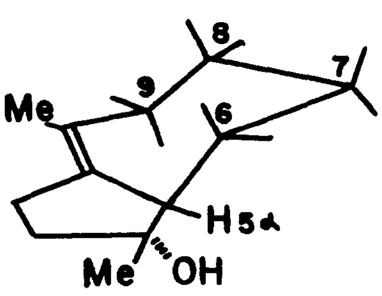
	A	B	Required from nmr coupling	
$H_{5\alpha}-H_{6\alpha}$	80°	120°	$H_{5\alpha}-H_{6}$	90°
$H_{5\alpha}-H_{6\beta}$	160°	0°		
$H_{6\alpha}-H_{7\alpha}$	80°	80°	$H_{6}-H_{7}$	90°
$H_{6\alpha}-H_{7\beta}$	30°	165°		

	A			Required from nmr coupling	
$H_{8\alpha}-H_{7\alpha}$	70°	$H_{8\beta}-H_{7\alpha}$	165°	$H_{7}-H_{8}$	65 or 110°
$H_{8\alpha}-H_{9\alpha}$	80°	$H_{8\beta}-H_{9\alpha}$	100°	$H_{8}-H_{9}$	65 or 110°
$H_{8\alpha}-H_{9\beta}$	30°	$H_{8\beta}-H_{9\beta}$	150°	$H_{8}-H_{9}$	30 or 150°

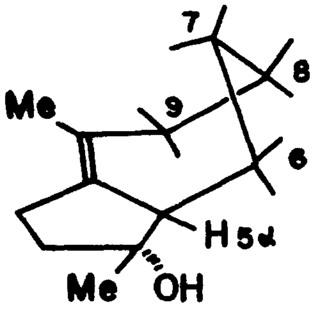
The proton on the carbon bearing the acetoxy group (H-6) must form dihedral angles of about 90° with H-5 and H-7 since both the couplings of H-6 with H-5 and -7 are near zero. An inspection of models shows that this is possible only if the cyclohexene system in V has chair form and all of H-5, -6 and -7 are placed on α-position.

The H-8 signal shows three couplings (10, 2.5 and 2.5) to the neighboured methylene at C-9 and H-7. That H-8 is placed on α-position is clear from the inspection of models as shown in Table I. Thus, shiromodiol diacetate and the cyclized product had to possess the relative configuration(I) and (V) respectively.

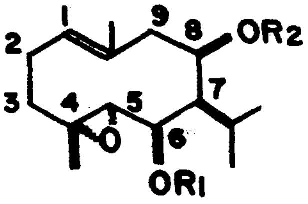
The absolute configuration of I was established from the ORD of β,γ-unsaturated chromophore in VII and VIII[1]. The ir. spectrum of the O-H streching region of the dilute carbontetrachloride solution of VII has an intramolecularly bonded hydroxy band at 3530 cm^{-1}, which indicates the existence of the carbonyl and hydroxyl group on same side of the plane put through ten-membered ring. The absorption maximum of the carbonyl in the ir. spectrum of VII, 1683 cm^{-1} shifted to 1708 cm^{-1} in VIII[5]. This also indicates that the hydroxy group in VII chelates with the carbonyl. The β,γ-unsaturated ketone chromophor in VII and VIII shows that the vinyl methyl group and the carbonyl group present on same side of the plane put through ten-membered ring. Thus, VII would be shown by the structure(C) or the enantiomer. The identities of the u.v. absorption maxima and the coupling constants of H-4 in VII and VIII[1] suggest that VIII also has same conformation

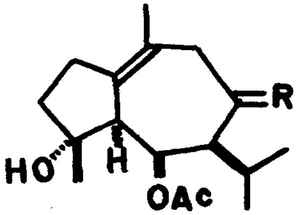


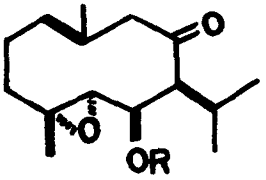
(A)



(B)







I. $R_1 = R_2 = Ac$

II. $R_1 = R_2 = H$

III. $R_1 = Ac$, $R_2 = H$

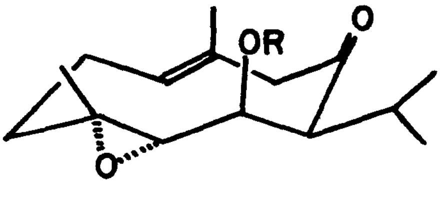
IV. $R_1 = Ac$, $R_2 = COC_6H_4-NO_2$

V. R = H, β-OH

VI. R = O

VII. R = H

VIII. R = Ac



C. R = H

D. R = Ac

with that of VII. VII and VIII show a negative Cotton effect[6] ($[\phi]_{326}$ -24200, $[\phi]_{280}$ +27200, a: 514, MeOH) and ($[\phi]_{326}$ -42500, $[\phi]_{290}$ +38300, a: 808 MeOH) respectively.

The high a-values reveals that in VII and VIII the β,γ-unsaturated ketone grouping forms an inherently dissymmetric chromophor[6]. From these data, VII and VIII were concluded to have the absolute conformation(C) and (D) respectively. Application of benzoate rule for the hydroxy group of III supports the above conclusion since the negative $\Delta[M]$ value ($[M]_D$ benzoate $-[M]_D$ alcohol= -148 -108= -256) indicates the s-configuration at C-8. Thus, shiromodiol diacetate was assigned to the absolute configuration(I).

Footnotes and References

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