Teucvin, a Novel Furanoid Norditerpene from *Teucrium viscidum var. Miquelianum*

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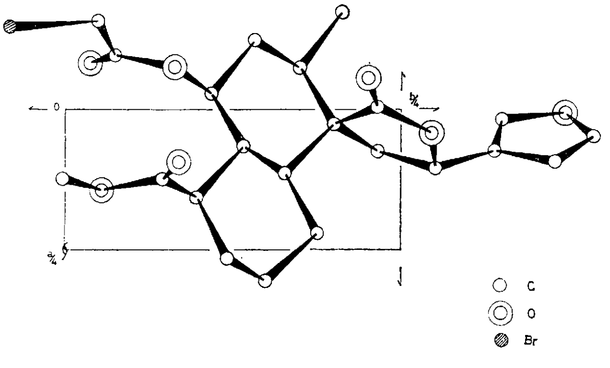
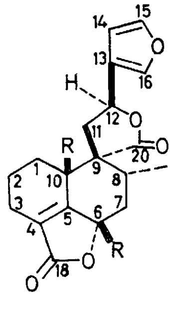
Summary The structure and absolute configuration of teucvin (I), a new norditerpene isolated from *Teucrium viscidum var. Miquelianum* has been determined by an *X*-ray crystallographic analysis of the bromo-derivative (IV) and from some of its reactions.

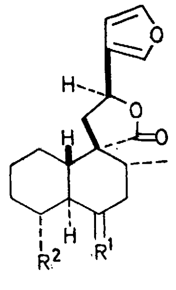
FROM the neutral fraction of the extracts of *Teucrium viscidum* Bl. *var. Miquelianum* (Maxim.) Hara (Labiatae), we have isolated a new norditerpene, teucvin (I), $C_{19}H_{20}O_5$, m.p. 207—208°, $[\alpha]_D + 88{\cdot}4°$ ($CHCl_3$), u.v., i.r., n.m.r., and mass spectral data were consistent with this structure. It showed pK_a' values of 8·4 and 6·5 by lactone titration in a mixture of methylcellosolve and water (8 : 2). Ehrlich reaction[1] for furan was positive. Teucvin, on heating with Na_2CO_3 in MeOH under reflux gave the keto-ester (II), $C_{20}H_{24}O_6$, m.p. 175—177°, which was converted into the bromoacetate (IV) *via* $NaBH_4$ reduction into (III), $C_{20}H_{26}O_6$, m.p. 207-210°, followed by acylation.



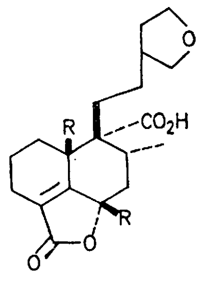
FIGURE



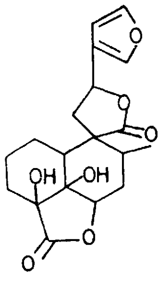
(I) R = H
(XI) R = D



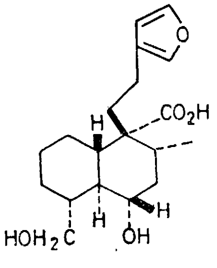
(II) $R^1 = O$; $R^2 = CO_2Me$
(III) $R^1 = \alpha$-OH, β-H; $R^2 = CO_2Me$
(IV) $R^1 = \alpha$-$OCOCH_2Br$, β-H, $R^2 = CO_2Me$
(VIII) $R^1 = \alpha$-OH, β-H; $R^2 = CH_2OH$



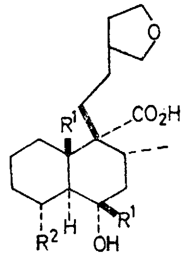
(V) R = H
(XII) R = D



(VI)



(VII)



(IX) $R^1 = H$; $R^2 = CO_2Me$
(X) $R^1 = H$; $R^2 = CH_2OH$
(XIII) $R^1 = D$; $R^2 = CH_2OH$

Single crystals of (IV), $C_{22}H_{27}O_7Br$, m.p. 167—170° (from MeOH–Et_2O), are colourless orthorhombic prisms of space group $P2_12_12_1$, $Z = 4$, $a = 12{\cdot}34$, $b = 29{\cdot}76$, $c = 6{\cdot}12$ Å, $U = 2248$ Å^3, and $D_m = 1{\cdot}408$. The *X*-ray intensity data around the *a* and *c* axes were measured visually from equi-inclination Weissenberg photographs taken with Cu-K_α radiation. The structure was solved by the heavy-atom method and refined by a block-diagonal least squares method to an *R*-factor of 14·0% for 1372 reflections. The absolute configuration of the molecule was determined from the anomalous *X*-ray dispersion effect of Br atoms on the Weissenberg films.[2] A perspective view of the molecular structure along the *c*-axis is shown in the Figure. Thus, the structure and absolute configuration of this bromoacetate were established as (IV).

The bromoacetate (IV) on hydrolysis with Na_2CO_3 in MeOH under reflux and subsequent Jones oxidation regenerated the keto-ester (II) *via* alcohol (III).

Hydrogenation of teucvin over Pd–C gave a hexahydro-derivative (V) showing λ_{max} (MeOH) 224 nm (ϵ 10,300), attributable to the α,β-unsaturated γ-lactone system.[3] Oxidation of teucvin with OsO_4 yielded a diol, $C_{19}H_{22}O_7$, m.p. 183—184°, whose spectroscopic data supported structure (VI). Teucvin was also shown to be positive for the colour reactions[4,5] characteristic of the α,β-unsaturated lactones. Thus, the structure of teucvin is shown as (I) except the configurations at C-6 and C-10.

Teucvin was subjected to the Birch reduction to afford a crystalline diol-carboxylic acid (VII), $C_{19}H_{36}O_5$, m.p. 210—212°, identical with the compound, m.p. 210—212°, derived *via* (VIII) from (III) by $LiAlH_4$ reduction followed by Birch reduction. Since the absolute configurations at C-6 and C-10 of (III) have been established from *X*-ray analysis of its bromoacetate (IV), those at C-6 and C-10 of teucvin are clarified to be *S* and *R*, respectively, unless the Birch reduction inverts their configurations.

Catalytic hydrogenation of compound (III) gave the saturated hydrogenolysis product (IX), which on reduction with $LiAlH_4$ yielded the diol-carboxylic acid (X). Compound (X) was also produced on Birch reduction of (V). Furthermore, teucvin was treated with Na_2CO_3 in refluxing MeOD to give [6,10-^{2}H]-teucvin (XI), $C_{19}H_{18}O_5D_2$, which on treatment with Na_2CO_3 in refluxing MeOH regenerated teucvin. Catalytic hydrogenation of (XI) yielded the carboxylic acid (XII), $C_{19}H_{24}O_5D_2$. Birch reduction of (XII) gave (XIII), $C_{19}H_{30}O_5D_2$, which corresponded to [6,10-^{2}H]-(X). These results confirmed the maintenance of the original configurations at C-6 and C-10 during the Birch reduction.

Thus, the structure and absolute configuration of teucvin were established as (I).

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