CHEMISTRY LETTERS, pp. 141-144, 1972. Published by the Chemical Society of Japan

STRUCTURES OF SECO-IRIDOIDS FROM LIGSTRUM OBTUSIFOLIUM SIEB. ET ZUCC.

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From spectroscopic evidence, the two seco-iridoids ligstroside and 10-hydroxyligstroside, isolated from Ligstrum obtusifolium Sieb. et Zucc., are assigned the structures (I) and (V), respectively.

Recently we reported the structure of syringopicroside, a new bitter glucoside from the leaves of Syringa vulgaris L. (lilac).1) Having been interested in the constituents of L. obtusifolium Sieb. et Zucc., on which lilacs are grafted as scions, we initiated this work.

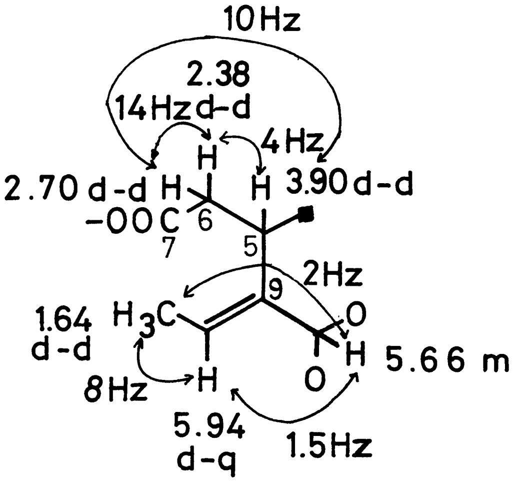
Repeated chromatography of methanol extract of the fresh leaves on silica gel afforded two amorphous glucosides,2) ligstroside (I) and 10-hydroxyligstroside (V). Although many attempts to crystallize these compounds failed, they appeared to be pure on tlc and from the NMR spectra of its derivatives.

Ligstroside (I), $[\alpha]_D$-110.7° (c=1.0, EtOH), gave an amorphous pentaacetate (II), $C_{35}H_{42}O_{17}$ (requires: C 56.67; H 5.68. found: C 57.21; H 5.76%). The spectroscopic data of II indicate the presence of the group $-OOC\overset{|}{C}=CH-O-$ [λmax 218 nm (ε12,700), υmax 1700, 1630 cm^{-1}, $\delta CDCl_3$ 7.42 ppm, s], $CH_3CH=C\langle$ (δ 1.64, d-d, J=8, 2 Hz, 5.94 ppm, d-q, J=8, 1.5 Hz), a carbomethoxy group (δ 3.66 ppm, s), four acetoxy groups (δ 2.00 ppm , 12H, s), and a p-hydroxyphenethyl ester grouping (δ 2.26, 3H, s; 2.86, 4.20 each 2H, t, J=8 Hz; 7.06 ppm, 4H AA'BB' type). The decoupling experiments revealed the presence of the partial structure (III). From the analogy with many other iridoids, the black square in III must be the residue $-(H_3COOC)C=CH-O-CH(OGlu)-$.3) These data seem to be explained in terms of the structure II. Finally this was confirmed by alkaline hydrolysis of I.

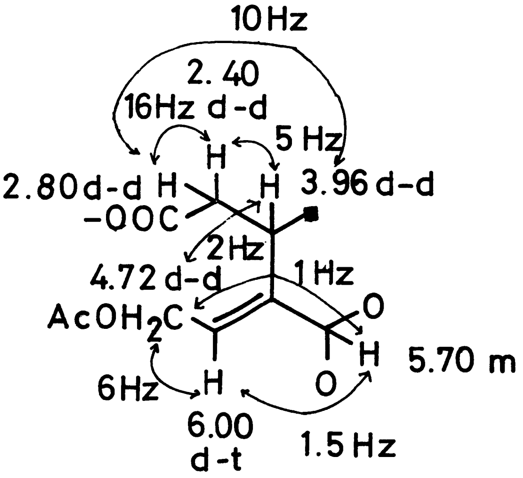
Mild alkaline hydrolysis of I gave p-hydroxyphenethyl alcohol and the residue was methylated and acetylated to give a tetraacetyl dimethyl ester (IV), mp 113-114°, which was identified with the authentic sample.4) Thus confirmed the structure of ligstroside as 3'-deoxyoleuropein (= I).

The other iridoid (V), $[\alpha]_D -156.8^{\circ}$ (c=1.02, EtOH) has similar spectroscopic properties to that of I. On acetylation this gave an amorphous hexaacetate (VI), $C_{37}H_{44}O_{19}\cdot H_2O$ (requires: C 54.71; H 5.72. found: C 54.21; H 5.58%). The spectroscopic data of VI are very similar to that of II except that VI has a group $AcCH_2CH{=}C\lessdot$ (δ 4.70, 2H, d-d, J=6, 4 Hz; 5.95 ppm, 1H, t, J=6 Hz) instead of a group $CH_3CH{=}C\lessdot$. [λmax 220 (ε10,600), 270 nm (ε830); νmax 1730, 1630, 1500 and 850 cm^{-1}; δ 2.04, 15H, s, 5OAc; 2.28, 3H, s, arom-OAc; 3.07, 3H, s, $COOCH_3$; 2.88, 4.22, each 2H, t, J=8 Hz; 5.68, 1H, s, H_1; 7.10, 4H, AA'BB' type aromatic protons; 7.44 ppm, 1H, s, H_3].

Mild alkaline hydrolysis of V gave p-hydroxyphenethyl alcohol and the residue was methylated and acetylated to give an amorphous pentaacetyl dimethylester (VII), $C_{28}H_{36}O_{17}\cdot H_2O$ (requires: C 50.75; H 5.78. found: C 50.77; H 5.62%), νmax 1750, 1700 and 1600 cm^{-1}, NMR (Fig. I). The decoupling experiments showed the presence of the grouping (VIII). When the protons at C_{10} was irradiated, there was observed NOE enhancement in the integrated area of H_5 proton. Thus confirmed the geometry of the double bond at C_9. From these data the structure V may be assigned for the second iridoid (= 10-hydroxyligstroside).



III



VIII

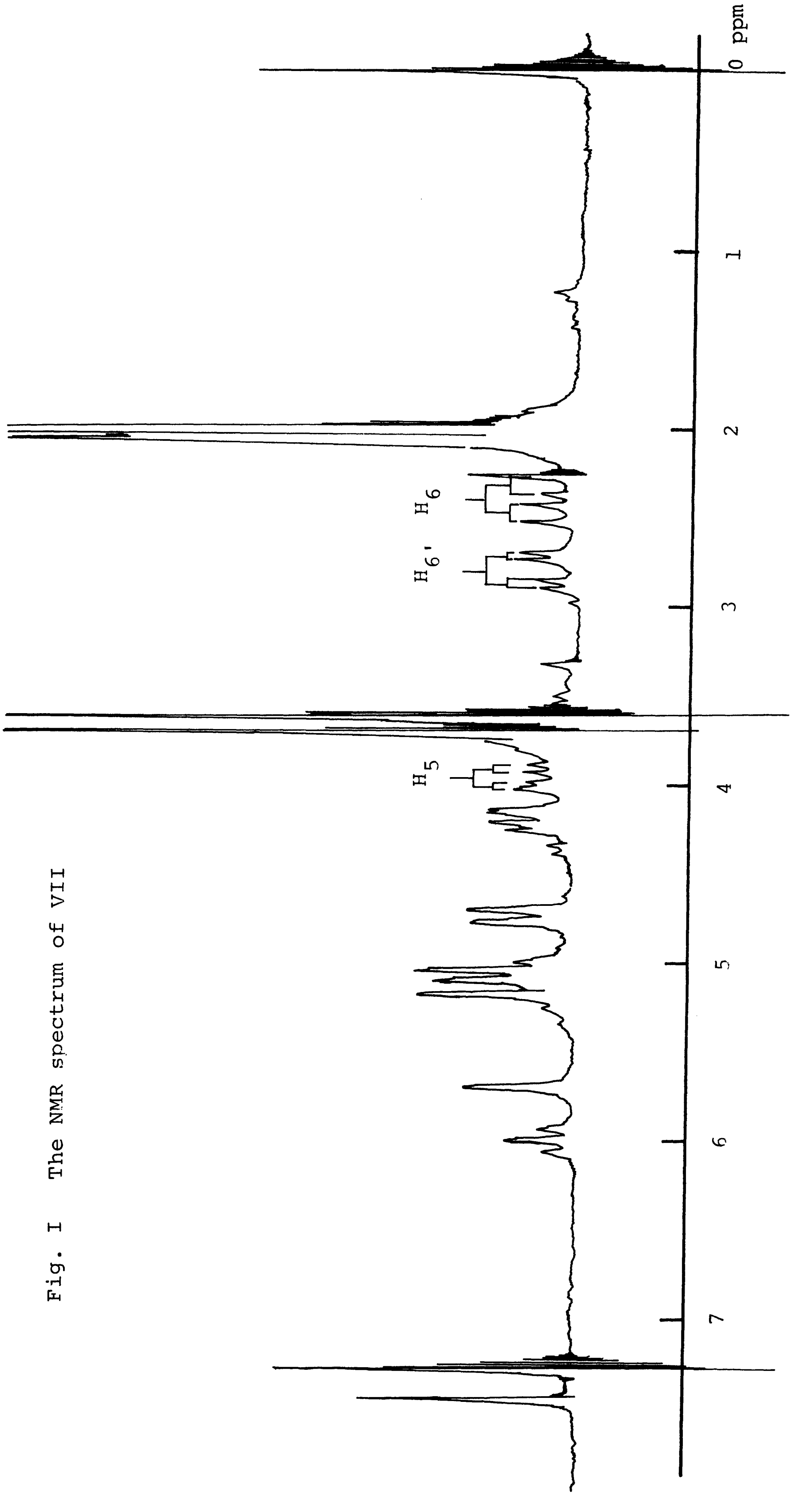
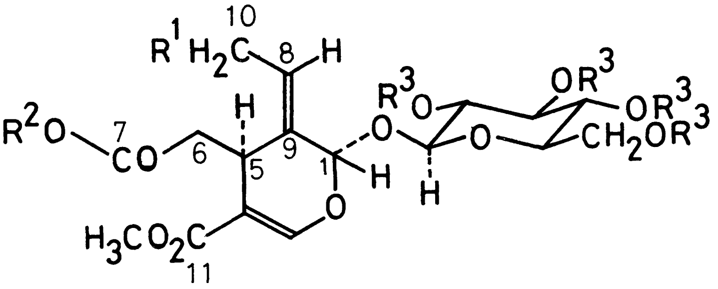


Fig. I The NMR spectrum of VII



(I) $R^1=R^3=H$; $R^2=-CH_2CH_2C_6H_4OH(p)$

(II) $R^1=H$; $R^2=-CH_2CH_2C_6H_4OAc(p)$; $R^3=Ac$

(IV) $R^1=H$; $R^2=CH_3$; $R^3=Ac$

(V) $R^1=OH$; $R^2=-CH_2CH_2C_6H_4OH(p)$; $R^3=H$

(VI) $R^1=OAc$; $R^2=-CH_2CH_2C_6H_4OAc(p)$; $R^3=Ac$

(VII) $R^1=OAc$; $R^2=CH_3$; $R^3=Ac$

References

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(Received December 11, 1971)