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THE STRUCTURE OF ISOSERICENINE, THE METHYL ESTER OF A NEW ELEMANE TYPE SESQUITERPENE ACID ISOLATED FROM NEOLITSEA SERICEA KOIDZ.

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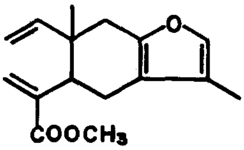
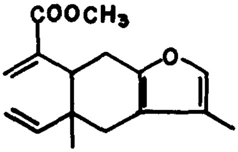
From the essential oil which was obtained from leaves of *Neolitsea sericea Koidz.*, Japanese name Shirodamo by steam distillation, the methyl ester of a new elemane-type sesquiterpene acid containing a furan ring was isolated, and its structure was determined as the formula I.

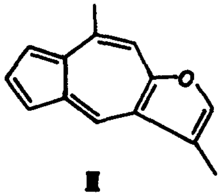
We propose the name isosericenine for this methyl ester, and here describe the evidence for the proposed structure.



I



II



III

The ester was isolated as an oily matter, b.p. 139°C/5 mm., n_D^{25} 1.5250 and $[\alpha]_D^{25}$ 0°, by fractional distillation and then elution chromatography. The fresh sample showed only one peak on gas chromatography (NGS, DEGS and Golay SE-30). This compound was very susceptible to autoxidation in contact with air.

The molecular formula of this compound is $C_{16}H_{20}O_3$ from the observation of the M^+ ion at m/e 260.140 (calcd., 260.141) in a high resolution mass spectrum, and the molecule contains a β-methyl furan ring, vinyl and tertiary methyl groups, and a terminal double bond attached to a methoxy carbonyl group.

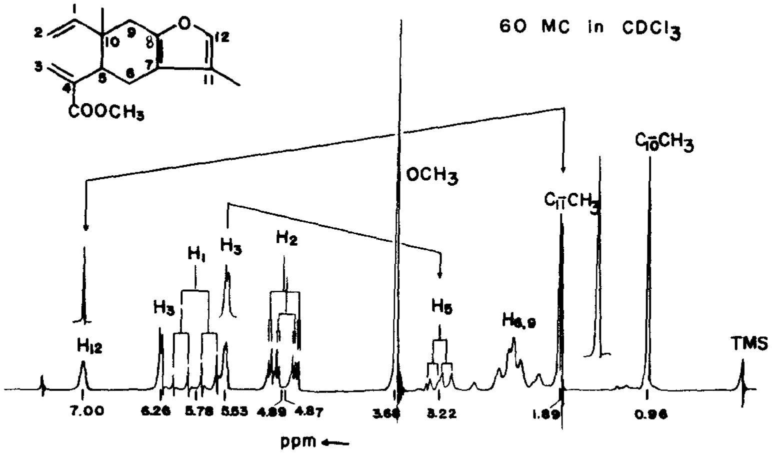
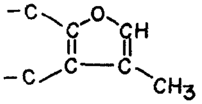
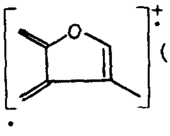
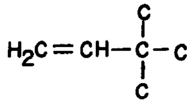


Fig. 1. NMR spectrum of isosericenine

This compound having absorption bands at 1551 and 1508 cm^{-1}, and λ_{max}^{EtOH} 209 mμ (ε 16000), showed a positive color reaction for the Ehrlich and Liebermann-Burchard tests, and produced a maleic anhydride adduct, m.p. 149 - 150°C. These facts suggest a furan system, and the NMR and mass spectra indicated more exactly the existence of a partial structure  : a methyl signal at 1.89 ppm (3H, d, J= 1.1 cps) and an aromatic proton at 7.00 ppm (1H, q, J= 1.1 cps) could be respectively assigned to a β-methyl substituent and an α-proton in the β-methyl furan system(1) by a double resonance experiment. The base ion of m/e 108.058 was attributed to the definitely characterized one,  (calcd., 108.058), in mass spectra of menthofuran(2) and alexandrofuran(3).

When the ester was hydrogenated over Adams catalyst in acetic acid, it absorbed hydrogen equivalent to two moles to produce tetrahydroisosericenine leaving the furan system completely intact (a positive color reaction). Five protons were found in the olefin region of the NMR spectrum of the original ester. Of these, three quartets (δ_A 4.87, δ_B 4.89 and δ_X 5.78 ppm, respectively 1H, J_{AB}= 1.7, J_{AX}= 10.0 and J_{BX}= 17.5 cps) were assigned to three vinyl protons of ABX type, and further the splitting pattern of the δ_X quartet indicates that a carbon atom adjacent to the vinyl double bond is quarternary$^{(4)}$; the existence of a partial structure



$H_2C{=}CH{-}\overset{C}{\underset{C}{C}}{-}C$ is sure. The other olefin signals at 5.53 (1H, m) and 6.26 ppm (1H, d, J= 1.2 cps) could be assigned to the methylene protons in a terminal double bond, which is jointed to a methoxy carbonyl group in a conjugated system as described below.

The ester exhibited absorption at 1133, 1245 and 1718 cm^{-1}, the last of which was shifted to 1736 cm^{-1} on catalytic hydrogenation. The saponification of the ester gave an acid of M^+ 246, which turned to the original ester by methylation with diazomethane. Hence, isosericenine is a methyl ester of α,β-unsaturated acid containing a terminal double bond.

An additional tertiary methyl group was seen on a singlet of 0.96 ppm (3H) and a $(M - CH_3)^+$ ion, m/e 245.

The above partial structures and the molecular formula give two possible formulae I and II. Isosericenine, however, is represented by the formula I, because its selenium dehydrogenation produced ujacazulene III in a good yield, which was identified by mass, UV and visible spectra.

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References

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