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SERICEALACTONE AND DEOXYSERICEALACTONE, METHYL ESTERS OF SESQUITERPENE ACIDS FROM NEOLITSEA SERICEA KOIDZ.

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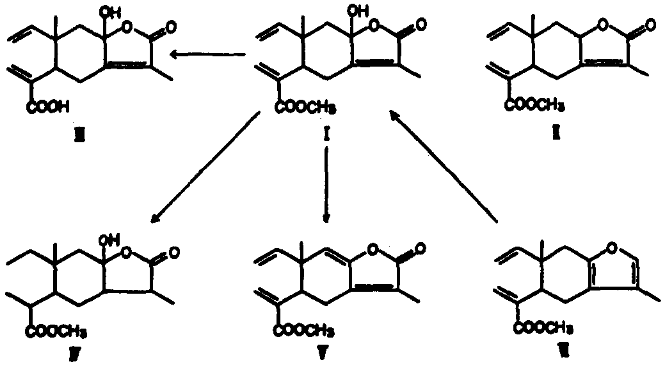
In addition to isosericenine (VI) which is the methyl ester of a new sesquiterpene acid reported in the previous communication[1)], two methyl esters of another elemane-type sesquiterpene acid containing a γ-hydroxy-α,β-butenolide system, and of its deoxy ester were isolated from an essential oil which was obtained from leaves of Neolitsea sericea Koidz.(Shirodamo in Japanese) by steam distillation, and those structures were determined as formulae I and II. We proposed the names sericealactone and deoxysericealactone for I and II respectively, and here present the evidence for the structure assignment.

A white crystalline mass isolated from a fraction, b.p. 139 - 148°C/5mmHg, of the essential oil by allowing to stand at a room temperature was separated into sericealactone, sparingly soluble needles of m.p. 150 - 151°C (the major constituent of the above fraction), and deoxysericealactone, easily soluble needles, m.p. 137°C (the minor constituent), by recrystallization from carbon tetrachloride.



Sericealactone (m.p. 150 - 151°C). This compound has the molecular formula of $C_{16}H_{20}O_5$ upon elementary analysis, molecular weight determination by the Rast method and appearance of a high intensity $(M - 18)^+$ ion in the mass spectrum, which did not have the parent ion. The NMR spectrum (Fig. 1) has a remarkable resemblance to that of isosericenine (VI), and by comparison with both the spectra the existence of the following several functional groups were deduced: an angular methyl group (1.18 ppm, s, 3H), a ABX type vinyl group attached to a tertiary carbon atom (δ_A 4.85, δ_B 4.87 and δ_X 5.60 ppm. J_{AX}= 17.5, J_{BX}= 9.5 and J_{AB}= 1.2 cps. 3H. $\nu^{CCl_4}_{max}$ 914, 995, 1641 and 3097 cm^{-1}), methine and methylene groups (1.50 - 2.90 ppm, m, 5H), a methyl group on a double bond (1.80 ppm, s, 3H) and methoxy carbonyl group (3.67 ppm, s, 3H; $\nu^{CCl_4}_{max}$ 1132 and 1712 cm^{-1}) conjugated with a terminal methylene group (5.54 and 6.28 ppm, each nearly singlet and 1H).

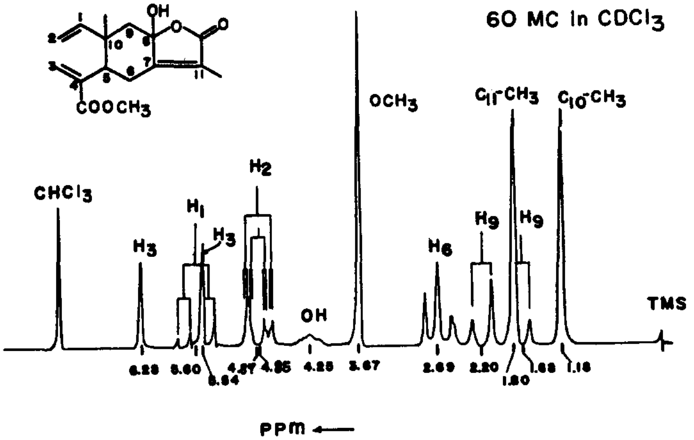


Fig. 1. NMR spectrum of sericealactone

In addition to these groups, sericealactone still contained a hydroxy group and an α,β-unsaturated γ-lactone system, which did not appear in the molecule of isosericenine; the hydroxyl group was indicated by the absorption band of $\nu^{CCl_4}_{max}$ 3310 cm^{-1} and the broad signal at 4.25 ppm, which was eliminated on the measurement using the deutelium exchange technique, and it was recognized as tertiary because of the absence of a carbinol proton in the neighborhood of ca. 4 ppm. The α,β-unsaturated γ-lactone system was shown by λ^{EtOH}_{max} 217 mμ(ε10,200) and $\nu^{CCl_4}_{max}$ 1736 cm^{-1} which was shifted to $\nu^{CCl_4}_{max}$ 1769 cm^{-1} after catalytic hydrogenation. Moreover, the absorption band of λ^{EtOH}_{max} 217 mμ was shifted to λ^{KOH}_{max} 262 mμ(ε6,670) in a methanolic potassium hydroxide solution. This shift of the absorption maximum indicates that the tertiary hydroxyl group and the α,β-unsaturated γ-lactone system mentioned above constitute a hemiketal lactone having a γ-hydroxyl-α,β-butenolide system[2].

On the other hand, sericealactone was confirmed to be identical with an autoxydation product of isosericenine (IR and NMR). This product was obtained, in a good yield (75%), by saking the benzene solution together with Adams catalyst in contact with oxygen.

The preceding spectrometric and chemical evidence, thus, indicates sericealactone to be represented by the structural formula I. The saponification of this compound produced a solid acid (formula III) of $C_{15}H_{18}O_5$ (elementary analysis, M^+ 260), the catalytic hydrogenation by using Adams catalyst in acetic acid consumed three molar equivalent of hydrogen to produce a saturated ester (formula IV): 1736 ($-COOCH_3$), 1769 (γ-lactone) and 3500 cm^{-1}(-OH), and the dehydation with thionylchloride produced an anhydro compound(formula V): M^+ 274, 968 (C=C) and 1743 cm^{-1}(α,β-butenoilde).

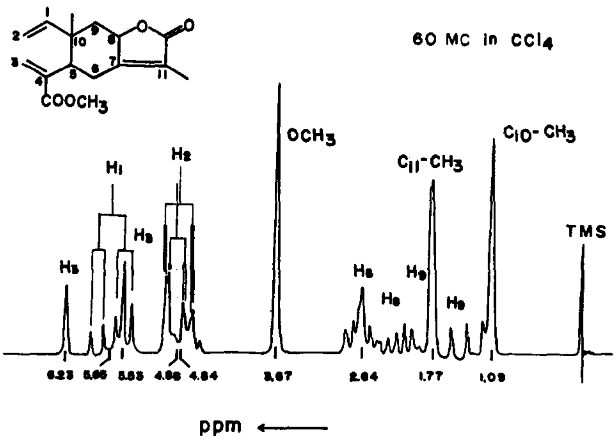


Fig. 2. NMR spectrum of deoxysericealactone

Deoxysericealactone, m.p. 137°C. Although the NMR spectrum of this compound (Fig. 2) did not have a hydroxyl signal (no change by deuteration), it could be almost closely superposed on that of sericealactone excepting the methylene and methine proton region, in which integral strength of the proton signals corresponds to 6H in contrast to 5H in the case of sericealactone. The mass spectrum exhibited the parent ion at m/e 276 which is smaller by 16 mass units than the molecular weight of sericealactone.

Hence, this compound is certain to have the molecular formula of $C_{16}H_{20}O_4$, and its structure should be represented by the formula II as the deoxy compound of sericealactone.

The authors are indepted to Professor Shô Itô of Tohoku University for his measurement of the NMR spectra.

References

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2. R. B. Woodward and R. H. Eastman, J. Am. Chem. Soc., **72**, 399 (1950).