

THE STRUCTURE OF SERICENINE AND SERICENIC ACID, THE  
NEW GERMACRANE TYPE SESQUITERPENOID, ISOLATED FROM  
NEOLITSEA SERICEA KOIDZ.

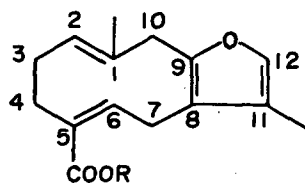
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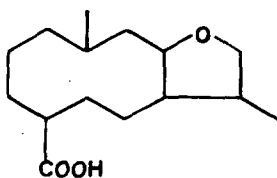
(Received in Japan 1 August 1968; received in UK for publication 27 August 1968)

In continuation of our study<sup>1)</sup> on furan-ring-containing sesquiterpenoids of the essential oil of Neolitsea sericea Koidz., a methyl ester of a new germacrane-type sesquiterpenoid containing a furan ring, which is thought to be a precursor of the furan-ring-containing sesquiterpenoids reported previously, and its free acid were isolated from ether extract of the leaves of the same plant. We wish to propose the names, sericenine (I) and sericenic acid (II), for these compounds respectively, and here to present the evidences for the proposed structure.

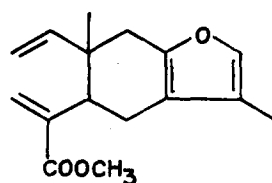


I R = CH<sub>3</sub>

II R = H



III



IV

A neutral portion of the extract, from which an acid portion was removed by treating it with 3% aqueous solution of sodium bicarbonate was chromatographed over a silica gel column by using n-hexane to collect a fraction exhibiting positive reaction for Ehrlich and Liebermann-Burchard color tests. The fraction was purified through thin layer chromatography, and sericenine was obtained as white needles, m.p. 115°C,  $[\alpha]_D^{20}$  0° (in EtOH).  $\lambda_{\max}^{\text{EtOH}}$  217  $\mu$  ( $\epsilon$  8840) and 209  $\mu$  ( $\epsilon$  8800).

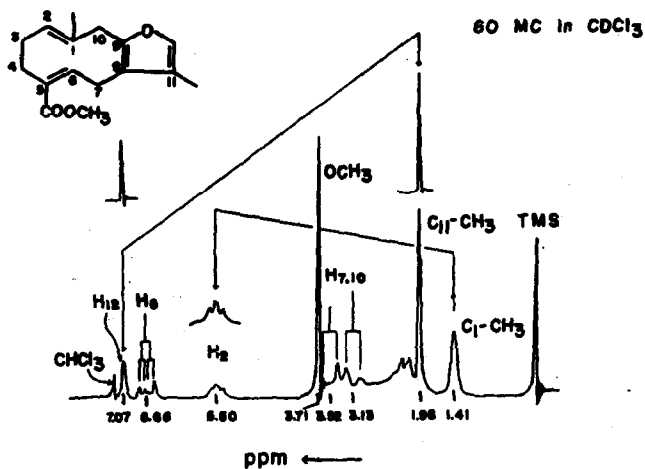


Fig. 1 NMR spectrum of sericenine

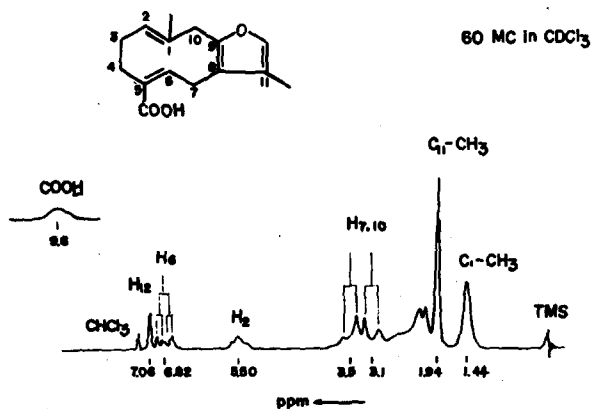



Fig. 2 NMR spectrum of sericenic acid

$\nu_{\text{max}}^{\text{KBr}}$  1550, 1706 and 3120  $\text{cm}^{-1}$ .  $m/e$  260 ( $M^+$ ).

The acid portion of the extract regenerated from the bicarbonate solution was also purified through elution chromatography and a small amount of sericenic acid was isolated as white powder, m.p. 203°C.  $[\alpha]_D^{20}$  0° (in EtOH).  $\nu_{\text{max}}^{\text{KBr}}$  1555, 1682, 2680, 3350  $\text{cm}^{-1}$ .  $m/e$  246 ( $M^+$ ).

Sericenine has a molecular formula of  $C_{16}H_{20}O_3$ . Its absorption bands,  $\nu_{\text{max}}^{\text{KBr}}$  1550 and 3120  $\text{cm}^{-1}$ , and absorption maximum,  $\lambda_{\text{max}}^{\text{EtOH}}$  207  $m\mu$  ( $\epsilon$  8800), together with the positive reaction in Ehrlich and Liebermann-Burchard color tests indicate the presence of a furan ring. The mass spectrum showed only one abundant peak at  $m/e$  108 which is attributed to an ion . Thus, it is certain sericenine has such a furan ring structure as in isosericenine.<sup>1)</sup>

The presence of characteristic peaks,  $m/e$  229 and 201, attributed to ( $M - OCH_3$ ) and ( $M - COOCH_3$ )<sup>+</sup> ions indicates sericenine to be a methyl ester. When the compound was refluxed with alcoholic potash, in fact, it produced an acid,  $C_{15}H_{18}O_3$ , showing  $\nu_{\text{max}}^{\text{KBr}}$  3350, 2680, 1682, 1555  $\text{cm}^{-1}$  and an acidic reaction against BCG indicator. This acid was identical with sericenic acid in spectrometry and the melting point, and returned to original sericenine by methylation with diazomethane. Sericenine was, hence, ascertained to be methyl ester of sericenic acid.

Sericenic acid took up 4 molar equivalent of hydrogen in the catalytic hydrogenation using Adams' catalyst in acetic acid and produced octahydro-acid, m.p. 162 - 163°C,  $m/e$  254 ( $M^+$ ), which was confirmed to be identical with a hydrogenolysis product (III), m.p. 164°C, of linderalactone<sup>2)</sup> by the admixing. On the other hand, sericenine was converted into isosericenine (IV)<sup>1)</sup> in good yield by heating it at 160 - 170°C for 15 min. under nitrogen atmosphere. These chemical evidences propose a germacrane skeleton for sericenine and sericenic acid. Namely these compounds consist of ten carbon-membered ring system carrying a methyl group on C-1 and the carboxyl group on C-5, and containing two double bonds.

In the NMR spectra of these compounds, the proton signal due to the methyl group held on C-1 was observed at 1.44 or 1.41 ppm (3H, s), which indicate the methyl group to be attached to a double bond. However, there is no evidence for the conjugation of the double bond with the furan ring. Accordingly, the double bond can be located between C-1 and C-2, the position of which is also supported by the fact that proton signals attributed to the C-10 methylene group appeared as a AB typ

broad quadruplet centered at 3.13 and 3.52 ppm (4H,  $J = 15$  cps, more clear in sericenic acid ) in overlapping with the proton signals of the C-7 methylene.

The absorption band,  $1706\text{ cm}^{-1}$ , in sericenine owing to the methoxy carbonyl group was shifted to  $1736\text{ cm}^{-1}$  by the catalytic hydrogenation, and the absorption maximum of sericenine,  $\lambda_{\text{max}}^{\text{EtOH}}$  217  $\mu$ , is in good agreement with a calculated value<sup>3)</sup> for the methyl ester of disubstituted  $\alpha,\beta$ -unsaturated acid (217  $\mu$ ). From these facts, it is certain that the carbonyl group held on C-5 also is attached to a double bond. Thus, the other double bond was restricted at C-4,5 or C-5,6 position. If the double bond locates at C-5,6 position, a AB type quadruplet may be expected for the proton signal of the C-7 methylene group. This expectation was satisfied by the fact that its methylene signal overlapped in the same chemical shift (3.13 and 3.52 ppm) as that of the C-10 methylene group, because C-7 and C-10 methylene groups come to the same circumstance.

These compounds were concluded to be 8,12-oxogermacra-1,4,7,11-tetraene-14-carboxylic acid and its methyl ester, the structures of which were reasonably supported by NMR spectra as seen in Fig. 1 and Fig. 2.

Irradiation of C-1 methyl protons in sericenine increased the integration of the signal of the C-6 proton by 24%. Such intramolecular nuclear Overhauser effect indicates that the C-6 proton is close to the C-1 methyl group.

#### References

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