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**Structures of Fischeric Acid & Isofischeric Acid,  
Two New Sesquiterpenes from  
*Neolitsea fischeri*\***

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From the roots of *Neolitsea fischeri* Gamble two new isomeric sesquiterpenes designated as fischeric acid (I) and isofischeric acid (II) have been isolated. These belong to the germacrane and elemene types of furano terpenes and their structures have been deduced on the basis of spectroscopic and degradative evidences. Fischeric acid (I) undergoes Cope rearrangement to give isofischeric acid (II).

IN continuation of our studies on the constituents of *Neolitsea* species<sup>1</sup>, we wish to report on the structures of two new furano sesquiterpenes isolated from the roots of *Neolitsea fischeri* Gamble. Fischeric acid (I), C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>, m.p. 158°, M<sup>+</sup> at *m/e* 246, λ<sub>max</sub> 212 nm (log ε 4.2), ν<sub>max</sub><sup>nujol</sup> 1690 and 1660 cm<sup>-1</sup>, and isofischeric acid (II), C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>, m.p. 120°, M<sup>+</sup> at *m/e* 246, [α]<sub>D</sub> 0°, ν<sub>max</sub><sup>nujol</sup> 1700 cm<sup>-1</sup>, were isolated

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from the hexane extract of the roots by chromatography on silica gel†.

Both the compounds are soluble in aq. NaHCO<sub>3</sub> and show positive Ehrlich test<sup>2</sup>. The presence of a β-methylfuran ring could be inferred from the NMR and mass spectra. The gross structures of fischeric acid and isofischeric acid are evident from their NMR spectra (Table 1) and the mass spectral fragmentations.

Fischeric acid on hydrogenation over PtO<sub>2</sub> in acetic acid gave an octahydro acid (III), m.p. 163°, identical with the acid obtained by the hydrogenolysis of linderolactone<sup>3</sup>. Treatment of (I) with diazomethane afforded a pyrazoline, m.p. 117-18°, to which we assign the structure (IV), on the basis of the available spectral data.

Isofischeric acid (II) on hydrogenation gave an octahydro acid, m.p. 107-8°, formulated as (V). It also formed a pyrazoline when treated with diazomethane.

From the essential oil of the leaves of *Neolitsea sericea* Koidz., Hayashi *et al.* have isolated the sesquiterpenes sericenine (VI)<sup>4,5</sup>, sericenic acid (VII)<sup>4,5</sup> and isocericenine (VIII)<sup>6</sup>. Since fischeric acid (I) differs in its physical and spectral properties from VII, it is apparently a geometrical isomer of sericenic acid. The carboxyl and the hydrogen on

†Satisfactory elementary analyses were obtained for all new compounds.

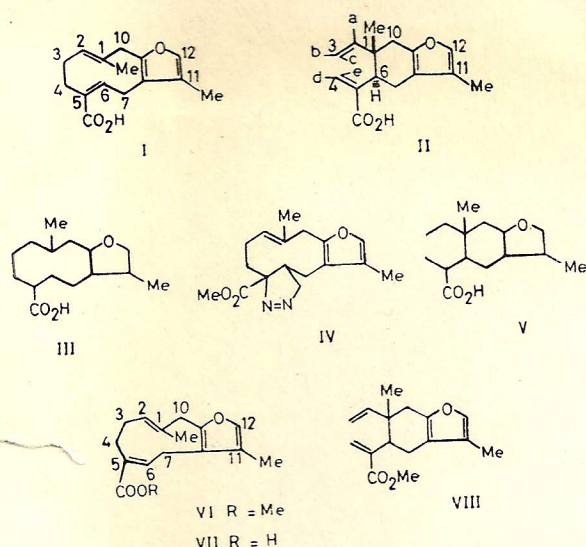


TABLE 1 — NMR SPECTRAL DATA OF FISCHERIC AND ISOFISCHERIC ACIDS

 [NMR spectra (CDCl<sub>3</sub>; 60 MHz) were taken with TMS as internal reference]

$\delta$ (ppm)	No. of protons	Multiplicity ( $J=Hz$ )	Proton assignment
FISCHERIC ACID (I)			
1.25	3	<i>d</i> (1)	C-1, CH <sub>3</sub>
1.95	3	<i>d</i> (1)	C-11, CH <sub>3</sub>
2.1-3.3	4	<i>m</i>	C-3, C-4, CH <sub>2</sub>
3.9	2	<i>q</i> (3; 11)	C-7, CH <sub>2</sub>
3.5	2	<i>s</i>	C-10, CH <sub>2</sub>
5.15	1	<i>t</i> (7.5)	C-2
5.7	1	<i>q</i> (3; 11)	C-6
7.1	1	<i>d</i> (1)	C-12
10.4	1	<i>s</i>	C-5, COOH
ISOFISCHERIC ACID (II)			
1.0	3	<i>s</i>	C-1, CH <sub>3</sub>
1.91	3	<i>d</i> (1.1)	C-11, CH <sub>3</sub>
2.2-2.9	4	<i>m</i>	C-7, C-10, CH <sub>2</sub>
3.2	1	<i>q</i> (6, 8)	C-6
4.91	1	<i>q</i> (1.1, 10)	C-3, (b)
4.92	1	<i>q</i> (1.1, 18)	C-3, (c)
5.66	1	<i>s</i> (W <sub>3</sub> ; 2.5)	C-4, (d)
6.45	1	<i>s</i> (W <sub>3</sub> ; 2.5)	C-4, (e)
5.84	1	<i>q</i> (10, 18)	C-2, (a)
7.05	1	<i>d</i> (1.1)	C-12
11.2	1	<i>s</i>	C-5, COOH

the 5,6-double bond in VI and VII have been shown to be in *cis* relationship to each other<sup>7</sup>. The vinyl methyl signal on C-1 in fischeric acid shows an abnormal upfield shift at  $\delta$  1.25 as in the case of

linderalactone<sup>8</sup>, furanodiene<sup>9</sup> and tamaulipin-A<sup>10,11</sup> which are derivatives of *trans-trans*-cyclodeca-1,5-diene, due to the shielding of the protons of the vinyl methyl on a *trans* double bond by the  $\pi$ -electrons of the 5,6-double bond<sup>1,12,13</sup>. In the case of neolinderalactone where the C-1 methyl is *cis* to the C-2 hydrogen<sup>14</sup>, the C-1 methyl shows the NMR signal at  $\delta$  1.6 and the compound does not undergo Cope rearrangement<sup>15</sup>. It is thus reasonable to assume that fischeric acid (I) is a geometrical isomer of sericenic acid (VII) where the configuration of the 5,6-double bond is reversed.

Fischeric acid (I) when heated at 230° underwent Cope rearrangement to give the starting material and isofischeric acid (II). On the assumption that the geometry of the double bonds in (I) is *trans-trans*, the rearrangement product (II) should be the *trans*-1,2-divinyl compound of the elemene type<sup>16-18</sup>.

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