

temp. The syrup obtained by the usual work-up was dissolved in Me<sub>2</sub>CO and treated with Jones reagent. To the Et<sub>2</sub>O extract of the reaction mixture was added an excess of CH<sub>2</sub>N<sub>2</sub>-Et<sub>2</sub>O and the mixture then concd. This product was then subjected to GC/MS using an OV-1 column.

The methyl ester mixtures obtained from **2** and **3** were treated as above to give samples for GC/MS analysis.

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## STRUCTURE OF (+)-RANGIFORMIC ACID\*

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**Key Word Index**—*Cladonia rangiformis*; Cladoniaceae; lichen; (+)-rangiformic acid; (+)-3S-methoxycarbonylheptadecane-1,2S-dicarboxylic acid.

**Abstract**—(+)-Rangiformic acid from the lichen *Cladonia rangiformis* has been shown to be (+)-3S-methoxycarbonylheptadecane-1,2S-dicarboxylic acid by an NMR selective decoupling experiment with (–)-rangiformic anhydride.

One hundred years ago Paterno [1] isolated an aliphatic compound which he named (+)-rangiformic acid from the lichen *Cladonia rangiformis*. The structure and stereochemistry of its demethylation product, (+)-nor-rangiformic acid, was later elucidated as heptadecane-1,2S,3S-tricarboxylic acid by Asahina and Sasaki [2] and Akermark [3], respectively.

Now we have localized the methyl ester group in (+)-rangiformic acid (**1**) at position 3 by <sup>13</sup>C NMR spectroscopy. (+)-Rangiformic acid gave (–)-rangiformic anhydride (**2**) on heating with acetyl chloride. The IR spectrum of **2** showed, besides the carbonyl band of the methyl ester group (1704 cm<sup>–1</sup>), two strong bands at 1770 and 1844 cm<sup>–1</sup> (Δ CO 74 cm<sup>–1</sup>), indicative of a five-membered anhydride [4]. To differentiate between the two possible structures **2** and **3**, we performed a <sup>13</sup>C NMR double-resonance experiment with **2**. On selective decoupling at the resonance of the –CO<sub>2</sub> Me protons with varying decoupling power, the originally complex signal of the –CO<sub>2</sub> Me carbonyl group at δ 170.66 was

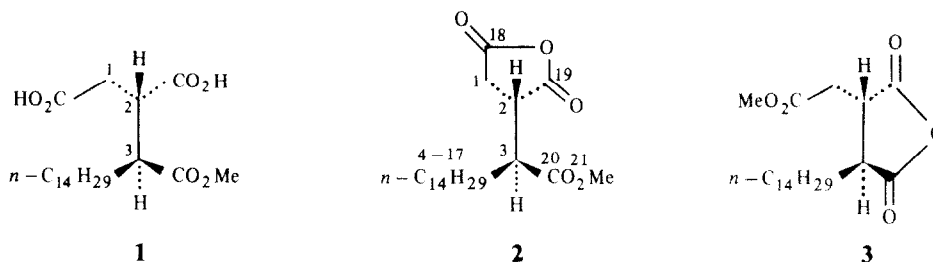
simplified to a doublet, thus proving structure **2**. Hence, (+)-rangiformic acid is (+)-3S-methoxycarbonylheptadecane-1,2S-dicarboxylic acid (**1**).

## EXPERIMENTAL

(+)-Rangiformic acid (**1**). **1** was obtained by extraction from *C. rangiformis* Hoffm., collected near Varna/Bulgaria in September 1981. Needles, mp 102–104° (MeOH–H<sub>2</sub>O) and [α]<sub>D</sub><sup>24</sup> + 14.2° (EtOH). IR ν<sub>max</sub><sup>KBr</sup> cm<sup>–1</sup>: 714, 726, 842, 900, 966, 1006, 1120, 1170, 1210, 1270, 1372, 1410, 1438, 1468, 1688, 1722, 2940, 3200. MS *m/z* (rel. int.): 368 [M – H<sub>2</sub>O]<sup>+</sup> (24), 350 (14), 336 (27), 322 (70), 308 (35), 290 (51), 280 (32), 264 (35), 228 (35), 214 (66), 210 (45), 200 (68), 196 (73), 182 (100), 168 (86), 154 (86), 140 (70), 132 (41), 126 (70), 112 (61), 98 (84), 84 (66).

(–)-Rangiformic anhydride (**2**). Heating **1** (0.2 g) with AcCl (20 ml) under reflux (2 hr), removal of excess AcCl (in vacuo) and crystallization of the residue from *n*-pentane gave **2** as plates, mp 50–51° and [α]<sub>D</sub><sup>24</sup> – 48.1° (CHCl<sub>3</sub>; *c* 1.175); C<sub>21</sub>H<sub>36</sub>O<sub>5</sub> (368.50). IR ν<sub>max</sub><sup>KBr</sup> cm<sup>–1</sup>: 712, 748, 884, 918, 968, 978, 1030, 1044, 1094, 1110, 1150, 1220, 1248, 1320, 1364, 1438, 1464, 1704 (–CO<sub>2</sub> Me), 1770, 1844 (anhydride-CO), 2860, 2940. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.86 (3H, *t*-Me), 1.22 (24H, *br s*, –(CH<sub>2</sub>)<sub>12</sub>–), 2.30–2.90 (4H, *m*, 2 × –CH<sub>2</sub>–), 2.73, 2.74, 2.77, 2.78 (1H, 2 × *d*, C-1-H), 2.90–2.99 (2H, *m*, C-2-H, C-3-H), 2.99, 3.00, 3.03, 3.05 (1H, 2 × *d*, C-1-H), 3.70 (3H, *s*, –CO<sub>2</sub> Me). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>): C-1: δ 33.59; C-2: 45.44; C-3: 42.41; C-

\*Part 139 in the series "Lichen Substances". For Part 138 see Huneck, S., Poelt, J., Ahti, T., Vitikainen, O. and Cogt, U., *Biol. Ressourcen Mongolischen Volksrepublik* (in press).



4-C-14: 26.50–30.37; C-15: 31.90; C-16: 22.65; C-17: 14.05; C-18: 172.39\*; C-19: 172.32\*; C-20: 170.66; C-21: 52.40 (values marked with \* can be exchanged). MS  $m/z$  (rel. int.): 368  $[M]^+$  (7), 350 (5), 337 (7), 322 (18), 308 (9), 294 (9), 290 (16), 223 (9), 214 (11), 210 (11), 200 (11), 196 (29), 182 (39), 168 (25), 154 (23), 140 (18), 126 (16), 109 (20), 95 (32), 81 (39), 74 (27), 69 (50), 55 (82), 43 (100). ORD (MeOH):  $[\alpha]_{350} - 975^\circ$ ,  $[\alpha]_{300} - 1544^\circ$ ,  $[\alpha]_{250} - 3577^\circ$ ,  $[\alpha]_{244} - 4146^\circ$ ,  $[\alpha]_{230} - 1382^\circ$ .

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## A FURTHER BITHIENYL DERIVATIVE FROM *BERKHEYA ZEYHERI*

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**Key Word Index**—*Berkheya zeyheri*; Compositae; thiophene derivative; acetylenic compound.

**Abstract**—The roots of *Berkheya zeyheri* afforded 2-acetoxymethyl-5-[but-1-in-1-yl]-bithienyl-(2'.5) while the aerial parts gave onopordopicrin.

In continuation of our investigations of representatives of the large genus *Berkheya* (Compositae tribe Arctothaeae) [1] we have studied the constituents of *B. zeyheri* (Sond. et Harv.) Oliv. et Hiern. subsp. *zeyheri*. The roots afforded lupeol and its  $\Delta^{12}$  isomer, taraxasterol, 2-[thienyl(2)-ethinyl]-5-[prop-1-in-1-yl]-thiophen [2], the bithienyl derivatives **1** [3] and its dihydro derivative **2**. The structure of the latter followed from the molecular formula and the  $^1\text{H}$  NMR spectrum (Table 1). In deuteriobenzene all signals of the thiophene protons could be assigned while these were overlapping in deuteriochloroform. The nature of the end groups could easily be deduced from the characteristic  $^1\text{H}$  NMR signals while the relative position of these groups could be assigned by comparing the chemical shifts of the  $\text{CH}_2\text{OAc}$  signal with that of similar compounds which showed that the magnitude of the deshielding effect of a thiophene ring is larger

Table 1.  $^1\text{H}$  NMR spectral data of compound **2** (400 MHz, TMS as internal standard)

	$\text{CDCl}_3$	$\text{C}_6\text{D}_6$
H-1	1.29 <i>t</i>	0.97 <i>t</i>
H-2	2.46 <i>q</i>	2.13 <i>q</i>
H-6	7.00 <i>m</i>	6.62 <i>d</i>
H-7		6.73 <i>d</i>
H-10		6.74 <i>br d</i>
H-11		6.93 <i>br d</i>
H-13	5.21 <i>br s</i>	4.96 <i>br s</i>
OAc	2.12 <i>s</i>	1.64 <i>s</i>

$J$  (Hz): 1, 2 = 7; 6, 7 = 10, 11 = 3.5; 10, 13 = 11, 13 ~ 0.5.