

(+)-ISORANGIFORMIC ACID, A LICHEN SUBSTANCE FROM *LECANORA STENOTROPA**

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Key Word Index—*Lecanora stenotropa*; Lecanoraceae; lichen; (+)-isorangiformic acid; (+)-2S-methoxycarbonyl-3S-heptadecanedicarboxylic acid.

Abstract—(+)-Isorangiformic acid from the lichen *Lecanora stenotropa* has been shown to be (+)-2S-methoxycarbonyl-3S-heptadecanedicarboxylic acid.

In continuation of our work on the chemistry of lichens the crustose species *Lecanora stenotropa* Nyl. which is related to *L. polytropia* (Ehrh.) Rabenh. has now been investigated. *L. stenotropa* is a characteristic plant of copper slate near Eisleben and contains (+)-isorangiformic acid, (+)-usnic acid, (+)-sodium usneate and zeorin.

(+)-Isorangiformic acid (**1**) (needles, mp 83–85°, $[\alpha]_D^{24} + 5.2^\circ$) on methylation with diazomethane, gave needles (mp 48–49°, $[\alpha]_D^{24} + 9.6^\circ$) methyl rangiformate (**2**). Saponification of **1** yielded (+)-norrangiformic acid (mp 105–108°, $[\alpha]_D^{24} + 7.5^\circ$). The absolute configuration of (+)-norrangiformic acid was determined by Åkermark [2] as (2S,3S)-heptadecanetricarboxylic acid (**3**). The position of the methylester group of (+)-rangiformic acid is still unknown. (+)-Isorangiformic acid gave on heating with acetyl chloride an anhydride (mp 92–94°, $[\alpha]_D^{24} + 13.4^\circ$) the IR spectrum of which contained, besides the carbonyl band of the methylester group (1702 cm⁻¹), two strong bands at 1758 and 1790 cm⁻¹, indicative of a six-membered anhydride [3]. Since norrangiformic acid

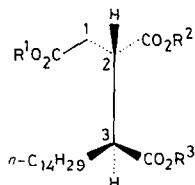
can give only one six-membered anhydride, formed from the carboxylic groups at C-1 and C-3, (+)-isorangiformic acid anhydride must have structure **4** and consequently (+)-isorangiformic acid is **1**. (+)-Rangiformic acid is either **5** or **6**. Experiments to differentiate between these structures are under way.

(+)-Sodium usneate has been isolated from a lichen for the first time.

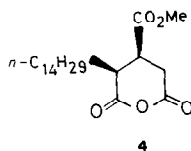
EXPERIMENTAL

Air-dried and ground *L. stenotropa* (786 g, GDR, Bezirk Halle, Kreis Hettstedt, on copper slate near Welfesholz; leg. S. Huneck, 3.9.1980, det. J. Poelt, 14.10.1980) was extracted with Et₂O. The ppt was recrystallized from MeOH–H₂O to give (+)-sodium usneate (33 mg, 0.004%): yellow flat needles (dec. above 240°), $[\alpha]_D^{24} + 275.4^\circ$ (Me₂CO; c 0.62); IR ν_{\max}^{KBr} cm⁻¹: 700, 738, 786, 810, 834, 882, 940, 980, 1004, 1038, 1068, 1116, 1134, 1180, 1238, 1284, 1320, 1380, 1450, 1470, 1516, 1620, 1690, 2700, 3000, 3500. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 225 (4.47), 290 (4.51). The Et₂O extract of the lichen was treated with NaHCO₃ (10%) and NaOH (1%); the NaHCO₃ fraction gave, after acidification and repeated crystallization from *n*-hexane and MeOH–H₂O, (+)-isorangiformic acid (**1**) (18 g, 2.29%): small needles; mp 83–85°; $[\alpha]_D^{24} + 5.2^\circ$ (MeOH; c 2.455); C₂₁H₃₈O₆ (386.51). IR ν_{\max}^{KBr} cm⁻¹: 724, 804, 864, 958, 1040, 1060, 1200, 1230, 1290, 1350, 1438, 1470, 1694 (–CO₂H), 1720 (–CO₂Me), 2870, 2940, 3200, 3500 (–CO₂H); ¹H NMR (100 MHz, CDCl₃): δ 0.83 (3H, *t*, –Me), 1.22 (24H, *br s*–(CH₂)₁₂–), 2.40–3.20 (4H, *m*, 2 × –CH₂–), 3.30 (2H, *m*, 2 × –CH–), 3.68 (2H, *s*, –CO₂Me), 9.78 (2H, *br s*, 2 × –CO₂H); MS *m/z* (rel. int.): 368 [M – H₂O]⁺ (69), 350 (55), 336 (57), 322 (92), 308 (79), 294 (79), 290 (84), 280 (69), 264 (79), 228 (69), 214 (87), 210 (87), 200 (90), 196 (94), 182 (100), 170 (94), 168 (99), 156 (89), 154 (99), 140 (92), 126 (91), 112 (85), 98 (92), 84 (92).

(+)-Methyl rangiformate (**2**). Methylation of **1** with CH₂N₂ in Et₂O gave **2**: mp 48–49° (MeOH); $[\alpha]_D^{24} + 9.6^\circ$ (CHCl₃; c 1.715); C₂₃H₄₂O₆ (414.57). IR ν_{\max}^{KBr} cm⁻¹: 730, 804, 856, 906, 968, 978, 1004, 1030, 1070, 1110, 1122, 1170, 1194, 1222, 1270, 1288, 1300, 1318, 1346, 1372, 1410, 1436, 1466, 1614 (–CO₂Me), 2850, 2930; ¹H NMR (100 MHz, CDCl₃): 0.80 (3H, *t*, –Me), 1.20 (24H, *br s*, –(CH₂)₁₂–), 2.30–2.90



	R ¹	R ²	R ³
1	H	Me	H
2	Me	Me	Me
3	H	H	H
5	Me	H	H
6	H	H	Me



*Part 131 in the series "Lichen Substances". For Part 130 see ref. [1]

(4H, *m*, $2 \times -\text{CH}_2-$), 3.00–3.25 (2H, *m*, $2 \times -\text{CH}-$), 3.58, 3.60, 3.61 (each 3H, *s*, $-\text{CO}_2\text{Me}$); ^{13}C NMR (50.32 MHz, CDCl_3): 13.99, 22.60, 28.70, 29.30, 29.49, 29.51, 32.26, 42.90, 46.10, 51.71 ($-\text{OMe}$), 52.04 ($-\text{OMe}$), 172.08 ($-\text{CO}-$), 173.29 ($-\text{CO}-$), 174.17 ($-\text{CO}-$); MS *m/z* (rel. int.): 414 $[\text{M}]^+$ (17), 383 (68), 382 (58), 350 (40), 322 (49), 295 (25), 269 (63), 242 (71), 228 (71), 218 (85), 210 (61), 196 (58), 186 (90), 154 (73), 146 (100), 126 (85), 114 (98), 98 (61), 84 (84).

(+)-*Norrangiformic acid* (3). Hydrolysis of **1** with KOH + MeOH gave **3**: mp 105–108° (MeOH); $[\alpha]_D^{24} + 7.5^\circ$ (MeOH; *c* 1.87); $\text{C}_{20}\text{H}_{36}\text{O}_6$ (372.49). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 670, 716, 734, 764, 792, 848, 882, 924, 1020, 1126, 1176, 1212, 1230, 1270, 1402, 1470, 1670 ($-\text{CO}_2\text{H}$), 1700 ($-\text{CO}_2\text{H}$), 2850, 2930, 3150 ($-\text{CO}_2\text{H}$); MS *m/z* (rel. int.): 354 $[\text{M} - \text{H}_2\text{O}]^+$ (54), 336 (73), 318 (38), 308 (77), 290 (75), 280 (84), 264 (70), 252 (57), 238 (49), 220 (61), 214 (67), 210 (61), 200 (81), 196 (87), 186 (80), 182 (98), 168 (96), 154 (91), 140 (95), 126 (86), 112 (93), 98 (100), 84 (95).

(+)-*Isorangiformic acid anhydride* (4). Heating **1** (0.3 g) with AcCl (7 ml) under reflux (2 hr), removal of excess AcCl (*in vacuo*) and crystallization of the residue from *n*-hexane gave **4**: needles, mp 92–94°; $[\alpha]_D^{24} + 13.4^\circ$ (CHCl_3 ;

c 1.74); $\text{C}_{21}\text{H}_{36}\text{O}_5$ (368.50). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 716, 742, 784, 818, 840, 866, 892, 928, 940, 964, 1000, 1014, 1040, 1094, 1190, 1210, 1240, 1280, 1300, 1338, 1380, 1436, 1464, 1702 ($-\text{CO}_2\text{Me}$), 1758, 1790 (anhydride $-\text{CO}-$), 2870, 2950.

The NaOH fraction of the Et_2O extract gave, after acidification and crystallization from CHCl_3 -MeOH, (+)-usnic acid (3.5 g, 0.44%): mp 198–200°; $[\alpha]_D^{24} + 492^\circ$ (CHCl_3 ; *c* 0.50).

The neutral part of the Et_2O extract yielded after chromatography on SiO_2 and crystallization from CHCl_3 -MeOH, zeorin (0.21 g, 0.026%) as double pyramids, mp 230–234°.

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TERPENES IN *PISTACIA* PLANTS: A POSSIBLE DEFENCE ROLE FOR MONOTERPENES AGAINST GALL-FORMING APHIDS

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Key Word Index—*Pistacia*; Anacardiaceae; aphids; triterpenes; monoterpenes.

Abstract—A re-investigation of *Pistacia vera* from southern Italy afforded, in addition to known compounds, two new monoterpenes (+)-9,10-cyclopropylterpinen-4-ol and (+)-9,10-cyclopropyl-terpin-2,4-diol and a novel triterpene triol $3\beta,11\alpha,13\beta$ -trihydroxyoleanane. The possible defence role of monoterpenes against gall-forming aphids is discussed briefly.

INTRODUCTION

The genus *Pistacia* includes many species widely distributed in the Mediterranean and Middle East areas which are often infected by gall-forming insects. A previous investigation of resins exuded from galls and trunks of several species [1] showed no significant differences in chemical composition.

Some of us recently reported [2] a comparative study on oleoresins from trunks of *Pistacia atlantica* plants originating in Israel and Iran. Both were found

to consist of euphane, dammarane and oleanane triterpenes, the only relevant difference being the presence in the oleoresin from Iranian specimens of two pinane monoterpenes. Interestingly, *P. atlantica* from Israel produces galls due to the aphid *Slavum wertheimae* (genus *Forda*) whereas the same species from Iran is gall-free although this insect lives in Iran and infects other *Pistacia* species growing in the same area [3]. We have now examined oleoresins from trunks of uninfected plants of *P. vera* from