First efficient synthesis of (±)-*erythro*-roccellic acid †

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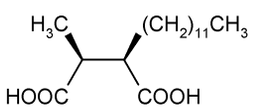
An easy, four-step route to (±)-*erythro*-2-dodecyl-3-methylbutanedioic acid (roccellic acid, **9**) with 60% overall yield has been described. Wittig reaction of the citraconimide–TPP adduct with dodecanal furnished the mixture of (*E*)- and (*Z*)-isomers **3** and **4**, which, on base-catalysed exocyclic to endocyclic double bond isomerisation, yielded maleimide **5**. Catalytic *cis*-hydrogenation of **5** using Adam's platinum dioxide catalyst followed by acid-catalysed hydrolysis of formed succinimide **8** gave desired (±)-*erythro*-roccellic acid **9**.

Introduction

(+)-Roccellic acid [(2*R*,3*S*)-2-dodecyl-3-methylbutanedioic acid, **1**] occurs in lichens[1,2] and it was first isolated in 1898. In the past century it has been isolated from the following lichen species: *Roccella capensis*,[3] *R. fuciformis*,[4,5] *R. hypomecha*,[6] *R. gayana*,[7] *R. fucoides*,[7,8] *R. condensata*,[9] *R. montagnei*,[10,11] *Dirinaria aegialita*,[12] *D. applanata*,[12] *D. confusa saxicola*,[12] *D. consimilis*,[12] *D. leopoldii*,[12] *Pyxine berteriana*,[12] *P. caesiopruinosa*,[12] *P. pungens*,[12] *Lobodirina cerebriformes*,[13] *L. mahuiana*,[14] *Acarospora chlorophana*,[15] *Lecanora riparia*,[16] *L. rupicola*,[17,18] *L. sordida*,[19,20] *Lepraria latebrarum*,[21] *L. aeruginosa*,[22] *Dirina lutosa*,[23] *Crocynea membranacea*[24,25] and more recently from *Haematomma nemetzii*[26] and *Tornabena scutellifera*[26] with a major contribution from Siegfried Huneck's group. The structural assignment of roccellic acid **1** has been made on the basis of analytical and spectral data.[17,19,24,26] Its absolute configuration was established by Åkermark by degrading **1** to its two isomeric monomethyl esters.[24,27] Roccellic acid **1** possesses antituberculosis activity[28–30] and concentration-dependent plant growth promoter[31–33]/inhibitor[33,34] activity. It is also used for (i) the synthesis of structural analogues of the antibiotic actinonin,[35] (ii) the precipitation of human serum albumin[36] and (iii) the preparation of coloured metal complexes.[37] To date, two syntheses[38,39] of unnatural (±)-*threo*-roccellic acid (major) are known starting from diethyl malonate and during these studies a small amount (25 mg) of (±)-*erythro*-roccellic acid has been obtained by an 8-step synthesis with 0.026% overall yield.[38] The provision of facile synthetic approaches to this bioactive natural product roccellic acid is a challenging task of current interest. Recently we have reported[40] the first coupling reaction of the citraconimide **2** and triphenylphosphine (TPP) adduct[41] with aliphatic aldehydes and used it for the synthesis of the recently isolated bioactive natural products chaetomellic acid A,[40] (±)-piliformic acid,[42] and tyromycin A.[43] We herein report yet another useful application of this coupling reaction to complete the first efficient synthesis of (±)-*erythro*-roccellic acid **9** by the *cis*-reduction of maleimide **5** to succinimide **8** employing a catalytic hydrogenation reaction with Adam's catalyst (Scheme 1).



(2*R*,3*S*)-2-Dodecyl-3-methylbutanedioic acid (**1**)

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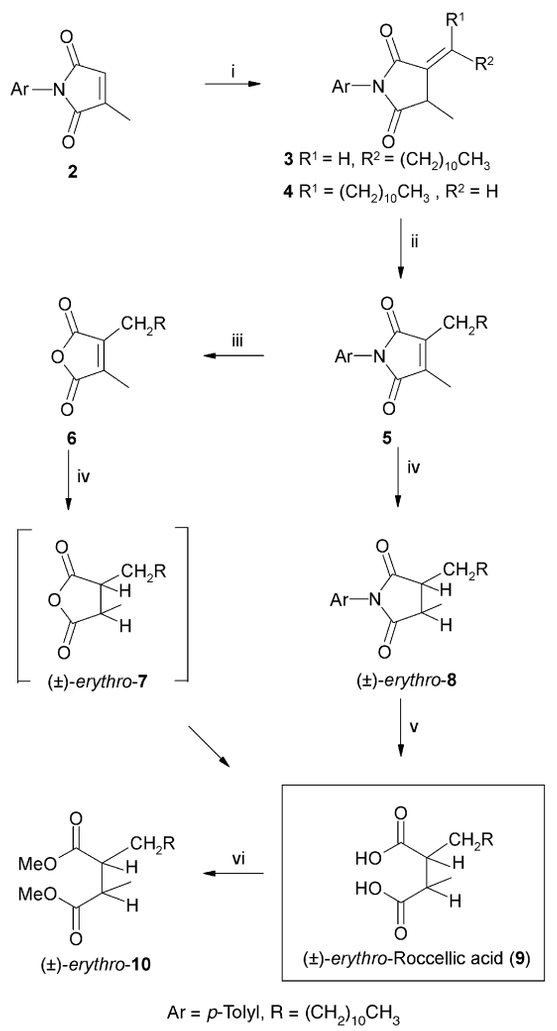

Scheme 1 *Reagents, conditions and yields*: (i) TPP, AcOH, dodecanal, reflux, 10 h (82%); (ii) TEA, THF, reflux, 48 h (98%); (iii) (a) KOH, THF, MeOH, H_2O, reflux, 2 h; (b) H^+/HCl (98%); (iv) Adam's catalyst, petroleum spirit, H_2, rt, 10 h (**9**: 60%; **8**: 95%); (v) CF_3COOH, conc. HCl, reflux, 48 h (98%); (vi) CH_2N_2, Et_2O, rt, 2 h, (98%).

Results and discussion

A mixture of equimolar amounts of citraconimide **2** and TPP on refluxing with 1.5 equivalents of dodecanal in glacial acetic acid for 10 h yielded a combination of geometric isomers **3** and

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4 in 82% yield by a Wittig reaction. The integration values for the vinylic protons in the ^{1}H NMR spectra of this mixture of geometric isomers (*E*)-**3** and (*Z*)-**4** revealed that they are formed in an 85 : 15 ratio. The mixture of *exo*-isomers **3** and **4** on refluxing with triethylamine–THF (1 : 1) for 48 h, underwent a smooth exocyclic to endocyclic carbon–carbon double bond isomerisation to yield dodecylmethylmaleimide **5** in 98% yield. On alkaline hydrolysis followed by acidification, the maleimide **5** gave the desired dodecylmethylmaleic anhydride **6** in 98% yield. We systematically studied the catalytic *cis*-hydrogenation reactions of maleimide **5** and disubstituted maleic anhydride **6** to obtain succinimide derivative **8** and succinic anhydride derivative **7** respectively. In our hands, the anhydride **6** and imide **5**, when subjected to catalytic hydrogenation with palladium on charcoal as catalyst in methanol, remained completely unreacted for 12 h at 50 psi pressure of hydrogen. The anhydride **6** in petroleum spirit on treatment with Adam's platinum dioxide catalyst at 50 psi pressure of hydrogen for 10 h followed by filtration, concentration and recrystallisation with acetone gave the desired (±)-*erythro*-roccellic acid **9** in 60% yield. We were unable to isolate the intermediate anhydride **7** under the present set of reaction conditions. The maleimide **5** underwent a very smooth catalytic *cis*-hydrogenation at rt in petroleum spirit with Adam's platinum dioxide catalyst at 50 psi hydrogen pressure in 10 h to yield the desired *cis*-succinimide derivative **8** in 95% yield. The reaction of maleimide **5** to succinimide **8** was much cleaner and more efficient compared to the conversion of **6** to **9** *via* **7**. The *cis*-succinimide derivative **8** on hydrolysis using refluxing mixture of acetic acid plus conc. hydrochloric acid (1 : 1) gave a mixture of *erythro*- and *threo*-isomers of roccellic acid, in a 2 : 1 ratio (by ^{1}H NMR, from the integration values of the methine protons) in 48 h with 98% yield. The *cis*-succinimide derivative **8** on hydrolysis in refluxing mixture of trifluoroacetic acid and conc. hydrochloric acid (1 : 1) gave a mixture of the desired *erythro*- and undesired *threo*-isomers with a much better proportion of the *erythro*-isomer (93 : 7, by ^{1}H NMR, from the integration values of the methine protons) in 48 h with 98% yield. Recrystallisation of the above mixture of *erythro*- and *threo*-isomers (93 : 7) from acetone gave the desired (±)-*erythro*-roccellic acid **9** in 80% yield. The formed acid **9** was further characterised as its dimethyl ester **10**. The analytical and spectral data obtained for (±)-*erythro*-roccellic acid **9** and its corresponding dimethyl ester **10** were in complete agreement with reported data.[2,17,38] The asymmetric catalytic hydrogenation[44–46] of maleimide **5** will provide an elegant route to the desired naturally occurring bioactive (+)-(2*R*,3*S*)-roccellic acid **1**.

In summary, we have demonstrated the first efficient four-step synthesis of (±)-*erythro*-roccellic acid **9** with 60% overall yield, starting from citraconimide **2** by a catalytic *cis*-hydrogenation pathway and the present strategy will be useful for obtaining several 2,3-dialkyl substituted succinic acid derivatives.

Experimental

Melting points were taken on a Büchi melting point B-540 apparatus and are uncorrected. The ^{1}H NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard on a Bruker AC 200 NMR spectrometer (200 MHz) and for roccellic acid **9** in pyridine-d_5 with TMS as an internal standard on a Bruker DRX 500 NMR spectrometer (500 MHz). The ^{13}C NMR spectra were recorded on Bruker AC 200 (50 MHz), Bruker MSL 300 (75 MHz) and Bruker DRX 500 NMR spectrometers (125 MHz). Mass spectra were recorded on a Finnigan Mat 1020 °C mass spectrometer at 70 eV. The FT-IR spectra were recorded on an FT-IR-8300 Shimadzu spectrometer and microanalyses were carried out on a Carlo-Erba instrument; column chromatographic separation was performed with ACME silica gel (60–120 mesh). Triphenylphosphine and dodecanal were obtained from Aldrich Chemical Co. Petroleum spirit refers to the fraction with distillation range 60–80 °C.

(±)-(*E*/*Z*)-2-Dodecylidene-3-methyl-*N*-(*p*-tolyl)succinimides 3 and 4

A mixture of citraconimide **2** (3.01 g, 15 mmol), TPP (3.93 g, 15 mmol) and dodecanal (4.14 g, 22.5 mmol) in glacial acetic acid (50 mL) was refluxed with stirring for 10 h. Acetic acid was distilled off *in vacuo* at 50 °C and the residue was dissolved in ethyl acetate (60 mL). The organic layer was washed successively with water (30 mL), brine (20 mL) and dried over Na_2SO_4. Concentration of the organic layer *in vacuo* followed by silica gel column purification of the residue using petroleum spirit–ethyl acetate (9 : 1) gave a mixture of **3** and **4** (**3** : **4** = 85 : 15 by ^{1}H NMR) (4.54 g, 82%); mp 49–52 °C; IR (Nujol) ν_{max} 1717, 1458 cm^{-1}; ^{1}H NMR δ_H 0.88 (t, *J* 6 Hz, 3 H), 1.27 (br s, 16 H), 1.45–1.60 (m, 2 H), 1.48 (d, *J* 6 Hz, 0.45 H, *Z*-isomer), 1.52 (d, *J* 6 Hz, 2.55 H), 2.20–2.36 (m, 1.7 H), 2.38 (s, 3 H), 2.74–2.92 (m, 0.3 H, *Z*-isomer), 3.34–3.59 (m, 1 H), 6.23 (dt, *J* 8 and 3 Hz, 0.15 H, *Z*-isomer), 6.92 (dt, *J* 8 and 3 Hz, 0.85 H), 7.20 (d, *J* 8 Hz, 2 H), 7.28 (d, *J* 8 Hz, 2 H); MS *m*/*z* 369 (M^+, 85%), 354 (4), 340 (4), 270 (5), 256 (8), 242 (100), 229 (28), 216 (47), 203 (80), 186 (8), 170 (4), 157 (4), 144 (4), 132 (12), 118 (18), 107 (46), 95 (62), 91 (29), 81 (55), 68 (82), 55 (9) (Calc. for $C_{24}H_{35}NO_2$: C, 78.00; H, 9.55; N, 3.80. Found: C, 78.16; H, 9.39; N, 3.92%).

2-Dodecyl-3-methyl-*N*-(*p*-tolyl)maleimide 5

A solution of the mixture of **3** and **4** (3.3 g) in THF (15 mL) and triethylamine (15 mL) was refluxed for 48 h with stirring. The reaction mixture was then allowed to reach rt, and was concentrated *in vacuo*; silica gel column chromatographic purification of the residue using petroleum spirit–ethyl acetate (9 : 1) gave pure **5** (3.23 g, 98%), mp 68–69 °C; IR (Nujol) ν_{max} 1710, 1690, 1650 cm^{-1}; ^{1}H NMR δ_H 0.89 (t, *J* 8 Hz, 3 H), 1.27 (br s, 18 H), 1.50–1.75 (m, 2 H), 2.05 (s, 3 H), 2.38 (s, 3 H), 2.46 (t, *J* 8 Hz, 2 H), 7.10–7.40 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 8.7, 14.0, 21.0, 22.6, 23.8, 28.1, 29.3, 29.6 (6 × CH_2), 31.9, 125.6, 129.5, 137.1, 137.2, 141.4, 159.7, 170.7, 171.1; MS *m*/*z* 369 (M^+, 85%), 256 (6), 228 (10), 215 (100), 203 (8), 107 (48), 91 (29), 81 (41), 67 (20), 55 (10) (Calc. for $C_{24}H_{35}NO_2$: C, 78.00; H, 9.55; N, 3.80. Found: C, 77.72; H, 9.78; N, 3.71%).

2-Dodecyl-3-methylmaleic anhydride 6

To the solution of imide **5** (1.11 g, 3 mmol) in a THF–methanol mixture (1 : 2, 18 mL) was added 30% aqueous KOH solution (10 mL) and the reaction mixture was refluxed for 2 h with stirring. The reaction mixture was concentrated *in vacuo* and the residue was acidified with dilute HCl, extracted with diethyl ether (3 × 50 mL) and the organic layer was washed with water (20 mL), brine (20 mL) and dried over Na_2SO_4. Concentration of the organic layer *in vacuo* followed by silica gel column chromatographic purification of the residue using petroleum spirit–ethyl acetate (9 : 1) furnished pure **6** as a thick oil (0.82 g, 98%); IR (Nujol) ν_{max} 1823, 1767, 1674, 1466 cm^{-1}; ^{1}H NMR δ_H 0.88 (t, *J* 6 Hz, 3 H), 1.26 (br s, 18 H), 1.45–1.70 (m, 2 H), 2.07 (s, 3 H), 2.46 (t, *J* 6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 9.2, 13.9, 22.5, 24.3, 27.4, 29.3, 29.5 (6 × CH_2), 31.8, 140.3, 144.6, 165.7, 166.1; MS *m*/*z* 281 (MH^+, 10%), 262 (18), 252 (12), 235 (13), 207 (20), 196 (14), 178 (42), 168 (29), 150 (15), 139 (10), 126 (95), 109 (12), 98 (26), 81 (33), 67 (30) (Calc. for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 73.05; H, 9.93%).

(±)-*erythro*-2-Dodecyl-3-methyl-*N*-(*p*-tolyl)succinimide 8

A mixture of maleimide **5** (1.1 g, 3 mmol) and Adam's catalyst (25 mg) in petroleum spirit (50 mL) was subjected to hydrogenation at 50 psi hydrogen pressure for 10 h at rt. The reaction

mixture was filtered through Celite and the filtrate was concentrated *in vacuo*. The silica gel column purification of the residue using petroleum spirit–ethyl acetate (9 : 1) gave succinimide **8** (1.05 g, 95%), mp 67–68 °C (from methanol); IR (Nujol) ν_{max} 1774, 1709, 1516, 1470 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ_H 0.91 (t, *J* 6 Hz, 3 H), 1.29 (br s, 20 H), 1.35 (d, *J* 6 Hz, 3 H), 1.60–1.95 (m, 2 H), 2.39 (s, 3 H), 2.85–3.20 (m, 2 H), 7.16 (d, *J* 8 Hz, 2 H), 7.28 (d, *J* 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 11.6, 13.9, 21.0, 22.6, 26.5, 27.6, 29.3, 29.5 (6 × CH_2), 31.8, 38.6, 43.8, 126.1, 129.6, 138.2, 138.4, 178.4, 179.3; MS *m*/*z* 371 (M^+, 24%), 265 (4), 216 (29), 203 (80), 175 (7), 134 (12), 107 (20), 91 (12), 69 (18) (Calc. for $C_{24}H_{37}NO_2$: C, 77.58; H, 10.03; N, 3.77. Found: C, 77.76; H, 10.14; N, 3.53%). Similarly, on catalytic hydrogenation, anhydride **6** (0.56 g, 2 mmol) furnished (±)-*erythro*-roccellic acid **9** (0.36 g, 60%).

(±)-*erythro*-Roccellic acid 9

Succinimide **8** (0.74 g, 2 mmol) was dissolved in trifluoroacetic acid–conc. hydrochloric acid (1 : 1, 15 mL) and the reaction mixture was refluxed for 48 h. The reaction mixture was kept aside at rt for 12 h and the white precipitate of roccellic acid was filtered *in vacuo* to obtain **9** (0.59 g, 98%) (*erythro* : *threo* = 93 : 7, proved by ^1H NMR). The mixture of *erythro*- and *threo*-roccellic acid (0.50 g, 93 : 7) was recrystallised from acetone (30 mL) to obtain pure (±)-*erythro*-roccellic acid **9** (0.40 g, 80%), mp 141–142 °C (from acetone); IR (Nujol) ν_{max} 1693, 1464, 1271, 1202 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz) δ_H 0.86 (t, *J* 5 Hz, 3 H), 1.20 (br s, 16 H), 1.30–1.45 (m, 2 H), 1.62 (d, *J* 10 Hz, 3 H), 1.53–1.75 (m, 2 H), 1.92–2.03 (m, 1 H), 2.10–2.23 (m, 1 H), 3.17–3.33 (m, 2 H); ^{13}C NMR (pyridine-d_5, 125 MHz) δ_C 14.2, 16.2, 22.8, 28.2, 29.5, 29.8 (6 × CH_2), 31.7, 32.0, 43.4, 50.0, 177.0, 177.7; MS *m*/*z* 282 (M^+, 1%), 254 (2), 227 (7), 209 (3), 170 (10), 156 (17), 132 (35), 97 (33), 83 (28), 69 (54) (Calc. for $C_{17}H_{32}O_4$: C, 67.96; H, 10.73. Found: C, 67.85; H, 10.65%).

Dimethyl ester of (±)-*erythro*-roccellic acid 10

A solution of (±)-*erythro*-roccellic acid **9** (0.30 g, 1 mmol) in ether (10 mL) was treated with a solution of diazomethane in ether at 0 °C, until the complete consumption of the starting material (2 h). The excess of diazomethane was quenched with acetic acid and the reaction mixture was concentrated *in vacuo*. Silica gel column chromatographic purification of the residue using petroleum spirit and ethyl acetate mixture (9 : 1) gave pure **10** as a thick oil (0.32 g, 98%); IR (neat) ν_{max} 1740, 1464, 1435, 1195 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ_H 0.87 (t, *J* 6 Hz, 3 H), 1.13 (d, *J* 6 Hz, 3 H), 1.23 (br s, 18 H), 1.30–1.50 (m, 2 H), 1.50–1.75 (m, 2 H), 2.58–2.78 (m, 2 H), 3.68 (s, 3 H), 3.69 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 14.0, 15.1, 22.7, 27.5, 29.4, 29.6 (6 × CH_2), 30.7, 31.9, 42.1, 48.6, 51.4, 51.7, 174.6, 175.3; MS *m*/*z* 328 (M^+, 1%), 298 (24), 267 (7), 242 (100), 184 (16), 170 (18), 160 (88), 128 (66), 111 (17), 101 (32), 91 (68), 81 (29), 69 (68), 55 (92) (Calc. for $C_{19}H_{36}O_4$: C, 69.47; H, 11.04. Found: C, 69.54; H, 11.23%).

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