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**DEFRAPLAST: NEW PLASTICISERS AND  
STABILISERS FROM UK-GROWN CRAMBE OIL  
(NOT TO BE PUBLISHED)**



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## 1. Synthetic experimental

### General Experimental

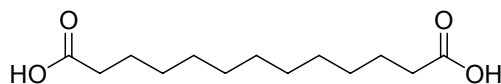
Ozone was produced with an Azkozon RMU16-16 ozone generator, fitted with an oxygen gas cylinder. Ozone gas was passed into the substrate through a stainless steel delivery tube and the mixture was vigorously stirred by a mechanical stirrer. At oxygen rate of 5.0 L/min; the ozone rate was 9.7 mmol/min.

NMR spectra were recorded on a Bruker AC-250 Spectrometer ( $^1\text{H}$  250 MHz,  $^{13}\text{C}$  63 MHz) (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, p = pentuplet, s = sextet, sp = septet, m = multiplet). All of the coupling constants ( $J$ ) were recorded in Hz.

Column chromatography was generally prepared with Davisil silica gel (40-60  $\mu$ ).

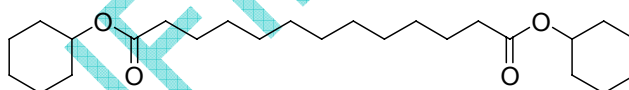
Infrared (IR) spectra were recorded on a Bruker Tensor 27 spectrometer. Liquid compounds were recorded as a liquid film. Solids were recorded as a KBr disc or using Nujol mull.

### Synthesis of brassylic acid: ozonolysis of erucic acid



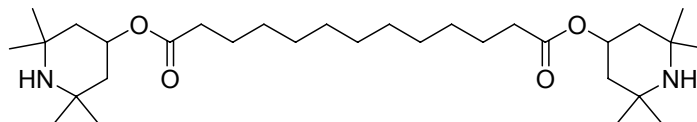
Erucic acid (600 g, 1.8 mol, 1.0 eq.) of 87% purity was mixed along with nonanoic acid (600 g, 3.8 mol, 2.1 eq.), into a 2L round-bottom flask equipped with a mechanical stirrer, a condenser, a digital thermometer and an outlet tube connected to the ozoniser. Ozone was passed through the mixture with continuous mechanical stirring. After five minutes, the temperature of the reaction rose to 40 °C, where it was kept stable with the aid of a water cooling bath. The extent of the reaction was measured by means of the rate of oxygen being consumed, at periodic intervals. The rate of ozone not consumed was monitored by titration of the outlet gas with potassium iodide buffer solution in water (0.3 M) at 1h (0.44 mmol/min), 2h (0.78 mmol/min), 3h (1.67 mmol/min), 4h (3.50 mmol/min), 5h (7.89 mmol/min) and 6h (9.50 mmol/min). <sup>13</sup>C NMR spectra were also recorded at 3h, 4h, 5h, and 6h to account for the disappearance of the double bonds. The reaction was stopped after 6h, and no more ozone was passed through. The reaction mixture was then warmed up to 75°C, at which decomposition of the ozonides started. The temperature was controlled by the use of alternate heating with a cold water cooling bath very slowly until it reached 110°C, over the period of 1h. Afterwards, oxygen was passed through the mixture during 2h at 110 °C. The resulting viscous oil was transferred to a three-necked round-bottom flask, where nonanoic acid was distilled at reduced pressure (0.025 mmHg, 82°C). The residue solidified when it cooled down to room temperature (350.2 g). This solid was dissolved in hot toluene (700 ml) and placed in the fridge for crystallisation. Filtration afforded the *title compound*, brassylic acid, as a white solid (233.0 g, 63.3%) mp 110–111 °C (lit., 110–112 °C);  $\nu_{\max}$  cm<sup>-1</sup> 3020, 2918, 2848, 1699, 1468, 1216, 929, 759, 669;  $\delta_{\text{H}}$  2.36 (4H, t, *J* 7.6), 1.64 (4H, m), 1.28 (14H, m);  $\delta_{\text{C}}$  185.8, 34.3, 29.6, 25.0.

### Synthesis of dicyclohexyl brassylate (PLB): tridecanedioic acid dicyclohexyl ester



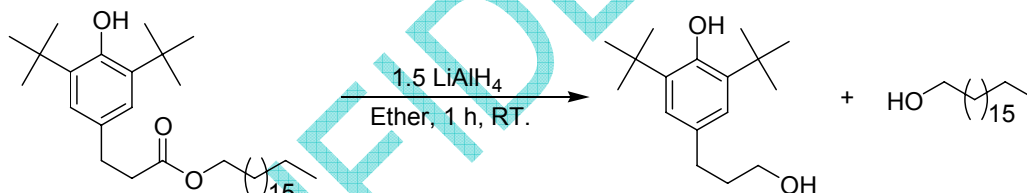
Brassylic acid (130.0 g, 532.0 mmol, 1.0 eq.), cyclohexanol (133.2 g, 1330.0 mmol, 2.5 eq.), *p*-toluene sulfonic acid (10.1 g, 190.0 mol, 0.1 eq.) and toluene (100 ml) were mixed altogether into a 500 ml three-necked round-bottom flask, equipped with a digital thermometer, heating-stirrer and a Dean-Stark apparatus. The mixture was brought to reflux and the water (70 ml) azeotropically distilled was collected. The reaction mixture was heated for an additional 30 minutes after all the water had already been collected. Afterwards, the reaction mixture was cooled down to temperature and an aqueous solution of sodium bicarbonate (210 ml, 1M) was added dropwise. The organic layer was separated and the aqueous phase was extracted with diethyl ether (3 x 100 ml). The combined organic fractions were dried over magnesium sulfate, filtered and evaporated under vacuum. The crude product was distilled under reduced pressure to distill off the toluene and the excess of cyclohexanol. The resulting brownish oil (190.4 g) was purified by column chromatography; eluting with petrol/diethyl ether (9:1) to afford the *title compound* as a white solid (130.2 g, 318.6 mmol, 60.0%) mp 24–25 °C;  $\nu_{\max}$  cm<sup>-1</sup> 2933, 2857, 1732, 1452, 1178;  $\delta_{\text{H}}$  4.59 (2H, m), 2.09 (4H, t, *J* 7.3), 1.65 (4H, m), 1.65 (4H, m), 1.57 (2H, s), 1.44 (4H, m), 1.22 (4H, m), 1.12 (22H, s);  $\delta_{\text{C}}$  173.1, 72.2, 34.8, 31.8, 29.6, 29.4, 29.3, 25.6, 25.2, 23.9; HRMS-*EI* (calculated *m/z* 409.3315; required *m/z* 409.3318) *m/z* 409.3 (12 %), 327.3 (12), 255.2 (11), 245.2 (19), 227.2 (100).

### Synthesis of tinuvin analogue (HABS): tridecanedioic acid bis-(2,2,6,6-tetramethyl-piperidin-4-yl) ester



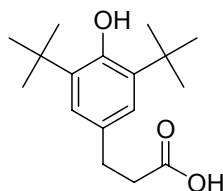
Brassylic acid (19.5 g, 80.0 mmol, 1.0 eq.), 2,2,6,6-tetramethyl piperidine-4-ol (37.7 g, 240.0 mmol, 2.5 eq.), *p*-toluene sulfonic acid (53.2 g, 280.0 mmol, 3.0 eq.) and xylene (10 ml) were mixed altogether into a 250 ml three-necked round-bottom flask, equipped with a digital thermometer, heater-stirrer and a Dean-Stark apparatus. The mixture was brought to reflux and the water (8.9 ml) azeotropically distilled was collected. Afterwards, the reaction mixture was cooled down to temperature and left standing overnight under chloroform (100 ml) and a saturated solution of sodium bicarbonate (200 ml). Then, more chloroform (100 ml) and water (300 ml) were added until clear solutions were obtained, followed by addition of sodium hydroxide aqueous solution (6M) until the pH=10. The organic layer was separated and the aqueous phase was extracted with chloroform (2 x 100 ml). The combined organic fractions were dried over magnesium sulfate, filtered and evaporated under vacuum. The resulting brownish oil (46.0 g) was purified by column chromatography; eluting with ethyl acetate to afford the *title compound* as an oil (31.3 g, 59.9 mmol, 75.1%);  $\delta_{\text{H}}$  5.17 (2H, m), 2.25 (4H, t, *J* 7.3), 1.89 (4H, dd, *J* 12.0 *J* 4.3), 1.59 (8H, t, *J* 6.7), 1.25 (28H, bs), 1.22 (12H, bs), 1.14 (12H, s);  $\delta_{\text{C}}$  173.6, 68.6, 51.8, 44.1, 35.0, 29.7, 29.5, 29.3, 29.1, 25.2.

### Reaction of irganox octadecyl ester with $\text{LiAlH}_4$



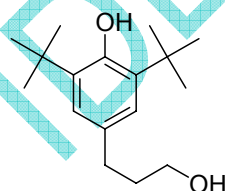
A solution of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid octadecyl ester (20.0 g, 37.6 mmol, 1.0 eq.) in diethyl ether (150 ml) was added portionwise to a well stirred suspension of  $\text{LiAlH}_4$  (3.6 g, 94.2 mmol, 2.5 eq.) in diethyl ether (200 ml), in a 500 ml three-necked round-bottom flask equipped with nitrogen line, condenser and addition funnel. After 1h stirring, methanol (15 ml) and saturated ammonium chloride solution (100 ml) were added, in that order. The organic phase was decanted and the residue extracted with diethyl ether (2 x 200 ml). The combined organic solutions were dried over magnesium sulfate and evaporated to give a white solid (20.5 g). TLC analysis revealed two spots in petrol/ether (50:50),  $R_{\text{F}} = 0.54$  and  $R_{\text{F}} = 0.48$ , corresponding to the two expected alcohol products.

### Synthesis of irganox acid



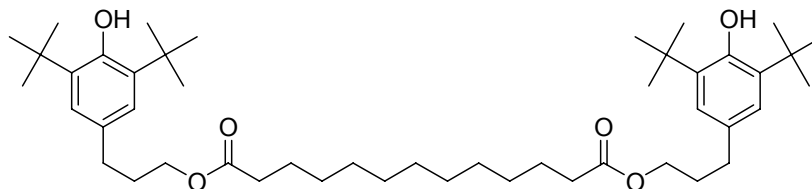
3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid octadecyl ester (200.0 g, 376.7 mmol, 1.0 eq.) was added portionwise to a solution of potassium hydroxide (52.9 g, 941.9 mmol, 2.5 eq.) in methanol (300 ml) in a 2L two-necked round-bottom flask, equipped with a reflux condenser. The mixture was brought to reflux for 1h, after which it was cooled down to room temperature. Then, water (1.5 L) was added. The organic layer was extracted with diethyl ether (3 x 200 ml), dried over magnesium sulfate and evaporated to give octadecan-1-ol (100.9 g, 99.2 %) as a light yellow solid. The aqueous layer was reacidified with hydrochloric acid (6M) and then extracted with diethyl ether (4 x 200 ml). The combined organic organic fractions were dried over magnesium sulfate and evaporated to give a light yellow solid (105.2 g). This yellow solid was dissolved in hot petroleum spirit (1L) and placed in the fridge for crystallisation. Filtration afforded the *title compound* as a white solid (96.6 g, 91.2%) mp 170-171 °C (lit., 172-175 °C);  $\nu_{\max}$   $\text{cm}^{-1}$  3637, 3020, 2961, 1708, 1434, 1215, 758, 669;  $\delta_{\text{H}}$  7.04 (2H, s), 5.12 (1H, s, -OH), 2.92 (2H, t,  $J$  7.9), 2.68 (2H, t,  $J$  7.9), 2.54 (6H, s), 1.46 (18H, s);  $\delta_{\text{C}}$  207.5, 179.3, 152.4, 136.1, 130.9, 124.9, 36.4, 34.5, 31.1, 30.9, 30.5.

### Synthesis of irganox alcohol



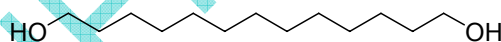
Irganox acid (50.0 g, 179.6 mmol, 1.0 eq.) was added dropwise over 1h to a suspension of  $\text{LiAlH}_4$  (10.2 g, 269.4 mmol, 1.5 eq.) in THF (200 ml), in a 2L round-bottom flask equipped with reflux condenser, mechanical stirrer, thermometer and Hershberg addition funnel under a positive pressure of nitrogen. The reaction mixture was heated under reflux for 2h. Afterwards, the mixture was cooled down to room temperature; ethyl acetate (20 ml) and aqueous  $\text{NH}_4\text{Cl}$  saturated solution (150 ml) were added dropwise, consecutively. The organic layer was decanted and the residue extracted with diethyl ether (3 x 200 ml). The combined organic layers were dried over magnesium sulfate, filtered and evaporated under vacuum to give an orange oil. This oil was dissolved in petroleum spirit (450 ml), and placed in the fridge for crystallisation. Filtration afforded the *title compound* as a white solid (45.0 g, 94.8%) mp 65-66 °C (lit., 64-67 °C);  $\nu_{\max}$   $\text{cm}^{-1}$  3644, 3362, 2955, 1435, 1232, 1055;  $\delta_{\text{H}}$  7.03 (2H, s), 5.09 (1H, s, -OH), 3.73 (2H, t,  $J$  6.4), 2.64 (2H, t,  $J$  7.9), 1.90 (2H, p,  $J$  7.1), 1.54 (1H, s, -OH), 1.46 (18H, s);  $\delta_{\text{C}}$  152.2, 136.2, 132.7, 125.2, 63.1, 35.1, 34.7, 32.5, 30.7.

### Synthesis of irganox ester stabiliser (HPB): tridecanedioic acid bis-[3-(3,5-di-tert-butyl-4-hydroxy-phenyl)-propyl] ester



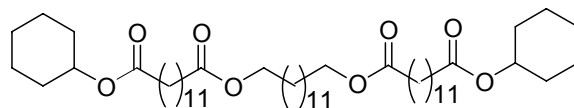
Brassylic acid (24.0 g, 98.2 mmol, 1.0 eq.), irganox alcohol (57.1 g, 216.1 mmol, 2.2 eq.), *p*-toluene sulfonic acid (1.9 g, 10.0 mmol, 0.1 eq.) and toluene (100 ml) were mixed altogether into a 500ml three-necked-round-bottom flask, equipped with a digital thermometer, heating-stirrer and a Dean-Stark apparatus. The mixture was brought to reflux and the water collected (3.7 ml) after 2h15min. The reaction mixture was heated for an additional 30 min after all the water had been collected. Afterwards, the reaction mixture was cooled down to temperature and an aqueous solution of sodium bicarbonate (30 ml, 1M) was added dropwise. The organic layer was separated and the aqueous phase was extracted with diethyl ether (3 x 100 ml). The combined organic fractions were dried over magnesium sulfate, filtered and evaporated under vacuum to give a crude product (76.9 g). The resulting crude oil was purified by column chromatography; eluting with petrol/diethyl ether 9:1 to afford the *title compound* as an oil (64.1 g, 88.5%);  $\nu_{\max}$   $\text{cm}^{-1}$  3544, 3068, 2944, 1734, 1436, 1391, 1361, 1234, 1121, 1024, 891, 787;  $\delta_{\text{H}}$  6.99 (4H, s), 5.08 (2H, s, -OH), 4.13 (4H, t, *J* 6.4), 2.62 (4H, t, *J* 6.4), 2.33 (4H, t, *J* 7.3), 1.95 (4H, p, *J* 7.3), 1.62 (8H, m), 1.46 (36H, s), 1.30 (10H, m);  $\delta_{\text{C}}$  174.3, 152.3, 136.1, 132.1, 125.1 (x2), 64.2, 34.7, 32.5, 31.0, 30.7, 29.8, 29.6, 25.4; HRMS-EI (calculated *m/z* 736.5483; required *m/z* 736.5642) *m/z* 736.5683 (42 %), 681.5 (12), 625.4 (100), 569.4 (81), 513.3 (33), 417.3 (20), 264.2 (22), 246.2 (65), 189.1 (69), 153.1 (59), 129.1 (55), 115.0 (50), 99.0 (45).

### Synthesis of brassylic alcohol



A solution of brassylic acid (40.0 g, 163.7 mmol, 1.0 eq.) in THF (200 ml) was added dropwise over a period of 1h to a suspension of  $\text{LiAlH}_4$  (13.7 g, 360.2 mmol, 2.2. eq.) in THF (800 ml) in a three-necked round-bottom flask equipped with mechanical stirring, nitrogen line and addition funnel at room temperature. The reaction mixture was brought to reflux and stirred for 1h. After cooling it down to room temperature, ethyl acetate (20 ml) and aqueous ammonium chloride saturated solution (150 ml), were added dropwise, successively. The reaction mixture was filtered and washed with ethyl acetate (200 ml). The organic phase was dried over magnesium sulfate, filtered and evaporated to give a light yellow solid, which was crystallised from hot ethyl acetate (300 ml) to afford the *title compound* as a white solid (34.1 g, 96.3%) mp 57-58 °C lit., (57-60 °C);  $\nu_{\max}$   $\text{cm}^{-1}$  3292, 3019, 2918, 2849, 1216, 759, 669;  $\delta_{\text{H}}$  3.53 (4H, t, *J* 6.4), 3.24 (2H, bs, -OH), 1.47 (4H, m), 1.21 (14H, s);  $\delta_{\text{C}}$  62.9, 32.9, 29.9, 26.1.

**Synthesis of oligomer plasticiser (PLOB): tridecanedioic acid cyclohexyl ester 13-(12-cyclohexyloxycarbonyl-dodecanoyloxy)-tridecyl ester**



Brassylic acid (365.9 g, 1497.5 mmol, 2.0 eq.), brassylic alcohol (162.0 g, 748.8 mmol, 1.0 eq.), cyclohexanol (150.0 g, 1497.5 mmol, 2.0 eq.), *p*-toluene sulfonic acid (28.5 g, 149.8 mmol, 0.2 eq.) and toluene (300 ml) were mixed together into a 2L three-necked round-bottom flask equipped with a Dean-Stark apparatus and a thermometer. The mixture was refluxed during 2h30min until all the water was collected (58.0 ml), and continued to be refluxed for an additional 30 minutes. Afterwards, the reaction mixture was cooled down to room temperature, an aqueous sodium bicarbonate solution (250 ml, 1M) was added dropwise, then water (200 ml) was added too. The organic phase was extracted with diethyl ether (3 x 400 ml), dried over magnesium sulfate, filtered and evaporated under vacuum to give a crude brown oil (596.0 g). This oil was decolourised over activated charcoal (100 g, 22.5 %) in hot petrol (1L) and then purified by chromatographic column with petrol/ether (80:20) to afford a mixture of oligomers as a white solid (432.0 g, 69.2%) mp 48-51 °C;  $\nu_{\max}$   $\text{cm}^{-1}$  1735, 1463, 1377, 1320, 1264, 1206, 1175, 722;  $\delta_{\text{H}}$  4.74 (2H, m), 4.04 (4H, m), 2.25 (8H, m), 1.80-1.67 (20H, m), 1.25 (58H, m);  $\delta_{\text{C}}$  174.3, 173.6, 72.6, 64.7, 35.1, 34.7, 31.9, 29.9, 29.6, 28.9, 26.3, 25.7, 25.4, 24.1; LSIMS (NOBA) (calculated m/z 833.6862; required m/z 833.6865), 833.7, 834.8, 835.8, 836.8, m/z 863.0 (78 %), 705.1 (10), 653.0 (24), 443.0 (79), 421.0 (42), 232.8 (100), 210.7 (82), 192.8 (33), 101.9 (13), 60.0 (42); MALDI: m/z 431.41 (rel. int., 1.0), 855.76 (0.8), 1280.08 (0.1).