

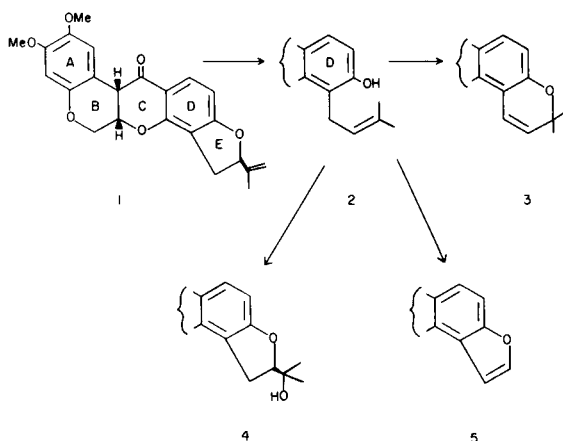
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The preparation of (-)-elliptone (**5**) from (-)-rotenone (**1**) via (-)-rot-2'-enonic acid (**2**) is described.

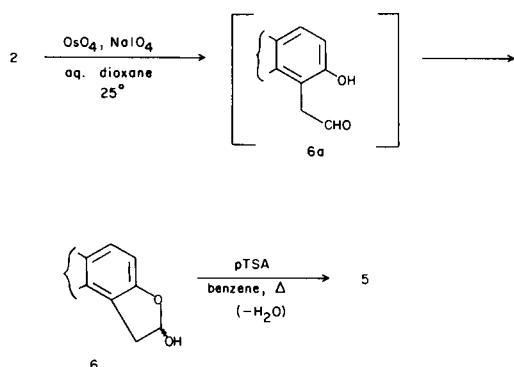
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In a recent communication (1), we described the use of (-)-rot-2'-enonic acid (**2**) (2a-d) in an efficient conversion of natural (-)-rotenone (**1**) to (-)-deguelin (**3**). Earlier, Crombie had employed **2** in a convenient synthesis of (-)-dalpanol (**4**) from **1** (3). We have further investigated the utility of **2** as a relay from **1** to other natural rotenoids and, in this note, report a short synthesis of natural (-)-elliptone (**5**), heretofore prepared only in racemic form (4).



Treatment of **2** with osmium tetroxide and excess sodium periodate, according to Crombie's procedure for oxidative cleavage of the $\Delta^{3'}$ double bond of rot-3'-enonic

Scheme 1



acid acetate (**3**), affords a crystalline mixture of diastereomeric lactols **6**, Scheme I, in moderate (35-40%) yield (**5**). Subsequent acid-catalyzed dehydration with *p*-toluenesulfonic acid (15 mole %) in refluxing benzene gives (-)-**5** (88%), identical with the natural material in all respects (6a-c).

EXPERIMENTAL

Melting points were determined on a Thomas Hoover "Uni-Melt" capillary melting apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded at 60 MHz on a Varian EM 360 A spectrometer, with tetramethylsilane used as an internal standard. Low resolution mass spectra were obtained on a Finnigan 4023 GC/MS/DS instrument operated in the electron impact mode (70 eV). Optical rotations were measured at ambient temperature on a Rudolph Model 62 polarimeter using a 1-dm. tube. Preparative layer chromatography was performed on Brinkmann 20 X 20 cm. glass plates coated (2 mm.) with silica gel 60-F254. Column chromatography was performed on columns packed with J. T. Baker ("Baker Analyzed") silica gel powder of 60-200 mesh particle size. Microanalyses were performed by Midwest Microlabs Inc.

1,2,12,12a-Tetrahydro-2-hydroxy-8,9-dimethoxy[1]benzopyrano[3,4-*b*]furo[2,3-*h*][1]benzopyran-6(6a*H*)one (**6**).

A mixture of 2.1 g. (5.3 mmoles) of rot-2'-enonic acid (**2**) (1,2a-d), osmium tetroxide (100 mg.) and sodium periodate (8.0 g., 40.4 mmoles) in 75 ml. of dioxane and 25 ml. of water was stirred at ambient temperature for 2 hours, after which an additional 50 ml. of 3:1 dioxane-water was added and the reaction continued for 2.5 hours. The mixture was filtered and the collected solid was washed with ether (50 ml.). Dilution of the combined filtrate and washings with 500 ml. of ether caused the separation of an aqueous phase. The organic layer was washed with water, dried (magnesium sulfate) and evaporated. Chromatography of the residue (1.6 g.) over 50 g. of silica with dichloromethane-acetone mixtures (to 95:5) as eluent yielded 0.7 g. (36%) of the epimeric mixture of lactols **6** m.p. 194-196° (dichloromethane); nmr (deuteriochloroform): δ 7.90 (d, 1, $J = 9$ Hz), 6.81 (s, 1), 6.72 (d, 1, $J = 9$ Hz), 6.50 (s, 1), 6.22 (m, 1), 4.94 (m, 1), 4.68 (dd, 1, $J = 12, 3.5$ Hz), 4.18 (d, 1, $J = 12$ Hz), 3.84 (s, 3), 3.80 (s, 3), 3.20 (m, 2).

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_7$: C, 64.86; H, 4.90. Found: C, 64.69; H, 4.86.

(-)-Elliptone (**5**).

A mixture of 0.5 g. (1.4 mmoles) of the lactols **6** and 150 mg.

of *p*-toluenesulfonic acid in 30 ml. of benzene was heated to reflux under nitrogen and refluxed for 1.5 hours. After cooling to room temperature, the solution was diluted with more benzene (20 ml.), washed with 5% sodium bicarbonate and brine and dried (magnesium sulfate). Evaporation left 0.44 g. of crude elliptone as a foam, which was purified by preparative layer chromatography utilizing dichloromethane-acetone (8:2) as eluent and subsequent crystallization from 1:1 benzene-petroleum ether (30-60°), m.p. 177-178° (lit. m.p. 171-172° (6c)); $[\alpha]_D^{25}$ -18.5° (c 1.0, benzene); nmr(deuteriochloroform): δ 7.93 (d, 1, J = 9 Hz), 7.60 (d, 1, J = 2 Hz), 7.18 (dd, 1, J = 9.0, 0.5 Hz), 6.95 (dd, 1, J = 2, 0.5 Hz), 6.81 (s, 1), 6.50 (s, 1), 5.10 (m, 1), 4.76 (dd, 1, J = 12, 3.5 Hz), 4.23 (d, 1, J = 12 Hz), 3.97 (d, 1, J = 3.5 Hz), 3.84 (s, 3); ms: m/e (relative intensity) 352 (84), 191 (95), 177 (88), 160 (65), 121 (70), 93 (73), 77 (83), 76 (100).

Anal. Calcd. for C₂₀H₁₆O₆: C, 68.16; H, 4.58. Found: C, 68.16; H, 4.42.

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