Compounds 1b-e prepared from eugenol (1a) were submitted to ozononation in methanol at 0°C, giving the 3-alkyl muconic acid dimethyl esters (2b-e). These were reduced to the corresponding 3-alkyl dimethyl esters of adipic acid (3b-e).

As part of a program of study of abundant natural products available in Brazil we turned our attention to the transformation of eugenol (1a) into aliphatic derivatives. Compounds 1b-e were prepared by usual methods from 1a and were submitted to ozononation in methanol.

The products from 1b-e were purified by silica gel chromatography and characterized as the 3-alkyl muconic acid dimethyl esters 2b-e. In all cases the yield was about 45% and the H NMR spectra showed the presence of a mixture of \( \Delta^2 \), \( \Delta^2 \), \( \Delta^2 \), and \( \Delta^2 \) isomers. These mixtures furnished in quantitative yield the corresponding adipates 3b-e by hydrogenation in EtOAc in the presence of Pd/C.

The derivatives 1f-g did not yield muconic acid derivatives when submitted to our ozononation condition. For 1f the main product was the methyl ester of veratic acid (20%) while for 1g a complex mixture of products was formed.

With the present method it is possible to prepare in 45% yield 3-alkyl muconic acid dimethyl ester and 3-alkyl adipic acid dimethyl ester. These aliphatic compounds can be utilized as interesting intermediates in synthetic works.

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References and notes


2. 1a = 1a', (CH3)2SO4, NaOH, H2O (87%); 1a = 1b, H2, AcOEt, Pd/C (100%); 1a = 1c, BF3·Et2O/NaBH4/THF, NaOH/H2O2/H2O, AcO/DMAP (79%); 1a = 1d, O2/AcOH, Zn, NaBH4/CH3OH, AcO/DMAP (82%); 1a = 1e, BF3·Et2O/NaBH4/THF, Jones, CH3N2/Sc2O3 (70%); 1a = 1f, KOH, CH3OH/O3, HOAc/Zn(OAc)2; 1a = 1g, NaBH4, CH3OH/Ac2O, DMAP (96%).


4. Depending on the experiment purified products containing slight different proportions of geometrical isomers \( \Delta^2 \) and \( \Delta^2 \) were obtained. This fact permits the interpretation of the H NMR spectra of the mixtures. The hydrogen atoms attached at C2 and C3 show identical chemical shifts and multiplicities in both geometrical isomers, while for hydrogen atoms at C2 and the methoxyl groups the chemical shifts differ. The same was observed for 2b-e. 2b (\( \Delta^2 \), \( \Delta^2 \)) (100 MHz, CDCl3) \( J = 7.06 \text{Hz} \), 1.26 (2H, d, \( J = 7.06 \text{Hz} \)), 1.69 (2H, d, \( J = 7.06 \text{Hz} \)), 2.58 (2H, td, \( J = 7.06 \text{Hz} \), 1.60 (2H, m, 0.88 (2H, t, \( J = 7.06 \text{Hz} \)), 2b (\( \Delta^2 \), \( \Delta^2 \)) (100 MHz, CDCl3) \( J = 7.06 \text{Hz} \), 1.26 (2H, d, \( J = 12.0 \text{Hz} \)), 2.58 (2H, m, 0.88 (2H, t, \( J = 7.06 \text{Hz} \)), 2.86 (2H, m, 0.88 (2H, t, \( J = 7.06 \text{Hz} \))), 3.46 (3H, s, CO2CH3), 3.84 (3H, s, CO2CH3), 2.48 (2H, m, 0.88 (2H, t, \( J = 7.06 \text{Hz} \))).