Synthesis of 2,3 : 7,8-Bis(polymethylene)-4*H*,9*H*-benzo[1,2-*b* : 4,5-*b*']dipyrans and Their Oxidation to the Corresponding Benzodilactones[1)]

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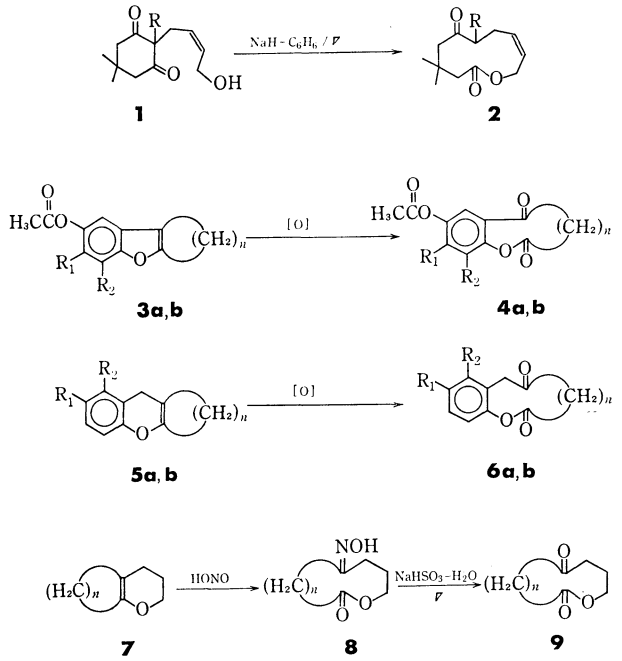
(Received June 27, 1977)

Four members of a new series of the title benzodipyrans have been synthesized through the alkylation of the pyrolidine-enamines of 6,7,8- and 12-membered cycloalkanones with 2,5-bis(dimethylaminomethyl)hydroquinone, followed by hydrolysis and subsequent cyclization of the intermediate products. Oxidation of these benzodipyrans with *m*-chloroperbenzoic acid (MCPBA) afforded the corresponding benzodilactones in 10—65% yield, the rest of the material being a mixture of hydroxylated carbonyl compounds.

We have recently reported the synthesis of several medium ring and macrocyclic keto lactones (**2**, **4**, **6**, **9**) by the intramolecular reverse Dieckmann reaction of 2,2-dialkyl-5,5-dimethyl-1,3-cyclohexanediones (**1**) as well as by various oxidative procedures, as shown in Chart 1.[2)] Although these synthetic keto lactones have only a distant resemblance with the natural antibiotic macrolides,[3)] yet it is noteworthy that a majority of these compounds as well as some of the synthetic intermediates have shown *in vitro* biological activity against one or the other of the following microorganisms: *Staphylococcus aureus*, *Escherichia coli*, *Bacillus megatherium*, *Candida albicans*, and *Leptomonas pessoai*.[4)] These promising bioassays encouraged us to explore the synthesis of symmetrical benzodilactones (**16**) from the title compounds (**15**), by procedures successfully developed in the case of benzo- and naphtho-fused keto lactones **6**.[2c)] We now report the results of this investigation.

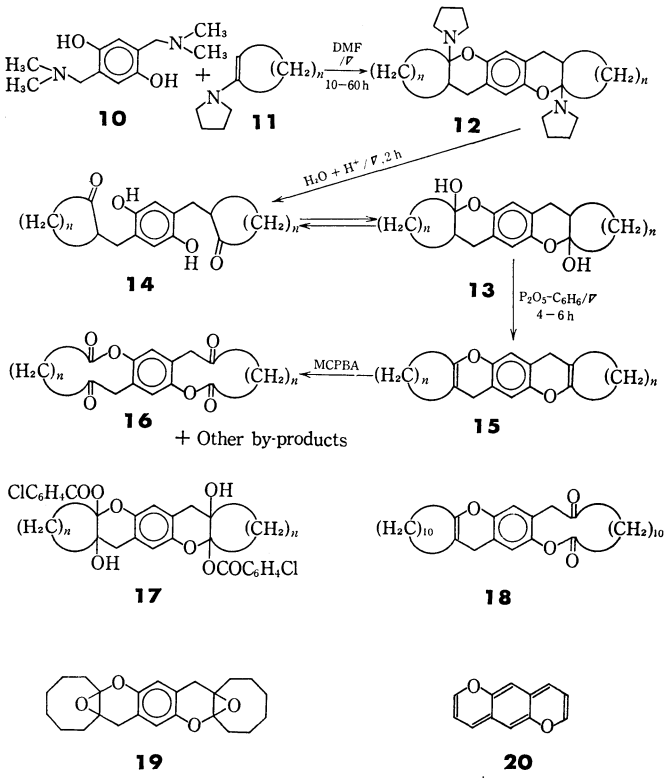
As the literature search in the ring index[5)] and chemical abstracts revealed that 4*H*,9*H*-benzo[1,2-*b*: 4,5-*b*']dipyran as well as its derivatives have not been described, we patterned the synthesis of the title compounds **15** after a successful route developed in the case of benzo- and naphthopyrans (**5a**,**b**), through the enamine alkylation of the Mannich bases derived from phenol and 2-naphthol.[2c,6a)] In contrast to the use of mono *o*-phenolic Mannich bases for the above purpose, there is no mention of the use of *bis* Mannich bases, derived from dihydric phenols, for the preparation of the corresponding dipyrans.[6)] We hereby describe that 2,5-bis(dimethylaminomethyl)hydroquinone[7)] (**10**) can be successfully employed for the synthesis of the title compounds **15**, as shown in Chart 2.

Although condensation between the Mannich base **10** and the enamine (**11**; n=4) could not be carried out in dioxane, according to the original method of Von Strandtmann,[6a)] the desired reaction could be successfully conducted in *N*,*N*-dimethylformamide (DMF).[2c)] The duration of reaction as well as its temperature had to be carefully controlled to obtain optimal results for



a: R_1=R_2=H, b: R_1=R_2=(CH=CH)$_2$,; n=4,5,6,10

Chart 1.



n=4,5,6,10

Chart 2.

each enamine. In most of the cases, the intermediate amino compound (**12**) was not isolated and was hydrolyzed *in situ* at the end of first step. However, in the case of enamine derived from cyclododecanone (**11**; $n=10$), the intermediate adduct (**12**; $n=10$) precipitated from the reaction mixture and was obtained as a coarse powder in 57% yield. Its hydrolysis in a two phase system containing benzene, water, and acetic acid, furnished the product (**14**; $n=10$) in 95% yield. On the other hand, the same product (**14**; $n=10$) could be obtained, in a slightly lower yield of an inferior quality, by direct hydrolysis of the reaction mixture.

Attempted extension of the present condensation to enamine derived from acetophenone[8] resulted in an intractable mixture of products.

One would expect an equilibrium between the cyclic form (**13**) and the acyclic form **14**. Moreover, the former could form diastereoisomers. In fact, only one of these compounds was present, in the solid state, entirely in the cyclic form (**13**; $n=4$), as evidenced by the absence of carbonyl absorption in its infrared spectrum, while the rest of the compounds ($n=5$, 6, 10) showed strong absorptions both in the OH and CO regions. The carbonyl absorption in these compounds (1681—1695 cm^{-1}) is shifted to lower wave numbers due to hydrogen bonding.[9] Attempted dehydration of these compounds in refluxing dioxane, containing catalytic amount of *p*-toluenesulfonic acid or phosphorus pentaoxide, proceeded in poor yield and was unsatisfactory. However, dehydration in benzene employing 2 molar equivalent of phosphorus pentaoxide furnished the desired benzodipyrans (**15**; $n=4$—6, 10) in 60—90% yield. The characteristic infrared absorption of these compounds (1692—1706 cm^{-1}) is in agreement with that observed in the corresponding benzopyran series.[2c]

One particular difficulty encountered in the present work was the poor solubility of most of the compounds described here, in the common organic solvents. Moreover, these compounds, especially the benzodipyrans **15**, suffer autoxidation while in solution. Therefore, crystallization of **14** and **15** was carried out in solutions containing catalytic amount of hydroquinone. Even so, mother liquors of benzodipyran (**15**; $n=10$) afforded, after silica gel column chromatography, a small quantity of a pure product which was characterized as keto lactone **18**, on the bases of its infrared (1751, 1712, 1695 cm^{-1}), and mass spectra. Similar autoxidations have already been observed in the benzo- and naphthopyran **5a**,**b** series.[2c]

As *m*-chloroperbenzoic acid (MCPBA) had proved to be the best reagent for the preparation of keto lactones **6a**,**b** from the corresponding benzo- and naphthopyrans **5a**,**b**[2c] the same reagent was used, with moderate success, in the present series. However, as the benzodipyrans **15** have two sites of reaction, the half oxidized and several other expected by-products, such as hydroxy ester (**17**), the corresponding tetrol, and combinations thereof become possible.[10] This made the isolation and purification of the desired products rather difficult in the present work. Under careful conditions, the desired dilactones **16** were obtained in 10—65% yields; the rest of the material being a mixture of products, showing both hydroxyl and carbonyl absorptions in the infrared spectrum.

Mechanistic considerations on the oxidation of cyclic enol ethers by MCPBA suggest that for optimal results, competitive reactions of the intermediate epoxide with *m*-chlorobenzoic acid and water be avoided.[10] Borowitz has attained this objective by employing 50% excess of the peracid in a limited volume of the solvent (CH_2Cl_2), the *m*-chlorobenzoic acid precipitates out of the reaction mixture as formed, because it is much less soluble than the corresponding peracid.[10] In an attempt to improve the present procedure, we treated benzodipyran (**15**; $n=6$) with MCPBA in the presence of potassium carbonate[11] and obtained the corresponding diastereoisomeric bis-epoxides (**19**; TLC, IR, NMR) as the exclusive products ($\approx$100%). Attempted posterior cleavage of this epoxide with MCPBA[10] or periodic acid in tetrahydrofuran[12] resulted in a complex mixture of products from which the isolation of the desired keto lactone appeared difficult (TLC).

Similarly, while the dipyran (**15**; $n=10$) was recovered unchanged from an attempted oxidation with potassium permanganate in acetone at room temperature, it gave complex mixture of products when ozonolyzed[2b,c] or oxidized with ruthenium tetraoxide ($RuCl_3$–$NaIO_4$) in dichloromethane–water.[13]

Due to poor solubility in most of the organic solvents, we could not obtain the NMR spectra of benzodilactones **16**. However, these products have been fully characterized by their elemental analysis, infrared and mass spectra. The molecular and fragmentation ions of these compounds are in accord with their structure, but the details of mass spectral studies will be reported elsewhere, along with other related series.

Experimental

Melting points (°C) are uncorrected and were determined on a Kofler block or, when mentioned, in capillary tube sealed under reduced pressure. The latter mps are sharper and more reproducible. The infrared (IR) spectra were taken as KBr discs on a Perkin Elmer 137 instrument and the absorption maxima (ν_{max}) are reported in wave numbers (cm^{-1}). ^1H NMR spectra were recorded on a Varian A60-D (60 MC) spectrometer and the reported values (δ ppm) are relative to internal TMS. As usual, s=singlet, m=multiplet, *etc.* The mass spectra were obtained on a Varian CH-7-spectrometer and the details will be published elsewhere; only the molecular ions (M^+) are reported here.

Progress of reaction was followed by thin layer chromatography (TLC) on silica gel G plates run in benzene, containing 5—10% ethanol. 2,5-Bis(dimethylaminomethyl)hydroquinone was prepared according to the procedure described by Caldwell and Thompson.[7] Enamines of cycloalkanones were prepared by the azeotropic method described by Stork *et al.* and in other literature references.[14] Nomenclature and numbering of the heterocyclic compounds is based on that described for the benzo[1,2-*b*: 4,5-*b'*]dipyran (**20**) in the Ring Index[5] and the Chemical Abstracts.[15]

*Condensation of 2,5-Bis(dimethylaminomethyl)hydroquinone (**10**) with Enamines (**11**; n=4,5,6,10).* General Procedure: A solution of the Mannich base (**10**; 10 mmol) and the desired

enamine (20 mmol) in *N*,*N*-dimethylformamide (40 ml) was heated in an oil bath (130—140 °C) during 10—60 h, while a slow stream of nitrogen was bubbled through the reaction mixture. At the end of the reaction, when the evolution of dimethylamine became neglegible, hot water (20 ml) was added, pH of the medium adjusted to 5—6 with 1 M hydrochloric acid and the heating continued another 1—2 h. The cooled reaction mixture was elaborated as described under individual compound.

*2,7-Dihydroxy-3,4,8,9-tetrahydro-2,3 : 7, 8-bis(tetramethylene)-2*H,7H-*benzo*[*1,2*-b: *4,5*-b']*dipyran* (**13**: n=*4*). The reaction between the Mannich base (**10**) and enamine (**11**; *n*=4) was complete in 10—12 h. The final product precipitated from the reaction mixture during the hydrolysis step and was filtered off. It was sparingly soluble in the common organic solvents: methanol, ethanol, 1-propanol, acetone, ethyl acetate, chloroform, carbon tetrachloride, benzene, ether, tetrahydrofuran, dioxane, glyme, *etc.* It was purified by refluxing in benzene–ethanol and filtering hot to obtain a faintly yellow powdery solid (80% yield), mp 221—223 °C (dec); ν_{max} 3436 and small absorption at 1672. Analytical sample was prepared by dissolving a small quantity in a large excess of hot 1,2-dichloroethane–ethanol and filtering hot. The filtrate was concentrated on a rotary evaporator till turbidity appeared, when it was allowed to crystallize affording white fine crystals, mp 232—234 °C (dec), with softening ≈226 °C; ν_{max} 3448; no absorption in the CO region. TLC of this compound (one spot only) revealed it to be most probably a single diastereomer. Found: C, 72.53; H, 8.08%. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93%.

2,5-Bis[*(2-oxocycloheptyl)methyl*]*hydroquinone* (**14**; n=*5*). Enamine (**11**; *n*=5) and the Mannich base (**10**) were allowed to react for 30 h. After hydrolysis, the cooled reaction mixture was extracted with chloroform and work-up as usual to obtain a solid (60%), which was crystallized from 1,2-dichloroethane–ethanol yielding shiny plates, mp 232—235 °C (dec); ν_{max} 3448, 1686. Found: C, 73.63; H, 8.43%. Calcd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44%.

2,5-Bis[*(2-oxocyclooctyl)methyl*]*hydroquinone* (**14**; n=*6*), was obtained in a manner just described above. Crystallization from benzene–ethanol afforded the pure product (47%) as fine white crystals, mp 228—230 °C (dec); ν_{max} 3436, 1681. Found: C, 74.46; H, 8.92%. Calcd for $C_{24}H_{34}O_4$: C, 74.58; H, 8.87%.

2,5-Bis[*(2-oxocyclododecyl)methyl*]*hydroquinone* (**14**; n=*10*), separated as an oily-solid from the reaction mixture. The supernatant was decanted and the product washed with water, followed by petroleum ether (40—60 °C). The residue was dissolved in benzene and treated with petroleum ether (40—60 °C) to afford a fine crystalline solid (50%). Further purification in the same solvent system furnished fine white crystals, mp 206—209 °C (dec); ν_{max} 3509, 1695. Found: C, 76.95; H, 10.09%. Calcd for $C_{32}H_{50}O_4$: C, 77.06; H, 10.10%.

*2,7-Di(1-pyrrolidinyl)-3,4,8,9-tetrahydro-2,3: 7,8-bis(decamethylene)-2*H,7H-*benzo*[*1,2*-b: *4,5*-b']*dipyran* (**12**; n=*10*). After ≈12 h of reaction between the Mannich base (**10**) and the enamine (**11**; *n*=10), a solid began to separate. At the end of reaction (60 h), the hydrolysis step was omitted. The reaction mixture was cooled, filtered and the product washed with benzene. On refluxing in a mixture of benzene–ethanol and filtering hot, the pure amino-adduct (**12**; *n*=10) was obtained as a coarse powder (57%), mp 200—206 °C (dec); ν_{max} 2959, 1497, 1458. This product (1 mmol) was refluxed (N_2) in a mixture of water (10 ml), acetic acid (2 ml) and benzene (20 ml), containing catalytic amount of hydroquinone. After ≈2 h, a solid began to float in the benzene layer. After a reflux of 6 h, the reaction mixture was cooled, the product filtered and washed successively with water and ethanol. The dry product (95%), mp 206—209 °C (dec) had infrared spectrum identical with the product (**14**; *n*=10) described above.

*Preparation of 2,3: 7,8-Bis(polymethylene)-4*H,9H-*benzo*[*1,2*-b: *4,5*-b']*dipyranes* (**15**; n=*4,5,6,10*). A suspension of diol **13** (*n*=4) (10 mmol) or a solution of the hydroxy ketones **14** (*n*=5,6,10) (10 mmol) in benzene (300—600 ml), containing phosphorus pentaoxide (20 mmol) and hydroquinone (50 mg), was refluxed (N_2) 2—6 h, till there was no more of the starting material (TLC). The cooled reaction mixture was decanted and allowed to stand over sodium carbonate decahydrate for 1 h, when the solvent was evaporated to obtain the desired product: **15** (*n*=4) was crystallized from benzene–ethanol to obtain faintly yellow, shiny plates (63%), mp 205—207 °C (dec); ν_{max} 1706; δ (CS_2) 1.5—2.4 (m, $8CH_2$), 3.1 (s, benzylic $2CH_2$), 6.3 (s, 2H aromatic). Found: C, 81.73; H, 7.54%. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53%.

15 (*n*=5) was obtained as yellowish shinyl plates (85%) from the same solvent system, mp 212—217 °C (dec); 234—235 °C (dec) in a sealed capillary tube; ν_{max} 1704. Due to its sparing solubility in $CHCl_3$, CCl_4, CS_2, and acetone, it was not possible to obtain its NMR spectrum. Found: C, 82.14; H, 7.88%. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13%.

15 (*n*=6) was also crystallized from the same solvents affording (61%) faintly yellow needles, mp 172—180 °C (dec); 188—190 °C in a sealed capillary tube; ν_{max} 1701; δ (CS_2) 1.4—1.8 (m, $8CH_2$), 1.9—2.4 (m, allylic $4CH_2$), 3.2 (s, benzylic $2CH_2$), 6.3 (s, 2H aromatic). Found: C, 82.45; H, 8.67%. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63%.

15 (*n*=10) was crystallized from chloroform to furnish (90%) shinyl cottony needles, mp 180—195 °C (dec); 212—213 °C in a sealed capillary tube; ν_{max} 1692; δ (CS_2) 1.2—1.8 (m, $16CH_2$), 1.9—2.4 (m, allylic $4CH_2$), 3.2 (s, benzylic $2CH_2$), 6.3 (s, 2H aromatic). Found: C, 83.04; H, 10.06%. Calcd for $C_{32}H_{46}O_2$: C, 83.06; H, 10.02%.

The hydroquinone derivatives **14** and the benzodipyranes **15** undergo autoxidation during prolonged heating while in solution. Consequently, these compounds were recrystallized as quickly as possible and in solutions containing catalytic amount of hydroquinone. Even so an oxidized product was isolated from the mother liquors of benzodipyran **15** (*n*=10), as described below.

Isolation of Benzopyran Lactone (**18**). Mother liquors of benzodipyran **15** (*n*=10) (1.3 g) were chromatographed on a silica gel (Merck; 80 g) column, eluted with benzene containing successively increasing amount (0—3%) of ethanol. 25 fractions of 20 ml were collected and fractions 10—15 combined on the basis of TLC examination. Recrystallization from absolute ethanol gave off-white, fluffy solid (≈15 mg), mp 158—160 °C; ν_{max} 1751, 1712, 1695; *m/e* 494 (M^+).

Oxidation of Benzodipyrans (**15**) *to Benzodilactones* (**16**). To obtain consistent results, the *m*-chloroperbenzoic acid (MCPBA) bought from the Aldrich Chemical Company (85%) was dried over $CaCl_2$, under reduced pressure, while the peracid bought from BDH was used without any further treatment. The following oxidation procedure is illustrative for the series.

Dilactone **16** (n=*4*): The solid benzodipyran (**15**; *n*=4; 147 mg, 0.5 mmol) was added, in small portions during 15—20 min, to a stirred solution of MCPBA (3 mmol, 0.52 g) in dichloromethane (6 ml), kept around 15—20 °C by a cold water bath and protected by a drying tube. Soon a white solid began to separate and stirring was continued till (1 h) all the starting material had been consumed (TLC). The reaction mixture was filtered and the solids washed with

carbon tetrachloride. The filtrate was evaporated to dryness and triturated with absolute ethanol to dissolve the soluble products, leaving an insoluble portion (96 mg). Similar treatment of the filter-cake gave 20 mg of an insoluble product. Both these insoluble residues were combined (116 mg) on the bases of their IR spectra, TLC, and mp 215—220 °C (dec). This product was sparingly soluble in common organic solvents. It was purified by a short reflux in a mixture of 1,2-dichloroethane–ethanol and filtering while hot, affording shiny plates (96 mg; 54%), mp 218—221 °C (dec). An analytical sample was prepared by recrystallization of a small portion from a large excess of the same solvent mixture, yielding thin plates, mp 224—231 °C (dec); 191—194 °C (dec) in a sealed capillary tube; ν_{max} ≈3448 (overtones), 1754, 1706; *m/e* 358 (M^+). Found: C, 66.89; H, 6.15%. Calcd for $C_{20}H_{22}O_6$ (358): C, 67.02; H, 6.19%.

Dilactone ***16*** *(n=5)*, was obtained in a similar manner to afford white needles (60%), mp 251—254 °C (dec), with softening ≈247 °C; ν_{max} ≈3472 (overtones), 1738, 1706; *m/e* 386 (M^+). Found: C, 68.14; H, 6.68%. Calcd for $C_{22}H_{26}O_6$ (386): C, 68.38; H, 6.78%.

Dilactone ***16*** *(n=6)*, was obtained as shiny white needles (65%), mp 260—261 °C (dec), with softening ≈233 °C; ν_{max} ≈3472 (overtones), 1745, 1709; *m/e* 414 (M^+). Found: C, 69.37; H, 7.32%. Calcd for $C_{24}H_{30}O_6$ (414): C, 69.55; H, 7.30%.

Dilactone ***16*** *(n=10)*, was obtained as white needles (10%) from absolute ethanol, mp 238—239 °C (dec); ν_{max} ≈3484 (overtones), 1754, 1712; *m/e* 526 (M^+). Found: C, 73.18; H, 8.96%. Calcd for $C_{32}H_{46}O_6$ (526): C, 72.97; H, 8.80%.

*Preparation of the Bis-epoxide (**19**).* To a suspension of MCPBA (2 mmol) and anhydrous potassium carbonate (10 mmol) in dichloromethane (5 ml) was added slowly a suspension of the benzodipyran (**15**; *n*=6) (116 mg, 0.33 mmol) in the same solvent (2 ml), with stirring at room temperature. After 6 h the reaction mixture was filtered and the solids washed with carbon tetrachloride. The filtrate was washed with water, dried over anhydrous sodium sulfate and evaporated to afford a crystalline product (116 mg), mp 129—135 °C; ν_{max} 2941, 1513, 1464; $\delta(CDCl_3)$ 1.2—2.6 (m, 12-CH_2), 3.0—3.6 (two superimposed broad AB quartets, benzylic 2CH_2; separated due to the two forms of the bis-epoxide), 6.5 (s, 2H aromatic). Attempted recrystallization of this product resulted in the opening of the epoxides (TLC, IR).

The above experiment repeated in the presence of a limited quantity of potassium carbonate (1.33 mmol), gave only the above epoxides.

*Attempted Further Oxidation of the Epoxide (**19**) with MCPBA.* A solution of the epoxide (64 mg, 0.15 mmol) in dichloromethane (2 ml) was added to a solution of the per acid (0.5 mmol) in the same solvent (2 ml). The reaction mixture was stirred at room temperature for 2 h, when it was diluted with chloroform and washed successively with 0.5 M sodium hydroxide and water. Drying and evaporation furnished a solid (55 mg) consisting of a complex mixture of products (TLC).

Similarly, attempted oxidation of the epoxide mixture (**19**) with periodic acid in tetrahydrofuran resulted in a complex mixture of products.

We thank Drs. O. E. Edwards and H. Séguin of the NRC, Ottawa, Canada, for some of the elemental analysis and H. B. Machado of the IE-UFMG, Belo Horizonte, Brazil, for the mass spectra of benzodilactones.

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