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Synthesis of Pipataline

Yoshimori OMOTE, Hinako TAZAWA, Yoshimori FUJINUMA and Noboru SUGIYAMA

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo

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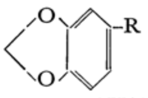
Atal *et al.*[1)] have recently reported the isolation of pipataline from *Piper peepuloides* Roxb. and proposed that its structure is 1-(3,4-methylenedioxyphenyl)-1-dodecene (I). In connection with our studies[2-4)] of melanin precursors we have synthesized pipataline (I) as a model catechol melanin precursor. The synthesis of pipataline consists of the addition of *n*-undecyl magnesium iodide to piperonal and the removal of the water.

Heating *n*-undecyl magnesiumiodide and piperonal under reflux for one hour gave an alcohol (II) as a colorless liquid, bp 200—220°C/10^{-3}—10^{-4} mmHg, this alcohol was then dehydrated, by aluminum oxide at 200°C for 30 min. The product (I) was extracted with ether and recrystallized from petroleum ether - ethanol to afford colorless crystals, mp 37°C. The spectral data of UV, IR and NMR, are in good agreement with those of natural pipataline.[1)]



I, R= $CH{=}CH(CH_2)_9CH_3$
II, R= $CH(OH)CH_2(CH_2)_9CH_3$

Experimental

***n*-Undecyl Iodide.** A mixture of *n*-undecyl alcohol (6 g), iodine (5.4 g), and red phosphorus (0.6 g) was heated at 110—120°C for 6 hr and then kept overnight at room temperature. The ethereal extract from the reaction mixture was washed with a 10% aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. The removal of the solvent gave *n*-undecyl iodide (6.2 g), which was then distilled at

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1) C. K. Atal, K. L. Dhar and A. Pelter, *Chem. & Ind.*, **1967**, 2173.

2) Y. Omote, U. Kurabayashi, A. Momose and N. Sugiyama, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **88**, 80 (1967).

3) Y. Omote, H. Yasuda, Y. Fujinuma and N. Sugiyama, *ibid.*, **89**, 594 (1968).

4) Y. Omote, Y. Fujinuma and N. Sugiyama, *Chem. Commun.*, **1968**, 190.

104—110°C/2 mmHg (lit.[5] 125°C/3 mmHg).

1-(3,4-methylenedioxyphenyl)-1-dodecanol (II). Piperonal (2.1 g) dissolved in ether (20 *ml*) was added to *n*-undecyl magnesiumiodide, prepared from magnesium (0.5 g) and *n*-undecyl iodide (3 g) in ether (25 m*l*), under cooling with ice water. The mixture was heated with stirring under reflux for one hour. To the mixture there was then added 3 N hydrochloric acid under cooling. The etheral layer from the acidified mixture was washed with a 40% aqueous sodium bisulfite and then with an aqueous sodium bicarbonate solution. After drying over anhydrous sodium sulfate, the solvent was evaporated, and to the residue there was added ethanol. Then the undissolved precipitates were filtered off and the ethanol solution was evaporated to give the alcohol (II) (0.7 g), which was distilled at 200—220°C/10^{-3}—10^{-4} mmHg in a molecular still. Found: C, 75.54; H, 9.85%. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87%. IR ν (liq. film) 3400, 2925, 1610, 1245 and 1043 cm^{-1}. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm 234, 288.

From the insoluble precipitates described above there was obtained a hydrocarbon (0.3 g), mp 43—44°C, mol wt (Rast)=341, IR ν^{KBr} 2900, 2840, 1470 and 718 cm^{-1}. This seems to be docosane (mp 47°C), probably resulting from the reaction of *n*-undecyl magnesiumiodide with *n*-undecyl iodide.

Pipataline (I). The alcohol (II) (0.35 g) was dehydrated by activated aluminum oxide (0.18 g) under a nitrogen atmosphere at 180—200°C for 30 min. The reaction mixture was then extracted with ether. The removal of the solvent and recrystallization from petroleum ether - ethanol gave pipataline as colorless crystals (50 mg), mp 37°C (lit.[1] 38°C). Found: C, 78.62; H, 9.78%. Calcd for $C_{19}H_{28}O_2$: C, 79.12; H, 9.79%. IR ν^{KBr} 2920, 2850, 1605, 1248 and 1040 cm.$^{-1}$ UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε) 262 (12700), 269 (12400) and 307 (6100). NMR τ ($CDCl_3$) 3.12(1H), 3.23 (2H, aromatic), 3.40 (1H,d,J=15 cps, olefinic), 3.7—4.1 (complex pattern, olefinic), 4.05 (methylendioxy), 7.6—8.0 (allylic), 8.2—8.9 (methylene), 8.95—9.3 (methyl).

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[5] "Beilsteins Handbuch der Organischen Chemie," (**1**), 66.