tion to a small vol. gave transparent crystals on standing which were recrystallized from MeOH, (0.023 g), mp 233–235°; IR $\nu_{max}^{KBr}cm^{-1}$: 3290, 1610, 890, 840, and 790; ^1H NMR (acetone-d_6): δ 1.55 (3H, *t*, $J=7$ Hz), 2.45 (3H, *s*), 2.55 (3H, *s*), 3.13 (2H, *br s*), 3.33 (2H, *q*, $J=7$ Hz), 7.17 (1H, *s*), 7.22 (1H, *d*, $J=9$ Hz), 7.45 (1H, *d*, $J=9$ Hz), 7.75 (1H, *d*, $J=9$ Hz), and 8.35 (1H, *d*, $J=9$ Hz); MS *m/z*: 266 $[M]^+$, 251, 236, 207, 189, 165, 118.

Conversion of juncusol to dehydrojuncusol. A mixture of juncusol diacetate (0.06 g) prepared according to ref. [3] and DDQ (0.06 g) in C_6H_6 (5 ml) was refluxed for 12 hr. After cooling, filtration, and evapn, the residue was directly hydrolysed in 2% KOH in MeOH (3 ml). The product after usual work-up gave a solid which proved to be a mixture juncusol and dehydrojuncusol when compared with authentic samples of these two compounds on TLC. Therefore, the product was subjected to PLC and the lower band, the minor product, after recovery and crystallization froL EtOAc–*n*-C_6H_{14} was found to be identical (mmp, IR and MS) to the natural dehydrojuncusol.

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AN IMPROVED HIGH YIELD SYNTHESIS OF DEHYDRODIEUGENOL

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Key Word Index—Neolignan; oxidative dimerization of eugenol.

Abstract—The oxidative coupling of eugenol with potassium ferricyanide in ammonium hydroxide produces the known neolignan, dehydrodieugenol in almost quantitative yield.

INTRODUCTION

Because of the importance of phenolic oxidative coupling reactions, classified as biogenetic type synthesis [1], oxidative coupling reactions have been the subject of most of the natural product chemists in this field. Amongst the known oxidizing agents employed for the last three decades [2], iron compounds, such as $FeCl_3$ and $K_3Fe(CN)_6$ are the most widely used phenol oxidants [3]. The ferricyanide–ferrocyanide is an unique system, the redox potential of which is unaffected by pH. Except in strong acid solutions, its oxidizing capacity is somewhat superior in alkaline than in acidic medium [4]. In the half reaction, the oxidizing species is a complex electron abstracting ion, which mimics biological systems of cytochrome type, where a 'one

$$Fe(CN)_6^{3-} + e \rightarrow Fe(CN)_6^{4-}$$

electron transfer' is involved. The primary action of potassium ferricyanide as a 'one electron abstracter' on a phenol, such as PhOH, is to generate the phenoxy radical. Through spreading the odd electron by resonance

over the *ortho–para* positions of the aromatic ring, the radical suffers homolytic coupling to products depending on the substitution pattern. This explains the formation of different types of phenolic compounds that are formed from such dimerization reactions [1–3].

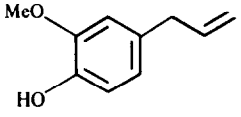
RESULTS AND DISCUSSION

Most of the known methods of oxidative dehydrogenation yield reaction mixtures of products which are difficult to isolate in pure forms. Our interest naturally, was to find a simplified reaction condition that would couple a phenol, such as eugenol (**1**), quantitatively into its dimer, dehydrodieugenol (**2**), by a one step reaction under mild conditions.

The modified procedure consists of the dropwise addition at room temperature of an aqueous solution of the iron complex $K_3Fe(CN)_6$, into a dilute solution of the phenol in acetone and ammonium hydroxide, a reaction which is at variance with the known methods [3]. After neutralizing the reaction mixture with cold dilute hydrochloric acid, at room temperature, the precipitated product was filtered, washed with distilled water and dried. The crude product was recrystallized from absolute ethanol as colourless plates. The identity of the product was established by comparison of its ^{13}C NMR, ^1H NMR and IR spectra with the known spectral data [5].

EXPERIMENTAL

Commercial eugenol (4-hydroxy-3-methoxyallylbenzene) was used without any further purification. Mps: uncorr. ^1H NMR: TMS as int. ref.



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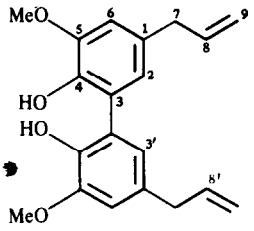

2

Dehydrodieugenol ($\Delta^{8,8'}$-4, 4′-*dihydroxy*-5,5′-*dimethoxy*-3,3′-*neolignan*) [6,7]. In a typical experiment, eugenol (15.4 g, 0.094 mol) was dissolved in technical grade Me_2CO (300 ml) and H_2O (150 ml), to which was added 25% NH_4OH (200 ml) and the mixture stirred for 10 min until a green-yellow colour developed. To this soln was then added dropwise a saturated aq. soln of $K_3Fe(CN)_6$ (31.0 g, 0.094 mol) over a period of 4–5 hr. More NH_4OH (200 ml) was then added to maintain the alkalinity in the reaction medium and the mixture stirred overnight. The reaction was neutralized by adding dil. HCl at room temp. and it was allowed to stand for 1 hr. A large quantity of solid pptd which was filtered, washed three times with distilled H_2O and dried (yield: 14.8 g, 98%). Recrystalization from absolute EtOH gave colourless plates, mp 105–106° (lit. [5] 106–107°), a sample prepared by the ferric chloride method [8] did not depress the mixed mp. ^1H NMR ($CDCl_3$/TMS): δ3.33 ($J = 6.5$ Hz, CH_2–7,7′), 3.79 (2xOMe), 4.96–5.18 (4H,*m*, CH_2-9,9′), 6.14 (2H,*m*,CH-8,8′), 6.69, 6.73 (CH-2,2′, CH-6,6′, CH-6,6′); ^{13}C NMR (20.0 MHz, $CDCl_3$):δ 40.02 (C-7, C-7′), 56.02 (2xOMe), 110.84 (C-6, C-6′), 115.59 (C-9, C-9′), 123.28 (C-2, C-2′), 124.75 (C-3, C-3′), 131.82 (C-1, C-1′), 137.79 (C-8, C-8′), 141.23 (C-4, C-4′), 147.44 (C-5, C-5′) and IR ν_{max}^{KBr} cm^{-1} 3360, 3280, 1600, 1495, 1460, 1260, 1150, 1050; acetate, oil, ^{13}C NMR (20.0 MHz, $CDCl_3$): δ 20.37 (2xCOMe), 40.03 (C-7, C-7′), 55.91 (2xOMe), 112.17 (C-6, C-6′), 116.08 (C-9, C-9′), 122.55 (C-2, C-2′), 131.34 (C-3, C-3′), 135.96 (C-8, C-8′), 138.04 (C-4, C-4′), 151.23 (C-5, C-5′) and 168.57 (2xOCOMe); IR ν_{max}^{KBr} cm^{-1}: 3010, 2945, 2850, 1770, 1640, 1590, 1470, 1370.

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