The Synthesis of (±)-Bakuchiol

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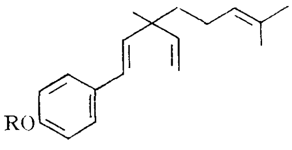
BAKUCHIOL is a monoterpenoid phenol occurring in the seeds of *Psoralea corylifolia* Linn. It has recently been shown, on the basis of spectroscopic and degradative evidence,[1] to have the structure (Ia). We report a synthesis of racemic (Ia) which confirms the structure of bakuchiol.

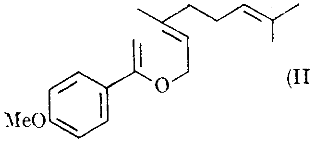
p-Methoxyacetophenone diethyl ketal was heated with geraniol and mercuric acetate in Diglyme at 160° for 2 hr. in order to effect the preparation and *in situ* Claisen rearrangement of (II). The product was the expected ketone (IIIa), 50%, the structure of which is confirmed by its spectral properties, $\lambda_{\max}$ (ethanol) 275 mμ (ϵ 12,400), $\nu_{\max}$ (film) 1688 and 1670 (C=O), 1642 (CH_2=CH), 1610 and 1515 (aryl), 1260 and 1035 (MeOAr), 1003 and 915 (CH_2=CH), 845 and 832 cm.$^{-1}$; n.m.r. (Perkin-Elmer 60, CCl_4): A_2B_2 quartet (4H) J = 9 c./sec. at τ 2·18 and 3·18 (aryl), doublet of doublets (1H) at τ 3·9—4·4 (C*H*=CH_2), multiplet (3H) at τ 4·8—5·35 (C*H*=C< and CH=CH_2), singlet (3H) at τ 6·30 (CH_3O), singlet (2H) at τ 7.20 (ArCO·CH_2·C), singlet (3H) at τ 8·86 (CH_3·C) and two singlets at τ 8·38 and 8·45 [CH=C(CH_3)$_2$] superposed on a multiplet at τ 7·9—8·7 (CH_2·CH_2).

Reduction of (IIIa) with sodium borohydride gave the alcohol (IIIb), $\nu_{\max}$ (film) 3380 (OH), 1065 (CHOH) cm.$^{-1}$; n.m.r.: τ 5·45 (ArC*H*·OH), τ 7·48 (OH; a broad band which disappeared after addition of D_2O). Dehydration of (IIIb) with phosphorus oxychloride in refluxing pyridine yielded (Ib), 76% from (IIIa), $\lambda_{\max}$ (ethanol) 261 mμ (ϵ 24,400), $\nu_{\max}$ (film) 1250 and 1040 (MeOAr), 1002 and 916 (CH_2=CH), 972 (*trans*-CH=CH) cm.$^{-1}$; n.m.r.: AB quartet (2H) J = 16 c./sec. at τ 3·78 and 4·00 (*trans*-CH=CH).

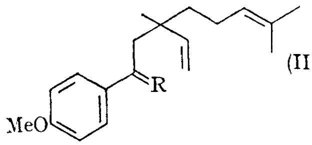
The ether (Ib) was demethylated by heating at 175° for 15 min. with methylmagnesium iodide.



(I) a; R=H
b; R=Me



(II)



(III) a; R=O
b; R=H,OH

The product was the phenol (Ia), 93%, λ_{max} (ethanol) 263 mμ (ϵ 17,200),† ν_{max} (film) 3300 (OH), 1640 ($CH_2{=}CH$), 1610 and 1520 (aryl), 1240 (ArOH), 1005 and 915 ($CH_2{=}CH$), 974 (*trans*-CH=CH) cm.$^{-1}$; n.m.r.: A_2B_2 quartet (4H) J = 8·5 c./sec. at τ 2·91 and 3·39 (aryl), AB quartet (2H) J = 16·5 c./sec. at τ 3·88 and 4·08 (*trans*-CH=CH), multiplet (2H) at τ 3·9—4·4 ($CH{=}CH_2$ and OH), multiplet (3H) at τ 4·8—5·4 ($CH{=}C$ and $CH{=}CH_2$), singlet (3H) at τ 8·84 ($CH_3{\cdot}C$), two singlets at τ 8·37 and 8·45 [$CH{=}C(CH_3)_2$] superposed on a multiplet at τ 7·8—8·7 ($CH_2{\cdot}CH_2$).

Comparison (u.v., i.r., n.m.r., and the t.l.c.) of this phenol with natural bakuchiol‡ shows that they are identical but for the optical activity.

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† Moving to 288 mμ (ϵ 17,600) on addition of alkali.

‡ We thank Dr. Sukh Dev for providing a sample of natural bakuchiol and for informing us of his alternative synthesis of racemic bakuchiol methyl ether prior to its publication (N. P. Damodaran and Sukh Dev, *Tetrahedron Letters*, 1967, in the press.).

[1] G. Mehta, U. R. Nayak, and Sukh Dev, *Tetrahedron Letters*, 1966, 4561.