A New Ketol, 1,7-Diphenyl-5-hydroxy-3-heptanone, and *trans*-Stilbene from *Alnus firma* Sieb. et Zucc. (BETULACEAE)

Yoshinori Asakawa

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

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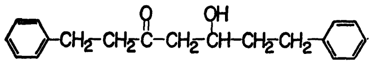
I wish to report at this time the occurrence in *A. firma* Sieb. et Zucc. of a new ketol and of *trans*-stilbene, and to outline the biosynthetic pathway of closely-related compounds, such as cinnamic acid, β-phenylethyl cinnamate, pinostrobin (5-hydroxy-7-methoxy-flavanone), and alpinetin (5-methoxy-7-hydroxy-flavanone), which exist together with II and the new ketol (I).

I



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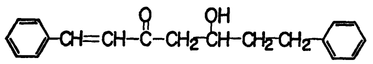
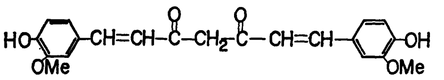
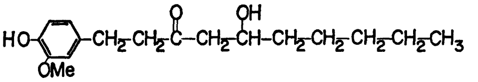


III



IV



Dihydroyashabushiketol (I). 1,7-Diphenyl-5-hydroxy-3-heptanone. The high-resolution mass-spectral measurement of I isolated from the benzene extract clearly established its molecular formula as $C_{19}H_{22}O_2$. The constituent (I), M^+ 282, mp 36.0—37.0°C, gives positive coloration with 2,4-DNP and with alkali-alkyl xanthate, and is shown by its spectral properties to possess a simple ketone group ($\lambda\lambda_{\max}^{\mathrm{EtOH}}$: 285 m$\mu$; 1706 cm^{-1}), a monosubstituted benzene ring (3060, 3020, 1600, 1490, 1450, 745 and 698 cm^{-1}), a non-conjugated benzene ring (248 mμ, 254, 261 and 268), active methylene (1409 cm^{-1}), and a hydroxyl group (3440 cm^{-1}). The NMR spectrum (60 MHz) of I in $CDCl_3$ indicates signals at 7.22 ppm (s, 10H, two monosubstituted benzene-ring protons), 4.07 ppm (quintet, 1H, J=7 Hz, $-CH_2-C\underline{H}OH-CH_2-$), 3.10 ppm (s, 1H, $O\underline{H}$), 2.80 ppm (m, 4H, $-C\underline{H}_2-CO-C\underline{H}_2-CHOH-$), 2.55 ppm (t, 4H, J=7 Hz, two $Ar-C\underline{H}_2-CH_2-$), and 1.66 ppm (m, 2H, $-CHOH-C\underline{H}_2-CH_2-$). The mass spectrum shows the parent ion at *m/e* 282, the base peak at *m/e* 91 $(C_7H_7)^+$, and other strong fragment ions at *m/e* 264 (M-18, m*=247.1), *m/e* 177 $(Ar-CH_2-CH_2-CO-CH_2-CH=\overset{+}{O}H)$, *m/e* 159 $(Ar-CH_2-CH_2-CO-CH=CH)^+$, *m/e* 148 $(Ar-CH_2-CH_2-CO-CH_3)^+$, *m/e* 133 $(Ar-CH_2-CH_2-CO)^+$, *m/e* 105 $(Ar-CH_2-CH_2)^+$, *m/e* 104 $(Ar-CH=CH_2)^+$, and *m/e* 43 $(CH_3-CO)^+$. The presence of *m/e* 39, 51, 65, and 77 suggests that I is a benzene derivative. These results have shown the structure of this ketol to be 1,7-diphenyl-5-hydroxy-3-heptanone. Furthermore, this was confirmed by the fact that the TLC R_f value, the mp, and the IR spectrum of I were all completely indentical with those of the hydrogenated product of yashabushiketol (II). In connection with a previous report,1) I wish to propose the name "dihydroyashabushiketol" for this compound. It is very interesting, from the standpoint of biochemistry, that the ketols (I) and (II) possess the same skeleton as the curcumin (III) isolated from *Curcuma longa* (ZINGIBERACEAE)2) and are partially similar to the structure of gingeron (IV) isolated from *Zingiber officinalis* Rosc. (ZINGIBERACEAE).3)

***trans*-Stilbene (V).** The colorless, leaflet crystals (M^+ 180, mp 120.0—121.0°C, R_f=0.75) isolated from the hydrocarbon portion was confirmed to be *trans*-stilbene by a study of the spectral data (UV,4) IR, NMR, and mass spectra5)).

It has been reported that oxygen-containing stilbene derivatives are widely distributed and coexist with flavones and flavanones in the family of Pinaceae.6) According to the shikimate-acetate biosynthesis pathway, dihydroyashabushiketol (I) and yashabushiketol (II) would be formed by the condensation of two molecules of cinnamic acid and a molecule of acetic acid. *trans*-Stilbene, flavanones (pinostrobin and alpinetin), and β-phenylethyl cinnamate would also result from a combination of acetic acid and shikimic acid pathways. It is very interesting, from the biochemical viewpoint, that free *trans*-stilbene and ketol I, ketol II, flavanones (pinostrobin and alpinetin), β-phenylethyl cinnamate, and cinnamic acid have been found to occur together in *A. firma* Sieb. et Zucc.

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3) H. Nomura, *Tohoku Riho*, **7**, 69 (1918).

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5) R. A. W. Johnstone and A. Millard, *Z. Naturforsch.*, **21a**, 604 (1966).

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