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A NEW KETOL FROM ALUNUS FIRMA SIEB. ET ZUCC. (BETULACEAE)[1]

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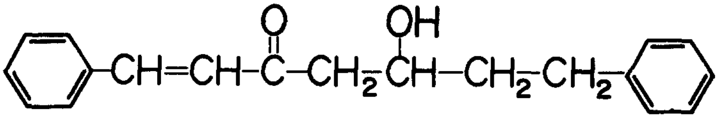
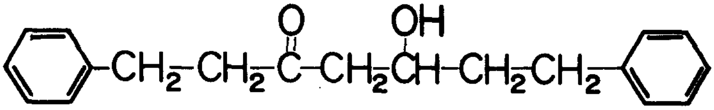
In the course of the investigation of viscous substances obtained from the buds of A. firma Sieb. et Zucc. (Betulaceae), a new ketol, $C_{19}H_{20}O_2$, was isolated, and its structure was determined as (I). We proposed the name Yashabushi-ketol for this compound.

Benzene extract of the buds was chromatographed on silica gel using ethyl acetate, and Yashabushi-ketol was isolated as a pure state. (TLC R_f value, 0.14 in benzene-ethylacetate, 19:1 v/v and R_f 0.52 in the same solvent, 3:2 v/v)

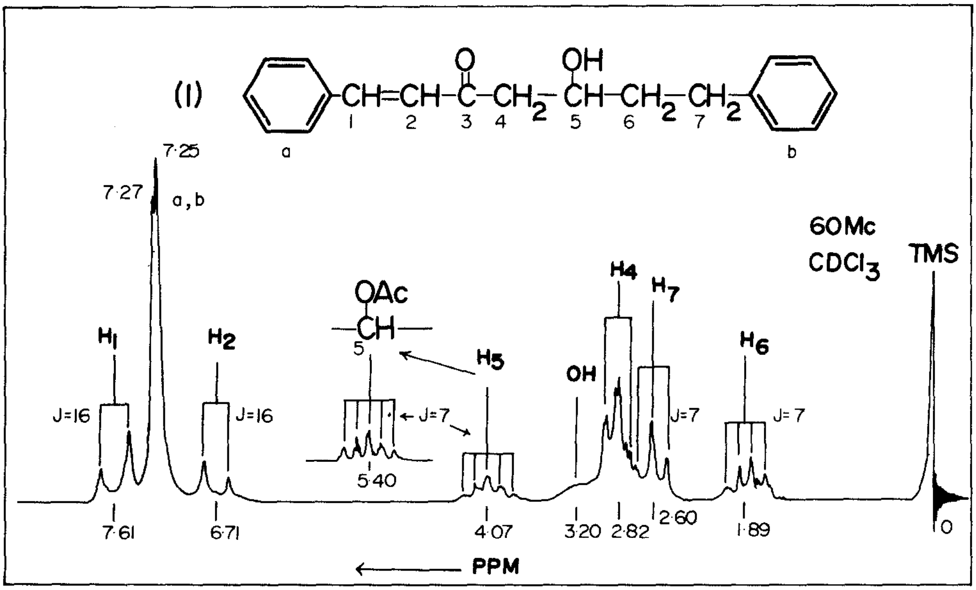
(I)



(II)

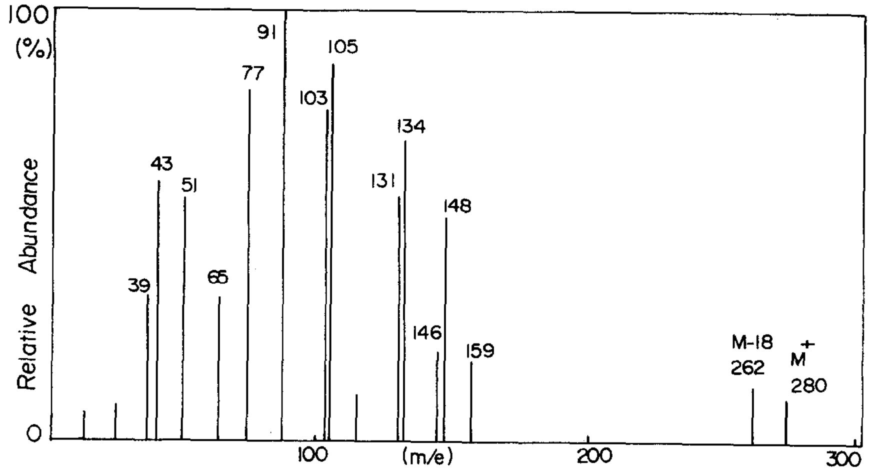


Ketol (I) gives colorless needles (from n-hexane), m.p. 59.5-60.5°C, $(\alpha)_D^{20}$, + 29.0° (c, 1.05, $CHCl_3$) and its color reactions (2,4-DNP and alkali-alkyl xanthate test) are characteristic of ketone and alcohol. Its UV spectrum in ethanol shows maxima at 217 (sh.), 227 and 289 mμ (ε, 22260, 7980 and 15120), suggesting the presence of an Ar-CH=CH-CO- group. The IR spectrum in nujol shows a band at 1703 cm^{-1} due to a carbonyl, bands at 3025, 1678 and 980 cm^{-1} for a trans double bond, 3090, 3050, 1607, 1574, 1490, 1447, 752 and 702 cm^{-1} due to a mono substituted benzene ring, at 1410 cm^{-1} for an active methylene and 3400 and 1100 cm^{-1} due to a secondary alcohol group. The NMR spectrum (Fig. 1) contains



Fig·1 NMR SPECTRUM of YASHABUSHI-KETOL (I)

the following signals: a pair of doublets at 7.61 and 6.71 ppm (J=16 cps, 1H each, Ar-C$\underline{H}$=C$\underline{H}$-CO-), two singlets at 7.27 and 7.25 ppm (10H, two monosubstituted benzene ring protons), quintet at 4.07 ppm (J=7 cps, 1H, -CH_2-C$\underline{H}$OH-CH_2-), multiplet at 2.82 ppm (2H, -CO-C$\underline{H}_2$-CHOH-), triplet at 2.60 ppm (J=7 cps, 2H, Ar-C$\underline{H}_2$-CH_2-), quartet at 1.89 ppm (J=7 cps, 2H, -CHOH-C$\underline{H}_2$-CH_2-Ar), and broad singlet at 3.20 ppm (1H, -CHO$\underline{H}$-) disappeared by D_2O. The mass spectrum (Fig. 2) of (I) shows the parent ion at m/e 280, and the base peak at m/e 91 attributed to an ion $C_7H_7^+$(tropylium ion). The presence of characteristic ions, m/e 77, 65, 51 and 39 indicates (I) to be an aromatic derivative, and m/e 262, attributed to M-18, indicates to be an alcohol. The other abundant ions are m/e 148 (CH_3-CO-CH_2-CH_2-Ar)$^+$, 134 (CHO-CH_2-CH_2-Ar)$^+$, 105 (CH_2-CH_2-Ar)$^+$, 103 (Ar-CH=CH)$^+$, 131 (Ar-CH=CH-CO)$^+$, 43 (CH_3-CO)$^+$ from 146 (Ar-CH=CH-CO-CH_3)$^+$, and 159 (Ar-CH=CH-CO-CH_2-CH_2)$^+$. Yashabushi-ketol (I) gave a dihydro derivative, $C_{19}H_{22}O_2$ (M^+282), m.p. 36.0-37.0°C and a monoacetate. The IR spectrum of dihydro-Yashabushi-ketol (II) dose not show the bands at 3025, 1678, 1574 and 980 cm^{-1} indicating the hydrogenation of trans double bond. In the mass spectrum of (II), m/e 131 and m/e 262 disappeared, and m/e 133 (Ar-CH_2-CH_2-CO)$^+$ and m/e 264 (M-18) newly appeared.



Fig· 2 MASS SPECTRUM of YASHABUSHI-KETOL (I)

On the basis of the above chemical and spectral evidences, the structure of Yashabushi-ketol was determined to be 1,7-diphenyl-1-heptene-3-one-5-ol (I).

According to shikimate-acetate biosynthesis pathway[2], Yashabushi-ketol (I) would be formed by the condensation of two molecules of cinnamic acid and one molecule of acetic acid. It is very interesting from the standpoint of biochemistry that in addition to Yashabushi-ketol (I), several closely related compounds, such as pinostrobin3)(5-hydroxy-7-methoxy flavanone), alpinetin4) (5-methoxy-7-hydroxy-flavanone), β-phenylethyl cinnamate5), cinnamic acid and trans-stilbene were also found in A. firma Sieb. et Zucc. (Betulaceae) in this work. Among five compounds, trans-stilbene was firstly isolated from natural substance.

References

1) Japanese name is Yashabushi.

2) T. Swain, Chemical Plant Taxonomy p. 102, Academic Press, London and New York. (1963).

3) 4) These two compounds were found in Ginger. S. Mongkolsuk and F. M. Dean, J. Chem. Soc., 4654 (1964).

5) A. Goris and H. Canal, Bull. chim. soc. France., 1982 (1936).