Phytochemistry, 1980, Vol. 19, pp. 2637 2638. Pergamon Press Ltd. Printed in England

0031 9422/80/1201 2637 $02.00/0

NONADECAN-7-OL-2-ONE, AN ALIPHATIC KETOL FROM *DIOSPYROS PEREGRINA*

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(*Revised received* 16 *April* 1980)

Key Word Index *Diospyros peregrina*; Ebenaceae; stem; nonadecan-7-ol-2-one; ketol.

Abstract—A new aliphatic ketol isolated from the stems of *Diospyros peregrina* was characterized as nonadecan-7-ol-2-one by analyses, MW determination, chemical degradation and spectroscopic data.

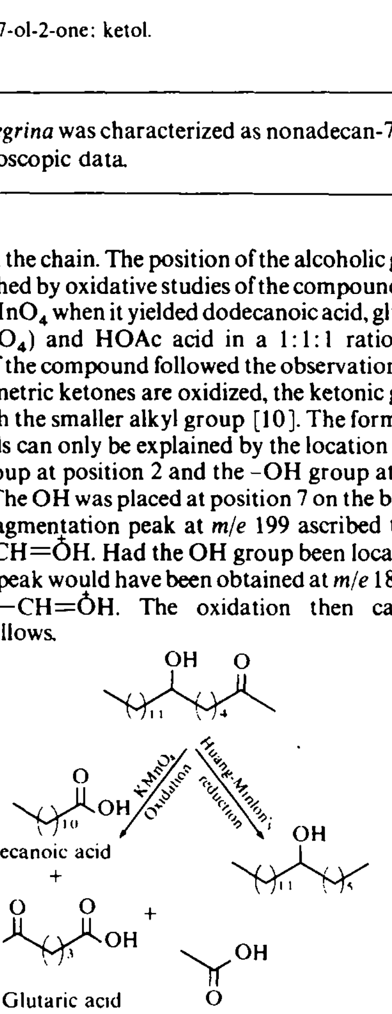
INTRODUCTION

Diospyros peregrina was selected for phytochemical investigation because of its reputed medicinal properties [1, 2] and also because a review of the literature showed that little chemical work had been done on the leaves [3] and bark [4] of this plant.

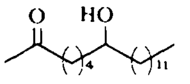
RESULTS AND DISCUSSION

The reported compound $C_{19}H_{38}O_2$ (M^+ 298), mp 75–78°, was isolated as a deposit from the EtOH concentrate of the stem. As the compound is a ketone (see later) the molecular formula indicates that there is no ethylenic linkage in the compound and this is further supported by the failure of the compound to decolourize Br_2 in CCl_4. By routine tests [5] and IR spectral studies (ν_{max}^{KBr} 2915, 2850, 1460, 1440, 1388, 1360 and 1170 cm^{-1}) [6], the compound was found to be aliphatic in nature. The compound contains an alcoholic group as it gave a positive test with ceric ammonium nitrate (ν_{max}^{KBr} 3400 cm^{-1}, ^{1}H NMR τ 5.77, OH) and formed a monoacetate, $C_{21}H_{40}O_3$, mp 54° (ν_{max}^{KBr} 1750 cm^{-1}). The alcoholic group was secondary (ν_{max}^{KBr} 1305 and 1110 cm^{-1}, ^{1}H NMR τ 6.2, CHOH) [6]. It also gave a positive test with 2,4-DNPH and formed a 2,4-dinitrophenylhydrazone, $C_{25}H_{42}O_5N_4$, mp 60°, showing the presence of an oxo group. The oxo group was ketonic (ν_{max}^{KBr} 1725 cm^{-1}), and not aldehydic, because the compound failed to give a positive Schiff's reagent test. The compound contained a $(>CH_2)_n$ grouping (^{1}H NMR τ 8.76, CH_2) where the value of n is >4, as shown by IR (ν_{max}^{KBr} 730 and 720 cm^{-1}) [7].

The compound gave a positive haloform test [8] indicating the presence of an acetyl function which was also supported by spectral studies (^{1}H NMR τ 8.02, COMe; MS m/e 43). The positive haloform reaction can also be given by a compound having a terminal CHOHMe group. In order to ascertain which of these two groups is at the end of the chain, the compound was reduced using the Huang-Minlon modification of the Wolff Kishner reduction [9]. The reduction product, mp 58 60°, gave an intense colour with ceric ammonium nitrate but it neither formed a 2,4-dinitrophenylhydrazone nor gave a positive haloform reaction, suggesting that the -COMe group occupies the terminal position in the chain. Thus the ketonic group is at position 2 in the chain. The position of the alcoholic group was established by oxidative studies of the compound with alkaline $KMnO_4$ when it yielded dodecanoic acid, glutaric acid ($C_5H_8O_4$) and HOAc acid in a 1:1:1 ratio. The oxidation of the compound followed the observation that, when asymmetric ketones are oxidized, the ketonic group remains with the smaller alkyl group [10]. The formation of these acids can only be explained by the location of the $>C{=}O$ group at position 2 and the -OH group at position 7 or 8. The OH was placed at position 7 on the basis of the mass fragmentation peak at m/e 199 ascribed to $Me(CH_2)_{11}-CH{=}\overset{+}{O}H$. Had the OH group been located at position 8 a peak would have been obtained at m/e 185 due $Me(CH_2)_{10}-CH{=}\overset{+}{O}H$. The oxidation then can be shown as follows.



On the basis of above chemical degradation supported by spectroscopic data the compound was assigned the following structure.



EXPERIMENTAL

The plant material was locally collected and was identified by the Botanical Survey of India, Allahabad.

Isolation and purification. The powdered, air-dried stem (2 kg) of *D. peregrina* was extracted exhaustively with hot EtOH for 120 hr. The total EtOH extract (2.5 l.) on concn and standing overnight at 0° deposited a brownish amorphous compound. It was purified by repeatedly dissolving it in EtOH, as a white amorphous compound which was crystallized from $CHCl_3$ MeOH (1:2), yield 800 mg, mp 75 78°. It was homogeneous by TLC, $CHCl_3$-petrol (1:1) R_f 0.36, $CHCl_3$ C_6H_6 (1:1), R_f 0.74. Found: C, 76.62; H, 12.71. Calc. for $C_{19}H_{38}O_2$: C, 76.51; H, 12.75%. IR: ν_{max}^{KBr} cm^{-1}: 3400, 2915, 2850, 1725, 1460, 1440, 1388, 1360, 1305, 1290, 1270, 1260, 1225, 1170, 1110, 1075, 940, 730 and 720. ^1H NMR (in $CDCl_3$): τ 9.12 (Me, 3 H), 8.76 (CH_2, 24 H), 8.02 (COMe, 3 H), 7.76 ($COCH_2$, 2 H), 7.65 ($CH_2-CHOH-CH_2$, 4 H), 6.2 (CHOH, 1 H), 5.77 (OH, 1 H). MS, m/e: 298 (M^+), 280 ($M^+ - 18$), 199 ($Me(CH_2)_{11}-CH=\overset{+}{O}H$), 169 ($\cdot CH_2(CH_2)_{10}-Me$), 155 ($\cdot CH_2(CH_2)_9-Me$), 141 ($\cdot CH_2(CH_2)_8-Me$), 129 ($MeCO(CH_2)_4CH=\overset{+}{O}H$), 127 ($\cdot CH_2(CH_2)_7-Me$), 113 ($\cdot CH_2(CH_2)_6-Me$), 86 ($-CH_2(CH_2)_3CH=\overset{+}{O}H$), 85 ($\cdot CH_2(CH_2)_4-Me$), 84 ($-CH_2(CH_2)_3C\equiv\overset{+}{O}$), 71 ($\cdot CH_2(CH_2)_3Me$), 58 ($CH_2=\underset{\overset{|}{+OH}}{C}-Me$), 57 ($\cdot CH_2(CH_2)_2-Me$), 43 ($Me-C\equiv O^+$), 31 ($CH_2=\overset{+}{O}H$).

Acetylation. The compound (100 mg) was acetylated with Ac_2O (7 ml) and pyridine (17 ml) by the usual method. The acetylated product was crystallized from $CHCl_3$-MeOH (1:1), mp 54°. Found: C, 74.0; H, 11.81. Calc. for $C_{21}H_{40}O_3$: C, 74.11; H, 11.76%. The percentage acetyl group was determined by the method of ref. [11] as described in ref. [12]. Found: COMe, 12 60. Calc. for $C_{19}H_{37}O_2$ (COMe): COMe, 12.64%.

2,4-Dinitrophenylhydrazone. 2,4-DNPH of the compound (100 mg) was prepared using 2,4-DNP (150 mg) in dioxan and conc HCl (2 ml) in the usual manner. The product was crystallized from aq. EtOH, mp 60°. Found: N, 11.68. Calc. for $C_{25}H_{42}O_5N_4$: N, 11.71%.

Reduction by Huang-Minlon's method. The compound (100 mg) was refluxed with diethylene glycol (1.3 ml), hydrazine hydrate (85%, 4.3 ml) and KOH (430 mg) in H_2O (6 ml) for 6 hr at 195 210° After refluxing, excess solvent was removed by distillation. The product obtained was purified on a column of neutral Al_2O_3 and eluted with MeOH. Repeated crystallizations from MeOH-$CHCl_3$ (1:1) afforded white flakes, mp 58–60°.

Oxidation. The compound (200 mg) was oxidized with aq. alkaline $KMnO_4$ (NaOH 10%, 6.6 ml; $KMnO_4$ 5%, 8 ml) for 12 hr. The soln was cooled and acidified with dil HCl. The ppt. MnO_2 was dissolved in an aq. soln of Na bisulphite and the soln filtered. The filtrate was again acidified with dil HCl and was cooled overnight at 0° when a white solid separated, which was filtered and washed with H_2O. The aq. filtrate was extracted with Et_2O. The white solid, crystallized from EtOH, $C_{12}H_{24}O_2$, mp 42°, was identified as dodecanoic acid by mp, amide formation, mp 97°, and also by mmp and co-chromatography with an authentic sample. The Et_2O extract was shown to be a mixture of HOAc and glutaric acids by co-PC with authentic samples. The extract was concd to a white solid which was crystallized from C_6H_6, $C_5H_8O_4$, mp 94–97° It was finally identified as glutaric acid by mp, amide formation, mp 173° and mmp with an authentic sample.

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