

(4);  $C_8H_7NO$  + 133 (95)  $C_7H_7N$  105 (100).

$$[\alpha]_{24}^{\lambda} = \frac{589}{-34.8} \frac{578}{-34.8} \frac{546}{-39.0} \frac{436 \text{ nm}}{-58.0} \quad (c = 1.0)$$

*Dehydroisosenetin* (7). Farbloses, zähes Öl, IR:  $>C=O$  1773, 1750, 1725  $\text{cm}^{-1}$ . MS:  $M^+$   $m/e$  387.131 (3%) (ber. für  $C_{20}H_{21}O_2N$  387.132);  $C_8H_7NO$   $^{7+}$  133(100);  $C_7H_7N$   $^{7+}$  105 (28).

$$[\alpha]_{24}^{\lambda} = \frac{589}{-45.6} \frac{578}{-46.1} \frac{546}{-48.8} \frac{436 \text{ nm}}{-89.0} \quad (c = 0.5)$$

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## LITERATUR

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A NEW PIPERIDINE ALKALOID FROM *PIPER PEEPULOIDES*

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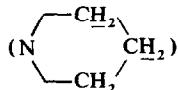
Key Word Index—*Piper peepuloides*; Piperaceae; 2-methoxy-4, 5-methylenedioxy cinnamoyl piperidine

The genus *Piper* has received considerable attention in recent years because of its reputation for producing a number of new chemical compounds, [1–8]. In earlier communications [1, 9, 10] we have reported the presence of a new pyrrolidine alkaloid, peepuloidin, from the leaves of *P. peepuloides* and from the fruits of the same plant a number of interesting compounds such as [+]–diacidesmin, pipataline, 5-hydroxy,3',4',7-trimethoxyflavone, 5-hydroxy-4', 7-dimethoxyflavone, *N*-isobutyl dodeca-*trans*-2-*trans*-4-dienamide, *N*-isobutyldeca-*trans*-2-*trans*-4-dienamide and sesamin. We now wish to report the isolation and structure elucidation of a new piperidine alkaloid from the leaves of *P. peepuloides*, identified as 2-methoxy-4, 5-methylenedioxy cinnamoyl piperidine.

The petrol extract of the leaves on repeated column chromatography over neutral  $Al_2O_3$  and repeated crystallisation furnished a white crystalline compound.

The compound analysed for  $C_{16}H_{19}NO_4$ ,  $M^+$ -289.1318 (Cal. for  $C_{16}H_{19}NO_4$ ,  $M^+$  289.1313); UV 333, 305 and 240 nm. The IR (KBr) spectrum of the compound showed characteristic bands for  $>C=O$  ( $1650 \text{ cm}^{-1}$ )

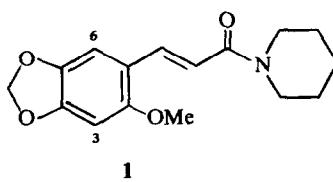
indicating the compound to be an amide and lack of an  $—NH$  stretching frequency demonstrated that it was a tertiary amide;  $C=C$  ( $1660 \text{ cm}^{-1}$ ) and methylenedioxy group ( $1260, 1040, 930 \text{ cm}^{-1}$ ). The 60 MHz PMR ( $CDCl_3$ ) spectrum of the compound showed a broad multiplet between  $\delta$  1.0 and 1.9 which is attributed to 6 protons



a triplet and a multiplet at  $\delta$  3.30 and 3.55 respectively

accounts for 4 protons ( $N$ — $CH_2$ —); a singlet at 3.75 has  $CH_2$  been assigned to 3 protons ( $O—Me$ ). A doublet at 5.85 (1H,  $J = 14 \text{ Hz}$ ), indicating a *trans* olefinic proton ( $\alpha$ ) adjacent to carbonyl; a singlet at 5.85 is due to two protons of methylenedioxy group. A doublet at 6.78 ( $J = 14 \text{ Hz}$ ) is assigned to one ( $\beta$ ) olefinic proton, singlets at  $\delta$  6.45 and 6.9 are attributed to C-3 and C-6 aromatic protons respectively. The MS is also in complete agreement with the proposed structure (1).

On hydrogenation ( $Pd/C$ ) the compound quickly absorbed one mole of  $H_2$  to give a waxy dihydro derivative ( $M^+$ -291). The  $KMnO_4$  oxidation of the compound furnished an acid mp 147–147.5° (lit., [11] mp 148–149°), identified as 2-methoxy-4, 5-methylenedioxy benzoic acid.



## EXPERIMENTAL

The air dried powdered leaves of *P. peepuloides* Roxb. (0.9 kg) were continuously extracted in a Soxhlet with petrol (bp 60–80°) for 75 hr. The extract was concentrated under red. pres. and the resultant viscous liquid was subjected to column chromatography over neutral  $Al_2O_3$  and eluted with different solvents in order of increasing polarity. The fractions eluted with  $C_6H_6$  gave a crude viscous liquid which on repeated column chromatography over

neutral  $\text{Al}_2\text{O}_3$  gave a dirty white crystalline compound, mp 90–92°. Repeated crystallization from petrol– $\text{Me}_2\text{CO}$  furnished a TLC pure, white crystalline compound (180 mg) mp 98–99°.  $R_f$  0.36, EtOAc–*n*-hexane, 1:1.

**Hydrogenation.** The compound (50 mg) in MeOH (200 ml) was hydrogenated over 10% Pd/C (40 mg) at room temp. and pres. Absorption of  $\text{H}_2$  was complete after 1 hr during which 1 mole of  $\text{H}_2$  was absorbed. The catalyst was filtered and the solvent removed under red. pres. leaving behind a viscous residue. The residue (40 mg) on purification by chromatography over neutral  $\text{Al}_2\text{O}_3$  yielded a TLC pure, white waxy compound,  $\text{C}_{16}\text{H}_{21}\text{NO}_4$ ,  $M^+ - 291$  ( $R_f$  0.42, EtOAc–*n*-hexane, 1:1).

**Oxidation.** To the compound (50 mg) dissolved in 3 ml  $\text{Me}_2\text{CO}$  was added  $\text{KMnO}_4$  in small batches and the mixture allowed to reflux. Addition of  $\text{KMnO}_4$  was stopped when a permanent pink colour persisted in the mixture.  $\text{MeCO}_2$  was removed and 1 ml of 10% KOH soln was added and filtered hot. The residue was washed with hot  $\text{H}_2\text{O}$  and the filtrate added to the alkaline aq. portion. The aq. soln was extracted with  $\text{Et}_2\text{O}$  to remove the unreacted alkaloid and then acidified with dil. HCl to pH 2. This was extracted  $\times 3$  with  $\text{Et}_2\text{O}$ , solvent removed and the residue chromatographed over Si gel. EtOAc fractions yielded a crystalline residue which on repeated crystallisation from  $\text{Me}_2\text{CO}$ –EtOAc (1:1) furnished a white crystalline compound (5 mg),  $\text{C}_9\text{H}_8\text{O}_5$ , mp 147–147.5°, identified as 2, methoxy-4,5-methylene-dioxy benzoic acid by PMR, IR and MS.

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