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ISOCODONOCARPINE FROM *CAPPARIS DECIDUA*

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Key Word Index—*Capparis decidua*; Capparidaceae; alkaloid; isocodonocarpine.

Abstract—A new spermidine alkaloid, isocodonocarpine, was isolated from the root bark of *Capparis decidua* and its structure elucidated by spectral studies including 2D NMR.

INTRODUCTION

The bark of *Capparis decidua* (Forssk.) Edgen (Capparidaceae) is reported to be used as a cure for asthma, inflammation and gout [1, 2]. Some species of *Capparis* have been investigated chemically and the isolation of stachydrine, β-carotene, sitosterol, rutin, isothiocyanate glucosides, hydrocarbons and fatty acids have been reported [3–8]. We have reported the isolation of capparisine [9] from *Capparis decidua*. The present communication reports the isolation and structure determination of a new spermidine alkaloid isocodonocarpine (**1**) from this plant.

RESULTS AND DISCUSSION

The crude alkaloidal mixture was separated from the alcoholic extract of the root bark of *C. decidua*. The repeated silica gel column chromatography of the crude alkaloidal material led to the isolation of pure compound **1** which was recrystallized from methanol. The name isocodonocarpine was assigned to compound **1**, with respect to the known compound codonocarpine (**2**). Isocodonocarpine gave a positive test for phenol with ferric chloride reagent.

The high resolution mass spectrum showed the molecular ion peak at *m/z* 465.2251 corresponding to molecular formula $C_{26}H_{31}N_3O_5$ (calcd. 465.2263). The UV spectrum displayed maxima at 218 (log ε = 3.730), 286 (log ε = 3.735) and a shoulder at 310 nm. These values are very close to those of capparisine [9], codonocarpine [10] and cadabicine [11].

The IR spectrum showed bands at 3200–3300 (*br*, OH and NH), 1660 (α, β-unsaturated amide) and 1600 cm^{-1} (aromatic ring). In the ^1H NMR spectrum a multiplet between δ 1.35 and 1.85 (6H) was assigned to three methylene groups and another multiplet between δ 2.8 and 3.1 (8H) was due to the four methylene groups adjacent to nitrogens. A singlet at δ 3.77 (3H) showed the presence of a methoxy group, attached to an aromatic ring. There were four doublets (J = 15.5 Hz, each 1H) at δ 5.82, 6.61, 7.20 and 7.47 from the olefinic protons of the *trans*-cinnamic acid residues. Two doublets at δ 6.71 (J = 8.5 Hz) and 6.55 (J = 8.9 Hz), which showed only *ortho*- but no *meta*-coupling, were attributed to H-25 and H-28, respectively. A doublet at δ 6.31 (J = 2.9 Hz) with only *meta*-coupling was due to H-27.

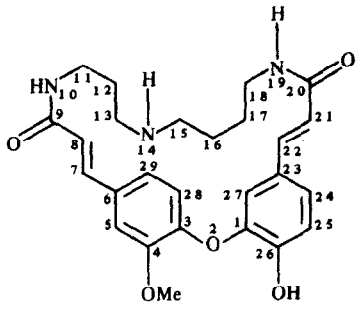
Another doublet at δ 6.92 was due to H-24, with an *ortho*- and a *meta*-coupling (J = 8.5 and 2.9 Hz). A doublet at δ 7.27 with an *ortho*-coupling (J = 8.9 Hz) and a *meta*-coupling (J = 2.8 Hz) was due to H-29, while a doublet at δ 7.70 (J = 2.8 Hz) with only *meta*-coupling was due to H-5.

These assignments were confirmed by 2D correlation of proton shifts through a COSY-45, and 2D, J-resolved experiments. The coupling interactions were established by a COSY-45 experiment. Two doublets of H-7 at δ 7.47 and H-8 at 6.61 were coupled with each other. Similarly two doublets of H-21 at δ 5.82 and H-22 at δ 7.20 were coupled with each other. A doublet of H-24 at δ 6.92 had cross peaks with H-25 (6.71) and H-27 (6.31). Similarly a doublet of H-29 at δ 7.27 had cross peaks with H-5 (7.70) and H-28 (6.55). A multiplet between δ 1.35 and 1.85 (6H) for 2 × H-12, 2 × H -16 and 2 × H-17 was coupled with another multiplet between δ 2.8 and 3.1 (8H) for 2 × H-11, 2 × H-13, 2 × H-15 and 2 × H-18.

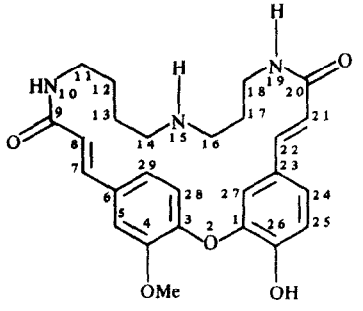
All these assignments show that the methoxy group and hydroxy group in this skeleton were attached to C-4 or C-26. Their exact positions in the skeleton were proved with the help of mass fragmentations of compound **1** (Fig. 1) and its acetate.

The high resolution mass spectrum of compound **1** and its diacetate showed several peaks that allowed the assignments of the propyl unit of spermidine to the phenyl ring bearing methoxy group (at C-4) and the butyl unit of spermidine to the other ring (bearing hydroxyl group at C-26). The peaks at *m/z* 234 of compound **1** and at *m/z* 276 of its acetate correspond to ions **3** and **4**, and show that hydroxyl group is attached at C-26 otherwise there should be a peak at *m/z* 248 in the mass spectrum of compound **1**, but it was not observed. The peaks at *m/z* 250 and 265 of compound **1** and at *m/z* 292 and 307 of its acetate correspond to ions **5–8**, respectively.

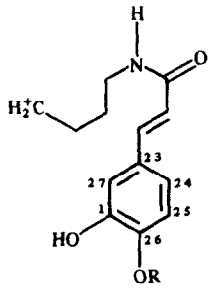
The mass spectral fragmentation proposed for cadabicine [11], (the structure of which was confirmed through X-ray analysis) should give rise to peaks at *m/z* 220, 248 and 262 in codonocarpine, but these fragments were not observed in isocodonocarpine. All the above assignments prove that the structure of isocodonocarpine (**1**) resembles that of codonocarpine (**2**) with the difference that the spermidine moiety is attached in the opposite manner. The difference in the melting points and the mass spectral



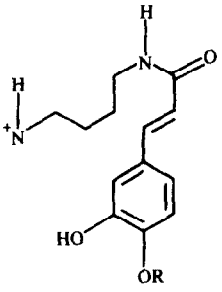
1



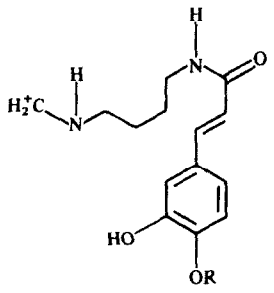
2



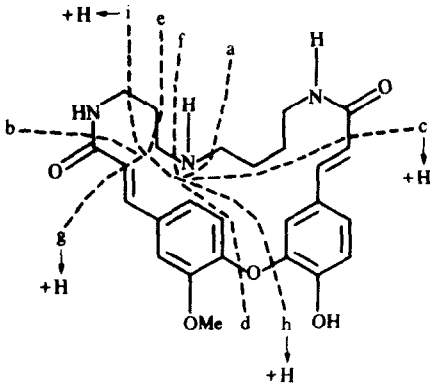
3 R = H *m/z* 234.1138 (calcd for $C_{13}H_{16}NO_3$, 234.1130)
4 R = Ac *m/z* 276.1239 (calcd for $C_{15}H_{18}NO_4$, 276.1235)



5 R = H *m/z* 250.13091 (calcd for $C_{13}H_{18}N_2O_3$, 250.13173)
6 R = Ac *m/z* 292.1398 (calcd for $C_{15}H_{20}N_2O_4$, 292.1423)



7 R = H *m/z* 265.1544 (calcd for $C_{14}H_{21}N_2O_3$, 265.1552)
8 R = Ac *m/z* 307.1661 (calcd for $C_{16}H_{23}N_2O_4$, 307.1657)



1	$[M]^+$	465 $(C_{26}H_{31}N_3O_5)^+$
2	[M -OMe]	435 $(C_{25}H_{29}N_3O_4)^+$
3	[a-b]	366 $(C_{22}H_{24}NO_4)^+$
4	[b-c]	265 $(C_{17}H_{13}O_3)^+$
5	[d-e]	265 $(C_{14}H_{21}N_2O_3)^+$
6	[d-f]	250 $(C_{13}H_{18}N_2O_3)^+$
7	[c-g]	235 $(C_{16}H_{11}O_2)^+$
8	[a-d]	234 $(C_{13}H_{16}NO_3)^+$
9	[h-i]	207 $(C_{11}H_{13}NO_3)^+$
10	[d-i]	189 $(C_{11}H_{11}NO_2)^+$
11	[b-d]	161 $(C_{10}H_9O_2)^+$
12	[d-g]	133 $(C_9H_9O)^+$

Fig. 1.

fragments observed for isocodonocarpine support structure **1**, and this conclusion is also supported by ^{13}C NMR spectrum (Table 1) and the DEPT experiment.

EXPERIMENTAL

Mp: uncorr, ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in DMSO-d_6 using TMS as int. standard. UV spectra were recorded in MeOH and IR spectra were taken in KBr disc.

Extraction of plant material. The root bark of *Capparis decidua* collected from Karachi was chopped into small pieces and then dried and powdered to provide the material which was extracted with EtOH. The residue obtained on evapn was partitioned

Table 1. ^{13}C NMR spectrum of isocodonocarpine (1)

C		C	
1	151.89	16	37.99
3	155.60	17	25.42
4	147.86	18	46.18/46.25*[c]
5	138.38	20	164.84[a]
6	134.57	21	123.64
7	137.75	22	138.07
8	125.85/125.93*	23	133.08
9	165.07[a]	24	122.53
11	43.93/44.00*[c]	25	110.06
12	25.63/25.68*	26	143.25
13	35.78[b]	27	121.12
15	38.41[b]	28	118.31
		29	118.61
		OMe	55.86

Doubling of peaks [11–13].
[a,b,c] Assignments may be reversed.

between EtOAc and H_2O. The aqueous layer was adjusted with NH_3 to pH 10 and extracted repeatedly with $CHCl_3$. The solvent was evapd to yield a brown gummy crude alkaloidal material. It was chromatographed on a silica gel column, eluted with $CHCl_3$–MeOH–NH_3 (40:9:1) afforded isocodonocarpine, which was recrystallized from MeOH and C_6H_6 as off-white crystals.

Isocodonocarpine (1). Mp 220–222° (decomp.); UV λ_{max}^{MeOH} nm (log ε); 218 (3.730), 286 (3.735), 310 (shoulder); IR ν_{max}^{KBr} cm^{-1}: 3300–3200 (OH), 1660 (α,β-unsaturated amide), 1600 (aromatic ring) HRMS: *m/z* (rel. int.): 465.2251 (19) (calcd for $C_{26}H_{31}N_3O_5$, 465.2263), 435.2158 (29) (calcd for $C_{25}H_{29}N_3O_4$, 435.2157), 366.16982 (16.5) (calcd for $C_{22}H_{24}NO_4$, 366.17052), 265.08511 (calcd for $C_{17}H_{13}O_3$, 265.08646), 265.1544 (calcd for $C_{14}H_{21}N_2O_3$, 265.1552), (*m/z* = 265 overall 58%), 250.13091 (10) (calcd for $C_{13}H_{18}N_2O_3$, 250.13173), 235.07622 (7), (calcd for $C_{16}H_{11}O_2$, 235.07586), 234.1138 (21) (calcd for $C_{13}H_{16}NO_3$, 234.1130), 207.09042 (4.3) (calcd for $C_{11}H_{13}NO_3$, 207.08953), 189.07759 (38.2) (calcd for $C_{11}H_{11}NO_2$, 189.07897), 161.06325 (100) (calcd for $C_{10}H_9O_2$, 161.06025), 133.06405 (76.5) (calcd for C_9H_9O, 133.06533), for ^1H NMR see Discussion and for ^{13}C NMR see Table 1. ^1H and ^{13}C NMR spectra showed doubling of several peaks which may be, due to slowly interconverting conformers *E* and *Z* with regards to the amide bond [11–13].

Isocodonocarpine diacetate. Compound 1 was treated with Ac_2O and pyridine, warmed slightly and kept overnight. On addition of ice the amorphous diacetate obtained which was crystallized from MeOH mp 212°; UV λ_{max}^{MeOH} nm (log ε), 206 (3.790), 275 (3.796) and 308 (shoulder); IR ν_{max} cm^{-1}: 1760 (phenolic acetate), 1660 (α,β-unsaturated amide), ^1H NMR: δ 1.98 (*s*, 3H) N-Ac and 2.33 (*s*, 3H) phenolic acetate. Other peaks were almost similar to compound 1; MS *m/z* (rel. int.): 549 $[M]^+$ (11), 507 $[M-CH_2CO]^+$ (21), 465 $[M-2\ CH_2CO]^+$ (17.5), 435 (27), 366 (19.4), 307 (28.2), 292 (9), 276 (16.4), 265 (25.8), 235 (6.2), 189 (40), 161 (100) and 133 (86.5).

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