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ALKALOIDS OF *LITSAEA LAETA* AND *L. SALICIFOLIA*

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Key Word Index—*Litsaea laeta*; *L. salicifolia*; Lauraceae; new noraporphine alkaloid; structure determination.

Abstract—The structure for laetine (2-hydroxy-1-methyl 10,11-methylenedioxy noraporphine), a new alkaloid from the bark of *Litsaea laeta* has been established. *N,O*-Dimethylharnovine and glaucine were also isolated from the same source. C-2 hydroxy aporphines are characteristic of *L. laeta*. Two known alkaloids, dicentrinone and nordicentrine, have also been isolated from the leaves of *L. salicifolia*.

In the course of our investigation on the bark of *Litsaea laeta* [1] we isolated another new noraporphine alkaloid, laetine (**1**), in addition to two known alkaloids, *N,O*-dimethylharnovine (**2**) and glaucine (**3**) of this group. The work on the leaves of *L. salicifolia*, which had not previously been investigated, led us to isolate two known alkaloids, dicentrinone (**4**) [2] and nordicentrine (**5**) [3]. The structure of **4** was established from mp, MS, UV and comparison of IR with that of an authentic sample and that of **5** was established by its conversion to **4** by a known reaction [2]. The presence of a minor alkaloid with M^+ *m/e* 321 was observed in the MS together with **5**.

Laetine **1** (mp 296° decomp.) which gave positive Meyer's and Dragendorff's tests, showed a M^+ (100%) at *m/e* 311 (for $C_{18}H_{17}NO_4$; high resolution mass for $M^+ - 1$, found: 310.10659, calc.: 310.1079) and optical rotation $[\alpha]_D^{25} - 23.7°$. The UV 270(4.06) and 307 (3.67) nm suggested a 1,2,10,11-tetrasubstituted aporphine skeleton [4], while the IR (KBr) gave a band at 3400–3500 cm^{-1} for both OH and NH groups. The ^1H NMR spectrum (DMSO-d_6, 270 MHz) exhibited signals at δ 3.67 (*s*, 3H, C-1 Me); 4.04 (*m*, 1H, 6aH), 5.97 (*s*, 1H) and 6.11 (*s*, 1H) two methylene protons of a methylenedioxy group; 6.75 (*s*, 1H, C-3H) and 6.87 (*s*, 2H, C-8 and C-9H). Other aliphatic protons appeared in the region between 3.0 and 2.5.

Catalytic hydrogenation (Pd–C in MeOH or Pt_2O in HOAc under pressure) had no effect on **1**. The presence of a phenolic hydroxyl group in **1** was confirmed by the formation of *O*-methyllaetine **7**.

The appearance of two methylenedioxy protons as singlets ruled out the position of that group between the C-1 and C-2 atoms [5].

The position of the OH group at the C-2 position was established by preparing the *N,O*-diacetate (**8**) from **1** by treatment with Ac_2O–Py at room temperature and studying its ^1H NMR spectrum. The ^1H NMR of **8** showed that the C-3 proton had shifted downfield to form a three-proton singlet together with C-8 and C-9 protons.

The isolation of 3 aporphine alkaloids, laetanine (**9**) [1], **1** and **2**, with a C-2 OH group might be chemotaxonomically important for *L. laeta*.

EXPERIMENTAL

Dried bark of *L. laeta* Benth HKf was collected from Sibsagar district, Assam during Sept.–Oct. 1977 and the phenolic and non-phenolic alkaloids extracted. From the non-phenolic part, 4 mg of pure **3** was isolated by repeated prep.-TLC on Si gel; mp 114°; UV λ_{max}^{EtOH} nm: 280 (4.2) and 303–304 (4.06); MS: M^+ *m/e* 355, 340, 338; IR (KBr) cm^{-1}: 1605, 1510. Phenolic alkaloids were passed over a neutral Al_2O_3 column to obtain 45 mg of a light coloured powder of **1** using EtOAc as eluent. C_6H_6–EtOAc (1 : 1) eluted 32 mg (crude) **2** which was further purified by repeated column and prep.-TLC to yield 9 mg of pure **2** (one spot on TLC). MS *m/e* M^+ 341, 326; UV λ_{max}^{EtOH} nm: 270 (3.91), 300 (3.5), IR cm^{-1}: 3400, 1600, 1420, 1410, 1260, 1050. ^1H NMR ($CDCl_3$): δ 7.0 (*d*, 1H), 6.88 (*d*, 1H), 6.75 (*s*, 1H), 3.9 (*s*, 3H, NMe), 3.63 (*s*, 3H, OMe), 3.44 (*s*, 3H, OMe) 2.58 (*s*, 3H, OMe) and other aliphatic protons appeared between 3.44 and 2.58.

Attempted hydrogenation of **2**. **2** (3 mg) was hydrogenated with Pt_2O–HOAc and Pd–C in MeOH under pres. for several hr. Hydrogenation did not occur.

Preparation of **7**. **1** (5 mg) was treated with CH_2N_2–Et_2O to obtain 2.5 mg of **7**. MS *m/e* M^+ 325; UV λ_{max}^{EtOH} nm: 269 (3.55) and 303 (3.24), Optical rotation: $[\alpha]_D^{25} = -14.8°$ (*c* 0.355 in EtOH).

Preparation of O-silyl derivative of **1**. **1** (1 mg) was treated with 1–2 drops of hexamethyldisilazane and warmed at 50–60° for 1 hr. MS *m/e* M^+ 383 for ($C_{21}H_{25}NO_4Si$).

Preparation of **8**. **1** (30 mg) was treated with Ac_2O–Py at room temp. for 18 hr. Solvent was removed under vacuum to yield **8**. IR (CCl_4) cm^{-1}: 1768 and 1650 for OAc and NAc bands respectively. ^1H NMR (CCl_4, 60 MHz): δ 2.15 (*s*, 3H,

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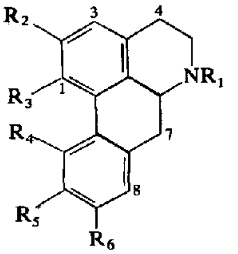

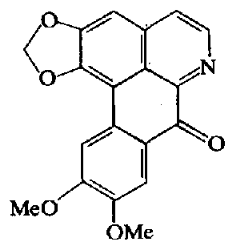

4

	1	2	3	5	7	8	9
R_1	H	Me	Me	H	H	Ac	H
R_2	OH	OH	OMe	O	OMe	OAc	OH
				CH_2			
R_3	OMe	OMe	OMe	O	OMe	OMe	OMe
R_4	O	OMe	H	H	O	O	H
	CH_2				CH_2	CH_2	
R_5	O	OMe	OMe	OMe	O	O	OH
R_6	H	H	OMe	OMe	H	H	OMe

OAc); 2.33 (*s*, NAc) 3.55 (*s*, 3H, OMe); 5.9 (*s*, 1H) and 6.11 (*s*, 1H) for methylenedioxy group; 6.75 (s, 3H, C-3, C-8 and C-9).

L. salicifolia *Roxb*. From 200 g of air-dried leaves, 90 mg crude non-phenolic alkaloid were obtained which were passed over a neutral Al_2O_3 column and the following fractions collected: Me_2CO–C_6H_6 (1 : 3) fraction A, 9 mg **2** and fraction B, 4 mg **4** Me_2CO–C_6H_6 (2 : 3) crystallized from Me_2CO. Dicentrinone (**4**), mp 295–297° (decomp); MS *m/e* M^+ 335 (100%) for $C_{10}H_{13}NO_5$, *m/e* 334 (50%), 320 (39%); 304 (24%); UV λ_{max}^{EtOH} (ε) nm: 249 (22 788), 271 (18 766), 309 sh (6903), 348 (7238), 387 (5630) and 415–421 (5254); $\lambda_{max}^{EtOH-HCl}$ (ε) nm: 260 (25 469), 290 (20 375), 378 (10 254) and 490–498 (2413) respectively. Nordicentrine (**5**), MS *m/e*: M^+ 325 for $C_{19}H_{19}NO_4$, *m/e* 324 (100%); UV λ_{max}^{EtOH} nm: 282 (max) and 305 (min).

Oxidation of **5** *to* **4**. **5** (5 mg) was treated with CrO_3 (200 mg) and 1 ml dry Py at room temp. for 2 hr. The product was passed through a neutral Al_2O_3 column and eluted with Me_2CO–C_6H_6 (1 : 4) to yield 0.5 mg of **4** which showed MS *m/e*: M^+ 335 (for $C_{19}H_{13}NO_5$), 334, 320 etc; UV λ_{max}^{EtOH} nm: 248, 271, 306–310 sh, 347 and 386. TLC gave identical R_f values to **4** in the following systems: EtOAc–C_6H_6 (1 : 3), EtOAc–C_6H_6 (1:1), EtOAc, MeOH–$CHCl_3$ (3 : 17) and EtOAc–C_6H_6 (3 : 17) using a triple development in each developing solvent.

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