Flemiphyllin triacetate (2). Flemiphyllin (7 mg) was dissolved in 0.7 ml of Ac_2O, pyridine (3 drops) added and the mixture gently refluxed on an oil bath for 6 hr and poured into crushed ice (50 g) while shaking. After 2 hr the product was filtered, washed throughly with H_2O and crystallized from petrol–C_6H_6, mp 117–118° (Found: C, 71.85; H, 6.68, $C_{36}H_{40}O_8$ requires C, 71.99; H, 6.66%).

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REFERENCES

1. Nageswara Rao, K. and Srimannarayana, G. (1983) *Phytochemistry* **22**, 2287.
2. Shinoda, J. (1928) *J. Pharm. Soc. (Japan)* **48**, 214.
3. Mabry, T. J., Markham, K. R. and Thomas, M. B. (eds) (1970) *The Systematic Identification of Flavonoids*, p. 41 and 253. Springer, Berlin.
4. Massicot, J., Marathe, J. P. and Heitz, S. (1963) *Bull. Soc. chim. Fr.* 2712.
5. Jackman, L. M. (1965) *Prog. Chem. Org. Nat. Prod.* **23**, 315.
6. Markham, K. R. and Mabry, T. J. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds) pp. 45–75. Chapman & Hall. London.
7. Komatsu, M., Tomimori, T., Hatayama, K., Makiguchi, Y. and Mikuriya, N. (1969) *Chem. Pharm. Bull (Tokyo)* **17**, 1299.
8. Hillis, W. E. and Horn, D. H. S. (1965) *Aust. J. Chem.* **18**, 531.
9. Horowitz, R. M. and Gentili, B. (1964) *Chem. Ind.* 498.
10. Markham, K. R., Mabry, T. J. and Swift, T. W. III (1968) *Phytochemistry* **7**, 803.
11. Gibbs, H. D. (1927) *J. Biol. Chem.* **72**, 649.
12. Ritchie, E., Taylor, W. C. and Shannon, J. S. (1964) *Tetrahedron Letters* 1437.
13. Deshpande, V. H., Rama Rao, A. V., Malavardan and Venkataraman, K. (1975) *Indian J. Chem.* **11**, 518.
14. Mabry, T. J. and Markham, K. R. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds) pp. 78–126. Chapman & Hall, London.
15. Pelter, A., Bradshaw, J. and Warren, R. F. (1971) *Phytochemistry* **10**, 835.
16. Ollis, W. D. and Sutherland, I. O. (1961) in *Recent Developments in the Chemistry of Natural Phenolic Compounds*, p. 74. Pergamon Press, New York.
17. Komatsu, M., Tomimori, T., Hatayama, K. and Mikuriya, N. (1970) *Yakagaku Zasshi* **90**, 463.

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BROUSSONETINE, A BISQUINOLYL-γ-BUTYROLACTONE FROM *BROUSSONETIA ZEYLANICA**

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Kew Word Index—*Broussonetia zeylanica*; Moraceae; wood; quinoline alkaloid; broussonetine.

Abstract—The wood of *B. zeylanica* (Moraceae) contains a new alkaloid broussonetine, identified as 3,4-bis(8-hydroxyquinolin-4-yl)-γ-butyrolactone.

The only *Broussonetia* species occurring in Sri Lanka is *B. zeylanica* (Thw.) Corner (= *Allaeanthus zeylanicus* Thw.) which is endemic to the country. The wood contains 4-formyl-8-hydroxyquinoline (**1**) [1] and 3,4′-dihydroxy-2,3′-bipyridine (**2**) [2]. Further investigation has revealed another minor quinoline alkaloid, broussonetine (**3**).

Broussonetine, $C_{22}H_{16}N_2O_4$, is soluble in dil. hydrochloric acid and dil. sodium hydroxide (yellow), gives positive tests with ferric chloride and Dragendorff's reagent and, like 8-hydroxyquinoline, forms a fluorescent complex with Mg^{2+} ions [3]. The UV spectrum shows λ_{max} at 252 and 333 nm. The presence of two 8-hydroxyquinoline moieties in the alkaloid is evident from the ^{13}C NMR spectrum; this reveals signals for 18 aromatic carbons which can be assigned as shown (Table 1) and bear a close resemblance to those of **1**. The ^1H NMR spectrum (DMSO-d_6) includes a 2H singlet at δ 9.71 (2 × OH), and in the aromatic region two overlapping doublets at δ 8.89 (H-2′ and H-2″, J = 4.6 Hz) coupled to

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Table 1. ^{13}C chemical shifts* and multiplicities for compounds **1**, **3** and 8-hydroxyquinoline (**5**)

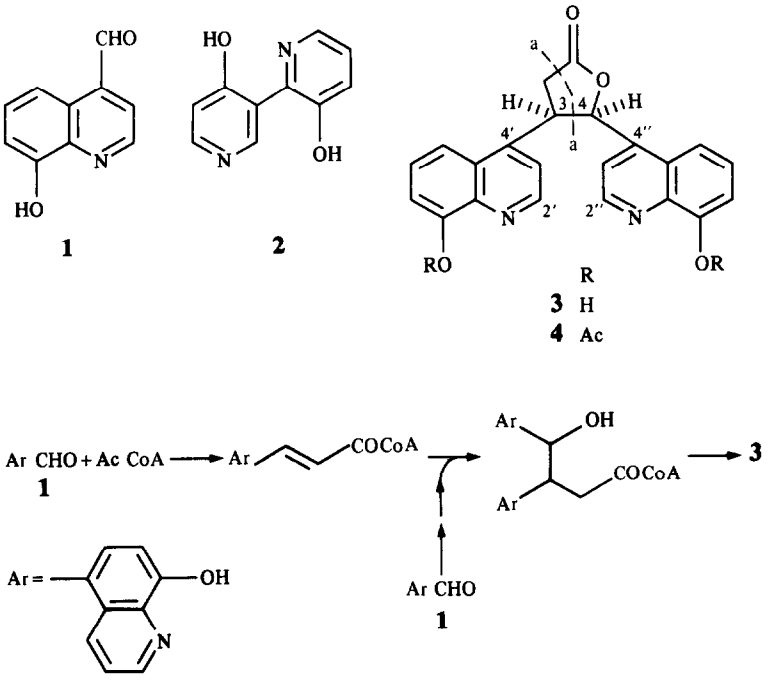
1		3		5	
C-2	148.08 *d*	C-2′ and C-2″	147.81 *d*	C-2	148.13 *d*
C-3	125.90 *d*	C-3′ and C-3″	112.76 *d*	C-3	121.80 *d*
C-4	153.46 *s*	C-4′ and C-4″	143.13 *s*, 145.04 *s*	C-4	136.03 *d*
C-4a	124.68 *s*	C-4′a and C-4″a	125.86 *s*, 127. 26 *s*	C-4a	128.83 *s*
C-5	114.36 *d*	C-5′ and C-5″	118.89 *d*, 119.06 *d*	C-5	117.77 *d*
C-6	130.50 *d*	C-6′ and C-6″	127.64 *d*, 127.85 *d*	C-6	127.52 *d*
C-7	111.70 *d*	C-7′ and C-7″	111.06 *d*, 111.21 *d*	C-7	111.30 *d*
C-8	157.16 *s*	C-8′ and C-8″	153.60 *s*, 153.66 *s*	C-8	153.32 *s*
C-8a	137.09 *s*	C-8′a and C-8″a	138.57 *s*, 136.60 *s*	C-8a	138.49 *s*
C-9	193.02 *d*				
		C-1	174.90 *s*		
		C-2	36.79 *t*		
		C-3	42.43 *d*		
		C-4	80.45 *d*		

*At 90.56 MHz in DMSO-d_6.

doublets at 7.97 (H-3″, J = 4.6 Hz) and 7.70 (H-3′, J = 4.6 Hz), respectively, double doublets at 7.09 (H-5′ or 5″, J = 1.0 and 8.60 Hz) and 7.01 (2H, H-7′ and H-7″, J = 1.0 and 7.40 Hz), and complex signals between 7.22 and 7.31 (H-5′ or 5″, H-6′ and H-6″). Extensive homonuclear decoupling of the 360 MHz ^1H spectrum established the presence of two sets of two and three adjacent protons showing that the 8-hydroxyquinoline moieties are substituted at either C-2, C-4, C-5 or C-7. That the 'substituents' are located at C-4′ and C-4″ in **3** follows from the H-2′, H-2″ and H-3′, H-3″ assignments, above, supported by the presence of the downfield doublet at δ 147.81 (2C) in the off-resonance proton decoupled ^{13}C NMR spectrum which clearly arises from C-2′ and C-2″, and from the observation that in the ^1H NMR spectrum of broussonetine diacetate (**4**) the signals from the protons *ortho*- and *para*- to the acetoxyls are all shifted downfield.

The remainder of the molecule is a fragment $C_4H_6O_2$ which must be a γ-butyrolactone unit (ν_{CO} 1775 cm^{-1}). In the ^1H NMR spectrum it shows signals at δ 6.71 (H-4, *d*, J = 7.4 Hz), 4.84 (H-3, *dt*, J = 7.4 and 8.6 Hz), 3.33 (H-2a, *dd*, J = 8.6 and 17.3 Hz) and 3.00 (H-2b, *dd*, J = 8.6 and 17.3 Hz) consistent with the structure 3,4-bis(8-hydroxyquinolin-4-yl)-γ-butyrolactone (**3**). In agreement the mass spectrum shows a major peak at m/z 171 (89%) corresponding to fragmentation at *a* in **3**. The $J_{3,4}$ value (7.4 Hz) and the downfield shift of H-4 indicate that the quinoline rings are *cis* to each other (*cf.* 3,4-diphenyl-γ-butyrolactone [4]).

Biosynthetically broussonetine (**3**) could arise from two



Scheme 1.

molecules of 1 and one of acetyl-CoA as summarized in Scheme 1.

EXPERIMENTAL

Dried, powdered, wood (3.75 kg) of *B. zeylanica* collected at Hasalaka, Sri Lanka, was successively extracted with hot light petroleum and hot C_6H_6. The C_6H_6 extract (12.0 g) was transferred to a column of silica gel (Merck, 30–70 mesh) and eluted with C_6H_6 containing increasing amounts of $CHCl_3$. The C_6H_6–$CHCl_3$ (49:1) eluates yielded (1), mp 155–156° (420 mg), C_6H_6–$CHCl_3$ (4:1) gave (2), mp 223–224° (130 mg), both identified by comparison with authentic samples previously isolated [2, 3], and C_6H_6–$CHCl_3$ (3:2) afforded broussonetine (3) as tiny crystals, mp 238–239° (from $CHCl_3$) (420 mg), $[\alpha]_D = 0°$ (*c* 0.11; DMF); (Found: C, 71.3; H, 4.5; N, 7.5%; $[M]^+$, 372.111. $C_{22}H_{16}N_2O_4$ requires C, 70.5; H, 4.3; N, 7.5%; $[M]^+$, 372.1110); UV λ_{max}^{MeOH} nm (log ε): 252 (4.19) and 333 (3.70); $\lambda_{max}^{MeOH-NaOH}$ nm: 271 (4.29), 344 (3.99) and 386 (4.07); IR ν_{max}^{KBr} cm^{-1}: 3300, 1775, 1570, 1510, 1470, 1405, 1365, 1330, 1270, 1225, 1160, 1130, 1050, 1015, 930, 750 and 690; MS (70 eV) *m/z* (rel. int.): 372 $[M]^+$ (100%), 344 (2), 328 (2), 172 (47), 171.0687 (89, $C_{11}H_9NO$ requires 171.0684), 170 (30), 145 (18), 143 (28), 142 (16), 117 (15). When treated with Ac_2O (1.0 ml) and pyridine (2.0 ml) broussonetine (20 mg) gave a diacetate (4); crystals, mp 162–163° (C_6H_6–petrol) (15.2 mg, 76%). (Found: $[M-CH_2CO]^+$, 414.1245. $C_{24}H_{18}N_2O_5$ requires 414.1215); IR ν_{max}^{KBr} cm^{-1}: 1775, 1755, 1601, 1591, 1500, 1470, 1410, 1370, 1310, 1210 *br*, 1180 *br*, 941, 771 and 755; ^1H NMR (360 MHz, $CDCl_3$); δ 2.50 and 2.52 (each 3H, *s*, OAc), 2.68 (1H, *dd*, *J* = 3.1 and 17.9 Hz, H-2a), 3.18 (1H, *dd*, *J* = 9.3 and 17.9 Hz, H-2b), 4.50 (1H, *dt*, *J* = 3.1 and 9.3 Hz, H-3), 6.51 (1H, *dd*, *J* = 0.7 and 3.1 Hz, H-4), 7.12–7.64 (8H, *m*, ArH), 8.97 and 9.00 (each 1H, *d*, *J* = 4.5 Hz, H-2 and H-2'); MS (20 eV) *m/z* (rel. int.): 456 $[M]^+$ (5%), 414 (18), 372 (100), 172 (37), 171 (67), 170 (26), 145 (14), 143 (21) and 117 (7).

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REFERENCES

1. Gunatilaka, A. A. L., Perera, J. S. H. Q., Sultanbawa, M. U. S., Brown, P. M. and Thomson, R. H. (1979) *J. Chem. Res.* (*S*) 61; (*M*) 779.
2. Gunatilaka, A. A. L., Sultanbawa, M. U. S., Surendrakumar, S. and Somanthan, R. (1983) *Phytochemistry* **22**, 2847.
3. Feigl, F. (1960) *Spot Tests in Organic Analysis*, 6th edn, p. 205. Elsevier, Amsterdam.
4. Mandel'shtam, T. V., Kolesova, S. V., Polina, T. V., Solomentsev, V. V. and Osmolovskaya, N. S., (1980) *J. Org. Chem. USSR* **16**, 1024.

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SATIVANINE-C: A CYCLOPEPTIDE ALKALOID FROM THE BARK OF *ZIZYPHUS SATIVA**

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Key Word Index—*Zizyphus sativa*; Rhamnaceae; cyclopeptide alkaloid; sativanine-C.

Abstract—From the bark of *Zizyphus sativa* a previously undescribed 13 membered cyclopeptide alkaloid, sativanine-C has been isolated. The structure of this new compound was elucidated by spectroscopic methods, its transformation product and by chemical degradation.

INTRODUCTION

As a part of our extended studies on the alkaloids of the Rhamnaceae we recently reported the isolation and characterization of five cyclopeptide alkaloids from *Zizyphus sativa* [2]. Extensive chromatography of the crude bases furnished a further previously unknown 13-membered cyclopeptide alkaloid (1). Its structure is related to nummularine-B (3) [3].

RESULTS AND DISCUSSION

The alkaloid was isolated from the polar fraction by TLC on silica gel. The molecular formula was determined by high resolution mass spectrometry as $C_{29}H_{43}N_5O_6$. The IR spectrum displayed characteristic secondary am-

*Part 34 in the series "The Alkaloids of Rhamnaceae". For Part 33 see ref. [1].