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TWO PHENAZINE DERIVATIVES, POLYCARTINE A AND B FROM IDESIA POLYCARPA MAXIM (FLACOURTIACEAE)

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Abstract: Two hydrogenated phenazines have been isolated from the fruits of Idesia polycarpa Maxim and their structures were determined by spectral and chemical means.

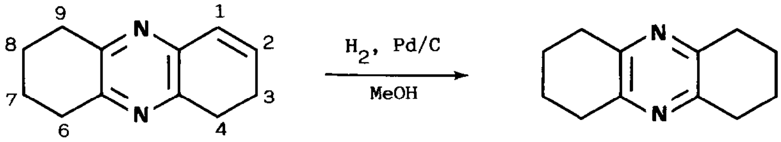
In the continuation of our chemical studies on the endemic plants of the Ryukyu Islands, we have investigated the constituents of Idesia polycarpa Maxim. This plant bears the conspicuously red fruits in winter which, as we noticed, are never eaten by birds. This observation prompted us to investigate the components of the fruits. Up to now compounds such as idesin,[1] gynocardin,[2] ryanodine,[3] poliothyrososide,[4] homaline,[5] and leucopelargonidine[6] have been obtained from the plants of Flacourtiaceae. We have now isolated two hydrogenated phenazines named polycartine A (1) and B (2). Although some phenazine derivatives have been found from bacteria,[7] few hydrogenated phenazines have been isolated from natural sources.[8] We describe the isolation of 1 and 2,and the determination of their structures in this paper.

The fruits (13 kg), which were collected in Iriomote Island and Okinawa Island, were crushed in a blender with a mixture of ethanol and aqueous hydrochloric acid. After removal of the solid residue by filtration, the filtrate was concentrated and partitioned between ether and water. The aqueous layer was basified with ammonium hydroxide and extracted with benzene. The organic phase was dried and concentrated to give a yellowish solid. The solid was purified by preparative TLC (silica gel; benzene—acetonitrile, 9:1) to afford 132 mg of 1 and 74 mg of 2. Repeated recrystallizations of 1 from aqueous methanol gave a pure sample of polycartine A (1) as pale yellowish crystals. Compound 2 was first purified by sublimation under reduced pressure and then recrystallized from aqueous methanol to afford analytically pure polycartine B (2) as pale yellowish needles.

Polycartine B was identified as 1,2,3,4,6,7,8,9-octahydrophenazine by comparison with a synthesized authentic sample.[9] To the best of our knowledge, there is only one precedent[8] for the isolation of 2 from natural sources.

Polycartine A, mp 69–71°C, exhibits the following physical data. UV$_{max}$ (MeOH): 260 and 323 nm. MS: m/z 187 (M^++1), 186 (M^+), 159, 144, 131, 96, and 68. IR (KBr): 3035, 2950, 2850, 1620, 1590, 1415, 1200, 1130, 1010, and 890 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ1.6–2.2 (4H, m, H-7 and H-8), 2.4–2.7 (2H, m, H-3), 2.7–3.2 (6H, m, H-4, H-6, and H-9), 6.3 (1H, ddd, J=9.9, 2.8, 2.8 Hz, H-2), and 6.5 (1H, d, J=9.9 Hz, H-1). ^{13}C NMR ($CDCl_3$): δ22.87 (t), 22.89 (t), 23.39 (t), 29.48 (t), 31.64 (t), 31.80 (t), 128.17 (d), 134.14 (d), 145.78 (s), 148.94 (s), 149.35 (s), and 149.54 (s). *Anal*. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.25; H, 7.63; N, 15.18.

Polycartine A, which is a new compound, has the spectral properties similar to polycartine B. The ^{1}H NMR spectrum, coupled with the ^{13}C NMR and IR spectra, shows the presence of a conjugated 1,2-disubstituted double bond [δ6.3 (1H, ddd, J=9.9, 2.8, 2.8 Hz) and 6.5 (1H, d, J=9.9 Hz)]. Hydrogenation of **1** with Pd/C in methanol gave **2**. Thus polycartine A (**1**) should be 3,4,6,7,8,9-hexahydrophenazine.



(**1**) (**2**)

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References:

1) T. Kubota and T. Tsuno, *Bot. Mag. Tokyo*, **79**, 770 (1966).
2) R. A. Coburn and L. Long Jr., *J. Org. Chem.*, **31**, 4312 (1966).
3) K. Wiesner, Z. Valenta, and J. A. Findlay, *Tetrahedron Letters*, 221 (1967).
4) V. Plouvier, *C. R. Acad. Sci. Paris Ser.*, D**268**, 1982 (1969).
5) M. Paris, G. Rattle, R. Sartat, and F. Xavievjarreau, *C. R. Acad. Sci. Paris Ser.*, C**266**, 37 (1968).
6) K. A. Nair and N. Ramigh, *Chemical Abstracts*, **75**, 1298 (1971); *Curr. Sci.*, **40**, 187 (1971).
7) (a) Wrede and Stack, *Z. Physiol. Chem.*, **181**, 58 (1929). (b) Clem and Macllwain, *J. Chem. Soc.*, 479 (1938). (c) Clemo and Daglish, *J. Chem. Soc.*, 1481 (1950). (d) Matsumura, *Nippon Kagaku Zasshi*, **81**, 515 (1960). (e) Moos and Rowen, *Arch. Biophys.*, **43**, 88 (1953).
8) B. Maurer and G. Ohloff, *Helv. Chim. Acta*, **59** (4), 1169 (1976).
9) P. A. S. Smith, *J. Am. Chem. Soc.*, **70**, 323 (1948).

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