Alkaloids of Berberis aristata - isolation of aromoline and oxyberberine

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Summary:Five alkaloids have been isolated from "rasaut", an extract of the root bark of Berberis aristata, which have been characterized as aromoline, oxyberberine, oxyacanthine, berbamine and berberine chloride.

Introduction

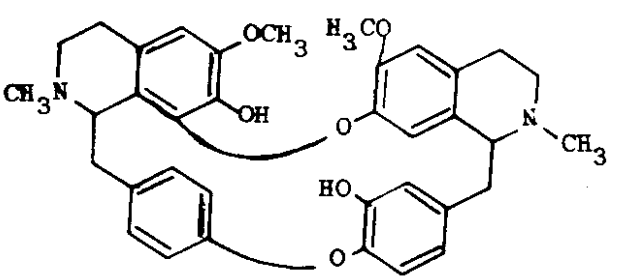
Berberis aristata [1] DC (family Berberidaceae) is found in the Himalayas from 6,000 to 10,000 ft and in the Nilgiri Hills. The extract made from the root bark of this plant is known as "rasaut" in the indigenous unani system of medicine and it is used in the treatment of skin diseases, menorrhagia, jaundice, infections of the eye and malarial fever. Ten alkaloids from roots of B. floribunda (B. aristata) have previously been reported. [2,3,4] These are oxyacanthine, berbamine, berberine, epiberberine, palmatine, dehydorcardoline, jatrorrhizine, columbamine, karachine and taxilamine. In the present work five alkaloids were isolated from "rasaut" which have been characterised as a aromoline, oxyberberine, oxyacanthine, berbamine and berberine chloride. Aromoline and oxyberberine have previously not been reported from this plant.

The identity of the isolated compounds was confirmed through comparisons of their IR, U.V., NMR, and mass spectra with those reported in the literature.

Experimental

Isolation of Berberine chloride, Berbamine, Oxyacanthine and Aromoline.

Rasaut (3 kg) was extracted with hot ethanol (10 litre). The extract was evaporated and the residue was acidified with 20% acetic acid (1 litre). The solution was then extracted exhaustively with chloroform (5 litre). The acidic aqueous extract was basified with 20% ammonium hydroxide solution (2 litre) to pH-9 and extracted to obtain the tertiary bases. Berberine chloride could be isolated by crystallisation from the aqueous layer. The chloroform layer was separated, dried(anhydrous Na_2SO_4) and evaporated to a brown residue.



Aromoline

The alkaloidal fraction(12 gm) was chromatographed on a neutral Al_2O_3 column (410 gm). Elution was carried out with petroleum-ether (2 litre), petroleum ether - ethylacetate-methanol (2 litre) and finally with methanol(1 litre). The ethylacetate and ethylacetate-methanol eluates afforded mixtures of berbamine and oxyacanthine and then aromoline. Berbamine and oxyacanthine

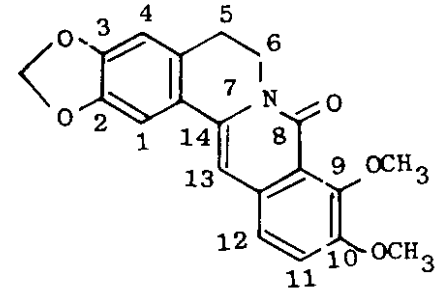
were further purified by separation on precoated t.l.c. sheets of Al_2O_3 neutral(Type E),using 85% acetone/15% methanol.

Aromoline (300 mg) was purified on a basic Al_2O_3 column(20 gm). The column was eluted first with ethylacetate and then with ethylacetate-methanol mixtures. The ethylacetate-methanol eluates gave aromoline on evaporation(30 mg, m.p. 173°C) IR($CHCl_3$): max 3350 cm^{-1} (OH); UV(MeOH): max 285 nm λ min 263; mass: m/e = 594 (M^+,100%), 382(46%), 381(85%), 367 (40%), 364(8%), 297(3%), 192(17%), 191 (75%), 174(17%), 168(14%); NMR ($CDCl_3$): δ 2.54, 2.56(2xNMe), 3.56, 3.76(2 xOMe), 6.32-7.45(10 x arom H).

Isolation of Oxyberberine

Rasaut (2 kg) was soaked for 12 hours in 10% acetic acid (5 litre), filtered and basified with 20% NH_4OH solution to pH-10. It was extracted with chloroform(20 litre) to obtain the tertiary bases. The chloroform layer was separated, dried(anhydrous Na_2SO_4) and evaporated to a brown residue. The alkaloidal fraction(8 gm)was chromatographed on a neutral Al_2O_3 column(280 gm). Elution was carried out with petroleum-ether, petroleum ether-ethylacetate, ethylacetate, ethylacetate-methanol and finally with methanol.

The petroleum ether-ethylacetate fraction afforded oxyberberine and other minor alkaloids. Oxyberberine was further purified by preparative t.l.c. using silica gel(G-60)plates(solvent system: ethylacetate 80%, petroleum-ether 20%), followed by a second preparative t.l.c.($CHCl_3$: MeOH,100:5, v/v system). UV(EtOH) λmax 233,290,340 nm, λ min 285,292.5 nm. NMR ($CDCl_3$, 360 MHz), δ 2.90(t,2H,J=6.OHz, H-5), 4.30(t, 2H, J=6.OHz, H-6), 3.96(s, 3H,OCH_3), 4.02(s,3H,OCH_3), 6.73 (s,1H, H-4), 6.72 (s, 1H, H-1), 7.32(d,J=7.3 Hz, H-12), 7.35(d, J=7.3Hz,2H,H-12). Mass m/e: 351 (M^+,55%),336(62%),322(61%),292(30%), 168(13%). Oxyberberine was further identified by direct chromatographic and spectroscopic comparisons with an authentic sample.



Oxyberberine

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