

THE ALKALOID OF *BERBERIS UMBELLATA*, WALL. PART I. ISOLATION AND EXAMINATION OF UMBELLATINE.

By R. CHATTERJEE.

From the stem bark of *Berberis umbellata* a new alkaloid of the molecular formula $C_{21}H_{21}O_3N$ has been isolated. It contains one methylenedioxy group, two methoxy groups and one imino group. The new alkaloid has been designated as umbellatine.

Berberine and several other alkaloids have been reported to be present in various species of the genus *Berberis* (N.O. Berberidaceae). An examination of *B. umbellata* has now been carried out with a view to find whether it contains any new alkaloid or not. The stem bark was collected from Darjeeling District in July. It has yielded a yellow crystalline alkaloid, m.p. $206-7^\circ$ (decomp.). The analytical data are in agreement with the molecular formula $C_{21}H_{21}O_3N$. As it appears to be a new alkaloid, it has been named "umbellatine."

Umbellatine has been found to contain two methoxy groups. It forms a crystalline methiodide and a yellow nitroso derivative which points to the presence of the nitrogen atom as a secondary amine; 5% gallic acid solution imparts a green colour to a solution of umbellatine in concentrated sulphuric acid, indicating the presence of a methylenedioxy group. The analytical data show the presence of one methylenedioxy group. It crystallises from water with 5.5 molecules of water of crystallisation. It contains half a molecule of water even on drying *in vacuo* at 110° and on raising the temperature to 120° , the colour of umbellatine changes from yellow to light brown. At higher temperatures umbellatine decomposes gradually; hence its remaining half molecule of water cannot be removed.

EXPERIMENTAL.

Isolation of Umbellatine.—The finely ground air-dried stem bark (1 kg.), obtained from Messrs. G. Ghose & Co., Darjeeling, was extracted by cold percolation with 90% alcohol during 10 days. The dark brown residue, after the removal of alcohol on the water-bath, was treated with cold water (500 c.c.) and filtered. The filtrate was extracted with light petroleum (b.p. $40-60^\circ$), to remove some oily matter. Moderately concentrated hydrochloric acid was then added to the aqueous extract to give 1% solution, which was allowed to stand for 2 hours. The crude hydrochloride of the

alkaloid gradually crystallised out and was filtered off. It was recrystallised from hot water as yellow, feathery needles, decomposing above 200° , yield 8.5 g.

The *hydrochloride* (5 g.) was dissolved in hot water and made alkaline with sodium hydroxide solution, when a yellow precipitate was obtained. It was collected and crystallised from hot water in yellow silky needles, m.p. $206-7^{\circ}$ (decomp.). The yield of pure umbellatine is 0.68% calculated on the amount of air-dried bark. [Found in a sample dried at 110° in *vacuo* over P_2O_5 : C, 59.0, 58.8; H, 5.33, 5.36; N, 3.2, 3.3; OMe, 14.4; CH_2O_2 , 2.95 (Clowes and Tollens, *Ber.*, 1899, **32**, 2841). Found in a sample dried at 120° in *vacuo* over P_2O_5 : C, 58.8; H, 5.33. $C_{21}H_{21}O_8N$, $\frac{1}{2}H_2O$ requires C, 59.4; H, 5.2; N, 3.3; OMe, 14.62; CH_2O_2 , 3.30 per cent].

Umbellatine is optically inactive. It is soluble in alcohol, methanol and hot water, sparingly soluble in cold water, acetone and chloroform and insoluble in benzene, ethyl acetate, ether and light petroleum ether.

Umbellatine forms crystalline hydrochloride, hybromide and hydriodide. Reactions with alkaloidal reagents are tabulated below:

Mayer's reagent	...	...	Pale yellow precipitate formed immediately.
Wagner's reagent	...	...	Orange precipitate formed immediately.
Picric acid	...	...	Pale yellow precipitate.
10% Potassium iodide solution	...	...	Yellow precipitate.
Acidified with conc. H_2SO_4 in a test tube and brought in contact with Cl_2 water	...	...	A blood red ring at the junction of the layers of two liquids.
Concentrated sulphuric acid	...	...	Dissolves with deep yellow colour changing to green.
Erdmann's reagent	...	...	Dissolves with a violet colour changing to blood-red and finally to yellow on long standing.
Froehde's reagent	...	...	Dissolves with a greenish yellow colour.
Mandelin's reagent	...	...	Yellow colour changing to red.
Conc. H_2SO_4 with $K_2Cr_2O_7$ powder	...	...	Green colouration on long standing.

Umbellatine Hydrochloride.—To a solution of umbellatine in hot water dilute hydrochloric acid was added drop by drop, till the precipitated hydrochloride settled down. On rewarming the mixture the hydrochloride dissolved and on cooling it crystallised as yellow feathery crystals, which charred without melting.

Umbellatine Chloroplatinate.—The chloroplatinate, prepared with a warm concentrated solution of umbellatine hydrochloride (0.3 g.) in water and platinic chloride (0.12 g.), separated as a yellow granular precipitate which was collected after heating on the water-bath for about 15 minutes. The

precipitate was well washed with hot water, and then collected and dried. Umbellatine chloroplatinate is a light yellow powder, which is insoluble in organic solvents and water, and which decomposes without melting. [Found: Pt, 15.71; M. W. 415. $(C_{21}H_{21}O_8N, HCl)_2 PtCl_4$ requires Pt, 15.72 per cent. M. W. 415].

Nitrosoumbellatine.—An ice-cold solution of umbellatine (1 mol.) in 10% acetic acid solution was treated with an ice-cold solution of sodium nitrite (1.5 mol.). A yellow granular precipitate was obtained, which was filtered after keeping the reaction mixture overnight at room temperature and was well washed first with 5% acetic acid solution and then with water. The nitroso derivative crystallised from alcohol in yellow glistening needles, m.p. 265-67° (decomp.). (Found: N, 6.9. $C_{21}H_{20}O_8N_2$ requires N, 6.4 per cent).

Umbellatine Methiodide.—A solution of umbellatine (1 mol.) in chloroform and methyl iodide (1.5 mol.) was allowed to stand at the room temperature for about 2 hours when a yellow crystalline methiodide separated. It was filtered, well washed with chloroform and dried; it chars without melting.

Further work is in progress.

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THE CHEMICAL LABORATORIES,
ST. JOSEPH'S COLLEGE, DARJEELING AND
UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA.

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