CHEMICAL EXAMINATION OF THE ROOTS OF *CENTAUREA BEHEN* LINN.

Isolation of Behnin

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Centaurea Behen or *Centaurea Behman*, commonly known in Hindustani as 'Lal Behman' and 'Rakta Barni' in Bengali, is an annual herb belonging to the Natural Order 'Compositæ'. It is cultivated throughout Northern India for the sake of its highly medicinal roots, which are used as remedial agents in various diseases.

Red Behman is a tuberous root consisting of a central part about 2″ in diameter, from which spring 5 or 6 tapering tubes $1\frac{1}{2}$″ to 2″ long and $\frac{1}{2}$″ to 1″ in diameter. At the top of the central tuber the scaly crown is 2″ in diameter. The external surface of the root is reddish brown and marked by numerous circular and longitudinal wrinkles, but internally there is a dull red woody central portion surrounded by a thick yellowish white horny layer. In the commercial article the root is sliced and the central woody part removed, but it is always associated with the white layer.

Red Behman, the drug of the ancient Persians, was introduced by the Arabs in the West. The drug is considered to be expelling flatulence and aphrodisiac by Dymock, Warden and Hooper.[1] Accordingly these are used in callous affections and jaundice as well as resolvents of phlegmatic humours.

In literature nothing has been mentioned regarding the chemical constituents of this plant. In view of its important medicinal properties however, the present authors have been tempted to put it to a thorough chemical examination in order to have an insight into the nature of its active principle. An account of the active principle of the root is given in this paper. It is indeed amazing that no alkaloid has been found in it as is mentioned by Kirtikar and Basu.[2] Instead, a resinous fatty matter, a saponin and a reddish white crystalline substance of the nature of a $\Delta^{\alpha\beta}$-unsaturated lactone have been isolated in small amounts and analysed. Most probably its medicinal property is due to the latter substance. It has been named 'Behnin', having a molecular formula $C_{24}H_{48}O_3$. Further it is

found to contain a methoxy group according to the determination made by micro-Zeissel's method.

Experimental

For extraction with different solvents, the dry root was crushed to fine powder and extracted in a Soxhlet's extractor in lots of 25 gm. each in order to ascertain the best solvent. The solvent was recovered by distillation in each case and the residue brought to a constant weight by keeping in a steam oven with the following results:—

1. *Alcohol extract* (15·7%).—Brown resinous mass, soluble in benzene but insoluble in water, giving a yellow colour with caustic soda, an intense red colour with concentrated sulphuric acid no precipitate with lead acetate, thus showing the presence of a lactone.

2. *Benzene extract* (10·5%).—Brown waxy residue, soluble in chloroform, insoluble in water, giving a yellow colour with caustic soda and red with strong sulphuric acid.

3. *Ethyl acetate extract* (4·36%).—Red resinous product, soluble in hot alcohol, neutral to litmus, yellow with caustic soda, decolourising bromine water, reducing potassium permanganate and finally giving a dirty green precipitate with ferric chloride.

4. *Chloroform extract* (10·4%).—Brown fatty residue, giving a beautiful yellow colour with alcoholic caustic potash.

5. *Aqueous extract* (23·2%).—A red brittle solid giving froths on heating the aqueous solution, precipitating with lead acetate and reducing Fehling's solution, probably due to sugars and tannins.

The powdered root on complete incineration left 14·85% water-soluble and 85·15% water-insoluble ash. The following radicals were detected:—

(*a*) In the water-soluble portion: SO_4CO_3, Cl, Na and K

(*b*) In the water-insoluble portion: CO_3, Al, Ca and Mg.

For exhaustive extraction 8 kg. of the powdered roots were extracted with alcohol three times, in lots of 2 kg. each, in a 5 litre flask. The extract was filtered hot and allowed to stand overnight, when it gave a buff coloured precipitate. It was filtered and the filtrate was set aside for further examination. The precipitate was washed with alcohol in order to remove the tannin and the colouring matter. On keeping in air, it could not be obtained dry on account of the presence of fatty and resinous matter in it. Hence it was repeatedly washed with petroleum ether to remove the impurities. The product was then extracted with hot alcohol

and animal charcoal a number of times and the solution filtered through a hot water filter funnel. After keeping for some time, the precipitate was filtered through a Buchner funnel under suction, washed with petroleum ether and dried in air. On crystallisation from alcohol slightly red crystalline leaflets, melting at 79·80° C. were obtained.

The previous filtrate already mentioned was distilled to recover the solvent and the residue poured into water to remove the sugars and tannins which were soluble in water. It could not be filtered due to the formation of an emulsion. Hence it was allowed to stand for two days, treated with common salt and heated in a beaker. On cooling, a slightly red precipitate was formed. It was filtered, dissolved in alcoholic caustic soda and precipitated with dilute sulphuric acid. This precipitate was filtered, washed with alcohol and dried in air. The above filtrates were combined and examined later on. On crystallisation of the precipitate alternately from benzene and methyl alcohol with the addition of animal charcoal crystalline leaflets sintering at 72° C. and melting at 79–80° C. were obtained. The whole operation was tedious and involved tremendous difficulties.

From the combined filtrates mentioned above a saponin was isolated but it was insufficient for further examination.

Properties.—It is a light buff coloured crystalline substance. It is soluble in chloroform, sparingly soluble in ethyl alcohol, benzene and methyl alcohol and insoluble in water. On boiling with water for a long time, it melts to an oily liquid which on cooling becomes resinous and greasy probably due to decomposition. When heated quickly, it decomposes completely with the evolution of black fumes and a luminous flame. On exposure to ordinary sun light, behnin assumes a yellow colour, but in strong direct sun light it is converted into a sticky yellow resin. It is insoluble in 5% aqueous caustic soda solution but on heating it dissolves slowly with a yellow colour. It develops an intense beautiful yellow colour with alcoholic caustic potash as in the case of $\Delta^{\alpha\beta}$-unsaturated lactones studied first by Thiele[3] and subsequently by Jacobs and Hoffmann.[4]

In strong sulphuric acid, it produces a red colour. It decolourises a solution of bromine in chloroform and a dilute alkaline solution of potassium permanganate. It does not give any colour with ferric chloride, nor does it reduce Fehling's solution. It gives a positive Salkowski's reaction producing a red tinge. In Liebermann-Burchard reaction, behnin turns green. It becomes intense yellow in strong nitric acid and gives no precipitate with lead acetate. Behnin gives no colour with an alkaline solution of sodium nitroprusside. It has been found to contain a methoxy group and

forms tetrabromo derivative. It has got no alcoholic hydroxy group, as it does not form any acetyl or benzoyl derivative. Thus both the remaining oxygen atoms account for the lactonic grouping. Results of a series of analyses and molecular weight determinations point to a molecular formula $C_{24}H_{48}O_3$. (Found: C = 75·18, 74·79; H = 12·66, 12·72; M.W. by Rast's camphor method = 372, 378. 408; $C_{24}H_{48}O_3$ requires C = 75·01; H = 12·5%; M.W. = 384.)

Estimation of Methoxyl Group.—The determination was conducted by the micro-Zeissel's method. (Found: OCH_3 = 7·94; $C_{23}H_{45}O_2$ (OCH_3) requires OCH_3 = 8·07%.)

Tetrabromo Derivative.—Behnin (0·2 gm.) was dissolved in chloroform (15 c.c.) and treated with a solution of bromine in chloroform. It was allowed to stand in dark for 4 hours and heated on a water-bath under reflux for half an hour. On evaporating the solvent, a semi-solid pasty mass was obtained. It was crystallised from alcohol in yellow needles melting at 67° C. (Found: Br, 45·12; $C_{24}H_{48}O_3Br_4$ requires Br, 45·45%.)

Summary

From the roots of *Centaurea Behen* a crystalline unsaturated lactone having a molecular formula $C_{24}H_{48}O_3$ has been obtained.

It has been found to contain a methoxy group and to yield a tetrabromo derivative.

REFERENCES

1. Dymock, Warden and Hooper *Pharmacographia Indica.*
2. Kiritkar and Basu .. *Indian Medical Plants.*
3. Thiele .. *Annalen*, 1901, **319**, 155.
4. Jacobs and Hoffmann .. *J. Biol. Chem.*, 1926, **67**, 333.