

CHEMICAL EXAMINATION OF THE SEEDS OF *DODONAEA VISCOSA*

Isolation of Dodonin, Dodogenin and a Fixed Oil

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Dodonea viscosa or Benmendu as it is known in Punjabi and Aliar in Hindi is an ever-green shrub belonging to the natural order of Sapindaceæ. It is met with throughout India, often growing wild, but generally cultivated in the form of a hedge for ornamenting gardens, roads, etc., and is also clipped into various artistic designs for this purpose. It is particularly abundant in the Punjab, United Provinces, Central Provinces, Bengal, Andhra Districts and Ceylon. In sheltered and moist places the plant is often found as a small tree with erect twiggy branches, but commonly it is a shrub from nine to twelve feet high.

The plant possesses a great repute in medicine. According to Kirtikar and Basu,¹ the leaves of the plant are used in baths and fomentations, and their powder is applied over wounds, burns and scalds. They are also considered to be very efficacious in rheumatism and possess great febrifugal properties. In the Punjab, the leaves made into a paste are applied in snake-bite. In South Africa the infusion of the green plant is often given in stomach disorders. In Peru the leaves are chewed like Coca leaves as a stimulant. The seeds of the plant also are reputed to have similar properties, as the leaves.

Since no work has been done on this plant and also in view of its medicinal importance, the present work was undertaken to find out the active principles present in the seeds, by systematic chemical examination.

The present authors working on the seeds of the plant have been able to isolate two compounds, one a glucoside melting at 182–86° C., and the other a deep yellow fixed oil in yields of 3.42 and 20.27% respectively. The systematic chemical examination of the fixed oil will be the subject of a separate communication, while in the present one the glucoside and particularly the product of its hydrolysis have been studied in detail.

The glucoside and the product of its hydrolysis have been named "Dodonin" and "Dodogenin" respectively. As Dodonin could not be

purified further, Dodogenin was made the subject of detailed study. It crystallises in fine small needles melting at 249° C., and has a molecular formula $C_{23}H_{36}O_8$. Dodogenin definitely contains a cyclopenteno-phenanthrene nucleus in the molecule as was found by Selenium dehydrogenation of the compound, when it gave the Diel's Hydrocarbon ($C_{18}H_{16}$). It does not contain any phenolic hydroxy group, but the presence of five alcoholic hydroxyls has been confirmed owing to the formation of penta-acetyl, penta-benzoyl and penta-*p*-nitrobenzyl derivatives.

EXPERIMENTAL

9.96 Kilos of the powdered seeds of the plant were extracted with petroleum ether (B.P. 40°-60° C.) in the cold in order to get rid of the fatty matter from the seeds. On distilling off the solvent a deep yellow fixed oil in an yield of 20.27% was obtained. The seeds after extraction with cold petroleum ether were next extracted with hot ethyl alcohol under reflux in lots of 1 Kilo at a time. The extracts were filtered hot and the solvent distilled off on a water-bath. The syrupy mass was allowed to stand overnight when some solid product settled down. This was filtered off and washed with ether. The mass was repeatedly dissolved in alcohol and precipitated with ether in order to free it from sugars. Thus 341 gm. of the material was obtained in white microneedles melting at 182-86° C., in an yield of 3.42%. The substance has been named "Dodonin".

Dodonin is very bitter in taste. It dissolves easily in water producing lathers. It is soluble in methyl and ethyl alcohols, acetic acid and phenol, while insoluble in benzene, ether and petroleum ether. It reduces Fehling's Solution readily.

As dodonin could not be obtained in quite pure form, it was hydrolysed by boiling with 5% HCl and the mass was allowed to cool when a crystalline precipitate settled down. It was filtered and repeatedly washed with water. It was then purified by treatment with animal charcoal in alcohol. Dodogenin was finally crystallised from alcohol-benzene mixture (1:4) in fine white needles melting sharp at 249° C.

Both Dodonin and Dodogenin are saturated compounds and thus do not add bromine. They neither reduce ammonical silver-nitrate, nor give Legal's test. Both the compounds give Liebermann-Burchard's and Salkowski's reactions promptly, indicating the presence of sterol nuclei in the molecules. They are insoluble in alkalies and do not give any colour with them. None of them give any colour with ferric chloride.

Dodogenin is soluble in methyl and ethyl alcohols. It is insoluble in water, acetone, chloroform, benzene, ether and petroleum ether. It also dissolves in acetic acid and pyridine easily. Dodogenin is insoluble in hot or cold HCl, and does not contain nitrogen in the molecule. It gives deep red colour with conc. H_2SO_4 . (Found: C= 62.73, 62.28, 62.79; H= 8.16, 8.06, 8.11 per cent.; M.W. Cryoscopic in phenol= 439.91, 440.82, 440.14; $C_{23}H_{36}O_8$ requires C= 62.72, H= 8.18 per cent.; M.W. 440.)

Acetylation of Dodogenin.—2 gm. of Dodogenin were dissolved in 5 c.c. of acetic anhydride, and to it 0.5 gm. of anhydrous sodium acetate were added. The mixture was refluxed in a boiling tube for about half an hour on the sand-bath. After this the hot mixture was poured into cold water. The compound which separated in fine crystalline form, was filtered and washed with water. It was recrystallised from alcohol-benzene mixture (1:2) in small needles melting at $190^\circ C$. It is soluble in ethyl and methyl alcohols, ethyl acetate and chloroform, while insoluble in water, benzene, ether and petroleum ether. (Found: C= 60.89, 60.90; H= 7.09, 7.06 per cent.; $COCH_3 = 33.32\%$; $C_{23}H_{31}O_8 (COCH_3)_5$ requires C= 60.92; H= 7.07%, and $COCH_3$ calculated for five acetyl groups in the molecule = 33.07%.)

Benzoylation of Dodogenin.—To a solution of 1 gm. of Dodogenin in 10 c.c. of pyridine, 5 c.c. of benzoyl chloride were added. The mixture was allowed to reflux for about half an hour on the sand-bath. The contents, while hot, were poured into cold water and kept overnight when a crystalline mass settled down. It was treated with excess of sodium carbonate solution, filtered and thoroughly washed with water. After drying, the product was recrystallised from ethyl acetate in small cubes and plates melting at $135^\circ C$. The benzoyl compound is soluble in alcohols, chloroform, and hot ethyl acetate, while quite insoluble in water, benzene, ether and petrol-ether. (Found: C= 72.55, 72.49; H= 5.89, 5.84; $C_{23}H_{31}O_8 (COC_6H_5)_5$ requires C= 72.50, H= 5.83%.)

p-Nitrobenzyl derivative.—To 1 gm. of Dodogenin dissolved in 5 c.c. of pyridine were added 2 gm. of *p*-nitrobenzyl chloride, and the mixture was refluxed on the sand-bath for about half an hour. On cooling, the crystalline mass, which settled down, was filtered, rapidly washed with alcohol and dried. The compound was recrystallised from alcohol-ether mixture (5:1) in very small needles melting at $165^\circ C$. It is soluble in alcohol and ethyl acetate, while insoluble in water, benzene, chloroform, acetone, ether and petrol-ether. (Found: C= 62.39, 62.41; H= 5.46, 5.55; $C_{58}H_{61}N_5O_{18}$ requires C= 62.42; H= 5.47%.)

Methylation of Dodogenin.—A suspension of 2 gm. of the substance in 200 c.c. of anhydrous acetone was treated with 8 c.c. of freshly distilled dimethyl sulphate and 20 gm. of anhydrous potassium carbonate. After refluxing for 30 hours on a water-bath the contents were cooled, filtered, and the residue washed with a little acetone. From the filtrate the solvent was distilled off and excess of water was added to the syrupy residue, when a crystalline mass settled down. It was filtered and washed with water. The compound was recrystallised from hot ethyl acetate in glistening rhombic needles melting at 132° C. The methylated derivative is soluble in acetone while Dodogenin is not. It is soluble in alcohol, chloroform and ethyl acetate, while insoluble in water, benzene, ether and petrol-ether. [Found: C= 65·90, 65·87; H= 9·11, 9·06; percentage of OCH₃= 30·41, 30·38 C₂₃H₃₁O₃ (OCH₃)₅ requires C= 65·88, H= 9·01; OCH₃ calculated for five methoxyl groups 30·39%.]

Selenium dehydrogenation of Dodogenin.—5 gm. of Dodogenin were intimately mixed with 25 gm. of Selenium metal powder and the mixture was taken in a combustion tube. The mixture was heated first at a lower temperature, while a slow current of dry hydrogen was passed through the tube. The temperature was gradually raised to 310° C., and the furnace was maintained at that temperature for about an hour. The compound, which sublimed in the receiver in orange-red plates was recrystallised from alcohol with the addition of a little ether in glistening orange-red plates melting at 122° C. It was found to be the Diel's Hydrocarbon (C₁₈H₁₆).

Fusion with NaOH.—2 gm. of the compound were gradually added to a molten mixture of 20 gm. of caustic soda and 1 c.c. of water in a nickel crucible maintained at 200° C. The reaction was vigorous and a lot of frothing took place during the reaction. The mass was finally heated at 300° C. for half an hour. The reaction was over when carbon dioxide was no longer evolved. The cold melt was dissolved in water and neutralised with dilute hydrochloric acid, when a white crystalline precipitate settled down, which was filtered, washed and dried. It was then crystallised from methyl alcohol in fine micro-needles melting at 224° C. It does not give any colour with ferric chloride. It is soluble in sodium hydroxide and carbonate solutions. It appears to be a carboxylic acid. It is also soluble in hot ethyl and methyl alcohols, and ethyl acetate, while insoluble in acetone, water and chloroform. (Found: C= 58·07, 58·11; H= 8·32, 8·30%; C₁₈H₃₄O₈ requires C= 58·7, H= 8·7%.)

Further work on the subject is in progress.

SUMMARY AND CONCLUSION

1. From the seeds of *Dodonaea viscosa* a glucoside (M.P. 182–86° C.) and a fixed oil have been obtained in yields of 3·42 and 20·27 per cent. respectively.

2. The glucoside and the product of its hydrolysis have been named “Dodonin” and “Dodogenin” respectively.

3. “Dodogenin” which has a molecular formula $C_{23}H_{36}O_8$ melts at 249° C. and contains a cyclo-penteno-phenanthrene nucleus in its molecule. In general properties it resembles the Sapogenins.

4. A number of derivatives of “Dodogenin” have been prepared and examined.

REFERENCES

1. Kirtikar and Basu .. *Indian Medicinal Plants*, 1, 641-43.