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SCANDENIN—A CONSTITUENT OF THE ROOTS OF *DERRIS SCANDENS*

E. P. CLARK

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Recently our attention was directed to a specimen of *Derris scandens* cultivated in a nursery at St. Petersburg, Fla. Since the plant grows well and can be propagated easily, it was important to know whether or not it contained rotenone. To obtain this information, M. J. Soule, upon whose property the plant grows, placed at our disposal a small quantity of the roots.

The roots were air-dried, ground, and extracted with ether. The extractive did not contain rotenone, but a mixture of several crystalline substances was obtained which, although showing no similarity to rotenone or allied products, appeared to be closely related among themselves.

The crystalline mixture was separated into three fractions. The first, which predominated and was the most readily obtained in a pure condition, was a new compound, $C_{26}H_{26}O_6$, m.p. 231°. It has been designated as "scandenin." The second compound, which was present in appreciable quantities and gave little trouble in separation, was lonchocarpic acid, previously found in *Lonchocarpus* sp. by Jones (1).

Lonchocarpic acid was identified by comparison with an authentic sample supplied by Jones (1). In these experiments lonchocarpic acid partly sintered between 200–205°, and melted sharply at 223° (corr.). The authentic sample, the compound from *Derris scandens*, and mixtures of both all behaved in this manner.

The third substance, m.p. 190°, was found only in small quantities. On the basis of its solubility in alkali, its melting point (190°), and its behavior toward the Durham test, it is thought to be robustic acid (2), but the meager yield and the difficulty of separating it from coexisting materials precluded exhaustive purification.

Scandenin has the formula $C_{26}H_{26}O_6$, and hence is isomeric with lonchocarpic acid. It crystallizes in rhombic plates and prismatic forms, which are biaxial with strong birefringence. The minimum index of refraction, N_α, is 1.483 ± 0.002, N_β and N_γ are both greater than 1.733. Owing to the limited supply of material available, only a superficial chemical study of the substance could be made. Some of the experiments, while indicating certain structures, could not be carried to a satisfactory conclusion, but the definite results obtained are as follows: Scandenin has one methoxyl and two free hydroxyl groups; it probably contains a *p*-hydroxybenzoyl grouping, although no oxime or semicarbazone could be obtained; it shows considerable unsaturation; it is somewhat acidic, dissolving in dilute aqueous alkalies; it forms relatively insoluble sodium and potassium salts; and, finally, it fails to give a reaction for a 2,2-dimethyl-Δ^3-chromene system (3, 4). The last fact strongly indicates the lack of relationship to the rotenone group of fish poisons.

These conclusions are based upon the following experiments: The methoxyl group was shown by analysis. The hydroxyl groups were shown by acetylation and by methylation with diazomethane. Acetylation occurred readily and quantitatively to give a diacetate, but diazomethane did not react so well. A dimethoxyscandenin was obtained, but the yield was extremely poor. The diacetate was insoluble in dilute potassium hydroxide, showing that the acidity of the substance was due to a phenolic hydroxyl group. Hydrogenation, with platinum catalyst, occurred readily, and approximately 3 moles of hydrogen were consumed. The *p*-hydroxybenzoyl group was shown to be present by the formation of *p*-hydroxybenzoic acid upon oxidation with alkaline hydrogen peroxide. The phenolic group being para to the carbonyl group accounts for the failure of scandenin to give a ferric chloride test.

EXPERIMENTAL

Preparation of scandenin. One kilogram of ground air-dried roots was exhaustively percolated with ether. While the solvent was being removed from the extract, several crops of crystals separated. In all, 5 grams of material which melted at 231° was obtained. This was dissolved in acetone, and the solution was clarified and decolorized by filtration through a thin bed of Norit. The acetone was replaced by gradual addition of methanol to the boiling concentrated solution until crystallization began. The slightly greenish product consisted mostly of thick rhombic plates together with some prismatic forms. The material, which was obtained in good yield, melted at 231° and further recrystallization failed to raise the melting point.

The material gave brilliant polarization colors when viewed with parallel polarized light (crossed nicols). Many fragments extinguished sharply, but others remained bright when the microscope stage was rotated. Birefringence was extremely strong, and in convergent polarized light (crossed nicols) partial biaxial interference figures were observed. These usually represented sections inclined to the acute bisectrix, but only one optic axis and a portion of the brush was visible. Occasionally sections occurred perpendicular to the optic axis. Only the lowest index, N_α, was measurable and had the value of 1.483 ± 0.002. Some fragments matched methylene iodide, with an index of 1.733, but N_β and N_γ were both greater than this value.[1]

Anal. Calc'd for $C_{26}H_{26}O_6$: Mol. wt., 434.5; C, 71.87; H, 6.03; one OCH_3, 7.14.

Found: Mol. wt., 422; C, 71.62; H, 6.05; OCH_3, 7.18.

Scandenin acetate. A mixture of 100 mg. of scandenin, 25 mg. of anhydrous sodium acetate, and 1 cc. of acetic anhydride was boiled 5 minutes, and then 25 cc. of water was added. When the mixture was stirred, a white crystalline material, which melted at 150°, separated. It was recrystallized from hot 95% methanol with no change of melting point. It was insoluble in dilute aqueous potassium hydroxide.

Anal. Calc'd for $C_{30}H_{30}O_8$: Mol. wt., 518.5; C, 69.49; H, 5.83; one OCH_3, 5.99; 2 acetyl, 16.6

Found: Mol. wt., 518; C, 69.54; H, 5.88; OCH_3, 5.86; acetyl, 16.2.

Scandenin dimethyl ether. One gram of scandenin was suspended in 100 cc. of ether containing an excess of diazomethane. The mixture was occasionally stirred and allowed to stand overnight, after which time all the scandenin had dissolved. When the ether was removed, the residue would not crystallize, and much material soluble in aqueous alkali was found to be present. It was therefore redissolved in ether and extracted with aqueous

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[1] The optical crystallographic data were determined by G. L. Keenan, Food and Drug Administration, Federal Security Agency, Washington, D. C.

potassium hydroxide. The portion remaining in the ether was obtained as a white crystalline product, which was recrystallized from methanol by the addition of water. The process was repeated until it had the constant melting point 129°. The quantity of material was only sufficient for a methoxyl determination.

Anal. Calc'd for $C_{29}H_{32}O_6$: 3 OCH_3, 19.54. Found: OCH_3, 19.96.

Action of alkaline hydrogen peroxide upon scandenin. One gram of scandenin was dissolved in 100 cc. of 0.2% warm aqueous potassium hydroxide, and oxidized with 15 cc. of 30% hydrogen peroxide added in 5-cc. portions. When the reaction subsided and frothing ceased, the solution was cooled, acidified with sulfuric acid, and distilled to collect any volatile fatty acids. The quantity obtained, calculated as acetic acid since its presence was indicated, was 83 mg., or a little more than 1 mole. Upon redistillation of the recovered acid according to the Dyer procedure (5), it was identified and shown to consist only of acetic acid.

The liquid residue from the first distillation was filtered and extracted with ether. The residue from the ethereal solution was dissolved in 1 cc. of water. This solution was frozen and then allowed to thaw slowly. A sticky product which remained adhering to the container was dried and sublimed. The sublimate, which melted at 213° and cleared at 215°, was identified as *p*-hydroxybenzoic acid by its failure to depress the melting point of a sublimed authentic sample of the acid.

Hydrogenation of scandenin. Two-tenths gram of scandenin in ethanol was reduced with hydrogen in the presence of reduced platinum oxide catalyst. Thirty-eight cubic centimeters, or approximately 3 moles, of hydrogen were consumed. Because of its poor crystallizing properties, the quantity available was insufficient to carry out a rigorous purification; hence no analysis of it is available. The experiment, however, does show the unsaturated nature of the compound.

Lonchocarpic and robustic acids. Further gradual concentration of the mother liquor from which scandenin was originally obtained gave several small quantities of crystals, melting unsharply between 193° and 195°, and a sticky mother liquor. The latter, when suspended in a small volume of ether, gave a small quantity of crystalline material which melted unsharply at 190°. All these crystalline fractions were united and digested in boiling benzene. The insoluble dried material melted at 220°. It was dissolved in acetone, the solution filtered through Norit, and the acetone replaced with methanol by boiling the liquid and adding the alcohol from time to time. Upon cooling, the solution crystallized, yielding prisms, rods, and plates which slightly sintered between 200–205°, then solidified, and melted sharply at 223° (1). Further recrystallization did not alter the melting point. A mixture with an authentic sample of lonchocarpic acid gave no depression of the melting point.

Upon cooling, the benzene mother liquor from the lonchocarpic acid gave a small crop of crystals, m.p. 185–210°. They were dissolved in methanol, and the solution was allowed to stand for several days. During this time some scandenin separated as large prisms. When these crystals were removed and water was added to the mother liquor, other crystals separated in the form of plates melting unsharply at 190°. After several recrystallizations the melting point became sharper. Because of its melting point, its solubility in alkali, and the evanescent, pale purple color given by the Durham test, it appeared to be robustic acid.

SUMMARY

The roots of *Derris scandens* have been examined for rotenone with negative results, but a new substance, scandenin, $C_{26}H_{26}O_6$, has been found. Lonchocarpic acid and possibly robustic acid have also been shown to be present.

Scandenin is isomeric with lonchocarpic acid. It contains one methoxyl,

two free hydroxyl groups, and probably a *p*-hydroxybenzoyl group. The acidic character of scandenin is probably due to a phenolic hydroxyl group.

BELTSVILLE, MD.

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