

The Constitution of Ayapanin.

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The leaves of *Eupatorium ayapana*, Vent. have been used in various parts of the world as a stimulant, tonic and diaphoretic. Dymock, Hooper and Warden (*Pharmacographia Indica*, Vol. II, p. 245) however remark: "The exaggerated ideas of its virtues formerly entertained are now exploded." In India the leaves or their infusion is still prescribed as an hæmostat. Dymock *et al* (*loc. cit.*) noticed the presence of an essential oil and a neutral crystalline substance, called ayapanin by them, which sublimed at 159-60° and imparted to concentrated sulphuric acid a faint yellow colour.

Recently Nag and Bose (*Trans. Bose Res. Inst.*, 1932-33, 8, 195) described the isolation, from the dried leaves of the plant, of a white crystalline substance, m.p. 110-12°, which was also called ayapanin. According to these authors ayapanin has the molecular formula, $C_{12}H_{10}O_4$. It dissolves in concentrated sulphuric acid with a violet colour and in potassium hydroxide with an yellow colour. Evidently Nag and Bose's ayapanin is different from that of Dymock *et al*. Bose and Nag (*Science and Culture*, 1936, 2, 163) have further described dibromoayapanin, $C_{12}H_8O_4Br_2$ and nitro-ayapanin, $C_{12}H_9O_4NO_2$.

From the fresh leaves of *E. ayapana* we have been able to isolate a crystalline product in an yield of 0.1%, i.e., 0.5% calculated on the dried material. From this product, which is a mixture, we have isolated a colourless substance, crystallising in plates and having m.p. 114-15°. This substance dissolved in aqueous potassium hydroxide with an yellow colour and in concentrated sulphuric acid with a deep violet fluorescence. Our compound is evidently identical with the ayapanin of Nag and Bose but in a purer form. Ayapanin has a faint coumarin-like odour especially when hot and was found to contain 17.2% methoxyl. The properties of our ayapanin are in good agreement with those of herniarin (7-methoxycoumarin) isolated from *Herniaria hirsuta*, Linn. (Barth and Herzig, *Monatsh.*, 1889, 10, 161). We have actually established the identity of our ayapanin with a synthetic specimen of 7-methoxycoumarin, which has previously been found in the flowers of *Matricaria chamomilla*, Linn. (Power and Browning, *J. Chem. Soc.*, 1914, 105, 2284) and in lavender oil (Ellmer, *Riechstoffind.*, 1927, p. 206).

Besides ayapanin, two other substances, m.p. 220-21° (which we shall call "ayapin") and m.p. 109° respectively, have been isolated from the same source. The constitution of these compounds will form the subject of a future communication. An account of the hæmostatic properties of ayapanin and ayapin will be published elsewhere.

EXPERIMENTAL.

Isolation of Ayapanin.—Fresh leaves of *E. ayapana* were boiled with eight times the weight of water for about 3 hours and filtered hot. The extraction was repeated twice. The combined filtrates, which showed a violet fluorescence somewhat masked by the light brown colour of the solution, were cooled and thoroughly extracted with chloroform. The chloroform extracts were dried over sodium chloride, and the solvent removed on the water-bath. The greenish brown crystalline residue was sublimed in vacuum (0.2 mm). A small quantity of a reddish oil which came over below 100° was rejected and the crystalline sublimate which passed over at 100-180° was collected; yield 0.1%. The sublimate was extracted with chloroform which dissolved all the ayapanin and a little of ayapin. The chloroform extract was evaporated to dryness and the residue distilled in vacuum, the fraction boiling at 130-140°/0.2 mm. being collected. The distillate was repeatedly fractionated and the fraction boiling at 120-25°/0.2 mm. was finally collected and twice recrystallised from hot water, when colourless plates, m.p. 114-15°, of ayapanin were obtained. (Found: OMe, 17.2. Calc. for $C_{10}H_8O_3$: OMe, 17.6 per cent).

7-Methoxycoumarin melted at 114-15° and there was no depression in m.p. on being mixed with ayapanin. They showed identical crystalline form under the microscope and their behaviour towards concentrated sulphuric acid and potassium hydroxide was also identical. The identity of ayapanin with 7-methoxycoumarin is thus firmly established.

We offer our best thanks to Sir P. C. Rây for the facilities given to one of us (A. C. R.) in carrying out this investigation.