

scribed. Attempts to prepare suitable compounds of type (VII) (compare Ring Index No. 2264) have been commenced. We shall follow the subsequent work of Buhle, Moore and Wisloge in this field with interest.

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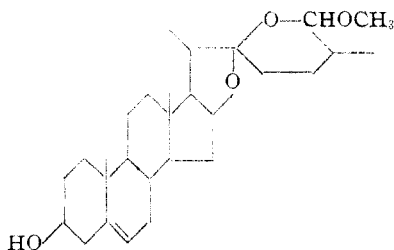
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### SAPONINS AND SAPOGENINS. XXIII. THE CONSTITUTION OF BETHOGENIN<sup>1</sup>

Sir:

We should like to propose the following structural formula for bethogenin.<sup>2,3</sup>



This proposal is based on the results previously reported and on new data which follow.

Reaction of bethogenin or its acetate with hydrogen bromide in acetic acid eliminates methoxyl and gives a diacetate, C<sub>31</sub>H<sub>46</sub>O<sub>6</sub>, m. p. 148–149°, [α]<sup>26</sup><sub>D</sub> – 161° in dioxane, which forms a dioxime, C<sub>31</sub>H<sub>45</sub>O<sub>6</sub>N<sub>2</sub>, m. p. 194–195°. Reduction of the hydrogen bromide reaction product with hydrogen and Adams platinum catalyst in alcoholic solution gives a dihydrodiacetate, C<sub>31</sub>H<sub>48</sub>O<sub>6</sub>, m. p. 116–117°, [α]<sup>22</sup><sub>D</sub> – 11° in dioxane. The ultraviolet absorption spectrum of this compound indicates that carbonyl still is present but a test with tetranitromethane for the double bond indicates that it has been reduced.

Reaction of bethogenin with hydroxylamine in pyridine gives a dioxime<sup>2</sup> C<sub>27</sub>H<sub>44</sub>O<sub>4</sub>N<sub>2</sub>, which no longer contains methoxyl.

(1) This Communication was submitted prior to the publication of the Communication by Marker and co-workers (THIS JOURNAL, 65, 1658 (1943)) in which a similar formula for bethogenin was proposed. The published reactions of bethogenin and kryptogenin are explainable by either formulation. On the basis of the formula for bethogenin proposed by us, kryptogenin would be a ketoaldehyde rather than a diketone. Preliminary tests by one of us (D. F.) indicate that this actually is the case. The product of the action of hydrogen bromide in glacial acetic acid on bethogenin is colored pink by Schiff reagent and gives a red color with 1,4-dihydroxynaphthalene in glacial acetic acid and hydrochloric acid [Raudnitz and Puluj, *Ber.*, 64, 2212 (1931)] while diosgenin and the diketo-compounds tigogenoic acid, chlorogenoic acid, and methyl chlorogenoate diacetate all give negative results with these reagents—C. R. NOLLER, M. R. BARUSCH and DAVID FRAZIER (August 16, 1943).

(2) Lieberman, Chang, Barusch and Noller, THIS JOURNAL, 64, 258 (1942).

(3) Noller and Barusch, *ibid.*, 65, 1435 (1943)

Several products of catalytic hydrogenation of bethogenin have been isolated. The absorption of one mole of hydrogen in the presence of platinum in alcoholic solution removes methoxyl to give a product which contains both a double bond and a carbonyl group and which forms a diacetate, C<sub>31</sub>H<sub>46</sub>O<sub>6</sub>, m. p. 142–144°, [α]<sup>24</sup><sub>D</sub> – 156° in dioxane. Exhaustive catalytic reduction of bethogenin in alcoholic solution gives C<sub>27</sub>H<sub>46</sub>O<sub>4</sub>, m. p. 203–208.6°, [α]<sup>25</sup><sub>D</sub> – 57.7° in dioxane. This product no longer contains a double bond or a carbonyl group. On reaction with acetic anhydride in pyridine it loses one molecule of water and forms a monoacetate, C<sub>29</sub>H<sub>46</sub>O<sub>4</sub>, m. p. 204–207.5°, [α]<sup>25</sup><sub>D</sub> – 62.2° in dioxane. On mixing with tigogenin acetate, m. p. 204–207.5°, [α]<sup>22.5</sup><sub>D</sub> – 64.0° in dioxane, no depression in melting point was observed.

We hope to be able to publish shortly the details of the above experiments and an interpretation of the reactions involved.

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### THE BOROHYDRIDES OF GALLIUM

Sir:

At the present time the borohydrides of three metals are known: lithium borohydride,<sup>1</sup> LiBH<sub>4</sub>; methylberyllium borohydride,<sup>2</sup> CH<sub>3</sub>BeBH<sub>4</sub>; beryllium diborohydride,<sup>2</sup> Be(BH<sub>4</sub>)<sub>2</sub>; and aluminum triborohydride,<sup>3</sup> Al(BH<sub>4</sub>)<sub>3</sub>. These compounds are of considerable interest because of their unusual chemical and physical properties. The aluminum and beryllium compounds are of particular interest because they are the most volatile derivatives of these metals known. It therefore seems desirable to extend the study of the borohydrides to other metals. In the present communication we wish to report preliminary observations on the borohydrides of gallium.

In a typical experiment, trimethylgallium was treated with an excess of diborane at room temperature. A small decrease in pressure was observed over a period of three hours. At the end of this time a metallic film suddenly appeared on the walls of the reaction vessel, accompanied by a rapid increase in the pressure, and the formation of non-condensable gas (hydrogen). The film was

(1) Schlesinger and Brown, THIS JOURNAL, 62, 3429 (1940).

(2) Burg and Schlesinger, *ibid.*, 62, 3425 (1940).

(3) Schlesinger, Sanderson and Burg, *ibid.*, 62, 3421 (1940).