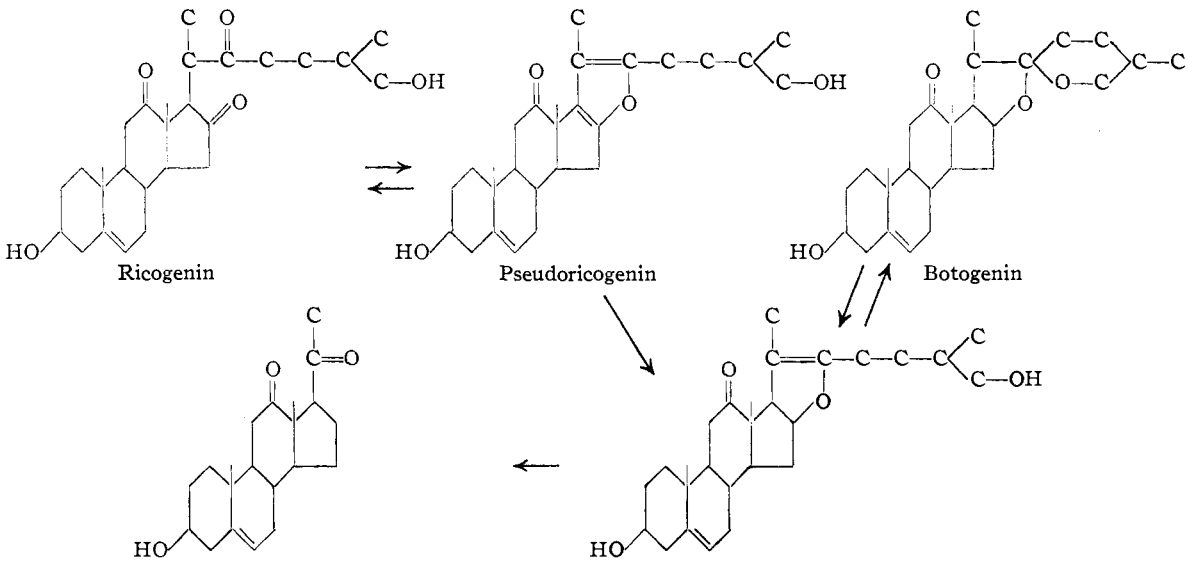
STEROIDAL SAPOGENINS, 173. 16-DEHYDROPREGNEN-5-OL-3-DIONE-12,20 FROM RICOGENIN, A NEW STEROIDAL SAPOGENIN

Sir:

In an extensive search for naturally occurring steroidal sapogenins having substituents in ring C which may be utilized for the synthesis of cortisone, the anti-arthritic hormone, a new saponide, riconin, m.p. 285–289° dec., was isolated from the mixture of glycosides occurring in *Dioscorea Macrostachya*.



Hydrolysis of riconin with alcoholic hydrochloric acid gave ricogenin, m.p. 225–227°. *Anal.* Calcd. for $C_{27}H_{40}O_5$: C, 72.9; H, 9.1. Found: C, 72.9; H, 9.1.

Ricogenin formed a diacetate, m.p. 195–197°, and contains three ketonic groups having the same side-chain structure as kryptogenin. *Anal.* Calcd. for $C_{31}H_{44}O_7$: C, 70.4; H, 8.4. Found: C, 70.2; H, 8.2.

Treatment of ricogenin with acetic anhydride at 195° for eight hours followed by hydrolysis gave pseudoricogenin, m.p. 220–222°. *Anal.* Calcd. for $C_{27}H_{38}O_4$: C, 76.0; H, 9.0. Found: C, 76.2; H, 9.0.

When heated with alcoholic hydrochloric acid for fifteen minutes, pseudoricogenin was converted into ricogenin, m.p. and mixed m.p. 225–227°. Catalytic reduction of the diacetate of pseudoricogenin, using palladium-on-barium sulfate as catalyst, saturated only the conjugated double bond in ring D, giving the diacetate of pseudobotogenin. This product upon alkaline hydrolysis followed by isomerization with alcoholic hydrochloric acid gave botogenin, m.p. and mixed m.p. 260–262°. *Anal.* Calcd. for $C_{27}H_{40}O_4$: C, 75.7; H, 9.4. Found: C, 75.5; H, 9.4.

Acetylation of this product gave botogenin acetate, m.p. and mixed m.p. 246–248°. *Anal.* Calcd. for $C_{29}H_{42}O_5$: C, 74.0; H, 9.0. Found: C, 74.1; H, 9.3.

The pseudobotogenin diacetate produced by the catalytic reduction of the diacetate of pseudoricogenin was oxidized with chromic anhydride in acetic acid, followed by hydrolysis,[1] giving 16-dehydropregnen-5-ol-3-dione-12,20 acetate, m.p. and mixed m.p. with the product prepared from naturally occurring botogenin, 225–227°. *Anal.* Calcd. for $C_{23}H_{30}O_4$: C, 74.8; H, 8.2. Found: C, 74.6; H, 8.1.

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(1) Marker, THIS JOURNAL, 71, 2656 (1949).

ALLO-PREGNAN-3,12,20-TRIONE

Sir:

The current interest in Kendall's substance E for rheumatoid arthritis has stimulated great interest in the search for starting materials for its synthesis. Recently, Marker reported the possibility of utilizing a steroidal sapogenin, botogenin, isolated from *Dioscorea Mexicana*.[1] Its degradation product was 5-pregnen-3(β)-ol-12,20-dione, characterized by conversion to *allo*-pregnan-3,12,-20-trione, m.p. 264°. The latter was identical with *allo*-pregnan-3,12,20-trione[2] from the degradation of hecogenin.

We have prepared an authentic sample of *allo*-pregnan-3,12,20-trione by an entirely different route and have found it completely different from the trione from hecogenin. Desoxycholic acid has been degraded to 12(α)-acetoxyprogesterone (I), m.p. 181°, $[\alpha]^{26}D$ +215°, $[\alpha]^{25}_{5461}$ +259° (chloroform), absorption maximum at 240mμ(log ε 4.14 in ethanol).[3] This compound (I) upon sodium–alcohol reduction followed by chromic acid oxidation furnished *allo*-pregnan-3,12,20-trione (II), m.p. 206–208°, $[\alpha]^{23}D$ +184°, $[\alpha]^{23}_{5461}$ +224° (chloroform), no maximum at 240mμ. *Anal.* Calcd. for $C_{21}H_{30}O_3$: C, 76.3; H, 9.2. Found: C, 76.0; H, 8.9. The reduction was also accomplished with hydrogen and Adams catalyst in acetic acid; subsequent hydrolysis and oxidation gave the same product (II). The course of these methods of reduction has been shown previously[4]

(2) Marker, Wagner and co-workers, *ibid.*, 69, 2167 (1947).

(3) Shoppee and Reichstein, *Helv. Chim. Acta*, 24, 351 (1941).

(4) Marker and Wittle, THIS JOURNAL, 59, 2704 (1937); Butenandt and Fleischer, *Ber.*, 68, 2094 (1935).