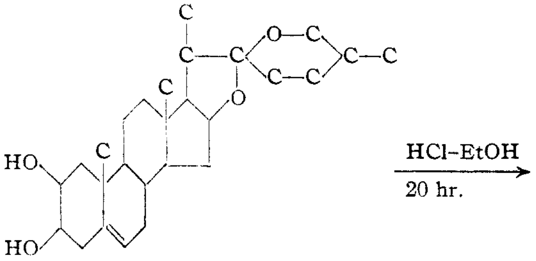
COMMUNICATIONS TO THE EDITOR

STEROLS. CLVIII. SAPOGENINS. LXX. THE STRUCTURE OF LILAGENIN

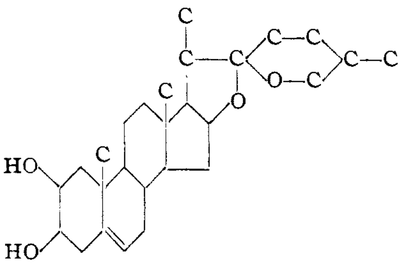
Sir:

Previously [THIS JOURNAL, **62**, 2620 (1940)] we reported the isolation in small amounts from *Lilium rubrum magnificum* of a new steroidal sapogenin, lilagenin, m. p. 245–246°. Boiling acetic anhydride formed a diacetate, m. p. 156°. Lack of material prevented further characterization of this substance. In our more recent plant studies, however, we have found a better source in *Lilium humboldtii*. The identity was established by the melting points, mixed melting points and analyses of the genin and its acetate as follows: genin, m. p. and mixed m. p., 242–246°. *Anal.* Calcd. for $C_{27}H_{42}O_4$: C, 75.3; H, 9.9. Found: C, 75.4; H, 9.9; diacetate, m. p. and mixed m. p., 153–155°. *Anal.* Calcd. for $C_{31}H_{46}O_6$: C, 72.3; H, 9.0. Found: C, 72.4; H, 9.0. Treatment of lilagenin with 2 *N* ethanolic hydrochloric acid for twenty hours gave yuccagenin (II) [THIS JOURNAL, **65**, 1199 (1943)], m. p. and mixed m. p., 244–246°. *Anal.* Calcd. for $C_{27}H_{42}O_4$: C, 75.3; H, 9.9. Found: C, 75.2; H, 10.0. The identity was further established by means of the diacetates, m. p. and mixed m. p., 176–178°. *Anal.* Calcd. for $C_{31}H_{46}O_6$: C, 72.3; H, 9.0. Found: C, 72.4; H, 9.2. Thus, lilagenin is not only isomeric with yuccagenin (II) but differs from the latter only in the *configuration of the side-chain.* Other pairs of isomeric sapogenins are similarly related [THIS JOURNAL, **65**, 1199 (1943)], namely, sarsasapogenin and smilagenin; texogenin and samogenin; yamogenin and diosgenin; neotigogenin and tigogenin. The first of each pair is converted to the other by treatment with ethanolic hydrochloric acid.

We reported erroneously [THIS JOURNAL, **62**, 2620 (1940)] on the basis of the analyses and an apparently negative bromine test, that lilagenin was isomeric with gitogenin ($C_{27}H_{44}O_4$) and its acetate with gitogenin diacetate ($C_{31}H_{48}O_6$). It so happens that the earlier analytical figures, namely, C, 75.1; H, 10.1 and C, 72.3; H, 9.2 for the first specimens of lilagenin and its acetate, respectively, agree equally well with the calculated values for the compositions $C_{27}H_{42}O_4$ and $C_{31}H_{46}O_6$, respectively. We now find that lilagenin (I) like yuccagenin (II) absorbs bromine in acetic acid more slowly than the other unsaturated sapogenins, such as diosgenin and yamogenin. This accounts for our previously reported negative bromine test. We propose structure I for lilagenin.



I. Lilagenin



II. Yuccagenin

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THE STRUCTURES OF OSAJIN AND POMIFERIN

Sir:

We have obtained evidence which in conjunction with that previously reported,[1] establishes the formulas of osajin, pomiferin, iso-osajin and isopomiferin.

The alkaline fusion of iso-osajin and isopomiferin yielded acetone and 2,2-dimethyl-5,7-chromandiol, identical with an authentic synthetic sample prepared from phloroglucinol according to the directions of Robertson and co-workers.[2]

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[1] M. L. Wolfrom and S. M. Moffett, THIS JOURNAL, **64**, 311 (1942), and preceding communications.

[2] W. Bridge, R. G. Heyes and A. Robertson, *J. Chem. Soc.*, 279 (1937); W. Bridge, A. J. Crocker, T. Cubin and A. Robertson, *ibid.*, 1530 (1937).