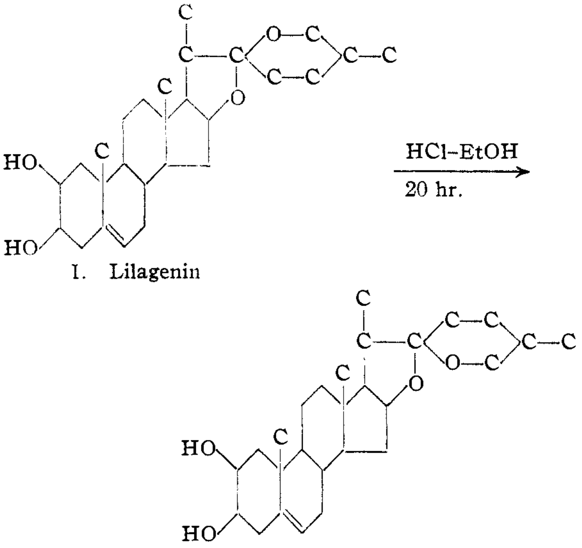
COMMUNICATIONS TO THE EDITOR

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

We thank Parke, Davis and Company for their assistance.

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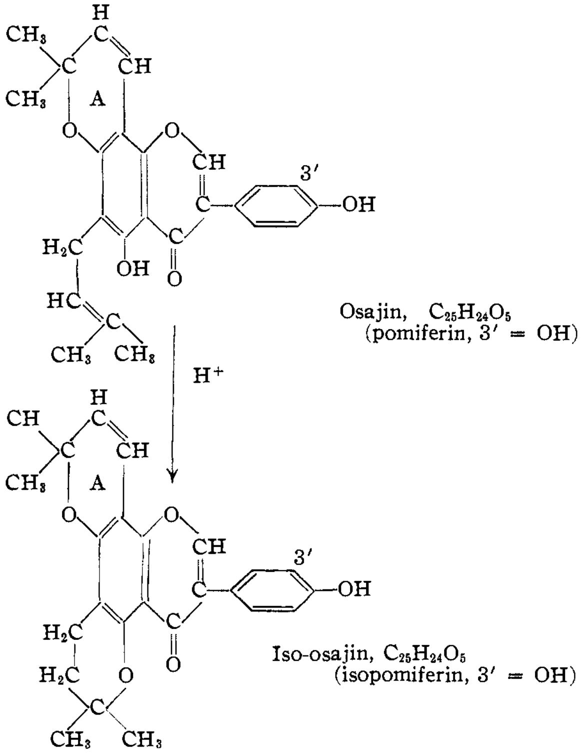
[1] M. L. Wolfrom and S. M. Moffett, This Journal, **64**, 311 (1942), and preceding communications.

[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).

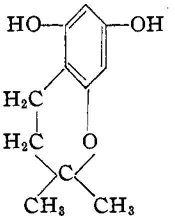


Osajin, $C_{25}H_{24}O_5$ (pomiferin, 3′ = OH)

H^+

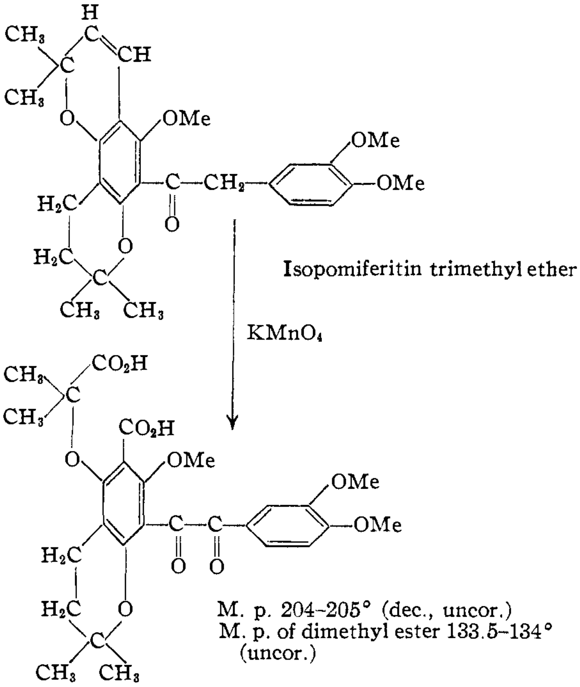
Iso-osajin, $C_{25}H_{24}O_5$ (isopomiferin, 3′ = OH)

The diacetate of the above was prepared and was likewise found identical with an authentic synthetic sample. Robertson and co-workers have recorded a sound proof of structure for 2,2-dimethyl-5,7-chromandiol.



2,2-Dimethyl-5,7-chromandiol

The formulation of ring A rests upon the known fact that such a structure yields acetone on alkaline fusion[2]; the pigments are optically inactive; and two $CH_3—C\lt$ groups are present. Further, absorption spectra measurements show clearly that the double bond of ring A is conjugated to the phloroglucinol structure while the double bond involved in the isomerization is not so conjugated. A permanganate oxidation product has been obtained from isopomiferitin trimethyl ether which is under further investigation but which very probably has the structure shown below and thus is analogous to the oxidation products obtained by Clark[3] from compounds likewise containing the 2,2-dimethyl-1,2-chromene structure.



Isopomiferitin trimethyl ether

$KMnO_4$

M. p. 204–205° (dec., uncor.)
M. p. of dimethyl ester 133.5–134° (uncor.)

Full details will be communicated at a later date. Experiments are in progress in this Laboratory with the aim of verifying these structures by synthesis.

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(3) E. P. Clark, THIS JOURNAL, **53**, 729 (1931); **54**, 3000 (1932).

SAPONINS AND SAPOGENINS. XXII. THE COMPOSITION AND CONSTITUTION OF BETHOGENIN

Sir:

The molecular formula, $C_{27}H_{40}O_6$, previously proposed for bethogenin[1] has been found to be in error. New analyses,[2] in which we have confidence, show bethogenin to have the formula $C_{28}H_{44}O_4$. *Anal.* Calcd. C, 75.62; H, 9.99. Found: C, 75.62, 75.69; H, 10.03, 10.02. **Acetate:** Calcd. for $C_{30}H_{46}O_5$: C, 74.02; H, 9.53. Found: C, 74.08, 73.98; H, 9.49, 9.57. **Benzoate:** Calcd. for $C_{35}H_{48}O_5$: C, 76.60; H, 8.82. Found: C, 76.58, 76.51; H, 8.86, 8.85.

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(1) Lieberman, Chang, Barusch and Noller, THIS JOURNAL, **64**, 2581 (1942).

(2) Analyses by Dr. E. W. D. Huffman, Denver, Colorado. Analyses on a test sample of chlorogenin were as follows: Calcd. for $C_{27}H_{44}O_4$: C, 74.95; H, 10.25. Found: C, 75.00, 74.90; H, 10.31, 10.31.