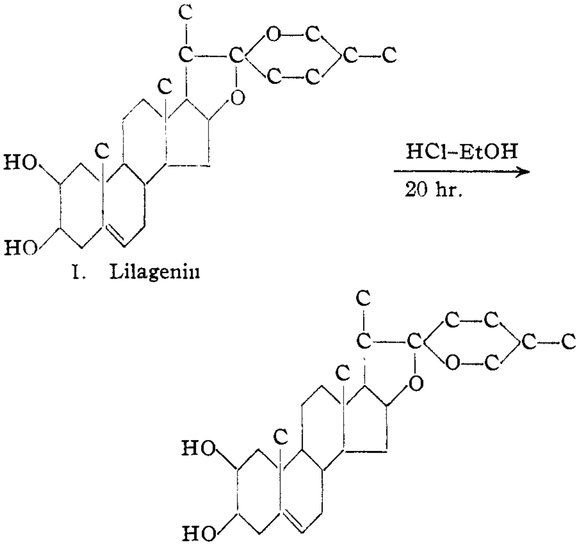
COMMUNICATIONS TO THE EDITOR

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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RECEIVED JUNE 12, 1943

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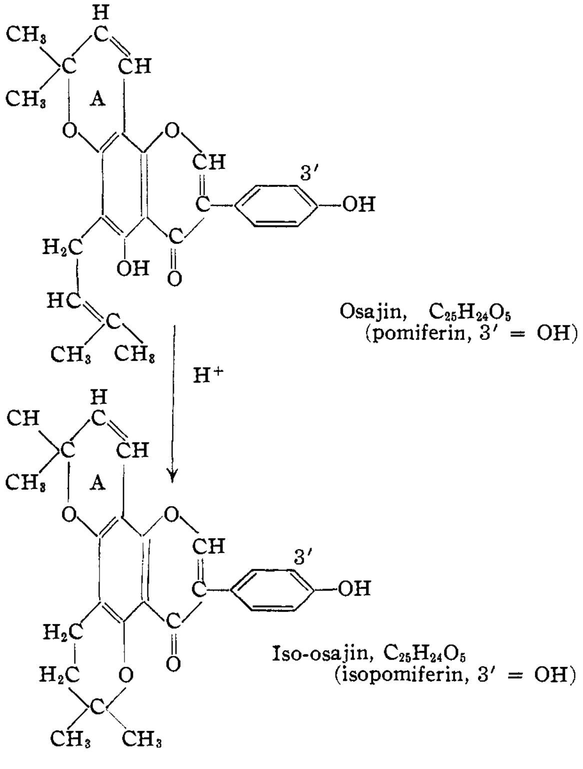
(1) M. L. Wolfrom and S. M. Moffett, THIS JOURNAL, **64**, 311 (1942), and preceding communications.

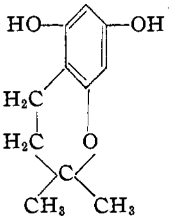
(2) W. Bridge, R. G. Heyes and A. Robertson, *J. Chem. Soc.*, 279 (1937); W. Bridge, A. J. Crocker, T. Cubin and A. Robertson, *ibid.*, 1530 (1937).



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

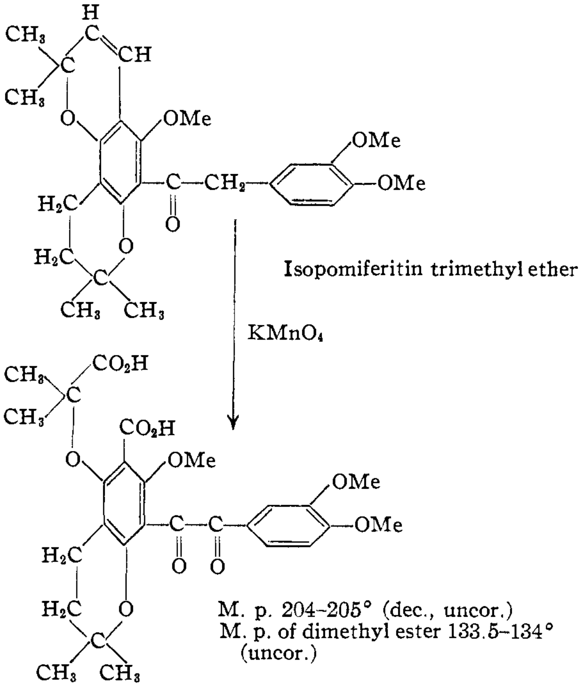
Iso-osajin, $C_{25}H_{24}O_5$ (isopomiferin, 3′ = OH)

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 $CH_3{-}C\leqslant$ 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

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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RECEIVED JUNE 16, 1943

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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.

We have found further that the additional carbon atom is present as a methoxyl group. Methoxyl determinations in this Laboratory on bethogenin were as follows: Calcd. for $C_{28}H_{44}O_4$, 6.97. Found: 6.68, 7.25, 6.82, 6.65. For bethogenin acetate, Calcd. for $C_{30}H_{46}O_5$, 6.37. Found, 6.15, 6.32. For bethogenin benzoate, Calcd. for $C_{35}H_{48}O_5$, 5.65. Found: 5.11.

Although bethogenin reacts with hydroxylamine in alcoholic pyridine solution[1] with the introduction of two nitrogen atoms, we find that bethogenin does not show typical carbonyl absorption in the ultraviolet. The absorption in alcohol rises almost regularly from λ 3500 to λ 2300 with only an inflection at λ 2850, log ϵ at this point being about 0.3. After treatment with hydrogen bromide in acetic acid, however, a product is obtained which gives an absorption spectrum typical of the isolated carbonyl group; $\lambda_{\text{max.}} = 2850$, $\log \epsilon = 1.77$. This would indicate that bethogenin is an enol ether but we are not prepared to suggest a structure for bethogenin until work in progress has been completed.

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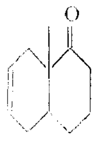
RECEIVED MAY 6, 1943

THE SYNTHESIS OF CONDENSED RING COMPOUNDS. X. *cis*-9-METHYL-8-KETO-2-OCTALIN AND *cis*-10-METHYL-1-VINYL-1,7-NAPHTHITADIENE[1]

Sir:

The addition of 1-methylcyclohexen-6-one to butadiene has yielded *cis*-9-methyl-8-keto-2-octalin (*cis*-10-methyl-7-naphthiten-1-one[2]), I, b. p. 67° at 0.5 mm., $n^{20}D$ 1.5042. Semicarbazone, m. p. 224.8–225° (dec., slight darkening at 224°). *Anal.* Calcd. for $C_{12}H_{19}ON_3$: N, 18.99; N found, 18.71, 18.93. In the presence of Adams catalyst, 0.94 millimole of the methyloctalone absorbed 1.88 millimoles of hydrogen.

The methyloctalone was converted by way of 5,10-*cis*-1-ethynyl-10-methyl-7-naphthiten-1-ol, b. p. 93–94° at 0.5 mm., $n^{20}D$ 1.5260, and 5,10-*cis*-10-methyl-1-vinyl-7-naphthiten-1-ol, b. p. 92° at 0.55 mm., $n^{22}D$ 1.5218, to *cis*-10-methyl-1-vinyl-1,7-naphthitadiene, II. The best reagent found so far for accomplishing the last step is phosphorus tribromide and pyridine. II, b. p. 66–67° at 0.45 mm., $n^{20}D$ 1.5284, maximum absorption at 2380 Å., ϵ 9400 in hexane and at 2380 Å., ϵ 10,000 in ethanol.[3] Hydrogen absorbed by 0.37 millimole of triene, 26.2 ml. at standard temperature and pressure; calcd. for three double bonds, 26.75 ml.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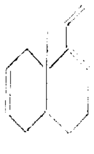
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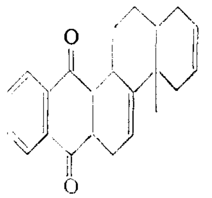
III

p-Naphthoquinone was heated with two equivalents of the triene at 110° in a sealed tube for forty-five minutes. Addition of methanol to the reaction mixture gave crystals, m. p. 183–185°. This material was recrystallized from ethanol with Norite and then from ethanol containing a little petroleum ether; yellow crystals, m. p. 191.8–192.8°. *Anal.* Calcd. for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 82.87, 82.83; H, 7.12, 7.15. This compound may have the structure III.

We are applying these reactions to the synthesis of steroids.

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(1) This work was supported by an allotment from the Special Research Fund (Bankhead–Jones Act of June 29, 1935). Not subject to copyright.

(2) For nomenclature see Butz and Joshel, THIS JOURNAL, **64**, 1311 (1942); decahydronaphthalene becomes *naphthitane* and carbon atoms are numbered in sequence.

(3) Obtained through the kindness of Mr. Harry Bastron. Compare with the maxima of related compounds in Booker, Evans and Gillam. *J. Chem. Soc.*, 1453 (1940).

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RECEIVED JUNE 11, 1943

ORIENTATION IN STRETCHED FILMS OF AMYLOSE TRIACETATE

Sir:

Starch (corn, wheat, and potato) can be separated by either water extraction or butanol precipitation[1] into two components, amylose and amylopectin. Amylose is the component extracted by water from swollen starch granules or precipitated by butanol from an autoclaved starch paste while amylopectin is the starch component remaining after separation of the amylose. Recently Whistler and Hilbert[2] have shown that amylose is capable of yielding strong pliable acetate films of high quality whereas only weak

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(1) T. J. Schoch, THIS JOURNAL, **64**, 2957 (1942).

(2) Roy L. Whistler and G. E. Hilbert, paper presented before the 105th meeting of the American Chemical Society, Detroit, Michigan, April, 1943, Division of Sugar Chemistry and Technology. Now in preparation for publication.

brittle films are produced from amylopectin acetate. The pliable amylose acetate films on stretching become birefringent and increase in tensile strength. This is evidence that a molecular orientation occurs within the film during stretching. The molecules constituting the film, therefore, most probably possess a highly anisodimensional or linear structure.

Confirmatory evidence that stretching produces orientation in these acetate films has been obtained by X-ray analysis. X-Ray diffraction patterns taken during the stretching of films clearly indicate a progressive change from an amorphous to a highly crystalline condition. Films which are stretched in hot water readily set to the new length when cooled and therefore can be easily handled in the elongated state. When elongated 400–600% the films produce a typical fiber pattern on exposure to X-rays (Fig. 1). The presence of discrete spots in the diffraction pattern is proof of the high degree of orientation attained by the film molecules and is further evidence that the molecules possess a linear nature. This is the first time a fiber pattern has been obtained with starch or its derivatives. Identical diffraction patterns are obtained from stretched acetate films prepared from either fractionated corn or potato starches. In each case a periodicity of 18.3 Å., occurs along the fiber (b) axis. While no experimental evidence was reported, French[3] claims that "oriented X-ray diffraction patterns from amylose films confirm previous unit cell determinations for granular (a-b) starches."

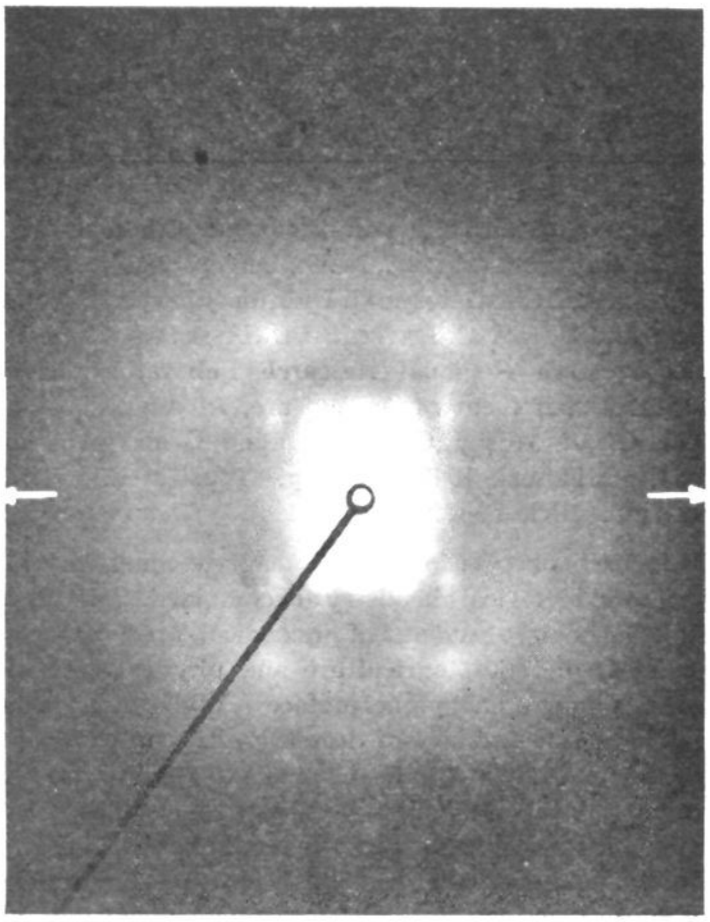

Fig. 1.—X-Ray pattern of stretched film of amylose triacetate (arrows indicate the direction of the fiber axis).

Although good patterns were obtained from unplasticized films, best patterns were obtained from films containing about 20% plasticizer (tricresyl phosphate, dibutyl phthalate, dibutyl tartrate, pentaerythritol tetraacetate). The diffraction patterns seem to be independent of the type of plasticizer used. Patterns were obtained with flat film technique by allowing a beam of unfiltered Cu $K\alpha$ X-rays to strike the stretched film at an angle of 90° to the surface. The specimen was mounted on the pinhole and a specimen to photographic film distance of 5 cm. was used. All the stretched films showed a small birefringence which was negative with reference to the axis of elongation.

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RECEIVED MAY 27, 1943

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[3] D. French, Doctor's Dissertation No. 696, Iowa State College, Ames, Iowa (1942); *Iowa State J. Science*, **17**, 62 (1942).