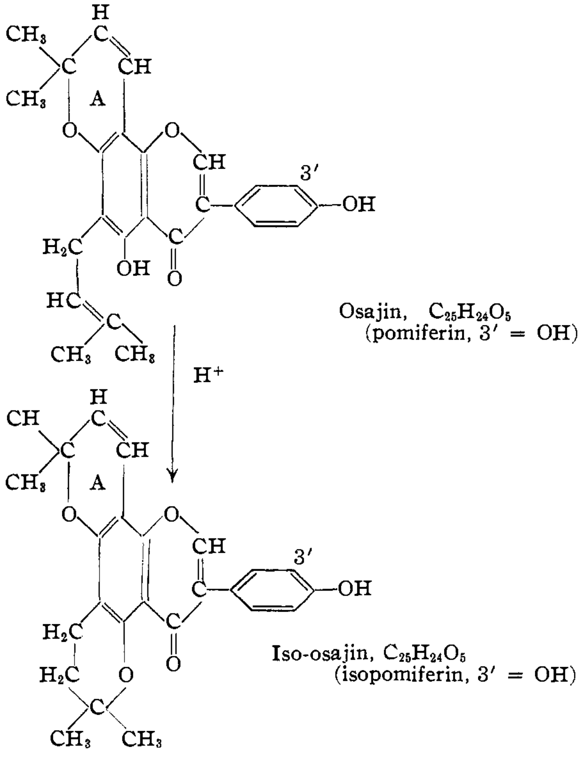
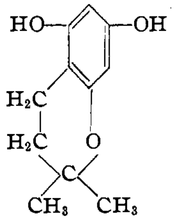


Osajin, $C_{25}H_{24}O_5$
(pomiferin, 3′ = OH)

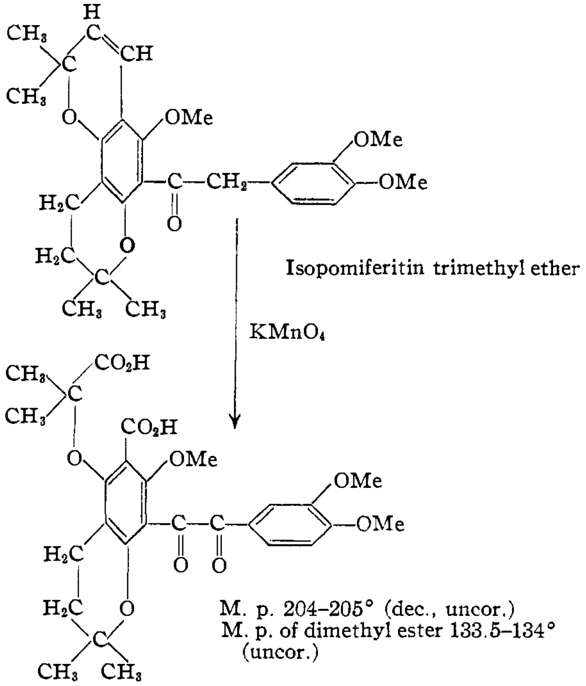
Iso-osajin, $C_{25}H_{24}O_5$
(isopomiferin, 3′ = OH)

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 $CH_3{-}C\Big\langle$ 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.

DEPARTMENT OF CHEMISTRY
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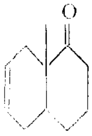
RECEIVED MAY 6, 1943

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

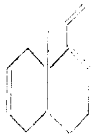
Sir:

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.

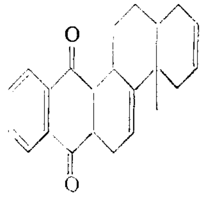
The methyloctalone was converted by way of 5,10-*cis*-1-ethynyl-10-methyl-7-naphthiten-1-ol, b. p. 93–94° at 0.5 mm., n^{20}D 1.5260, and 5,10-*cis*-10-methyl-1-vinyl-7-naphthiten-1-ol, b. p. 92° at 0.55 mm., n^{22}D 1.5218, to *cis*-10-methyl-1-vinyl-1,7-naphthitadiene, II. The best reagent found so 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.



I



II



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.

BUREAU OF ANIMAL INDUSTRY WALTER NUDENBERG
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BELTSVILLE, MARYLAND LEWIS W. BUTZ

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] 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).

(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.