Phenylglycerosazone: m. p. 132°; reported[1,5] m. p. 132°.

Hydroxymethylglyoxime: m. p. 134–135°. Reported[5] m. p. 168°.

*Anal.* Calcd. for $C_3H_6O_3N_2$: N, 23.7. Found: N, 23.4.

An aqueous solution of the dioxime gave a red color with cobalt acetate in the presence of sodium acetate. On careful addition of dilute sodium hydroxide to this solution a green base was precipitated.

## Summary

1. The alcoholate of the trimer of hydroxypyruvic aldehyde was prepared free from sulfur derivatives.

2. The quinoxaline derivative, phenylosazone, and dioxime were prepared.

BALTIMORE, MD.

RECEIVED FEBRUARY 28, 1938

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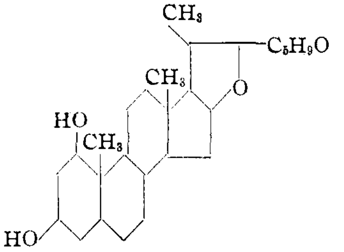
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

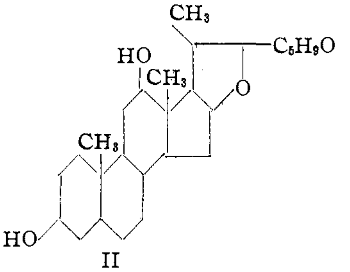
# Saponins and Sapogenins. VI. Surface Films of Chlorogenin and Derivatives

BY C. R. NOLLER

In the last paper of this series[1] the tentative formulas, I and II, based on chemical evidence,



I



II

were proposed for chlorogenin. Formula II was favored because the ketodibasic acid obtained on oxidation did not appear to be either an $\alpha$- or a $\beta$-keto acid as would be required by formula I. The second hydroxyl group was assigned to position 12, since the diketone forms a dioxime which would not be expected if the hydroxyl group is at position 11.

Recent work on the surface films of structurally related compounds[2] indicates that those molecules having one or two hydroxyl groups in the end-ring give incompressible films in which the molecules stand on end and occupy an area that is predicted by models of the compounds. Cholestanol-6 and $\Delta^{4,5}$-cholestenol-7 ($\psi$-cholesterol) having hydroxyl groups in the second ring give highly compressible films indicating that the molecules are tilted or lying flat at low pressures.[3] Hence it was expected that if formula II is a possibility for chlorogenin, the molecules in surface films would lie flat at low pressures and give a highly compressible film. The data plotted in curve I show that this is actually the case. The molecules occupy at low pressures an even larger area than $\psi$-cholesterol, the film being gaseous at very low pressures. At higher pressures the curve appears as if it will coincide with that for gitogenin

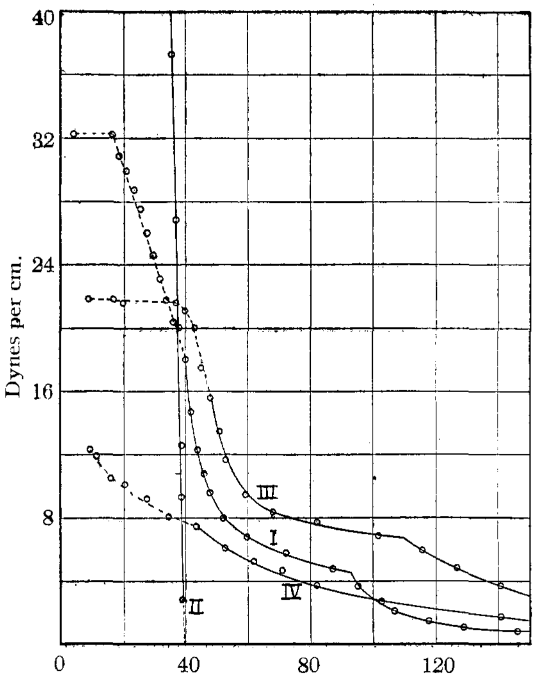


Fig. 1.—Pressure-area curves for surface films of: I, chlorogenin; II, gitogenin; III, chlorogenin diacetate; IV, diketone from chlorogenin.

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(1) Noller, THIS JOURNAL, 59, 1092 (1937).

(2) Askew, Farmer and Kon, *J. Chem. Soc.*, 1399 (1936).

(3) Adam, Askew and Danielli, *Biochem. J.*, 29, 1786 (1935).

but contraction begins at a pressure of about 15 dynes per centimeter and at higher pressures the film collapses. However, it remains mobile as shown by dusting with talc, even at 32 dynes per centimeter.

The data for gitogenin (curve II) were obtained using a sample kindly supplied to us several years ago by Dr. W. A. Jacobs of the Rockefeller Institute for Medical Research. The value of 39.5 Å. for the area per molecule at zero pressure is identical with that obtained previously[2] and served to check our technique and procedure. Evidently under pressure the molecules of chlorogenin can be made to stand on end and occupy an area very close to that occupied by gitogenin, thus furnishing additional evidence for the close relationship in the structure of these two compounds.

Chlorogenin diacetate gives a curve, III, which is very similar to that for chlorogenin except that the lower attraction of the acetate groups for water is manifest in the greater tendency to remain in the gaseous state and the greater instability of the close packed film. The diketone obtained by the oxidation of chlorogenin (curve IV) shows no tendency to form a close packed film but collapses at pressures of about 6 dynes per centimeter.

## Experimental

The surface pressures were measured on a Cenco Hydrophil Balance by the general procedure developed by Adam and his co-workers.[3] The solvent used was a mixture of eight parts by volume of purified cyclohexane and two parts of purified dioxane. From 0.01 to 0.02 g. of compound was weighed accurately into a tared glass-stoppered 25-cc. Erlenmeyer flask and dissolved in 10–20 cc. of solvent with warming if necessary. After cooling to room temperature the flask was stoppered and the weight of solvent determined.

For placing the solution on the surface a 1-cc. ground-glass syringe was used, whose tip was drawn out and ground so that small drops would form and leave the pipet without wetting the outer surface of the tip. The tip was fitted with a small cap by means of a ground joint to prevent evaporation during the weighing of the syringe. The space between plunger and barrel of the syringe was sealed by a narrow band of glycerol.

All films were spread on 0.02 *N* hydrochloric acid. The films were not examined for collapse with a dark ground illuminator[3] but the phenomenon of contraction was observed shortly before collapse was obvious.

## Summary

Measurements on surface films of chlorogenin, chlorogenin diacetate and the diketo derivative are in agreement with the view that the two hydroxyl groups are in different rings in the molecule. They also confirm the close relationship in structure previously assumed to exist between chlorogenin and gitogenin.

Stanford University, Calif. Received May 4, 1938

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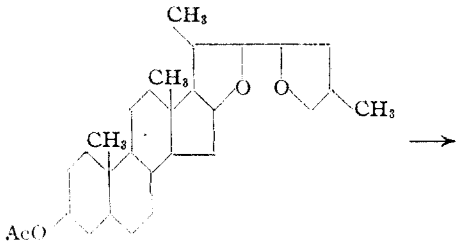
[Contribution from the Department of Chemistry of Stanford University]

# Saponins and Sapogenins. VII. The Structure of the Side Chain of Chlorogenin

By F. M. McMillan and C. R. Noller

In previous chemical investigations on the structure of chlorogenin,[1] it has been assumed that the two unreactive oxygen atoms of chlorogenin are in a side chain whose structure is similar to that of the isomeric compound gitogenin and of other steroid sapogenins. This side chain is generally believed to consist of two tetrahydrofuran rings, the chief chemical evidence being the oxidation of tigogenin acetate[2] to an acid and a lactone as formulated in the equation



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(1) Noller, This Journal, **59**, 1092 (1937); **60**, 1629 (1938).

(2) Tschesche and Hagedorn, *Ber.*, **68**, 1412, 2247 (1935).