IRIDIN, THE GLUCOSIDE OF THE IRIS ROOT.

By G. DE LAIRE AND FERD. TIEMANN.

Monacetylirigenin, $C_{18}H_{15}O_8(COCH_3)$.—Diacetylirigenin loses one acetyl easily if heated for a few minutes in alcoholic solution with a little soda. The monacetyl derivative forms no double compound with chloroform, but it dissolves in it readily at the ordinary temperature and may be distinguished in this way from irigenin. From chloroform monacetylirigenin separates in fine, white needles melting at 169°.

ANALYSIS.—CALCULATED FOR $C_{20}H_{18}O_9$.

	Per cent. C.	Per cent. H.
Calculated	59.70	4.48
Found	59.75	4.74

Decomposition of Irigenin.—By heating with concentrated alkalies irigenin is decomposed according to the equation

$$C_{18}H_{16}O_8 + 3H_2O = CH_2O_2 + C_{10}H_{12}O_5 + C_7H_8O_4$$
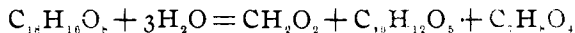
into formic acid, CH_2O_2, an aromatic oxy-acid, $C_{10}H_{12}O_6$, which we call iridinic acid and a phenol which we call iretol.

An alkaline irigenin solution is decomposed differently in presence of oxygen. The decomposition must take place, therefore, with exclusion of air. It is best effected as follows: Fifteen grams irigenin and thirty cc. water are placed in a 500 cc. pressure flask. The air is displaced by hydrogen, ninety grams of a solution of caustic potash (sp. gr. 1.33) corresponding to about thirty grams KOH added, the flask closed as quickly as possible and heated on the water bath for five to six hours. After opening the flask it is acidified at once with thirty grams sulphuric acid which has been diluted with twice the bulk of water. In a well-conducted operation no precipitate will separate from the light yellow acid solution. The formic acid may be distilled off quantitatively in a stream of water vapor; about three hours are necessary. If it is not desired to determine the formic acid, the acid solution is shaken ten to twelve times with ether. The watery residue from the evaporation of the ether is freed from formic acid by distillation in water vapor.

The air in the retort is now replaced by a stream of hydrogen and a boiling saturated solution of barium hydroxide added until the contents are alkaline. The stream of hydrogen is then exchanged for one of carbon dioxide, which precipitates the excess of barium hydroxide. The filtrate from barium carbonate is exhausted with ether. In this way the greater part of the barium iridinate separates in crystals, while the ether takes up the iretol. This is left by distilling off the ether as a syrup, which after some time sets to a mass of crystals. The iridinic acid is obtained by decomposing the barium salt with sulphuric acid and evaporating the filtrate from the barium sulphate.

We have measured the formic acid produced in this reaction. In doing this we have not forgotten that by the prolonged action of hot alkali upon iridinic acid and iretol small amounts of other volatile organic acids are formed as by products. We have determined by comparison with pure iridinic acid and iretol how far the yield of formic acid is affected, and corrected the results obtained in accordance therewith. According to the above equation 100 parts irigenin should give 13.06 per cent. formic acid, 58.9 per cent. iridinic acid, and 43.3 per cent. iretol. We have obtained from 100 parts irigenin as a mean of many determinations: 10.23 per cent. formic acid, forty to forty-five per cent. iridinic acid, and thirty-three to thirty-five per cent. iretol.

In view of the ease with which the product of this reaction decomposes and the fact that secondary decompositions even with careful working cannot be entirely avoided we may conclude with safety from the above figures that the decomposition of iridin as expressed by the above equation corresponds to the facts.

Formic acid, CH_2O.—The formic acid split off from irigenin is identified by its reducing action upon salts of mercury and sil· ver. We have also converted it into ethyl formate as well as into a sodium salt. The latter when analyzed gave:

	Per cent. Na.
Calculated	33.83
Found	33.94

Iridinic acid, $C_{10}H_{12}O_5$.—Iridinic acid is easily purified by recrystallizing from boiling benzene. It forms colorless prisms

melting at 118°, dissolves in water, alcohol, ether, chloroform, acetone and boiling benzene, is less easily dissolved by cold benzene, and is insoluble in light petroleum.

<div align="center">ANALYSIS.</div>

	Calculated for $C_{10}H_{12}O_5$.	Found	
C	56.60	56.45	56.56
H	5.66	5.87	5.85

Heated above its melting point it splits up into carbon dioxide and a phenol which we call iridol.

Iridinic acid is a strong acid. It expels carbonic acid from the carbonates of the metals of the alkalies and alkaline earths and saturates the alkaline hydroxides molecule for molecule. Titration with caustic soda gave the following results:

<div align="center">For formation of
$C_9H_{11}O_2CO_2Na$
is requisite.</div>

Calculated	9.83 per cent. Na
Found	9.80 per cent. Na

The alkaline salts and the calcium salt of iridinic acid are deliquescent. The barium salt, however, crystallizes well. Its composition corresponds to the formula $Ba(C_{10}H_{11}O_5)_2 + 5H_2O$. The water of crystallization is lost at 105°.

<div align="center">ANALYSIS.</div>

	Per cent. H_2O
Calculated for $5H_2O$	13.87
Found	13.90

A barium determination in the dried salt gave:

	Per cent. Ba.
Calculated for $Ba(C_{10}H_{11}O_5)_2$	24.51
Found	24.58

The esters of iridinic acid are formed by passing hydrochloric acid gas through solutions of iridinic acid in the different alcohols.

Methyl iridinate, $C_9H_{11}O_3(CO_2CH_3)$ is a viscous oil, boiling above 360°.

<div align="center">ANALYSIS.</div>

	Calculated for $C_{11}H_{14}O_5$.	Found.
C	58.41	58.16
H	6.19	6.30

Ethyl iridinate, $C_9H_{11}O_3(CO_2C_2H_5)$ forms a yellow oil which cannot be distilled without decomposition at the ordinary atmospheric pressure.

ANALYSIS.

	Calculated for $C_{12}H_{16}O_5$.	Found.
C	60.00	59.74
H	6.67	6.52

Besides the hydroxyl of the carboxyl group iridinic acid contains a second hydroxyl, whose hydrogen is easily replaced by acyls and alkyls.

Benzoyl iridinic acid, $C_9H_{10}O_2(OCOC_6H_5)(CO_2H)$ is obtained by shaking an alkaline solution of iridinic acid with benzoyl chloride. The substance is precipitated from the alkaline solution by means of hydrochloric acid and recrystallized from alcohol. Its melting point is 131°.

ANALYSIS.

	Calculated for $C_{17}H_{16}O_6$.	Found.
C	64.56	64.58
H	5.07	5.24

Acetyliridinic acid, $C_9H_{10}O_2(OCOCH_3)(CO_2H)$ is formed by heating iridinic acid with acetyl chloride. The excess of acetyl chloride is driven off on the water bath, the residue dissolved in benzene and precipitated with light petroleum. This compound is easily soluble in water, alcohol, ether, benzene, and chloroform, and insoluble in light petroleum, and melts at 125°. Alkalies separate from it acetic acid with great ease. As a control of the composition we have effected this saponification and determined by titration the acetic acid resulting from distillation with sulphuric acid.

100 parts $C_{12}H_{14}O_6$ should give 23.62 parts $C_2H_4O_2$
100 " " have given 24.21 " "

Methyliridinic acid, $C_9H_{10}O_2(OCH_3)(CO_2H)$ crystallizes in white plates easily soluble in water, alcohol, ether, and benzene, insoluble in light petroleum, and melts at 120°. To prepare it iridinic acid is digested in methyl alcohol solution with sodium methylate and methyl iodide. Under these conditions the methyl ester of methyliridinic acid is formed, which by evapo-

ration of the methyl alcohol separates as an oil and is converted
by saponification with alkali into methyliridinic acid.

<div style="text-align:center">ANALYSIS.</div>

	Calculated for $C_{11}H_{14}O_5$.	Found.
C	58.41	58.22
H	6.15	6.15

Silver Methyliridinate, $C_9H_{10}O_2(OCH_3)CO_2Ag$ is precipitated
from the solution of the ammonium salt as a gelatinous mass
and obtained by recrystallization from alcohol in beautiful white
needles.

Action of Hydriodic Acid upon Iridinic Acid.—By boiling with
hydriodic acid, methyl iodide is formed from iridinic acid from
which it is evident that it contains methoxyl. We have applied
Zeisl's method of methoxyl determination to iridinic acid and
obtained the following results:

<div style="text-align:right">Per cent. OCH_3.</div>

Calculated for $2(OCH_3)$ in $C_{10}H_{12}O_5$ 29.25
Found 33.13

Iridinic acid therefore contains two methoxyl groups and its
formula in accordance with the experiments so far described
may be written $C_7H_4(OCH_3)_2(OH)(CO_2H)$.

Iridol, $C_9H_{12}O_3 = C_7H_6(OCH_3)_2(OH)$.—The phenol derived
from iridinic acid by splitting off carbon dioxide must have the
same formula as that just obtained for the acid. Iridol is ob-
tained by dry distillation of iridinic acid. At 239° a colorless
oil passes over which solidifies in the receiver to large white
crystals melting at 57°. Iridol is nearly insoluble in cold water,
but is easily dissolved by alcohol, ether, ethyl acetate, benzene,
chloroform, and caustic alkali. Ferric chloride colors the alco-
holic solution violet.

<div style="text-align:center">ANALYSIS.</div>

	Calculated for $C_9H_{12}O_3$.	Found	
Per cent. C	64.22	63.81	63.88
Per cent. H	7.14	6.98	7.05

Iridol is a true phenol and is converted on heating with chloro-
form and caustic alkali into two isomeric aldehydes. One,
which belongs to the ortho series, is colored a deep yellow by
caustic alkalies like salicylic aldehyde. The second, which is a

derivative of paroxybenzaldehyde does not give this reaction. It crystallizes in white needles which melt at 88°.

Benzoyliridol, $C_7H_5(OCH_3)_2OCOC_6H_5$, is obtained by shaking an alkaline solution of iridol with benzoyl chloride. It dissolves easily in alcohol, ether, and chloroform, as well as in ethyl acetate and crystallizes in white plates which melt at 68°.

ANALYSIS.

	Calculated for $C_{16}H_{16}O_4$.	Found.
Per cent. C	70.59	70.31
" H	5.88	5.94

Methyliridol, $C_7H_5(OCH_3)_3$, is obtained by the action of methyl iodide upon a methyl alcohol solution of iridolsodium. It is a colorless oil, boiling at 236°–237°.

ANALYSIS.

	Calculated for $C_{19}H_{14}O_3$.	Found.
Per cent. C	65.95	65.62
" H	7.69	7.71

By oxidation with potassium permanganate methyliridol is converted into *trimethylgallic acid*, $C_6H_2CO_2H(OCH_3)_3$, 3.4.5, which melts at 168°.

ANALYSIS.

	Calculated for $C_{10}H_{12}O_5$	Found.
Per cent. C	56.60	56.49
" H	5.66	5.78

In order to identify the trimethylgallic acid sharply, we have converted it into gallic acid on the one hand by digestion with hydriodic acid, and on the other hand we have prepared it by methylating gallic acid. Finally we have determined that by dry distillation silver trimethylgallate gives the trimethyl ether of pyrogallol, melting at 47° and boiling at 235°, and that this is converted into pyrogallol when it is heated to 150°–160° in closed tubes with dilute hydrochloric acid.

Trimethylgallic acid and the trimethyl ether of pyrogallol have been known for a long time. W. Will[1] prepared them by permethylating gallic acid and pyrogallol, and G. Körner[2] has shown that the syringic acid obtained by him from the gluco-

[1] *Ber. d. chem. Ges.*, **21**, 607 and 2023.

[2] *Gazz. Chim. Ital.*, **18**, 216.

side of the elder (dimethylgallic acid) is converted by methylating into trimethylgallic acid of melting point 168°. We have found the properties of the compound in question to be exactly those which W. Will gives it.

Constitution of Iridol.—Trimethylgallic acid is formed from methyliridol by the oxidation to carbonyl of a methyl group attached to the benzene nucleus. Methyliridol corresponds therefore to the formula,

$$C_6H_2(\overset{1}{C}H_3)(\overset{3.4.5}{OCH_3})_3;$$
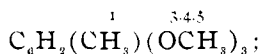
it is the trimethyl ether of homopyrogallol, $C_6H_2(\overset{1}{C}H_3)(\overset{3.4.5}{OH})_3$. Iridol contains one hydroxyl in place of one of the three methoxyl groups of methyliridol. We have already observed that iridol is transformed by chloroform and alkali into two isomeric aldehydes. It must therefore contain two hydrogen atoms in the benzene nucleus, of which one occupies the ortho, the other the para position with reference to the phenol hydroxyl. Only the formula
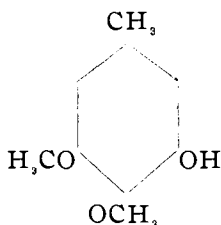

is in accordance with these facts.

There are other grounds for this view. A. W. Hofmann has isolated two phenols from the acid constituents of wood tar boiling between 250°–290°, of which one, boiling at 265°, is a dimethyl ether of homopyrogallol[1] while the phenol boiling at 285° bears the same relation to propylpyrogallol[2]. If we exchange the methyl in the methoxyl groups of these phenols for hydrogen we obtain triatomic phenols which show the characteristic reactions of pyrogallol. For this reason A. W. Hofmann considered these phenols derivatives of pyrogallol.

[1] *Ber. d. chem. Ges.*, **12**, 1371.
[2] *Ber. d. chem. Ges.*, **8**, 67; **11**, 327.

Nitric acid converts the dimethyl ether of propylpyrogallol into the dimethyloxylated quinone[1], $C_6H_2O_2(OCH_3)_2$, melting at 249°. In the first named compound the propyl and hydroxyl groups must occupy the para position with reference to each other. W. Will[2] has shown that the trimethyl ether of Hofmann's propylpyrogallol is converted by potassium permanganate into trimethylgallic acid melting at 168°. The above dimethyl ether of propylpyrogallol must therefore have the formula

$$C_3H_7$$

H₃CO————OCH₃

OH
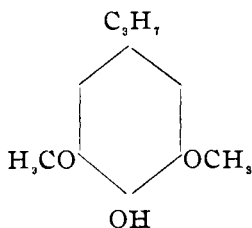
It is *a priori* probable that the lower homologue of the above phenols—the dimethyl ether of homopyrogallol—has an analogous constitution. We have, in fact, determined that the neutral methyl ether of the phenol boiling at 265°, prepared by A. W. Hofmann, of which a large sample was at our disposal, had the same properties and the same constitution as the trimethyl ether of homopyrogallol prepared from iridol. Both compounds are converted by the aboxydation of the methyl group attached to the nucleus into trimethylgallic acid melting at 168°.

The dimethyl ether of pyrogallol from the wood tar and iridol are isomeric methyl derivatives of the same homopyrogallol. The properties of the two isomers differ materially as the following summary shows:
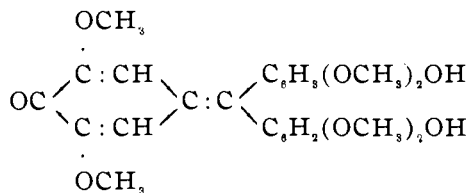
	Dimethyl ether of homopyrogallol from wood tar.	Iridol.
Melts at	36°	57°
Boils at	265°	239°
Benzoyl derivative melts at	118°	68°

By means of a very remarkable method which is analogous

[1] A. W. Hofmann. *Ber. d. chem. Ges.*, 11, 332.

[2] *Ber. d. chem. Ges.*, 21, 2025.

to the formation of rosanilin by the oxidation of a mixture of toluidin and analin, namely, fusion with sodium hydroxide in contact with air, the mixture of the dimethyl ether of homo· pyrogallol boiling at 265° and of the dimethyl ether of pyrogallol is converted as A. W. Hofmann has shown[1] into eupittonic acid, $C_{20}H_{26}O_9$, the constitution of which, in view of the studies made in the last few years of the triphenylmethane colors should be expressed by the symbol:

$$OC\underset{C:CH}{\overset{C:CH}{<}}\overset{OCH_3}{\underset{OCH_3}{\cdot}}C:C\underset{C_6H_2(OCH_3)_2OH}{\overset{C_6H_3(OCH_3)_2OH}{<}}$$

To such a condensation, however, only a dimethyl ether of homopyrogallol constituted according to the formula

$$
\begin{array}{c}
CH_3 \\
\text{(benzene ring)} \\
H_3CO \qquad OCH_3 \\
OH
\end{array}
$$
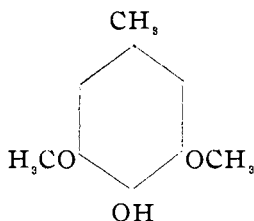
can lend itself.   Its isomer, iridol, which under like conditions gives no trace of eupittonic acid or an isomeric eupittonic acid must therefore have the formula,

$$
\begin{array}{c}
CH_3 \\
\text{(benzene ring)} \\
H_3CO \qquad OH \\
OCH_3
\end{array}
$$
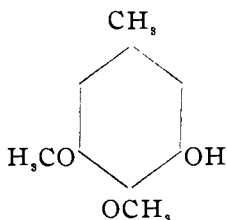
This gives to iridol the same constitution as our experiments.

[1] *Ber. d. chem. Ges.*, **12,** 1377.

Constitution of Iridinic Acid and Methyliridinic Acid.—Iridinic acid is carboxylated iridol and its composition must correspond to one of the three formulas

(1)
CH,
CO,H
H,CO
OH
OCH,

(2)
CH,
HO,C
H,CO
OH
OCH,

(3)
CH,COOH
H,CO
OH
OCH,
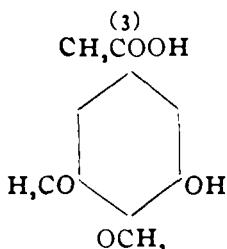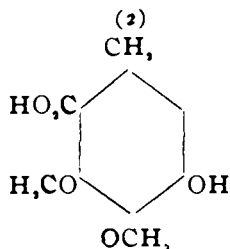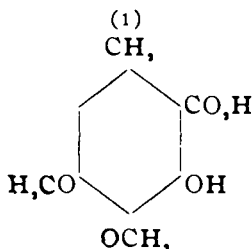
while the constitution of methyliridinic acid is expressed by one of the two formulas

(1)
CH,
CO,H
H,CO
OCH,
OCH,

(2)
CH,CO,H
H,CO
OCH,
OCH,
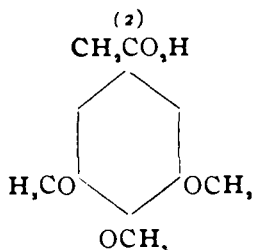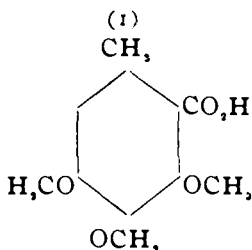
The experiments described below give the further explanation of the constitution of iridinic and methyliridinic acids.

(*a*) *Dibrommethyliridinic Acid,* $C_6Br_2(O\overset{2.6}{C}H_3)_2(\overset{1}{C}H_2CO_2H)$.—If a solution of methyliridinic acid in dilute acetic acid is poured into an excess of bromine water an acid separates in compact crystals which is easily soluble in alcohol and ether. It melts

at 152° and is formed from **methyliridinic** acid by the substitution of two bromine for two **hydrogen** atoms.

<div align="center">

ANALYSIS.

	Calculated for $C_{11}H_{12}Br_2O_4$	Found.
Per cent. Br	41.66	41.36

</div>

The formation of this acid shows at once that of the two formulas considered for methyliridinic acid the second is correct.

(*b*) *Dibromtrimethylgallic Acid.*—Dibrommethyliridinic acid is a very stable compound which may be recrystallized from hot dilute nitric acid without change. If it is heated with nitric acid of sp. gr. 1.2, action takes place accompanied by the evolution of red vapors and soon leads to a profound decomposition of the dimethyliridinic acid used. If, however, the action is stopped at the proper time by the addition of water, which can be determined by the precipitation of crystals instead of an oil, and the solid compound separating dissolved in very dilute nitric acid, dibromtrimethylgallic acid will crystallize out in long lustrous needles which when pure melt at 143°. For comparison we have prepared dibromtrimethylgallic acid by pouring a solution of trimethylgallic acid in dilute acetic acid into excess of bromine water, and find the acid obtained in these different ways to be identical.

<div align="center">

ANALYSIS.

	Calculated for $C_{10}H_{10}Br_2O_4$	Found.
Per cent. Br	43.24	43.54

</div>

Experiment shows that methyliridinic acid contains two hydrogen atoms directly attached to the benzene nucleus. We have not been able to convert dibrommethyliridinic acid into dibrommethylgallic acid by heating it with potassium permanganate. The potassium permanganate is indeed reduced by heating for a long time and a small part of the dibrommethyliridinic acid destroyed; but by far the larger part of the acid remains unattacked.

(*c*) *Trimethylgallic Acid from Methyliridinic Acid.*—Methyliridinic acid is, on the contrary, readily oxidized to trimethylgallic acid, melting at 168°, by means of potassium permanga-

nate. In carefully conducted oxidations in the course of the transformation an extremely unstable intermediate product, which is difficult to isolate and which is probably the ketonic acid derived from methyliridinic acid, $C_6H_2(OCH_3)_3COCO_2H$, and which we have not followed further.

(To be continued.)

ON CARBORUNDUM.

(CARBIDE OF SILICON.)

BY DR. OTTO MÜHLHAEUSER.

THIS new material stands next to diamond, not only in its composition, but in its internal and external properties, in the extraordinary brilliancy of its crystals, and in the extreme hardness which makes it such an efficient and powerful abrasive material.

It is an American invention, having been discovered by Edward G. Acheson, of Monongahela City, Pa., who carried the invention to commercial success with extraordinary energy in the face of many obstacles.

The product is obtained by heating a mixture of 100 parts sand, twenty-five parts salt and twenty-five parts coke in an electrical furnace for several hours. The alternating current used has finally a strength of about 500 amperes and a difference of potential of fifty volts.

The mixture yields a mass in which we can distinguish shells and layers of different character and nature. Around the carbon core we find a layer of graphite. The latter is surrounded by a thick shell of carborundum crystals. This shell of carborundum is enveloped in a thin sheet of amorphous carbide of silicon; surrounding and incasing these three products of the reaction is the original mixture in an essentially unchanged condition.

(1) *The Graphite.*—The graphite is located around the carbon core and is covered by the carborundum crystals. It is connected with the latter, forming one large elypsoid of crystals whose rays are arranged radially to the axis of the elypsoid or