The ether-insoluble fraction of this mixture consists largely of eriodictyol (m.p. 271°), the presence of which in lemons has now been established unequivocally. The ether-soluble fraction contains a number of other aglycones which, upon standing, deposit a small quantity of a crystalline, chromatographically homogeneous flavonol, m.p. 274–275°, λ_{max} 259 and 378 mμ. Analytical data for the compound (Calcd. for $C_{17}H_{14}O_8$: C, 59.0; H, 4.08; CH_3O, 17.9. Found: C, 58.8; H, 4.27; CH_3O, 18.7), its tetraacetate (m.p. 155–156°; calcd. for $C_{25}H_{22}O_{12}$: C, 58.4; H, 4.31; CH_3O, 12.1. Found: C, 58.3; H, 4.37; CH_3O, 12.4) and its tetra-ethyl ether (m.p.[2] 116 and 130°; calcd. for $C_{25}H_{30}O_8$: C, 65.4; H, 6.59; CH_3O, 40.6. Found: C, 65.6; H, 6.68; CH_3O, 40.9) establish it as a dimethoxytetrahydroxyflavone. Methylation with excess methyl sulfate yields gossypetin hexamethyl ether (3,5,7,8,3′,4′-hexamethoxyflavone) (m.p.[2] and mixed m.p. 148–150° and 168–169°), while methylation with three moles of methyl sulfate yields 5-hydroxy-3,7,8,3′,4′-pentamethoxyflavone (m.p. and mixed m.p. 156–157°). The compound is, therefore, a dimethyl ether of gossypetin having a free 5-hydroxy group. It is the first representative of this flavonol to be found in citrus and has been named *limocitrin*.

The location of one of the methoxy groups at the 3′-position is proved by the isolation of vanillic acid from the alkaline cleavage products. That the other methoxy group must be located at the 8-position is shown by the facts that limocitrin, unlike flavones containing a free 5,8-dihydroxy group, does not undergo aerial oxidation to deeply colored substances in alkaline solution and fails to give the gossypetone reaction when treated with *p*-benzoquinone in alcohol. It follows that the structure of limocitrin is 3′,8-dimethoxy-3,5,7,4′-tetrahydroxyflavone.

This structural assignment has been confirmed by various spectral measurements. Thus, a free 7-hydroxy group is indicated by the shift of the short wave length band from 259 to 282 mμ in the presence of sodium acetate,[3] while a free 3,4′-dihydroxy group is indicated by the disappearance of the long wave length band in 0.002 *N* sodium ethoxide solution.[3] The absence of an *o*-dihydroxy group is shown by the failure of the bands to shift in the presence of boric acid–sodium acetate.[4] The structure suggested is the only dimethyl ether of gossypetin which can accommodate these spectral data.

The identification of other aglycones in the mixture is in progress.

[2] Double melting point.

[3] L. Jurd and R. M. Horowitz, *J. Org. Chem.* (in press).

[4] L. Jurd, *Arch. Biochem. Biophys.*, **63**, 376 (1956).

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RECEIVED OCTOBER 31, 1957

A NEW AND SELECTIVE METHOD OF OXIDATION

Sir:

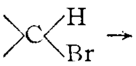
We have found that the oxidation  $>C\begin{smallmatrix}H\\Br\end{smallmatrix} \rightarrow$ $>C{=}O$ can be achieved simply by dissolving the halide in dimethyl sulfoxide. In the majority of cases studied thus far the reaction proceeds at room temperature. Table I summarizes our findings. Extension of this reaction is being explored as is also the matter of mechanism.

TABLE I

OXIDATION OF >CHBr to >C=O

Halide	Product	Yield, %
$C_6H_5COCH_2Br$	C_6H_5COCHO	71
p-Br-C_6H_4-$COCH_2Br$	*p*-Br-C_6H_4-$COCHO^a$	84
p-Cl-C_6H_4-$COCH_2Br$	*p*-Cl-C_6H_4-COCHO	69
p-C_6H_5-C_6H_4-$COCH_2Br$	*p*-C_6H_5-C_6H_4-$COCHO^a$	85
p-NO_2-C_6H_4-$COCH_2Br$	*p*-NO_2-C_6H_4-COCHO	72
$C_6H_5CHBrCOC_6H_5$	$C_6H_5COCOC_6H_5{}^b$	95
p-NO_2-C_6H_4-CH_2Br	*p*-NO_2-C_6H_4-CHO	48

[a] Isolated as the hydrate. [b] At 45° for 44 hours.

As a typical example: *p*-bromophenacyl bromide (15.98 g.) is dissolved in 100 ml. of dimethyl sulfoxide at room temperature. After nine hours the solution is poured into ice-water and extracted with diethyl ether; the extracts are washed with water and dried over anhydrous magnesium sulfate. Removal of the ether *in vacuo* yields 14.6 g. of a slightly pasty, pale yellow, solid. One recrystallization from ethyl *n*-butyl ether gives 11.2 g. (84% yield) of white needles, m.p. 123–124°. *Anal.* Calcd. for $C_8H_5O_2Br \cdot 0.5\ H_2O$: C, 43.27; H, 2.72; Br, 35.90. Found: C, 43.58; H, 2.87; Br, 35.73. This hydrate is quantitatively converted to the hemi-acetal (m.p. 62–63°) by dissolving it in hot absolute ethanol and evaporating the solution to dryness *in vacuo*. *Anal.* Calcd. for $C_8H_5O_2Br \cdot C_2H_5OH$: C, 46.3; H, 4.25; Br, 30.8. Found: C, 46.2, 46.2; H, 4.28, 4.32; Br, 30.9; 30.9. The glyoxal hydrate gives a *bis*-semicarbazone: m.p. 253–254°. *Anal.* Calcd. for $C_{10}H_{11}BrN_6O_2$: C, 36.71; H, 3.39. Found: C, 36.91; H, 3.46.

Periodic acid oxidation of *p*-bromophenyl glyoxal results in a 98% yield of *p*-bromobenzoic acid and an 88% yield of formic acid. In contrast, from the keto alcohol *p*-BrC_6H_4-CO-CH_2OH, on treatment with periodic acid, an 87% yield of *p*-bromobenzoic acid and a 61% yield of formaldehyde is obtained.

The foregoing simple procedure is not satisfactory with benzyl bromides. However, by raising the temperature, and using acetonitrile as a solvent, pure *p*-nitrobenzaldehyde has been obtained in 48% yield from *p*-nitrobenzyl bromide.

Acknowledgment.—This work has been supported by the Explosives Department of E. I. du Pont de Nemours and Co., Inc., and the Air Force of the United States.[1]

[1] Under Contract No. AF 18 (600)–310 monitored by the Office of Scientific Research, Air Research and Development Command.

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RECEIVED JULY 16, 1957