needles, m.p. 117~118° (reported[3]) m.p. 118~119°), $[\alpha]^{16}_{D}$ −19.5° (c=1.0, $CHCl_3$). *Anal.* Calcd. for $C_{14}H_{20}O_9S$: C, 46.15; H, 5.53. Found : C, 46.20; H, 5.58. This substance was identical with the substance prepared from (I) and potassium methylmercaptide according to the method of Helferich, *et al.*[3]

Phenylosazone of (III) and Glucuronolactone—A solution of 0.5 g. of (III), 2 g. of phenylhydrazine, and 2 cc. of 50% AcOH dissolved in 20 cc. of H_2O was heated on a steam bath to a clear solution, and the osazone appeared as yellow needles following evolution of H_2S. After cool, the resulting crystals were collected and washed with cold H_2O and EtOH. Recrystallization from pyridine-H_2O gave pale yellow needles, m.p. 171~172°, $[\alpha]^{16}_{D}$ −15° (c=1.0, pyridine).

This substance was identical with the compound prepared similarly from glucuronolactone and apparently different from the osazone of m.p. 125°, prepared from D-glucopyranuronic acid.

The authors are grateful to Chugai Pharmaceutical Co. Ltd., for the supply of glucuronolactone.

Summary

1-Thio-β-D-glucopyranurono-6,1-thiolactone was prepared by hydrolysis of methyl 2,3,4-tri-O-acetyl-1-thio-β-D-glucopyranuronate 1-ethylthionocarbonate which was prepared from methyl 2,3,4-tri-O-acetyl-1-bromo-1-deoxy-α-D-glucopyranuronate and potassium ethylxanthate. Methylation of this compound with diazomethane and subsequent acetylation afforded methyl (methyl 2,3,4-tri-O-acetyl-1-thio-β-D-glucopyranosid)uronate.

(Received February 15, 1960)

UDC 547.572.3:543.41[546.791]

189. Morizo Ishidate[*1] and Yasuhiro Yamane[*2] :

Detection of β-Diketones with Uranyl Ion.

(*Faculty of Pharmaceutical Sciences, University of Tokyo,*[*1] *and*
Pharmaceutical Faculty, University of Chiba[*2])

In the previous papers, the authors reported that enolisable β-diketones are liable to form a stable chelate compound with uranyl ion, producing a yellow color.[1~3] Geyer[4] and Sakaguchi[5] also reported that 1-hydroxyanthraquinone and tetracycline derivatives which possess a phenolic β-diketone in the molecule similarly produce chelate compound with the same metal. It seemed possible to apply this color reaction for the detection of compounds having enolisable β-diketone or phenolic β-diketone group.

For the detection of β-diketones, the color reaction with iron(III) chloride[6,7] or titanium(III) chloride[8] has usually been employed. As these color reactions take place similarly

---

[*1] Hongo, Tokyo (石館守三).
[*2] Inohana, Chiba (山根靖弘).
1) M. Ishidate, Y. Yamane : Yakugaku Zasshi, **77**, 386(1957).
2) Y. Yamane : *Ibid.*, **77**, 391(1957).
3) *Idem* : *Ibid.*, **77**, 396(1957).
4) B.P. Geyer : J. Am. Chem. Soc., **64**, 1649(1942).
5) T. Sakaguchi, *et al.* : Yakugaku Zasshi, **78**, 177(1958).
6) H.B. Pulsifer : J. Am. Chem. Soc., **26**, 967(1904).
7) R.P. Linstead, B.G.L. Weedon : "A Guide to Qualitative Organic Chemical Analysis," 17(1956). Butterworths Scientific Publications, London.
8) F. Weygand, E. Csenees : Ber., **85**, 45(1952).

with phenols and enols, they are not applicable for the selective detection of β-diketones in the presence of phenols and the like. It was now found that under an appropriate condition uranyl ion provides a specific and more sensitive reaction for characterisation and detection of β-diketones than iron(III) chloride or titanium(III) chloride.

Experimental

Reagents—2% $UO_2(AcO)_2$ solution : 2 g. of purified $UO_2(AcO)_2$ dissolved in H_2O to make 100 cc.

5% $TiCl_3$ solution : 15% $TiCl_3$ solution (1st grade reagent, J. I. S.) diluted to 5% solution with H_2O and stored in tightly stoppered vessel.

2% $FeCl_3$ solution : 2 g. of $FeCl_3$ dissolved in H_2O to make 100 cc.

Five kinds of parallel experiments were carried out as follows : Procedures A and B : Reaction with UO_2^{+2} in neutral and acidic media, respectively. Procedures C, D, and E : Reaction with $TiCl_3$ and $FeCl_3$ for comparison. The compounds to be tested were prepared as 0.2% or 0.5% solution in EtOH or H_2O.

Procedure A : 1 cc. of test solution + 1 drop of 2% $UO_2(AcO)_2$ solution.
Procedure B : Procedure A + 1 drop of glacial AcOH.
Procedure C : 1 cc. of test solution + 1 drop of 5% $TiCl_3$ solution.
Procedure D : Procedure C + 1 drop of pyridine.
Procedure E : 1 cc. of test solution + 1 drop of $FeCl_3$ solution.

The results of color reaction with compounds having β-diketone, phenolic β-diketone, phenol, enol, etc. are summarized in Table I.

Discussion

R-CO-CH_2-CO-R′ Type Compounds : This type of β-diketones generally gives deep yellow color with uranyl ion in both neutral and acid media (procedures A and B), green with titanium(III) ion, and red with iron(III) ion.

R-CO-CH(R″)CO-R′ : The derivatives of β-diketone in which one of the hydrogens in active methylene is replaced by alkyl group often show negative reaction with uranyl ion, especially in acid medium. This fact corresponds to the finding that the methylene-substituted β-diketones gave negative reaction on enol test (bromine absorption test). Therefore, this type of β-diketones is considered to be not stable enough for the formation of uranyl chelate compound.

Phenolic β-diketones : β-Phenol ketones like 8-hydroxynaphthoquinone and 2-methylhydroxynaphthoquinone show negative reaction by the procedure B, but positive by procedure A. On the other hand, anthraquinone derivatives such as alizarin and the like show positive color reaction. Salicylaldehyde and tetracycline analogs similarly give marked coloration by both procedures. These phenolic β-diketones give coloration with iron(III) and titanium(III) ions.

Phenols : Phenols give color reaction by the procedures C and D with titanium(III) ion, procedure E with iron(III) ion, and procedure A with uranyl ion, but negative to procedure B. Therefore, procedure B is a suitable method for distinguishing β-diketones from phenols. The compounds of carboxylic acids, monoketones, aldehydes, and R_1-CO-NH-CO-R_2 type never give coloration with uranyl ion. α-Diketones such as 2,3-butanedione or benzil are also negative. The fact that the reaction is positive in acetoacetic ester and ascorbic acid may be due to the presence of a functional group similar to β-diketone in their molecules. The colored precipitate formed in the case of 2,5-dihydroxy-*p*-benzoquinone is not a chelate compound, but is a formation of a stable salt in acetic acid.

The colored chelate compounds of enolic and phenolic β-diketones with uranyl ion are illustrated in Chart 1.

These chelate compounds are generally stable in acetic acid. On the other hand, phenols will give color reaction with uranyl ion in neutral solution[9] by the formation of a salt-

---

[9] A. Müller : Z. anorg. Chem., **109**, 240(1920).

Table I. Color Reaction of β-Diketone and Related Compounds

Compound \ Procedure	A	B	C	D	E
[$R-CO-CH_2-CO-R'$]					
2,4-Pentanedione	Y	p Y	R	R→Oppt	R
1-Phenyl-1,3-butanedione	〃	Y	B G	G→Y	〃
1,3-Diphenyl-1,3-propanedione	〃	〃	G	G→Yppt	〃
1-(2-Furyl)-3-phenyl-1,3-propanedione	d Y	d Y	〃	d Gppt	〃
1-Phenyl-3-(4-pyridyl)-1,3-propanedione	〃	〃	〃	G→Yppt	〃
1-*o*-Nitrophenyl-3-phenyl-1,3-propanedione	Y	Y	〃	〃	〃
1-*m*-Nitrophenyl-3-phenyl-1,3-propanedione	〃	〃	〃	〃	〃
1-*p*-Nitrophenyl-3-phenyl-1,3-propanedione	〃	〃	〃	〃	〃
1-*o*-Methoxyphenyl-3-phenyl-1,3-propanedione	d Y	d Y	〃	G→Y	〃
1-*m*-Methoxyphenyl-3-phenyl-1,3-propanedione	〃	〃	〃	〃	〃
1-*p*-Methoxyphenyl-3-phenyl-1,3-propanedione	〃	〃	〃	G→Yppt	〃
1-*m*-Aminophenyl-3-phenyl-1,3-propanedione	O	O	〃	〃	〃
1-*p*-Aminophenyl-3-phenyl-1,3-propanedione	O R	O	Br	Br→Yppt	〃
1-*p*-Carboxyphenyl-3-phenyl-1,3-propanedione	Y	Y	G	Yppt	〃
[$R-CO-CH(R'')-CO-R'$]					
1-Phenyl-2-methyl-1,3-butanedione	Y	—	B	B→Y	V
1-Phenyl-2-ethyl-1,3-butanedione	〃	±	〃	—	R V
1,3-Diphenyl-2-methyl-1,3-propanedione	—	—	—	—	—
1,3-Diphenyl-2-ethyl-1,3-propanedione	—	—	—	—	—
[Phenolic β-Diketones]					
5-Hydroxy-1,4-naphthoquinone	R	—	V	V R	R
2-Methyl-8-hydroxy-1,4-naphthoquinone	〃	—	〃	〃	〃
Alizarin	B V	d G	G	Vppt	d V
Quinalizarin	B	R	d G	Bppt	Bl
Alizarin S	R V	〃	d V	V Rppt	d R
Aureomycin	O Y	O Y	O→Gppt	Oppt	R
Terramycin	O	O	O→G	〃	〃
Achromycin	O Y	O Y	d G	O Rppt	〃
Salicylaldehyde	O	p Y	B→O	Yppt	d Br
[Phenols and Enols]					
Phenol	p O	—	—	V→Yppt	Br
Pyrocatechol	O	—	R	Oppt	R
Pyrogallol	d R	—	〃	d Oppt	〃
Phloroglucine	p O	—	—	Y	—
o-Aminophenol	Br	—	—	—	R
o-Nitrophenol	O	—	O	Yppt	Br
Ethyl *p*-hydroxybenzoate	Y	—	—	—	Y
1-Naphthol	O	—	O	Yppt	Br
2-Nitroso-1-naphthol	d R	—	Br	Br	d R
Ethyl acetoacetate	Y	p Y	O Y	—	O R
Ascorbic acid	O	O	O R	Br	Br
2,5-Dihydroxy-*p*-benzoquinone	Oppt	Oppt	V	Brppt	Brppt
[α-Diketones]					
2,3-Butanedione	—	—	—	—	—
Benzil	—	—	V	Brppt	—
1,2-Naphthoquinone	—	—	R	R	R
[Miscellaneous]					
Anthranilic acid	Y	—	—	—	—
Phthalic acid	—	—	—	—	—
Potassium sodium tartrate	p Y	—	—	—	—
Benzaldehyde	—	—	—	—	—
Acetophenone	—	—	—	—	—
Acetone	—	—	—	—	—
Diacetamide	—	—	—	—	—
Benzoylacetamide	—	—	—	—	—
Dibenzamide	—	—	—	—	—
Benzoin	—	—	—	—	—
Diethyl malonate	—	—	—	—	—

B : blue Br : brown Bl : black G : green O : orange R : red V : violet
Y : yellow d : deep p : pale ppt : precipitation — : no coloration

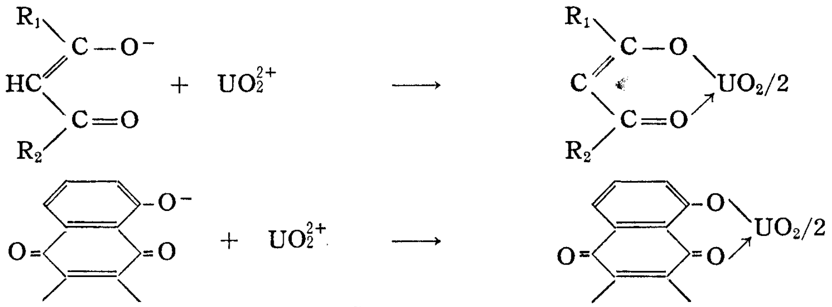

Chart 1.

like uranyl phenoxide which is discolored in acid medium by decomposition. These β-diketones which hardly form enol never produce chelate compound, as for example, 1,3-diphenyl-2-methyl-1,3-propanedione and 1,3-diphenyl-2-ethyl-1,3-propanedione which show negative reaction both to titanium(III) and iron(III) ions, and likewise do not form chelate compounds.

The procedure recommended for correct coloration is as follows :

A sample (1~5 mg.) is dissolved in 1 cc. of ethanol or water and one drop of 2% uranyl acetate solution is added. If β-diketone is present, the color reaction appears just as shown in Table I. In case phenols are present at the same time, one drop of glacial acetic acid should be added to this solution. The color reaction due to phenols will disappear at once and interfering effect of phenols can be removed. Sensitivity of the reaction is estimated in some derivatives of β-diketones as shown in Table II.

Table II. Comparison of Sensitivity of the Color Reaction

Procedure Compound	Detection limit (γ/cc.)			
	A	B	C	E
2,4-Pentanedione	50	200	20	40
1,3-Diphenyl-1,3-propanedione	5	10	40	100
1-(2-Furyl)-3-phenyl-1,3-propanedione	5	10	50	100
1-Phenyl-3-(4-pyridyl)-1,3-propanedione	5	10	10	100
1-*p*-Methoxyphenyl-3-phenyl-1,3-propanedione	5	10	25	100
2-Methyl-8-hydroxy-1,4-naphthoquinone	50	—	20	100
Alizarin	10	500	25	50
Achromycin	5	10	50	50
Salicylaldehyde	1(mg.)	5(mg.)	200	200
Ethyl acetoacetate	2(〃)	30(〃)	1(mg.)	1(mg.)

Summary

For the detection of compounds having enolisable or phenolic β-diketone group, the method employing uranyl ion was found to be recommendable by the fact that it is more selective and sensitive than the known methods using titanium(III) or iron(III) ion which gives color reaction both with β-diketones and phenols. The reaction with uranyl ion proposed here is based on the formation of a colored chelate compound which is stable in an acetic acid medium.

(Received April 18, 1960)