crystal by means of three-dimensional Fourier summations. The revised parameters yield structure factors which are in better agreement with the observed data. Two features of the structure are significantly different from those of the original determination: The C–N bond distance is 1.50 Å. and is no longer anomalously short; and the two C–O distances in the carboxyl group differ by 0.06 Å., indicating that hydrogen bond formation causes one of the resonating structures to be favored over the other, an effect which is substantiated by the inequality of the C–C–O bond angles.

PASADENA, CALIF. RECEIVED AUGUST 22, 1949

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

The Polarographic Behavior of the Neptunium(III)–Neptunium(IV) Couple in Chloride and Perchlorate Solution

BY J. C. HINDMAN AND EVELYN S. KRITCHEVSKY

It has been reported previously[1] that the uranium(III)–uranium(IV) couple is reversible at the dropping mercury electrode in acid chloride and perchlorate solutions and, further, that the potential of the couple is independent of hydrogen ion concentration at acidities above 0.05 molar. These data have been interpreted as showing that the U^{+4} (hydrated) ion exists in acid solution in the absence of a complexing agent. Confirmation of this conclusion has been obtained by direct measurement of the amount of acid liberated on the addition of anhydrous uranium tetrachloride to an aqueous chloride solution.[2] Since plutonium(IV) is known to exist as Pu^{+4} (hydrated) in acid perchlorate solutions[3] and thorium(IV) is present as Th^{+4} (hydrated) under similar conditions,[4,5] the only tetrapositive ion in the actinide series for which data were not available was the neptunium(IV) ion. Potential measurements of the hydrogen ion dependence of the neptunium(III)–neptunium(IV) couple were therefore considered.

Hindman, Magnusson and LaChapelle[6] have reported that the reversible oxidation potential of this couple is −0.137 ± 0.005 volt in molar hydrochloric acid. Since this potential is within the range of polarographic determination, this method of measurement was used. Investigations of perchlorate as well as chloride solutions were undertaken since there is some evidence that chloride forms weak complexes with these tetrapositive ions.[1,2,7]

Experimental

The polarograms described in this report were obtained with a Sargent Model XX potentiometric pen chart recording polarograph calibrated according to the method of Lingane.[8] The diffusion currents reported were determined from a line drawn through the mid-point of the recorder pen oscillations using either damping position 1 or 2 of the polarograph. Operation of the present instrument under these conditions gave a value of the diffusion current constant for the lead ion in 1 *M* potassium chloride within ±1% of that reported by Lingane and Loveridge.[8a] The experimental procedure and apparatus were, in general, similar to those previously described.[1] Electromotive force values in the vicinities of the half-wave potentials were determined with a Leeds and Northrup type K_2 potentiometer. All values of half-wave potentials reported in this work have an experimental error of ±0.004 volt. This error includes any error in measurement caused by the *iR* drop in the solutions. An H-cell[9] was used with a sintered glass disc and an agar-agar plug separating the two compartments. A saturated ammonium chloride agar bridge[10] was used for the perchlorate solutions. A saturated KCl-agar bridge was used for the chloride solutions. The reference electrode and anode was a saturated calomel electrode.

Air was removed from the solutions with pre-purified nitrogen. Redistilled water was used. All measurements were carried out at 25.0 ± 0.2°. Al values of the current reported have been corrected for the residual current.

Neptunium(IV) solutions in 5 *M* perchloric acid were prepared by hydrogen reduction from neptunium(V) solutions using a platinum black catalyst. Neptunium(IV) solutions in 1 *M* perchloric acid were prepared by the dissolution of solid anhydrous neptunium tetrachloride in the acid. Neptunium(IV) solutions in hydrochloric acid were prepared by precipitation of the hydroxide with ammonia from perchloric acid solutions of neptunium(IV) and redissolution in concentrated acid. The neptunium(III) chloride and perchlorate solutions were prepared by hydrogen reduction of the neptunium(IV) solutions. All of the polarograms were made on solutions approximately 0.007 *M* in neptunium except where otherwise noted. The concentrations of the neptunium solutions were determined by radiometric assay.

Results and Discussion

Analyses of the polarographic reduction waves were made by the equation of Heyrovsky and Ilkovic.[11]

$$E_{\text{d.e.}} = E_{1/2} - \frac{0.05915}{n} \log \frac{i}{i_{\text{d}} - i} \qquad (1)$$

---

[1] E. S. Kritchevsky and J. C. Hindman, THIS JOURNAL, **71**, 2096 (1949).

[2] J. C. Hindman and E. S. Kritchevsky, unpublished data.

[3] J. C. Hindman, to appear as Paper No. 4.4 Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series.

[4] J. Kasper, Ph.D. Thesis, Johns Hopkins Univ., Baltimore, Md., 1941.

[5] J. C. Hindman and E. S. Kritchevsky, unpublished data.

[6] J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, THIS JOURNAL, **71**, 687 (1949).

[7] J. C. Hindman, data to appear in Chapter IV, Vol. 14A of the Plutonium Project Record of the National Nuclear Energy Series.

[8] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **18**, 734 (1946).

[8a] J. J. Lingane and B. Loveridge, THIS JOURNAL, **66**, 1425 (1944); **68**, 395 (1946).

[9] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

[10] C. N. Murray and S. F. Acree, *Bur. Stds. Jour. Research*, **7**, 713 (1931).

[11] J. Heyrovsky and D. Ilkovic, *Coll. Czechoslov. Chem. Comm.*, **1**, 198 (1935).

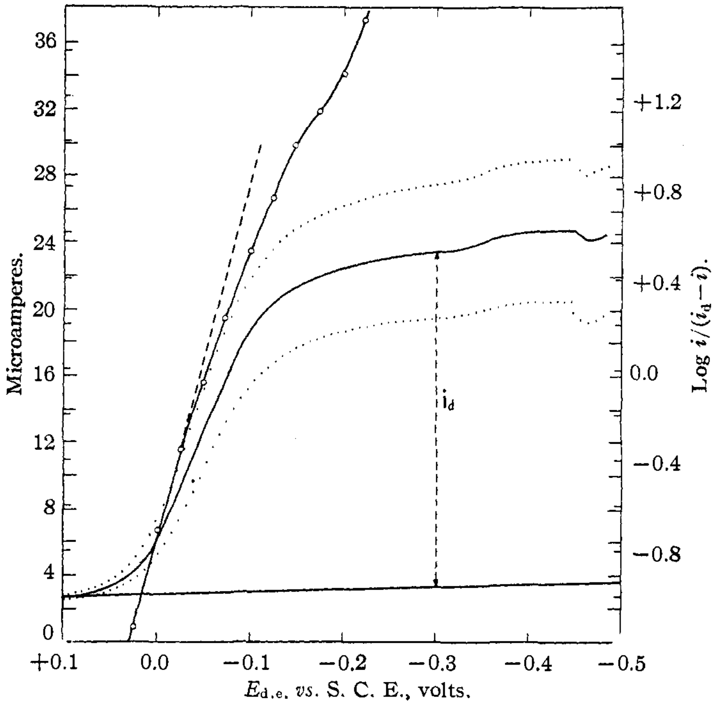

Fig. 1.—Neptunium(IV) polarogram in 1.0 M $HClO_4$: . . . , extent of pen excursions of recording polarograph; -O-, experimental line of log $i/(i_d - i)$ vs. $E_{d.e.}$ plot; --, extension of straight line portion of log $i/(i_d - i)$ vs. $E_{d.e.}$ plot; i_d, diffusion current.

The data on the behavior of the neptunium(III) and (IV) in chloride solution are summarized in Table I. The half-wave potential of the couple in chloride solution satisfies the necessary criteria of reversibility: (1) the half-wave potential is independent of the ratio of Np(III) to Np(IV) and (2) analyses of the slopes by plots of $E_{d.e.}$ *versus* log $[i - (i_d)_a]/[i_d)_c - i]$ in all cases gave a straight line with values of 1/slope (column 3, Table I) in good agreement with the value of n = 0.059 for a one electron change.

Polarograms of neptunium(IV) in perchloric acid were not always symmetrical about the half-wave point. In these cases the diffusion current changed gradually with changing potential at potentials more negative than the half-wave potential and only slowly reached a constant value of the diffusion current. Analyses of the waves for these solutions did not give a straight line. This phenomenon is illustrated in Fig. 1. The values of the slopes recorded in Table II were determined on the straight portion of the $E_{d.e.}$ *versus* log $[i - (i_d)_a]/[(i_d)_c - i]$ plots for those solutions having asymmetric polarographic waves. In addition, it was found that, although mixtures of neptunium(III) and neptunium(IV) gave a smooth continuous curve, the half-wave potential varied with the ratio of neptunium(IV) to neptunium(III). Pure neptunium(IV) solutions gave half-wave potentials 30–40 millivolts more negative than the half-wave potential of neptunium(III) with mixtures of the two oxidation states giving half-wave potentials falling between the two extremes. It would therefore appear that the neptunium(III)–neptunium(IV) couple in perchloric acid is not completely reversible at the dropping mercury electrode. As shown by the data in Table III the reversibility of the couple is no greater in 5 molar perchloric acid than in one molar. In view of the behavior in the 5 M acid it appears unlikely that the irreversibility is due to an electrode process involving hydroxy ions,

TABLE I

POLAROGRAPHIC BEHAVIOR OF THE NEPTUNIUM(III)–NEPTUNIUM(IV) COUPLE IN CHLORIDE SOLUTION

Approximate Np(IV)/Np(III) ratio	Average values of $E_{1/2}$ volts	Average values 1/slope	Detns.
	1.0 Molar Hydrochloric Acid		
100/0	−0.104 ± 0.003	0.060 ± 0.002	10
80/20	− .107	....	1
90/10	− .102 ± 0.000	.059	2
70/30	− .1035 ± 0.0005	.0585 ± 0.005	2
50/50	− .099	.058	1
45/55	− .102	....	1
30/70	− .099	....	1
15/85	− .102 ± 0.000	.0615	2
3/97	− .102	....	1
0/100	− .102 ± 0.001	.060	3
	0.10 Molar Hydrochloric Acid–0.90 Molar Sodium Chloride		
100/0	−0.101 ± 0.0003	0.059	3
85/15	− .100	....	1
50/50	− .101	.059	1
30/70	− .100	....	1
0/100	− .101	.060	1

TABLE II

POLAROGRAPHIC BEHAVIOR OF THE NEPTUNIUM(III)–NEPTUNIUM(IV) COUPLE IN MOLAR PERCHLORIC ACID

Approximate Np(IV)/Np(III) ratio	Average values of $E_{1/2}$ volts	Average values of 1/slope	Detns.
100/0	−0.099 ± 0.006	0.066 ± 0.002	9
90/10	− .091	.069	1
70/30	− .088	.067	1
50/50	− .081	.074	1
40/60	− .078	.068	1
35/65	− .076	.068	1
25/75	− .076 ± 0.003	.070 ± 0.000	2
15/85	− .068 ± 0.001	.070 ± 0.002	2
10/90	− .076 ± 0.001	.069 ± 0.000	2
0/100	− .064 ± 0.005	.064 ± 0.001	4

TABLE III

POLAROGRAPHIC BEHAVIOR OF THE NEPTUNIUM(III)–NEPTUNIUM(IV) COUPLE IN 5 MOLAR PERCHLORIC ACID

No.	Micro-amp. current	Microamps. per millimole	$E_{1/2}$	1/Slope	$D_{Np(IV)} \times 10^5$
1	6.743	3.089	−0.044	0.068	0.642
2	6.696	3.067	− .048	.069	.633
3	6.219	2.849	− .052	.072	.546
4	6.541	2.996	− .060		.604

but rather that the hydrated ion of neptunium (IV) is itself not reversibly reduced at the dropping mercury electrode.

A number of other electrode reactions are known where the reduction of the aquo ions is a polarographically irreversible process.[12,13] It is noteworthy that in the presence of chloride ions these reactions are rendered more reversible. Heyrovsky[13] has suggested that the electrode process may involve a chloro complex of the cation.

The irreversibility of the electrode process in perchlorate solutions is also interesting from another point of view. The difficulty in obtaining polarographically reversible waves in the uranium(III)–uranium(IV) system in perchloric acid has been previously discussed[1,14] although under conditions similar to those described in this paper the uranium perchlorate system was reversible. If the electrode process involves a dehydration effect, it would appear reasonable to assume that the slightly smaller radii of the neptunium ions might increase the stability of the aquo complexes just enough to make the couples polarographically reversible in one case and not in the other. In this connection it would be of interest to know the behavior of the plutonium(III)–plutonium(IV) couple at the dropping mercury electrode. Unfortunately such a study is not feasible since the oxidation potential of the couple is too negative.

It should be noted that the polarographic irreversibility of the neptunium couple in perchloric acid does not necessarily imply a thermodynamic irreversibility at an inert electrode. Further studies of this system using as indicator electrode either platinum or mercury are contemplated.

In conclusion two other observations should be noted: (1) In Table IV are values of the diffusion coefficients of neptunium(III) and neptunium(IV) in molar perchloric acid. These diffusion coefficients were calculated from the Ilkovic equation[15] using the values of the diffusion

$$i_d = 605nD^{1/2}Cm^{2/3}t^{1/6} \qquad (2)$$

currents in microamperes per millimole per liter and the capillary constant $m^{2/3}t^{1/6}$, mg.$^{2/3}$ sec.$^{-1/2}$

TABLE IV

DIFFUSION COEFFICIENTS OF NEPTUNIUM(III) AND NEPTUNIUM(IV) IN 1 *M* PERCHLORIC ACID

Neptunium concn., moles/liter	i_d in micro-amps.	$m^{2/3}t^{1/6}$ mg.$^{2/3}$ sec.$^{-1/2}$	$D \times 10^5$	Voltage of measurement
0.00699 *M* Np(IV)	19.47	1.969	0.547	−0.3
	19.53		.551	
	20.08		.582	
		Av.	.560	
0.00709 *M* Np(III)	20.77	1.909	.643	0.0
	20.84		.648	
		Av.	.645	

It was necessary to determine these coefficients in perchloric acid since an accurate value of the diffusion current in hydrochloric acid cannot be obtained due to the interference of the anodic wave of the reaction $2\ Cl^- + 2\ Hg^0 \rightleftarrows Hg_2Cl_2 + 2e^-$ with the reduction wave of the neptunium. The diffusion coefficient $D_{Np^{+3}} = 0.645 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ is very close to the value $D_{U^{+3}} = 0.65 \times 10^{-5}$ cm.^{2} sec.$^{-1}$,[1] found for uranium(III) in tenth molar perchlorate solution. The diffusion coefficient, $D_{Np^{+4}} = 0.56 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ is somewhat smaller than the corresponding value, $D_{U^{+4}} = 0.66 \times 10^{-5}$ cm.^{2} sec.$^{-1}$,[1] found for uranium(IV) in tenth molar perchlorate solution. The lower value of the diffusion coefficient found for neptunium(IV) is probably explained by the slow approach to an equilibrium value of the diffusion current observed in the neptunium(IV) polarograms. If a formal oxidation potential[16] for the reaction

$$Np(III) \rightleftarrows Np(IV) + e^- \qquad (3)$$

is defined by the equation

$$E_f = E^0 - 0.0591 \log \frac{f_{Np^{+4}}}{f_{Np^{+3}}} = -E_{1/2} + E_{cal} + 0.059 \log \left(\frac{D_{Np^{+3}}}{D_{Np^{+4}}}\right)^{1/2} \qquad (4)$$

where E^0 is the thermodynamic oxidation potential, E_{cal} is the standard oxidation potential of the calomel electrode, −0.245 v., $f_{Np^{+4}}$ and $f_{Np^{+3}}$ are the respective activity coefficients of the Np^{+4} and Np^{+3} ions, and $D_{Np^{+3}}$ and $D_{Np^{+4}}$ their respective diffusion coefficients, calculation gives for this formal potential in molar hydrochloric acid a value of −0.142 ± 0.005 volt. This value compares favorably with the value of −0.137 ± 0.005 volt obtained by classical e.m.f. measurements.[6]

Summary

Polarographic measurements have been made of the neptunium(III)–neptunium(IV) couple in perchloric and hydrochloric acids.

---

(12) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 281-285.

(13) J. Heyrovsky, Faraday Soc. Discussion, 1947, 1, p. 212.

(14) W. E. Harris and I. M. Kolthoff, THIS JOURNAL, **67**, 1484 (1948).

(15) Reference 12, p. 38.

(16) Two conventions are used in reporting potentials in this paper. The polarographic convention, corresponding to reduction at the dropping mercury electrode, is used in reporting the half-wave potentials. The thermodynamic convention, corresponding to writing the reaction with the electrons on the right side of the equations, is used in reporting the oxidation potentials.

The couple is polarographically reversible in hydrochloric acid giving an oxidation potential (thermodynamic convention) for the reaction $Np(III) \rightleftarrows Np(IV) + e^- $ of -0.142 ± 0.005 volt. The hydrogen ion independence of the couple between 0.1 and 1.0 molar hydrochloric acid is interpreted as supporting the conclusion that the neptunium(III) and neptunium(IV) ions are Np^{+3} (hydrated) and Np^{+4}(hydrated) in non-complexing acid media.

The neptunium(III)-neptunium(IV) couple is polarographically irreversible in perchloric acid. The difference in polarographic behavior of the tri-positive and tetra-positive ions of neptunium and uranium in perchlorate media is discussed.

CHICAGO 80, ILLINOIS RECEIVED AUGUST 3, 1949

CONTRIBUTION FROM THE SLOAN-KETTERING INSTITUTE FOR CANCER RESEARCH AND THE DIVISION OF CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL OF CANADA[1]]

Studies in Steroid Metabolism. IX. Further Observations on the Infrared Absorption Spectra of Ketosteroids and Steroid Esters

BY R. NORMAN JONES, P. HUMPHRIES AND KONRAD DOBRINER

It has been reported in previous publications[2,3] that the frequency of the carbonyl stretching vibration in the infrared spectra of steroids is characteristic of the type of carbonyl group present and of its location in the molecule. These observations have been applied to the elucidation of the structure of steroids isolated from urine.[4,5] During the past year the spectra of an additional one hundred and eighty steroids have been examined. The results of these measurements, which are reported in this paper, confirm and extend the correlations between spectra and structure previously established.

In Table I are listed the frequencies of the carbonyl stretching maxima of additional compounds of types discussed previously.[2,3] These data are in good agreement with those reported earlier and call for no detailed comment.

TABLE I

CARBON-OXYGEN DOUBLE BOND STRETCHING VIBRATIONS IN STEROIDS, NEW DATA SUPPORTING PREVIOUSLY ASSIGNED FREQUENCIES

(All measurements in solution in carbon disulfide[a]).

In the compounds described here, the configuration of the 17-hydroxyl group is designated β if it is the same as that in testosterone. This is the *inverse* of the convention employed in the previous publications in this series (references 2, 3, 5, 10). The sources of the individual compounds are indicated by superscripts to footnotes at the end of the table. In some cases derivatives (acetates, methyl esters, or epoxides) were prepared at the Sloan-Kettering Institute; this is indicated by an asterisk following the reference to the donor of the original compound.

Non-Carbonyl Compounds.—The following showed no absorption bands between 1650 and 1800 cm.$^{-1}$: estranol-17β,[12] estranediol-3,17β,[12] $\Delta^{5,7,9}$-estratrienol-17β,[12] $\Delta^{1,3,5:10}$-1-methylestratrienediol-3,17β,[3] $\Delta^{1,3,5:10}$-1-methyl-17-(1-methylheptyl)-estratrienol-3,[3] Δ^{5}-androstenol-3β,[23] Δ^{16}-androstenol-3α,[19] Δ^{16}-etiocholenol-3α,[19] Δ^{16}-etiocholenol-3β,[19] uranediol-3β,11,[12,17] Δ^{5}-cholestene,[7] $\Delta^{2,4}$-cholestadiene,[5] ergostane,[7] $\Delta^{8:14}$-ergostene,[7] Δ^{22}-ergostene,[1] lumisterol,[7] vitamin D_2,[11] Δ^{7}-5-isoergostenol-3α,[1] Δ^{22}-5-isoergostene,[1] $\Delta^{7,22}$-5-isoergostadiene.[1]

Monocarbonyl Compounds

I. **3-Ketones.** (1716–1719 cm.$^{-1}$).—Allopregnanone-3,[21] allopregnanediol-17α,20-one-3,[21] uranol-11-one-3,[12] tigogenone,[18] $\Delta^{8:14}$-ergostenone-3,[1] Δ^{22}-ergostenone-3.[1]

II. **7-Ketones** (1710–1713 cm.$^{-1}$).—Pregnanone-7,[21] cholestanone-7.[7]

III. **17-Ketones** (1742–1745 cm.$^{-1}$).—3-Methoxy-(*dl*)-isoequilenin,[10] equilenone-17,[10] isoequilenone-17,[10,26] $\Delta^{1,3,5:10}$-3-methoxyestratrienone-17,[3] $\Delta^{1,3,5:10}$-1-methylestratrienol-3-one-17,[3] $\Delta^{1,3,5:10}$-3-methoxy 1-methylestratrienone-17,[3] 9,11-epoxyetiocholanol-3α-one-17.[22*]

IV. **20-Ketones** (1706–1710 cm.$^{-1}$).—$\Delta^{1,3,5:10}$-3-Methoxy-17-acetyl-estratriene,[3] pregnanol-3β-one-20,[12] $\Delta^{(2 \text{ or } 3),11}$-pregnadienone-20,[21] allopregnanone-20.[21]

V. **3-Acyl Esters** (1735–1739 cm.$^{-1}$).—$\Delta^{1,3,5:10}$-17-Ethynylestratrienediol-3,17-acetate-3,[9] androstanol-3α-acetate,[23*] androstanol-3β-acetate,[23*] Δ^{5}-androstenol-3β-acetate,[23*] Δ^{5}-17-ethynylandrostenediol-3β,17-acetate-3,[9] Δ^{16}-androstenol-3α-acetate,[19*] Δ^{16}-etiocholenol-3α-acetate,[19*] Δ^{16}-etiocholenol-3β-acetate,[19*] pregnanol-3β-acetate,[12*] Δ^{23}-3α-acetoxy-24,24′-diphenylcholene,[5] ergostanol-3β acetate,[7] lumistanol-3β-acetate,[7] lumisteryl acetate.[7]

VI. **17-Acyl Esters** (1737–1742 cm.$^{-1}$).—$\Delta^{1,3,5:10}$-1-Methylestratrienediol-3,17β-acetate-17,[3] androstanol-17β-acetate,[17*,23*] $\Delta^{3,5}$-androstadienol-17β-acetate,[27] etiocholanediol-3α,17α-acetate-17.[5,14]

VII. **Alkyl Esters of Steroid Carboxylic Acids** (1737–1742 cm.$^{-1}$).—$\Delta^{1,3,5:10}$-3-Methoxy-17-carbomethoxy-estratriene,[3] etioallocholanic acid M.E.,[15] 3α-hydroxyetiocholanic acid M.E.,[13*] 3β-hydroxyetioallocholanic acid M.E.,[15] Δ^{5}-3β-hydroxyetiocholenic acid M.E.,[2,15] Δ^{11}-3α-hydroxyetiocholenic acid M.E.,[13*] 3α-hydroxybisnorcholanic acid M.E.,[13] Δ^{11}-3α-hydroxybisnorcholenic acid M.E.,[13] Δ^{11}-3α-hydroxynorcholenic acid M.E.,[13,24] cholanic acid M.E.,[24] 3α,12α-dihydroxycholanic acid E.E.,[24] Δ^{5}-3β-hydroxycholenic acid M.E.,[5] Δ^{11}-3α,9α-epoxycholenic acid M.E.,[13,24]

VIII. **3-Aryl Esters** (1719–1724 cm.$^{-1}$).—Δ^{5}-Cholestenol-3β-benzoate,[4] Δ^{5}-cholestenediol-3β,4β-benzoate-3,[4,16] 5α,6α-dichlorocholestanol-3β-benzoate,[1] 5α,6β-dichlorocholestanol-3β-benzoate.[1]

IX. **$\Delta^{3,5}$-Diene-ol-3 Acyl Ester** (1754–1758 cm.$^{-1}$).—$\Delta^{3,5}$-Cholestadienol-3β-acetate.[24]

Dicarbonyl Compounds

X. **Δ^{4}-3,11-Diketones** (1674–1677:1710 cm.$^{-1}$).—Δ^{4}-Urenedione-3,11.[12]

XI. **3,17-Diketones** (1719:1742–1745 cm.$^{-1}$).—Estranedione-3,17.[12]

---

[1] Published as Contribution No. 2066 from The Laboratories of The National Research Council of Canada.

[2] Jones, Williams, Whalen and Dobriner, THIS JOURNAL, **70**, 2024 (1948).

[3] Jones, Humphries and Dobriner, *ibid.*, **71**, 241 (1949).

[4] Dobriner, *Acta de L'Union Internationale Contre le Cancer*, **6**, 315 (1948).

[5] Jones and Dobriner, *Vitamins and Hormones*, **7**, 294 (1949).