2,4-dinitrophenylhydrazone of the ethyl ester (from B) melted at 171.5–172°. *Anal.* Calcd. for $C_{13}H_{16}O_6N_4$: C, 48.2; H, 4.97; N, 17.3. Found: C, 48.0; H, 4.80; N, 17.0). Some first order rates of decarboxylation, determined manometrically near *p*H 5 in the presence and absence of metal ions, are shown in the table below.

	Monoester B		Diacid C	
Metal ion	Concn. of metal ion, m./l.	k, min.$^{-1}$	Concn. of metal ion, m./l.	k, min.$^{-1}$
None		0.075		0.0032
Cu^{++}			0.001	.14
	0.01	.069	.01	*ca.* 1.6
Al^{+++}	.01	.070	.001	0.13
Ni^{++}	.01	.075	.01	.022
Mn^{++}	.01	.066	.01	.0046

Thus metal salts strongly catalyze the decarboxylation of the diacid, C, but do not affect the rate of decarboxylation of the monoester, B. Since no enol form of α,α-dimethyloxaloacetic acid is possible, it is clear that the *keto* acid (like dimethylacetoacetic acid[6]) undergoes decarboxylation. Further, these experiments show that the metal ion catalysis of the decarboxylation of dimethyloxaloacetic acid requires the formation of a complex between the metal ion and the carboxyl group gamma to the one lost; presumably the metal ion is also coördinated with the carbonyl oxygen atom. By analogy, these conclusions also apply to the decarboxylation of oxaloacetic acid itself.

The investigation of these reactions is continuing.

[6] K. Pedersen, THIS JOURNAL, **51**, 2098 (1929); **58**, 240 (1936).

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DEGRADATION PRODUCTS OF PSEUDOHECOGENIN

Sir:

It has been shown that "*allo*-pregnan-3,12,20-trione" from pseudohecogenin does not agree in properties with *allo*-pregnan-3,12,20-trione prepared from 12(α)-acetoxyprogesterone.[1] We have now reinvestigated "16-*allo*-pregnen-3,12,20-trione" from pseudohecogenin. From its method of synthesis and analysis, it was assumed to be an α,β-unsaturated triketone containing a molecule of water of crystallization.[2] However, we find that this material does not show an absorption maximum in the ultraviolet typical for α,β-unsaturated ketones, that it is unchanged by conditions of hydrogenation with palladium catalyst and that *it is actually identical with the compound designated as "allo-pregnan-3,12,20-trione,"* also assumed to contain a molecule of water of crystallization. It is not changed by hot acetic anhydride and pyridine, which suggests that the "molecule of water" might be a tertiary hydroxyl group at C-17. Mild chromic acid oxidation gives impure starting material in agreement with the results of Reichstein and Gatzi[3] for this ketol system. It is noteworthy that mild oxidation of the isomeric D-homo derivative is reported to give an acidic product.[4]

Hydroxyl groups in steroids have been associated with infrared absorption maxima at 3570 to 3620 cm.$^{-1}$ along with a carbonyl harmonic band at 3300 to 3475 cm.$^{-1}$ if a ketone group is also present.[5] It was hoped that such data (Fig. 1) would support the assignment of a hydroxyl group to this substance; however, the results are inconclusive. A scarcity of material has curtailed further work.

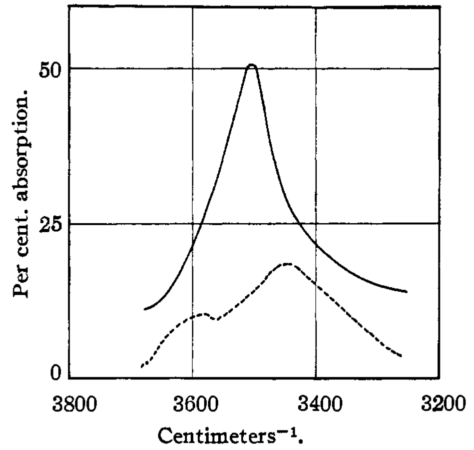

Fig. 1.—Infrared absorption spectra in carbon disulfide solution: ...., 17(α)-hydroxyprogesterone; ——, degradation product from pseudohecogenin.

Although it is not possible to state definitely the structure for this product, it becomes clear that the non-identity of it with *allo*-pregnan-3,12,20-trione is not necessarily due to an incorrect assignment of the C-12 oxygen in hecogenin and botogenin.[6]

We thank Parke, Davis and Company for their help.

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[1] Wagner, Moore and Forker, THIS JOURNAL, **71**, 3856 (1949).

[2] Marker, Wagner and co-workers, *ibid.*, **69**, 2167 (1947).

[3] Reichstein and Gatzi, *Helv. Chim. Acta*, **21**, 1497 (1938).

[4] Ruzicka, Gatzi and Reichstein, *ibid.*, **22**, 637 (1939).

[5] Jones, *et al.*, THIS JOURNAL, **70**, 2024 (1948).

[6] At the time that this communication was in preparation, Marker, *ibid.*, **71**, 3856 (1949), presented further evidence that the degradation of pseudobotogenin diacetate can lead to a 17-hydroxy steroid.