filtrate was evaporated to a sirup which, on being triturated with 95% ethanol, deposited white crystals. These were filtered off, washed with cold 95% ethanol, and dried to yield 1.77 g. (18.2%) of 3,3-diphenylphthalide, m.p. 117.5–118.5°. Identification was made by a mixed melting point with an authentic specimen, and by comparison of the infrared absorption spectrum with that of an authentic specimen.

Run III.—A solution of 12.3 g. (0.045 mole) of trityl methyl ether and 0.091 mole of *n*-butyllithium in 100 ml. of diethyl ether was distilled under nitrogen until most of the solvent had been removed. A red color developed during this time. Ninety ml. of toluene was added to the residue, and the resulting mixture was refluxed for 24 hours and then hydrolyzed with iced, dilute sulfuric acid. The organic layer was separated and evaporated to yield a dark brown sirup. This material, and all fractions later obtained from it, were exceptionally difficult to purify. Some tarry crystals were obtained by refluxing the sirup with benzene and cooling; an additional crop of crystals was obtained by evaporating the benzene filtrate and triturating the residue with a mixture of acetone and carbon tetrachloride. The combined crystals (3.1 g., m.p. 123–131°) were dissolved in benzene and chromatographed on alumina, using benzene as an eluent. Most of the fractions so obtained were sirups or tars. Several semi-crystalline fractions were combined and recrystallized from a mixture of benzene and 95% ethanol to yield 1.91 g. (17.5% crude yield) of yellow solid, m.p. 128–139°. The product was dissolved in methanol, treated with Norit A, and filtered. The filtrate was evaporated to yield a yellow solid, which was dissolved in benzene and chromatographed on alumina, using petroleum ether (b.p. 60–70°) as an eluent. The crystalline fractions so obtained were extracted with a small volume of boiling methanol. The undissolved material weighed 0.40 g. (3.8%) and melted at 145–147°. A mixed melting point with an authentic specimen of 9-phenylfluorene was undepressed.

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CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY
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Low Pressure Catalytic Hydrogenation of Nitroparaffins

BY DON C. IFFLAND AND FRANK A. CASSIS, JR.

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Although low pressure catalytic hydrogenation of aromatic nitro-compounds is routine, few applications to nitroparaffins have been reported. The use of Raney nickel and hydrogen as low as six atmospheres pressure is reported to reduce nitroparaffins to amines[1]; however, the use of platinum and hydrogen is referred to as "mainly for aromatic nitro compounds."[2] Hydrogenation at two to three atmospheres pressure with palladium in the presence of oxalic acid is stated to yield hydroxylamine derivatives from nitroparaffins.[3] Recently a study of the use of nitro compounds (including nitroethane) as hydrogen acceptors in the presence of platinum catalyst has been described[4]; however, neither the isolation of the hydrogenation products nor yields were reported.

In view of this, the impression is frequently obtained that catalyzed low pressure hydrogenation of nitroparaffins to amines is unsatisfactory. We have found that platinum-catalyzed low pressure (two to three atmospheres) hydrogenation of simple nitroparaffins in 95% ethanol produces aliphatic amines in good yield and is a convenient laboratory operation. The per cent. conversion to amine and melting point for phenylthiourea derivatives of the amines isolated are summarized in Table I.

TABLE I

CONVERSION OF RNO_2 TO RNH_2 BY LOW PRESSURE CATALYTIC HYDROGENATION

R	Conversion to RNH_2,[a] %	Amine isolated, %	M.p. C_6H_5NCS derivatives, °C.
CH_3–	48	..	111–112[b]
C_2H_5–	79	..	102–103[b]
n-C_3H_7–	83	69	64–65[b]
i-C_3H_7–	88	64	100–101[c]
n-C_4H_9–	91	76	62–63

[a] These values are based on the titration of an aliquot with standard acid; see Experimental. [b] M. L. Willard and M. Z. Jones, THIS JOURNAL, **62**, 2876 (1940), report the following values: methyl, 112–113°; ethyl, 101–102°; *n*-propyl, 64°; *n*-butyl, 63°. [c] O. C. Dermer and J. W. Hutcheson, *Proc. Oklahoma Acad. Sci.*, **23**, 60 (1943), report 102°.

The addition of a trace of hydrochloric acid in the hydrogenation solvent did not affect the conversion to amine or the time required for the reduction. The introduction of as little as 1% by volume of acetic acid in the solvent increased the time required for the reduction by as much as 140–150% but did not change the conversion. With higher concentrations of acetic acid the effect of increasing the time of hydrogenation was more pronounced. This effect of acetic acid in the hydrogenation of nitroparaffins is consistent with the observations of Line, Wyatt and Smith[4a] in their hydrogenation of nitroethane.

Experimental

The following procedure was used for reducing all nitroparaffins indicated in Table I. Two-tenths mole of freshly distilled 2-nitropropane was dissolved in 100 ml. of 95% ethyl alcohol containing 0.1 g. of platinum oxide catalyst and shaken for nine hours at room temperature with hydrogen at two to three atmospheres pressure in a Parr low pressure hydrogenation apparatus. By this time the theoretical amount of hydrogen had been absorbed to reduce the nitro group to an amine. The hydrogenation was slightly exothermic. The reduction mixture was filtered, diluted with 100 ml. of water, acidified with about 0.25 equivalent of 85% phosphoric acid and distilled until the distillate was free of alcohol. The aqueous solution remaining was made alkaline with 25% aqueous sodium hydroxide and distilled through a 15-cm. Vigreux column until about 100 ml. of distillate was collected in a receiver containing 100 ml. of water. The receiver was cooled in an ice–water-bath. The distillate was diluted to exactly 250 ml.; titration of the amine in a 5.00-ml. aliquot required 35.10 ml. of 0.100 *N* hydrochloric acid using methyl red indicator. The yield of amine was 88%.[5]

A 200-ml. aliquot of the aqueous amine solution was saturated with potassium carbonate keeping the temperature at 0 to 5° and the amine which separated was carefully decanted and dried with sodium hydroxide pellets. Six grams of isopropylamine was obtained which distilled at 32–36°. The isolated amine yielded a substituted phenyl-

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(1) K. Johnson and E. F. Degering, THIS JOURNAL, **61**, 3194 (1939).

(2) H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 389 (1943).

(3) E. Schmidt, A. Ascherl and L. Mayer, *Ber.*, **58**, 2430 (1925).

(4) (a) L. E. Line, B. Wyatt and H. A. Smith, THIS JOURNAL, **74**, 1808 (1952); (b) H. W. Smith and W. C. Bedoit, *J. Phys. Colloid Chem.*, **55**, 1085 (1951).

(5) The validity of the titration was demonstrated by a blank measurement on a solution of 100 ml. of alcohol containing 0.0750 mole of pure isopropylamine. By the above procedure the 5.00-ml. aliquot required 14.75 ml. of 0.100 *N* hydrochloric acid indicating a recovery of 0.0737 mole or 98% of the original amine.

thiourea[6] which melted at 100–101° and gave no depression when mixed with authentic phenylisopropylthiourea.

Repetition of this reduction using 0.2 mole of 2-nitropropane and differing only by the addition of 0.2 ml. of 36% hydrochloric acid resulted in an 87% conversion to amine in nine hours. Modification of the original procedure with the addition of 1.0 ml. of glacial acetic acid increased the time required to 13 hr. and the conversion was 89%. When 10.0 ml. of glacial acetic acid was added only 35% of the required hydrogen was absorbed in 40 hr. and the experiment was discontinued.

The reduction of nitromethane proceeded more slowly than the other nitro compounds and when 0.2 g. of catalyst was used in the above procedure 38 hr. were necessary for absorption of 91% of the required amount of hydrogen.

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(6) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 193.

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Components of Podophyllin. X.[1] Relation of α-Peltatin to β-Peltatin

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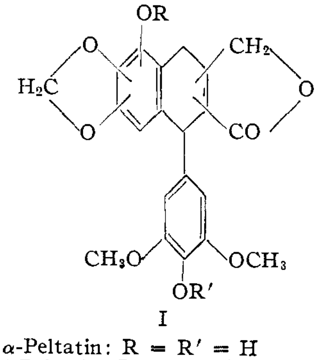
In a previous communication,[2] the empirical formula $C_{22}H_{22}O_8$ was proposed for α-peltatin, which would make it an isomer of β-peltatin and podophyllotoxin. However, it was pointed out that the analyses of the compound and of some of its derivatives were equally consistent with an alternate formula, $C_{21}H_{20}O_8$. A renewed investigation of the methyl ethers derived from the peltatins has now demonstrated unequivocally that the latter formula is actually correct and that α-peltatin itself is 4′-demethyl-β-peltatin, as indicated in formula I.



I

α-Peltatin: R = R′ = H
β-Peltatin: R = H, R′ = CH_3

In the original experiments,[2] treatment of α- and of β-peltatin with diazomethane gave levorotatory methyl ethers, m.p. 124–126°, $[\alpha]_{\mathrm{D}}$ −116° or −118°, which were believed not to be identical since mixtures of the two gave a melting point depression of a few tenths of a degree. Similarly, a slight melting point depression was noticed with mixtures of α-peltatin-B dimethyl ether (m.p. 180–183°, $[\alpha]_{\mathrm{D}}$ +10.0°) and β-peltatin-B methyl ether (m.p. 183–184°, $[\alpha]_{\mathrm{D}}$ +9.4°), prepared with dimethyl sulfate and alkali.

When the methylation with diazomethane was now repeated, products were obtained which after several recrystallizations melted at 162.6–163.6° and had $[\alpha]_{\mathrm{D}}$ −120°. Samples from α-peltatin and from β-peltatin showed no mixed melting point depression and, furthermore, had indistinguishable infrared absorption spectra (Fig. 1). This established their identity. It has not been possible to prepare again the material, m.p. 124–126°. At the beginning of the present reinvestigation, previously obtained samples, 3 to 4 years old, still showed the original melting points; recrystallization from ethanol, however, yielded material melting at 162.6–163.6°. It seems that the two substances are polymorphic modifications. Similar polymorphism had already been encountered in the case of podophyllotoxin.[3]

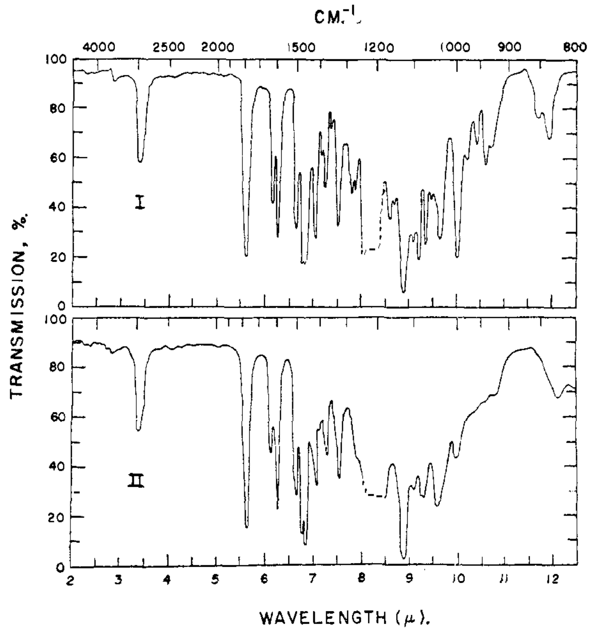


Fig. 1.—Infrared spectra in chloroform: I, β-peltatin-A methyl ether (α-peltatin-A dimethyl ether); II, β-peltatin-B methyl ether (α-peltatin-B dimethyl ether).

Methylation with dimethyl sulfate gave material, m.p. 183.8–184.6°, $[\alpha]_{\mathrm{D}}$ +11°. Here again, the identity of the products obtained from α- and β-peltatin was proven by the mixed melting point and by the infrared spectra (Fig. 1). Since the presence of two phenolic hydroxyl groups in α-peltatin renders the compound sensitive to autoxidation in alkaline solution, the previously used alkylation procedure[2] had to be modified in order to obtain a pure product.

The identity of the methyl ethers of α- and β-peltatin in both the "A" and "B" series[2] demonstrates that β-peltatin is a monomethyl-α-peltatin. This, together with the results of the oxidation of the ethyl ethers[2] proves that α-peltatin is 4′-demethyl-β-peltatin (I, R = R′ = H).

The infrared spectra of the methyl ethers (Fig. 1) substantiate the previous assumption[2] that a lactone ring is present in the peltatins and indicate further that it is a γ-lactone ring. The carbonyl band lies in the range commonly associated with

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(1) Paper IX: A. W. Schrecker and J. L. Hartwell, THIS JOURNAL, 74, 5676 (1952).

(2) J. L. Hartwell and W. E. Detty, *ibid.*, 72, 246 (1950).

(3) J. L. Hartwell and A. W. Schrecker, *ibid.*, 73, 2909 (1951).