Communications TO THE EDITOR

Occurrence of 1-Nitro-2-phenylethane in *Ocotea pretiosa* and *Aniba canelilla*[1]

Sir:

The present communication is concerned with the isolation and identification of the compound responsible for the cinnamon odor of the Brazilian trees *Ocotea pretiosa* (Nees) Mez[2] and *Aniba canelilla* (H.B.K.) Mez[3] (family *Lauraceae*). In both cases the light petroleum ether soluble portion of the benzene extract of the plant material, submitted to chromatography on alumina (activity I) and eluted with benzene, furnished at first fractions rich in methyleugenol and later on fractions with a strong cinnamon-like odor. These, or (in an alternative procedure) the essential oil obtained from vapor distillation of the plant material, were dissolved in light petroleum ether. The solution was extracted exhaustively with 3% aqueous sodium hydroxide. Continuous percolation of chloroform through the alkaline layer removed an oil which was rectified by vacuum distillation.

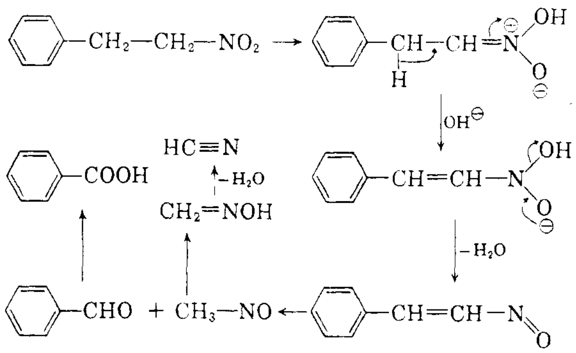
Ocotea pretiosa wood (yield 0.1%) and bark, as well as *Aniba canelilla* wood (yield 0.7%) and bark (yield 0.6%) furnished the same compound when processed in this way; a colorless oil, d^{25}_{25} 1.122, n^{25}_{D} 1.527, b.p. 130–135° (14 mm.). Calcd. for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.27; O, 21.17. Found: C, 64.04; H, 6.22; N, 8.88; O, 20.69. C—CH_3, N—CH_3, and O—CH_3 groups were absent. The infrared spectrum showed two strong peaks at 6.45 and 7.25μ (primary nitro group[4]), two peaks of medium intensity at 13.30 and 14.30μ (monosubstituted benzene nucleus), and feeble absorption maxima at 8.50, 9.25, 9.72, 11.60μ *inter al.*

Oxidation with hot alkaline potassium permanganate afforded benzoic acid in 60% yield. Hydrogenation at atmospheric pressure, over 10% palladium on charcoal catalyst, resulted in the uptake of 3 mol. of hydrogen and led to β-phenylethylamine (infrared bands at 3.1, 6.28, 13.33, 14.30μ); m.p. of picrate, undepressed by admixture of an authentic specimen, 170–171° (lit. 171°[5]).

Alkaline degradation (30 min. boiling with 3% sodium hydroxide solution or 60 min. boiling with N alcoholic potassium hydroxide) yielded benzoic acid (about 15% of the quantity theoretically available from $C_8H_9NO_2$) and hydrocyanic acid (about 20% of the quantity theoretically available from the N of $C_8H_9NO_2$).

The evidence allows the substance to be formulated as 1-nitro-2-phenylethane. This compound is known by synthesis[6] and direct comparison of the natural isolate with a synthetic specimen by physical, organoleptic, and spectral criteria proved their identity. Surprisingly, the authors of the synthesis[6] do not mention the quite obvious cinnamon odor and flavor of the compound.

The products of alkaline degradation, subsequently obtained also from synthetic 1-nitro-2-phenylethane, were at first difficult to explain. However, their formation may be rationalized by alkali catalyzed transformation of the nitro compound into ω-nitrosostyrene[7] which by reverse aldol condensation would give benzaldehyde (and subsequently benzoic acid) and nitrosomethane. It is known that the latter isomerizes readily into formaldoxime[8] and this we have shown to decompose into hydrocyanic acid under the conditions of our alkaline degradation.



1-Nitro-2-phenylethane is the first organic compound to be isolated from plants which possesses as the sole function a nitro group. Very few other natural nitro derivatives have been described. In higher plants apparently only β-nitropropionic acid (as the glucoside)[9] and the aristolochia acids I[10] and II[11] were found.

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(1) The authors wish to thank Dr. B. Gilbert, Dr. Roderick A. Barnes, and Dr. Walter B. Mors for useful discussion and the Conselho Nacional de Pesquisas, Brazil, for financial aid.

(2) W. B. Mors, M. Taveira Magalhães, and O. R. Gottlieb, *Perf. Essent. Oil Record,* **50,** 26 (1959).

(3) See E. Gildemeister and F. Hoffmann, *The Volatile Oils,* 2nd ed., Vol. II, p. 500, John Wiley & Sons, New York (1916).

(4) N. Kornblum, H. E. Ungnade, and R. A. Smiley, *J. Org. Chem.,* **21,** 377 (1956).

(5) H. Decker and W. Kropp, *Ber.* **42,** 2078 (1909).

(6) W. Borsche and F. Sinn, *Ann.,* **553,** 260 (1942).

(7) This transformation is essentially an intramolecular oxidation-reduction involving the nitro group and the possibility for an intramolecular equivalent cannot be eliminated by the present data.

(8) K. H. Mueller, *J. Am. Chem. Soc.,* **77,** 3459 (1955).

(9) C. L. Carter and W. J. McChesney, *Nature* **164,** 576 (1949).

(10) M. Pailer, L. Belohlav, and E. Simonitsch, *Monatsh* **87,** 249 (1956).

Full details of the work on the two species mentioned will be reported later.

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(11) M. Pailer and A. Schleppnik, *Monatsh.*, **88**, 367 (1957).

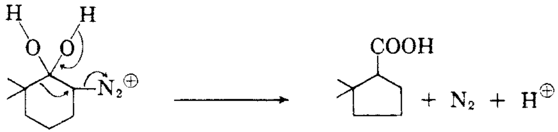
Deamination of α-Aminoketones

Sir:

Observation that nitrous acid deamination of a primary aminoketone derived from the alkaloid lycoctonine[1] gave an acid led us to consider the possibility that aliphatic α-aminoketones would give acids by Favorskii-type rearrangement on deamination.

We have now shown that 2-aminocyclohexanone hydrochloride[2] (prepared by stannous chloride reduction of 2-oximinocyclohexanone) gives up to 57% yields of carboxylic acid when treated with aqueous nitrous acid. This proved to be mainly cyclopentanecarboxylic acid (amide m.p. 179°; anilide, m.p. 165°, showing no melting point depression with authentic derivatives). Similarly, 2-amino-6,6-dimethylcyclohexanone (hydrochloride m.p. 182°, *Anal.*, Calcd. for $C_8H_{16}ONCl$: C, 54.08; H, 9.07; N, 7.82. Found: C, 53.47; H, 9.00; N, 7.92) gave a 25% yield of acid. This was mainly a saturated monocyclic acid $C_8H_{14}O_2$ (anilide, m.p. 125°, *Anal.*, Calcd. for $C_{14}H_{19}ON$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.49; H, 8.57; N, 6.44) which on mechanistic grounds and by analogy to the product from 2-aminocyclohexanone should be 2,2-dimethylcyclopentanecarboxylic acid (I). This assignment was supported by its infrared spectrum, which had the pair of peaks characteristic of a *gem*-dimethyl group (ν_{max} 1370 and 1385 cm.$^{-1}$, liquid film), and by the NMR spectrum of its methyl ester, which had two unsplit methyl signals at 186 and 199 c.p.s. (60 Mc, water reference). In addition, the spectrum contained signals due to a single hydrogen with a large chemical shift flanked by one methylene (triplet with J = 6.5 c.p.s. centered about +118 c.p.s.).

We suggest that the positive charge on the amine salt and diazonium ion aid hydration of the carbonyl, and that I is formed by the following mechanism:



I

Close analogs are found in the deamination of cyclic α-aminoalcohols[3] and the silver ion initiated rearrangement of α-bromoketones.[4]

Attempts to prepare I by vigorous alkaline treatment of 2-chloro-6,6-dimethylcyclohexanone (m.p. 62°, ν_{max} 1720 cm.$^{-1}$ as Nujol mull. *Anal.*, Calcd. for $C_6H_{13}OCl$: C, 59.81; H, 8.15; Cl, 22.07. Found: C, 59.65; H, 8.09; Cl, 22.33) and by the action of silver nitrate in aqueous alcohol[4] on 2-bromo-6,6-dimethylcyclohexanone (m.p. 58°. *Anal.*, Calcd. for $C_6H_{13}OCl$: C, 46.84; H, 6.38. Found: C, 47.05; H, 6.26) failed to yield more than traces of carboxylic acid. Hence the above deamination may prove a useful alternative to the Favorskii reaction when one carbon alpha to the carbonyl is quaternary.[5] The neutral products of the reaction are under investigation.

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(1) Unpublished work by O.E.E.

(2) H. E. Baumgarten and F. A. Bower, *J. Am. Chem. Soc.*, **76**, 4561 (1954).

(3) G. E. McCasland, *J. Am. Chem. Soc.*, **73**, 2293 (1951); D. Y. Curtin and S. Schmukler, *J. Am. Chem. Soc.*, **77**, 1105 (1955).

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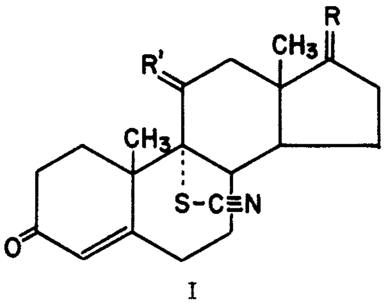
(5) R. B. Loftfield, *J. Am. Chem. Soc.*, **73**, 4707 (1951).

Synthesis of 9α- and 11β-Thiocyano Steroid Analogs

Sir:

With the intention of finding antimetabolites of steroidal hormones, some thiocyano derivatives of corticoids and androgens (Ia–f and IIIa–b) have been synthesized.



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(a) R = α-OH, -CO—CH_2OH
R′ = β-OH, -H
(b) R = α-OH, -CO—CH_2OAc
R′ = β-OH, -H
(c) R = =O
R′ = β-OH, -H
(d) R = α-OH, -CO—CH_2OH
R′ = =O
(e) R = α-OH, -CO—CH_2OAc
R′ = =O
(f) R = =O
R′ = =O