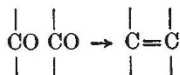


Herzig and Pollak³ prepared a monoxime of O-trimethylbrazilone, m.p. 203–205° (decomp.). Repetition of this preparation has now yielded two forms of the monoxime; one (from aqueous alcohol) consisted of fine needles, m.p. 197° (decomp.) (found: C, 63.9; H, 5.4; N, 3.9 per cent) and the other (from alcohol) of small prisms m.p. 208–210° (decomp.) (found: C, 64.3; H, 5.4; N, 3.8; calc. for C₁₉H₁₉O₆N: C, 63.9; H, 5.3; N, 3.9 per cent). A mixture of the two forms decomposed at an intermediate temperature, and they appear to be polymorphic because crystallization of the form with melting point 208–210° under appropriate conditions yields the needle form, which is slowly reconverted into the substance with the higher melting point when it is left to stand in the mother liquor.

The explanation of the change



in the course of the reaction between O-trimethylbrazilone and phenylhydrazine must clearly involve the propinquity of the carbonyls in the large ring structure; but the postulation of a radical change in the bonds contained in these groups is now excluded.

R. E. RICHARDS

Physical Chemistry Laboratory,

M. L. TOMLINSON

Dyson Perrins Laboratory,
Oxford.
June 8.

¹ Gilbody and Perkin, *J. Chem. Soc.*, **81**, 1040 (1902).

² Perkin and Robinson, *J. Chem. Soc.*, **93**, 498 (1908). Perkin, Ray and Robinson, *J. Chem. Soc.*, 2096 (1927); 1054 (1928).

³ Herzig and Pollak, *Ber.*, **36**, 398 (1903).

Structure of α -Fagarine

THE more significant experimental facts for basing the structure of α -fagarine, one of the alkaloids isolated from *Fagara coco*¹, were the presence of one methylimino group, two methoxyls and one dioxymethylene group, and the formation of *m*-methoxybenzaldehyde by oxidation². α -Fagarine behaves as a tertiary base, since it does not react with nitrous acid and also lacks rotatory power.

A tertiary base, with a methylimino group and giving *m*-methoxybenzaldehyde by oxidation, may have a structure: $R - \text{N} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{OCH}_3$ (*m*), as

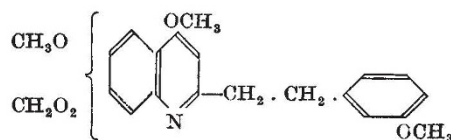


oxidation experiments with similar simpler bases have shown³. A substance of this type might be expected to be degraded by the action of tetranitromethane as similar bases are⁴, and also by hydrogenolysis under the action of palladium-charcoal.

Fagarine was found to be resistant to both types of degradation. We believe, then, that the methylimino group, that was determined in two laboratories (in our laboratory, Slotta and Haberland's⁵ method was employed) and isolated as methylamine when α -fagarine is heated with soda-lime, is an artefact. The methylimino group determined could be a resistant methoxyl that is only split off at higher temperatures than usual, or that transposes to a

methylimino group under the action of the reagents. The methylamine isolated would also result from a molecular transposition.

This type of reaction could be expected from a γ -methoxyquinoline, and accordingly the following structural formula for α -fagarine is now proposed:



similar to the structures of cusparine, galipine and galipoline, all alkaloids from angostura bark, a plant belonging to the family Rutaceae, as is the case with *Fagara coco* (Gill.) Engl., from which α -fagarine was isolated.

Thus the first formula proposed, C₁₉H₂₃NO₄, should be changed to C₂₁H₂₁NO₅. The carbon and hydrogen determinations of the free base given in our paper² agree well with the new formula. Fagarine salts gave lower values for carbon than those expected.

We have carried out a series of determinations of the halogens of the salts and the methiodide of α -fagarine, which differentiate clearly between the formulae C₁₉H₂₃NO₅ and C₂₁H₂₁NO₅, and obtained figures that agree with the last one. (Hydrochloride: calc., Cl, 8.91; found, 8.13. Hydrobromide: calc., Br, 17.85; found, 18.28. Hydroiodide: calc., I, 25.67; found, 25.64. Methiodide: calc., I, 24.97; found, 24.47).

When α -fagarine is treated with dilute nitric acid, a nitro-derivative is obtained which gives a crystalline nitrate melting at 254–55° and of formula C₂₁H₂₀NO₅·NO₂·NO₃H (calc.: C, 53.05; H, 4.21; N, 8.84; found: C, 52.85; H, 5.10; N, 8.90). This nitro-derivative gives a picrate melting at 255–57°, C₂₁H₂₀NO₅·NO₂·C₆H₃N₃O₇ (calc.: C, 50.54; H, 3.59; found: C, 50.53; H, 3.96).

The absorption spectrum of α -fagarine, for which we are indebted to Dr. H. Puente, also supports the quinoline structure. It presents an absorption maximum at 285 m μ and is very similar to the absorption spectrum of quinoline, with a maximum about 280 m μ , and to that of 4-quinolymethyl ether, with a maximum about 280–285 m μ , as determined by Ewing and Steck⁶. An N-methyl quinolone structure would explain the methylimino determination and the isolation of methylamine, but leaves unexplained the formation of a methiodide and the similarity of the absorption spectrum of the base to those of quinoline and its derivatives.

V. DEULOFEU

R. LABRIOLA

B. BERINZAGHI

Laboratorio de Química Orgánica,

Facultad de Ciencias Exactas,

Físicas y Naturales,

Buenos Aires.

May 24.

¹ Deulofeu, V., Labriola, R., and De Langhe, J., *J. Amer. Chem. Soc.* **64**, 2326 (1942).

² Deulofeu, V., Labriola, R., and Berinzaghi, B., *J. Org. Chem.*, **12**, 217 (1947).

³ Labriola, R., Ishii, M., and Mariani, I., *An. Asoc. Quim. Arg.*, **33**, 156 (1945).

⁴ Labriola, R., Dorronsoro, I., and Verruno, O., paper read before the Fourth South American Chemical Congress, Santiago, Chile, March 1948.

⁵ Slotta, K. H., and Haberland, G., *Ber.*, **65**, 127 (1932).

⁶ Ewing, G. W., and Steck, E. A., *J. Amer. Chem. Soc.*, **68**, 2181 (1946).