by the color of the ferric chloride test, and by the abnormally low frequency of the carbonyl absorption in the infrared absorption spectrum (1740 cm.$^{-1}$ in chloroform) as contrasted to the characteristic γ-lactone carbonyl absorption (1765 cm.$^{-1}$ in chloroform) observed for the methyl ether.[2]

Synthesis was effected through the pyridine-piperidine catalysed condensation of 3-methoxyphthalic anhydride with malonic acid, hydrolysis of the resulting 3-methylene-7-methoxyphthalide to 2-acetyl-6-methoxybenzoic acid, and reduction of this intermediate to 7-methoxy-3-methylphthalide by sodium amalgam. This product, which was obtained in low yield, is identical with that derived from terramycin as indicated by melting points, mixed melting point, and the identity of their infrared absorption spectra. Several alternative synthetic routes yielded 4-hydroxy-3-methylphthalide rather than the desired product.

(2) R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

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RECEIVED SEPTEMBER 7, 1951

DEGRADATION OF SOLASODINE

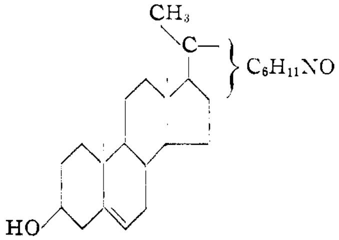
Sir:

In view of the present acute interest in new sources for steroids we wish to report the degradation of solasodine to a pregnane derivative.

To solasodine, the aglycone of the alkaloidal glycoside solasonine obtainable from a number of *Solanum* species[1] has been assigned a steroidal structural formula mainly, because it yielded Diels' hydrocarbon[2,3] in the selenium dehydrogenation.

By treatment of solasodine (m.p. 197–201°[4] $[\alpha]^{20}D$ −98.5°, *c*, 0.396, methanol; calcd. for $C_{27}H_{43}NO_2$: C, 78.40; H, 1048; N, 3.39. Found: C, 78.17; H, 10.29; N, 3.45, acetate, m.p. 191–193°) with acetic anhydride, oxidation of the reaction product with chromic acid anhydride in acetic acid, and subsequent hydrolysis with methanolic potassium hydroxide, we obtained a semicrystalline mass which was chromatographed, acetylated and again chromatographed twice over alumina (previously washed with ethyl acetate). We eventually isolated 3β-acetoxy-$\Delta^{5,16}$-pregnadiene-20-one (of m.p. 172–174°, $[\alpha]^{20}D$ −24.5 ± 4°, *c*, 0.449, ethanol, calcd. for $C_{23}H_{32}O_3$: C, 77.49; H, 9.05. Found: C, 77.38; H, 9.39) and 3β-acetoxy-16α-methoxy-Δ^5-pregnen-20-one of m.p. 157–159°. The identity of these compounds was established by determination of the mixture-melting points, and the comparison of the infrared spectra[5] with authentic samples. A small amount of a third compound not as yet identified (m.p. 198–200.5°, $\lambda_{max.}$ 240, 280) could also be isolated. In addition, a considerable amount of acidic products was formed in the oxidation.

The isolation of the above pregnane derivatives establishes the partial structural formula I for solasodine. One point of attachment of the nitrogen-containing portion is fixed at C-20. The other point is probably at position 16.



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RECEIVED AUGUST 27, 1951

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(1) Henry, "The Plant Alkaloids," 4th ed., The Blakiston Company, Philadelphia, Pa., 1949, p. 666.

(2) Rochelmeyer, *Arch. Pharm.*, **274**, 543 (1936).

(3) See also Rochelmeyer, *ibid.*, **275**, 336 (1937); **277**, 329 (1939); Rochelmeyer, Stützel and Cheu, *ibid.*, **282**, 92 (1944); Briggs, *et al.*, *J. Chem. Soc.*, 1, 3, 12 (1942); 3013, 3020 (1950).

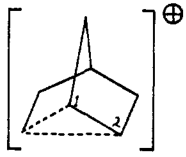
(4) All melting points reported were taken on the Kofler block and are uncorrected.

(5) By Mrs. Phyllis B. Humphries, of this Laboratory.

THE NATURE OF THE INTERMEDIATE IN THE SOLVOLYSIS OF NORBORNYL DERIVATIVES[1,2]

Sir:

It has been suggested[3] on the basis of solvolysis rate and stereochemical considerations that the solvolysis of *exo*- and *endo*-norbornyl *p*-bromobenzenesulfonates in acetic acid proceeds by a bridged "non-classical" carbonium ion having a structure (I) like that proposed[4] for the cationic intermediate involved in the rearrangement of camphene hydrochloride to isobornyl chloride. The desirability of tracer experiments to confirm structure I has been pointed out earlier[5] and, as part of an investigation of the mechanisms of reaction of norbornyl derivatives, solvolysis reactions of *exo*- and *endo*-norbornyl-2,3-C^{14}_2 *p*-bromobenzenesulfonates are being studied in several solvents.



I

Solvolysis of the *exo*-isomer (II) in acetic acid via intermediate I would be expected to yield equal[6] parts of *exo*-norbornyl-2,3-C^{14}_2 and *exo*-norbornyl-1,7-C^{14}_2 acetates since positions 1 and 2 must become equivalent if I is to have a plane of sym-

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(1) Supported by the program of research of the U. S. Atomic Energy Commission under Contract AT(30-1)-905.

(2) Presented at the Symposium on Reaction Mechanisms at the 75th Anniversary Meeting of the American Chemical Society, September 7, 1951.

(3) S. Winstein and D. S. Trifan, THIS JOURNAL, **71**, 2953 (1949); S. Winstein and D. S. Trifan, Abstracts of April, 1951, Meeting of the American Chemical Society, 53M, 54M.

(4) T. P. Nevell, E. de Salas and C. L. Wilson, *J. Chem. Soc.*, **1188** (1939).

(5) J. D. Roberts, R. E. McMahon and J. S. Hine, THIS JOURNAL, **72**, 4237 (1950).

(6) Neglecting differences in reaction rate between C^{12} and C^{14} atoms (isotope effect).