l-abietic acid and 2% neoabietic acid. The observed specific rotation and the calculated specific rotation were in excellent agreement, −93 and −92°, respectively.

Isolation of Isomerization Products of Levopimaric Acid.—Five-gram samples of levopimaric acid were allowed to isomerize the desired lengths of time and the isomerization stopped by pouring the solution into water and removing the precipitated resin acids by ether extraction. The product was isolated as described above in the isomerization of *l*-abietic acid.

Analysis of Products of Isomerized Levopimaric Acid.—The specific rotation, ultraviolet absorption analysis, levopimaric acid content and chromatographic analysis were obtained on each product isolated. A summary of these analyses and the calculated specific rotations and specific extinction coefficients is recorded in Table III. The identity of palustric, *l*-abietic and neoabietic acids was confirmed by isolation by means of large scale chromatography. Acids with specific rotations of +71.2, −104.5 and +160°, respectively, were obtained.

OLUSTEE, FLORIDA

COMMUNICATIONS TO THE EDITOR

THE COMPOUND Fe_3S_4 (SMYTHITE) FOUND IN NATURE

Sir:

We have found minute, plate-like crystal inclusions in calcite crystals from Bloomington, Indiana, to be a new iron sulfide, with chemical and physical properties similar to those of pyrrhotite. The crystals are opaque, have a dark bronzy color, and are strongly ferromagnetic, but they give a wholly distinct powder diffraction pattern. Insufficient material is available for quantitative chemical analysis, even by microtechniques, but an ideal formula, Fe_3S_4, is postulated on the basis of our study of the crystal structure by X-ray diffraction methods. The mineral is named smythite (pronounced smīth'īte) in honor of Professor C. H. Smyth, Jr., who was one of the earliest to recognize the occurrence of pyrrhotite in sedimentary rocks.

Microanalytical techniques by X-ray fluorescence, confirmed by qualitative microchemical tests, have shown the major metallic constituent to be iron, with a small amount of nickel also present. A satisfactory microchemical test also was obtained for sulfur. Buerger precession X-ray photographs of single crystals show that they are rhombohedral with a probable space group $R\bar{3}m$ ($D^5_{3\alpha}$), and hexagonal unit cell dimensions a_0 = 3.47 Å., c_0 = 34.5. This unit cell accounts quantitatively for the powder pattern. The specific gravity as measured by flotation is 4.06 ± 0.03, in good agreement with the value 4.09 as calculated from the unit cell with contents $3Fe_3S_4$.

The formula was first arrived at through a study of the crystal structure, which shows a striking relationship to that of pyrrhotite. The similarity of dimensions (pyrrhotite is hexagonal with space group $P6_3/mmc$, a_0 = 3.44 Å., c_0 = 5.68, $6 \times c_0$ = 34.1) indicates that a similar type of structure is involved, but the rhombohedral symmetry shows that the basic pyrrhotite framework is interrupted periodically to produce layers. A structure has been evolved which gives a reasonable agreement between observed and calculated diffraction intensity. The pyrrhotite-layer structure hypothesis leads directly to the formula Fe_3S_4.

The compound Fe_3S_4 has long been postulated, usually by analogy to the minerals linnaeite (Co_3S_4, spinel structure) and violarite ($FeNi_2S_4$, spinel structure), but its existence never has been proved. For example, Sidot[1] claimed to have prepared Fe_3S_4 by the reaction of magnetite (Fe_3O_4) with H_2S at red heat, but attempts by de Jong and Willems[2] and Fontana[3] to repeat this and other previously reported syntheses were unsuccessful. So far we have not been able to achieve synthesis of smythite by fusion or by precipitation from water solutions.

A more detailed description of the occurrence, properties, and structure of smythite will be published at a later date.

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[1] Th. Sidot, *Compt. rend.*, **66**, 1257 (1868).

[2] W. F. de Jong and H. W. V. Willems, *Z. anorg. allgem. Chem.*, **161**, 311–5 (1927).

[3] C. Fontana, *Atti acad. Lincei*, [6] **5**, 579–81 (1927).

U. S. GEOLOGICAL SURVEY R. C. ERD
WASHINGTON 25, D. C. H. T. EVANS, JR.

RECEIVED MARCH 22, 1956

12α-HALO DERIVATIVES OF 11β-HYDROXYPROGESTERONE

Sir:

The enhancement of adrenocorticoid activity by substitution of a halogen atom in the 9α-position of 11β-hydroxy or 11-ketopregnane derivatives was first reported from this laboratory[1] and has since been demonstrated to be of broader significance.[2] In examining available data for possible generalizations concerning the dependence of biological activity upon chemical structure one cannot fail to note the consistent parallelism between adrenocorticoid action and the electronegativity (−I effect) of the 9α-substituent.[3] Such a relationship suggested the view that enhancement in activity might be the

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[1] J. Fried and E. F. Sabo, THIS JOURNAL, **75**, 2273 (1953).

[2] (a) J. Fried and E. F. Sabo, *ibid.*, **76**, 1455 (1954); (b) J. Fried, J. E. Herz, E. F. Sabo, A. Borman, F. M. Singer and P. Numerof, *ibid.*, **77**, 1068 (1955); (c) R. F. Hirschman, R. Miller, R. E. Beyler, L. H. Sarett and M. Tishler, *ibid.*, **77**, 3166 (1955); (d) J. Fried, K. Florey, E. F. Sabo, J. E. Herz, A. R. Restivo, A. Borman and F. M. Singer, *ibid.*, **77**, 4181 (1955); (e) J. Fried, *Ann. N. Y. Acad. Sci.*, **76**, 573 (1955).

[3] This relationship does not apply to halogens only but also to other substituents, *e.g.*, OH, OCH_3, OC_6H_5. A convenient numerical expression of the electro-negativity of a substituent is the pK_a of the correspondingly α-substituted acetic acid. *Cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 737.