hours. Filtration and Claisen distillation followed by fractionation gave compound XII, ethyl methyldiethoxysilylmethylcyanoacetate 120 g. (0.46 mole), b.p. 140° (8 mm.), $n^{20}D$ 1.4291, d^{20} 1.017, in 46% yield.

Anal. Calcd. for $C_{11}H_{21}O_4SiN$: Si, 10.8; sap. equiv. (hydrolysis of ester group only), 259; MR_D, 65.73. Found: Si, 11.0; sap. equiv., 253; MR_D, 65.74.

To prevent hydrolysis of the nitrile group very mild conditions were used for the determination of the saponification equivalent. Samples were allowed to stand at room temperature with 1 *N* potassium hydroxide in butyl cellosolve for 1 hour.

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[CONTRIBUTION FROM THE NAVAL STORES STATION, U. S. DEPARTMENT OF AGRICULTURE[1]]

Acid Isomerization of Levopimaric Acid

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The isomerization of levopimaric acid with hydrochloric, acetic, nitric, sulfuric, phosphoric and chloroacetic acids was followed by observing the changes in specific rotation. The hydrochloric acid isomerization was studied closely by stopping the isomerization at several points and analyzing the products by partition chromatography, ultraviolet absorption analysis, and levopimaric acid determination. In all these products palustric, *l*-abietic and neoabietic acids were present. Isomerization with acetic and sulfuric acids also produced these acids, although the maximum amounts of palustric and neoabietic acids produced by acid isomerization were much smaller than the amounts produced by thermal isomerization of levopimaric acid. Isomerization of *l*-abietic acid with hydrochloric acid yielded a product that contained palustric and neoabietic acids.

The work described in this paper was undertaken in order to establish the composition of the products formed by acid-catalyzed isomerization of levopimaric acid. Previous investigations of the acid isomerization of levopimaric acid[2-4] established that when hydrochloric acid was used as the catalyst, the change in specific rotation was observed to pass through a minimum, and Dupont[2] suggested the possibility of the formation of an unstable isomer at this point.

The discovery of palustric acid[5] in pine oleoresins and rosins suggested that this acid might be the intermediate isomer in the isomerization of levopimaric acid to *l*-abietic acid. Investigations with partition chromatography showed that a complete analysis of the isomerization products of levopimaric acid was possible. Studies of the products of thermally isomerized levopimaric acid[6] in this Laboratory established that palustric acid is one of the intermediate products of the thermal isomerization of levopimaric acid to *l*-abietic acid. A similar study has been made of the acid isomerization of levopimaric acid.

The changes in specific rotation during the isomerization of levopimaric acid with hydrochloric, acetic, nitric, phosphoric, sulfuric and chloroacetic (in two solvents) acids were followed (Table I). Concentrations of the acid catalyst were chosen so that the minimum point of specific rotation would be reached in two or three hours whenever possible. Since the specific rotations of the resin acids differ in various solvents and since three different solvents were used in these isomerizations, the specific rotations of *l*-abietic, levopimaric and neoabietic acids in the more common organic solvents are listed in Table II.

TABLE I

CHANGES IN SPECIFIC ROTATION[a] DURING THE ISOMERIZATION OF LEVOPIMARIC ACID WITH ACIDS

Acid	HCl	HCl	H_2SO_4	Acetic	Acetic	H_3PO_4	Chloroacetic	Chloroacetic	HNO_3
Normality	0.12	0.12	0.25	5	17.6	5.3	4.5	2.2	0.25
Solvent	95% EtOH	Abs. EtOH	Abs. EtOH	Abs. EtOH	Glacial acetic acid	Abs. EtOH	Abs. EtOH	Benzene	95% EtOH
Hours isomerized	Specific rotation								
0[b]	−275°	−275°	−275°	−265°	−275°	−275°	−275°	−250°	−275°
1/4	−159	− 78	−110			−160	−206	−124	−208
0.5	−135	− 71	−100			−143	−182	− 96	−188
1	− 91	− 70	− 94	−271	−252	−109	−174	− 48	−156
1.5	− 80	− 72	− 94		−247	− 95	−161	− 37	−133
2	− 74	− 76	− 94		−239	− 90	−147	− 34	−125
3	− 74	− 79	− 94		−228	− 88	−126	− 34	−106
4	− 74	− 84	− 94		−216	− 87	−112	− 34	− 93
5	− 74	− 87			−205	− 87	−103	− 34	− 93
8	− 74	− 88	− 93		−181	− 87	− 95	− 34	− 89
19	− 81			−255	−114				
24	− 88	− 93	− 92		−102	− 88	− 91	− 35	− 89
48	− 93	− 94	− 93		− 77	− 88	− 92	− 36	
72				−156	− 72				
96					− 72				

[a] Resin acids exhibit different specific rotations in different solvents. [b] Extrapolated values.

(1) One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) G. Dupont, *Compt. rend.*, **172**, 1373 (1921).

(3) R. Lombard, *Bull. soc. chim. France*, 1186 (1948).

(4) P. F. Ritchie and L. F. McBurney, THIS JOURNAL, **71**, 3736 (1949).

(5) V. M. Loeblich, D. E. Baldwin and Ray V. Lawrence, *ibid.*, **77**, 2823 (1955).

(6) V. M. Loeblich, D. E. Baldwin, R. T. O'Connor and Ray V. Lawrence, *ibid.*, **77**, 6311 (1955).

TABLE II

SPECIFIC ROTATIONS OF RESIN ACIDS IN VARIOUS SOLVENTS

Solvent	$[\alpha]_D$ levopimaric acid[a]	$[\alpha]_D$ *l*-abietic acid[b]	$[\alpha]_D$ neoabietic acid[a]
Ethanol	−275°	−103.1°	+160.1°
Methanol	−274.2	− 99.2	+154.1
Benzene	−250.9	− 21.5	+155.2
Isoöctane	−286.2	− 60.6[a]	+142.6
Heptane	−273.3	− 62.2[a]	+147.7
Cyclohexane	−280.4	− 70.1	+157.0
Chloroform	−258.9	− 81.6	+158.1
Ether	−269.7	−110.7	+162.6
Acetone	−268.4	− 80.3	+160.1
Dioxane		−107.3	
Acetic acid	−265[c]	− 82.2	

[a] 1% solution. [b] 2% solution. [c] Extrapolated value.

pimaric acid in the final equilibrium mixture. This same equilibrium was obtained by isomerizing *l*-abietic acid with hydrochloric acid, thereby explaining the fact that pure *l*-abietic acid is not obtained by isomerizing levopimaric acid with hydrochloric acid. Rather this same equilibrium mixture will result, requiring recrystallization to give *l*-abietic acid with a specific rotation of −105°. This is in agreement with the observation of Lombard and Frey[7] that pure *l*-abietic acid with a specific rotation of −112° changed to a specific rotation of −90 to −95° on treatment with H^+.

Products from isomerization of levopimaric acid with sulfuric acid and glacial acetic acid were analyzed and contained palustric, *l*-abietic and neoabietic acids (Table III).

TABLE III

ANALYSES OF PRODUCTS OF ACID-ISOMERIZED LEVOPIMARIC ACID

Time isomerized	$[\alpha]_D$ (2% EtOH)	α at 241 mμ	Levopimaric acid content, %	Chromatographic analyses, % Palustric	*l*-Abietic	Neoabietic	Recov.	Calcd. $[\alpha]_D$	Calcd. α at 241 mμ
				0.1 *N* HCl[a]					
20 min.	−155	30	59	9	23	9	100	−166	29
1.5 hr.	− 79	62	7	12	72	6	97	− 76	62
2 hr.	− 74	63	0	12	84	2	98	− 76	66
19 hr.	− 81	73	0	6	90	3	99	− 83	72
24 hr.	− 88	72	0	5	91	2	98	− 88	72
48 hr.	− 93	76	0	3	95	2	100	− 94	75
				0.4 *N* H_2SO_4[a]					
20 min.	−108	69	14	3	76	7	100	−105	66
3 hr.	− 92	72	4	3	87	5	99	− 88	71
				Glacial acetic acid					
24 hr.	−111	62	13	5	78	4	100	−108	64

[a] 95% EtOH used as the solvent.

Using 0.1 *N* hydrochloric acid in 95% ethanol solution as the catalyst, a minimum specific rotation of −74° was reached in two hours which then rose slowly to −93° at the end of 48 hours. This pronounced minimum is characteristic of the hydrochloric acid isomerization and was not caused by other acids used.

Products from the hydrochloric acid catalyzed isomerization with specific rotations of −155, −79, −74, −81, −88 and −93° were isolated and then investigated by partition chromatography, ultraviolet absorption analysis and levopimaric acid determination (Table III). In a previous publication,[6] the completeness of analysis of such products has been discussed. All these products contained palustric, *l*-abietic and neoabietic acids although the concentrations of palustric and neoabietic acids were generally lower than the concentrations found in the thermally isomerized levopimaric acid products. Specific extinction coefficients and specific rotations calculated from the results of chromatographic analyses are in excellent agreement with the observed values. The concentration of palustric acid reached a maximum of 12% at the point of minimum specific rotation and decreased to 3% at the end of the isomerization. The concentration of *l*-abietic acid increased throughout the isomerization until a final equilibrium mixture of 3% palustric, 95% *l*-abietic and 2% neoabietic acids was reached. There was no detectable amount of levo-

Experimental

Preparation of Levopimaric Acid.—A modification[6] of the procedure of Harris and Sanderson[8] was used to separate levopimaric acid from pine oleoresin. The levopimaric acid used in these isomerizations had a specific rotation of −275° and was shown by chromatographic and ultraviolet absorption analyses to contain more than 97% levopimaric acid.

Specific Rotation Changes During Isomerization of Levopimaric Acid.—Levopimaric acid was weighed into a volumetric flask, the solvent added, and solution effected before the acid catalyst was added whenever it was possible. (Glacial acetic acid and chloroacetic acid solutions were added directly to the levopimaric acid.) Timing started immediately upon the addition of the acid catalyst. The solution was sealed in a polarimeter tube and readings were generally taken every ten minutes until the isomerization was complete; 2% solutions of levopimaric acid were used. A summary of the specific rotation changes observed is recorded in Table I. Specific rotations of levopimaric, neobietic and *l*-abietic acids in different solvents are recorded in Table II.

Isomerization of *l*-Abietic Acid.—A 0.5 *N* hydrochloric acid solution of *l*-abietic acid, $[\alpha]_D$ −104.2°, was prepared using absolute ethanol and concentrated hydrochloric acid. The specific rotation decreased to −97.9° at the end of one hour, −95.9° at the end of two hours, −94.0° at the end of four hours, and −93.6° at the end of five hours. At the end of 24 hours the specific rotation was still −93.6°.

The product was precipitated with water and extracted into ether. The ether solution was washed free of hydrochloric acid, dried over sodium sulfate and evaporated on a vacuum pump. Chromatographic analysis of the crystalline product showed the presence of 4% palustric acid, 93%

(7) R. Lombard and J. M. Frey, *Bull. soc. chim. France*, 1194 (1948).

(8) G. C. Harris and T. F. Sanderson, THIS JOURNAL, **70**, 334 (1948).

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 smĭth'ite) 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_{3d}), 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.

(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
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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

(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_2H_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.