

of air. The temperature was raised gradually (to prevent spattering of the melt) to a fixed temperature at which it was held constant for twelve to twenty-four hours. The products were periodically removed from the furnace, ground in a mortar and again heated. Products obtained over the range 150 to 1020° were examined by X-ray analysis and the diffraction patterns of several unidentified phases were obtained. From the mixture in which the ratio La/Co = 1, an essentially homogeneous product was obtained between 800 and 970°. It appeared to be contaminated by a small amount of lanthanum oxide. Chemical analysis showed that the valence of cobalt in this product is 3. Subsequent study of the diffraction patterns of the 700° products from mixtures in which the ratio La/Co ranged from 0.5 to 3, showed the presence of the same phase strongly contaminated with other phases. From these results it is reasonable to conclude that the composition of the persistent phase is LaCoO₃. Further justification for this conclusion was obtained by the determination of the structure.

The diffraction pattern (given in Table I) resembled that of a perovskite structure except that many lines appeared as doublets and a few as triplets. This was taken as an indication that the structure was slightly distorted from the cubic. A tentative value (3.82 Å.) was obtained for the pseudo-cubic unit cell dimension by assuming that the innermost reflection was due to the 100 plane. Upon this basis, the other lines of the pattern were indexed. It was found that reflections corresponding to the 100, 200,

TABLE I

X-RAY DIFFRACTION PATTERN OF LaCoO₃

I = Intensity; VS = Very strong; S = Strong; M = Medium; W = Weak; VW = Very weak; VVW = Extremely weak

<i>d</i>	<i>I</i>	$h^2 + k^2 + l^2$
3.82	M	1
2.721	VS	2
2.681	VS	2
2.213	M	3
2.178	W	3
1.911	S	4
1.719	VVW	5
1.701	VVW	5
1.568	S	6
1.545	M	6
1.360	M	8
1.348	M	8
1.275	VVW	9
1.213	M	10
1.204	M	10
1.154	VW	11
1.143	VW	11
1.108	W	12
1.091	VW	12
1.068	VVW	13
1.055	VVW	13
1.027	M	14
1.021	W	14
1.013	W	14
0.956	W	16
0.906	VW	18
0.896	VW	18
0.860	VW	20
0.851	VW	20
0.820	VW	22
0.806	VW	22
0.786	W	24
0.782	W	24

300 and 400 planes were all single lines while those due to such planes as 110, 111, 210, 221, etc., were doublets or triplets. This points to a rhombohedral unit cell the interplanar spacings for which can be calculated from the equation

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + hl + kl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$

where α is the interaxial angle.

The value for α was found to be 90°42'. The obtuse angle was chosen on the basis of the relative intensities of pairs of reflections when compared with the number of equivalent reflections that could be obtained from a set of planes. Table II gives the computed and observed values of d^* ($d^* = \lambda/d = 2 \sin \theta$). Since excellent agreement was obtained, the unit cell dimension was recalculated using the equation given above. It was found to be 3.82 ± 0.01 Å.

TABLE II

A COMPARISON OF VALUES OF d^* obs. AND d^* calcd.

Plane	d^* obs.	d^* calcd.
100	0.403	0.403
$\bar{1}10$.566	.567
110	.574	.574
$\bar{1}11$.695	.695
111	.707	.707
200	.806	.806
$\bar{2}10$.896	.897
210	.905	.906
$\bar{2}11, 2\bar{1}1$.982	.983
211	.997	.997
$\bar{2}20$	1.133	1.133
220	1.147	1.147
300	1.208	1.209
$\bar{3}10$	1.270	1.270
310	1.279	1.279
$\bar{3}11, 3\bar{1}1$	1.335	1.334
311	1.347	1.347
$\bar{2}22$	1.390	1.391
222	1.412	1.413
$\bar{3}20$	1.442	1.445
320	1.460	1.461
$\bar{3}21, 3\bar{2}1$	1.500	1.501
$3\bar{2}\bar{1}$	1.508	1.510
321	1.520	1.522
400	1.611	1.612
$\bar{3}30, 4\bar{1}1$	1.700	1.701
330, 411	1.719	1.720
$\bar{4}20$	1.795	1.794
420	1.812	1.811
$\bar{3}32, 33\bar{2}$	1.883	1.884
332	1.913	1.912
$\bar{4}22$	1.959	1.962
422	1.970	1.970

The density of LaCoO₃ was found to be 7.2 g./c.cm. which corresponds to one formula weight per unit cell.

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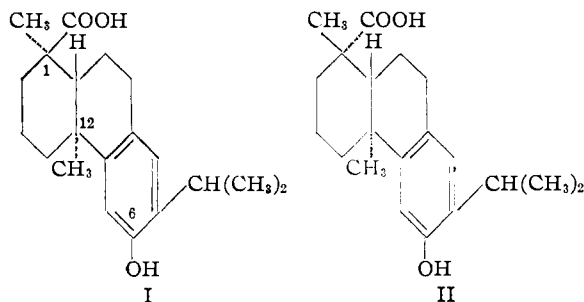
7-Isopropylpodocarpinol

BY MANUEL M. BAIZER, MARILYN KARNOWSKY AND W. G. BYWATER

Campbell and Todd¹ have shown that 6-hydroxydehydroabiatic acid (I) differs from

(1) Campbell and Todd, THIS JOURNAL, 64, 928 (1942).

7-isopropylpodocarpic acid (II) only in the configuration of the methyl and carboxyl groups at C₁.



Since 6-hydroxydehydroabietinol ($-\text{COOH}$ of I replaced by $-\text{CH}_2\text{OH}$) possesses a relatively high order of estrogenic activity,² it was of interest to prepare the isomeric 7-isopropylpodocarpinol ($-\text{COOH}$ of II replaced by $-\text{CH}_2\text{OH}$) and to test its biological activity.³

Podocarpic acid, obtained from rimu resin, was converted by the previously described⁴ sequence of reactions to methyl O-methyl-7-isopropylpodocarpate which was reduced to O-methyl-7-isopropylpodocarpinol (III) in 93% crude yield⁵ by means of lithium aluminum hydride.⁶ III was demethylated in 40% yield to the free phenol by treatment with potassium hydroxide in diethylene glycol at 210–220° for four hours.⁷

7-Isopropylpodocarpinol was assayed for estrogenic activity by the Laboratory of Industrial Hygiene, Inc.⁸ Of a group of ten rats receiving 1.5 micrograms of sample per animal 30% showed positive response; under similar conditions 1.1 micrograms of estrone produced a 50% positive response. When the dosage level of the sample was raised to 2.8 micrograms per rat, 40% of ten animals showed positive response, compared again with 50% response to 1.1 micrograms of estrone.

Experimental

O-Methyl-7-isopropylpodocarpinol.—A solution of 4.7 g. of lithium aluminum hydride in 200 ml. of dry ether was prepared in a one-liter three-necked flask equipped with a reflux condenser, mercury-sealed stirrer and dropping funnel. All outlets were protected by drying tubes containing anhydrous calcium chloride and Ascarite. Then a solution of 10 g. of methyl O-methyl-7-isopropylpodocarpate⁴ in 75 ml. of dry ether was added dropwise with stirring. The mixture was stirred for three days at room temperature. Cracked ice was added followed by 250 ml. of dilute sulfuric acid. The layers were separated, the

(2) Fieser and Campbell, *THIS JOURNAL*, **61**, 2530 (1939); Fieser and Fieser, "Natural Products Related to Phenanthrene," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1949, p. 69.

(3) Brandt and Ross, *Nature*, **161**, 892 (1948), report that podocarpinol is estrogenic.

(4) Sherwood and Short, *J. Chem. Soc.*, 1006 (1938); Campbell and Todd, *THIS JOURNAL*, **62**, 1292 (1940).

(5) Zeiss, *et al.*, *THIS JOURNAL*, **70**, 1981 (1948), similarly reduced the des-isopropyl ester to the corresponding alcohol in 93% yield.

(6) Metal Hydrides, Inc., Beverly, Mass.

(7) Optimum conditions for this step were not determined.

(8) Laboratory of Industrial Hygiene, Inc., 76 Madison Ave., New York 16, N. Y.

aqueous layer extracted once with ether, the ether solutions combined, washed with water and dried over anhydrous sodium sulfate. The ether solution was distilled to dryness and the residue crystallized from ethanol. The yield, in two crops, was 8.5 g. (93%). A sample after one recrystallization from ethanol melted at 83–85°.

Anal. Calcd. for $\text{C}_{21}\text{H}_{30}\text{O}_2$: C, 79.69; H, 10.19. Found: C, 79.57; H, 10.30.⁹

7-Isopropylpodocarpinol.—A mixture of 5.4 g. of O-methyl-7-isopropylpodocarpinol, 18.9 g. of potassium hydroxide and 135 ml. of diethylene glycol was heated under a reflux condenser for four hours at 210–220° (internal temperature) with stirring. The mixture was cooled, diluted with one liter of water and acidified with dilute sulfuric acid. The precipitated solid was removed by filtration. The filtrate was extracted with four 100-ml. portions of ether; the previously removed solid was dissolved in the ether. The ether solution was washed with three 25-ml. portions of 5% sodium hydroxide,¹⁰ then with water and dried over anhydrous sodium sulfate. The solution was distilled to dryness. The residue upon crystallization from ethanol-hexane gave, in several crops, 1.6 g. of product and 1.1 g. of recovered starting material (40% yield based upon net material entering reaction). Recrystallized from ethanol-hexane, the phenol-alcohol melted at 185.4–186.4°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{30}\text{O}_2$: C, 79.43; H, 10.00. Found: C, 79.31; H, 9.80⁹.

(9) Schwarzkopf Microanalytical Laboratory, Middle Village, L. I., N. Y.

(10) The phenolic group in 7-isopropylpodocarpinol is highly hindered. The product is practically insoluble in aqueous alkali, but the caustic wash removes some colored material which interferes with the crystallization.

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The Interaction of Aluminum Bromide and Sodium Iodide

By J. L. DANIEL AND N. W. GREGORY

The properties of fused mixtures of aluminum halides and other metallic halides have been studied extensively, particularly by Plotnikov^{1,2} and others^{3,4} in Russia. Considerable evidence for the existence of addition compounds has been observed. In mixtures of alkali metal halides and aluminum halides, electrochemical studies provide results which indicate the presence of negative ions containing aluminum. The ion AlX_4^- has been postulated frequently. Al_2X_6 can be sublimed away from addition compounds in systems of this type at high temperatures.

The electrical properties of mixtures of sodium chloride and aluminum bromide have been explained by Mezhenii⁴ in terms of ionization into Na^+ and AlBr_3Cl^- . Evidence for the existence of a corresponding type of mixed halide ion has also been found in the system $\text{AlBr}_3-\text{NaI}-\text{C}_2\text{H}_5\text{Br}$.²

(1) V. A. Plotnikov and U. I. Shvartsman, *J. Phys. Chem. (U. S. S. R.)*, **12**, 120 (1938).

(2) V. A. Plotnikov and V. N. Dumarevskaya, *Zapiski Inst. Khim., Akad. Nauk., U. R. S. S.*, **7**, 383 (1940).

(3) E. L. Starokadomskaya, *J. Gen. Chem. (U. S. S. R.)*, **9**, 840 (1939).

(4) Y. F. Mezhenii, *Zapiski Inst. Khim., Akad. Nauk., U. R. S. S.*, **7**, 373 (1940).