

metric methods. Molybdenum contents down to 0.01 % can be determined. This corresponds to about 0.004 mg of molybdenum in 10 ml of the final solution or to a diffusion current of 0.02–0.03  $\mu\text{A}$ . The error of the analysis is assessed at about  $\pm 5\%$  (rel.), or  $\pm 0.01\%$  (abs.), whichever is the larger.

A typical polarogram is shown in Fig. 1. The molybdenum wave is found at  $-1.00$  or  $-1.01$  V; Meites<sup>7</sup> found  $E_{1/2} -1.111$  V or  $-0.927$  V, depending on the concentration of the electrolyte. Most of the samples produced a wave with  $E_{1/2}$  about  $-0.3$  V. It has not been possible to identify the substance producing this wave; it is not bismuth.

**Interferences.** With the purpose of finding any interfering substances, and of identifying, if possible, the substance producing the wave at  $-0.3$  V, a series of metals were examined. Cerium IV, titanium IV, thorium VI, tin IV, niobium V, tantalum V, arsenic V, antimony V, cobalt II, and nickel II did not produce any wave. Solutions of copper II, thallium III, zirconium IV, bismuth III, and uranium VI, in the electrolyte were reduced, but these metals were eliminated by the fusion. Zinc II, cadmium II, lead II, vanadium V, chromium IV and tungsten VI produced polarographic waves, persisting after fusion, but none of these waves interfered with the molybdenum wave. The values of  $E_{1/2}$  are shown in Table 2.

**Acknowledgements.** Thanks are due to Nordisk Mineselskab, A/S, for the analysed samples of molybdenum ore, to Kryolitselskabet Øresund A/S for permission to publish this paper, to H. Pauly, Ph. D., J. Bjerrum, professor, Ph.D., and H. Buchwald, chief analyst, for valuable discussions and good advice.

- Sandell, E. B. *Ind. Eng. Chem. Anal. Ed.* **8** (1936) 336.
- Grimaldi, F. S. and Wells, R. C. *Ind. Eng. Chem. Anal. Ed.* **15** (1940) 315.
- Dobritskaya, Yu. I., *Pochvovedenie* **1957** No. 3, 91; *cf. Anal. Abstr.* **5** (1958) No. 3931.
- Hope, R. P. *Anal. Chem.* **29** (1957) 1053.
- Winterstein, C. *Erzmetall* **10** (1957) 549.
- Kanevskii, E. A. and Shvartsburd, L. A. *Zavodskaya Lab.* **7** (1940) 283; *cf. Chem. Abstr.* **34** (1940) 5782<sup>8</sup>.
- Meites, L. *Anal. Chem.* **25** (1953) 1752.
- Meites, L. *Polarographic Techniques*, New York 1955, p. 65.

Received May 3, 1961.

*Acta Chem. Scand.* **15** (1961) No. 4

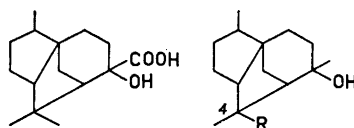
## The Structure of Cedrolic Acid

JARL RNEBERG

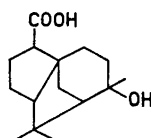
*Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden*

Recently a saturated, tricyclic hydroxy acid,  $\text{C}_{15}\text{H}_{24}\text{O}_3$ , was isolated from the heartwood of the American desert juniper, *Juniperus utahensis* Lemm.<sup>1</sup> The name cedrolic acid and the structure 2 are proposed for this compound, which appears to be the first naturally occurring sesquiterpene hydroxy acid described. Small amounts of three other compounds of the same class have since been isolated from heartwood of *Juniperus* species<sup>2,3</sup>.

Cedrolic acid melts over a wide range (m.p. 181–187°). The sharp-melting methylester (3, m.p. 98.0–98.5) was reduced to a diol<sup>1</sup> (4, m.p. 130–131°). This diol has now been oxidised with chromic acid in pyridine to the hydroxy aldehyde 5, which on reduction by the Huang-Minlon procedure gave cedrol (6) in good yield.



- 1  
2 R =  $-\text{COOH}$  3 R =  $-\text{COOCH}_3$   
4 R =  $-\text{CH}_2\text{OH}$  5 R =  $-\text{CHO}$   
6 R =  $-\text{CH}_3$



7

Of the possible structures 1, 2 and 7 for cedrolic acid, 1 can be eliminated because the acid formed on dehydration from cedrolic acid is not  $\alpha,\beta$ -unsaturated<sup>1</sup>. Evidence against 7 is obtained from the infrared spectra of cedrolic acid, its methylester, the diol 4 and the hydroxy aldehyde 5. These spectra have only a single peak in the  $1375\text{ cm}^{-1}$  region, indicating the absence of a *gem*-dimethyl group in the above compounds.

The carbon-methyl value for cedrolic acid and its dehydration product<sup>1</sup> is in better agreement with structure 2 for cedrolic acid than with 7.

The proton magnetic resonance spectrum of cedrolic acid methylester was compared with that of cedrol<sup>4</sup> and agrees with structure 2 for the acid but not with 1 or 7.

The absolute configuration of cedrol was elucidated by Stork and Clarke<sup>5</sup> in connection with the total synthesis of this compound. Büchi and co-workers<sup>6</sup> have recently confirmed the absolute configuration of cedrene.

So far it has not been possible to determine the configuration at C<sub>4</sub> in cedrolic acid (2). On attempted lactonisation (acetic anhydride, pyridine) the formation of a strained 5-membered ring lactone in very low yield was indicated (IR).

The PMR spectrum of cedrolic acid methylester and a comparison between the infrared spectra of this compound in a polar and a nonpolar solvent (*cf.* Ref.<sup>7</sup>) gave no indication of any hydrogen bonding between the ester carbonyl and the alcoholic hydroxyl group. The  $pK_{MCS}^*$ -values<sup>8,9</sup> of cedrolic acid ( $pK_{MCS}^* = 8.37$ ) and that of its dehydration product<sup>1</sup> ( $pK_{MCS}^* = 8.23$ ) are close to one another.

*Experimental.* Melting points, taken on a hot stage, are uncorrected.

The carbon-methyl value of cedrolic acid (m.p. 181–187°,  $[\alpha]_D -47^\circ$ ) was redetermined (*cf.* Ref.<sup>1</sup>. Found: CH<sub>3</sub>-(C) 9.9; 10.9. C<sub>15</sub>H<sub>24</sub>O<sub>3</sub> requires CH<sub>3</sub>-(C) (one) 6.0).

*Hydroxy aldehyde (5).* A solution of the diol 4 (0.50 g, prepared as described previously<sup>1</sup>) in dry pyridine (7 ml) was added to chromic acid (1.00 g) in the same solvent (20 ml) and left for 11 h at room temperature. Methanol (10 ml) was then added, and after an additional hour the reaction mixture was diluted with ice-cold sodium hydroxide (20 ml) and extracted with ether. The ether solution was first washed with ice-cold hydrochloric acid (2 N) to remove pyridine and then with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to dryness. The residue (401 mg) was recrystallised from light petroleum and from methanol-water yielding the hydroxy aldehyde 5, m.p. 62–64°,

$[\alpha]_D -77^\circ$  (c, 2.2, CHCl<sub>3</sub>). (Found: C 75.9; H 10.2. C<sub>15</sub>H<sub>24</sub>O<sub>3</sub> requires C 76.2; H 10.2.) Infrared spectrum (in KBr): 3 480 m, 2 695 m, 1 721 cm<sup>-1</sup>s. 2,4-Dinitrophenylhydrazone, m.p. 172–174°. (Found: N 13.9. C<sub>21</sub>H<sub>28</sub>O<sub>5</sub>N<sub>4</sub> requires N 13.5.)

*Cedrol from the hydroxy aldehyde.* The hydroxy aldehyde 5 (102 mg) was refluxed for 1 h with a mixture of potassium hydroxide (280 mg), hydrazine hydrate (99–100 %, 0.31 ml) and ethylene glycol (3.5 ml, redistilled). The temperature of the reaction mixture was then raised to 200° while some water was removed by distillation. The mixture was then refluxed (at about 230°) under oxygen-free nitrogen for 4 h, cooled, diluted with water (25 ml) and extracted with light petroleum. The extract was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated, leaving a crystalline residue (89 mg). This was chromatographed on basic alumina (Broekmann, Grade II), eluting with benzene containing an increasing amount of ether. Pure ether eluted the main product (74 mg) which was recrystallised from ethanol (95 %), m.p. 85–86°,  $[\alpha]_D 10^\circ$  (c, 3.1). The product was identified (mixed m.p., IR) as cedrol.

*Acknowledgements.* My thanks are due to Professor H. Erdtman for his interest in this work, to Miss G. Hammarberg for spectral measurements and to the *Swedish Natural Science Research Council* for financial support.

1. Runeberg, J. *Acta Chem. Scand.* **14** (1960) 797.
2. Pettersson, E. and Runeberg, J. *Acta Chem. Scand.* **15** (1961) 713.
3. Runeberg, J. *Acta Chem. Scand.* **15** (1961) 721.
4. Forsén, S. and Runeberg, J. *To be published.*
5. Stork, G. and Clarke, F. H., Jr. *J. Am. Chem. Soc.* **77** (1955) 1072.
6. Büchi, G., Erickson, R. E. and Wakabayashi, N. *J. Am. Chem. Soc.* **83** (1961) 927.
7. Åkermark, B. *Acta Chem. Scand.* **15** (1961). *In the press.*
8. Simon, W. *Helv. Chim. Acta* **41** (1958) 1835.
9. Arya, V. P., Erdtman, H. and Kubota, T. *Tetrahedron* **1961**. *In the press.*

Received June 22, 1961.