

Table 1. Physical constants of sandaracopimaric and cryptopimaric acids and their methyl esters.

Compound	m.p.	$[\alpha]_D$ (EtOH)	Reference
Sandaracopimaric acid	173°	-18.8°	2
»	172°	-16.7°	3
»	169°	-20°	7
»	171°	-20°	Present work
Cryptopimaric acid	159-161°	-19°	10
»	160-162°	-21.7°	12
»	166-168°	-22°	11
»	168-170° *	-	Present work
Methyl cryptopimarate	63-64°	-25.6°	11
»	68-69°	-	Present work

* softening at 163°

racopimaric acid and its methyl ester, Professor H. H. Bruun for a sample of cryptopimaric acid and Dr. W. Simon for the titration of sandaracopimaric acid. Thanks are also due to the Ciba Fellowship Trust for a Post-doctoral fellowship (V.P.A.) and to the Swedish Technical Research Council for financial support.

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The Preparation of the Aldehyde of Kojic Acid (Comenaldehyde)

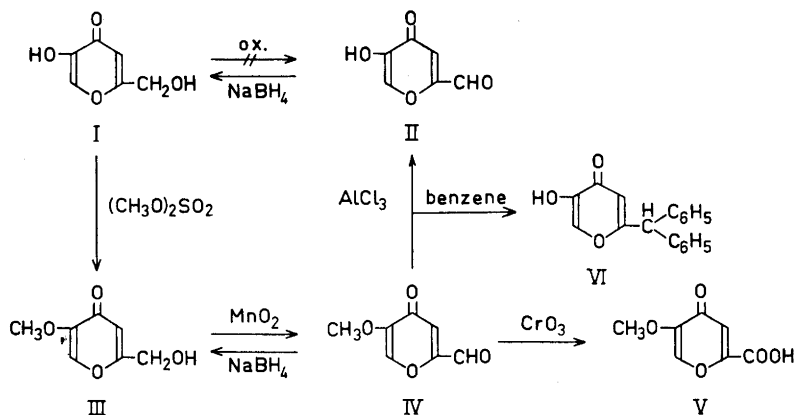
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Many derivatives of kojic acid (I) have been described but all attempts to synthesize its aldehyde (II, comenaldehyde, 2-formyl-5-hydroxy- γ -pyrone) have been unsuccessful.¹

Both the oxidation of the hydroxymethyl group of kojic acid with mild oxidizing agents² and the reduction of comenyl chloride by Rosenmund's method³ did not give the aldehyde II. Yabuta, who established the structure of kojic acid, concluded that comenaldehyde was a very unstable substance.³

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Previous oxidations of kojic acid mono-methyl ether (III, 2-hydroxymethyl-5-methoxy- γ -pyrone) yielded comenic acid methyl ether (V). KMnO_4 in acetone solution⁴, conc. HNO_3 ,⁵ and air in the presence of catalysts⁶ have been applied as oxidizing reagents. The 2-formyl-5-methoxy- γ -pyrone (IV) had not been obtained.

We recently⁷ found that the γ -pyrone aldehyde IV can be prepared when a solution of III in benzene is refluxed for one hour in the presence of active manganese dioxide⁸. From the filtered solution IV crystallizes in colorless needles that sublime on heating (m.p. 202°C; Found: C 54.75; H 3.91; Calc. for $\text{C}_7\text{H}_6\text{O}_4$: C 54.55; H 3.92; IR spectrum: $\nu_{\text{C}=\text{O}}$ 1705 cm^{-1}). The yield of IV was 50–70%. With phenylhydrazine IV forms a phenylhydrazone (m.p. 205–206°C; Found: N 11.50; Calc. for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3$, N 11.47).

When IV was oxidized by $\text{CrO}_3/\text{H}_2\text{SO}_4$ in acetone,⁹ V was formed immediately (yield 90%). Comenic acid methyl ether was also obtained by direct oxidation of III by $\text{CrO}_3/\text{H}_2\text{SO}_4$ in acetone (yield 70%).

Reduction of IV by NaBH_4 in ethanol did not attack the γ -pyrone group but gave III in about 70% yield.

Attempted demethylation of IV by the action of pyridine hydrochloride at 185°C resulted only in decomposition products. Treatment of IV in boiling benzene with an excess of AlCl_3 gave a colorless crystalline product, probably 2-(diphenylmethyl)-5-hydroxy- γ -pyrone, VI (m.p. 150–152°C; Found: C 77.24; H 5.17; Calc. for $\text{C}_{18}\text{H}_{14}\text{O}_3$: C 77.68; H 5.07; IR spectrum: ν_{OH} 3200 cm^{-1} ; red color with FeCl_3).

When the 2-formyl-5-methoxy- γ -pyrone (IV) was heated with AlCl_3 without a sol-

vent at 120°C for 3 h, the hitherto unknown comenaldehyde was formed almost quantitatively. (Found: C 51.51; H 2.96; Calc. for $\text{C}_9\text{H}_4\text{O}_4$: C 51.44; H 2.88; IR spectrum: $\nu_{\text{C}=\text{O}}$ 1718 cm^{-1} ; ν_{OH} 3230 cm^{-1} ; red color with FeCl_3).

The comenaldehyde forms colorless prismatic needles, m.p. 162–163°C, and can easily be purified by sublimation or recrystallization from chloroform.

Formulation of the structure of II as 2-formyl-5-hydroxy- γ -pyrone was supported by its reduction with NaBH_4 in ethanol to kojic acid.

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