

Short Communications

The Identity of Cryptopimaric Acid and Sandaracopimaric Acid

V. P. ARYA, C. ENZELL, H. ERDTMAN

Organisk-Kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

and R. RYHAGE

Masspektrometrlaboratoriet, Kemiska Institutionen, Karolinska Institutet, Stockholm, Sweden

Sandaracopimaric acid has been isolated from the resin of *Tetraclinis articulata*, (Vahl) Masters, ("Sandarac resin")¹⁻³. It belongs to the pimaric acid group of diterpenes⁴ and its structure and configuration (I) has recently been settled⁵⁻⁷. The acid, on titration gave the pK^*_{MCS} -value⁸ 7.92 which is in good agreement with the presence of a *trans* A/B ring junction and an equatorial carboxyl group⁹.

Cryptopimaric acid* has been isolated from the resin¹⁰ and heartwood¹¹** of

* Added in proof: Apsimon et al. (*J. Chem. Soc.* 1961 752) recently obtained a small amount (about 5 %) of dihydrosandaracopimaric acid as the only identifiable hydrogenation product of a cryptopimaric acid preparation (m.p. 160-162°, $[\alpha]_D -20^\circ$). From isomerisation experiments they conclude that, in spite of the high negative rotation, their acid contained mainly isopimaric and/or "Ukitas acid" and in addition a small amount of sandaracopimaric acid. We have found that a mixture of authentic sandaracopimaric and isopimaric acid (ca. 1:20) melts at 110-148°. "Ukitas acid" has not been available for comparison. It is possible that many cryptopimaric acid preparations have been impure.

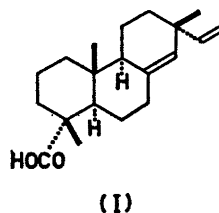
** There referred to as *isopimaric acid*.

Cryptomeria japonica, D. Don, and also shown to belong to the pimaric acid group¹⁰. Stenhagen et al.¹²⁻¹⁴, on the basis of infra-red, mass spectrometric (cf. Ref.¹⁵) and surface-balance studies, have suggested a structure for cryptopimaric acid identical with that later proposed for sandaracopimaric acid⁵⁻⁷. The structure, however, has recently been questioned¹⁶.

The mass spectrum of methyl sandaracopimarate, recorded in a mass spectrometric investigation of the diterpenes¹⁷, was identical with that of methyl cryptopimarate¹². The physical constants (Table I) of the two acids show a striking similarity and indicate that they are in fact identical.

Sandaracopimaric acid and cryptopimaric acid showed an undepressed mixed melting point (168-170°) whilst the melting point of a mixture of sandaracopimaric acid and *isopimaric acid* exhibited a large depression (ca. 30°). Similarly the mixed melting point of methyl sandaracopimarate and methyl cryptopimarate was not depressed (68-69°). The infra-red spectra of sandaracopimaric and cryptopimaric acids were superimposable.

It follows, therefore, that these acids are identical. The name sandaracopimaric acid has priority over cryptopimaric acid and the latter name may be deleted.



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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)

HANS-DIETER BECKER*

Institutionen för organisk kemi, Chalmers Tekniska Högskola, Göteborg, Sweden

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

* Present address: University of Wisconsin, Madison, Wis., U.S.A.