THE OCCURRENCE OF α-AMYRIN AND URSOLIC ACID IN THE LEAVES OF Ilex paraguariensis

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Received November 28, 1939

In Argentina, Uruguay, and Brazil, a beverage called maté, an infusion of the leaves of *Ilex paraguariensis*, is extensively used as tea. This has created special interest in this plant material, and as a result, chemical investigation of its constituents has been undertaken. The writer, working in this field, has isolated two constituents, namely, α -amyrin and ursolic acid. From a phytochemical standpoint, the discovery that α -amyrin occurs in *Ilex paraguariensis* is significant, as it is the first report of its occurrence in a plant of the Aquifoliaceae family, to which *Ilex paraguariensis* belongs. The fact that α -amyrin and ursolic acid occur together in this plant leads to the belief that the plant converts α -amyrin to ursolic acid. This is in harmony with the findings of Goodson (1), who has shown that ursolic acid is an oxidation product of α -amyrin.

While this is the first time ursolic acid has been reported as a constituent of the leaves of *Ilex paraguariensis*, attention is directed to a paper by Hauschild (2) in which he reports that he isolated from the leaves of *Ilex paraguariensis* a substance that he thought was a sterol, and consequently named matésterol. However, from a comparison of the analysis and other descriptive data of Hauschild's compound with those of ursolic acid, it appears that the two materials are identical. This is further confirmed by the fact that in the present work no indications of a typical sterol were found in the extractives studied.

EXPERIMENTAL

alpha-Amyrin. Chloroform treatment of finely-ground leaves of Ilex paraguariensis yielded 10% of extractives. A solution of 10 g. of these extractives in 200 cc. of 5% ethanolic potassium hydroxide solution was refluxed for 3 hours. Water was then added to the solution, and the mixture was extracted with petroleum ether. The material obtained after the petroleum ether was removed was a yellow, semicrystalline mass. Its solution in acetone was decolorized with carbon, and evaporated until crystallization began. The crude crystals melted at 175-178°. These were recrystallized from acetone (yield 0.43 g.), and then melted at 183-185°. The purified material had a specific rotation of $[\alpha]_{2}^{20} + 90.9^{\circ}$ (c = 0.958 in benzene), and when it was mixed with an authentic sample of α -amyrin,¹ there was no depression of the melting point.

Anal. Calc'd for C₈₀H₅₀O: C, 84.50; H, 11.73.

Found: C, 84.33; H, 11.91.

alpha-Amyrin acetate. A solution of 0.25 g. of the above α -amyrin in 2.5 cc. of acetic anhydride was boiled for 30 minutes. As the solution cooled, crystallization took place, and 0.25 g. of material was obtained. When this was recrystallized from acetic acid it melted at 217-219° and had a specific rotation of $[\alpha]_{\alpha}^{\infty}$ +76.1° (c = 1.316 in benzene). When the purified substance was mixed with an authentic sample of α -amyrin acetate, no depression of the melting point occurred.

alpha-Amyrin benzoate. This compound was made by boiling for 30 minutes a solution of 0.1 g. of α -amyrin and 0.6 cc. of benzoyl chloride in 2.5 cc. of pyridine. After the reaction-mixture was cooled, it was poured into water, and the mixture was extracted with ether. The ethereal extract was dissolved in methanol, from which the benzoate crystallized. It melted at 193-195°, and it did not depress the melting point of an authentic sample of α -amyrin benzoate.

alpha-Amyrone. This product was prepared from the *Ilex* α -amyrin according to the directions of Ruzicka, Muller, and Schellenberg (3). It melted at 123-125°, and it did not depress the melting point of an authentic sample of amyrone.

The following is a comparison of certain properties of authentic α -amyrin and some of its derivatives as reported by Professor Ruzicka and the corresponding data concerning α -amyrin obtained from the leaves of *Ilex paraguariensis*.

MATERIAL	M.P., °C.	C, %	Н, %	[¤]D	ACETATE M.P., [°] C.	[¤]D	BEN- ZOATE M.P., °C.	AMY- RONE M.P., °C.
α-amyrin Ruzicka	176–179	84.50	11.73	+89°	224-225	+77.°	195	125
par	183–185	84.33	11.91	+90.9°	221-222	+76.1°	193	125

Ursolic acid. After storage at 0° for some days, an ethereal extract of ground leaves of *Ilex paraguariensis* yielded a deposit of crude ursolic acid. An ethanolic solution of this material was decolorized with carbon and evaporated until it crystallized. Crystals melting at 279-282° were obtained. Upon recrystallization, this gave a product which melted at 283.5-285°. $[\alpha]_{D}^{30}$ (c = 1.363 in pyridine) was +65.9°.

Ursolic acid diacetate. This compound was prepared by boiling a solution of 50 mg. of the above ursolic acid in 0.9 cc. of acetic anhydride. Upon cooling the solution, the diacetate crystallized. The product melted at 200-201°, became solid at 204-205°, and remelted above 300°. Van der Haar (4) reports the first melting point of ursolic acid as 200-201° and the second melting point as 320-322°.

Monoacetylursolic acid. This substance was prepared by boiling one-half hour an ethanolic solution of the above diacetylursolic acid. After recrystallization from ethanol it melted at 283-285°. $[\alpha]_{p}^{20}$ (c = 0.468 in chloroform) was +61°.

Some of the properties of ursolic acid and derivatives as reported in the literature,

¹ The authentic samples of α -amyrin and its derivatives were kindly furnished by Professor Ruzicka of Zurich.

properties of Hauschild's matésterol follow:								
SUBSTANCE	M.P., °C.	C. %	Н. %	[¤]D	DIACETATE	MONOACETATE		

the same data obtained with ursolic acid from Ilex paraguariensis, and the recorded

SUBSTANCE	M.P., °C.	C, %	Н, %	[α]D	M.P., °C.			
						M.p., °C.	[¤]D	
Ursolic acid	284-285	78.88	10.6	+67.5°ª	200-201	289-290	+62.49	
Ursolic acid from <i>Ilex par</i>	283.5-285			65.9°	200-201	283–285	+61.°	
schild	276-278	78.14	10.7	+65.0° ⁵	-	274-276		

a In ethanolic potassium hydroxide.

b In pyridine.

SUMMARY

Ursolic acid and α -amyrin have been isolated from the leaves of *Ilex* paraguariensis,

Matésterol described by Hauschild appears to be somewhat impure ursolic acid.

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