[CONTRIBUTION FROM THE INSTITUTO DE QUÍMICA AGRÍCOLA, MINISTÉRIO DA AGRICULTURA]

The Chemistry of Rosewood. III. Isolation of 5,6-Dehydrokavain and 4-Methoxyparacotoin from *Aniba firmula* Mez

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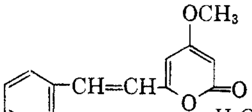
From the wood of *Aniba firmula* Mez there were isolated benzoic acid, 4-methoxy-6-piperonyl-α-pyrone (4-methoxyparacotoin) and 4-methoxy-6-(β-styryl)-α-pyrone (5,6-dehydrokavain). This latter compound, isolated for the first time from a natural source, has been known by synthesis since 1939. The relationship to the previously described arylpyrones from other plants of the same genus and to the styrylpyrones from *kava* root is pointed out.

Aniba firmula (Nees et Mart.) Mez (family *Lauraceae*) is a tree closely related to the two species of rosewood studied in former articles.[1,2] Its wood is fragrant and finds use in popular perfumery. Although it is not commercially exploited for the production of essential oil, it is sometimes called *louro rosa* (rose laurel) due to a certain similarity of its odor with that of true rosewood.[3] Of all *Aniba* species, this has the widest geographical distribution, reaching from the extreme north of South America, over the Brazilian and Peruvian Amazon, as far south as the Brazilian states of Minas Gerais and São Paulo.[4]

The material investigated was collected in the vicinity of Rio de Janeiro. From the benzene extract of the finely ground wood three cystalline substances could be isolated. One was recognized as benzoic acid. The second was found to be identical with 4-methoxyparacotoin, previously described from *Aniba Duckei* Kostermans and *A. rosaeodora* Ducke.[1] The third compound, greenish yellow crystals, $C_{14}H_{12}O_3$, m.p. 138–140°, appeared to be new. Its ultraviolet and infrared spectra were notably similar to those of 4-methoxyparacotoin and anibine.[1] The presence of a δ-lactone ring was therefore assumed likely. In fact, the substance showed reactions in every way analogous to the pyrones from rosewood. Oxidation with permanganate yielded benzoic acid; when boiled with alkali, cinnamic acid resulted. At room temperature, the compound dissolved in ethanolic potassium hydroxide and from the yellow solution crystals of a dipotassium salt slowly separated out. The infrared spectrum of this salt closely resembles that of the analogous salts from anibine and 4-methoxyparacotoin; the formation of all these salts takes place with loss of the methoxyl group present in the original compounds. Acidification of the potassium salt yielded a yellow degradation product, $C_{12}H_{12}O_2$, m.p. 85°. This was evidently a product of decarboxylation, as indicated not only by the molecular formula, but also by the infrared spectrum, which was again similar to those of the β-diketones, the corresponding degradation products of the two mentioned pyrones. One characteristic feature in the infrared was a strong band at 6.03 μ, persisting through the whole degradation, and presumably indicating the presence of a carbon-carbon double bond. Subsequently, the degradation product $C_{12}H_{12}O_2$ was identified as cinnamoylacetone by comparison with a synthetic specimen.

These data allow the establishment of structure I, 4-methoxy-6-(β-styryl)-α-pyrone, for the new compound from *Aniba firmula.*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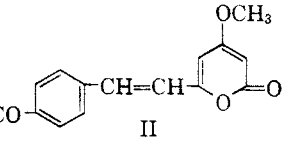
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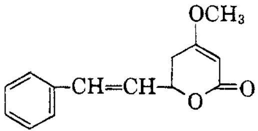
III

A search of the literature showed that the formulated substance had been synthesized by Z. Macierewicz in 1939.[5] Through the courtesy of Dr. Stefania Drabarek, University of Warsaw, we came into possession of a sample of the synthetic compound. The two substances proved to be identical.

This substance, now isolated for the first time from a natural source, is related not only to the

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[1] W. B. Mors, O. R. Gottlieb, and C. Djerassi, *J. Am. Chem. Soc.*, **79**, 4507 (1957).

[2] O. R. Gottlieb and W. B. Mors, *J. Am. Chem. Soc.*, **80**, 2263 (1958).

[3] Other popular names are *canela rosa* and *canela sassafrás*. This latter name should not be confused with the North American sassafras, *Sassafras albidum* (Nutt.) Nees, nor with the Brazilian sassafras of commerce, *Ocotea pretiosa* (Nees) Mez, which belong to the same family. *Aniba fragrans* Ducke (popular name *macacaporanga*), a species restricted to a small area in the Lower Amazon Basin [*A.* Ducke, *Arq. Jard. Bot. Rio de Janeiro,* **4**, 189 (1925); *Anais da Primeira Reunião Sul-Americana de Botânica* (*Rio de Janeiro*), **3**, 59 (1938)], is considered by Kostermans to be identical with *A. firmula*. A chemical examination of this disputed species is planned.

[4] A. J. G. H. Kostermans, Revision of the *Lauraceae. V.*, *Rec. trav. bot. neerl.*, **35**, 921 (1938). Recently material has been collected even in the state of Santa Catarina (I. de Vattimo, private communication).

[5] Z. Macierewicz, *Sprawozdania Posiedzén Towarz. Nauk. Warszaw. Wydział III. Nauk. Mat. Fiz.*, **32**, 37 (1939); *Roczniki Chem.*, **24**, 144 (1950).

arylpyrones from rosewood and the *coto* barks,[1] but also to the styrylypyrone yangonin (II)[6] and the styryldihydropyrones methysticin[7] and kavain (III)[8] from *kava* root (*Piper methysticum* Forst., family *Piperaceae*). Thus I becomes 5,6-dehydrokavain.

EXPERIMENTAL[9]

Extraction procedure. The wood was reduced to sawdust and then extracted exhaustively with benzene in a Soxhlet apparatus. After concentration, a small quantity of basic material was removed with dilute hydrochloric acid.

Benzoic acid. The benzene solution was next extracted several times with aqueous sodium bicarbonate. Acidification yielded a precipitate which was separated and dried. Vacuum sublimation yielded colorless crystals, m.p. 121–122°, identified as benzoic acid by mixture melting point and infrared spectral comparison with an authentic sample.

A small additional amount of acidic material was extracted with 3% aqueous sodium hydroxide, but was not further investigated.

Essential oil. The remaining benzene solution was evaporated and the semisolid residue exhaustively extracted with boiling petroleum ether. This procedure removed an essential oil in 1.3% yield calculated on the extracted wood.

5,6-Dehydrokavain (I) *and 4-methoxyparacotoin.* The residue insoluble in petroleum ether was dissolved in benzene and chromatographed on alkaline alumina. Elution with benzene yielded first 5,6-dehydrokavain (I) (yield 0.5%) and subsequently 4-methoxyparacotoin (yield 0.2%). The latter substance was crystallized from ethanol. Colorless needles, m.p. 222–224°. Its identity was established by comparison (mixture melting point and infrared spectrum) with a specimen of 4-methoxyparacotoin from *Aniba Duckei*.

Compound (I) was crystallized from ethanol and purified by sublimation *in vacuo*. Greenish yellow crystals, m.p. 138–140°, $[\alpha]_D$ 0° (c, 4 in $CHCl_3$,c); $\lambda_{max}^{CHCl_3}$ 5.80, 6.02, 6.15, 6.38μ; λ_{max}^{EtOH} 230 mμ (log ε 4.13), 255 mμ (log ε 4.10), 343 mμ (log ε 4.37); λ_{min}^{EtOH} 245 mμ (log ε 3.92), 275 mμ (log ε 3.72).

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30; one OCH_3, 13.60. Found: C, 73.18; H, 5.20; OCH_3, 13.71.

Oxidation of 5,6-dehydrokavain (I) (123 mg.) with potassium permanganate in acetone at room temperature yielded benzoic acid (40 mg.), purified by vacuum sublimation, m.p. 122°, identified by mixture melting point and infrared spectral comparison with an authentic sample.

Alkaline cleavage of 5,6-dehydrokavain (I). (*a*) *With boiling alkali.* A solution of 198 mg. of 5,6-dehydrokavain (I) in 20 ml. of 0.5 *N* aqueous ethanolic potassium hydroxide were heated under reflux for 3 hr. After dilution with water, chloroform removed 75 mg. of an oil. The liquid was then acidified and again extracted with chloroform. Evaporation of the solvent left 44 mg. of a slightly yellow, crystalline mass. Recrystallization from petroleum ether–chloroform (1:1) and subsequent sublimation *in vacuo* yielded colorless crystals of cinnamic acid, m.p. 131–133°, proved to be identical by mixture melting point determination and infrared comparison with an authentic specimen.

(*b*) *At room temperature.* A solution of 200 mg. of 5,6-dehydrokavain (I) was left at room temperature in 35 ml. of 1*N* ethanolic potassium hydroxide. After 2 hr., crystals began separating out, increasing slowly in quantity with time. They were filtered off after 18 hr. and washed with absolute ethanol yielding 104 mg. yellow crystals, m.p. 230° dec.; λ_{max}^{Nujol} 6.04, 6.23μ.

Anal. Calcd. for $C_{13}H_{10}O_4K_2$: K, 25.36. Found: K, 26.11; OCH_3, 0.00.

Acid degradation. A solution of 250 mg. of the potassium salt in 5 ml. of water was acidified with a few drops of hydrochloric acid. The resulting yellow precipitate (96 mg.) of cinnamoylacetone was filtered and crystallized from aqueous ethanol affording yellow crystals, m.p. 85°. $\lambda_{max}^{CHCl_3}$ 6.02, 5.28μ.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.07; H, 6.46.

Identity with a synthetic specimen of cinnamoylacetone prepared by condensation of ethyl cinnamate and acetone in ether solution in the presence of sodium,[10] was established by direct comparison (mixture melting point and infrared spectrum).

Comparison of natural and synthetic 5,6-dehydrokavain. Mixture melting point determination showed no depression and the ultraviolet and infrared spectra of the two samples were superimposable.

Acknowledgments. We wish to pay tribute to the late Dr. J. G. Kuhlmann, notable Brazilian botanist, who did not live to see this work concluded. Our first material of *Aniba firmula* was collected at his suggestion and was identified by him. We are also grateful to Dr. Paulo Agostinho Matos Araujo, chief of the Section of Wood Technology, Forest Service, Ministry of Agriculture, who supplied us with additional wood samples. Recognition is due to Dr. Ida de Vattimo, Botanical Garden, Rio de Janeiro, for her orientation in the botanical aspects pertaining to the family *Lauraceae*. We are indebted to Dr. Stefania Drabarek, University Warsaw, for a generous sample of synthetic 4-methoxy-6-(β-styryl)-α-pyrone as well as for reprints of the Polish papers. Finally, we wish to express our appreciation to the Conselho Nacional de Pesquisas, Brazil, for financial aid.

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(6) I. Chmielewska and J. Cieślak, *Roczniki Chem.*, **28**, 38 (1954).

(7) W. Borsche, C. H. Meyer, and W. Peitzsch, *Ber.*, **60**, 2113 (1927).

(8) W. Borsche and W. Peitzsch, *Ber.*, **63**, 2414 (1930).

(9) All melting points were determined on the Kofler block. Ultraviolet spectral measurements were performed with a Beckman model DU spectrophotometer. We are indebted to Mrs. Dolores Phillips and Miss Birgitte Bach, Spectrophotometric Laboratory, Wayne State University, Detroit, Mich., for the infrared spectral measurements and to Dr. A. Bernhardt, Mühlheim, Germany, for the microanalyses.

(10) H. Ryan and J. M. Dunlea, *Proc. Roy. Irish Acad.*, **32**, 1 (1913); *Chem. Abstr.*, **8**, 1106 (1914).