

times for compounds injected singly and in solutions permitted unambiguous identification. Ratios of retention times show that the partitioning liquid is affecting separation although the brick support itself exhibits some selectivity.

Elimination of the inert carrier gas is potentially useful in non-analytical applications of gas chromatography. The method is a unique way of using relatively high molecular weight carrier gases.

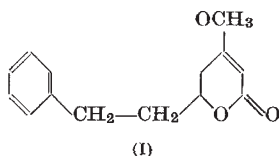
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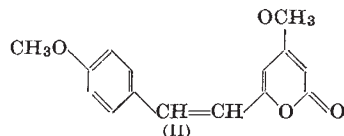
¹ Porter, R. S., and Johnson, J. F., *Nature*, **183**, 391 (1959).

A New Carbonyl Compound from *Piper methysticum* Forst.

THE rhizomes of *Piper methysticum* Forst. are the raw material from which the Polynesians and other Pacific island peoples prepare their ceremonial (and soporific) beverage 'awa (also known as kawa of kava-kava). The chemical constituents of 'awa root were first studied over a hundred years ago, but the most extensive investigation was carried out by Borsche and co-workers¹ some thirty years ago. While Borsche established the structure of several constituents, none of these compounds, curiously enough, was found to possess physiological activity. This negative result led to the surmise that activity is perhaps introduced during the preparation of the drink which involved chewing of the root². Van Veen³ in 1938 showed that a substance, marindinin, was responsible for the drug action of 'awa. Marindinin, however, was later shown to be identical with Borsche's dihydrokawain⁴ (I), a substance previously found to have no physiological activity⁵.

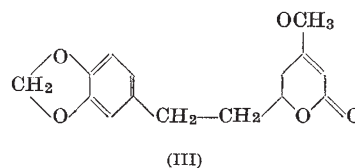


The unresolved state in which this problem had remained for many years induced us some time ago to initiate a chemical re-investigation. The recent upsurge of interest in 'awa originating from several laboratories⁶⁻⁸ prompts us to report our preliminary findings at this time. The Polish workers⁶ re-investigated one of Borsche's compounds, yangonin, and corrected its structure from a γ -pyrone to an α -pyrone (II). The German workers⁷ established for the first



time beyond doubt that the 'awa constituent dihydro-methysticin (III) possesses sedative activity. The Riker group⁸ substantiated this finding and in addition isolated a new substance designated 'compound A' of empirical composition $C_{14}H_{12}O_3$.

In our work 'awa root was dried, milled and extracted in a Soxhlet with ethanol for 31 hours.



(The material was collected by Dr. C. E. Swanholm of this Laboratory at Waihole, Island of Oahu, and its identity was established by comparison with an authentic specimen in the Bernice P. Bishop Museum collection.) The solid residue after evaporation of the solvent *in vacuo* was refluxed with ether and filtered while warm to remove insoluble material. Upon cooling of the ethereal solution a yellow solid separated. This solid after two recrystallizations from ethanol melted at 115–118° C. and was found to be identical with dihydromethysticin (III) by comparison with the published information on this compound and by elemental analysis (performed by Dr. A. Bernhardt, Mülheim, Germany). The infra-red spectrum (Nujol mull) of (III) exhibited the bands reported by the Riker group⁸ as well as a series of bands at 8–11 μ characteristic for the dioxymethylene grouping⁹.

The ethereal mother liquor from which dihydro-methysticin had been removed was washed successively with acid and base and the ether was removed *in vacuo*. The resulting residue was dissolved in methanol and treated with Girard's reagent *T* according to Vogel's¹⁰ procedure. The resulting carbonyl components were distilled, yielding as the major fraction a yellow oil, b.p. 104° C./0.4 mm. From spectral considerations this oil appeared to contain a dioxymethylene grouping and a carbonyl function conjugated with olefinic unsaturation. A crystalline 2,4-dinitrophenylhydrazone of this oil melted at 204–207° C. (from ethyl acetate). Its infra-red spectrum agreed with previously made assignments of functional groups. The combustion analysis of the derivative supported an empirical composition of $C_{11}H_{10}O_3$, although this formulation cannot be considered entirely established.

Further work on this and other minor constituents of *P. methysticum* is in progress. In this connexion it is worth noting that recent work in this laboratory¹ established the presence of alkaloids in this plant to the extent of 0.012 per cent (based on dry root). This finding is in fair agreement with an earlier alkaloid report¹².

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¹ Borsche, W., and Lewinsohn, M., *Chem. Ber.*, **66**, 1792 (1933).

² Titcomb, M., *J. Polynesian Soc.*, **57**, 105 (1948).

³ Van Veen, A. G., *Geneeskundig Tijdschr. Nederland. Indie* **78**, 1941 (1938).

⁴ Van Veen, A. G., *Rec. trav. chim.*, **58**, 521 (1939).

⁵ Borsche, W., and Blount, B. K., *Chem. Ber.*, **66**, 803 (1933).

⁶ Chmielewska, I., Ciślak, J., Górczyńska, K., Kontnik, B., and Pitakowska, K., *Tetrahedron*, **4**, 36 (1958).

⁷ Hänsel, R., and Beiersdorff, H. U., *Naturwiss.*, **45**, 573 (1958).

⁸ Klohs, M. W., Keller, F., Williams, R. E., Toekes, M. I., and Cronheim, G. E., *J. Med. Pharm. Chem.*, **1**, 95 (1959).

⁹ Briggs, L. H., Colebrook, I. D., Fales, H. M., and Wildman, W. C., *Anal. Chem.*, **29**, 904 (1957).

¹⁰ Vogel, I., "A Textbook of Practical Organic Chemistry", 3rd ed., p. 977 (London, 1956).

¹¹ Swanholm, C. E., St. John, H., and Scheuer, P. J., *Pacific Sci.* (in the press).

¹² Winzheimer, E., *Arch. Pharm.*, **246**, 338 (1908); *Chem. Abst.*, **3**, 429 (1909).