

It was of interest to determine what effect the type of strain present in norbornylene exerted upon the dipole moment. The moment was therefore measured in the customary way in heptane solution, and it was found to have the value of 0.40 D. This value may be compared with those found for the ordinary *cis* olefins cyclooctene<sup>5</sup> (0.43 D) and cyclodecene<sup>7</sup> (0.44 D). Clearly the strain in the norbornylene case, which although considerable in terms of energy,<sup>8</sup> is inconsequential in its effect on the dipole moment.

The calculation of a dipole moment from dielectric constant measurements is a tedious process with a desk calculator. If six or seven experimental measurements are taken, the whole calculation, including rechecking and correcting of errors requires the better part of a day. We have therefore applied automatic computing methods, utilizing an IBM 650 computer, to the solution of this problem. Large digital computers of this general class are now rather generally available, and are ideally suited to solving lengthy problems of this kind. Advances in automatic programming made in the last few years now make it possible for the average chemist to program and use such a computer with much less difficulty than is commonly supposed. The program was first prepared and checked by calculating known moments from available data. To calculate a dipole moment now that the program is available, the experimental data (weights, dielectric constants, *etc.*) are put directly onto punched cards, which takes about 15 min. The computer is then able to read the program and data cards, do the calculations, including the two least squares fittings, and punch out all of the desired data ( $N_2$ ,  $d_{1,2}$ ,  $\epsilon_{1,2}$ ,  $P_{2\infty}$ , and  $\mu$ ) in about 3 min.

#### EXPERIMENTAL

**Materials.** The norbornylene (obtained from the reaction of ethylene with dicyclopentadiene<sup>9</sup>) was redistilled before use, b.p. 97°, m.p. 44.0–44.5° (sealed capillary). The heptane solvent was purified as described earlier.<sup>8</sup> The apparatus used for the dielectric constant measurements has been described.<sup>10</sup>

**Calculations.** The general procedure of Halverstadt and Kumler<sup>11</sup> as described earlier<sup>7</sup> was used as the basis for the program. The program was initially written in the RUNCIBLE<sup>12</sup> language. This program was translated by RUNCIBLE into the SOAP<sup>13</sup> input program, which was in turn converted by SOAP to the machine language program in the usual way.<sup>14</sup>

(7) N. L. Allinger, *J. Am. Chem. Soc.*, **79**, 3443 (1957).

(8) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

(9) J. Meinwald and N. J. Hudak, *Org. Syntheses*, **37**, 65 (1957).

(10) M. T. Rogers, *J. Am. Chem. Soc.*, **77**, 3681 (1955).

(11) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(12) "Revised Unified New Compiler with IT Basic Language Extended."

(13) "Standard Optimum Assembly Program."

(14) RUNCIBLE I, Computing Center, Case Institute of Technology, Cleveland, Ohio, 1958.

The actual experimental data, the weight of the empty flask, flask plus sample, flask plus sample plus solvent, cell constant, condenser correction, absolute temperature, and so on were placed on punched cards. The program and data were then run into the computer. The program instructed the computer to read the data and calculate  $N_2$ ,  $d_{1,2}$ , and  $\epsilon_{1,2}$  and then calculate from these quantities  $d_1$ ,  $\epsilon_1$ ,  $\alpha$  and  $\beta$  by the method of least squares. After these least squares lines were available, the computer continued by testing the experimental points against the least squares lines and it would have discarded any point which was further from the line than an amount  $\delta$ .

A new line would then have been calculated omitting these discarded points. The value of  $\delta$  was introduced into the computer as data, and so may be varied from one calculation to the next. In this particular case the points were all within 0.0002 in mole fraction of the  $N_2$  vs.  $d_{1,2}$  line and within 0.0004 in dielectric constant of the  $\epsilon_{1,2}$  vs.  $N_2$  line, hence none were discarded. The probable error in the moment is estimated at 0.05 D. The computer then continued by calculating A, B, and C, and then  $P_{2\infty}$ . The molar refractivity, calculated by hand from tables,<sup>15</sup> was inserted into the computer with the data. (Atomic polarization was neglected. In other cases it could be inserted with the molar refractivity if desired.) The moment was then calculated, and all of the desired quantities were punched by the computer as output. The output data are listed in Table II.

TABLE II  
DIPOLE MOMENT DATA FOR NORBORNYLENE IN HEPTANE  
AT 25°C.

$N_2$	$d_{1,2}$	$\epsilon_{1,2}$
0.0239207	0.680836	1.9141
0.0201392	0.680294	1.9126
0.0144320	0.679471	1.9117
0.0101019	0.678902	1.9099
0.0026978	0.677821	1.9081
0.0000000	0.677423	1.9077
$\alpha = 0.26746$	$\beta = 0.14122$	$\epsilon_{1,2} = 1.9075$
$d_1 = 0.677447$	$P_{2\infty} = 32.889$	$\mu = 0.398D$

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(15) J. A. Leermakers and A. Weissberger, in H. Gilman, "Organic Chemistry," Vol. II, Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1947, p. 1751.

#### Identity of Compound A from Kava Root with 5,6-Dehydrokavain

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We established the structure 4-methoxy-6-( $\beta$ -styryl)- $\alpha$ -pyrone for a compound isolated from the

wood of *Aniba firmula* (Nees et Mart.) Mez (family Lauraceae).<sup>1</sup> Simple 6-substituted 4-methoxy- $\alpha$ -pyrones seem to be quite rare in nature. Before our work on South American *Aniba* species<sup>2</sup> only the Polynesian kava root, *Piper methysticum* Forst. (family Piperaceae), had been known to contain representatives of this class of compounds.<sup>3</sup> One of them is kavain, 4-methoxy-6-( $\beta$ -styryl)-5,6-dihydro- $\alpha$ -pyrone, from which we derived the name 5,6-dehydrokavain for the substance isolated from *Aniba firmula*.

Recently Klohs *et al.*<sup>4</sup> re-examined the extractives of kava root and, in addition to the already known constituents, isolated a new, optically inactive substance, m.p. 138–139°, which they designated compound A. The formula C<sub>14</sub>H<sub>12</sub>O<sub>3</sub> was assigned to it and ultraviolet and infrared spectra were determined. All their data are in exact agreement with those of our substance from *Aniba firmula*.<sup>1</sup> Direct comparison by mixture melting point and infrared spectral comparison of 5,6-dehydrokavain with a sample of compound A kindly supplied by Dr. M. W. Klohs, Riker Laboratories, Inc., Northridge, Calif., confirmed the identity of the two substances.

It is interesting to recall that this substance, 4-

methoxy-6-( $\beta$ -styryl)- $\alpha$ -pyrone, was synthesized 20 years ago by Macierewicz<sup>5</sup> as a model compound for yangonin. Later, Chmielewska and Cieślak<sup>6</sup> proved the correct structure of yangonin to be its simple derivative 4-methoxy-6-(p-methoxy- $\beta$ -styryl)- $\alpha$ -pyrone and not a  $\gamma$ -pyrone as previously admitted.<sup>7</sup>

Among the different constituents of kava root, whose pharmacological investigation was undertaken by Klohs *et al.*,<sup>4</sup> yangonin and compound A fall distinctly into a separate class. Contrary to the four other compounds tested, they did not antagonize clonic strychnine convulsions and death in mice, or potentiate sodium pentobarbital-induced sleeping time. The identity of compound A having been established, it becomes among the members of the group the only one which shares with yangonin the true pyrone structure (the others being dihydropyrones). The observed effects on the central nervous system can thus be associated with a definite structural feature of these constituents of kava root.

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(1) O. R. Gottlieb and W. B. Mors, *J. Org. Chem.*, **24**, 17 (1959); preliminary note in *Anais acad. brasil. ciênc.*, **30**, 527 (1958).

(2) See also W. B. Mors, O. R. Gottlieb and C. Djerassi, *J. Am. Chem. Soc.*, **79**, 4507 (1957); O. R. Gottlieb, M. T. Magalhães and W. B. Mors, *Tetrahedron Letters*, **1959**; *Anais assoc. brasil. quim.*, **18**, 37 (1959).

(3) W. Borsche and M. Lewinsohn, *Ber.*, **66**, 1792 (1933) and preceding papers of the series.

(4) M. W. Klohs, F. Keller, R. E. Williams, M. I. Toekes and G. E. Cronheim, *Journal of Medicinal and Pharmaceutical Chemistry*, **1**, 95 (1959).

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

(6) I. Chmielewska and J. Cieślak, *Roczniki Chem.*, **28**, 38 (1954); I. Chmielewska, J. Cieślak, K. Gorczyńska, B. Kontnik, and K. Pitakowska, *Tetrahedron*, **4**, 36 (1958).

(7) For a complete historical background, see D. Herbst, W. B. Mors, O. R. Gottlieb, and C. Djerassi, *J. Am. Chem. Soc.*, **81**, 2427 (1959).