(1)

addition we have obtained further proof of the structure of this acid by the isolation of geronic acid (as its semicarbazone) in 34 per cent yield on ozonolysis, and by a quantitative hydrogenation (3·9 ethylenic bonds.)

Arens and van Dorp obtained the expected hydroxy-ester as the main product of their Reformatsky reaction and partially converted it into the ester of (I) by dehydration with anhydrous oxalic acid. In our experience the deliberate dehydration procedure is unnecessary, hydrolysis of the crude product either before or after distillation at $10^{-2}$ mm. giving material from which the fully conjugated acid (I) is readily isolated.

Although methyl sorbate can be brominated readily with N-bromosuccinimide to the ω-*bromo-ester*, numerous attempts to condense this vinylogue of the ω-bromocrotonate, with β-ionone, have failed completely to give any of the desired ester of the $C_{19}$ acid. It had been intended to extend the synthesis, by using the ω-bromo-methylsorbate, to obtain the $C_{20}$ acid corresponding to vitamin A.

We have converted the acid (I) into its *chloride* and at the present time the reaction of this substance with cadmium dimethyl is being studied. At the same time work is in progress on the condensation of the acyclic $C_{14}$ and $C_{15}$ aldehydes[2,3] with ω-bromocrotonate, and the related $C_{17}$ and $C_{18}$ ketones[3] with bromoacetate, in attempts to obtain acyclic acids related to vitamin $A_2$ on the assumption that vitamin $A_2$ is the lycopene analogue of vitamin A[4].

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## Absorption of Basic Dyes by Jute

IT is well known that jute fibre has a strong natural affinity for basic dyes. This was formerly ascribed to the presence of tannins in the fibre[1]. Analysis of a fairly large number of jute samples of different qualities in this Laboratory has shown that though the plant contains some tannin, the retted fibre is practically free from it. According to Chowdhury and Mitra[2], acid constituents of the fibre, such as uronic acids, are responsible for this affinity. Some attribute it to the presence of lignin in the fibre. According to Parsons[3], for example, "delignified jute no longer has this property". The same statement also occurs in the latest edition of Whittaker's book[4]. Correct information in this regard is very important from the industrial point of view, for basic dyes are extensively used in dyeing jute, and if lignin be really the cause of absorption, fully bleached jute would not take up the dye unless mordanted.

In the course of our work on the isolation of cellulose from jute fibre, it has been observed that jute, completely delignified by means of sodium chlorite, absorbs, under identical conditions, practically the same amount of methylene blue as the original fibre. Further work has revealed that jute, delignified by different methods, behaves more or less similarly so far as the absorption of basic dyes is concerned. Some of the results of dye absorption measurements are shown below. Exhaustion of the dye-bath was determined colorimetrically, using a Kleet colorimeter of the Duboscq type. The figures given in the table do not, however, represent the equilibrium absorption values which are, in all cases, considerably higher (in the case of raw jute and chlorite cellulose, the values are 21·33 and 32·9 respectively). The details of these experiments will be published elsewhere.

| Sample | | Dye absorption (millimoles/100 gm.) |
| --- | --- | --- |
| Raw jute, defatted | .. .. | 5·51 |
| Cross and Bevan cellulose | | 5·13 |
| Norman and Jenkins's „ | .. | 5·73 |
| Chlorine dioxide „ | .. | 5·49 |
| Sodium chlorite „ | .. | 5·44 |
| Filter Paper (Whatman No. 42) | .. | 1·45 |

(Fibre-liquor ratio = 1 : 50 ; pure methylene blue (Grübler) in millimolar solution (unbuffered) ; temperature, 22–25° C. ; time, 2 hr.)

Even alpha-cellulose, prepared from any of these celluloses, absorbs a considerable amount of basic dyes (4·41 millimoles methylene blue per 100 gm.). Malachite green and acriflavine give similar results.

It would appear, therefore, that the presence of lignin is not responsible for the high absorption of basic dyes by jute. As regards the composition of the cellulose obtained by different methods, it has been shown[5] that, unlike other reagents, sodium chlorite removes no important constituent besides lignin.

The ash alkalinity (milliequivalents of acid required to neutralize ash obtained from 100 gm. of the bone-dry material) of jute fibre is high—11·07 for the fibre used in these experiments—but this does not appear to be related directly to the absorption of basic dyes. When this figure is reduced to 0·73 by treatment with deci-normal hydrochloric acid at room temperature, the dye absorption value remains practically unchanged. The acid value (milliequivalents of alkali required to neutralize the acid liberated from 100 gm. of the bone-dry material) of the cation-free fibre, or cellulose prepared therefrom, appears to be connected with the absorption of basic dyes. Work in this direction is in progress.

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## The Two Heats of Atomization of Carbon

IN a recent communication, Sidgwick and Springall[1] have referred to the current division of opinion between two different values for the heat of atomization of carbon, and the apparent support for the higher value (∼ 170 kcal./gm.-atom) forthcoming from the figures they calculate for the energies of the Hg—C links in $HgMe_2$, $HgEt_2$ and $HgPh_2$.

In calculating these energy values, the heat of atomization of carbon into the ground, or $^3P$, state was employed, that is, the quantity Herzberg[2] has termed $L_1$. This procedure is justifiable only for compounds containing divalent carbon, it having been pointed out twelve years ago[3] that the imaginary dissociation of organic molecules into atoms normally leads to carbon atoms in the $^5S$ state (that is, the lowest energy-level corresponding to tetravalence), and that the energy difference between the $^5S$ and $^3P$ states must be taken into consideration when calculating the energies of carbon links for compounds in which the carbon is tetravalent. Neglect to consider the excitation energy of the $^5S$ state is mainly responsible for the apparent conflict in experimental values and the state of confusion that at present dominates the thermochemistry of carbon, failure to distinguish between bond energies and energies of dissociation being a subsidiary cause.

This subject is fully reviewed by us in a forthcoming paper in which it is shown that virtually all experimental quantities can be brought into alignment. Consideration of the energies required to remove a hydrogen atom from molecules of methane and ethane, and of the energies of reorganisation of the resulting radicals, indicates that the heat of sublimation of carbon into free atoms in the $^5S$ state is of the order 190 kcal./gm.-atom. With certain tacit assumptions, Cherton[4] has independently deduced the same figure from a spectroscopic study of acetylene. This quantity, which we have termed $L_2$, leads in turn to a satisfactory assignment of values to the strengths of carbon bonds, including the more reasonable value ∼ 22 kcal. for the Hg—C link in $HgMe_2$, it being assumed that the mean C—H bond energies in ethane and $HgMe_2$ are not widely different. The excitation energy of $^5S$ carbon has not been experimentally determined, but there is strong chemical evidence for believing the estimate of 100 kcal. by Bacher and Goudsmit[5] to be roughly 50 per cent in excess of the true value.

In the light of the foregoing, there remains no sound evidence to support $D(CO) = 11·11$ eV. and $L_1 = 170$ kcal., the arguments of Kynch and Penney[6] in favour of these values being based on false premises, including the tacit assumption that the $^3P$ and $^5S$ states of carbon are at one and the same energy-level : and the recent speculations of Gaydon and Penney[7] are vitiated by the employment of this erroneous figure for $D(CO)$. By far the most probable value for $L_1$ remains Herzberg's figure, 125 kcal. (corresponding to $D(CO) = 9·14$ eV.), which at least must be regarded as being of the right order.

Direct measurement of the equilibrium conditions obtaining at the triple point of carbon[8] provides excellent confirmation of this figure, as can be demonstrated by reference to the hypothetical curves of Goldfinger and Jeunehomme[9], whereas the observed vapour pressure is several hundred times larger than that necessitated by $L_1 = 170$ kcal. Moreover, to Herzberg's additional arguments[10] must be added other supporting considerations dealt with in our paper.

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