

2. 5-Acetyl-8-hydroxyquinoline oxime on treatment either with thionyl chloride or with concd. sulfuric acid gives 5-acetamino-8-hydroxyquinoline.

TOKYO, JAPAN

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[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, MARBURG A. L., GERMANY]

## THE TITRIMETRIC AND SPECTROMETRIC ANALYSIS OF KETO-ENOL MIXTURES. ALPHA-PHENYLACETOACETIC ESTER

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In a recent paper<sup>1</sup> on the keto-enol equilibrium in  $\alpha$ -phenylacetoacetic ester, Post and Michalek have attempted to determine the percentage of the enolic modification, both titrimetrically and spectrometrically. Indirect titration with bromine, by the Kurt Meyer method, gave them an average value of 28.6% of enol, whereas, from its molecular refraction, they calculate the impossible value of 137.13%, which they attribute to the "anomalous" structure of the phenyl group.

These authors also mention, incidentally, that from its molecular refraction the enol content of the unsubstituted acetoacetic ester is 59.2%, whereas, according to the bromine titrations, it contains only 7.7%.

These statements make it appear that spectrochemistry would lead to entirely false results with substances of this type and would not be useful for the analysis of keto-enol mixtures.

However, these authors have overlooked the fact that this problem of the apparent contradiction between the results of the bromine titrations and those of spectrochemistry has long since been investigated and explained.<sup>2</sup>

It has been found that both methods in reality give results which are in sufficient agreement, if certain well-known spectrochemical regularities are correctly taken into account.

Post and Michalek<sup>3</sup> arrive at their values for the enol content by comparing the experimental molecular refraction with the values which they calculate, theoretically, on the basis of atomic refractions. By this procedure, however, correct values are obtained only for the keto forms; those for the enol forms are too low. The molecules of the enolic acetoacetic ester contain a conjugated system of double bonds, the exaltation of which is increased by the hydroxyl group attached to it,<sup>4</sup> since the partial valences

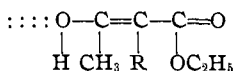
<sup>1</sup> Post and Michalek, *THIS JOURNAL*, **52**, 4358 (1930).

<sup>2</sup> K. v. Auwers, *Ann.*, **415**, 169 (1918); K. v. Auwers and H. Jacobsen, *ibid.*, **426**, 161 (1921).

<sup>3</sup> Post and Michalek state erroneously that their values have been calculated with the old Brühl refraction equivalents, whereas they have actually used the new Eisenlohr values. It may be mentioned, incidentally, that the accompanying reference number 9, as well as numbers 5 and 7 are not apropos.

<sup>4</sup> K. v. Auwers, *Ber.*, **44**, 3514 (1911).

of the oxygen atom, together with the double bond, form a sort of "cumulative" conjugation, as can be seen from the formula



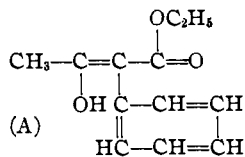
It has been previously shown<sup>5</sup> that by considering all the factors that should be taken into account, the molecular refraction for 100% enolic acetoacetic ester is calculated to be 34.42 instead of 32.62, and this value coincides exactly with the results of Knorr's observations. Furthermore, it has been shown that, according to its molecular refraction, the enol content of the equilibrium ester is 8%, which is in excellent agreement with the titrimetrically determined value. Therefore there is no contradiction, in this case, between the two methods.

**$\alpha$ -Phenylacetoacetic Ester.**—Post and Michalek calculate the enol content of this compound, refractometrically, from the following figures.

| 100% Ketone (calcd.) | Found | 100% Enol          |
|----------------------|-------|--------------------|
| 55.66                | 57.10 | 56.71 <sup>6</sup> |

The third of these figures is, for the reasons previously given, too low. The correct value for the molecular refraction can be approximated with a sort of accuracy by taking into account the following facts.

The specific exaltation of  $\beta$ -hydroxycrotonic ester, *i. e.*, the pure enol of acetoacetic ester, has been found to be +1.38. However, substituents introduced into a conjugated system exert an influence on its spectrochemical behavior. The  $\alpha$ -phenylacetoacetic ester molecule contains a "crossed" conjugation, as shown by the structural formula (A).



The optical activity of a crossed conjugation, compared to that of a simple conjugation, varies both according to the nature of the parent system and the kind of "disturbing" substituent. In the case under consideration it can be concluded from analogies, which will not be discussed here, that the specific exaltation of the phenylated acetoacetic ester will be approximately as great as that of the parent substance, or at least will not be greater, and probably will be somewhat smaller. Assuming the two to be equal, the molecular exaltation of the pure enol of phenylacetoacetic ester is +2.84, *i. e.*, the molecular refraction of this substance is not 56.71 but 59.56. Then it follows from Post and Michalek's experimental value that the equilibrium ester contains 36.6% enol and not 137.13%.

This value is about 10% higher than those determined titrimetrically by other authors, for their observations yield an average of 26.8%.<sup>7</sup>

<sup>5</sup> K. v. Auwers, Ref. 4, p. 3530.

<sup>6</sup> The actual values are 55.68 and 56.72.

<sup>7</sup> Post and Michalek calculate, from their investigations, the somewhat higher value of 28.6%.

The difference might mean that the specific exaltation of the phenyl derivative is not equal to that of the parent substance, as assumed; but then it would follow, from the amount of enol which the authors found titrimetrically, that the specific exaltation of the enol of phenylacetoacetic ester, is higher than that of the enol of acetoacetic ester, and therefore that the exalting effect of the crossed conjugated systems is greater than that of simple conjugations. This is, however, in the light of previous spectrochemical experience, unlikely.

Therefore it is necessary to consider the possibility that the indirect bromine titration of  $\alpha$ -phenylacetoacetic ester results in too low values, for this has already been established with certainty for various sorts of substances containing the atomic arrangement<sup>8</sup> —C=C—C=O.



In order to clear this up, I have repeated, in collaboration with Dr. E. Wolter, to whom I extend my sincere thanks for his valuable assistance, the spectrometric and titrimetric investigation of  $\alpha$ -phenylacetoacetic ester.

We used both a collection preparation, which was redistilled, and a preparation that was freshly made according to Dimroth and Feuchter's modified directions<sup>9</sup> of Beckh's method.<sup>10</sup> Both preparations had the same properties; they boiled at 141° under a pressure of 9 mm.

#### SPECTROCHEMICAL CONSTANTS

$d_4^{16.5}$  1.08915;  $d_4^{20}$  1.086;  $n_D^{16.5}$  1.51065;  $n_{\text{He}}^{16.5}$  1.51513;  $n_D^{16.5}$  1.52630;  $n_{\gamma}^{16.5}$  1.53610;  
 $n_{\text{He}}^{20}$  1.5136

| Calculated for.....  | $M_\alpha$ | $M_D$ | $M_\beta - M_\alpha$ | $M_\gamma - M_\alpha$ |
|--|------------|-------|----------------------|-----------------------|
| $\text{C}_{12}\text{H}_{14}\text{O} < \text{O}_2 \sqrt[3]{3}$ (206.11) | 55.32      | 55.68 | 1.16                 | 1.86                  |
| Found  | 56.66      | 57.08 | 1.45                 | 2.36                  |
| M. E.  | +1.34      | +1.40 | +0.29                | +0.50                 |
| Sp. E.   | +0.65      | +0.68 | +25%                 | +27%                  |

These data agree satisfactorily with the observations of Post and Michalek; further determinations were therefore considered unnecessary.

**Bromine Titrations.**—The following titrations, for which samples from both preparations were used, were carried out by the indirect method of Kurt Meyer, in Jena glass vessels. The first two trials were heated for twenty minutes after the addition of potassium iodide, numbers III and IV for thirty minutes and numbers V and VI, one hour.

|     | Substance, g. | N/10 $\text{Na}_2\text{S}_2\text{O}_3$ , <sup>a</sup> cc. | Enol, % |
|-----|---------------|---|---------|
| I   | 0.4379        | 16.4  | 38.6    |
| II  | .3458         | 12.8  | 38.1    |
| III | .3732         | 14.3  | 39.5    |

<sup>8</sup> K. v. Auwers and H. Jacobsen, Ref. 2, p. 165.

<sup>9</sup> Dimroth and Feuchter, *ibid.*, 36, 2243 (1903).

<sup>10</sup> Beckh, *Ber.*, 31, 3160 (1898).

|    | Substance, g. | N/10 $\text{Na}_2\text{S}_2\text{O}_8$ , <sup>a</sup> cc. | Enol, % |
|----|---------------|---|---------|
| IV | 0.4379        | 16.5  | 38.8    |
| V  | .4385         | 17.3  | 40.7    |
| VI | .3579         | 13.9  | 40.0    |

<sup>a</sup> These volumes were calculated by means of the factors of the solutions actually used.

It is apparent that the length of heating has no material effect on the result. This means that conversion was, in every case, complete, and therefore that the indirect procedure is applicable to this substance.

In order to be absolutely certain, the enol content was determined directly, in a final experiment, and verified by indirect titration.

VII Subs., 0.2640 g.; N/10 Br,<sup>a</sup> 10 cc. = 39.0% Enol; N/10  $\text{Na}_2\text{S}_2\text{O}_8$ ,<sup>a</sup> 9.9 cc. = 38.7% Enol

The average of all the determinations is 39.2% enol, a value which is approximately that deduced from the refractive index.

It is impossible to state why Post and Michalek found a materially lower value, although their preparation had the same physical constants as that which we investigated. The supposition that in their investigation of the ester it had become more ketonic in alcoholic solution can hardly be correct, for we found the higher values of the enol content, also, when the solutions had stood for several hours or had come to room temperature.

The noteworthy fact that  $\alpha$ -phenylacetoacetic ester enolizes to a much greater extent than  $\alpha$ -alkyl acetoacetic esters<sup>11</sup> can be explained, following Post and Michalek, by the ionizing influence which the phenyl group exerts on the  $\alpha$ -hydrogen atom. It may, however, also be due to the fact that there is present in the enol of that compound the atomic arrangement ( $\text{C}_6\text{H}_5\text{—C=C—}$ ) which is actually characteristic of styrols. It is known that  $\Delta^2$ -styrols,  $\text{C}_6\text{H}_5\text{—C—C=C—}$ , have a tendency to pass over into the  $\Delta^1$ -isomers, whereas a shift of the double bond in the opposite direction does not take place. In contrast to this, in the olefinic acid a mutual inter-conversion of  $\Delta^1$  and  $\Delta^2$  is possible. Therefore the system

$$\begin{array}{c} \text{—C=C—C=O} \\ | \quad | \\ \text{HO} \quad \text{C}_6\text{H}_5 \\ | \quad | \\ \text{—C—C—C=O} \\ || \quad | \\ \text{O} \quad \text{C}_6\text{H}_5 \end{array}$$

will show a stronger resistance to conversion into

$$\begin{array}{c} \text{—C—C—C=O} \\ || \quad | \\ \text{O} \quad \text{C}_6\text{H}_5 \end{array}$$

than the enols of acetoacetic ester and its alkyl derivatives, and this must result in an increase in the enol content of the equilibrium ester.

### Summary

1. The rule that titrimetric and spectrometric determinations of the enol content of tautomeric mixtures gives results in satisfactory agreement holds also for  $\alpha$ -phenylacetoacetic ester.

<sup>11</sup> Dieckmann [*Ber.*, 55, 2476 (1922)] has already pointed out the high "enol constants" of phenyl derivatives.

2. Titrimetrically, the enol content of this substance is found to be 39.2% and spectrometrically 36–37%, therefore materially higher than for  $\alpha$ -alkyl acetoacetic esters.

3. For  $\alpha$ -phenylacetoacetic ester, in contrast to  $\alpha$ -alkylacetoacetic ester, the direct bromine titration is just as applicable as the indirect bromine titration.

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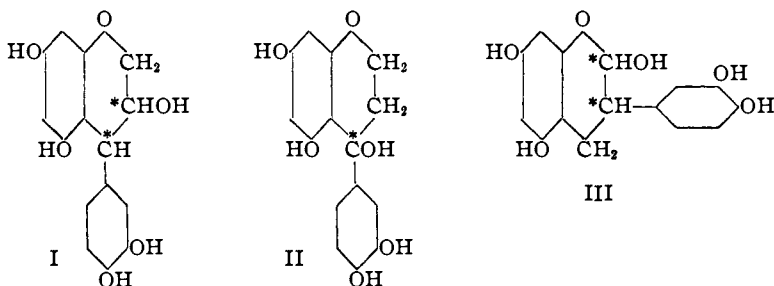
### STEREOISOMERIC CATECHINS

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Six stereoisomers are to be expected from acacatechin (I) and three from iso-acacatechin (II), but so far only four have been identified in Nature, namely, *l*- and *dl*-acacatechin and *l*- and *dl*-iso-acacatechin.



The present communication describes two new stereoisomeric catechins, *d* acacatechin and *d*-iso-acacatechin. *d*-Acacatechin accompanied by *dl*-acacatechin was found in mahogany wood from South America and the West Indies and in the Australian Kinos from *Eucalyptus viminalis*, Lab., *E. Leucosylon*, Müll. and *Angophora intermedia* D. C., whereas *d*-iso-acacatechin only was identified in the heartwood of *Anarcadium occidentale*, L. Of the other plant materials investigated in the course of the present work, the Malabar Kinos from *Myristica Malabarica*, Larn. and *Pterocarpus Marsupium*, Roxb., and the Australian Kino from *Eucalyptus corymbosa*, Smith, were found to contain *l*-acacatechin and *dl*-acacatechin, whilst Chinese rhubarb, Guarana paste, Kola nuts and the leaves of *Uncaria gambir*, Roxb. and of *Uncaria acida*, Roxb. all contain *d*-gambir-catechin and *dl*-gambir-catechin.

The investigation, in view of their red-brown color suggesting the presence of catechin, was also extended to the following plant materials: oak