On the Magnetic Susceptibilities of Troponoid-System. I : Diamagnetism of Hinokitiol (-Thujaplicin) and -Thujaplicin

On the Magnetic Susceptibilities of

Troponoid-System. I

Diamagnetism of Hinokitiol (β-Thujaplicin)*

and α-Thujaplicin

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Synopsis

The diamagnetic susceptibilities of hinokitiol (β-thujaplicin) and α-thujaplicin in powdered crystal form have been measured and the structures of the tropolone-ring are discussed.

The observed molar susceptibilities obtained in the present experiments are $-(102\pm1)\times10^{-6}$ for hinokitiol, $-(100\pm3)\times10^{-6}$ for α-thujaplicin (colourless, m.p. 34°), and $-(97\pm2)\times10^{-6}$ for α-thujaplicin (light yellow, m.p. 24°).

These observed data have been compared with calculated values, which were computed by use of the four methods ; the Pascal's additive law, the Slater-Angus method, Langevin's formula referring to the diamagnetism for the planar orbit, and the theory of diamagnetic anisotropy of molecular orbitals (London's method), with the result that there are six π-electrons, within each tropolone-ring of these compounds, which are able to revolve along the closed circuit constructed out of the periphery of seven membered ring. As a necessary consequence of this condition, it follows the ionization between one of the carbon atoms in the ring system and the oxygen atom in the carbonyl group, assuming the former a positive charge and the later a negative one.

I. Introduction

T. Nozoe, one of the authors, has isolated an enolic substance $(C_{10}H_{12}O_2)$ from the essential oil contained in *Chamaecypris taiwanensis* in 1936 and named it hinokitiol.[1] After that, the substance was confirmed by Nozoe to be an unsaturated ring compound of seven members[2] and further identified by Erdtman to be β-thujaplicin by the mixed melting method. The organic chemical constitutions of the β-compound and its α-isomer were determined by the synthetic

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** The Chem. Inst., Fac. Sci.

(1) T. Nozoe, Bull. Chem. Soc., Japan, **11** (1936), 295 ;

  T. Nozoe and S. Katsura, J. Pharm. Soc., Japan, **64** (1944), 181.

(2) T. Nozoe, Science of Drugs, 3 (1949), 174.

(3) T. Nozoe, S. Seto, K. Kikuchi, T. Mukai, S. Matsumoto and

  M. Murase, Proc. Japan Acad., **26** (1950), No. 7, 43.

(4) T. Nozoe, Y. Kitahara and S. Itô, Proc. Japan Acad., **26** (1950), No. 7. 47.

method.[3][4]   With the view of researching the special properties of π-electrons in various seven membered, unsaturated ring compounds from the stand point of magneto-chemistry, we have measured, in the first place, the magnetic suscepti-bilities of the above two compounds in the state of powdered crystals.

II. Experimental

As it is difficult, in general, to have a good supply of samples for susceptibility measurements, the modified Gouy method has been adopted, so as to be able to put up with about 0.2g. of sample in weight. A part of schematic representation of the equipment is shown in Fig. 1. P's are pole pieces of an electromagnet; FFCF system is made of quartz glass; F is a quartz fiber of 0.5 mm in diameter; C is a cylinder of 5 mm in outside diameter, 6 cm in length and about 1.7g in weight and volume scales are graduated. W is a plumb of about 2.5g. The upper part of the system is connected with one of the stirrups of a semi-micro balance; the lower end of cylinder (C) is in a uniform magnetic field between the pole faces of the strong magnet, the upper end of the sample contained in the cylinder is in a region where the field gradient is not maximum; that is, the maximum position of the field gradient lies half-way between the two ends of the sample.

In entering upon the measurement, at first C is made vacant and the weight change, ΔW, of the FCW system is previously measured by passing a definite electric current to the electromagnet. Then the powdered sample is uni-formly charged into C, and its volume and weight are measured, then the weight change of the sample caused by the same magnetic field strength, under the same condition with the former case, is observed. And then pure water with the same volume as the sample is charged into C and the weight change of water by the magnetic field, under the same condition with the former case, is measured. Taking the specific susceptibility, χ_g, of water as -0.720×10^{-6}, χ_g of the sample is arithmetically obtained, because of the proportional relationship between the specific susceptibility and the weight change, caused by the definite magnetic field, per unit mass of sample. Whereas the weight change of an empty vessel by the magnetic field contains the susceptibility of air in it. When the strict result is required,

Fig. 1.

it is necessary to make corrections for air of the same volume with those of the sample and water. Making the corrections in accounts, the following relation should be established at room temperature:
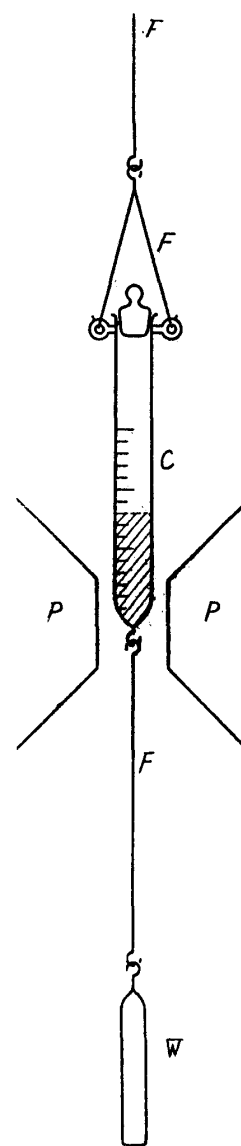
$$10^6 \times \chi_s = \frac{\Delta W_s \cdot d_{H_2O}}{\Delta W_{H_2O} \cdot d_s}\left(10^6 \times \chi_{H_2O} - \frac{0.0294}{d_{H_2O}}\right) + \frac{0.0294}{d_s}. \quad \cdots \cdots (1)$$

Here,

χ_{H_2O}, χ_s: the specific susceptibilities of water and the sample.

ΔW_s, ΔW_{H_2O}: the weight changes of the sample and water in the unit volume.

d_s, d_{H_2O}: the specific gravities of the sample and water.

0.0294×10^{-6}: the volume susceptibility $(\kappa)^*$ of air at 20°C.

An example: In case of the strength of maganetic field, in the homogeneous region, was 20,000 Oersteds, the weight change of 4.00mg was perceived for 0.16290g of water and that of 3.04mg for 0.13966g of crystalline powder of hinokitiol occupying the same volume as in the case of water. From the formula (1), the following value is obtained:

$$\chi_g \text{ of hinokitiol} = -0.630 \times 10^{-6}.$$

By neglecting the correction for air, the above value· becomes -0.638×10^{-6} and the values for 1 mole (χ_M) are -103×10^{-6} and -105×10^{-6}, respectively. From the repeated measurements, χ_M of hinokitiol was obtained, by making the correction for air:

$$\chi_M = -(102 \pm 1) \times 10^{-6}. \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

$C_{10}H_{12}O_2$

Hinokitiol
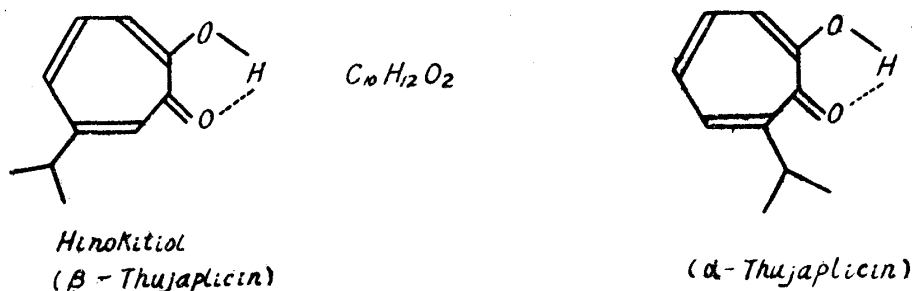
$(\beta - Thujaplicin)$

$(\alpha - Thujaplicin)$

Fig. 2.

The sample of hinokitiol used in the above experiment was the crystal obtained from natural source,[1] recrystallized and purified by distillation under reduced pressure. As α-thujaplicin, a synthetic substance[4] of m.p. 34°C was used. On the other hand a substance of m.p. 24°C was afterwards obtained, which was assumed to be the stereo-isomer of the compound of m.p. 34°C. The measurements were also carried out on the two compounds, the result being as follows:

m.p. 34°C-compound (colorless): $\chi_M = -(100 \pm 3) \times 10^{-6}$ $\cdots\cdots(3)$

m.p.24°C-compound (light yellow): $\chi_M = -(97 \pm 2) \times 10^{-6}.$ $\cdots(4)$

III. Discussion

In order to explain the chemical charcteristics and stability of troponoid compounds, one of the present authors has recently proposed a system of resonance structures that can be devided into the following five types[5]:
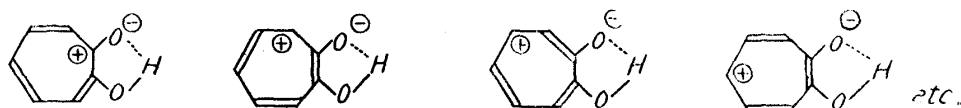
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* Taking the absolute temperature as T, $\kappa_{(T)} = \frac{2.52 \times 10^{-3}}{T^2}$.

(5) T. Nozoe, Proc. Japan Acad., 26 (1950), No. 9, 30;
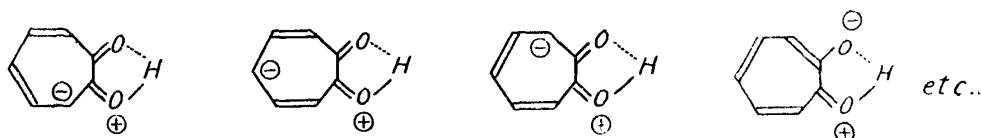   T. Nozoe, Sci. Rep. Tôhoku Univ., Ser. I, 34 (1950), 119.
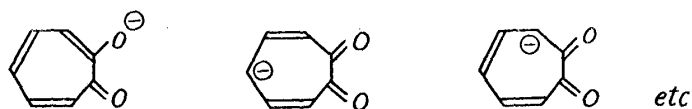
(A) *Non-ionic type* (2 *structures*);
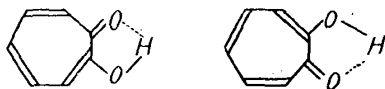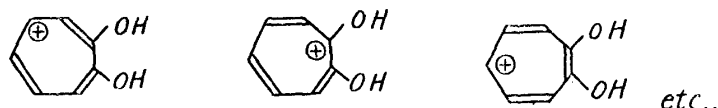

(B) *Cationoid type* (14 *structures*);

(C) *Anionoid type* (8 *structures*);

(D) *Tropoxylate anion* (5 *structures*);

etc

(E) *Conjugate acid cation* (9 *structures*);

etc..

Among these five types, (A), (B) and (C) are thought to be the fundamental types of the resonance constitutions in the molecule of the tropolone system, while, in cases of the single component and of the ground state, the type-(C) has been considered to be excepted owing to the results of dipole moment measurements on the tropolone compounds by Kurita, Nozoe and Kubo.[6] (D) and (E) will have their meaning according to their pH values in case of solutions or will get much weight in case of intermolecular compounds or complex salts. Therefore, as in the present case, wherein the powdered crystals as a single body are taken as the object of the measurement, it is sufficient to discuss whether (A) or (B) will occupy more important roll than the other.

(i) The case of type-(A).

From the magnetochemical stand point of view, there are two distinct different

(6) Y. Kurita, T. Nozoe and M. Kubo, J. Chem Soc., Japan,. **71** (1950), 543 ; Y. Kurita, T. Nozoe and M. Kubo, Bull. Chem. Soc., Japan, **24** (1951), 10.

cases concerning the diamagnetic contribution from the mobile π-electrons in organic compounds; the one is in the case of conjugated aliphatic case, and the other is in the case of aromatic one. The simplified models of the two cases are schematically represented in Fig. 3-(a) and -(b).
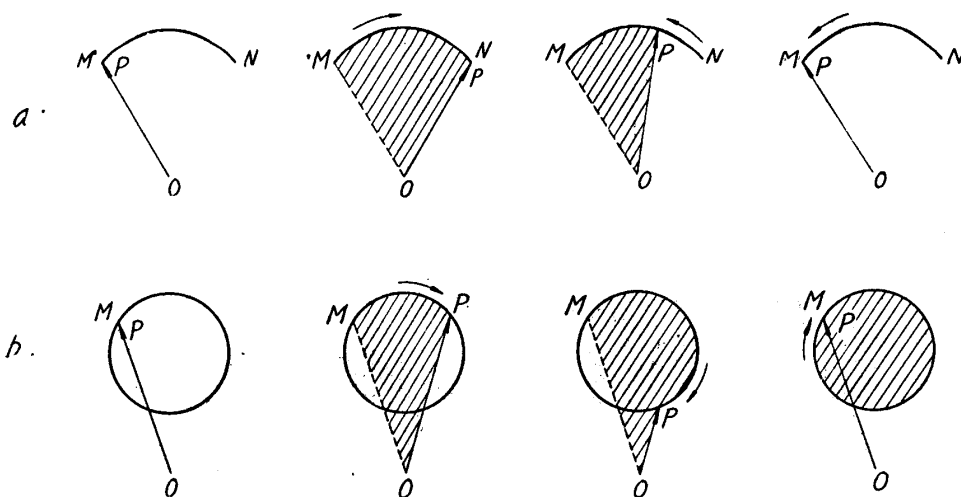

Fig. 3.

In Fig. 3-(a), consider the area described by the radius vector, OP, having O as its center, starting from the point M and coming back again from N to M tracing the heavy line MN. The resultant area from this operation is zero from the vector concept of view. Assuming MN to be the path of an electron, the diamagnetic contribution due to the round trip of the electron along such an open circuit is zero. The type-(A) corresponds to the present case. Looking the case from the standpoint of chemical constitution of the type-(A), it is characteristic that two adjacent carbon atoms, directly combining with oxygen atoms, have no chance to constitute the double bond between them. In short, whether the above model circuit is a closed one or an open one will determine the existence or absence of the diamagnetic contribution from the moving π-electrons.

In case of getting the calculated values of χ_M in the case of type-(A), it is sufficient to apply the additive law in unsaturated aliphatic compounds to the calculation, according to the former empirical facts.[7] Owing to Pascal's method, the following value is obtained for the type-(A) of hinokitiol and α-thujaplicin,* and there is a large difference comparing with the measured values shown in (2), (3) and (4).

$$\chi_M = \Sigma \chi_A = 4C(|^-) + 6C(|^=) + 12H + (O=) + (-O-) = -82.2 \times 10^{-6}. \cdots\cdots(5)$$

Table 1 shows the values of the atomic increments used in (5). The left side part of the table was obtained by using the values of Pascal as the fundamental

(7) G. Hazato, J. Chem. Soc., Japan, **64** (1943), 483 ;

      H. Shiba and G. Hazato, Bull. Chem. Soc., Japan, **22** (1949), 92 ;

      A. Pacault, Bull. Soc, Chim., **16** (1949), D 371 ;

      G. Berthier M. Mayot and B. Pullman, J de physique et Rad., **12** (1951), 717.

  * Cf. Table 1.

ones. Among these, the value of C(|=), showing the double bond carbon, is obtained by adding a quarter of the constitutive correction constant of the butadiene type to that of C(|-)[7].

(ii) The case of type-(B).

Table 1.

	$\chi_A \times 10^6$		$\chi_A \times 10^6$
C(|-)	−6.00	C⁺¹	−3.3
C(|=)	−3.36	C⁻¹	−10.0
H	−2.93	O⁺¹	−2.7
–O–	−4.61	O⁻¹	−6.7
O for C=O	+1.73	H⁺	0

Fig. 3-(b) shows the case, in which the electron revolves along a closed circuit and an effective area closed by the circuit remains, notwithstanding the position of the center O. The value of the effective area should be constant, even when the closed circuit has the open branches. In this case, the magnitude of diamagnetism caused by the movement of electron is proportional to the projected area on the perpendicular plane to the magnetic field direction. Assuming the closed area of the circuit to be that of the molecule and to be perpendicular to the direction of the magnetic field; and also a molecule in which an even member (p) of electrons can revolve along the circuit, the susceptibility caused by the movement of these electrons for 1 mole is shown as follows:

$$\varDelta K_M = -\frac{e^2 N}{4\,n_0 C^2}\sum_p r^2. \quad\cdots\cdots(6)$$

This is a classical formula of the diamagnetism concerning the planar orbit proposed by Langevin. By substituting the known physical constants for numerical values expressed in C. G. S. and E.M.U. units, the following formula is obtained:

$$\varDelta K_M = -2.83 \times \frac{6}{4}\sum_p r^2 \times 10^{10}. \quad\cdots\cdots(6')$$

Here, r is the radius of the circuit above mentioned and expressed in centimeter unit.

Assuming the average inter atomic distance between the adjacent carbons of tropolone-ring to be 1.40 Å,[8] and the ring to be a plane of regular heptagon, the radius of the circumscribed circle becomes 1.61Å. Substituting this value in (6') and putting $p=6$ according to the model (B):

$$\varDelta K_M = -66.0 \times 10^{-6}. \quad\cdots\cdots(7)$$

In the case of powdered or liquid sample, the projection of r^2 (proportional to the area) to the plane perpendicular to the magnetic field should be one third of the above value, owing to the average meaning:

$$\overline{\varDelta K_M} = \frac{1}{3}(-66) \times 10^{-6} = -22 \times 10^{-6}. \quad\cdots\cdots(7')$$

Now, the terms shown by $\sum\chi_A$ and $\varDelta K_M$ can be regarded as the isotropic and the anisotropic terms respectively.[7] To obtain the calculated full value, a value corresponding to that of expressed by (5); the isotropic part, should be added to that of (7'); the anisotropic one. In this case, the following value is obtained from the value of table 1 as the isotropic part:

(8) cf. J. M. Robertson, J. Chem. Soc. (London), **1951**, 1222.

$$\Sigma\chi_A = 12H + 6C(\parallel) + 3C(\mid\mid) + C^{+1} + O^{-1} + (-O-) = -87.9 \times 10^{-6}. \cdots (8)$$

Although substituting $H^+ + 11H$ for 12H, and $2O^{-1}$ for $O^{-1} + (-O-)$, the value becomes -87.1×10^{-6}, showing the difference is very small. In conclusion, the following is obtained as the calculated full value for the type-(B):

$$\chi_M = -109 \times 10^{-6}. \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(9)$$

The value of C^{+1} in table 1 used in the calculation of (8) was obtained, according to the calculating method of Angus,[9] by adding the difference between the value (-7.8×10^{-6}) of χ_A of neutral C and $C^{+1}(-5.1 \times 10^{-6})$ to the value (-6.00×10^{-6}) of $C(\mid\mid)$ of Pascal. The values of C^{-1}, O^{-1} and O^{+1} were calculated by the same method.

The above calculation was made from the standpoint of classical theory. On the other hand, applying the London's approximate method of molecular orbitals[10] to the model of the type-(B), the value corresponding to (7) is as follows and near to that of (7):

$$\Delta K_M = -69 \times 10^{-6}. \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(10)$$

For introducing the result of (10), the method of first order approximation due to the model of the ring part only is adopted, neglecting the mutual interactions of π-electrons between the C–O and O–H bonds respectively. One of the reasons of these neglections is as follows:

$$\text{\Large$>$}C=O \ \rightarrow \ \text{\Large$>$}C^+ - O^-, \qquad \text{and}$$

$$\text{\Large$>$}C-O-H \ ; \ \text{\Large$>$}C-O^- + H^+.$$
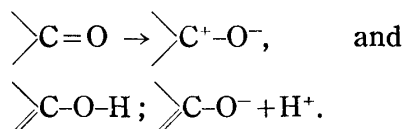
Owing to the ionization, the mutual interaction of π-electrons between C–O bond is assumed to be very small, if any. And other reason is that the C–O bond is a branched part of the ring model and belongs to a kind of Fig. 3-(a). On the other side, in case of adopting such a model that the regular heptagon with two C–O branches, neglecting the corrections which are to be introduced in Coulomb and resonance integrals, in every vertex and side respectively in the heptagon and in each CO groups as well, it has been obtained that the value of $\overline{\Delta K_M}$ is -0.11×10^{-6}; a very small contribution from the mobile π-electrons, which is much the same as in the case of type-(A) or Fig. 3-(a). Moreover, it is questionable how much corrections for Coulomb integral and resonance one in the C–O group should be adopted, for which the authors have no proper vista at present. For these reasons, in the calculation of the result of (10) also, the introductions of the corrections were neglected.

By comparing the measured results (2), (3) and (4) with the calculated value of (9), there remains no further question to be discussed in estimating the large contribution of the type-(B) in the results of present crystalline compounds. But it is questionable whether the differences between the three measured values are due to the constitutional differences between the isomers or not, and there

(9)　W. R. Angus, Proc. Roy. Soc. London, **A136** (1932), 569.

(10)　F. London, J. de physique, **8** (1937), 397.

occurs no good idea to us, for the present, to give an exact quantitative explanation to the fact from the magnetochemical stand point. Still more, as the calculated value of (9) has larger diamagnetic value compared with the three measured ones, there is a possibility to suppose the compound to be a hybrid constitution between the types of (A) and (B) or (B) and (C). But it is also difficult to decide on estimating the definite contribution from either type of them, which depends upon the reliability of the approximate degree of the calculation method, and that of the magnitude of r adopted in (6') or (10) formula. However, the present result does not deny the support of the hybrid constitution between (A) and (B). When the hybrid constitution is brought to consideration, the authors wish to lay emphasis on the necessity to estimate the weight of type (B) higher than the other.

Recently, Doering and Knox proposed many models for the constitution of tropolone.[11] Among the models shown in their paper, the Ic model is, after all, completely the same type with (B) in our case.[5] From the result of the infrared absorption spectra, they perceived that the C–O band of tropolone shifted to the longer wave side by about $100^{-1}cm$ than that of ordinary carbonyl group, the cause of which was largely attributed to the contribution of the type-Ic corresponding to the type-(B). In other words, the amount of the double bond character of CO combination can be less estimated than that of carbonyl. And, as the compound does not show paramagnetism, it has no property of free radical, so that there is a possibility to form a dipolar ion, which may be helped by the adjacent H^+ ion and is resulted for giving a chance to have the double bond between the two carbon atoms within the adjacent CO groups, by which six π-electrons can settle down in the ring of seven members. Therefore, the authors' conclusion obtained by the standpoint of magnetochemistry does not qualitatively contradict not only with the view of Doening and Knox but also with the measuring results[6] of the dipole moments by Kurita, Nozoe and Kubo.

(11)   W. von E. Doering and L. M. Knox, J. Am. Chem. Soc., **73** (1951), 828.