The filtrate from the first precipitation was chromatographed on filter paper using 77% ethanol as solvent to show the presence of DL-β-phenylalanine in the hydrolysate.

DL-β-Phenylalanine-N-acetic Acid Hydrochloride.—Sixty mg. of the DL-β-phenylalanine-N-acetic acid was converted to the hydrochloride[2] to give 50 mg. of material, m.p. 203–206° dec. (lit.[2] 200–201°).

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(7) Federal Security Agency, Public Health Service.

A Note on the Occurrence of Panstroside[1]

BY ROBERT FOPPIANO AND M. R. SALMON

RECEIVED MARCH 19, 1952

v. Euw and Reichstein[2] have reported on the glycoside content of the seeds of *Strophanthus petersianus*, Klotzsch, from which they isolated sarmentocymarin, sarmentogenin and three new substances identified as No. 792, 793 and 794. We find that in addition the seeds of this species contain panstroside which we isolated in a crude yield of 0.035%.

The seeds were received from Mr. P. Topham, Nyasaland, Africa, through the courtesy of the New York Botanical Garden. A flowering specimen and a mericarp sent as botanical vouchers for the seeds were identified as *S. petersianus* at the New York Botanical Gardens. We wish to thank Mr. Topham for the collection and Mr. Joseph Monachino for the botanical examination of this sample.

Panstroside frequently crystallizes slowly or not at all[3] and may be easily overlooked. When the presence of this glycoside is suspected we regularly crystallize the chloroform extract from acetone from which panstroside crystallizes more readily than from methanol and ether.

Experimental

The seeds (1111 g.) were extracted as previously described.[4] The chloroform extract on concentration gave 2.58 g. (0.23%) of crude total glycoside. This was dissolved in about 10 cc. of acetone, and allowed to crystallize in the refrigerator. We obtained 366 mg. of crude panstroside, $[\alpha]_D$ +25°; m.p. 210–219°. An additional 19 mg. was isolated by chromatography of the mother liquors.

Recrystallization of this panstroside gave preparations that agreed in rotation and melting point with our former preparations but the absorption spectrum showed that a small amount of impurity was retained tenaciously. It was accordingly chromatographed on alumina, and from the eighth and ninth fractions eluted with chloroform and chloroform-methanol (99:1), 193 mg. of panstroside was obtained after crystallization from methanol; $[\alpha]_D$ +27°. Panstroside was recrystallized three times and yielded 154 mg.; $[\alpha]_D$ +31.0°; m.p. 222–228°; Keller–Kiliani test negative; legal test positive. Color test with 84% sulfuric acid pink becoming red in 2 min., developing a blue edge in 3 min., and becoming blue in 20 min. The mixed melting point with panstroside from *S. intermedius* showed no depression. Ultraviolet absorption spectrum maximum at 218 mμ, log ε 4.23; plateau at 265–280 mμ, log ε 1.93.

Anal. Calcd. for $C_{30}H_{44}O_{11}$: C, 62.06; H, 7.64. Found: C, 61.84, 61.63; H, 7.43, 7.61.

We wish to thank Dr. W. G. Bywater for advice and suggestions and the Upjohn Company for encouragement and support.

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(1) J. v. Euw, H. Hess, P. Speiser and T. Reichstein, *Helv. Chim. Acta*, **34**, 1821 (1951).

(2) J. v. Euw and T. Reichstein, *ibid.*, **33**, 1551 (1950).

(3) See for example J. v. Euw and T. Reichstein, *ibid.*, **33**, 2153 (1950).

(4) M. R. Salmon, Eric Smith and W. G. Bywater, THIS JOURNAL, **73**, 3824 (1951).

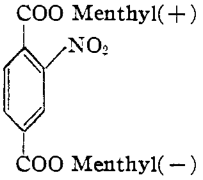
Active (+) Menthyl (−) Menthyl Nitroterephthalates

BY P. J. HEARST AND C. R. NOLLER

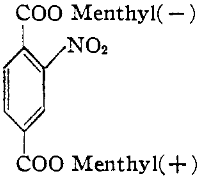
RECEIVED APRIL 25, 1952

Compounds containing two like asymmetric groups of opposite configuration, A(+) and A(−), and no other asymmetric groups, but which nevertheless have molecular asymmetry, are of interest in that they have some bearing on the entrenched idea of internal compensation. It might be argued that the rotation of A(+) should cancel that of A(−) or that, if it did not, the rotation of the compound would be small. An example of such compounds would be those of the type (+)A-Z-X-Y-Z-A(−) and (−)A-Z-X-Y-Z-A(+), where X, Y and Z are not asymmetric. It is difficult to be certain that this type of compound has not been discussed or prepared previously, but an examination of several available books on stereochemistry and a search of the literature for likely specific compounds have not revealed a reference to this aspect of the problem.

We have prepared one pair of enantiomorphs of this type, namely, the 1-(+)menthyl 4-(−)menthyl 2-nitroterephthalate (I) and the 1-(−)menthyl 4-(+)menthyl 2-nitroterephthalate (II). These compounds have specific rotations in benzene solution of +59.1 and −59.7°, respectively. Thus the molecular asymmetry not only confers activity on these compounds, but the rotation is appreciable.



I



II

Experimental

Nitroterephthalic acid was prepared from terephthalic acid in 78% yield by a procedure essentially the same as that of Wegscheider[1] except that 70% nitric acid and 30% fuming sulfuric acid were used instead of fuming nitric acid and pyrosulfuric acid. It was converted to the (−)**menthyl ester** by the procedure of Cohen and de Pennington[2] except that, in the preparation of the acyl chloride, twice the calculated amount of phosphorus pentachloride was used and a small amount of phosphorus oxychloride was added to start the reaction. The purified ester, obtained in over-all yield of 59%, melted at 86–88°; $[\alpha]^{25}_D$ −159° (*c* 1.996 in benzene).

1-(−)**Menthyl 2-nitroterephthalate** was obtained in 42% yield by the partial saponification of the (−)menthyl ester.[2] After crystallization from aqueous ethyl alcohol, it melted at 73.5–75°, compared to the 75° previously reported. Recrystallization from hexane, however, raised the melting point to 128.5–129.5°. A determination of neutralization equivalents showed that the product melting at 75° contains one molecule of water of crystallization, whereas that melt-

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(1) R. Wegscheider, *Monatsh.*, **21**, 621 (1900).

(2) J. B. Cohen and H. S. de Pennington, *J. Chem. Soc.*, **113**, 57 (1918).

ing at 129° is anhydrous; $[\alpha]^{25}\text{D}$ −128° (c 2.029 in 95% alcohol). In addition to the half menthyl ester, the half methyl ester, presumably formed by ester exchange from the methanolic potassium hydroxide solution, was isolated in 15% yield.

1-(−)Menthyl 4-(+)menthyl 2-nitroterephthalate was prepared by refluxing 3.49 g. of 1-(−)menthyl 2-nitroterephthalate with 5 cc. of pure thionyl chloride for one hour and removing the excess thionyl chloride at reduced pressure. To the residue was added 1.56 g. of (+)menthol[3] in 25 cc. of pyridine. After 24 hours the mixture was worked up in the usual way, and gave 4.09 g. of product that crystallized on standing. Recrystallization to constant melting point from 95% alcohol gave 2.76 g., m.p. 99.5–100.5°; $[\alpha]^{25}\text{D}$ −59.7° (c 2.011 in benzene).

Anal. Calcd. for $C_{28}H_{41}O_6N$: C, 68.97; H, 8.48. Found: C, 69.08, 69.29; H, 8.53, 8.40.

(+)Menthyl 2-nitroterephthalate was prepared by the same procedure used to make the (−)menthyl ester. It melted at 86–88°; $[\alpha]^{25}\text{D}$ +158° (c 2.031 in benzene). It was converted to the half ester, 1-(+)**menthyl 2-nitroterephthalate**, m.p. 127.5–128.5°; $[\alpha]^{25}\text{D}$ +127° (c 2.00 in 95% alcohol). The half ester was converted to 1-(+)**menthyl 4-(−)menthyl 2-nitroterephthalate**, m.p. 99.5–100.5°; $[\alpha]^{25}\text{D}$ +59.1° (c 2.006 in benzene).

Anal. Calcd. for $C_{28}H_{41}O_6N$: C, 68.97; H, 8.48. Found: C, 69.03, 69.02; H, 8.48, 8.45.

A mixture of equal amounts of the two enantiomorphic esters melted at 80–87°.

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[3] J. Read and W. J. Grubb, *J. Soc. Chem. Ind.*, **51**, 329T (1932).

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Effect of Nearest Neighbor Substrate Interactions on the Rate of Enzyme and Catalytic Reactions

BY TERRELL L. HILL

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The object of this note is to illustrate with a simple example an approximate method of taking into account explicitly the effect of substrate interactions on the rate of surface-catalyzed reactions.

Let us consider nearest neighbor interactions on a surface with a large number B of equivalent adsorption sites. The problem of a linear enzyme, with B not necessarily large, has been discussed by Botts and Morales.[1] Consider the system (S is the substrate, S′ the product)

$$\text{S}\left(\begin{matrix}\text{solution, concentration } c;\\ \text{or gas, pressure } p\end{matrix}\right) \underset{k_{-1}^{\circ}}{\overset{k_1^{\circ}}{\rightleftarrows}} \text{S (adsorbed)} \qquad (1\text{a})$$

$$\text{S (adsorbed)} \xrightarrow{k_2^{\circ}} \text{S}' \text{ (solution; or gas)} \qquad (1\text{b})$$

The desorption of S′ is assumed fast enough that the number of S′ molecules on the surface is negligible.

In the absence of interactions we write the rates of the separate reactions as

$$v_1^{\circ} = k_1^{\circ}c(1-\theta) \qquad (2)$$
$$v_{-1}^{\circ} = k_{-1}^{\circ}\theta,\ v_2^{\circ} = k_2^{\circ}\theta$$

where $\theta = N/B$ and N is the number of adsorbed S molecules. Let the interaction free energy[2] between nearest neighbor S molecules be w_a, and between S and S′ nearest neighbors w'_a. At steady state, with N adsorbed S molecules, we assume that the probabilities of the various possible configurations of the adsorbed phase are given by a Boltzmann distribution (*i.e.*, the *adsorbed phase* is in *internal* equilibrium); the quasi-chemical approximation[3] is used to represent this equilibrium.

A consequence of the quasi-chemical approximation is the following: of the z sites nearest neighbor to a filled site, the probability that j will be filled is

$$P_j^{(f)} = \frac{z!}{j!(z-j)!}\, p^{z-j}(1-p)^j \qquad (3)$$

where

$$p = 2(1-\theta)/(\beta+1) \qquad (4)$$
$$\beta^2 = 1 - 4\theta(1-\theta)[1-\exp(-w_a/kT)]$$

Also, the probability that next to an empty site j will be filled is

$$P_j^{(e)} = \frac{z!}{j!(z-j)!}\, r^{z-j}(1-r)^j \qquad (5)$$

where

$$r = (\beta+1-2\theta)/(\beta+1) \qquad (6)$$

We assume that the rate constant for an S molecule being adsorbed onto an empty site with j nearest neighbor filled sites can be written as

$$k_1(j) = k_1^{\circ}\exp(-jw_b/kT) \qquad (7)$$

That is, the increase in the free energy of activation per nearest neighbor is w_b. Then the rate constant for an S molecule leaving a site with j nearest neighbor filled sites is

$$k_{-1}(j) = k_{-1}^{\circ}\exp[j(w_a - w_b)/kT] \qquad (8)$$

Similarly, the rate constant for an S′ molecule leaving a site with j nearest neighbor filled (with S) sites is written as

$$k_2(j) = k_2^{\circ}\exp[j(w'_a - w'_b)/kT] \qquad (9)$$

The over-all rates in the presence of interactions are then

$$v_1 = c(1-\theta)\sum_{j=0}^{z} k_1(j)P_j^{(e)} \qquad (10)$$

$$v_{-1} = \theta\sum_{j=0}^{z} k_{-1}(j)P_j^{(f)} \qquad (11)$$

$$v_2 = \theta\sum_{j=0}^{z} k_2(j)P_j^{(f)} \qquad (12)$$

Equation (12) gives the desired rate of formation of product. Implicit in writing eq. (12) is the assumption that an S′ molecule, once formed, leaves the surface before the local nearest neighbor distribution determined by S–S interactions has time to readjust to S–S′ interactions. When simplified, eq. (12) leads to

$$v_2(\theta) = k_2^{\circ}\theta\left[\frac{2(1-\theta)}{\beta+1-2\theta}\right]^z\left(1 + \frac{2\theta\{\exp[(w'_a - w'_b - w_a)/kT] - 1\}}{\beta+1}\right)^z \qquad (13)$$

The other rates become

$$v_1 = k_1^{\circ}c(1-\theta)f(\theta) \qquad (14)$$

$$v_{-1} = k_{-1}^{\circ}\theta\left[\frac{2(1-\theta)}{\beta+1-2\theta}\right]^z f(\theta) \qquad (15)$$

$$f(\theta) = \left\{1 + \frac{2\theta[\exp(-w_b/kT) - 1]}{\beta+1}\right\}^z$$

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[1] D. J. Botts and M. F. Morales, to be published.

[2] E. A. Guggenheim, *Trans. Faraday Soc.*, **44**, 1007 (1948).

[3] R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1939, Chap. 10.