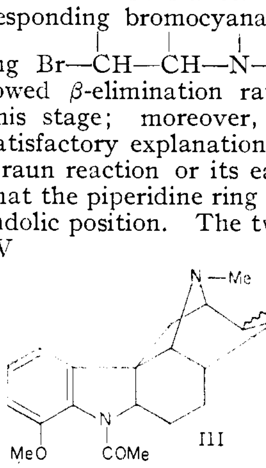
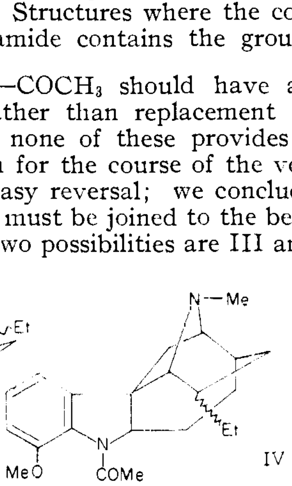
N, 11.27) in which hydrogen replaces bromine; there is no evidence of unsaturation and there is no NH band in the infrared spectrum of the debrominated substance. Structures where the corresponding bromocyanamide contains the grouping $\mathrm{Br{-}\overset{|}{C}H{-}\overset{|}{C}H{-}\overset{|}{N}{-}COCH_3}$ should have allowed β-elimination rather than replacement at this stage; moreover, none of these provides a satisfactory explanation for the course of the von Braun reaction or its easy reversal; we conclude that the piperidine ring must be joined to the beta indolic position. The two possibilities are III and IV

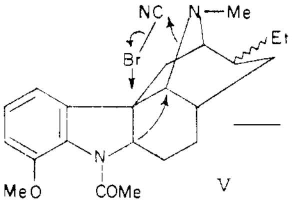


III

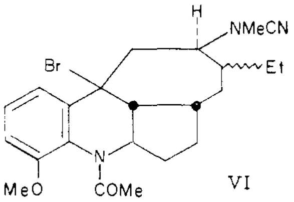


IV

Although we know of no experimental evidence as yet conclusively eliminating either of these, the structure III is preferred for biogenetic reasons.[6] On the basis of III the abnormal von Braun degradation is interpreted in terms of a rearrangement transition state (V) meeting eminently well all stereoelectronic requirements. The bromocyanamide, then formulated as VI, in fact does not appear to contain the CHBr grouping, for no new peak is evident in the region (*ca.* 1090 cycles, as in isopropyl bromide) expected in its NMR spectrum.



V



VI

Acknowledgment.—We wish to thank Dr. E. Schlittler for a generous gift of aspidospermine, Dr. Aksel Bothner-By for his assistance with the NMR spectrometer and Dr. S. M. Nagy for the analyses. The work is supported by grants from Research Corporation and from the National Institutes of Health.

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(6) The expression (III) is sufficiently similar in relevant detail to that proposed by Openshaw (*cf.* "Structural Relations of Natural Products," by R. Robinson, Oxford University Press, Oxford, 1955, p. 117) and by Witkop (ref. 1d) so that Openshaw's biogenesis could be adapted to fit. A simpler, and perhaps preferable, scheme pictures the biogenetic derivation of III with appropriate Mannich/aldol condensations of precursors formed from tryptophan and phenylalanine, where the phenylalanine suffers typical ring cleavage, but between its *ortho* and *meta* positions, to give a *butylidenesuccindialdehyde equivalent.*

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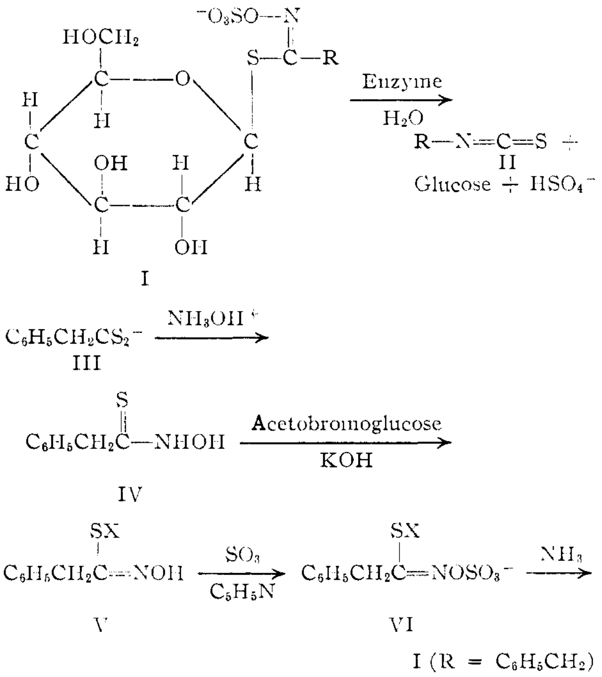
FIRST SYNTHESIS OF A MUSTARD OIL GLUCOSIDE; THE ENZYMATIC LOSSEN REARRANGEMENT

Sir:

We have proved analytically that sinigrin is the potassium salt of I ($\mathrm{R = H_2C{=}CHCH_2}$)[1] and rearranges during enzymatic cleavage to allyl isothiocyanate (II, $\mathrm{R = H_2C{=}CHCH_2}$). All the two dozen or more known natural isothiocyanates and thioöxazolidones are believed to arise similarly from precursors of type I, possibly varying in the carbohydrate portion. We have now synthesized the glucotropaeolate ion I ($\mathrm{R = C_6H_5CH_2}$), a natural source of benzyl isothiocyanate, and confirmed the new structure of the class.

Ethereal magnesium dithiophenylacetate (III), prepared[2] by addition of benzylmagnesium chloride to carbon disulfide, was treated[3] with aqueous hydroxylamine hydrochloride at 0° to furnish, in 33% over-all yield from benzyl chloride, **phenylacetothiohydroxamic acid**[4] (IV), m.p. 73–74.2°, $\lambda_{\max.}$ 267 mμ in methanol (log $\epsilon_{\max.}$ *ca.* 3.9).[5] After IV had reacted with 0.9 equivalent each of potassium hydroxide and acetobromoglucose in 1:3 methanol–acetone during 6 hours at room temperature,[3,6] there was obtained, in 47% yield from acetobromoglucose, **S-β-D-1-(tetraacetylglucopyranosyl)-phenylacetothiohydroximic acid**[4] (V), m.p. 163.8–164.1°, $[\alpha]^{32}_{\mathrm{D}}$ −9.6° (chloroform), without accessible ultraviolet absorption maximum (in methanol log



$$\mathrm{\underset{III}{C_6H_5CH_2CS_2^-}} \xrightarrow{\mathrm{NH_3OH^+}}$$

$$\mathrm{\underset{IV}{C_6H_5CH_2\overset{\overset{\displaystyle S}{\|}}{C}{-}NHOH}} \xrightarrow[\mathrm{KOH}]{\text{Acetobromoglucose}}$$

$$\mathrm{\underset{V}{C_6H_5CH_2\overset{\overset{\displaystyle SX}{|}}{C}{=}NOH}} \xrightarrow[\mathrm{C_5H_5N}]{\mathrm{SO_3}} \mathrm{\underset{VI}{C_6H_5CH_2\overset{\overset{\displaystyle SX}{|}}{C}{=}NOSO_3^-}} \xrightarrow{\mathrm{NH_3}}$$

$$\mathrm{I\ (R = C_6H_5CH_2)}$$

X = tetraacetyl-β-D-1-glucopyranosyl

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(1) M. G. Ettlinger and A. J. Lundeen, THIS JOURNAL, **78**, 4172 (1956). Dr. J. Waser and Mr. W. H. Watson, Jr., are studying sinigrin by X-ray diffraction.

(2) A. Kjaer, *Acta Chem. Scand.*, **6**, 327 (1952).

(3) *Cf.* L. Cambi, *Atti reale accad. Lincei, Rend. classe sci. fis., mat. e nat.*, [5] **18**, I, 687 (1909).

(4) Obtained analytically pure.

(5) The thiohydroxamic acid could be stored below 0°, but decomposed[3] in a few days at 30° and puffed when heated in bulk to *ca.* 100°, giving phenylacetonitrile and sulfur. The substance was tolerably stable in aprotic solvents, but a methanolic solution deposited sulfur quantitatively during 24 hours at room temperature. Solid sodium phenylacetothiohydroxamate kept 10 weeks at room temperature afforded N,N′-dibenzylthiourea in 25% yield by Lossen rearrangement.

(6) *Cf.* C. B. Purves, THIS JOURNAL, **51**, 3619 (1929).

ϵ *ca.* 2.9 at 250 mμ, 4.2 at 210 mμ).[7] With pyridine–sulfur trioxide in pyridine overnight at room temperature, V furnished the tetraacetylglucotropaeolate ion VI, isolated as the monohydrated potassium salt, m.p. 186.5–187° dec. (lit.[8] 187–189° dec.), $[\alpha]^{32}\text{D}$ $-22.6°$ (water), identified by infrared spectrum with specimens derived[8] from nature. The ion was also isolated, in 53% yield from V, as **tetramethylammonium tetraacetylglucotropaeolate,**[4] m.p. 182.5–183.5° (anhydrous form), $[\alpha]^{28}\text{D}$ $-18.9°$ (water), converted in 94% yield by methanolic ammonia[8,9] to anhydrous **tetramethylammonium glucotropaeolate,**[4] the salt of I ($R = C_6H_5CH_2$), m.p. 188–189.2° dec., $[\alpha]^{28}\text{D}$ $-16.7°$ (water). The glucotropaeolate was identical with a sample isolated from *Tropaeolum majus* seed by adsorption of an extract[8] on anion exchange resin and elution with tetramethylammonium hydroxide.[10] When the synthetic glucotropaeolate was treated with the usual protein fraction of yellow mustard, benzyl isothiocyanate (II, $R = C_6H_5CH_2$) was rapidly[11] formed in quantitative yield and was determined and isolated as benzylthiourea.

We thank Drs. O.-E. Schultz, A. Kjaer, and R. Gmelin for samples of glucotropaeolin tetraacetate, The National Science Foundation for a predoctoral fellowship (A. J. L.), and The Robert A. Welch Foundation for financial support.

(7) Ammonolysis of V afforded S-β-D-1-glucopyranosylphenylacetothiohydroximic acid, m.p. *ca.* 115° (hydrate), $[\alpha]^{28}\text{D}$ $-44°$ (water), which was attacked by myrosin, if at all, with not more than one fiftieth of the rate of cleavage of the sulfated analog I ($R = C_6H_5CH_2$) and was not converted to benzyl isothiocyanate. The likelihood that rearrangement of I and departure of the sulfate and glucosyl groups are simultaneous renders dubious the accepted division of myrosin into thioglucosidase and sulfatase.

(8) O.-E. Schultz and W. Wagner, *Arch. Pharm.*, **288**, 525 (1955). Other monohydrated samples of natural or synthetic origin melted as low as 140–150° (dec.).

(9) A. Kjaer and R. Gmelin, *Acta Chem. Scand.*, **10**, 335 (1956).

(10) On isolation of amorphous potassium glucotropaeolate and hydrolysis to phenylacetic acid, see O.-E. Schultz and R. Gmelin, *Arch. Pharm.*, **287**, 342 (1954).

(11) The glucotropaeolate was cleaved to mustard oil approximately twice as fast as was natural glucosinalbate.

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RECEIVED FEBRUARY 8, 1957

RELAXATION PHENOMENA AND CONTACT ANGLE HYSTERESIS

Sir:

We wish to advance a kinetic mechanism for contact angle hysteresis as observed by Bartell and Bjorklund[1] on high energy smooth surfaces. Verwey[2] has presented evidence for the existence of an ice-like structure at the water–vacuum interface, and Grahame[3] has found evidence for a similar structure at the water–mercury interface. Recently Bockris, Mehl, Conway and Young[4] have proposed that water is oriented in an ice-like structure at the water–copper interface, and that its dielectric relaxation time there is about 10^{-6} sec. (as compared to 10^{-10} sec. for bulk water at room temperature).

These findings appear relevant to contact angle hysteresis on smooth surfaces. The measurement of a contact angle involves displacement of a periphery formed by the three-phase junction across one of the phases. There is a natural length associated with this process, namely, the peripheral thickness l. Just as the surface of discontinuity between two phases is not a mathematical surface, so the periphery is not a mathematical curve, but will have a thickness of the same order of magnitude as the surface of discontinuity. This latter thickness is normally taken as the distance over which concentration gradients are appreciable (at equilibrium), and is of the order of magnitude of molecular dimensions. A parallel definition of peripheral thickness can be made, and it should be of the same order of magnitude. There is a natural time associated with this process, namely, the relaxation time τ of the most slowly relaxing molecule at the periphery. There is therefore a natural displacement velocity $V_N = l/\tau$. Let V be the actual displacement velocity; then if $V << V_N$ the displacement should be quasistatic and all boundary tensions operating at the periphery should be equilibrium tensions, but if $V >> V_N$, then at least the most slowly relaxing molecule will be disoriented at the periphery, and boundary tensions at the periphery (which determine the contact angle) at interfaces involving this molecule will exceed their equilibrium values. On standing, the disoriented molecules will orient and the periphery will move, but at a velocity approximating V_N.

Now $l \sim 10^{-8}$ cm., and if we assume $\tau \sim 10^{-3}$ sec. it is possible to rationalize the experiment of Bartell and Bjorklund[1] involving substantial equality of contact angles formed by advanced and immediately (but slowly) receded water drops in the mercury–water–heptane system. Even more extreme time effects should be expected in systems such as water–heptane–silica, since adsorption at the water–silica boundary appears to involve formation of a surface silicic acid. If $\tau \sim 1$ sec. for this process, $V_N \sim 10^{-8}$ cm./sec. or about 0.01 mm./day. Most observers would consider such a drop motionless.

We are indebted to the American Petroleum Institute for support, in the form of a Research Grant-in-Aid, for research leading to the preceding conclusions. Work was performed in part in the Ames Laboratory of the U. S. Atomic Energy Commission.

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RECEIVED FEBRUARY 7, 1957

(1) F. E. Bartell and C. W. Bjorklund, *J. Phys. Chem.*, **56**, 453 (1952).

(2) E. J. W. Verwey, *Rec. trav. chim.*, **61**, 564 (1942).

(3) D. C. Grahame, *J. Chem. Phys.*, **23**, 1725 (1955).

(4) J. O'M. Bockris, W. Mehl, B. E. Conway and L. Young, *ibid.*, **25**, 776 (1956).

CRYSTALLINE PHOSPHORUS PENTANITRIDE, P_3N_5

Sir:

Phosphorus nitrides generally are reported to be amorphous. In one exception,[1,2] a crystalline

(1) H. Moureu and P. Rocquet, *Bull. soc. chim.*, [5] **3**, 1801 (1936).

(2) H. Moureu and G. Wetroff, *ibid.*, [5] **4**, 918 (1937).