Zukunftsaufgaben hingewiesen, wie zum Beispiel die Aufklärung der Proteinkomponenten von Vitamin-Enzymen, und schliesslich wird die zunehmende Bedeutung der Vitamine auf dem Lebens- und Futtermittelsektor hervorgehoben.

### Literature

*General*


W. H. SEBRELL JR. and R. S. HARRIS (Eds.), *The Vitamins*, 2nd edn. (Academic Press, New York and London 1967 ff.), vol. 1–5.

R. TSCHESCHE, F. REIFF, F. v. WERDER, W. NÜBLING, R. STROHECKER, U. SCHWIETER, H. GUTMANN, H. MAYER and O. ISLER, in *Ullmanns Encyklopädie der technischen Chemie*, 3rd edn. (Ed. W. FOERST; Urban & Schwarzenberg, München, Berlin and Wien 1967), vol. 18, p. 177.

R. S. HARRIS, K. V. THIMANN, G. F. MARRIAN, D. J. INGLE, I. G. WOOL and J. A. LORAINE (Eds.), *Vitamins and Hormones, Advances in Research and Applications* (Academic Press, New York and London 1943 ff.), vol. 1 ff., e.g. vol. 18 (1960) (Vitamins A and Carotene), vol. 20 (1962) (Vitamins E), vol. 22 (1964) (Vitamin $B_6$), vol. 24 (1966) (Vitamins K and Related Quinones), vol. 26 (1968) (Vitamin-Related Anemias).

A. F. WAGNER and K. FOLKERS, *Vitamins and Coenzymes* (Interscience Publ., New York 1964).

G. BRUBACHER, W. HAUSHEER, O. WISS and G. HUSCHKE, in *Handbuch der Lebensmittelchemie* (Ed. J. SCHORMÜLLER; Springer-Verlag, Berlin, Heidelberg and New York 1965), vol. 1, p. 933.

T. W. GOODWIN, *The Biosynthesis of Vitamins and Related Compounds* (Academic Press, London 1963).

P. KARLSON, *Kurzes Lehrbuch der Biochemie*, 7th edn. (Georg Thieme Verlag, Stuttgart 1970).

R. A. MORTON, Int. Z. Vitaminforsch., *Fat-soluble vitamins*, *38*, 5 (1968).

O. ISLER, U. SOLMS and J. WÜRSCH, in *International Encyclopaedia of Food and Nutrition* (Ed. H. M. SINCLAIR; Pergamon Press, Oxford, in press), vol. 9.

G. WALD, Angew. Chem. *80*, 857 (1968).

O. ISLER, Chim. Ind., Milano *49*, 1317 (1967).

O. ISLER and U. SCHWIETER, Dt. med. J. *16*, 576 (1965).

H. H. INHOFFEN, Angew. Chem. *72*, 875 (1960).

O. ISLER and M. MONTAVON, Bull. Soc. chim. France, *Water-soluble vitamins, 1965*, 2403.

A. GRÜSSNER and W. SCHLEGEL, in *Ascorbinsäure*, Wissenschaftliche Veröffentlichungen der Deutschen Gesellschaft für Ernährung (Ed. K. LANG; Steinkopff Verlag, Darmstadt 1965), vol. 14, p. 1.

E. DE RITTER, in *Encyclopedia of Chemical Technology*, 2nd edn. (KIRK-OTHMER; Interscience Publishers, New York 1968), vol. 17, p. 445.

E. L. R. STOKSTAD and J. KOCH, Physiol. Rev. *47*, 83 (1967).

F. LYNEN, Biochem. J. *102*, 381 (1967).

F. LYNEN, Pure appl. Chem. *14*, 137 (1967).

F. LYNEN, Angew. Chem. *77*, 929 (1965).

H. HOLZER, Angew. Chem. *73*, 721 (1961).

R. B. WOODWARD, Pure appl. Chem. *17*, 519 (1968).

Y. YAMADA, D. MILJKOVIC, P. WEHRLI, B. GOLDING, P. LÖLIGER, R. KEESE, K. MÜLLER and A. ESCHENMOSER, Angew. Chem. *81*, 301 (1969).


# SPECIALIA

Les auteurs sont seuls responsables des opinions exprimées dans ces brèves communications. – Für die Kurzmitteilungen ist ausschliesslich der Autor verantwortlich. – Per le brevi comunicazioni è responsabile solo l'autore. – The editors do not hold themselves responsible for the opinions expressed in the authors' brief reports. – Ответственность за короткие сообщения несёт исключительно автор. - El responsable de los informes reducidos, está el autor.

## Dissociation of Magnesian Calcites

Thermal studies of natural and synthetic calcites have been reported extensively and the dissociation temperature for calcite varies between 840 °C and 990 °C in the literature[1–5]. Lattice parameters of calcite modify with the substitutional impurity in solid-solution within calcite structure. Such systematic variations of lattice parameters with composition of calcite are indicated[6–8]. The present study concerns the changes in dissociation patterns with $Mg^{++}$ in the calcite lattice.

Pure calcite (synthetic), pure dolomite (synthetic), magnesian calcite (synthetic $Ca_9Mg_1$ composition) from Tem-Pres Research Inc. (USA) and natural magnesian calcite (from Bihar, India) are chosen in the present study. Differential thermal analysis was carried in air with Du Pont thermal analyzer with $Al_2O_3$ as inert material at 20 °C/min heating rate. The Figure indicates the dissociation patterns for these samples. For calcite (Figure, pattern 1), though the endothermic reaction starts around 600 °C, it is interesting to note that the peak occurs at 798 °C which is lower than the literature values. With artificial mixtures of synthetic calcite and 20% dolomite (synthetic), the thermal pattern indicates no shift in dissociation temperature of calcite (Figure, pattern 2). This may be that both these members have their dissociation in the same temperature range. However, with synthetic


[1] C. W. BECK, Am. Miner. *35*, 985 (1950).

[2] F. L. CUTHBERT and R. A. ROWLAND, Am. Miner. *32*, 111 (1947).

[3] R. A. W. HAUL, Am. Miner. *37*, 166 (1952).

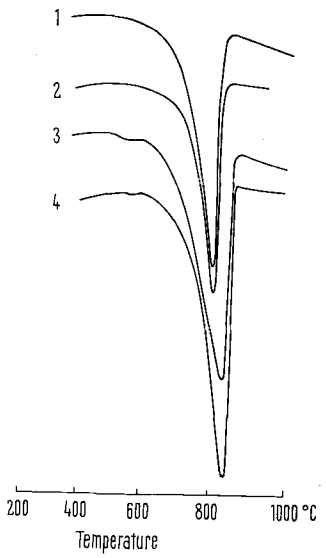
[4] R. I. HARKER and O. F. TUTTLE, Am. J. Sci. *253*, 274 (1955).

[5] J. L. KULP, P. KENT and P. F. KERR, Am. Miner. *36*, 643 (1951).

[6] K. W. ANDREWS, Mineralog. Mag. *29*, 85 (1950).

[7] J. R. GOLDSMITH, D. L. GRAF and O. I. JOENSUU, Geochim. cosmochim. Acta *7*, 212 (1955).

[8] J. R. GOLDSMITH and D. L. GRAF, Am. Miner. *43*, 84 (1958).




Differential thermal patterns for (1) pure synthetic calcite, (2) mixture of pure calcite with 20% pure dolomite, (3) magnesian calcite (synthetic with $Ca_9Mg_1$ composition) and (4) natural magnesian calcite.

magnesian calcite a shift in the dissociation to 830 °C is noticed. A similar shift to 842 °C is observed with natural magnesian calcite (Figure, patterns 3 and 4). A shallow endothermic peak around 565 °C was also seen in both these cases.

The present study thus indicates that the dissociation of magnesian calcites is a function of the nature and extent of impurity in the lattice, and that presence of dolomite in a physical mixture with calcite does not affect the dissociation trend of calcite. A systematic differential thermal study with magnesian calcites of differing composition would be of considerable importance of estimation of the extent of $Mg^{++}$ present in solid-solution in natural magnesian calcites. In such studies, however, the grain size and other affecting parameters need to be properly controlled.

*Zusammenfassung.* Es wurde die Dissoziationstemperatur für verschiedene synthetische und natürliche Calcite und Mg-Calcite bestimmt. Die Dissoziationstemperatur ist abhängig vom Mg-Gehalt des Gitters.

K. V. G. K. Gokhale and T. C. Rao

*Indian Institute of Technology, Kanpur-16 (India), 9 October 1969.*

## Cocsulin: a New Bisbenzylisoquinoline Alkaloid from *Cocculus pendulus* Diels[1]

Confirmation of anticancer and hypotensive activity in the alkaloid fraction from leaves and stem of *Cocculus pendulus* Diels[2] has led to further chemical investigations and the isolation of pendulin, a new biscoclaurine base[3]. We now report a second new base, provisionally designated as cocsulin, from this fraction.

Cocsulin, $C_{35}H_{34}N_2O_5$[4] ($M^+$, 562), mp 272–274 °, $[\alpha]_D$ + 280 °, formed a picrate mp 194–196 °. Its IR-spectrum with maxima at 2907, 1621, 1575, 1504, 1453, 1372, 1269, 1198, 1119, 831 and 778 $cm^{-1}$ indicated the presence of hydroxyl and ether functions and its substituted aromatic nature. The UV-spectrum of cocsulin was typical of a bisbenzylisoquinoline; a maximum at 284 nm shifting bathochromically to 304 nm on addition of alkali[5]. With $H_2SO_4$-$HNO_3$, cocsulin gave a blue coloration characteristic of bisbenzylisoquinoline alkaloids having a diphenylene dioxide function[6].

The NMR-spectrum of cocsulin integrated for 34 protons: 2 NMe singlets at $\tau$ 7.44 and 7.62, 1 OMe singlet at $\tau$ 6.15, 4 benzylic, 8-ring methylene and 2-ring methylene protons at $\tau$ 6.75, 7.29 and 5.98 respectively, and 10 aromatic protons (a shielded singlet at $\tau$ 3.86, a 2-proton singlet at $\tau$ 3.16 and a 7-proton multiplet between $\tau$ 2.40–3.39).

Treatment of methanolic solutions of cocsulin with diazomethane and diazoethane yielded *O*-methylcocsulin, $C_{36}H_{36}N_2O_5$ ($M^+$, 576) mp 212–214 °, $[\alpha]_D$ + 289 °, and *O*-ethylcocsulin, $C_{37}H_{38}N_2O_5$ ($M^+$, 590) mp 214–216 °, $[\alpha]_D$ + 225 °, respectively. The IR-spectrum of these compounds showed the absence of free hydroxyl functions and their NMR-spectra were similar to that of cocsulin except for an additional OMe singlet at $\tau$ 6.0 in the spectrum of *O*-methylcocsulin and an *O*-ethyl triplet at $\tau$ 8.48 and quartet at $\tau$ 5.74 (J, 11 Hz) in the spectrum of *O*-ethylcocsulin.

Comparison of *O*-methylcocsulin with an authentic sample of isotrilobine[7] established their identity. Cocsulin, isomeric with trilobine was, therefore, an *O*-demethylated derivative of isotrilobine, a *bis*benzylisoquinoline isolated from *Cocculus trilobus, Cocculus sarmentosus*[7] and *Stephania hernandiflora*[8]. In confirmation, cocsulin yielded a dimethiodide, $C_{38}H_{42}IN_2O_5$, identical in all respects to isotrilobine dimethiodide[9] and Hofmann degradation of this compound yielded a methine, $C_{38}H_{40}N_2O_5$, mp 114–117 °, that appeared identical with the reported isotrilobine methylmethine[10].

The location of the hydroxyl group of cocsulin followed from a consideration of the mass spectra of cocsulin and *O*-methylcocsulin. The $M^+$ peak in both spectra were prominent. The most important diagnostic peaks in the spectra of the trilobine type of alkaloids are those due to a doubly-charged ion m/e 175 (I) and a prominent ion m/e 350 (II)[11]. Both these peaks are present in the

[1] Communication No. 1436 from Central Drug Research Institute.
[2] D. S. Bhakuni, M. L. Dhar, M. M. Dhar, B. N. Dhawan and B. N. Mehrotra, Indian J. exp. Biol., in press.
[3] N. C. Gupta, D. S. Bhakuni and M. M. Dhar, in press.
[4] Satisfactory C, H and N analysis of all reported compounds obtained. Optical rotations were routinely determined in $CHCl_3$, UV-spectra in EtOH, IR-spectra in KBr and 60 Mcs NMR-spectra in $CDCl_3$ with TMS as an internal standard.
[5] A. W. Sangster and K. L. Stuart, Chem. Rev. *65*, 69 (1965).
[6] M. Tomita and J. Kunitomo, J. pharm. Soc. Japan *52*, 139 (1932).
[7] H. Kondo and T. Nakazato, J. pharm. Soc. Japan *532*, 461 (1926). – M. Tomita and S. Ueda, J. pharm. Soc. Japan *78*, 194 (1958).
[8] M. Tomita and S. Ueda, J. pharm. Soc. Japan *79*, 977 (1959).
[9] H. Kondo and M. Tomita, J. pharm. Soc. Japan *48*, 659 (1928).
[10] H. Kondo and M. Tomita, J. pharm. Soc. Japan *50*, 1035 (1930); Justus Liebig's Annln. Chem. *497*, 104 (1932).
[11] D. C. Jongh, S. R. Shrader and M. P. Cava, J. Am. chem. Soc. *88*, 1052 (1966). – M. Tomita, T. Kikuchi, T. Fujitani, A. Kato, H. Furukawa, Y. Aoyagi, M. Kitano and T. Ibuka, Tetrahedron Letters *857* (1966). – J. Baldas, Q. N. Porter, I. R. C. Bick and M. J. Vernengo, Tetrahedron Letters *2059* (1966).