isobutyric acid and 5 g. of red phosphorus at 70–80°. The excess bromine was removed by evaporation under diminished pressure and the residue cooled in ice while 20 cc. of methanol was added. On fractional distillation, 14.4 g. (25%) of methyl α-bromoisobutyrate was obtained; b. p. 52° (19 mm.),[7] n^{20}_D 1.4410; d^{20}_4 1.331; M^{20}_D (calcd.), 34.71; M^{20}_D (found), 35.01.

Anal. Calcd. for $C_5H_9O_2Br$: Br, 44.15. Found[6]: Br, 43.14.

The physical properties of this ester changed appreciably on standing for a few hours since hydrogen bromide is evolved with extreme ease. This accounts for the low bromine content of the product. The physical properties recorded above were observed immediately after distillation.

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[7] Wheeler and Barnes, *Am. Chem. J.*, **24**, 79 (1900).

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The Identity of Obaculactone, Evodin and Dictamnolactone with Limonin[1]

BY MILTON S. SCHECHTER AND H. L. HALLER

Several investigators[2,3] have isolated from the extractives of the bark of the amur cork tree (*Phellodendron amurense* Rupr.) a colorless, crystalline, optically active compound, which melts with decomposition at 292–293° and possesses the properties of a dilactone. The compound was named "obaculactone" by Fujita and Wada,[2] who were the first to describe it. On the basis of combustion analyses and molecular weight determinations they assigned the formula $C_{15}H_{16}O_6$ to obaculactone, but subsequent studies have shown this formula to be in error. The molecular formula $C_{26}H_{30}O_8$ is now generally accepted as correctly representing the composition of the compound.

In 1934 Fujita, Kaku and Kutani[4] showed that obaculactone is identical with evodin and with dictamnolactone. Evodin was first isolated by Keimatsu[5] in 1902 from the benzene extractives of the fruit of *Evodia rutaecarpa* Hook. f. and Thoms., and subsequently by several investigators from the fruits of other species of *Evodia.* Dictamnolactone was first described by Thoms and his co-workers[6] who obtained it from the extractives of white dittany (*Dictamnus albus* L.). The latter workers surmised that evodin and dictamnolactone were identical but were unable to make a direct comparison. The identity of the three compounds was established[4] by mixture melting point determinations and specific rotations in neutral and alkaline solution. In acetone all three compounds are levorotatory; $[\alpha]_D$ about $-123°$. In ethanolic potassium hydroxide solution they are dextrorotatory; $[\alpha]_D$ about $+30°$.

None of the early formulas assigned to the lactone were correct. In 1933 Chen and Chen[7] proposed the formula $C_{26}H_{30}O_8$. Mayeda[8] confirmed this and suggested that some of the previous difficulties in the determination of the molecular formula may have been due to the fact that the lactone crystallizes from acetic acid with one mole of acetic acid of crystallization. The lactone melts with decomposition, and melting points ranging from 280 to 293° have been reported for obaculactone, evodin and dictamnolactone by the several investigators.

A recent communication by Higby[9] describes the isolation of limonin from the pulp and seeds of the Valencia orange. This colorless, crystalline compound was first obtained by Bernay[10] in 1841 from the seeds of several varieties of citrus. Limonin has been shown to be an optically active dilactone, and combustion analyses and molecular weight determinations indicate it to possess the formula $C_{26}H_{30}O_8$. Koller and Czerny[11] have reported that limonin melts with decomposition at 280° (uncor.), whereas Higby found 292° (cor.). Citrolimonin, which is considered by Feist and Schulte,[12] by Koller and Czerny, and by Higby as being identical with limonin, is reported to melt with decomposition at 304° (Kofler micro melting point apparatus) by the first-mentioned workers.

In the course of our studies on the insecticidal properties of the fruit of the amur cork tree, the results of which will be reported elsewhere, obaculactone has been obtained from the ether and the acetone extracts of the fruit. The compound, when recrystallized by solution in acetone followed by the addition of ethanol, melted with decomposition at 299–300° (cor.).[13] When recrystallized from glacial acetic acid, it melted with decomposition at 297–298° (cor.). An aqueous

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[1] Not subject to copyright.

[2] Fujita and Wada, *J. Pharm. Soc. Japan*, **51**, 506 (1931), (in German 52).

[3] Kaku, Cho and Orita, *ibid.*, **52**, 593 (1932), (in German 73).

[4] Fujita, Kaku and Kutani, *ibid.*, **55**, 67 (1935).

[5] Keimatsu, *ibid.*, No. **248**, 979 (1902).

[6] Thoms, *Ber. deut. pharm. Ges.*, **33**, 68 (1923).

[7] Chen and Chen, *J. Am. Pharm. Assoc.*, **22**, 716 (1933).

[8] Mayeda, *J. Pharm. Soc. Japan*, **55**, 90 (1935).

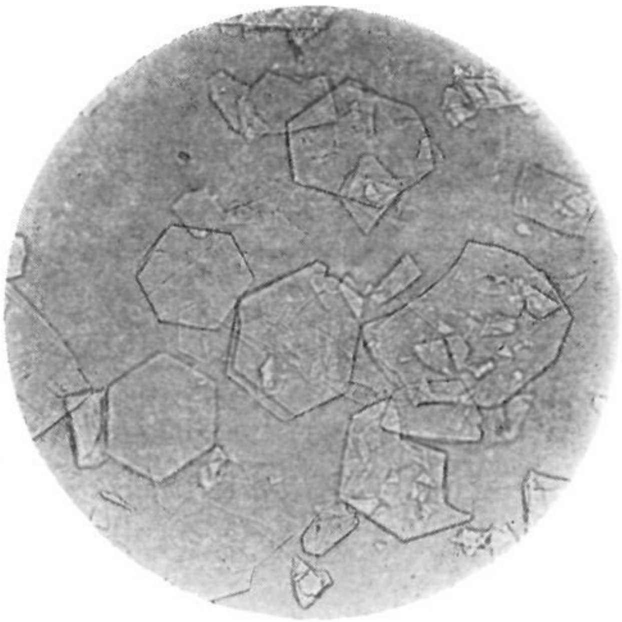
[9] Higby, THIS JOURNAL, **60**, 3013 (1938).

[10] Bernay, *Ann.*, **40**, 317 (1841).

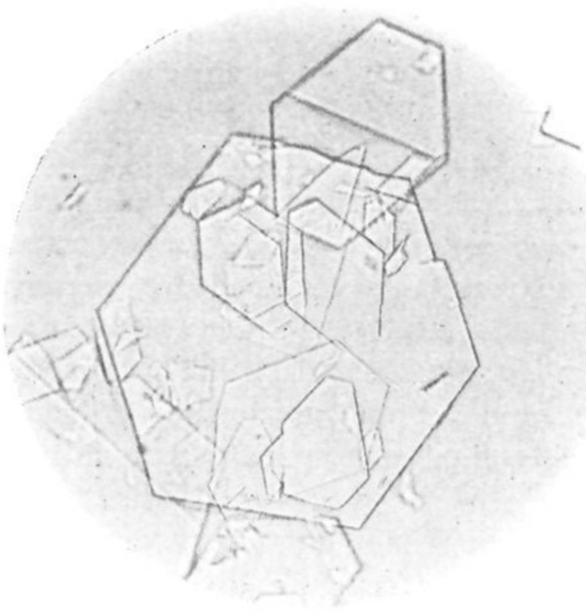
[11] Koller and Czerny, *Monatsh.*, **67**, 248 (1936); **70**, 26 (1937).

[12] Feist and Schulte, *Ber.*, **69**, 1322 (1936).

[13] All the melting point determinations reported were made in open melting point capillaries, using a total immersion thermometer calibrated by the National Bureau of Standards, Washington, D. C.



Obaculactone (× 77).



Limonin (× 193).

Fig. 1.

ethanol solution of the lactone has an intensely bitter taste. It is insecticidally inert.

Some of the chemical properties recorded for obaculactone have been confirmed by us. It is a dilactone, dissolves in concentrated sulfuric acid with the formation of an intense red brown color, and does not absorb bromine in chloroform solution. It does not possess alkoxyl groups, or reactive carbonyl or hydroxyl groups. Contrary to the statement of Fujita and Wada,[2] it has been found that obaculactone absorbs hydrogen slowly on catalytic hydrogenation with the formation of a mixture of products. A study of these products will form the subject of a future communication.

Obaculactone recrystallized from a mixture of ethanol and acetone and then dried in an Abderhalden drier at 100° gave the following analytical data:

Anal. Calcd for $C_{26}H_{30}O_8$: C, 66.35; H, 6.43; mol. wt., 470. Found: C, 66.39, 66.20; H, 6.52, 6.50; mol. wt. (Rast), 445; equiv. wt. (sodium hydroxide titration), 240. *Optical rotation:* 0.0888 g. in 10 cc. of acetone at 20.5° rotated $-2.29°$; l = 2.0 dm.; $[\alpha]^{20.5}\text{D}$ $-129°$. 0.0844 g. in 5 cc. of 0.5 N ethanolic potassium hydroxide and 5 cc. of water at 20.5° rotated $+0.55°$; l = 2.0 dm.; $[\alpha]^{20.5}\text{D}$ $+32.6°$.

The melting point, the rotation in neutral solution, the behavior toward alkali, and the identity of the molecular formula of obaculactone and limonin led us to believe that the two were the same. Through the courtesy of Dr. M. B. Matlack, Food Research Division, Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture, we obtained a sample of limonin isolated by him from orange seed. When recrystallized from ethanol or from glacial acetic acid the compound melted with decomposition at 297–298° (cor.). A mixture of equal parts of limonin and obaculactone also melted with decomposition at 297–298° (cor.).

The optical rotations of limonin in acetone solution and in 0.25 N aqueous ethanol potassium hydroxide solution were practically identical with the values obtained for obaculactone in these solvents.

Obaculactone and limonin recrystallized from ethanol consisted of colorless, micaceous, six-sided plates and were found to be identical microscopically.[14] Refractive indices (determined by immersion in oily liquids): $n_\alpha = 1.563$; n_β = indet.; $n_\gamma = 1.582$; both ± 0.002. In parallel polarized light (crossed nicols) the birefringence is moderate, usually first-order grays being shown. There appears to be no definite elongation. In convergent polarized light (crossed nicols) the plates were found to extinguish sharply, indicating that the plane of the optic axes is approximately parallel to the broad face of the plates so that interference figures could not be expected. Therefore, the refractive indices were determined by a variation of the statistical method, plates showing maximum double refraction for obtaining n_α and n_γ being selected.

The foregoing results indicate clearly that obaculactone and limonin are identical.

Since obaculactone, evodin, dictamnolactone, limonin, and citrolimonin are the same compound, it would appear desirable to retain one name and discard the others. As the compound was first

(14) We are indebted to George L. Keenan, of the Food and Drug Administration, U. S. Department of Agriculture, for the photomicrographs and for the optical crystallographic data reported here.

obtained by Bernay, who designated it "limonin," we suggest that this name be retained.

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
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Mechanism of Nuclear Isomer Separation Process

BY G. T. SEABORG, G. FRIEDLAENDER AND J. W. KENNEDY

It has been shown that the energy released during the radioactive transition from an upper to a lower isomeric state of an atomic nucleus can be used to effect a chemical separation of two genetically related nuclear isomers and this discovery has provided a powerful method for the study of nuclear isomerism.[1,2,3,4] These so-called *isomeric transitions* have been the source of activation energy for many interesting chemical reactions and offer a unique method for a study of chemical activation.[1–6] We wish to report briefly some experiments which we have performed for the purpose of elucidating the mechanism of the chemical separation process.

The small amount of recoil energy, about 5.6 kcal. per mole,[7] acquired in the majority of the cases by the Br^{80} atom as the result of the emission of an internal conversion electron during an isomeric transition in a Br^{80} nucleus, seemed to be too small to account for the bond rupture and activation experiments (sometimes 100% efficient[1]) observed with bromine compounds. We have performed experiments with the isomeric transitions[3] in radioactive Te^{127} and Te^{129}, where the recoil energies are again very small. Internal conversion electrons are emitted in these cases and the recoil energies[3] of the tellurium atoms are 9.2 and 6.6 kcal. per mole for Te^{127} and Te^{129} respectively. We made a quantitative study of the change of telluric acid to tellurous acid which occurs when the radioactive Te^{127} or Te^{129} nucleus in the telluric acid undergoes a transition from its upper to its lower isomeric state. The experiments show, for both Te^{127} and Te^{129}, that the isomeric transitions effect reduction of telluric to tellurous acid with approximately 100% yield in aqueous solution at room temperature or even when frozen to the temperature of liquid air.

These experiments suggest, in view of the very small recoil energies involved, that the bond rupture and activation occurs, not as a result of the recoil energy, but as a consequence of the high state of electronic excitation which results from the vacancy in the K- or L-shell created by the emission of the internal conversion electron. A direct test of this view could be obtained by determining whether or not bond rupture could be initiated by an isomeric transition in which the transition gamma-ray undergoes very little internal conversion. Just such a case[8] is radioactive Zn^{69}, where the transition gamma-rays are largely *unconverted* and are of such an energy as to impart 40 kcal. of energy to the recoiling zinc atoms. We compared the effectiveness of the Zn^{69} transition in producing bond rupture with that of Te^{127} and Te^{129} under comparable conditions, namely, with the zinc and tellurium in the form of their gaseous diethyl compounds at 110°. The separation of the radioactivity corresponding to the lower isomeric state, as shown by its presence on the walls of the containing vessel (where fragments of the ruptured molecules collected), made it evident that again the isomeric transitions in Te^{127} and Te^{129} had been effective in producing an isomer separation process, while in the case of the zinc diethyl no separation was observed. The tellurium isomers were separated either in the presence or absence of electrically charged plates while the zinc isomers were not separable in any case. It is difficult to see how the isomer separations observed in tellurium compounds can be attributed to the recoil energy involved, since the recoil energy in the case of zinc is roughly five times greater and yet produces no separation in a similar molecule with similar bond energies.

These results lead to the not unexpected[6] conclusion that the state of high electronic excitation which exists after the loss of an internal conversion electron is responsible for the accompanying isomer separation process. For example, the tellurium atom is excited after K-shell conversion to the extent of 32 Kev. (740,000 kcal. per mole) or after L-shell conversion to 4.9 Kev. (110,000 kcal. per mole). During the electronic rearrangement which follows, the molecule should have ample opportunity to dissociate by reaching

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(1) E. Segrè, R. S. Halford and G. T. Seaborg, *Phys. Rev.*, **55**, 321 (1939).

(2) D. C. DeVault and W. F. Libby, *ibid.*, **55**, 322 (1939).

(3) G. T. Seaborg, J. J. Livingood and J. W. Kennedy, *ibid.*, **57**, 363 (1940).

(4) A. Langsdorf, Jr., and E. Segrè, *ibid.*, **57**, 105 (1940).

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(6) J. E. Willard, THIS JOURNAL, **62**, 256 (1940).

(7) G. E. Valley and R. L. McCreary, *Phys. Rev.*, **56**, 863 (1939).

(8) J. W. Kennedy, G. T. Seaborg and E. Segrè, *ibid.*, **56**, 1095 (1939).