Vc: Colorless prisms from methanol, m.p. 276° (decomp.); yield 27%.

Anal. Calcd. for $C_{11}H_{17}N_3O_2$: C, 59.20; H, 7.63; N, 18.80. Found: C, 59.53; H, 7.62; N, 18.87.

High pressure hydrogenations of IIb, IIc, Vb, and Vc. General procedure. A mixture of one part of IIb (or IIc, Vb, Vc) and 1–2 parts of copper chromite in 20–30 parts of dioxane (v.) was submitted to hydrogenation at 250° and 130 atmospheres (initial pressure) for 1 hr. In the case of IIb or IIc, the reaction mixture was filtered, dry hydrogen chloride was passed into the filtrate, and dioxane was removed under reduced pressure. After adding water to the residue, it was made basic with potassium carbonate, the base was extracted with ether, the extract was washed and dried, the ether was evaporated, and the remaining material was distilled. In the case of Vb or Vc, the filtrate was directly stripped under reduced pressure and the residual oil was distilled. *Pyrrolizidine* (IIIb), b.p. 135°, yield 55%, formed a picrate, longish yellow needles from ethanol, m.p. 253° (decomp.). A mixed melting point with the sample prepared by the method of Leonard, *et al.*[3] showed no depression. *Indolizidine* (IIIc): b.p. 70–80° (bath temp.)/30 mm., yield 66%. *Picrate:* yellow needles from ethanol, m.p. 233°. A mixed melting point with the sample prepared by the method of Leonard, *et al.* showed no depression. *2-Methyl-hexahydropyrido[3,4,5-g,h]-pyrrolizidine* (VIb): b.p. 70–90°/4 mm., yield 40%. This was dissolved in ethanol containing sulfamic acid and the separated sulfamate solidified on standing for several days. It melted at 127° and was difficult to recrystallize because of its hygroscopic nature. The salt was dissolved in water, the solution was made basic with potassium hydroxide, and the base was extracted with ether. The purified oil distilled at 70–72°/4 mm.

Anal. Calcd. for $C_{10}H_{18}N_2$: C, 72.24; H, 10.91; N, 16.85. Found: C, 72.35; H, 10.91; N, 16.70.

Monohydrate crystallized from this oil on standing in air. Recrystallization from petroleum ether gave colorless prisms, m.p. 160°.

Anal. Calcd. for $C_{10}H_{18}N_2.H_2O$: C, 65.17; H, 10.94; N, 15.21. Found: C, 65.41; H, 10.70; N, 15.38.

2-Methyl-hexahydropyrido[3,4,5-h,i]-indolizidine (VIc): b.p. 140–180° (bath temp.)/12 mm., yield 54%. Purified base prepared through its flavianate distilled at 145–150° (bath temp.)/12 mm.

Anal. Calcd. for $C_{11}H_{20}N_2$: C, 73.28; H, 11.18; N, 15.55. Found: C, 73.01; H, 11.01; N, 15.32. *flavianate:* yellow needles from water, m.p. 267° (decomp.).

Anal. Calcd. for $C_{11}H_{20}N_2.2C_{10}H_6N_2O_8S$: C, 46.05; H, 3.96; N, 10.04. Found: C, 46.33; H, 3.90; N, 9.92.

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Infrared Spectra of Some Naturally Occurring Flavonoids

G. E. INGLETT[1]

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Numerous infrared spectra of some naturally occurring flavonoids have been recorded for rapid structural elucidation of these structures in the course of studying the occurrence of flavonoids in allergenic pollens. Flavonoid pigments have been found to be widely distributed in pollen. In 1919 Heyl isolated a quercetin glucoside and isorhamnetin from ragweed pollen.[2] Stevens, Moore, and Baer[3] have recently shown a quercetin glucoside from giant ragweed pollen to be isoquercitrin. Some of the other flavonoids isolated from pollen are rutin,[4] isorhamnetin-3,4′-diglucoside,[5,6] and a isorhamnetin-3-trisaccharide.[7]

EXPERIMENTAL

Materials: Samples of apiin (5,7,4′-trihydroxyflavone-7-apioside), chrysosplenin (5,4′-dihydroxy-6,7,3′-trimethoxyflavone-3-glucoside), luteolin-7-glucoside (5,3′,4′-trihydroxyflavone-7-glucoside), pectolinarin (5-hydroxy-6,3′-dimethoxyflavone-7-rhamnoglucoside), reynoutrin (5,7,3′,4′-tetrahydroxyflavone-3-xyloside), robinin (5,4′-dihydroxyflavone-3-robinobio-7-rhamnoside), chrysosplenetin (3,5,4′-trihydroxy-6,7,3′-trimethoxyflavone), and luteolin (5,3′,4′-trihydroxyflavone) were kindly supplied by Dr. Tashichiro Nakaoki. Dr. Richard Kuhn kindly supplied samples of isorhamnetin (3,5,7,4′-tetrahydroxy-3′-methoxyflavone) and 3,4′-dihydroxy-5,7,3′-trimethoxyflavone, and Dr. Simon H. Wender kindly supplied the samples of apigenin-7-rhamnoglucoside (5,7,4′-trihydroxyflavone-7-rhamnoglucoside) and naringin (5,7,4′-trihydroxyflavanone-7-rhamnoglucoside). The sample of flavone was kindly sent to us by Dr. T. S. Wheeler. Dactylin (isorhamnetin-3,4′-diglucoside) was isolated from timothy pollen.[6]

Infrared spectra. The spectral data recorded in Table I were obtained by a recording Perkin-Elmer infrared spectrometer, Model 21. The flavonoids were dissolved in dimethylformamide and placed on a micro silver chloride plate. The solvent was removed by means of an infrared heat lamp. A smooth film of flavonoid was deposited on the plate. A drop of Nujol on the film gave sharp spectra.

DISCUSSION

Hergert and Kurth[8] in 1953 reported some infrared spectral studies on some flavanones, flavones, chalcones, and acetophenones. The small number of naturally occurring flavones and flavonols employed in their study did not make it possible to assign any specific absorption region for the carbonyl band. In the present study, the naturally occurring flavonoids recorded in Table I reveal a specific carbonyl region for naturally occurring flavones and flavonols. The flavones, apigenin-7-rhamnoglucoside, apiin, pectolinarin, luteolin, and luteolin-7-glucoside, recorded in Table I have carbonyl absorption bands between 1660 cm.$^{-1}$ and 1655 cm.$^{-1}$

The flavonols, chrysosplenetin, chrysosplenin, dactylin, isorhamnetin, quercetin, quercitrin, rey-

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[1] Present address: Box 345, Corn Products Refining Co., Argo, Ill.

(2) F. W. Heyl, *J. Am. Chem. Soc.* **41**, 1285 (1919).

(3) F. A. Stevens, D. Moore, and H. Baer, *J. Allergy*, **22**, 165 (1951).

(4) M. S. El Ridi, L. A. Strait, and M. H. A. Wafa, *Arch. Biochem. Biophys.*, **39**, 317 (1952).

(5) R. Kuhn and I. Löw, *Ber.*, **77**, 196 (1944).

(6) G. E. Inglett, *Nature*, **178**, 1346 (1956).

(7) G. Tappi and E. Menziani, *Gazz. chim ital.*, **85**, 703 (1955).

(8) H. L. Hergert and E. F. Kurth, *J. Am. Chem. Soc.*, **75**, 1622 (1953).

TABLE I

Hydroxyl and Carbonyl Frequencies of Some Naturally Occurring Flavonoids

Compound	Hydroxyl, Cm.$^{-1}$	Carbonyl, Cm.$^{-1}$	Flavone-Flavonoid, Δ Cm.$^{-1}$
	Flavones		
Flavone	...	1660	0
Apigenin-7-rhamnoglucoside	3330	1658	2
Apiin	3240	1660	0
Luteolin	3220	1655	5
Luteolin-7-glucoside	3160	1658	2
Pectolinarin	3320	1658	2
	Flavonols		
Chrysosplenetin	3320	1658	2
Chrysosplenin	3300	1658	2
Dactylin	3220	1655	5
Isorhamnetin	3160	1655	5
Quercetin	3340	1655	5
Quercitrin	3280	1655	5
Reynoutrin	3140	1652	8
Robinin	3240	1655	5
Rutin	3300	1655	5
	Flavanones		
Flavanone	...	1680	0[a]
Hesperidin	3340	1639	41[a]
Naringin	3360	1639	41[a]

[a] Flavanone-flavonoid values.

noutrin, robinin, and rutin, have carbonyl absorption bands between 1652 cm.$^{-1}$ and 1658 cm.$^{-1}$ as shown in the table. The difference (Δ cm.$^{-1}$) of the parent flavone minus the flavonoid is very small for the flavones and considered to be within the experimental error of the parent flavone carbonyl frequency. The flavones listed in Table I have hydroxyl group at the C—5 position adjacent to the carbonyl group with the exception of the parent compound, flavone. The lack of difference of the naturally occurring flavone carbonyl frequencies from the parent flavone would suggest the lack of hydrogen bonding in these substances. This does not seem reasonable, nor can it be rationalized on the basis of the shifts observed for hydrogen bonding for similar substituted substances.[9–11] The interpretation of these anomalies by Hergert and Kurth appears to be sufficient.

The flavonols differ from the flavones by having a hydroxyl or glycosidic linkage at the C-3 position. This added opportunity for hydrogen bonding of the C-3 hydroxyl group with the carbonyl for the flavonoids, isorhamnetin, quercetin, and chrysosplenetin, did not make itself apparent. Likewise the C-5 hydroxyl containing flavonols do not reveal an appreciable difference (Δ cm.$^{-1}$) between the flavonol carbonyl frequency and the parent flavone.

The flavanone carbonyl absorption frequencies are in sharp contrast to the flavones as also noted by Hergert and Kurth. The parent flavanone has a carbonyl absorption band at 1680 cm.$^{-1}$ and the substituted flavanones, hesperidin, and naringin, have carbonyl absorption bands at 1639 cm.$^{-1}$ This shift of 41 wave numbers to the longer wave length is evidence of hydrogen bonding in these flavonoids.

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[9] M. St. C. Flett, *J. Chem. Soc.*, 1441 (1948).

[10] B. Cleverley, Ph.D. Thesis, University of New Zealand, 1953.

[11] M.-L. Josien, N. Fuson, J.-M. Lebas, and T. M. Gregory, *J. Chem. Phys.*, 21, 331 (1953).

Syntheses of DL-β-Aminobutyric Acid and Its N-Alkyl Derivatives

Albert Zilkha and Joseph Rivlin

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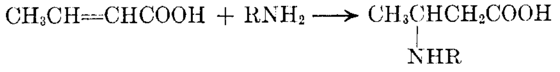
Only a few *N*-alkyl derivatives of β-aminobutyric acid are reported in the literature.[1,2] They were usually prepared in low yield by reduction of the intermediate imino derivative obtained by the reaction of the appropriate amine with ethyl acetoacetate.[1,2] Some esters of these compounds were prepared by the reaction between amines and ethyl crotonate,[3] which requires a long reaction time and usually gives low yields.

In this paper is given a simple synthesis of these compounds based on the direct addition of amines to crotonic acid. It was found that the addition of amines to the double bond in neutral solvents such as dioxane or benzene did not take place and only the amine salts of crotonic acid were formed. However, under the influence of basic solvents such as pyridine or α-picoline, the addition of primary aliphatic amines readily took place; the less reactive secondary amines and aromatic amines did not interact with the double bond.

The reaction was carried out by heating one mole of crotonic acid with one mole of amine in pyridine at 120–130° for 1–2 hours, and proceeded according to the following scheme:



$$CH_3CH{=}CHCOOH + RNH_2 \longrightarrow CH_3\underset{\displaystyle NHR}{\underset{|}{C}}HCH_2COOH$$

The *N*-alkyl derivatives of DL-β-aminobutyric acid usually crystallized out directly on cooling; otherwise the pyridine solution was evaporated to dryness *in vacuo* and the oily residue crystallized from hot acetone.

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[1] C. A. Skita and C. Wulff, *Ann.*, **453**, 190 (1927).

[2] J. Décombe, *Ann. Chim.*, **18**, 81 (1932).

[3] K. Morsch, *Monatsh.*, **60**, 50 (1932).