tane solution dried (Na_2SO_4). The solvent was distilled at atmospheric pressure using a 12-cm vacuum-jacket spiral wire filled column. The residue was distilled through a short-path still, bp 72–73° (18 mm), to yield 10.55 g (73%) of 98% (GC) pure hydrocarbon. The product displayed spectral characteristics identical with the reported values.[4,5]

***exo*-4,7-Dimethyl-5,6-diphenylpentacyclo$[8.2.2.1^{4,7}.0^{2,9}.0^{3,8}]$-pentadeca-5,11,13-trien-15-one (4b).** In a 250-ml, round-bottomed flask equipped with a reflux condenser were placed tricyclo$[4.2.2.0^{2,5}]$deca-3,7,9-triene (**2**, 10.15 g, 0.078 mol), 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer (20.0 g, 0.04 mol),[14] and dry benzene (100 ml). The solution was refluxed with magnetic stirring under a nitrogen atmosphere until the red color disappeared (~40 h) and cooled to room temperature, and ether (75 ml) was added. The white precipitate was filtered, washed with cold ether, and dried under reduced pressure at 25° to yield 21.1 g (70%) of exo isomer **4b**. An analytical sample was recrystallized from CCl_4–MeOH: mp 182–184° dec; NMR ($CDCl_3$) δ 1.19 (s, 6), 1.72–1.93 (m, 4), 3.62 (m, 2), 6.26–6.58 (overlapping triplets, apparent quintet, 4, J = 4 Hz), 6.78–7.30 (m, 10); ir (KBr) 696, 722, 760, 781, 809, 1395, 1440, 1755, and 2930 cm^{-1}; mass spectrum m/e 390 (M^+), 362 (M^+ − CO), 284 (M^+ − CO − benzene), 258.

Anal. Calcd for $C_{29}H_{26}O$: C, 89.19; H, 6.71. Found: C, 88.96; H, 6.76.

The filtrate was concentrated to a viscous oil, which was dissolved in hot CCl_4 (25 ml), and diluted with hot absolute EtOH (100 ml). The solution was rotary evaporated to 60 ml, the precipitate filtered, and the solid washed with EtOH. The filtrate was further concentrated to yield a product of lesser purity. A total of 7.1 g (22%) of product was obtained from the ethanolic solution, and these crops were enriched in the endo isomer: NMR ($CDCl_3$) δ 1.34 (s, 6), 1.88–2.30 (m, 4), 3.50–3.94 (m, 2), 6.25 (t, 2, J = 3.5 Hz), 6.51 (t, 2, J = 3.5 Hz), 6.85–7.32 (m, 10).

Bicyclo[2.2.2]octa-2,5,7-triene (1). To a quartz irradiation well equipped with a magnetic stirrer and a dry ice condenser was added a solution of **4b** (7.80 g, 20 mmol) in dry tetrahydrofuran (125 ml) and the solution was purged with dry nitrogen for 1 h. The solution was irradiated through a Vycor filter with a Hanovia 450-W lamp and the progress of the reaction followed by TLC (10% EtOAc–90% ligroin). After a 6-h period only traces of starting material remained and the irradiation was terminated. The reaction solution was transferred to a 250-ml, round-bottomed flask, the solution freeze–thaw degassed (five cycles, 25 μ), and the volatile material vacuum transferred to a 250-ml, round-bottomed flask cooled in liquid nitrogen; a thick yellow residue remained in the distillation flask. An additional 20 ml of tetrahydrofuran was added to the residue, and the vacuum transfer repeated. The combined tetrahydrofuran solution was concentrated by distillation through a 40-cm spinning-band column at atmospheric pressure to leave 7.26 g of solution (10.7 mol % barrelene by NMR analysis, yield 1.07 g, 51%) which contained benzene and cyclooctatetraene as trace contaminants. Pure barrelene was isolated by preparative gas chromatography (15 ft × 0.25 in., 2.5% SE-30, 120°) and a neat sample displayed spectral properties identical with the literature values.[2,3]

***exo*-1,6-Dimethyl-7,8-diphenyltricyclo$[4.2.1.0^{2,5}]$nona-3,7-dien-9-one (5b).** A sublimer containing **4a** (100 mg, 0.256 mmol) was heated at 160° under aspirator vacuum for 2 h. The white sublimate was collected, yield 70 mg (87%) of **5b**, and was resublimed under identical conditions: mp 132–135°;[16] NMR (CCl_4) δ 1.19 (s, 6), 3.09 (s, 2), 6.52 (s, 2), 6.88–7.32 (m, 10);[17] ir (CCl_4) 699, 848, 891, 907, 928, 970, 1010, 1070, 1170, 1185, 1280, 1370, 1445, 1485, 1770, 2900, and 3000 cm^{-1}; mass spectrum m/e 312 (M^+), 286 (M^+ − C_2H_2), 284, (M^+ − CO, base peak), 258.

Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: C, 88.37; H, 6.29.

***exo*-4,7-Dimethyl-5,6-diphenylpentacyclo$[8.2.2.1^{4,7}.0^{2,9}.0^{3,8}]$-pentadeca-5,13-dien-15-onedicarboxylic Acid Anhydride (6).** A suspension of crude *endo*-tricyclo$[4.2.2.0^{2,5}]$deca-3,9-diene-7,8-dicarboxylic acid anhydride (12.2 g, 0.06 mol), 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer (15.7 g, 0.03 mol), and 100 ml of toluene was heated under reflux for 24 h; the bright red color of the monomeric dienone gradually disappeared. The suspension was cooled in an ice bath, and the product filtered. To the filtrate there was added 100 ml of ether and a second crop of crystals was obtained. The combined crops were dried under vacuum: yield 27.6 g (98%); mp 278–280°; NMR ($CDCl_3$) δ 1.20 (s, 6), 2.02 (broad s, 4), 3.01 (t, 2, J = 2 Hz), 3.35 (m, 2), 6.45 (t, 2, J = 4 Hz), 6.80–7.30 (m, 10); ir (KBr) 750, 809, 915, 1085, 1220, 1770, and 1850 cm^{-1}; mass spectrum m/e 462 (M^+), 434 (M^+ − CO), 258.

Anal. Calcd for $C_{31}H_{26}O_4$: C, 80.50; H, 5.67. Found: C, 80.71; H, 5.48.

Bicyclo[2.2.2]octa-2,5-diene-7,8-dicarboxylic Anhydride (7). A solution of **6** (924 mg, 2 mmol) in dry tetrahydrofuran (30 ml) was placed in a Vycor tube fitted with a stopcock, the tube was cooled in ice water in a transparent quartz Dewar flask, and the solution was degassed with nitrogen. At ice temperature, the solution was irradiated for 9 h in a Rayonet reactor using 254-nm light sources. A small amount of solid material was filtered, and the solution treated twice with small portions of ligroin and the resulting solids removed. Finally, a 25-ml portion of ligroin was added and the flocculent precipitate filtered and dried (0°, vacuum) to give 190 mg (54%) of material of about 90% purity (NMR analysis): mp 70–80° dec; NMR ($CDCl_3$) δ 3.20 (t, 2, J = 1.5 Hz), 4.12 (m, 2), 6.54 (t, 2, J = 3.5 Hz); ir ($CHCl_3$) 824, 914, 930, 960, 1010, 1080, 1230, 1295, 1345, 1775, 1845, 2920, and 3020 cm^{-1}.

A small amount of **7** was recrystallized by dissolving it in a minimal amount of tetrahydrofuran at room temperature, followed by the addition of 4 volumes of ether. The resulting solution was chilled for 12 h and the crystalline precipitate was filtered (~30% recovery), mp 70–80% (dependent upon heating rate).

Anal. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 68.14; H, 4.83.

Registry No.—**1**, 500-24-3; **2**, 21604-76-2; **3**, 51447-09-7; **4a**, 57496-75-0; **4b**, 57526-53-1; **5b**, 30450-25-0; **6**, 57496-76-1; **7**, 57496-77-2; 2,5-dimethyl-3,4-diphenylcyclopentadienone, 26307-17-5.

References and Notes

(1) This work was supported by the National Science Foundation, Grant MP573-04662.

(2) H. E. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82,** 1514 (1960); H. E. Zimmerman, G. I. Grunewald, R. M. Paufler, and M. A. Sherwin, *ibid.*, **91,** 2330 (1969).

(3) G. N. Taylor, *J. Org. Chem.*, **37,** 2904 (1972).

(4) M. Auram, E. Sliam, and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **636,** 184 (1960).

(5) H. H. Westburg and H. J. Dauben, *Tetrahedron Lett.*, 5123 (1968); E. N. Cain, R. Vukov, and S. Masamune, *Chem. Commun.*, 98 (1969); E. Vedejs, *ibid.*, 536 (1971).

(6) L. T. Scott and M. Jones, Jr., *Chem. Rev.*, **72,** 182 (1972); L. A. Paquette, W. E. Volz, M. A. Beno, and G. D. Christoph, *J. Am. Chem. Soc.*, **97,** 2562 (1975); E. Vedejs and E. S. C. Wu, *ibid.*, **97,** 4706 (1975).

(7) T. Wickersham, J. P. Li, and E. J. Warawa, *Synthesis*, 399 (1975).

(8) W. G. Dauben and L. N. Reitman, *J. Org. Chem.*, **40,** 835 (1975).

(9) C. M. Anderson, J. B. Bremner, H. H. Westberg, and R. N. Warrener, *Tetrahedron Lett.*, 1585 (1969).

(10) B. M. Trost and F. Chen, *Tetrahedron Lett.*, 2603 (1971); K. Wiesner, P. Ho, R. C. Jain, S. F. Lee, S. Oida, and A. Phillip, *Can. J. Chem.*, **51,** 1448 (1973).

(11) A small amount of benzene is formed by thermal decomposition of the hydrocarbon **2.** Thus, the thermolysis time should be kept to the minimum necessary for complete reaction.

(12) These compounds are known photoproducts of barrelene.

(13) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560,** 1 (1948).

(14) J. D. Rose and F. S. Statham, *J. Chem. Soc.*, 69 (1950).

(15) Progress of the reaction is conveniently followed by the disappearance of carbonyl absorption in the infrared spectrum.

(16) C. M. Anderson, I. W. McCay, and R. N. Warrener, *Tetrahedron Lett.*, 2735 (1970).

(17) The endo isomer was produced along with the exo isomer when a mixture of the pentacyclic ketones was pyrolyzed, but the endo isomer was never isolated in pure form. The new NMR bands attributed to it occurred at δ 1.26 (s, 6), 2.96 (s, 2), 6.06 (s, 2), and 6.83–7.26 (m, 10).

Oxidation of Secondary Alcohols with Ozone[1]

William L. Waters,* Anthony J. Rollin,
Cindy M. Bardwell, Jeffrey A. Schneider,
and Thomas W. Aanerud

Department of Chemistry, University of Montana,
Missoula, Montana 59801

Received October 15, 1975

The ozonation of alcohols has received only scattered attention throughout the literature.[2] Primary interest has been a mechanistic interpretation of the oxidation process. However, since we[1,3] and others[2] have noted fairly rapid

Table I

Alcohol	Registry no.	% ketone yield	Alcohol	Registry no.	% ketone yield
2-Propanol	67-63-0	83	2-Nonanol	628-99-9	57
2-Butanol	78-92-2	72	4-Nonanol	5932-79-6	68
2-Pentanol	6032-29-7	69	4-Decanol	2051-31-2	71
3-Pentanol	584-02-1	81	5-Decanol	5205-34-5	65
2-Hexanol	626-93-7	66	2,4-Dimethyl-3-pentanol	600-36-2	83
3-Hexanol	623-37-0	74	Cyclopentanol	96-41-3	53
2-Heptanol	543-49-7	62	Cyclohexanol	108-93-0	65
3-Heptanol	589-82-2	82	Cycloheptanol	502-41-0	74
4-Heptanol	589-55-9	70	Cycloheptanol		65[4]
2-Octanol	123-96-6	71	Cyclooctanol	696-71-9	69
4-Octanol	589-62-8	66	Cyclododecanol	1724-39-6	61

and complete conversion of alcohols to ketones upon ozonation, it was decided that a potentially useful synthetic oxidation method had presented itself. We tested the general applicability of this method by ozonizing 21 acyclic and cyclic secondary alcohols in methylene chloride at 0 °C.

Results and Discussion

Yield data for these oxidations are summarized in Table I.

The results indicate that ozonation gives ketone yields quite comparable to other oxidation methods.[5] Moreover VPC and ir analysis showed no residual alcohol in the raw product mixtures, whereas the more common oxidation processes frequently leave some unreacted alcohol.[6] Under the stated ozone flow conditions complete oxidation of 10–20 mmol of alcohol required 40–60 min at 0 °C.[7] The ketone products were essentially inert to "overozonation".[8]

As noted previously,[2,3] ozonation of alcohols, and most other functional groups, causes a certain amount of carbon–carbon scission. Likewise the present study showed minor yields of mono- and dibasic acids from the acyclic and cyclic alcohols, respectively. The nonvolatile acids were conveniently removed by either an aqueous bicarbonate wash or flash distillation prior to analysis. No other product impurities could be detected.[9]

The general utility of alcohol oxidation via ozonation is, of course, somewhat limited. Since the oxidation rate of alcohols is clearly many times slower than the addition of ozone to a carbon–carbon π bond,[2,3] the use of alkenols or alkynols is ruled out. The presence of other ozone reactive functional groups, e.g., aldehydes, amines,[10] etc., is also excluded. Finally, the rather slow rate of alcohol oxidation itself,[2] coupled with the necessity of ozonating at pressures close to atmospheric, appear to make large-scale oxidations impractical.[4]

However, ozonation, as an oxidation method, does offer some attractive advantages when compared to existing procedures. On a small preparative scale the alcohol is gently converted to ketone in a neutral organic medium[11] at a relatively low temperature. The side reactions which sometime accompany highly acidic or basic media and/or high temperatures are therefore eliminated. The work-up following ozonation is obviously quite simple, involving only simultaneous ozone quenching and carboxylic acid removal with an aqueous basic iodide wash.[9,12] Distillation to remove unreacted alcohol is unnecessary. Finally, the cost of the oxidizing agent itself, excluding the ozonator,[13] is minuscule when compared to that for most of the common oxidants.

Experimental Section

Welsbach T-408 and Airox C2P-9C ozonators were used to generate 3–5% O_3–O_2 mixtures at rates of 15–70 mmol of O_3 per hour. Rate of ozone flow was calculated by the standard iodide–thiosulfate method.[14]

Ozonations were generally carried out at 0 °C in a 100-ml three-necked flask with 1–2 g (10–20 mmol) of alcohol as a 1–2% w/v solution in CH_2Cl_2. The reaction solution also contained 10–20 mmol of nitromethane as an internal VPC standard. The reaction vessel was fitted with an inlet tube, magnetic stirrer, and a dry ice reflux condensor in series with an aqueous KI trap.

After ca. 45 min of ozonation, the reaction solution was washed with 20 ml of a 1 M aqueous KI–$NaHCO_3$ solution. The organic phase was dried with $MgSO_4$ and analyzed by VPC on 10 ft × 0.25 in. 10% SE-30, 20% DEGS, and 10% Carbowax columns. Identification of ketone products was accomplished by both comparing the peak retention times with those of the known ketones and by VPC collection and subsequent ir analysis of each peak.[15] Yields were calculated by using the VPC integration data coupled with the detector sensitivity calibration curves for each nitromethane–ketone mixture.

Registry No.—Ozone, 10028-15-6; 2-propanone, 67-64-1; 2-butanone, 78-93-3; 2-pentanone, 107-87-9; 3-pentanone, 96-22-0; 2-hexanone, 591-78-6; 3-hexanone, 589-38-8; 2-heptanone, 110-43-0; 3-heptanone, 106-35-4; 4-heptanone, 123-19-3; 2-octanone, 111-13-7; 4-octanone, 589-63-9; 2-nonanone, 821-55-6; 4-nonanone, 4485-09-0; 4-decanone, 624-16-8; 5-decanone, 820-29-1; 2,4-dimethyl-3-pentanone, 565-80-0; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; cyclododecanone, 830-13-7.

References and Notes

(1) This research was supported by the National Science Foundation, Grant GP-18317, and the University of Montana Foundation. A preliminary report of this work was presented at the 30th Annual NWRACS Meeting, Honolulu, Hawaii, June 1975.

(2) See, for example, C. Harries and K. Langheld, *Hoppe-Seyler's Z. Physiol. Chem.* **51**, 373 (1907); J. von Euw and T. Reichstein, *Helv. Chim. Acta.*, **27**, 821 (1944); A. Lardon and T. Reichstein, *ibid.*, **37**, 443 (1954); E. P. Oliveto, H. Q. Smith, C. Gerold, R. Rausser, and E. B. Hershberg, *J. Am. Chem. Soc.*, **78**, 1414 (1956); M. C. Whiting, A. J. N. Bolt, and J. H. Parish, *Adv. Chem. Ser.*, **77**, 4 (1968); T. M. Hellman and G. A. Hamilton, *J. Am. Chem. Soc.*, **96**, 1530 (1974); A. Y. Gerchikov, E. P. Kuznetsova, and E. T. Denisov, *Kinet. Katal.*, **15**, 509 (1974).

(3) W. L. Waters, P. E. Pike, and J. T. Rivera, *Adv. Chem. Ser.*, **112**, 78 (1972).

(4) This yield of ketone was obtained from the oxidation of 20 g (0.18 mol) of alcohol. Complete disappearance of cycloheptanol required a 4-h reaction time.

(5) I. T. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods", Wiley-Interscience, New York, N.Y., 1971, pp 386–396.

(6) For example, we have found that the two-phase Jones oxidation procedure [H. C. Brown, C. P. Garg, and K. Liu, *J. Org. Chem.*, **36**, 387 (1971)] commonly leaves 3–6% unreacted alcohol.

(7) Oxidation was faster at higher temperatures, but was accompanied by an increase in the percentage of carbon–carbon scission. We are currently investigating Whiting's findings (ref 2) that a catalytic amount of sodium borohydride or sodium acetate reduces this unwanted side reaction.

(8) At 0 °C the oxidation cleavage of ketones is five to ten times slower than alcohol oxidation.

(9) Since the by-products of the reaction are O_2 H_2O, and a small amount of RCOOH (see Whiting et al., ref 2), samples of the product mixture were analyzed by VPC after shaking either with a solid KI–NaS_2O_3 mixture or with aqueous KI–$NaHCO_3$.

(10) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(11) Oxidations were also carried out in CCl_4, $CHCl_3$, and $(CH_3)_2CO$. All solvents gave identical products and similar reaction rates.

(12) Alternatively, excess O_3 can be conveniently removed by purging the solution with N_2.

(13) The appearance of a number of relatively inexpensive air-cooled ozon-

ators on the market, coupled with the expanding investigation of O_3 water purification, has made ozonation available to most laboratories.

(14) See, for example, E. P. Parry and D. H. Hern, *Environ. Sci. Technol.*, **7**, 65 (1973).

(15) Ir spectra of the VPC collected ketones agreed closely with those from the literature. Sources: C. J. Pouchert, "The Aldrich Library of Infrared Spectra", Aldrich Chemical Co., Milwaukee, Wis., 1970; "Sadtler Standard Spectra", Sadtler Research Laboratories, Philadelphia, Pa.

Isolation and Identification of β-Citraurol, a C_{30} Carotenoid in Citrus[1]

Urs Leuenberger and Ivan Stewart*

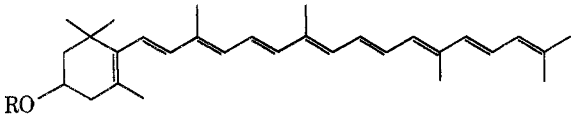
Agricultural Research and Education Center, University of Florida, IFAS, Lake Alfred, Florida 33850

Roy W. King

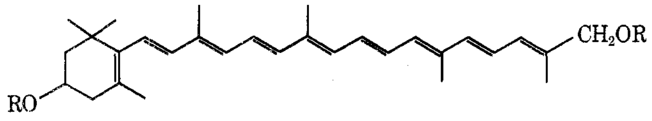
Chemistry Department, University of Florida, Gainesville, Florida 32611

Received July 10, 1975

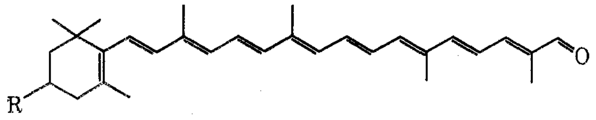
Reported occurrences of 8′-apocarotenoids in nature are not common. From a known total of 311 naturally occurring carotenoids Straub[2,3] lists only four C-30 compounds. Two of these, 8′-apo-β-caroten-8′-al (**3a**) and β-citraurin (**3b**), are found in citrus peel. The latter pigment is the major contributor to the red color of tangerines and the bright color of oranges.[4,5] More recently, 3-hydroxy-5,8-epoxy-5,8-dihydro-8′-apo-β-caroten-8′-al was found in orange juice[6] and β-citraurinene (8′-apo-β-caroten-3-ol, **1a**) was identified as a major pigment in citrus peel.[7] Also recently, Taylor and Davies[8,9] reported a group of acyclic C-30 carotenoids from bacteria.



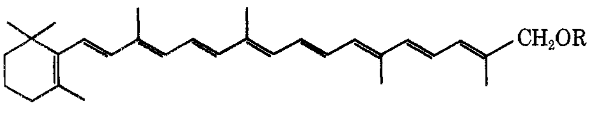
1a, R = H **1b**, R = Ac



2a, R = Acyl **2b**, R = H **2c**, R = Ac



3a, R = H **3b**, R = OH **3c**, R = OAc



4a, R = H **4b**, R = Ac

In this paper, we describe the isolation and structure elucidation of a new C_{30} carotenoid, β-citraurol, from peel of the citrus hybrid Robinson (Orlando tangelo × Clementine mandarin). This carotenoid with the structure of 8′-apo-β-caroten-3,8′-diol (**2b**) is not believed to have previously been reported to occur in nature. Curl reported the synthesis of β-citraurol from β-citraurin.[10]

β-Citraurol (**2b**) occurs as a diester in the peel as determined by a significant change in R_f on TLC following saponification. Acetylation of the carotenoid indicated two hydroxyl groups, yielding a monoester as an intermediate. The natural diester (**2a**), the diol (**2b**), and the diacetate (**2c**) showed similar visible spectra typical for a β,ψ chromophore with λ_{max} 403, 425, and 450 nm in *n*-hexane. There was no shift in the visible spectrum after treatment with HCl in EtOH[11] and a color test with HCl on TLC was negative. These tests along with a failure to reduce the oxygen with lithium aluminum hydride indicated the absence of an epoxide or a furanoid oxide.

Most of the studies on β-citraurol reported in this paper were made on the diacetate ester. The ester was more easily isolated than the alcohol and previous work with similar compounds would suggest that the esterified form is more stable.[7] β-Citraurol diacetate (**2c**) exhibited a molecular ion at *m/e* 518. Fragments due to the loss of acetic acid at *m/e* 458 (M − 60) and 398 (M − 120) confirmed the presence of two hydroxyl groups. Typical ester bands were exhibited in the infrared spectrum at 1740 and 1245 cm^{-1}.

The positions of the OH groups were investigated by several means. Smooth saponification and acetylation reactions ruled out a tertiary alcohol as well as a hydroxyl group in position C-2.[12] Oxidation with *p*-chloranil yielded a reddish compound with chromatographic and spectral properties identical with those of β-citraurin (**3b**) indicating one allylic hydroxyl group.

The above mentioned structural features were ultimately confirmed by the NMR data. The doublet of the geminal methyl groups at 1.08 and 1.12 ppm as well as the broad signal of the single proton at C-3 at ca. 5.05 ppm point to a secondary ester configuration of a 3-hydroxy-β-end group ring. A singlet at 1.98 ppm was associated with the three in-chain methyl groups, while the end-of-chain methyl yielded a singlet at 1.85 ppm. These signals together with the singlet of two protons at 4.58 ppm demonstrated an ester of a primary alcohol group at C-8′. Finally, the structure was confirmed when the diacetate of β-citraurol was synthesized from β-citraurin and the synthetic product was found to have identical chromatographic, spectroscopic, and chemical properties with the diacetate made from the natural occurring diol.

The finding of β-citraurol brings the known 8′-apocarotenoids to seven, with five of these found in citrus fruit. The presence of this number of similar compounds suggests that the biosynthesis of β-citraurin may not be a degradation product of C_{40} compounds as proposed[13] but rather it may form through a new pathway for C_{30} compounds.

A novel fragmentation of β-citraurol diacetate in the mass spectrometer was observed with both the natural and synthetic compounds. It is well known in carotenoid chemistry that acetic acid esters of nonallylic hydroxy carotenoids have a fragment M − 60 (M − acetic acid). The allylic ester of β-citraurol at C-8′ showed not only a loss of acetic acid but also two significant fragments, one at M − 44, loss of C_2H_4O, and a second fragment at M − 58, loss of $C_2H_2O_2$. The intensity of *m/e* 474 varied from 1.8 to 77% compared with the molecular ion and *m/e* 460 varied from 6.3 to 108% depending on the probe temperature.

The fragments *m/e* 474 and 460 have the same compositions as compounds **3c** and **1b**, respectively. Therefore, the decomposition of **2c** into **3c** and **1b** is not excluded. The relatively high temperatures required (>200°C) and the variable fragment intensities suggest thermal rather than electron-impact induced reactions. Compound **1b** does not exhibit a similar fragmentation, but gives only the M − 60 peak. However, 8′-apo-β-caroten-8′-ol acetate (**4b**) also gives fragments of M − 44 and M − 58 as found with **2c**. This would suggest that these two fragments are characteristic for the allylic end-of-chain acetate ester. Gross et al.[14] report for a similar allylic end-of-chain ester of 5,8-epoxy-5,8-dihydro-10′-apo-β-caroten-3,10′-diol diacetate a frag-