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(PIB/POP)*

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OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: EPA Registration No. 053201. (DEB # 6879). Methyl Bromide Reregistration Letter and Attachments From the Methyl Bromide Industry Panel (MBIP) Dated May 25, 1990. (No MRID #).

FROM: Nancy Dodd, Chemist *Nancy Dodd*  
Tolerance Petition Section II  
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Health Effects Division (H7509C)

THRU: Michael T. Flood, Ph.D., Acting Section Head  
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TO: Walter C. Francis, Acting Product Manager #32  
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and

Larry Schnaubelt  
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Special Review and Reregistration Division (H7508C)

Introduction

The MBIP has submitted a letter dated May 25, 1990 and attachments which address DEB's comments in a review dated February 22, 1990 (N. Dodd) regarding a protocol for postharvest fumigation of dried fruits and nuts. Issues regarding the protocol have also been discussed in meetings on April 12 and May 3, 1990 (see memorandums of conferences from N. Dodd dated May 2 and 17, 1990) and as a response to a letter dated December 29, 1989 (see N. Dodd memorandum dated May 18, 1990).

Conclusion/Recommendation

1. DEB recommends that MBIP modify their protocols to incorporate the following comments:
  - a. Bridging data will be necessary to support residue data from small chambers. (Refer to Conclusion #1 in the Detailed Considerations section of this review.)
  - b. Duplicate samples and duplicate chambers will be acceptable provided results are similar. If results are not similar, the study may have to be repeated with triplicate chambers and triplicate samples. (Refer to Conclusion #2 in the Detailed Considerations section of this review.)
  - c. Storage stability data are not needed for samples analyzed within 12 hours of sampling. For samples stored longer than 12 hours, spiked samples should be handled just as the treated samples are to determine loss between treatment and analysis. (Refer to Conclusion #9a in the Detailed Considerations section of this review.)
  - d. If the MBIP expects some packages to be fumigated more than once, residue data reflecting multiple treatments of packages will be needed. Alternatively, the labels should be revised to restrict the number of fumigations of packages to one. (The MBIP's approach would not work unless no detectable residues could be certified in the commodity at the time of refumigation.) (Refer to Conclusion #10 in the Detailed Considerations section of this review.)
  - e. MBIP should select a minimum time interval between refumigations for each commodity and revise labels so that refumigations will not occur within that time interval. Then the proposed studies should be conducted with refumigations occurring at the selected minimum time intervals. (Refer to Conclusion #11 in the Detailed Considerations section of this review.)
  - f. Residue data should be provided for each individual commodity or for the representative crops of the crop groups [40 CFR 180.34(f)(9)]. Bridging data for dried fruit as suggested by

the MBIP are not acceptable. (Refer to Conclusion #20 in the Detailed Considerations section of this review.)

- g. A label restriction limiting the number of postharvest applications to three for nuts would be acceptable. Then a crop group tolerance for the tree nuts crop group would be possible, if supported by residue data on almonds, pecans, and English walnuts. Residue data would also be needed for pistachios and any other nut which is not listed in the tree nuts group in 40 CFR 180.34(f). (Refer to Conclusion #21 in the Detailed Considerations section of this review.)

2. The MBIP should refer to the "Detailed Considerations" section of this review for discussions of issues upon which the MBIP and DEB have now reached agreement.

Note to PM: This entire review should be forwarded to the MBIP.

#### DETAILED CONSIDERATIONS

DEB's statements from the February 22, 1990 review of the dried fruit and nut protocol are listed below, followed by the MBIP's response and DEB's conclusions.

##### DEB's Statement #1

Commercial size chambers should be used. This conclusion may be reconsidered if additional data are provided which show that residues in commodities in large scale and small (28.3 l) chambers are similar.

##### MBIP's Response #1

The MBIP states that there is "no significant difference between small chambers and a well-defined commercial chamber." The major problem with using commercial chambers involves lack of control of variables (such as temperature, humidity, aeration, chamber tightness, etc.) which affect residue levels. (Refer to the MBIP's submission dated May 25, 1990 for their detailed discussion.)

##### DEB's Conclusion #1

DEB concludes that small chambers will be adequate for postharvest fumigation provided that bridging data are provided which indicate that residues in small chambers (28.3 l) and commercial chambers are similar. One study on

raisins has been submitted. One study on Eureka walnuts should be provided to satisfy the requirement for dried fruits and nuts.

DEB's Statement #2

Triplicate chambers and triplicate samplings from each chamber at each sampling time should be kept in the protocols.

MBIP's Response #2

"RESPONSE, DFNI: Table 2A, under each Crop section of protocols, as an example, shows no significant difference between MB concentration. Because the analysis of each sample will be triplicated and previous data between chamber replications and number of samples from a chamber is non-significant, we feel that duplication of chambers and samples should be more than sufficient."

DEB's Conclusion #2

DEB concludes that duplicate samples and duplicate chambers will be acceptable provided results are similar. If results are not similar, the study may have to be repeated with triplicate chambers and triplicate samples.

DEB's Statement #3a

The dosage rates in the protocols are consistent with the registered rates.

MBIP's Response #3a

"RESPONSE, DFNI: Dose rate is okay."

DEB's Conclusion #3a

No further comment is necessary.

DEB's Statement #3b

The 24-hour exposure times in the protocols are appropriate.

MBIP's Response #3b

"RESPONSE, DFNI: Exposure time is O.K."

DEB's Conclusion #3b

No further comment is necessary.

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DEB's Statement #4a

Additional data comparing residues resulting from different treatment temperatures and the same exposure period are needed for dried fruits and nuts. The worst residue case may involve a high temperature for exposure (absorption) and low temperatures for aeration and storage (desorption).

MBIP's Response #4a

"RESPONSE, DFNI: The worst residue case cited is not possible because treatment and aeration temperatures will be the same. As the data indicates that low temperatures are the worst case, low temperatures should be used in the study."

DEB's Conclusion #4a

Since most data indicate that low exposure and storage temperatures result in higher residues, DEB concludes that the protocol temperature of 50 °F (10 °C) for exposure and aeration will be acceptable. [50 °F (10 °C) is considered to be a low temperature since the boiling point of MeBr is 4.5 °C.]

DEB's Statement #4b

Since temperature is an important factor affecting residues, DEB concludes that the labels for dried fruits and nuts will need to specify treatment and aeration temperatures. For example, the labels will need to limit the fumigation and aeration temperatures to 50 °F or above if low temperatures result in higher residues and the studies are therefore conducted at 50 °F.

MBIP's Response #4b

"RESPONSE, DFNI: Minimum treatment temperature is currently on the label and should remain on it. Because aeration temperature will be the same as treatment temperature, it is pointless to list aeration temperature on the label. Also, it is not possible to commercially control aeration temperature."

DEB's Conclusion #4b

DEB agrees that the minimum treatment temperature (50 °F or 10 °C) should be on the label.

DEB agrees that it is not necessary to specify aeration temperature on the label.

DEB's Statement #5

DEB concludes that a 30 percent load factor will be appropriate provided the labels are revised to limit fumigations to chambers with load factors of 30 percent or higher.

MBIP's Response #5

"RESPONSE, DFNI: It is O.K. for label to show 30 percent load factor."

DEB's Conclusion #5

No further comment is necessary.

DEB's Statement #6a

Labels for dried fruits should be revised to prohibit vacuum fumigation.

MBIP's Response #6a

"RESPONSE, DFNI: We do not feel prohibiting vacuum fumigation on dried fruits is necessary. See DFNI Response 6b."

DEB's Conclusion #6a

DEB agrees that it is not necessary to prohibit vacuum fumigation on the label. Residue data reflecting normal atmospheric pressure (NAP) will cover both NAP and vacuum treatments. (See Discussion/Conclusion #6b.)

DEB's Statement #6b

Data reflecting both NAP and vacuum treatment of nuts should be provided since DEB cannot determine from one comparison study on walnuts that use of NAP on nuts will cause higher residues than use of a vacuum chamber.

MBIP's Response #6b

"RESPONSE, DFNI: The CT product for NAP is over twice as much as vacuum and greater sorption at NAP. Therefore, test should be conducted at NAP. This should apply to all dried fruits and nuts. Vacuum fumigation is no longer than 4 hours while NAP fumigation is often 24 hours."

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DEB's Discussion #6b

Figure 7 submitted in the walnut section of the protocol for dried fruits and nuts indicates that residues resulting from NAP treatments are higher than for vacuum fumigation.

Residue levels increase with increasing treatment time as well as with increasing treatment rate.

Previous discussions with the MBIP of residues resulting from NAP vs. vacuum fumigation did not consider the shorter exposure time on the label for vacuum fumigation.

DEB's Conclusion #6b

DEB concludes that data reflecting normal atmospheric pressure (NAP) will cover both NAP and vacuum treatments.

DEB's Statement #7

Concerning the King et al. headspace method, recoveries from spiked substrates and the limit of detection for each commodity must be reported.

MBIP's Response #7

"RESPONSE, DFNI: A calibration curve will be done for each commodity. Detection levels of .1 ppm MeBr on nuts and .01 ppm MeBr on dried fruits will be verified. Control samples will be spiked and compared to the calibration curve each day."

DEB's Conclusion #7

The recovery issue is satisfied.

DEB notes that a successful EPA method trial (W. Hazel, PP#5F3300, May 28, 1987) has been conducted for oranges at fortification levels of 0.01 and 0.05 ppm, for wheat at 0.005 and 0.01 ppm, and for walnuts at 0.05 and 0.1 ppm.

DEB also notes that FDA has been sent a PAM II Cover Sheet listing product applicability to "oranges, walnuts, and wheat" and to "various commodities" and the detection limit as 0.002 ppm.

DEB's Statement #8

The first sampling should occur when the MeBr concentration reaches 5 ppm. Perhaps the timing of the fumigation could be scheduled so that the 5 ppm level is reached during the day. It should be noted that this initial

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sampling time will require a label statement such that commodities may not be removed from fumigation chambers until MeBr concentration in chamber air is 5 ppm or less.

MBIP's Response #8

"Response, DFNI: This issue is already addressed on labels and was required by the label improvement program."

DEB's Conclusion #8

No further comment is necessary.

DEB's Statement #9a

Samples should be analyzed within 12 hours of sampling, or handled as described in the excerpt from the Residue Chemistry Chapter of the Methyl Bromide Registration Standard below:

"Analyses must be conducted as soon as possible (perhaps within 12 hours) after sampling and/or samples must be stored in impermeable containers. If stored in leakproof containers, analysis of headspace samples as well as the sample itself may be required if preliminary studies indicate that a significant amount of methyl bromide in the treated sample volatilizes into the gaseous phase of storage containers during a typical sample storage period. A problem may arise estimating the volume of the gaseous phase once the sample has been introduced. To increase confidence in residue determinations, spiked samples of each crop should be handled just as the treated samples are to determine the loss between treatment and analysis."

MBIP's Response #9a

"RESPONSE, DFNI: Nut samples will be run in 12 hours. If a delay of greater than 12 hours occur for dried fruits, data shows, Table 13 under Raisin section of protocols, that freezing the samples up to 4 weeks could be permitted."

DEB's Conclusion #9a

Storage stability data are not needed for samples analyzed within 12 hours of sampling. For samples stored longer than 12 hours, spiked samples should be handled just

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as the treated samples are to determine loss between treatment and analysis.

DEB's Statement #9b

Residue data "must be accompanied by data regarding storage length and conditions of storage of samples analyzed. These data must be accompanied by data depicting stability of residues under the conditions and for the intervals specified."

MBIP's Response #9b

"RESPONSE, DFNI:

1. The time that samples are removed from storage will be recorded.
2. Temperatures (which will be at storage temperature or below) from the time the samples are taken until extraction will be recorded.
3. The time that samples go into the blender will be recorded."

DEB's Conclusion #9b

No further comment is necessary.

DEB's Statement #10

The protocol regarding one fumigation of packaged commodities is acceptable provided that the labels will be revised to restrict the number of fumigations of packages to one. This would mean that packages which are fumigated with MeBr immediately after packaging could not be refumigated if returned to the packager. This may also mean that some recordkeeping system (such as stickers or codes on the package labels) would be needed by the MeBr fumigators so that the restriction is practical.

MBIP's Response #10

"RESPONSE, DFNI: Consumer packages will normally be fumigated one time. The rare exception might be consumer packages being recalled to the processor. In this case it may be necessary to fumigate again, but only after residues are equal to or less than .1 ppm MeBr on nuts and .01 ppm MeBr on dried fruits. The label could state that these levels must be reached before refumigation of consumer packages. This issue needs to be discussed further with the Agency."

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DEB's Conclusion #10

If the MBIP expects some packages to be fumigated more than once, residue data reflecting multiple treatments of packages will be needed. Alternatively, the labels should be revised to restrict the number of fumigations of packages to one. (The MBIP's approach would not work unless no detectable residues could be certified in the commodity at the time of refumigation.)

DEB's Statement #11

The MBIP should select a minimum time interval between refumigations for each commodity and revise labels so that refumigations will not occur within that time interval. Then the proposed studies should be conducted with refumigations occurring at the selected minimum time intervals.

MBIP's Response #11

"RESPONSE, DFNI: The residue test will determine the time interval to reach .1 ppm MeBr on nuts and .01 ppm MeBr on dried fruits. How this is to be addressed on the label needs to be discussed."

DEB's Conclusion #11

The issue raised in DEB's Statement #11 remains unresolved.

DEB's Statement #12a

The number of fumigations of bulk commodities as specified in the dried fruits and nuts protocols are acceptable except for walnuts.

MBIP's Response #12a

"RESPONSE, DFNI: Number of fumigations on dried fruits is O.K."

DEB's Conclusion #12a

No further comment is necessary. (See 12b for comments on walnuts.)

DEB's Statement #12b

Since walnuts may be fumigated five or more times before packaging, the walnut studies should be conducted with five fumigations of bulk walnuts.

MBIP's Response #12b

"RESPONSE, DFNI: After meeting with walnut handlers on the issue of number of treatments with MeBr, it was decided that the number of treatments should be restricted to three treatments. It is O.K. for the label to restrict the treatments on nuts to three times."

DEB's Conclusion #12b

A label restriction which limits the number of postharvest applications to nuts to three would be acceptable.

DEB's Statement #13

The following information should also be reported on Form A: commodity moisture, chamber humidity, method of MeBr introduction, rate of air circulation, and mechanism for air circulation.

MBIP's Response #13

"RESPONSE, DFNI: Commodity moisture, chamber humidity, method of MeBr introduction, rate of air circulation, and mechanism of air circulation will be recorded for each lot of commodity."

DEB's Conclusion #13

No further comment is necessary.

DEB's Statement #14a

Thompson seedless, which accounts for approximately 98 percent of the U.S. raisin crop, is an acceptable variety of raisins for the studies.

MBIP's Response #14a

"RESPONSE, DFNI: Okay to use Thompson Seedless."

DEB's Conclusion #14a

No further comment is necessary.

DEB's Statement #14b

The French prune variety, which accounts for approximately 90 percent of the U.S. prune crop, is an acceptable variety for the studies.

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MBIP's Response #14b

"RESPONSE, DFNI: Okay to use French prune."

DEB's Conclusion #14b

No further comment is necessary.

DEB's Statement #14c

The Deglet Noor date variety, which is the most common variety, is an acceptable variety for the studies.

MBIP's Response #14c

"RESPONSE, DFNI: Okay to use Deglet Noor."

DEB's Conclusion #14c

No further comment is necessary.

DEB's Statement #14d

The Adriatic variety of fig is an acceptable variety for the studies.

MBIP's Response #14d

"RESPONSE, DFNI: Okay to use Adriatic."

DEB's Conclusion #14d

No further comment is necessary.

DEB's Statement #14e

Residue data on both the Eureka variety and the Hartley variety of walnuts are needed.

MBIP's Response #14e

"RESPONSE, DFNI: Will use worst case - Eureka. Refer to Table 9 in Walnut section of protocol."

DEB's Discussions #14e

In the review dated February 22, 1990, DEB indicated that residue data on the "worst case" variety are needed to set tolerances. DEB also indicated that data on the leading variety would also probably be useful for risk assessment

purposes. However, residue data on the Eureka variety (a minor variety with the highest residues) can be used for both purposes.

DEB's Conclusion #14e

The Eureka variety is an acceptable variety for the studies.

DEB's Statement #14f

The Nonpareil variety of almond is acceptable for use in the studies.

MBIP's Response #14f

"RESPONSE, DFNI: Okay to use Nonpareil."

DEB's Conclusion #14f

No further comment is necessary.

DEB's Statement #14g

The Kerman variety of pistachio, which accounts for approximately 99 percent of the U.S. pistachio crop, is an acceptable variety for the studies.

MBIP's Response #14g

"RESPONSE, DFNI: Okay to use Kerman."

DEB's Conclusion #14g

No further comment is necessary.

DEB's Statement #14h

The Stewart variety of pecan is an acceptable variety for the studies.

MBIP's Response #14h

"RESPONSE, DFNI: Okay to use Stewart."

DEB's Conclusion #14h

No further comment is necessary.

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DEB's Statement #15a

Residue data are needed for raisins, prunes, and figs in bulk bins (such as wooden bins), cartons with liners, consumer packages with liners, and consumer packages without liners.

MBIP's Response #15a

"RESPONSE, DFNI: Okay as stated."

DEB's Conclusion #15a

No further comment is necessary.

DEB's Statement #15b

Residue data are needed on bulk nonpitted dates in bins (such as wooden bins), nonpitted dates in lined cartons, and dates in consumer packages with and without liners.

MBIP's Response #15b

"RESPONSE, DFNI: Okay as stated."

DEB's Conclusion #15b

No further comment is necessary.

DEB's Statement #15c

Residue data are needed on walnuts, almonds, pistachios, and pecans in bulk bins (such as wooden bins), in cartons with liners, and in consumer packages with and without liners.

MBIP's Response #15c

"RESPONSE, DFNI: Consumer packages for nuts do not have liners, thus will not be used in test."

DEB's Conclusion #15c

DEB concludes that residue data are needed on walnuts, almonds, pistachios, and pecans in bulk bins (such as wooden bins), in cartons with liners, and in consumer packages (without liners).

DEB's Statement #16a

To establish a tolerance on most nuts, only nutmeats must be analyzed. For almonds, hulls as well as nutmeats

must be analyzed according to DEB's Residue Chemistry Guidelines.

MBIP's Response #16a

"RESPONSE, DFNI: Nutmeats will be analyzed. As label currently states, hull treatments on almonds is not allowed."

DEB's Conclusion #16a

Since the label will restrict postharvest fumigation of almonds in hulls, residue data on almond hulls will not be needed for postharvest uses.

DEB's Statement #16b

Since MBIP has indicated that almonds in hull are not fumigated with MeBr, DEB concludes that a restriction on the labels should be added which prohibits fumigation of almonds in hulls so that DEB can be sure that this will never occur. Otherwise, residue data on almond hulls resulting from fumigation of almonds in hull would be needed (see above).

MBIP's Response #16b

"RESPONSE, DFNI: Okay to put on label."

DEB's Conclusion #16b

See Conclusion 16a above.

DEB's Statement #17

Residue data for both in-shell and shelled walnut nutmeats are needed.

MBIP's Response #17

"RESPONSE, DFNI: Even though the data does not show very much difference between in-shell and shelled walnut nutmeats, the shelled nutmeat residue is slightly higher, thus will be used in tests. CT product in Table 11A, under Walnut section of protocols, shows higher CT product for nutmeats."

DEB's Discussion #17

Based on Figure 11 of the Walnut section of the dried fruit and nut protocol, DEB concluded that residues were higher in in-shell walnut meats at days 1 and 6 after treatment and slightly higher for shelled walnut meats 2 and 9 days after treatment. However, the differences are probably

not significant after the first day.

DEB's Conclusion #17

DEB will accept residue data reflecting fumigation of shelled walnut nutmeat.

DEB's Statement #18

Since residues in shelled almond nutmeats are higher than in in-shell nutmeats, only data on shelled almond nutmeats are needed.

MBIP's Response #18

"RESPONSE, DFNI: Okay to use shelled almond nutmeats."

DEB's Conclusion #18

No further comment is necessary.

DEB's Statement #19

Residue data for both in-shell and shelled pecan and pistachio nutmeats are needed unless data are provided which show that residues are higher from one type of treatment.

MBIP's Response #19

"RESPONSE, DFNI: Because the data on almonds and walnuts show a higher residue on shelled nutmeats and the fact that the shell obviously absorbs MeBr, we do not see the point to confirm this on each nut, see Table 12, in walnut section in which in-shell had higher dose than nutmeats, but nutmeats still gave highest residues."

DEB's Conclusion #19

DEB will accept residue data reflecting fumigation of shelled pecan and pistachios nutmeats, based on the data from almonds and walnuts.

DEB's Statement #20

Residue data should be provided for each dried specialty or cut fruit unless crop group tolerances are sought. However, data for peaches may be used to support use on nectarines. If crop group tolerances are desired, data on representative crops as discussed in 40 CFR 180.34(f)(9) would be needed. Other requirements discussed under 40 CFR 180.34(f) must also be met.

MBIP's Response #20

"RESPONSE, DFNI: Cynthia Deyrup indicated in her visit to California that, because of the similarities of dried fruits, complete residue test would not have to be run on all dried fruits. If we used prunes, raisins, dates, and figs for the residue test, bridging data would be acceptable if residue analysis indicate the other dried fruits residues fall within the four dried fruits being tested. Because the other dried fruits did fall within the ranges of the four test dried fruits, we do not feel it would be necessary to do additional residue tests on the other dried fruits, see Figure 2 in Bridging Data section. Also, note attached Table A, Comparison of Dried Fruits, which shows similar total fat content for all the dried fruits. As MB is soluble in fat, the data in Figure 2, under Bridging section of protocols, is supported by Table A."

DEB's Conclusion #20

Residue data should be provided for each individual commodity or for the representative crops of the crop groups [40 CFR 180.34(f)(9)]. Bridging data for dried fruit as suggested by the MBIP are not acceptable.

DEB's Statement #21

Residue data should be provided for each nut. A crop group tolerance for the tree nuts group as discussed in 40 CFR 180.34(f) is probably not appropriate since the number of fumigations for the nuts of concern varies from two to six.

MBIP's Response #21

"RESPONSE, DFNI: At Cynthia's suggestion, we will test representative nuts within the nut group-almonds, walnuts, pecans, and pistachios. Because bridging data indicates the other nuts fall within the residues of the four nuts to be tested, we do not feel it would be necessary to do additional residue tests on the other nuts, see Figure 5 in Bridging Data section. Also, note attached Table B, Comparison of Nuts, which shows similar total fat content for all the nuts. As MB is soluble in fat, the data in Figure 5, under Bridging section of protocols, is supported by Table B. For all nuts, the maximum number of fumigations will be three. Therefore, the nut crop group should be acceptable."

DEB'S Conclusion #21

A label restriction limiting the number of postharvest applications to three for nuts would be acceptable. Then a crop group tolerance for the tree nuts crop group would be

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possible, if supported by residue data on almonds, pecans, and English walnuts. Residue data would also be needed for pistachios and any other nut which is not listed in the tree nuts group in 40 CFR 180.34(f).

cc: R.F., S.F., Circulation (6), PP#5F3300, N. Dodd (DEB), Methyl Bromide Registration Standard File - W. Boodee, R. Schmitt (DEB), Larry Schnaubelt (SRRD), PM#32, C. Furlow (PIB/FOD, H7506C)

RDI:M. Flood:7/18/90:R. Loranger:7/19/90  
H7509C:DEB:CM#2:Rm. 800D:X1681:KENCO:nd:7/23/90

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