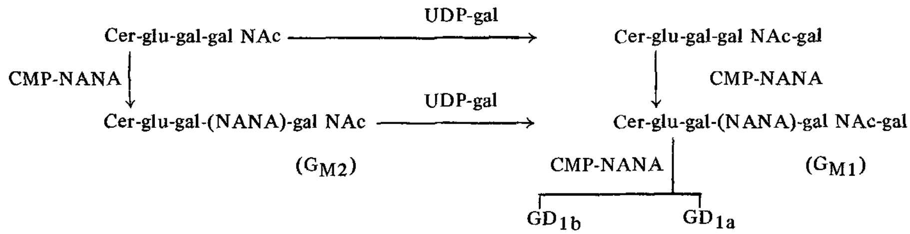

FIG. 3.

ceramide-glu-gal-gal NAc, also accumulates in this disease (20,22). There is little, if any, increase in the G_{M3} levels in pathological material (20). These three lines of evidence would tend to mitigate against a precursor role of G_{M3} for the other brain gangliosides. The glycosphingolipid composition of mouse neuroblastoma and human and rat glioma cells grown in tissue culture has been reported (23). G_{M3} was the only ganglioside present in the gliomas. In the neuroblastoma cells G_{M3} was undetectable, while G_{M2} and its corresponding asialo derivatives were abundant. They concluded, therefore, that G_{M3} does not serve as a precursor of the higher ganglioside homologues (23).

Two possible pathways are explained by Figure 3.

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Determination of the Position of Ethylenic Linkages in Lipids

ABSTRACT

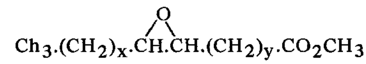
A new procedure for determining the position of ethylenic linkages in lipids involves oxidation of the corresponding epoxides with ethereal periodic acid. The oxidation products are identified by standard techniques such as nuclear magnetic resonance spectroscopy, mass spectrometry and gas liquid chromatography.

The present communication describes a convenient method for determining the position of olefinic linkages in lipids. It is based upon a report (1) that epoxides can be cleaved with a solution of periodic acid in ether or tetrahydrofuran. The new method involves converting the unsaturated material into the corresponding epoxide, followed by oxidation of the latter with an ethereal solution of periodic acid, and identification of the resulting aldehydes by nuclear magnetic resonance spectroscopy (NMR), mass spectrometry (MS), or gas liquid chromatography (GLC); a convenient procedure involves combination of NMR with MS, or GLC-MS. It may be illustrated by the following examples.

Methyl oleate was converted by oxidation with perlauric acid (2,3) into the corresponding epoxide (methyl *cis*-9,10-epoxyoctadecanoate) (I; x = 7, y = 7). To a stirring solution of this epoxy-ester (45 mg, 1.4 mmole) in dry ether (1 ml) was added a suspension of periodic acid (50 mg, 2.2 mmole) in dry ether (5 ml) [the suspension was prepared by vigorously stirring powdered periodic acid dihydrate (100 mg) in dry ether (10 ml) for 1 hr], and the mixture stirred for 1 hr [the reaction, followed by thin layer chromatography (TLC) and GLC was complete after this period]. It was then poured into water (5 ml), extracted with ether (20 ml), and the ethereal extract washed with 10% aqueous potassium hydrogen carbonate (5 ml), water 3 x 5 ml) and brine (5 ml). After removal of the solvents the products were separated by preparative thin layer chromatography (PLC) on a silica gel plate (20 x 20 cm x 1 mm, HF 254 + 366). Development with a mixture of light petroleum (bp 60-80 C) and ether (9:1, 3 passes) gave the aldehyde (II; x = 7) and the oxo-ester (III; y = 7). The aldehyde showed τ 0.26 (1H, *t*, J 1.8 Hz, $-C\underline{H}O$), 7.60 (2H, *m*, $-C\underline{H}_2.CHO$), 8.40 (2H, *m*, $-C\underline{H}_2.CHO$), 8.73 [10H, *s*, $-(C\underline{H}_2)_5.CH_2.CH_2.CHO$], 9.13 (3H, *t*, J 6 Hz, terminal CH_3), and m/e (%): 44 (65), 57 (100), 98 ($\underline{M}$-44) (30), 114 ($\underline{M}$-28) (2.3), 124 ($\underline{M}$-18) (1.7), 141 ($\underline{M}$-1) (2), 142 ($\underline{M}^+$) (1.7). The oxo-ester showed τ 0.26 (1H, *t*, J 1.8 Hz, $-C\underline{H}O$), 6.35 (3H, *s*, $-CO_2C\underline{H}_3$), 7.60 (*m*, $-C\underline{H}_2.CHO$) and 7.70 (*t*, J 7 Hz, $-C\underline{H}_2.CO_2CH_3$) (together 4H), 8.39 (*m*, $-C\underline{H}_2.CH_2.CHO$ and $-CH_2.CH_2.CO_2CH_3$) and 8.68 [*s*, $-(CH_2)_3-$] (together 10H), and m/e (%): 44 (16), 57 (18), 74 (100), 87 (96), 111 ($\underline{M}$-75) (57), 112 ($\underline{M}$-74) (7), 115 ($\underline{M}$-71) (13), 143 ($\underline{M}$-43) (66), 154 ($\underline{M}$-32) (7), 155 ($\underline{M}$-31) (40), 158 ($\underline{M}$-28) (26), 168 ($\underline{M}$-18) (1.6), 185 ($\underline{M}$-1) (0.6).

The same products were obtained on subjecting methyl *trans*-9,10-epoxyoctadecanoate to the above procedure.

Methyl *cis*-13,14-epoxydocosanoate (I; x = 7, y = 11) gave by the same procedure the aldehyde (II; x = 7) and the oxo-ester (III; y = 11). The latter showed τ 0.24 (1H, *t*, J 1.8 Hz, $-C\underline{H}O$), 6.33 (3H, *s*, $-CO_2C\underline{H}_3$), 7.60 (*m*, $-C\underline{H}_2.CHO$) and 7.70 (*t*, J 7 Hz, $-C\underline{H}_2.CO_2CH_3$) (together 4H), 8.38 (4H, *m*, $-C\underline{H}_2.CH_2.CHO$ and $-C\underline{H}_2.CH_2.CO_2CH_3$), 8.72 [14H, *s*, $-(CH_2)_7-$], and m/e (%): 74 (100), 87 (45), 167 ($\underline{M}$-75) (9), 171 ($\underline{M}$-71) (7.5), 199 ($\underline{M}$-43) (14.5), 211 ($\underline{M}$-31) (4), 214 ($\underline{M}$-28) (6), 224 ($\underline{M}$-18) (0.5), 241 (M-1) (0.5).



(I)

$CH_3(CH_2)_x.CHO$ + $OHC.(CH_2)_y.CO_2CH_3$

(II) (III)

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Ricinoleic Acid in *Linum mucronatum* Seed Oil

ABSTRACT

Linum mucronatum seed oil contains 15% ricinoleic [(+)-12-D-hydroxy-*cis*-9-octadecenoic] acid, previously unknown